Doctoral Thesis

Tropospheric nitrogen dioxide from GOME and SCIAMACHY measurements over the alpine region
Strengths and limitations

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TROPOSPHERIC NITROGEN DIOXIDE FROM GOME AND SCIAMACHY MEASUREMENTS OVER THE ALPINE REGION: STRENGTHS AND LIMITATIONS

A dissertation submitted to the
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Summary

Nitrogen oxides, NO\(_x\) \(\equiv\) NO + NO\(_2\), are among the most important trace gases in the troposphere, the lowest and approximately 10 km deep layer of the earth’s atmosphere. Due to their high reactivity, nitrogen oxides are involved in many chemical reactions taking place in ambient air including the formation of ozone. The investigation of such processes requires knowledge about the NO\(_x\) concentration in the troposphere and its distribution. Roughly 10 years ago, the Global Ozone Monitoring Experiment (GOME) spectrometer onboard the ERS-2 satellite for the first time enabled the determination of space-borne vertical tropospheric column densities (VTCs) of nitrogen dioxide (NO\(_2\)). In contrast to ground-based or airborne measurements, space-borne NO\(_2\) retrievals provide a global coverage within only a few days. However, the processing of the measured UV-visible radiance spectra to retrieve tropospheric NO\(_2\) columns is complex. It requires radiative transport modelling and uses a number of (a priori) assumptions on the state of the atmosphere. While pollution hot spot regions are visible in a qualitative sense, the quantitative use of space-borne data on a pixel-to-pixel basis is more challenging. In this work, the quality of space-borne NO\(_2\) VTCs in particular with regard to their use for air pollution monitoring and modelling in Switzerland is explored based on data from GOME and from the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY). The data are provided by the University of Bremen and the Royal Netherlands Meteorological Institute (KNMI).

A first case study is dedicated to exceptionally high NO\(_2\) columns detected from the GOME spectrometer above a dense cloud cover on 17 February 2001. Clouds are a major problem for tropospheric NO\(_2\) retrievals because they hinder to a large extent the penetration of solar radiation into the lower troposphere and hence into the polluted planetary boundary layer. The case study demonstrates that NO\(_2\) columns can be severely in error when NO\(_2\) pollution layers are lifted above a cloud cover and when this process is not accurately reflected in the a-priori NO\(_2\) profiles used in the retrieval. By combining the GOME NO\(_2\) columns with trajectory calculations the transboundary (i.e. cross-border) transport of the NO\(_2\) pollution towards the Alpine region is estimated. The case study demonstrates that significant pollution transport can occur in connection with fronts and, for this episode, contribute by more than 50\% to NO\(_2\) concentration levels measured at ground sites in the Alpine region.

The general quality of GOME NO\(_2\) VTCs is investigated by a detailed long-term comparison of NO\(_2\) VTCs for clear sky and cloudy conditions with coincident ground-based tropospheric NO\(_2\) columns. The latter are deduced from in situ measurements operated in the Swiss Plateau and at different altitudes in the Alps. By applying averaging kernel (AK) information, a more detailed interpretation of the difference between the two column data sets can be given: the method allows to quantify the contribution to the total difference that is due to the difference between the shapes of the a priori NO\(_2\) profile and the profile derived from ground-based measurements. The study indicates a good agreement between the two independent NO\(_2\) column quantities for anticyclonic clear sky conditions (pixel cloud fraction \(\leq 0.1\)) with GOME being on average slightly lower by -7\% than the ground-based data. In general, the shapes of the a priori and the ground-based NO\(_2\) profiles are found to be similar.
A poorer agreement is found for the cloudy cases (pixel cloud fraction $\geq 0.75$) with a mean relative difference of 60% and GOME data on average overestimating the ground-based columns. In contrast to the clear sky cases, a clear improvement is achieved when the ground-based profiles are first multiplied with the AK. This suggests that a significant part of the difference between the two column data sets is due to uncertainties in the a priori NO$_2$ profile shape.

In a third study, both seasonal NO$_x$ lifetime estimates (derived from the comparison of SCIAMACHY NO$_2$ VTCs with a Swiss NO$_x$ emission inventory) and the comparison of seasonal NO$_2$ VTCs derived from GOME and SCIAMACHY provide evidence for a systematic underestimation of SCIAMACHY NO$_2$ VTCs above the Swiss Plateau during the winter season. A possible explanation not discussed in literature previously is the use of inaccurate pixel surface heights taken from coarse resolution global models in the retrieval. The marked topography in the Alpine region can lead to deviations of several hundred meters between assumed and real mean surface height over the extension of a pixel. The resulting error is estimated based on selected clear sky SCIAMACHY NO$_2$ VTCs over the Swiss Plateau and two fixed a priori NO$_2$ profiles. For a profile shape with the bulk of the NO$_2$ residing near the ground an effect of nearly 40% on the computed NO$_2$ columns is found. This result suggests that over regions with a marked topography, inaccurate pixel surface pressures can be among the most important error sources for tropospheric retrievals. This is particularly true if the satellite pixel resolution is significantly higher than the resolution of the a priori information used in the data retrieval.
Zusammenfassung

