SCIAMACHY tropospheric NO$_2$ over Switzerland: estimates of NO$_x$ lifetimes and impact of the complex Alpine topography on the retrieval

D. Schaub$^1$, D. Brunner$^1$, K. F. Boersma$^2$, J. Keller$^3$, D. Folini$^1$, B. Buchmann$^1$, H. Berresheim$^{4,5}$, and J. Staehelin$^5$

$^1$Empa, Swiss Federal Laboratories for Materials Testing and Research, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland
$^2$School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA
$^3$Paul Scherrer Institute (PSI), 5232 Villigen PSI, Switzerland
$^4$German National Meteorological Service, DWD/MOHp, 82383 Hohenpeissenberg, Germany
$^5$Swiss Federal Institute of Technology (ETH), Universitätsstrasse 16, 8092 Zurich, Switzerland

Received: 23 November 2006 – Published in Atmos. Chem. Phys. Discuss.: 12 January 2007
Revised: 9 November 2007 – Accepted: 21 November 2007 – Published: 7 December 2007

Abstract. This study evaluates NO$_2$ vertical tropospheric column densities (VTCs) retrieved from measurements of the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) above Switzerland and the Alpine region. The close correlation between pixel averaged NO$_x$ emission rates from a spatially and temporally highly resolved inventory and the NO$_2$ VTCs under anticyclonic meteorological conditions demonstrates the general ability of SCIAMACHY to detect sources of NO$_x$ pollution in Switzerland. This correlation is further used to infer seasonal mean NO$_x$ lifetimes carefully taking into account the influence of the strong diurnal cycle in NO$_x$ emissions on these estimates. Lifetimes are estimated to 3.6 ($\pm 0.8$) hours in summer and 13.1 ($\pm 3.8$) hours in winter, the winter value being somewhat lower than previous estimates. A comparison between the 2003-2005 mean NO$_2$ VTC distribution over Switzerland and the corresponding 1996–2003 mean from the Global Ozone Monitoring Experiment (GOME) illustrates the much better capability of SCIAMACHY to resolve regional scale pollution features. However, the comparison of seasonal averages over the Swiss Plateau with GOME and ground based in situ observations indicates that SCIAMACHY exhibits a too weak seasonal cycle with comparatively high values in summer and low values in winter. A problem likely contributing to the reduced values in winter (not reported in earlier literature) is the use of inaccurate satellite pixel surface pressures derived from a coarse resolution global model in the retrieval. The marked topography in the Alpine region can lead to deviations of several hundred meters between the model assumed and the real pixel-averaged surface height. A sensitivity study based on selected clear sky SCIAMACHY NO$_2$ VTCs over the Swiss Plateau and two fixed a priori NO$_2$ profile shapes indicates that inaccurate pixel surface pressures affect retrieved NO$_2$ columns over complex terrain by up to 40%. For retrievals in the UV-visible spectral range with a decreasing sensitivity towards the earth’s surface, this effect is of major importance when the NO$_2$ resides close to the ground, a situation most frequently observed during winter.

1 Introduction

Nitrogen dioxide is an important air pollutant. It can affect human health and plays a major role in the production of tropospheric ozone (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000). The bulk of NO$_x$ (NO$_x$=NO+NO$_2$) is emitted by the high-temperature combustion of fossil fuel in the highly industrialised continental regions in the northern mid-latitudes. Important natural sources are biomass burning and the microbial production in soils of the non-polar continental surface. At higher altitudes in the troposphere NO$_x$ is directly injected into the troposphere by lightning and aircraft emissions (IPCC, 2001). NO$_x$ is primarily emitted as NO which oxidises to NO$_2$ within a few minutes. The NO$_2$ concentration is affected by the partitioning of NO$_x$ into NO and NO$_2$ which depends on the abundance of ozone and reactive organic compounds as well as on solar light intensity and temperature, and which therefore changes with altitude and with time of day in the troposphere. NO$_x$ is removed from the troposphere mainly by conversion to nitric acid (HNO$_3$). During daytime, HNO$_3$ is formed through the
reaction of NO$_2$ with the OH radical. At night, a two step reaction mechanism forms nitrogen pentoxide (N$_2$O$_5$) which further reacts on surfaces and aerosol to HNO$_3$ (Dentener and Crutzen, 1993). HNO$_3$ is finally removed by dry and wet deposition (Kramm et al., 1995). Typical lifetimes of NO$_x$ are of the order of 4 to 20 h depending on season (Seinfeld and Pandis, 1998). This is supported by results presented in this study inferred from the combination of SCIAMACHY NO$_2$ VTCs with a high-quality NO$_x$ emission inventory. The reverse approach, that is the computation of NO$_x$ emissions from satellite column observations based on a priori knowledge of NO$_x$ lifetimes or NO$_2$ column to NO$_x$ emission ratios taken from a model, has recently become an important tool in top-down emission estimation for regions where sources are not well known (e.g. Martin et al., 2003).

Although the NO$_2$ concentration in Switzerland decreased during the last 15 years the Swiss NO$_2$ annual ambient air quality standard of 30 µg·m$^{-3}$ ($\approx$16 ppb) is still exceeded in polluted areas (FOEN, 2005) and there has been a stagnation or even a slight increase in NO$_2$ in recent years (Hueglin et al., 2006). Monitoring of nitrogen oxides therefore plays an important role for the assessment of reduction measures. Complementary to ground-based monitoring networks which provide detailed information of local near-surface air pollution, space-borne instruments such as the Global Ozone Monitoring Experiment (GOME) (Burrows et al., 1999) and the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) (Bovensmann et al., 1999) provide area-wide data of NO$_2$ vertical tropospheric column densities (VTCs) with global coverage within a few days. The gradually improving resolution of space-borne UV/VIS instruments (GOME pixel size: 320×40 km$^2$, SCIAMACHY: 60×30 km$^2$, occasionally 30×30 km$^2$, Ozone Monitoring Instrument (OMI): up to 13×24 km$^2$ at nadir) increasingly allows to detect NO$_2$ pollution features on a regional scale. However, these space-borne data and their complex retrieval are still recent and evolving techniques and validation is therefore needed. Schaub et al. (2006) summarised different validation campaigns of GOME and SCIAMACHY NO$_2$ data and carried out a detailed comparison of GOME NO$_2$ VTCs retrieved by KNMI (Royal Dutch Meteorological Institute) and BIRA/IASB (Belgian Institute for Space Aeronomy) with NO$_2$ profiles derived from ground-based in situ measurements at different altitudes in the Alpine region.

In this paper we evaluate SCIAMACHY NO$_2$ VTCs over Switzerland and the Alpine region with regard to their use for air quality monitoring and modelling on a regional scale and over a complex topography. The observations are compared to a high quality NO$_x$ emission inventory in order to test the ability of SCIAMACHY to detect the distribution of NO$_x$ pollution sources on the scale of a small country. This comparison is further used to infer seasonal mean NO$_x$ lifetimes carefully taking into account the influence of the strong diurnal cycle in NO$_x$ emissions on these estimates.

The significantly enhanced potential of SCIAMACHY as compared to the Global Ozone Monitoring Instrument GOME regarding the resolution of regional scale NO$_x$ pollution features is demonstrated by a comparison of multi-annual mean distributions of the two instruments over Switzerland. In addition, mean seasonal cycles representative for the Swiss Plateau are calculated for both instruments and compared to each other as well as to NO$_2$ columns deduced from ground-based in situ measurements carried out at different altitudes. From this comparison evidence is found that SCIAMACHY underestimates the amplitude of the seasonal cycle over the Swiss Plateau.

In the last part of this study the potential effects of the complex topography over the Alpine region on the retrieval are investigated. Based on a sensitivity analysis applied to selected SCIAMACHY pixels it is demonstrated that the use of a coarse resolution topography in the retrieval can indeed lead to significant systematic errors in NO$_2$ VTCs over the Swiss Plateau. The results are relevant for any region of the globe with a marked orography and highlight the need for a more accurate representation of this parameter in future satellite retrievals.

2 Data

2.1 KNMI/BIRA GOME and SCIAMACHY tropospheric NO$_2$ observations

Nadir measurements from GOME on board ESA’s ERS-2 satellite and from SCIAMACHY on board ESA’s Envisat satellite are used in the present study. Depending on whether the focus is the whole domain of Switzerland or only the densely populated Swiss Plateau, our analyses will be
restricted to pixels with centre coordinates within the region of interest ROI_{CH} or ROI_{SP}, respectively (Fig. 1).