Stickoxide, \( \text{NO}_x \) (\( \equiv \text{NO} + \text{NO}_2 \)), gehören zu den wichtigsten Spurengasen in der Troposphäre, der untersten, etwa 10 km dicken Luftschicht der Erdatmosphäre. Aufgrund ihrer grossen Reaktivität nehmen die Stickoxide an zahlreichen in der Umgebungsluft ablaufenden chemischen Reaktionen teil und spielen insbesondere bei der Bildung von Ozon eine entscheidende Rolle. Zur Erforschung solcher Prozesse werden Kenntnisse über die \( \text{NO}_x \)-Konzentration und -Verteilung benötigt. Vor etwas mehr als 10 Jahren konnten zum ersten Mal troposphärische Vertikalsäulenkonzentrationen (TVS) von Stickstoffdioxid (\( \text{NO}_2 \)) aus Messungen des GOME (Global Ozone Monitoring Experiment) Spektrometers an Bord des ERS-2 Satelliten gewonnen werden. Im Gegensatz zu boden- oder Flugzeug-gestützten Messungen liefern Satellitenmessungen \( \text{NO}_2 \)-Daten mit einer globalen Abdeckung innerhalb von wenigen Tagen. Das Verfahren zur Berechnung der \( \text{NO}_2 \)-TVS aus den gemessenen UV-sichtbaren Strahlungsspektren ist allerdings äusserst komplex und stützt sich auf Strahlungstransportmodelle sowie auf (a priori) Annahmen zum Zustand der Atmosphäre. So sind Regionen mit erhöhter Luftverschmutzung in den Daten in qualitativer Hinsicht zwar deutlich sichtbar, doch die quantitative Verwendung einzelner Satellitenpixel stellt eine grosse Herausforderung dar. Im Hinblick auf deren Nutzung für die Beobachtung von Luftschadstoffen untersucht die vorliegende Arbeit deshalb die Qualität von \( \text{NO}_2 \)-TVS der Spektrometer GOME und SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric Chartography), welche von der Universität Bremen und dem Königlich-Niederländischen Meteorologischen Institut (KNMI) prozessiert wurden.

Eine erste Fallstudie widmet sich aussergewöhnlich hohen \( \text{NO}_2 \)-TVS, die aus GOME-Messungen oberhalb einer ausgedehnten Wolkendecke am 17. Februar 2001 gewonnen wurden. Wolken sind problematisch, weil sie die Sonnenstrahlung praktisch nicht passieren lassen. Deshalb können kaum Informationen über die \( \text{NO}_2 \)-Mengen in der verschmutzten Grenzschicht gewonnen werden. Die Fallstudie zeigt, dass \( \text{NO}_2 \)-Säulen stark fehlerbehaftet sein können, wenn \( \text{NO}_2 \)-Verschmutzung über die Wolkendecke angehäuft und dieser Prozess in a priori \( \text{NO}_2 \)-Profilen für die Datenprozessierung ungenügend abgebildet ist. Durch Kombination der GOME-Säulen mit Luftmassenträgerkonzentrationen wird der grenzüberschreitende Transport der \( \text{NO}_2 \)-Verschmutzung in die alpine Region abgeschätzt. Die Fallstudie demonstriert den ausgeprägten Verschmutzungstransport im Zusammenhang mit einer Front und zeigt auf, dass dieses Transportereignis einen Beitrag von über 50% zu den gemessenen \( \text{NO}_2 \)-Konzentrationen an Bodenstationen in der alpinen Region geliefert hat.

Um die generelle Qualität von GOME \( \text{NO}_2 \)-TVS zu ermitteln, werden letztere unter Schönwetter- und Wolkenbedingungen mit \( \text{NO}_2 \)-Säulen verglichen, welche aus Bodenmessungen in verschiedenen Höhen im Alpenraum abgeleitet werden. Die Verwendung von averaging kernel (AK)-Information ermöglicht dabei eine detaillierte Interpretation der Differenz zwischen den beiden Säulen-Datensätzen: die Methode erlaubt die Quantifizierung desjenigen Anteils an der Differenz, welcher auf den Unterschied zwischen den zwei Profilformen zurückzuführen ist, dem a priori \( \text{NO}_2 \)-Profil und dem aus den Bodendaten abgeleiteten \( \text{NO}_2 \)-Profil.

Für antizyklonale Schönwetter-Bedingungen (Wolkenanteil in Satellitenpixeln \( \leq 0.1 \)) findet sich eine gute Übereinstimmung zwischen den beiden unabhängigen \( \text{NO}_2 \)-
TVS. Die mittlere relative Differenz bezüglich der bodengestützten NO2-Säulen beträgt -7(±40)%, wobei letztere von den GOME-Säulen im Mittel leicht unterschätzt werden. Generell sind die Formen der a priori NO2-Profile und der aus den Bodendaten abgeleiteten NO2-Profile unter Schönwetter-Bedingungen ähnlich. Eine schlechtere Übereinstimmung zeigt sich für die Wolkenfälle (Wolkenanteil in Pixeln ≥ 0.75). Die GOME-Säulen liegen hier im Mittel um 60(±118)% über den bodengestützten Werten. Anders als bei den Schönwetterfällen wird die Differenz deutlich geringer, wenn die bodengestützten Profile vorgängig mit dem AK multipliziert werden. Dies deutet darauf hin, dass ein beträchtlicher Teil der Differenz zwischen den Säulen-Datensätzen auf ungenaue a priori NO2-Profilformen zurückzuführen ist.

In einer dritten Studie weisen sowohl die Abschätzung saisonaler NOx-Lebensdauern (abgeleitet aus SCIAMACHY NO2-TVS und einem Schweizerischen NOx-Emissionsinventar) als auch der Vergleich saisonal gemittelten Säulen von GOME und SCIAMACHY auf eine systematische Unterschätzung der winterlichen SCIAMACHY NO2-TVS über dem Schweizerischen Mittelland hin. Eine mögliche Erklärung dafür sind ungenaue mittlere Pixel-spezifische Bodenhöhen, welche aus grob aufgelösten globalen Modellen abgeleitet und in der Datenprozessierung verwendet werden. Die ausgeprägte alpine Topographie kann zu Abweichungen von mehreren hundert Metern zwischen der angenommenen und der tatsächlichen mittleren Bodenhöhe führen. Für eine Auswahl von Schönwetter-SCIAMACHY-NO2-TVS über dem Schweizerischen Mittelland wird der resultierende Effekt abgeschätzt. Dabei werden zwei (fixe) a priori NO2-Profile verwendet. Für eine Profilform mit dem Grossteil des NO2 in Bodennähe wird ein Effekt von nahezu 40% auf die resultierenden NO2-Säulen berechnet. Über einer Region mit ausgeprägter Topographie können ungenaue mittlere Pixel-spezifische Bodenhöhen demnach eine der bedeutendsten Fehlerquellen für NO2-TVS sein; insbesondere dann, wenn die Auflösung der Satellitenpixel deutlich höher ist als diejenige der in der Datenprozessierung verwendeten Modelle.
1 Introduction

Three keywords known to every regular newspaper reader dominate the discussion about the earth’s atmosphere: “summer smog”, “ozone hole” and “greenhouse effect”. For the chemical processes standing behind these, nitrogen oxides (\(\text{NO}_x \equiv \text{NO} + \text{NO}_2\)) play an important direct, or at least indirect role. Besides the abundance of the main atmospheric constituents – nitrogen (\(\text{N}_2, 78\%\)), oxygen (\(\text{O}_2, 21\%\)) and argon (\(\text{Ar}, <1\%\)) – \(\text{NO}_x\) exhibits tiny concentrations in the order of one part per billion (ppb), i.e. one \(\text{NO}_x\) molecule per one billion \(\left(10^9\right)\) air molecules. At first glance, one might be surprised that compounds of such extremely low abundance play a key role in atmospheric chemistry at all. However, it is precisely this small abundance that mirrors the short chemical lifetime of \(\text{NO}_x\) which is caused by its high reactivity and its involvement in a large number of chemical processes. The investigation of these processes requires high quality \(\text{NO}_x\) concentration data. Whereas \(\text{NO}_x\) measurements at ground-based in situ sites have been operated for decades, satellite-borne spectrometers only for roughly 10 years enable the measurement of tropospheric \(\text{NO}_2\) (Fig 1.1). Such measurements have the advantage of providing a global coverage within a relatively short time. Particularly for nitrogen species, this is a critical issue because of the non-uniform distribution of \(\text{NO}_x\) emissions, their short chemical lifetime and the meteorological transport, resulting in a spatially and temporally highly variable \(\text{NO}_x\) concentration distribution. A disadvantage of (tropospheric) space-borne retrievals is the uncertainty of the resulting data product, most pronounced in the presence of clouds. The objective of the present thesis is the evaluation of the quality of tropospheric \(\text{NO}_2\) retrievals from the Global Ozone Monitoring Experiment (GOME) and the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) with regard to their use for air pollution monitoring and modelling in Switzerland.

![Figure 1.1. Mean tropospheric NO\(_2\) columns over central Europe between 2003 and 2005 calculated from clear sky SCIAMACHY data (pixel cloud fraction \(\leq 0.1\)) provided by KNMI.](image)
1.1 A short history of air pollution

The following section gives a short summary on the history of air pollution based on Brimblecombe (1987) and the free online encyclopaedia Wikipedia (www.wikipedia.org).