The GOME and SCIAMACHY observations are obtained at approximately 10:30 and 10:00 local time and individual pixels cover an area of 320\times40 \, km^2 and 60\times30 \, km^2, respectively. The GOME and SCIAMACHY measurement principles are described in Burrows et al. (1999) and Bovensmann et al. (1999), respectively. The NO\textsubscript{2} VTCs studied in this work are the product of a collaboration between KNMI and BIRA/IASB. Both GOME and SCIAMACHY NO\textsubscript{2} data are publicly available on a day-by-day basis via ESA’s TEMIS project (Tropospheric Emission Monitoring Internet Service, www.temis.nl).

The first retrieval step is based on the Differential Optical Absorption Spectroscopy (DOAS) technique (Platt, 1994; Vandeaele et al., 2005): a polynomial and a modelled spectrum are fitted to the logarithm of the ratio of earthshine radiation to solar irradiance in the spectral window from 426.3–451.3 nm. The modelled spectrum accounts for spectral absorption features of NO\textsubscript{2}, O\textsubscript{3}, O\textsubscript{2}-O\textsubscript{2}, H\textsubscript{2}O, and the filling-in of Fraunhofer lines by Raman scattering (“Ring effect”). Scattering by clouds, aerosols, air molecules and the surface is described by a low-order polynomial. This first retrieval step results in the slant column density (SCD) of NO\textsubscript{2}, which can be interpreted as the column integral of absorbing NO\textsubscript{2} molecules along the effective photon path from the sun through the atmosphere to the spectrometer.

The second retrieval step separates the stratospheric contribution from the total SCD (Boersma et al., 2004). For KNMI retrievals this is achieved with a data-assimilation approach using the TM4 global chemistry transport model (CTM) (Dentener et al., 2003). The tropospheric SCD (SCD\textsubscript{trop}) results from the subtraction of the stratospheric estimate from the total SCD.

In the third retrieval step, the SCD\textsubscript{trop} is converted into a VTC by applying the tropospheric air mass factor (AMF\textsubscript{trop}). Following Palmer et al. (2001) and Boersma et al. (2004), the retrieved SCIAMACHY NO\textsubscript{2} VTC (X_{SCIA}) is calculated as

\[ X_{SCIA} = \frac{N_{trop}}{M_{trop}(x_{a}, b)} = \frac{N_{trop} \cdot \sum x_{a,l}}{\sum m_{l}(b) \cdot x_{a,l}} \]  

(1)

where \( N_{trop} \) denotes the tropospheric slant column density, \( M_{trop} \) the tropospheric air mass factor, \( x_{a,l} \) the layer specific subcolumns from the a priori profile \( x_{a} \), and \( m_{l} \) the altitude-dependent scattering weights. These weights are calculated with the Doubling Adding KNMI (DAK) radiative transfer model (Stamnes, 2001) and best estimates for forward model parameters \( b \), describing surface albedo, cloud parameters (fraction, height) and pixel surface pressure. The a priori NO\textsubscript{2} profiles for every location and all times are obtained from the TM4 CTM. Cloud fraction and height are retrieved from the TM4 retrieval scheme for clouds from the Oxygen A band (FRESCO) algorithm (Koelemeijer et al., 2001). Since the TM4 model is driven by meteorological data of the European Centre for Medium-Range Weather Forecasts (ECMWF) the surface pressures in TM4 are taken from the ECMWF model on the 2\(^2\) \times 3\(^\circ\) resolution of the TM4 model. The surface pressure for an individual satellite pixel is linearly interpolated to the pixel location (hereafter ECMWF/TM4 surface pressure).

The different error sources in tropospheric NO\textsubscript{2} retrievals have been discussed extensively in Boersma et al. (2004) for GOME and error propagation studies have shown that SCIAMACHY errors are similar (Boersma et al., 2007). Based on this work, errors for both GOME and SCIAMACHY NO\textsubscript{2} VTCs are estimated on a pixel-to-pixel basis and additionally provided in the TEMIS data sets. However, these studies have not included the effect of errors in surface pressure. The present work will show that, over a complex topography, an inadequate treatment of this parameter may lead to significant errors which tend to be larger for an instrument with a higher spatial resolution such as SCIAMACHY as compared to GOME.

2.2 Swiss NO\textsubscript{x} emissions

Swiss NO\textsubscript{x} emissions amount to 33.2 kt N/y with traffic, industry, agriculture/forestry and residential activities contributing 58%, 24%, 12% and 6%, respectively, for the year 2000 (FOEN, 2005). The present study employs an hourly resolved NO\textsubscript{x} emission inventory for Switzerland available on a 3\times3 km\textsuperscript{2} grid. It combines the following basic data sets:

- Road traffic emissions of NO\textsubscript{x} for the reference year 2000 with a spatial resolution of 250 m prepared by the consulting company INFRAS, Switzerland. The data set includes an average diurnal variation. Long-term trends of annual totals recently published in Keller and Zbinden (2004) were used to interpolate the emissions between 2000 and 2005.

- NO\textsubscript{x} emissions from residential activities, heating, industry, off-road traffic and agriculture/forestry for the reference year 2000 with a spatial resolution of 200 m and accounting for seasonal variations prepared by the company Meteotest, Switzerland. Data sets for other years of interest were calculated on the basis of trends provided by the Swiss Federal Office for the Environment (FOEN, 1995).

Additional information on the emission inventory is summarised in Keller et al. (2005). Total emission inventories are usually based on a large number of input variables. Each of these parameters – and, thus, also the resulting total emission inventory – are affected by uncertainties. Their assessment is a challenging task which needs further assumptions (e.g. Kühlewien and Friedrich, 2000). For the 3\times3 km\textsuperscript{2} Swiss NO\textsubscript{x} emission inventory an accuracy of \pm 15–20% is estimated in FOEN (1995). Kühlewien (2004) further pointed out increasing errors in emission inventories for increasing spatial resolutions. Thus, due to integration of the 3\times3 km\textsuperscript{2}
Fig. 2. Diurnal cycle of NO\textsubscript{x} emissions (in g (N) km\textsuperscript{-2} h\textsuperscript{-1}) over Switzerland. The solid line is the hourly emission flux from the Swiss emission inventory (in winter) averaged over the domain of Switzerland. The three other lines illustrate the effect of the exponential decay of NO\textsubscript{x} for three selected lifetimes \(\tau\). This decay leads to a reduced contribution of the emissions released at a given time of the day to the NO\textsubscript{x} column \(M\) measured at the SCIAMACHY overpass time, see Eq. (5) (a). Effective NO\textsubscript{x} emission rate \(E_{\text{eff}}\) as a function of lifetime \(\tau\). The dashed line is the daily mean emission rate (average of solid line if panel a) (b).

resolved emission data over the SCIAMACHY pixel size of 60 × 30 km\textsuperscript{2} in the present work, the above given error of 20% is considered as a reasonable upper limit, which will be assumed in this study.

3 Methods

3.1 Comparison of NO\textsubscript{2} VTCs with a high resolution emission inventory for the estimation of mean NO\textsubscript{x} lifetimes

In Sects. 4.1.1 and 4.1.2 NO\textsubscript{2} VTCs will be compared to the Swiss NO\textsubscript{x} emission inventory for SCIAMACHY pixels located entirely within the Swiss boundaries. A representative emission rate is computed for each NO\textsubscript{2} VTC by averaging the gridded inventory data over the area of the pixel. The comparison is restricted to clear sky pixels (cloud fraction < 0.1) and anticyclonic conditions. Meteorological conditions are deduced from the Alpine Weather Statistics described in MeteoSwiss (1985). The Alpine Weather Statistics distinguishes between advective and convective classes based on pressure gradients in surface charts. Anticyclonic conditions are a subset of the convective class and are characterized by fair weather and low surface level winds of typically less than 15 km/h. Significant long-range advection of air pollutants is unlikely to occur under these conditions, at least in the boundary layer. Therefore, a close association between the emission distribution and the NO\textsubscript{2} column field is expected.