“As soon as I had gotten out of the heavy air of Rome and from the stink of the smoky chimneys thereof, which, being stirred, pouted forth whatever pestilential vapors and soot they had enclosed in them, I felt an alteration of my disposition.”

Seneca, 61 A.D.

The statement from Lucius Annaeus Seneca – often known simply as Seneca or Seneca the Younger, a Roman philosopher, statesman and dramatist (Fig. 1.2) – reveals that pernicious effects of air pollution are not a new phenomenon. This is probably one of the first documents of air pollution at all.

Roughly twelve hundred years later, in the 13th century, coal began to replace wood for domestic heating. It was during that time when King Edward I prohibited the burning of coal in order to protect the health of his subjects. This first recorded legislation dates from 1273 and marks the start of air pollution control. In the 1500s, it is understood that Elizabeth I banned the use of coal while the Parliament was sitting with the penalty of death.

In the 17th century, John Evelyn wrote Fumifugium or The Inconveniencie of the Aer and Smoak of London as a call to clean up the city of London (Fig. 1.3). To combat the pollution problem, Evelyn proposed moving such industries as breweries and lime-burners to locations far outside of London to prevent the soot from settling in the city. Further, Evelyn suggested a correlation between the death rate indicated in London’s ‘bills of mortality’ (documents that listed births and the numbers and causes of deaths) and the incidence of particularly severe fogs. His conclusions have been substantiated by the detailed records of foggy weather kept by his contemporary, the astrologer John Gadbury, who described the coincidence between the arrivals of two “Great Stinking Fogs” (later often called the “London smog”) in mid-November 1679 and the unusual rise in deaths in the bills of mortality.
The industrial revolution was the major technological, socioeconomic and cultural change that took place during the late 18th and early 19th century. It began in Britain, spread throughout the world and led to environmental pollution as we know it today. The emergence of great factories and consumption of immense quantities of coal and other fossil fuels gave rise to unprecedented air pollution. In the 20th century a number of severe smog episodes stimulated the discussion about the issue of air pollution and its impact on human health. Most famous is the Great London Smog from December 1952. Then, the combustion of coal and emissions from power plants together with a temperature inversion inhibiting the vertical mixing – and, thus, the dilution of the pollution – led to a 5 day episode of the worst smog that ever occurred in London. During the Great London Smog, an excess number of 4000 deaths were to complain. The air pollution was characterised by large sulphur dioxide (SO$_2$) and particle concentrations, which since then is known as the London, winter or sulphurous smog. Whereas, today, the sulphurous air pollution is of minor importance for our region because air pollution control measures successfully and significantly reduced the SO$_2$ emissions during the 1980s (e.g. FOEN, 2005), problems with high particulate concentrations still remain to be solved. Another air pollution type that remains problematic is the so-called summer or photochemical smog, which is characterised by enhanced near ground ozone (O$_3$) concentrations. Vegetation damages in the Los Angeles area due to photochemical air pollution has first been described by Middleton et al. (1950). Over Europe, the background concentration of ozone has increased by more than a factor of 2 since pre-industrial times (Volz and Kley, 1988). An ozone increase of a factor of 2.2 at the Alpine site of Arosa for the second half of the last century has been reported by Staehelin et al (1994). The increasing summertime ozone concentrations are caused by increasing emissions of nitrogen oxides and other precursors such as carbon monoxide (CO), methane (CH$_4$) and reactive organic compounds (ROC).
current century, primarily the continuing increase of CH$_4$ and NO$_x$ emissions is expected to result in continuously increasing tropospheric ozone (Prather et al., 2003). Today, the most pronounced increase in emissions takes place in economically rapidly developing countries such as China. Based on space-borne NO$_2$ observations from GOME and SCIAMACHY above polluted regions there, Richter et al. (2005) and Van der A et al. (2006) reported on a highly significant increase of NO$_2$ tropospheric column amounts of up to 50% over the last decade.

Towards the end of the 20$^{th}$ century, two other problematic topics related to air pollution have been increasingly focused on, namely the “(anthropogenic) greenhouse effect” and the “ozone hole”.

The greenhouse effect, first discovered by Joseph Fourier in 1824, is the radiative forcing process by which atmospheric gases (the so-called “greenhouse gases”, e.g. water vapour, carbon dioxide, methane, ozone and others) warm a planet due to absorption and re-emission of infrared radiation. One has to distinguish between the “natural” and the “anthropogenic” greenhouse effect: the first is of fundamental importance for the development of life on our planet, as it is responsible for a liveable temperature regime. The anthropogenic greenhouse effect, on the other hand, is the additional radiative forcing induced by the dramatic increase of greenhouse gas emissions due to the increasing combustion of coal and fossil fuels taking place since the industrial revolution. Due to the long atmospheric lifetime of the majority of the greenhouse gases of several to up to hundreds of years, these gases accumulate in the atmosphere around the globe (IPCC, 2001). Both the predicted increase as well as the increase rate of the mean global temperature due to anthropogenic activity is unprecedented for the history of climate on our planet and will probably be one of the largest challenges for mankind ever. For this reason, the United Nations Framework Convention on Climate Change (UNFCCC) established the Kyoto Protocol requiring that developed countries decrease their greenhouse gas emissions by 5% relative to 1990 emission levels until 2008-2010.

A second problem of global scale was discovered in the second half of the 20$^{th}$ century. Mid of the 1980s, substantial reductions of up to 70% in the total ozone column were observed during the austral (southern hemispheric) spring (Farman et al., 1985). This seasonal decrease in the total ozone over the earth's Poles (most pronounced over Antarctica) is commonly referred to as the "ozone hole". The ozone depletion takes place in the stratosphere, the atmospheric layer between 12 and 50 km altitude. There, the ozone molecules absorb ultraviolet (UV) sunlight harmful to the biota on the earth’s surface. In the 70ies it was found that catalytic reaction cycles including atomic chlorine and bromine play an important role in the anthropogenic destruction of stratospheric ozone. Again, the global scale of this problem is due to the involvement of long lived substances: the primary source of the above mentioned halogen atoms in the stratosphere is the photodissociation of chlorofluorocarbon (CFC) and bromofluorocarbon (halon) compounds. These can persist in the troposphere for hundreds to thousands of years and, thus, slowly move into the stratosphere. In order to slow down the stratospheric ozone destruction, the Montreal Protocol was signed in 1987. It bans the production of ozone-depleting substances such as CFCs and halons.

Due to their high reactivity, nitrogen oxides play an important direct or indirect role for many of the so far mentioned air pollution issues. For example, nitrogen species catalyse the ozone production near the earth’s surface and are therefore jointly responsible for summertime photochemical smog episodes. Because ozone is also a
greenhouse gas, nitrogen oxides additionally play a role for the greenhouse effect. They further affect the global warming by their reaction with the hydroxyl radical (OH). The latter in turn decomposes greenhouse gases such as methane. In the stratosphere, nitrogen oxides catalytically destruct ozone themselves and are additionally involved in other ozone destructing reaction cycles by offering pathways for the deactivation of ozone depleting substances. The role of NO\textsubscript{x} for the chemistry of both the stratosphere and the troposphere is described in more detail in section 2.1.

1.2 Detecting air pollution from space
In order to investigate and understand air pollution issues, but also to evaluate air pollution control measures, the measurement of the corresponding atmospheric species is crucial. For decades, air quality monitoring and modelling has mainly been based upon ground-based point measurements and limited aircraft measurement campaigns. In contrast, the emerging space-borne measurements have the advantage of a global view and can therefore provide measurements for regions not covered by ground-based stations (Fig. 1.4).

Figure 1.4. Global mean tropospheric NO\textsubscript{2} columns based on SCIAMACHY retrievals for the year 2004 (image processed by KNMI; available on http://www.temis.nl).

Because satellites carrying measurement devices orbit the earth outside the atmosphere and detect the latter from a “remote” location, such measurements are “remote sensing” techniques. Such techniques exploit the fact that each atmospheric gas is characterised by its absorption and emission spectra describing how the molecules respond to different frequencies of radiation. Space-borne remote sensing
instruments measure the resulting spectral features over a range of wavelengths. These signatures are then used to derive information on the atmospheric composition. Atmospheric absorption is dominated by water vapour (H$_2$O), carbon dioxide (CO$_2$), and ozone. Smaller contributions originate from methane and other trace gases. Whereas broadband spectrometers can be used for measurements of the dominant gases, high spectral resolution spectrometers are required to measure optically thin trace species, since they produce weaker signals. The spectral windows containing the molecule specific signatures that are exploited in the data retrieval strongly differ for different molecules. For the NO$_2$ retrieval, signatures in the UV-visible wavelength range are used to estimate its abundance in the atmosphere. However, this so-called “retrieval” is far from being straightforward. The processing requires the modelling of the radiative transfer in the atmosphere. Further, it is based on the inclusion of a priori information on the state of the atmosphere, e.g. a priori NO$_2$ profiles derived from chemistry transport models (CTMs). Obviously, space-borne data – and in particular tropospheric retrievals – can be affected by a number of error sources. The retrieval of vertical tropospheric NO$_2$ columns from GOME and SCIAMACHY measurements – the data used in the present thesis – is a 3-step process whose principles are described in section 2.2. In the same section, an overview over other instruments enabling the retrieval of NO$_2$ can be found.

1.3 Thesis outline

Tropospheric retrievals of space-borne measurements can be affected by large errors. The aim of the present thesis is the assessment of satellite data in terms of quality and usability for air pollution monitoring and modelling. With the focus on tropospheric NO$_2$ over Switzerland and adjacent regions, the scientific questions can be summarised as follows:

1. Can space-borne NO$_2$ vertical tropospheric column densities (VTCs) observed above clouds be used for air pollution modelling?