The NO\textsubscript{x} emissions released at the location of the column are considered as the main flux of NO\textsubscript{x} into the column which, in an equilibrium state, is balanced by the chemical and physical (i.e. deposition) losses in the column. Neglecting transport and assuming first order losses only and steady state, we can write

\[
\frac{dM}{dt} = E - k \cdot M = 0, \tag{2}
\]

with \(M\) the amount of NO\textsubscript{x} in the column (in g (N) km\textsuperscript{-2}), \(E\) the NO\textsubscript{x} emission flux (in g (N) km\textsuperscript{-2} h\textsuperscript{-1}), and \(k\) the first order loss rate. Reforming yields

\[
M = \frac{1}{k} \cdot E = \tau \cdot E, \tag{3}
\]

with \(\tau\) the lifetime of NO\textsubscript{x} in the column. The lifetime can thus be obtained as the slope in a correlation plot of \(M\) versus \(E\). In order to account for inaccuracies in both the observed columns and the emission rates, the slopes are calculated using weighted orthogonal regression (York, 1966). NO\textsubscript{x} columns \(M\) are computed from the product of SCIAMACHY tropospheric NO\textsubscript{2} VTC and simulated NO\textsubscript{x}/NO\textsubscript{2} ratios, both contributing to the error in \(M\). The SCIAMACHY NO\textsubscript{2} VTC \(1 \sigma\) error estimates are taken from the TEMIS data file where error estimates are provided for each individual pixel (Boersma et al., 2004). Errors introduced by the uncertainty in NO\textsubscript{x}/NO\textsubscript{2} column ratios are described later. For the NO\textsubscript{x} emission fluxes averaged over the individual SCIAMACHY pixels an error of 20% is assumed (Sect. 2.2).

The basic assumption of steady state has also been made in earlier studies by Leue et al. (2001), Beirle et al. (2003) and Kunhikrishnan et al. (2004). It disregards the horizontal NO\textsubscript{x} transport into and out of the column. This transport, however, can lead to a smearing because the net effect of transport will be negative for regions with large sources and positive for the surrounding areas. The smearing effect is also depending on the prevailing meteorology (e.g. wind speed and direction) and the chemical lifetime. For mapping isoprene emissions from space-borne data, Palmer et al. (2003) determined typical smearing length scales. For NO\textsubscript{x} lifetimes in the order of hours to one day, this length scale is ~100 km (Martin et al., 2003). While neglecting the effect of transport is well justified for the large size of GOME pixels as
in the study of Martin et al. (2003), this might be problematic for SCIAMACHY data with a much smaller pixel size of 60×30 km². However, as described above, our analysis is restricted to clear sky pixels and anticyclonic weather conditions associated with low wind speeds, i.e. rather stagnant air, and fast photochemistry reducing the importance of horizontal transport in the boundary layer. Significant transport over larger distances (e.g. from highly polluted regions in adjacent countries to Switzerland as described in Schaub et al. (2005) for a frontal passage) is therefore considered to be unimportant for these conditions.

SCIAMACHY NO₂ VTCs are converted to NOₓ VTCs by employing representative values for the seasonal mean NO₂/NO ratio. The latter depends on the abundance of ozone and reactive organic compounds as well as on solar radiation and temperature. Thus, the ratio varies both spatially (horizontally and vertically) and seasonally. For the United States and based on 106 NOₓ monitoring data sets measured at different distances from the predominant emission sources, Chu and Meyer (1991) recommended a national default value for the NO₂/NO ratio of 3. NOₓ measurements performed since 1999 at an elevated rural site at the edge of the Swiss Plateau (Rigi, 47°04′N, 8°28′E, 1030 m a.s.l.) using a standard chemiluminescence detector for the measurement of NO and a photolytic converter for the selective conversion of NO₂ to NO (Steinbacher et al., 2007) indicate a seasonal variation of monthly mean ratios of between 1.6 (January) and 4.0 (August) for anticyclonic clear sky conditions and a time window between 10:00 and 12:00 UTC (Steinbacher, personal communication). Instead of using ratios from in-situ observations valid only for the altitude of the measurement site, we here apply seasonal mean tropospheric (0–8 km) column NO₂/NO ratios obtained from the TM4 model. The ratios are based on model output over Switzerland on clear days. Unfortunately, only output for 12:00 UTC (13:00 LT) was available. Nevertheless, these TM4 column ratios are assumed to be representative for the SCIAMACHY overpass time (10:00 LT) and are found to be surprisingly close to the ratios observed in situ at Mount Rigi. Vertical model profiles indicate that the NO₂/NO ratio changes only little in the lowest 1 to 2 km where most of the NO₂ resides, which likely explains the good agreement with the ratios measured at a single altitude. Above the planetary boundary layer, the ratios decrease rapidly but the free troposphere contributes only little to the total column above Switzerland.

The ratios finally applied are 3.0 (±0.7) for spring (MAM), 4.0 (±0.6) for summer (JJA), 2.8 (±1.0) for autumn (SON), and 1.5 (±0.5) for winter (DJF), where values in brackets represent the 1σ variability of the column ratios between individual days. The uncertainty in these ratios is added to the uncertainly in the SCIAMACHY NO₂ VTC to obtain an estimate for the uncertainty of the NOₓ VTCs M finally used in the calculation of seasonal mean lifetimes according to Eq. (3). It is interesting to note that these ratios do not change significantly when cloudy days are included in the analysis, probably due to the compensating effects of reduced photolysis rates (increasing the ratio) and at the same time reduced O₃ concentrations (reducing the ratio) on cloudy days. Obtaining an emission rate $E$ representative for the time of the SCIAMACHY overpass (10:00 LT corresponding to 09:00 UTC over Switzerland) is not straightforward due to the strong diurnal cycle in NOₓ emissions. If NOₓ has a short lifetime then only the emissions released during a few hours preceding the satellite overpass contribute to the NO₂ VTC measured by SCIAMACHY. If the lifetime is longer, however, then also emissions of the previous night and the previous day become relevant. This problem is illustrated in Fig. 2a showing the average diurnal cycle of NOₓ emissions over Switzerland in winter (solid line). Also shown are the effective contributions of the emissions to the measured column if we assume three different NOₓ lifetimes $\tau$ of 4, 10, and 20 h (dotted and dashed-dotted lines).

The problem can be formulated as follows: The amount of NOₓ released at a given hour $t_i$ of the day over a period $\Delta t=1$ h (i.e. $E_i \cdot \Delta t$, where $E_i$ is the emission rate at hour $i$ given by the solid line in Fig. 2a) decays exponentially with a time constant $\tau$. The column amount $M$ accumulated by all emissions released during $n$-hours preceding the overpass can thus be expressed as:

$$M = \sum_{i=1}^{n} E_i \cdot e^{-\frac{(t_{\text{SCIA}}-t_i)}{\tau}} \cdot \Delta t,$$

where $t_{\text{SCIA}}-t_i$ is the time difference between the SCIAMACHY overpass and the NOₓ release in hours. Values of $E_i \exp(-1(t_{\text{SCIA}}-t_i)/\tau)$ are shown in Fig. 2a for three different lifetimes $\tau$. Combining this equation with Eq. (3) we can compute an effective emission rate $E_{\text{eff}}$ relevant for a given
The effective emission rate is thus a weighted mean of the original emissions with weights given by an exponential decay with time constant $\tau$. Values of $E_{\text{eff}}$ are shown in Fig. 2b as a function of lifetime $\tau$. For comparison, the daily mean emission rate is also shown (dashed line). For short lifetimes lower than about 7 h the effective emission rate is higher than the daily mean because only the high morning emissions including the early morning traffic peak are relevant. For longer lifetimes the low emission rates of the previous night become important reducing $E_{\text{eff}}$ below the daily mean value. It is important to notice that the effective emission rate depends not only on the NO$_x$ lifetime but also on the time of the satellite overpass. Such complicating effects need to be carefully considered for instance in NO$_x$ emission inversion studies using a combination of model information and satellite observations to obtain improved emission estimates.

Now we are facing the problem that, for the calculation of lifetime $\tau$ according to Eq. (3), we have to use an effective emission rate which itself is depending on $\tau$. This problem can be solved iteratively with

$$\tau_i = \frac{M}{E_{\text{eff}}(\tau_{i-1})},$$

where in each step $(i)$ the emission $E_{\text{eff}}$ is adjusted to the lifetime obtained from the previous step $(i-1)$ using Eq. (6). The iteration is found to converge quickly within no more than 4 steps. Lifetime estimates based on this approach will be presented in Sect. 4.1.2.
Table 1. Seasonal NO$_x$ lifetime estimates based on a weighted orthogonal regression and lifetime-dependent effective emission rates for two different cloud fraction limits. Stated uncertainties correspond to the standard deviations of the slopes determined by the regression.

| Cloud fraction limit | $\tau_{NO_x}$ (h) MAM ($\pm$ std. dev.) | $\tau_{NO_x}$ (h) JJA ($\pm$ std. dev.) | $\tau_{NO_x}$ (h) SON ($\pm$ std. dev.) | $\tau_{NO_x}$ (h) DJF ($\pm$ std. dev.) |
|----------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| 0.1                  | 4.93 (±1.39)                           | 3.60 (±0.78)                           | 6.10 (±0.81)                           | 13.12 (±3.78)                          |
| 0.2                  | 5.95 (±1.05)                           | 3.64 (±0.60)                           | 6.45 (±0.75)                           | 16.04 (±3.16)                          |

The sensitivity study is then carried out for a subset of clear sky SCIAMACHY pixels and two fixed a priori NO$_2$ profiles only. The AMF$_{top}$ and NO$_2$ VTCs are first calculated for the ECMWF/TM4 surface pressure $p_{surf}$ as in the original retrieval and then recalculated for the effective surface pressure $p_{eff}$ deduced from the aLMo topography $h_{eff}$ using again the ground based vertical pressure profiles. The criteria for the pixel subset are i) anticyclonic clear sky meteorological conditions (Alpine Weather Statistics; MeteoSwiss, 1985), ii) pixel cloud fraction $\leq$0.1, and iii) a small standard deviation $\leq$65 m of the aLMo 7x7 km$^2$ grid cell heights enclosed within a SCIAMACHY pixel, the latter ensuring that the reprocessing is done for pixels over a flat region in the vicinity of the Alps rather than directly over the mountains. The resulting SCIAMACHY pixels are located above the rather flat north-eastern Swiss Plateau (Fig. 3) but their surface pressure $p_{surf}$ is still strongly influenced by the proximity of the Alps at the coarse ECMWF/TM4 resolution.

The sensitivity analysis is performed for two characteristic (and fixed) CTM a priori NO$_2$ profile shapes (Fig. 4). In a first profile (a), the bulk of NO$_2$ is residing near the ground. This profile is applied to pixels sampled during the cold part of the year (November-March) as it is expected to occur over polluted regions during the winter months when vertical mixing is generally weak or non-existing. The second profile (b) is applied to the subset of SCIAMACHY pixels sampled between April and August. It shows a much lower NO$_2$ abundance near the ground representing either a profile over a remote location or a summertime profile resulting from enhanced vertical mixing. As shown in Fig. 4 the use of a different surface pressure scales the profile vertically. The other retrieval (or forward model) parameters including surface albedo, cloud fraction and height, solar zenith angle and so on are kept constant.

4 Results and discussion

4.1 SCIAMACHY NO$_2$ VTCs versus NO$_x$ emissions in Switzerland

4.1.1 Qualitative comparison

Figure 5a shows the comparison between SCIAMACHY NO$_2$ VTCs and the corresponding 09:00–10:00 UTC NO$_x$ emission rates for anticyclonic clear sky (cloud fraction $\leq$0.1) conditions together with a simple linear regression ($n=243$). This simple comparison is limited by a number of factors: The relation between NO$_2$ VTCs and the corresponding NO$_x$ emissions is expected to change with different meteorological conditions which influence the lifetime of NO$_x$ as well as the NO$_x$/NO$_2$ column ratio. Even though the comparison is restricted to anticyclonic conditions, some transport of NO$_x$ into and out of the column may still make a non-negligible contribution to the column budget. In addition, using emission rates from a fixed release time interval is not the best possible choice as discussed in Sect. 3.1.

Nevertheless, the resulting correlation coefficient of $R=0.72$ indicates that the collocated emissions explain more than 50% of the variance in the NO$_2$ VTCs. From this we may conclude that SCIAMACHY is able to observe the sources of air pollution from space even though its sensitivity is strongly decreasing towards the earth’s surface.

Figure 5b shows the sensitivity of the correlation coefficient to the upper limit selected for the cloud fraction; i.e., only SCIAMACHY pixels with cloud fractions lower than or equal to this limit are taken into account. The comparison is carried out for all meteorological conditions (square symbols) as well as for anticyclonic conditions only (circles). The better correlations for the anticyclonic cases support our hypothesis that transport effects play a much smaller role under these conditions which are typically characterized by low wind speeds and rather homogeneous air masses (e.g. no passages of fronts). The general trend of decreasing correlations with increasing cloud fraction thresholds can be understood from clouds screening NO$_2$ located below. Moreover, in cloudy situations, the retrieved column is more strongly affected by the a priori assumption for the vertical NO$_2$ profile as was shown by Schaub et al. (2006). Note that the levelling off of the correlation coefficients for high upper cloud fraction limits in Fig. 5b is mainly due to the small number of cases that are additionally taken into account (denoted by the number of data points additionally shown in Fig. 5).

4.1.2 NO$_x$ lifetime under anticyclonic clear sky conditions

As described in Sect. 3.1 the NO$_x$ lifetime can be deduced from the slope of a correlation plot of NO$_x$ columns $M$ versus the corresponding emission rates $E$ if both are provided in

www.atmos-chem-phys.net/7/5971/2007/  Atmos. Chem. Phys., 7, 5971–5987, 2007
suitable units. Instead of using emission rates from a fixed time interval as in the previous section, effective emission rates $E_{\text{eff}}$ are used in the following calculated according to the iterative method described in Sect. 3.1.

The seasonal mean lifetimes are summarised in Table 1 and shown in Fig. 7 together with other estimates based on published data.

For summer, a large number of estimates is available
- from measurements in power plant plumes: 5 h (Ryerson et al., 1998), 2.8 and 4.2 h (Nunnermacker et al., 2000) and 6.4 h (Stillman, 2000),
- from measurements in urban plumes: Boston: 5.5 h (Spicer, 1982), Nashville: 2.0 h (Nunnermacker et al., 2000), Zurich: 3.2 h (Dommen et al., 1999),
- from GOME NO$_2$ VTCs above Germany: 6.0 h (Beirle et al., 2003) and
- zonal mean in the boundary layer (0–2 km) from the GEOS-CHEM CTM: 3.0 h (Martin et al., 2003).

For spring, Martin et al. (2003) calculated a mid-latitude NO$_x$ lifetime from the GEOS-CHEM model of 8 h. For the winter season, Martin et al. (2003) and Beirle et al. (2003) reported on NO$_x$ lifetimes of 19 and 21 h, respectively.

Additional NO$_x$ lifetimes have been estimated here for the main daytime loss mechanism which is the oxidation of NO$_2$ by OH to form HNO$_3$. These estimates are based on pressure ($\sim$960 hPa) and temperature values representative for the Swiss Plateau and on OH concentrations taken from the BERLIOZ and the SLOPE96 campaigns as well as from long-term OH measurements carried out at Hohenpeissenberg. The BERLIOZ campaign took place at a distance of 50 km from Berlin; the SLOPE96 campaign focused on polluted air masses travelling from the city of Freiburg to the Schauinsland Mountain (south-western Germany); the Hohenpeissenberg station is located in Southern Germany at an altitude of 985 m a.s.l. From a pollution point of view, all regions are similar to the conditions encountered over the Swiss Plateau. For an assumed temperature of 298 K and based on OH concentrations taken from the BERLIOZ and the SLOPE96 campaigns with noon-time values of $(4–8) \times 10^6$ cm$^{-3}$ (Volz-Thomas et al., 2003; Mihelcic et al., 2003) and $(7–10) \times 10^6$ cm$^{-3}$ (Volz-Thomas and Kolahgar, 2000), respectively, the resulting mean daytime NO$_x$ lifetimes in summer are estimated to be 4.6 h and 3.0 h. Seasonally averaged 09:00–10:00 UTC OH concentrations determined from clear sky OH measurements at Hohenpeissenberg carried out between 1999 and 2005 (Rohrer...
Fig. 7. Seasonal NO$_x$ lifetimes (and standard deviations) over the Swiss Plateau under anticyclonic clear sky conditions estimated in this study. Results from other studies are shown for comparison. These data have been deduced from campaigns in the U.S. (Spicer, 1982; Ryerson et al., 1998; Nunnermacker et al., 2000; Sillman, 2000) and in the Swiss Plateau (Dommen et al., 1999), from GOME NO$_2$ VTCs over Germany (Beirle et al., 2003) and from the GEOS-CHEM model (Martin et al., 2003). Additionally, mean NO$_x$ lifetimes against oxidation to HNO$_3$ are calculated for (i) 960 hPa and 298 K with OH concentrations of (4–8) $\times$ 10$^6$ cm$^{-3}$ measured during the BERLIOZ campaign (Volz-Thomas et al., 2003; Mihelcic et al., 2003) and of (7–10) $\times$ 10$^6$ cm$^{-3}$ measured during the SLOPE96 campaign (Volz-Thomas and Kolahgar, 2000) as well as for (ii) seasonally averaged OH concentrations measured by Rohrer and Berresheim (2006) with 960 hPa and assumed temperatures for the summer, spring/fall and winter seasons of 298 K, 288 K and 278 K, respectively.

and Berresheim, 2006; Berresheim, unpublished data, 2006) are used together with assumed temperatures for summer, spring/fall and winter of 298 K, 288 K and 278 K, respectively, to estimate NO$_x$ lifetimes of 6.1, 3.9, 8.2 and 21.0 h for MAM, JJA, SON and DJF, respectively.