2. What is the quality of GOME NO$_2$ VTCs under clear sky and cloudy conditions with a special focus on the a priori NO$_2$ profile shape?

3. What is the reliability of SCIAMACHY NO$_2$ VTC retrievals over the Alpine region and how are they affected by the topography?

After elaborating the scientific background in section 2, section 3 addresses the first question by carrying out a case study. Although clouds obscure the NO$_2$ below and represent a significant error source for the retrieval, a dense cloud cover with a known height could also provide an outstanding situation, because the high albedo above the cloud leads to a high sensitivity of the space-borne measurement to the trace gas of interest. Nevertheless, NO$_2$ columns above clouds are not directly usable for near-ground air pollution monitoring. Section 3 presents a method based on trajectories which implicitly estimates the additional sub-cloud NO$_2$ distribution in order to model concentrations at ground stations. The method is applied to a transboundary (or cross-border) pollution transport episode which led to high above cloud NO$_2$ VTCs observed by GOME over middle Europe.
The second question is addressed in section 4 where NO$_2$ VTCs retrieved from GOME measurements are compared to coincident ground-based tropospheric NO$_2$ columns. The ground-based columns are deduced from in situ measurements at different altitudes in the Alps for 1997 to June 2003, yielding a unique long-term comparison of GOME NO$_2$ VTC data with independently derived tropospheric NO$_2$ profiles. A first comparison relates the GOME retrieved tropospheric columns to the tropospheric columns obtained by integrating the ground-based NO$_2$ measurements. For a second comparison, the tropospheric profiles constructed from the ground-based measurements are first multiplied with the averaging kernel (AK) of the GOME retrieval. The second approach makes the comparison independent from the a priori NO$_2$ profile used in the GOME retrieval. This allows splitting the total difference between the column data sets into two contributions: one that is due to differences between the a priori and the ground-based NO$_2$ profile shapes, and another that can be attributed to uncertainties in both the remaining retrieval parameters (such as, e.g., surface albedo or aerosol concentration) and the ground-based in situ NO$_2$ profiles. The work described in section 4 is the first detailed validation study that

- carries out a comparison with in situ measurements through inclusion of AK information,
- investigates tropospheric NO$_2$ retrieval errors under cloudy situations.

Section 5 addresses the third question by relating SCIAMACHY NO$_2$ VTCs over Switzerland and the Alpine region to a temporally and spatially highly resolved NO$_x$ emission inventory available for Switzerland. The relation between the two quantities is used to estimate seasonal NO$_x$ lifetimes over the Swiss Plateau (the densely populated Swiss lowlands). Second, seasonally averaged NO$_2$ VTCs from SCIAMACHY are compared to those from GOME. Both studies provide evidence for a systematic underestimation of SCIAMACHY NO$_2$ columns over the Swiss Plateau, particularly during the winter season. Inaccurate satellite pixel surface heights as a possible reason for this and a sensitivity study for SCIAMACHY pixels over the Swiss Plateau are discussed.

The thesis ends with section 6 containing the conclusions and outlook.
References


2 Scientific background

First, an overview over the nitrogen chemistry in the atmosphere is given. More precisely, the role of NO\textsubscript{x} in the stratospheric ozone destruction and – in more detail (due to the further focus on the troposphere) – the tropospheric ozone production is described. Further, characteristics of tropospheric NO\textsubscript{x} such as its removal, vertical distribution and absorption of radiation are described. This is followed by introducing the principles of measuring nitrogen oxides in the troposphere from space-borne spectrometers and at ground-based in situ measurement sites commonly used for air pollution monitoring.

2.1 Nitrogen oxides in the atmosphere

Due to their high reactivity, nitrogen oxides NO\textsubscript{x} \(\equiv NO + NO_2\)\(^{1}\) including nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}) are among the most important constituents in the atmosphere. Nitrogen oxides can affect human health when inhaled and are known to damage ecosystems by their role in eutrophication (the enrichment of an ecosystem with chemical nutrients) or acid rain. Further, nitrogen species play a key role in the chemistry of important species such as ozone (O\textsubscript{3}) and the hydroxyl radical (OH), the latter also known as the detergent of the atmosphere. Therefore, NO\textsubscript{x} indirectly contributes to the global warming caused by tropospheric O\textsubscript{3}. On the other hand, Solomon et al. (1999) pointed out the direct effect of NO\textsubscript{2} as an absorber of solar radiation in the visible spectral range. It was observed that, during episodes with high production of NO\textsubscript{2}, the incoming solar radiation can be reduced at the ground by about 5-12\%. This effect, however, is of minor significance because the chemical lifetime of NO\textsubscript{x} is short and respective episodes are spatially and temporally limited. A further indirect influence of NO\textsubscript{x} on the “greenhouse effect” emanates from the fact that nitrogen oxides react with OH radicals. The latter in turn decompose greenhouse gases like for instance methane (CH\textsubscript{4}).