Figure 6 shows for each season the SCIAMACHY NO$_x$ columns for anticyclonic clear sky conditions plotted against the corresponding effective NO$_x$ emission rates $E_{\text{eff}}$. Additionally, the linear fits obtained by the weighted orthogonal regression are shown. The relatively small intercepts suggest that under anticyclonic conditions the background NO$_x$ plays a rather marginal role and the SCIAMACHY observations are dominated by the local NO$_x$ emissions. The slopes of the linear fits correspond to the seasonal mean lifetimes. The effective emission rates used in the figure optimally correspond to these lifetimes as assured by the iterative adjustment (Eq. 7).

The comparison of our NO$_x$ lifetimes with independent estimates generally shows a reasonable agreement though our values tend to be at the lower end, in particular in winter. A possible reason is that our estimates are only valid for clear sky situations. In Fig. 7 the dashed line shows additional lifetimes calculated for a higher cloud fraction limit of 0.2. For this higher threshold all lifetimes become larger (see also Table 1). The uncertainty ranges, on the other hand, become smaller because a larger number of data points can be included in the calculation of the slopes. A higher cloud fraction reduces the amount of solar radiation reaching the boundary layer. This in turn decreases the OH concentrations (Rohrer and Berresheim, 2006) which likely explains the larger lifetimes for the higher threshold. The Hohenpeissenberg OH data have been obtained for clear sky days with cloud fractions $\leq$ 1 octa (0.125), too. However, the wintertime lifetime estimate is significantly higher than the SCIAMACHY based estimate for a comparable cloud fraction of 0.1. This may be an indication that nighttime conversion to HNO$_3$ and deposition may be more important losses of NO$_x$ in winter than reaction with OH during daytime. The lifetime estimates of Martin et al. (2003) represent monthly mean values not restricted to clear sky days. There is no obvious discrepancy from our estimates assuming that our values would become larger if even higher cloud fractions would be allowed.

All other estimates are implicitly representing clear sky or at least fair weather conditions, too. The different summertime estimates, for instance, were obtained in the framework of studies dedicated to the investigation of photochemical ozone production focussing on sunny days, or were derived from clear sky satellite observations. Our summertime value of about 3.6 h is well in the range of these estimates. In particular, it is in excellent agreement with another study carried out over Switzerland by Dommen et al. (1999) which obtained a lifetime of 3.2 h (Fig. 7).

Neglecting horizontal transport (smearing effect) could also contribute to an underestimation of lifetimes using our approach. Even though we are focussing on anticyclonic conditions, transport effects may still play a role in particular during winter when a long lifetime (> 10 h) allows for transport over distances larger than the extension of SCIAMACHY pixels despite low wind speeds (< 15 km/h).

4.2 Comparison of GOME and SCIAMACHY NO$_2$ VTCs over Switzerland

SCIAMACHY can better resolve regional structures of air pollution over Switzerland than GOME owing to the much smaller pixel size. This is demonstrated by Fig. 8 showing multi-annual mean NO$_2$ VTC distributions from (a) GOME (1996–2003) and (b) SCIAMACHY (2003–2005) mapped onto a fine 0.125° × 0.125° grid. For each grid cell a mean VTC has been computed by averaging over all clear sky pixels covering the given cell. Whereas the SCIAMACHY data can resolve the large contrast between the Alpine region (blue shadings) and the Swiss Plateau these differences are smeared out in the GOME data. In addition, SCIAMACHY...
can “see” individual population centres such as the areas of Zurich, Basel or the Rhine valley along the border between France and Germany. Elevated values are also seen around the cities of Lausanne and Geneva. All these details are missing in the GOME data. Interestingly, the area of Berne does not stand out even in the SCIAMACHY data, possibly due to the specific location of this city in between the Jura Mountains and the Alps.

For a more quantitative comparison seasonally averaged GOME and SCIAMACHY NO$_2$ VTCs have been calculated from all clear sky pixels with centre coordinates located within the region ROI$_{SP}$ (see Fig. 1) covering the polluted regions of the Swiss Plateau ($7°$ E – $9.5°$ E, $47°$ N – $47.75°$ N) only. Restricting the comparison to this region reduces the influence of the complex Alpine terrain as much as possible, which is particularly relevant for the large GOME pixels (Schaub et al., 2006). In Fig. 9a the resulting SCIAMACHY NO$_2$ VTCs are on average higher than the GOME columns in spring, summer and autumn. Somewhat higher values can be expected for SCIAMACHY because the extended GOME pixels always include less polluted regions outside of the Swiss Plateau. Surprisingly, the SCIAMACHY wintertime values are lower than the ones from GOME, the difference being more pronounced for the median than for the mean values. However, the GOME value in winter is only based on 7 individual pixels. Anticyclonic conditions are typically associated with the formation of fog over the Swiss Plateau during winter which likely explains the poor availability of clear sky pixels.

In order to improve the statistics the cloud fraction threshold has been relaxed to 0.2 in Fig. 9b. For this threshold a reasonable sample size of 32 pixels is available in winter. The differences between SCIAMACHY and GOME become significantly smaller in this case, not only in winter. The relative amplitude of the seasonal cycle (winter maximum – summer minimum), however, remains about 25% lower in the SCIAMACHY data as compared to GOME as highlighted in panel (c) where the values are scaled to the annual average. Again, the differences are more pronounced for the median values which are thought to be a more robust quantity as they are less susceptible to outliers.

For comparison, seasonally averaged NO$_2$ columns estimated from NO$_2$ data measured in situ between January 1997 and June 2003 at 15 ground-based sites at different altitudes in Switzerland and Southern Germany are also shown in Fig. 9c. The elevated sites are assumed to detect NO$_2$ concentrations representative for the appropriate height in the (free) troposphere over flat terrain. These measurements, together with boundary layer in situ measurements and an assumed mixing ratio of 0.02 ppb at 8 km, are used to construct NO$_2$ profiles. The latter are subsequently integrated to tropospheric NO$_2$ columns. Details on the data set and method are given in Schaub et al. (2006). For the present study, the ground-based in situ data set has been restricted to all clear sky days as flagged by the sunshine and high fog parameters from the Alpine Weather Statistics (MeteoSwiss, 1985). The columns are reaching down to an assumed mean Swiss Plateau height of 450 m a.s.l. The normalised seasonal variation of the ground-based data agrees reasonably well with the variation observed by GOME, in particular regarding the large differences between summer and winter. Similarly pronounced seasonal variations of space-borne NO$_2$ VTCs over industrialised regions have also been reported by Petritoli et al. (2004), Richter et al. (2005), van der A et al. (2006) and Uno et al. (2006). The seasonal amplitude in the SCIAMACHY data, however, is lower than in both GOME and ground-based observations: For the median values the amplitude is reduced by more than a factor of two. For the means the reduction is about 25% as mentioned earlier. This suggests that SCIAMACHY values over the Swiss Plateau are possibly underestimated in winter and/or overestimated in summer. It is important to note that this conclusion is only drawn here for the specific KNMI/BIRA retrieval. As has been shown by van Noije et al. (2006) there...
are substantial differences in seasonal variations obtained by different groups using different retrieval algorithms. Moreover, our analysis is limited by the fact that SCIAMACHY and GOME have been sampled differently in space and time and, thus, a perfect agreement is not expected. Nevertheless, the reduced seasonal cycle in SCIAMACHY data may be related to a problem in the retrieval over complex orography discussed in the next section.