2.1.1 NO\textsubscript{x} emissions in the troposphere

IPCC (2001) estimated the global NO\textsubscript{x} emissions. A summary of “best” source estimates and emission locations are listed in Table 2.1. Obviously, there is a high spatial variability in the sources of NO\textsubscript{x}. The major one, the combustion of fossil fuel, is man-made and therefore mainly located at highly industrialised regions over the continents in the northern mid-latitudes. During high-temperature combustion processes, NO is produced from the reaction

\[
N_2 + O_2 \rightarrow 2NO
\]  

\hspace{1cm} (2.1)

\(^{1}\) Stratospheric NO\textsubscript{x} is often defined as the odd nitrogen family: \(NO_{x} = N + NO + NO_2 + NO_3 + 2\timesN_2O_5 + HNO_4 + CIONO_2\) (Brasseur and Solomon, 1986). In this thesis the above definition (\(NO_{x} = NO + NO_2\)) is used.
Smaller amounts of NO\textsubscript{2} are released due to the further oxidation of NO. The fractions of emitted NO and NO\textsubscript{2} on the total NO\textsubscript{x} depends on the specific conditions during the different combustion processes. The fraction of the total NO\textsubscript{x} which is emitted as NO is generally assumed to be $\geq 90\%$ \textit{(Finlayson-Pitts and Pitts, 1986)}. Biomass burning, in contrast to the anthropogenic sources, predominantly takes place in the tropical regions of the globe. A further significant source is the microbial production in soils of the non-polar continental surface. Besides the main sources being located at the earth’s surface, NO\textsubscript{x} is in situ injected into the atmosphere by lightning, decomposition of nitrous oxide (N\textsubscript{2}O) in the stratosphere and aircraft emissions. The following sections highlight the role of nitrogen oxides for the chemistry of both the stratosphere and the troposphere.

Table 2.1. Summary of NO\textsubscript{x} source estimates \textit{(IPCC, 2001)} and emission locations. Recent estimates suggest ship emissions to additionally contribute 3.6 \textit{(Endresen et al., 2003)} to 6.9 Tg[N]yr\textsuperscript{-1} \textit{(Corbett and Köhler, 2003)}.

<table>
<thead>
<tr>
<th>Source</th>
<th>Emission (Tg[N]yr\textsuperscript{-1})</th>
<th>Principal location of emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil fuel combustion</td>
<td>33.0</td>
<td>Northern hemisphere mid latitude continental surface</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>7.1</td>
<td>Tropical continental surface</td>
</tr>
<tr>
<td>Soil microbial production</td>
<td>5.6</td>
<td>Non-polar continental surface</td>
</tr>
<tr>
<td>Lightning</td>
<td>5.0</td>
<td>Tropical continent, troposphere</td>
</tr>
<tr>
<td>Stratospheric decomposition of N\textsubscript{2}O</td>
<td>$&lt;0.5$</td>
<td>Stratosphere</td>
</tr>
<tr>
<td>Aircraft</td>
<td>0.7</td>
<td>Northern hemisphere, 30°-60° N, 10 km altitude</td>
</tr>
<tr>
<td>Total</td>
<td>51.9</td>
<td></td>
</tr>
</tbody>
</table>

2.1.2 NO\textsubscript{x} in the stratosphere

Stratospheric NO\textsubscript{x} plays a role for the retrieval of space-borne tropospheric NO\textsubscript{2} columns insofar as an estimation of the stratospheric part of the NO\textsubscript{2} column is required. This stratospheric NO\textsubscript{2} column is then subtracted from the total column yielding the tropospheric NO\textsubscript{2} column (sects. 2.2.3 and 2.2.4). The importance of nitrogen oxides in the stratosphere results from both their ability to catalytically destruct ozone and the interactions with the O\textsubscript{3}-destroying ClO\textsubscript{x}- and HO\textsubscript{x}-cycles. The dominant stratospheric source of NO\textsubscript{x} is the decomposition of N\textsubscript{2}O. The latter can be photolysed or react with an excited oxygen atom produced by the photolysis of O\textsubscript{3}, leading to reaction channel 2.2 producing NO:

\[
\text{N}_2\text{O} + \text{O}(^{1}\text{D}) \rightarrow 2\text{NO} \tag{2.2}
\]

\[
\rightarrow \text{N}_2 + \text{O}_2 \tag{2.3}
\]
Crutzen (1970, 1971) postulated the catalytic destruction of ozone by NO and NO₂, which, in the middle and upper stratosphere (above ~25 km), follows reactions 2.4 - 2.6:

\[
\begin{align*}
O_3 + h\nu &\rightarrow O_2 + O \quad (2.4) \\
NO_2 + O &\rightarrow NO + O_2 \quad (2.5) \\
NO + O_3 &\rightarrow NO_2 + O_2 \quad (2.6) \\
\text{net } 2O_3 + h\nu &\rightarrow 3O_2
\end{align*}
\]

Due to the abundance of atomic oxygen decreasing with altitude in the lower stratosphere, the photolysis of NO₂ into NO and O becomes more important there than reaction 2.5. This favours the photostationary equilibrium state, where no net ozone destruction takes place (see also sect. 2.1.3).