4.3 Influence of inadequate treatment of Alpine surface topography on NO₂ VTC retrievals

4.3.1 GOME and SCIAMACHY pixel surface pressures

Errors of GOME NO₂ VTC retrievals were initially discussed by Richter and Burrows (2002) and Boersma et al. (2004). The methods and error budgets of the TEMIS retrievals applied to GOME, SCIAMACHY and OMI data are described in more detail in Blond et al. (2007) and Boersma et al. (2007). They reported on the following retrieval parameters inducing inaccuracies in the AMF calculation, which is the major error source for tropospheric retrievals over polluted regions: the a priori NO₂ profile shape, the surface albedo, cloud characteristics (fraction and height) and aerosol concentration. Here, we propose an additional source for systematic errors only relevant over complex topography: the mean surface pressure (or height) assumed for the retrieval of an individual pixel. This influence has not been investigated in the literature so far. As discussed in Sect. 3.2 the surface pressure \( p_{\text{surf}} \) used in the retrieval is obtained from the TM4 model at coarse resolution (ECMWF/TM4 surface pressure). While for large parts of the globe this will be sufficiently accurate, the low resolution may lead to problems over complex topography such as the Alpine region, in particular if there is a large mismatch in resolution between the satellite pixels and the surface pressure data set.

This is illustrated in Fig. 10 for the situation over the Alpine region. In a coarsely resolved model, the topography is averaged over extended grid elements, typically leading to an underestimation of the effective elevation of mountains.

Fig. 9. Seasonal mean and median NO₂ VTCs from GOME and SCIAMACHY over the ROI_SP (Fig. 1) for cloud fractions \( \leq 0.1 \) 76, 175, 129 and 86 SCIAMACHY pixels and 52, 95, 33 and 7 GOME pixels were available for the four seasons MAM, JJA, SON and DJF, respectively (a). Same as above but for cloud fractions \( \leq 0.2 \). Number of SCIAMACHY pixels per season: 144, 256, 236, and 141; GOME: 106, 154, 88, 32 (b). Seasonal mean and median NO₂ VTCs from GOME, SCIAMACHY, and derived from ground-based in situ NO₂ measurements normalised to the annual mean value. Ground-based in situ columns per season: 139, 165, 69 and 78 (c).

Fig. 10. Illustration of the problem arising for highly resolved satellite pixels over a marked topography when retrieved with coarsely resolved input parameters. The red and blue lines denote the averaged real surface height at the location of individual SCIAMACHY and GOME pixels, respectively. Further, the real topography and the topography given in a coarsely resolved global model are indicated. Over the large GOME pixel extension, the mean height given by a coarsely resolved model better approximates the averaged real surface height than for the smaller SCIAMACHY pixels.
and an overestimation of the effective ground height in the surrounding area. Because the size of SCIAMACHY pixels is much smaller than the size of a model grid cell, it can be expected that the mean model heights $h_{\text{surf}}$ (thin dotted line) show a larger deviation from the effective pixel-averaged surface heights $h_{\text{eff}}$ for the smaller SCIAMACHY pixels (thick red lines) than for GOME (thick blue line).

Figure 11 presents histograms of the differences $\Delta h = h_{\text{surf}} - h_{\text{eff}}$ between ECMWF/TM4 based surface elevations $h_{\text{surf}}$ and effective heights $h_{\text{eff}}$ for all GOME pixels of the years 1996–2003 (b) and SCIAMACHY pixels of the years 2003–2005 (a) over the domain ROI$_{\text{CH}}$ (Fig. 1). Figure 12 displays the corresponding pixel centre locations color-coded by the values of $\Delta h$. The following conclusions can be drawn:

- Due to the smoothed topography in ECMWF/TM4, the surface heights of the GOME and SCIAMACHY pixels are underestimated over the Alps and overestimated over the Swiss Plateau (Fig. 12).

- Lower minimum and higher maximum values of $\Delta h$ are found for SCIAMACHY pixels (Figs. 11 and 12). This can be expected due to the smaller pixel size of SCIAMACHY compared to GOME (Fig. 10).

This demonstrates that certain retrieval parameters, such as the mean pixel surface pressure, can become increasingly inaccurate with increasing resolution of the satellite data if the spatial resolution of the parameters is not improved accordingly. In the following section, the effect of an inaccurate pixel surface pressure on the resulting NO$_2$ VTC is investigated for selected SCIAMACHY columns.

4.3.2 Sensitivity study for selected SCIAMACHY pixels

Figure 13 shows an idealized NO$_2$ profile over the Swiss Plateau where $h_{\text{surf}} > h_{\text{eff}}$. The profile which would be used in the retrieval reaching down to pressure $p_{\text{surf}}$ is shown in black, the profile scaled to the higher effective surface pressure $p_{\text{eff}}$ in red. Over the Alps the situation would be reversed. Following Eq. (1) (Sect. 2.1) and the formulation for the AMF$_{\text{trop}}$ given there, the following systematic errors due to inaccurate surface heights are expected:

- For positive $\Delta h$ ($h_{\text{surf}} > h_{\text{eff}}$, e.g. over the Swiss Plateau, Figs. 12) the near-ground NO$_2$ pollution is in reality located at a lower level than assumed in the retrieval. The retrieval therefore associates the high near-ground pollution with a too high sensitivity (thin dotted line in Fig. 13). This leads to an overestimated AMF$_{\text{trop}}$ and, thus, to an underestimated NO$_2$ VTC.

- For negative $\Delta h$ ($h_{\text{surf}} < h_{\text{eff}}$, e.g. over the Alps, Fig. 12) a tendency towards overestimation of the NO$_2$ VTCs is expected.

The effect of inaccurate pixel surface pressures is investigated for selected SCIAMACHY pixels following the method described in Sect. 3.2. Table 2 presents an overview of the selected pixels and the results obtained by the sensitivity analysis. For the selected pixels over the northeastern Swiss Plateau (see Fig. 3) the surface pressures $p_{\text{surf}}$ and $p_{\text{eff}}$ differ by about 50 hPa, corresponding to about 450 m.

The mean relative change in the AMF$_{\text{trop}}$ due to the changing pixel surface pressure is $-27.2 \pm 1.3\%$ and $-11.7 \pm 1.8\%$ for the profile shapes A and B (Fig. 4), respectively. The mean relative change in the resulting NO$_2$ VTCs is $+37.5 \pm 2.4\%$ and $+13.3 \pm 2.4\%$, respectively. Obviously, the
Fig. 12. Differences between pixel surface heights used in the retrieval and effective surface heights averaged over the respective pixels ($h_{surf} - h_{eff}$) for all GOME (1996–2003) (a) and SCIAMACHY (2003–2005) (b) pixels located over ROI$_{CH}$ (Fig. 1). The ($h_{surf} - h_{eff}$) value for a pixel is indicated at its corresponding centre coordinate.

5 Summary and conclusions

This study has evaluated SCIAMACHY NO$_2$ VTCs above Switzerland and the Alpine region. The clear relationship between a spatially and temporally highly resolved Swiss NO$_x$ emission inventory and SCIAMACHY NO$_2$ columns under anticyclonic meteorological conditions has demonstrated the ability of SCIAMACHY to detect the main NO$_x$ pollution features in Switzerland. The decreasing correlation between the two quantities when taking into account cloudy pixels indicates that SCIAMACHY is less likely to accurately detect sources of air pollution in cloudy situations. From the relation between the SCIAMACHY data and the NO$_x$ emission inventory, seasonal NO$_X$ lifetime estimates have been computed. This computation is complicated by the strong diurnal cycle in NO$_x$ emissions which leads to a coupling between the estimated lifetimes and the relevant emission rate. A method has been demonstrated here solving this problem.
using an iterative approach. A NO$_x$ lifetime of 3.6±0.8 h has been obtained for summer, in good agreement with previous estimates and with lifetimes deduced from published OH concentrations measured during daytime. In winter, the lifetime is much longer on the order of 13.1±0.8 h to 16.0±3.2 h for cloud fraction limits of 0.1 and 0.2, respectively. The larger lifetime for the higher threshold is consistent with fewer OH radicals being present during more cloudy conditions. These values are lower than previous estimates but no firm conclusion can be drawn due to the small number of data available for comparison in winter. Nevertheless, an underestimation of the wintertime NO$_x$ lifetime based on the SCIAMACHY measurements can not be ruled out.

A comparison of SCIAMACHY and GOME NO$_2$ VTCs has shown the advantage of better resolved space-borne data with regard to monitoring the NO$_2$ pollution distribution on a regional scale. However, the quantitative comparison of multi-year seasonal averages provides evidence for a reduced amplitude in the seasonal cycle of SCIAMACHY with comparatively high values in summer and low values in winter. This has further been supported by a comparison with the seasonal variation of NO$_2$ VTCs derived from ground-based in situ measurements which shows a better agreement with GOME.

A problem likely contributing to an underestimation of SCIAMACHY NO$_2$ VTCs over the Swiss Plateau in winter is the use of inaccurate satellite pixel surface pressures derived from a coarse resolution global model in the retrieval. It has been found that the marked topography in the Alpine region can lead to deviations of several hundred meters between assumed and pixel-averaged real surface heights. The sensitivity of the retrieved NO$_2$ VTCs to this problem has been estimated based on selected clear sky SCIAMACHY pixels over the Swiss Plateau and two predefined a priori NO$_2$ profile shapes. An effect of 10–15% has been found for the profile characteristic of summer conditions and of 30–40% for the winter profile. In winter, large concentrations of NO$_x$ are accumulating near the surface due to reduced vertical mixing and a long lifetime. Together with the strongly decreasing sensitivity of UV/VIS instruments towards the surface this results in an enhanced sensitivity to surface pressure errors in winter. Our lifetime estimates for winter may thus be regarded as lower limits. The true lifetimes may be up to 40% higher as they proportionally scale with the NO$_2$ columns.

### Table 2

| Date       | Orbit, pixel number | Cloud fraction | $p_{surf}$ from ECMWFM4 (hPa) | $p_{eff}$ from al,Mo (hPa) | AMF$_{trop}$ calc. for $p_{surf}$ | AMF$_{trop}$ calc. for $p_{eff}$ | rel. change AMF$_{trop}$ (%) | rel. change NO$_2$ VTC (%) |
|------------|----------------------|----------------|-----------------------------|---------------------------|----------------------------------|---------------------------------|-------------------------------|---------------------------|
| **Profile A (Fig. 4)** |                      |                |                             |                           |                                  |                                 |                               |                           |
| 10 Mar 04  | 71117                | 0.02           | 912.22                      | 964.22                    | 1.023                            | 0.776                          | −24.1                         | +31.8                     |
| 22 Jan 05  | 6574                 | 0.01           | 903.92                      | 956.62                    | 1.315                            | 0.941                          | −28.4                         | +39.7                     |
| 17 Nov 05  | 8731                 | 0.01           | 899.13                      | 948.72                    | 1.326                            | 0.958                          | −27.8                         | +38.4                     |
| 17 Nov 05  | 8732                 | 0.01           | 906.25                      | 958.03                    | 1.308                            | 0.942                          | −28.0                         | +38.9                     |
| 17 Nov 05  | 8764                 | 0.01           | 895.73                      | 950.36                    | 1.315                            | 0.944                          | −28.2                         | +39.3                     |
| 23 Nov 05  | 7493                 | 0.07           | 919.30                      | 970.80                    | 1.214                            | 0.904                          | −27.2                         | +37.3                     |
| 23 Nov 05  | 7559                 | 0.00           | 912.22                      | 958.68                    | 1.257                            | 0.916                          | −27.1                         | +37.2                     |
| 26 Nov 05  | 7701                 | 0.06           | 884.32                      | 941.34                    | 1.215                            | 0.890                          | −26.7                         | +36.5                     |
| **Profile B (Fig. 4)** |                      |                |                             |                           |                                  |                                 |                               |                           |
| 17 Apr 04  | 51383                | 0.01           | 899.71                      | 953.97                    | 1.109                            | 0.972                          | −12.4                         | +14.1                     |
| 12 May 04  | 7726                 | 0.02           | 903.72                      | 955.69                    | 1.106                            | 0.933                          | −15.6                         | +18.5                     |
| 21 Jul 04  | 8674                 | 0.01           | 913.20                      | 963.67                    | 1.004                            | 0.889                          | −11.5                         | +12.9                     |
| 21 Jul 04  | 8691                 | 0.03           | 916.65                      | 963.47                    | 0.963                            | 0.858                          | −10.9                         | +12.2                     |
| 09 Aug 04  | 8645                 | 0.01           | 905.58                      | 959.25                    | 0.936                            | 0.835                          | −10.7                         | +12.1                     |
| 03 Jul 05  | 8645                 | 0.09           | 912.73                      | 962.94                    | 0.897                            | 0.803                          | −10.5                         | +11.7                     |
| 10 Aug 05  | 8614                 | 0.01           | 905.79                      | 962.17                    | 0.895                            | 0.801                          | −10.5                         | +11.7                     |
representative. It is thus unlikely that the inadequate description of the Alpine topography is the only reason for the different amplitudes of the seasonal cycle observed by GOME and SCIAMACHY.

For the purpose of air pollution monitoring on a regional scale, highly resolved space-borne data are of great value. However, we further conclude from this study that in order to fully exploit the potential of such data, the forward parameters used in the retrieval should be available on a scale matching the size of the satellite pixels. This not only applies to surface pressure but also to albedo and a-priori NO2 profiles. This is of increasing importance with regard to the decreasing pixel sizes of new instruments from 320×40 km2 (GOME) to 60×30 km2 (SCIAMACHY) to 13×24 km2 (OMI).

Acknowledgements. This work was funded by the Swiss Federal Office for the Environment (FOEN) and supported through ACCENT/Troposat-2. For providing information on ground-based NO2 measurements in Switzerland we acknowledge the Swiss National Air Pollution Monitoring Network (NABEL) and M. Steinbacher. TM4 model data used for the computation of NO2/NO column ratios have been generated within the EU project QUANTIFY and were kindly provided by E. Meijer and P. van Velthoven (KNMI). Furthermore we thank I. DeSmedt and M. Van Roozendael (BIRA/IASB) and H. Eskes and R. van der A (KNMI) for their work on making available the TEMIS GOME and SCIAMACHY NO2 data set used in this study, and the two referees who substantially contributed to the improvement of the manuscript.

Edited by: T. Wagner

References

Beirle, S., Platt, U., Wenig, M., and Wagner, T.: Weekly cycle of NO2 by GOME measurements: a signature of anthropogenic sources, Atmos. Chem. Phys., 3, 2225–2232, 2003, http://www.atmos-chem-phys.net/3/2225/2003/.

Beirle, S., Platt, U., Wenig, M., and Wagner, T.: Highly resolved global distribution of tropospheric NO2 using GOME narrow swath mode data, Atmos. Chem. Phys., 4, 1913–1924, 2004, http://www.atmos-chem-phys.net/4/1913/2004/.

Blond, N., Boersma, K. F., Eskes, H. J., 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.

Boersma, K. F., Eskes, H. J., and Brinksma, E. J.: Error analysis for tropospheric NO2 retrieval from space, J. Geophys. Res., 109, D04311, 2004.

Boersma, K. F., Eskes, H. J., Veefkind, J. P., Brinksma, E. J., van der A, R. J., Snel, 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/.

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.

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.

Chu, S. H. and Meyer, E. L.: Use of ambient ratios to estimate impact of NOx sources on annual NO2 concentrations, Proceedings, 84. Annual Meeting and Exhibition of the Air and Waste Management Association, Vancouver, B.C., 16–21 June 1991, 91-180.6, 16 pp., 1991.

Dentener, F. J. and Crutzen, P. J.: Reaction of N2O5 on tropospheric aerosols: impact on the global distributions of NOx, O3 and OH, J. Geophys. Res., 98, 7149–7163, 1993.

Dentener, F. J., 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/.

Donnen, J., Prévôt, A. S. H., Hering, A. M., Staffelbach, T., Kok, G. L., and Schilllowski, R. D.: Photochemical production and aging of an urban air mass, J. Geophys. Res., 104, D5, 5493–5509, 1999.

Eskes, H. J.: Combined retrieval, modeling and assimilation approach to GOME NO2, in GOA final report, European Commission 5th framework programme 1998–2002, EESD-ENV-99-2, 116–122, Eur. Comm., De Bilt, Netherland, 2003.

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.

FOEN (Swiss Federal Office for the Environment, BAFU): Vom Menschen verursachte Luftschadstoffemissionen in der Schweiz von 1900 bis 2010, Schriftenreihe Umwelt Nr. 256, 1995.

FOEN (Swiss Federal Office for the Environment, BAFU): NABEL – Luftbelastung 2004, Schriftenreihe Umwelt Nr. 388, 2005.

Hueglin, C., Buchmann, B., and Weber, R. O.: Long-term observation of real-world road traffic emission factors on a motorway in Switzerland, Atmos. Environ., 40, 3696–3709, 2006.

IPCC, Climate Change 2001: The Scientific Basis, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK and New York, USA, 2001.

Jaeglé, L., Jacob, D. J., Wang, Y., Weinheimer, A. J., Ridley, B. A., Campos, T. L., Sachse, G. W., and Hagen, D. E.: Sources and chemistry of NOx in the upper troposphere over the United States, Geophys. Res. Lett., 25, 1705–1708, 1998.

Keller, J., Andreani-Aksoyoglu, S., Tinguely, M., and Prévôt, A. S. H.: Emission Scenarios 1985–2010: Their Influence on Ozone in Switzerland, PSI Bericht Nr. 05–07, Paul Scherrer Institut, Villigen PSI, 2005.

Keller, M. and Zbinden, R.: Luftschadstoffemissionen des Strassenverkehrs 1980–2030, Schriftenreihe Umwelt Nr. 355, FOEN (Swiss Federal Office for the Environment), 2004.

Koelmeijer, 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.
Kramm, G., Dlugi, R., Dollard, G. J., Foken, T., Mölders, N., Müller, H., Seiler, W., and Sievering, H.: On the dry deposition of ozone and reactive nitrogen species, Atmos. Environ., 29, 3209–3231, 1995.

Kühlein, J.: Uncertainties in the arithmetical determination of pollutant emissions from road traffic and demands on future models, PhD thesis, University of Stuttgart, 2004.

Kühlein, J. and Friedrich, R.: Uncertainties of modelling emissions from road transport, Atmos. Environ., 34, 4603–4610, 2000.

Kunihikshnan, T., Lawrence, M. G., von Kuhlmann, R., Richter, A., Ladstätter-Weissenmayer, A., and Burrows, J. P.: Analysis of tropospheric NO$_2$ over Asia using the model of atmospheric transport and chemistry (MATCH-MPIC) and GOME-satellite observations, Atmos. Environ., 38, 581–596, 2004.

Leue, C., Wenig, M., Wagner, T., Klimm, O., Platt, U., and Jaehne, B.: Quantitative analysis of NO$_x$ emissions from Global Ozone Monitoring Experiment satellite image sequences, J. Geophys. Res., 106, 5493–5505, 2001.

Martin, R. V., Jacob, D. J., Chance, K., Kurosu, T. P., Palmer, P. I., and Evans, M. J.: Global inventory of nitrogen oxide emissions constrained by space-based observations of NO$_2$ columns, J. Geophys. Res., 108, D17, 4537, doi:10.1029/2003JD003453, 2003.

MeteoSwiss: Alpine Weather Statistics (Alpenwetterstatistik – Witterungskalender: Beschreibung der einzelnen Parameter), MeteoSwiss, Switzerland, 1985.

Mihelcic, D., Holland, F., Hofzumahaus, A., Hoppe, L., Konrad, S., Müggen, P., Pätz, H.-W., Schäfer, H.-J., Schmitz, T., Volz-Thomas, A., Bächmann, K., Schlomski, S., Platt, U., Geyer, A., Aliche, B., and Moortgat, G. K.: Peroxy radicals during BERLIOZ at Pabststett: measurements, radical budgets and ozone production, J. Geophys. Res., 108, D4, 8254, doi:10.1029/2003JD003104, 2003.

Nunnermacker, L. J., Kleinman, L. I., Imre, D., Daum, P. H., Lee, Y.-N., Lee, J. H., Springer, S. R., and Newman, L.: NO$_x$ lifetimes and O$_3$ production efficiencies in urban and power plant plumes: analysis of field data, J. Geophys. Res., 105, D7, 9165–9176, 2000.

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, 14539–14550, 2001.

Palmer, P. I., Jacob, D. J., Fiore, A. M., Martin, R. V., Chance, K., and Kurosu, T. P.: Mapping isoprene emissions over North America using formaldehyde column observations from space, J. Geophys. Res., 108, D6, 4180, doi:10.1029/2002JD002153, 2003.

Petritoli, A., Bonasoni, P., Giovanelli, G., Ravegnani, F., Kostadinov, I., Bortoli, D., Weiss, A., Schaub, D., Richter, A., and Forteza, F.: First comparison between ground-based and satellite-borne measurements of tropospheric nitrogen dioxide in the Po basin, J. Geophys. Res., 109, D15307, doi:10.1029/2004JD004547, 2004.

Platt, U.: Differential optical absorption spectroscopy (DOAS), Chem. Anal. Series, 127, 27–83, 1994.

Richter, A. and Burrows, J. P.: Tropospheric NO$_2$ from GOME measurements, Adv. Space Res., 29, 1673–1683, 2002.

Richter, A., Burrows, J. P., Nüss, H., Granier, C., and Niemeier, U.: Increase in tropospheric nitrogen dioxide over China observed from space, Nature, 437, doi:10.1038/nature04092, 2005.

Rohrer, F. and Berresheim, H.: Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, Nature, 442, 184–187, 2006.

Ryerson, T. B., Buhr, M. P., Frost, G. J., Golden, P. D., Holloway, J. S., Hübler, G., Jobson, B. T., Kuster, W. C., McKeen, S. A., Parrish, D. D., Roberts, J. M., Sueper, D. T., Trainer, M., Williams, J., and Fehsenfeld, F. C.: Emissions lifetimes and ozone formation in power plant plumes, J. Geophys. Res., 103, D17, 22 569–22 583, 1998.

Schaub, D., Boersma, K. F., Kaiser, J. W., Weiss, A. K., Eskes, H. J., and Buchmann, B.: Comparison of GOME tropospheric NO$_2$ columns with NO$_2$ 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., Weiss, A. K., Kaiser, J. W., Petritoli, A., Richter, A., Buchmann, B., and Burrows, J. P.: A transboundary transport episode of nitrogen dioxide as observed from GOME and its impact in the Alpine region, Atmos. Chem. Phys., 5, 23–37, 2005, http://www.atmos-chem-phys.net/5/23/2005/

Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics – from air pollution to climate change, John Wiley and Sons, New York, 1998.

Sillman, S.: Ozone production efficiency and loss of NO$_x$ in power plant plumes: photochemical model and interpretation of measurements in Tennessee, J. Geophys. Res., 105, D7, 9189–9202, 2000.

Solomon, S., Portmann, W., Sanders, R. W., Daniel, J. S., Madsen, W., Bartram, B., and Dutton, E. G.: On the role of nitrogen dioxide in the absorption of solar radiation, J. Geophys. Res., 104, 12 047–12 058, 1999.

Spicer, C. W.: Nitrogen oxide reactions in the urban plume of Boston, Science, 215, 4536, 1095–1097, 1982.

Stamnes, P.: Spectral radiance modelling in the UV-Visible Range, in IRS 2000: Current problems in Atmospheric Radiation, Edited by: Smith, W. L. and Timofeyev, Y. M.: A. Deepak Publ., Hampton (VA), 2001.

Steinbacher, M., Zellweger, C., Schwarzenbach, B., Bugmann, S., Buchmann, B., Ordoñez, C., Prevot, A. S. H., and Hueglin, C.: Nitrogen dioxide measurements at rural sites in Switzerland: Bias of conventional measurement techniques, J. Geophys. Res., 112, D11307, doi:10.1029/2006JD007971, 2007.

Uno, I., He, Y., Ohara, T., Yamaji, K., Kurokawa, J.-I., Katayama, M., Wang, Z., Noguchi, K., Hayashida, S., Richter, A., and Burrows, J. P.: Systematic analysis of interannual and seasonal variations of model-simulated tropospheric NO$_2$ in Asia and comparison with GOME-satellite data, Atmos. Chem. Phys. Disc., 6, 11 181–11 207, 2006.

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 NO$_2$ over China, J. Geophys. Res., 111, D12317, doi:10.1029/2005JD006594, 2006.

Vandaele, A. C., Fayt, C., Hendrick, F., et al.: An intercomparison campaign of ground-based UV-visible measurements of NO$_2$, BrO, and OCIO slant columns: Methods of anal-
ysis and results for NO\textsubscript{2}, J. Geophys. Res., 110, D08305, doi:10.1029/2004JD005423, 2005.

van Noije, T. P. C., Eskes, H. J., Dentener, F. J., Stevenson, D. S., et al.: Multi-model ensemble simulations of tropospheric NO\textsubscript{2} compared with GOME retrievals for the year 2000, Atmos. Chem. Phys., 6, 2943–2979, 2006, http://www.atmos-chem-phys.net/6/2943/2006/.

Volz-Thomas, A., Geiss, H., Hofzumahaus, A., and Becker, K.-H.: Introduction to special section: photochemistry experiment in BERLIOZ, J. Geophys. Res., 108, D4, 8252, doi:10.1029/2001JD002029, 2003.

Volz-Thomas, A. and Kolahgar, B.: On the budget of hydroxyl radicals at Schauinsland during the Schauinsland Ozone Precursor Experiment (SLOPE96), J. Geophys. Res., 105, D1, 1611–1622, 2000.

York, D.: Least-square fitting of a straight line, Can. J. Phys., 44, 1079–1086, 1966.