Two other cycles destroying ozone in the stratosphere are the ClOₓ- (Molina and Rowland, 1974) and the HOₓ-cycle which similarly to NOₓ destroy ozone through reactions 2.7-2.9:

\[
\begin{align*}
O_3 + h\nu &\rightarrow O_2 + O \quad (2.7) \\
XO + O &\rightarrow X + O_2 \quad (2.8) \\
X + O_3 &\rightarrow XO + O_2 \quad (2.9) \\
\text{net } 2O_3 + h\nu &\rightarrow 3O_2
\end{align*}
\]

where X = Cl or OH. The NOₓ molecules are linked to these cycles by offering a pathway for deactivation of radicals as indicated by reactions 2.10 and 2.11:

\[
\begin{align*}
NO_2 + ClO(+M) &\rightarrow ClONO_2(+M) \quad (2.10) \\
NO_2 + OH(+M) &\rightarrow HNO_3(+M) \quad (2.11)
\end{align*}
\]

where M denotes a further reactant, usually N₂ or O₂, which absorbs the energy released during the reaction. Outside the wintertime polar stratosphere, ClONO₂ is a nighttime reservoir for chlorine, since it photolyses back to Cl and NO₃ or ClO and NO₂ during the day. In the very cold polar stratosphere, however, ClONO₂ can rapidly react with HCl on ice surfaces producing Cl₂ and adsorbed HNO₃. The particles containing HNO₃ can subsequently sediment to lower altitudes and, thus, remove NOₓ from the stratosphere (denitrification). This prevents the chlorine deactivation and the chlorine cycle can further destroy ozone (Fahey et al., 1989).

Reaction 2.11 denotes the main sink for stratospheric NOₓ, because HNO₃ is relatively stable in the lower part of the stratosphere and can therefore be transported to the troposphere.

At night, the OH radical required for reaction 2.11 is absent and the loss of NOₓ takes place through the oxidation of NO₂ with O₃ to NO₃. Whereas the latter rapidly photolyses back to NO₂ during the day, it further reacts with NO₂ to N₂O₅ in an equilibrium reaction during night. After sunrise, N₂O₅ is photolysed back to NO₂. As a
result of these reactions, NO\textsubscript{x} undergoes a diurnal variation with low values in the morning and higher ones in the afternoon.

The availability of solar radiation affects the latitudinal distribution of NO\textsubscript{x} in the stratosphere and leads to an increase of NO\textsubscript{x} towards the summer pole. Going from the equator towards the winter pole, NO\textsubscript{x} only slightly increases (until \(\sim 35^\circ\text{N}\)) and decreases further northward. This can also be seen in space-borne total NO\textsubscript{2} column retrievals (Fig. 2.1).

![Figure 2.1. Global mean total NO\textsubscript{2} columns averaged from SCIAMACHY retrievals for July 2005 and February 2006 (images processed by KNMI; available on http://www.temis.nl).](image)

The stratospheric mixing ratio of NO\textsubscript{2} is similar to the mixing ratio found near the earth’s surface over the polluted continents and can reach 10 ppb at an altitude of 30-35 km \cite{Warneck2000}. However, due to the much lower pressure in the stratosphere, the absolute molecule number is distinctly lower than near the polluted ground. Sioris \textit{et al.} \cite{Sioris2003} investigated stratospheric NO\textsubscript{2} profiles and found NO\textsubscript{2} number densities of around \(2 \times 10^9\) molecules cm\textsuperscript{-3}. For comparison, in the polluted boundary layer, NO\textsubscript{2} number densities can be larger by one to two orders of magnitude. Nevertheless, the resulting stratospheric NO\textsubscript{2} columns are similar to or even exceeding the tropospheric NO\textsubscript{2} columns over large parts of the world, as can be seen when comparing the total columns denoted in Figure 2.1 with the tropospheric columns from Figures 1.1 and 1.4. Only over polluted industrialised regions, the tropospheric NO\textsubscript{2} columns clearly exceed the stratospheric contribution. This has implications for the uncertainty of tropospheric NO\textsubscript{2} retrievals as discussed in section 2.2.4.

\subsection*{2.1.3 NO\textsubscript{x} and photochemistry in the troposphere}

In the troposphere, the lowest atmospheric layer reaching from the surface to up to around 12 km altitude, nitrogen oxides play a key role in the production of ozone. The primary source of NO\textsubscript{x} is NO, which can rapidly react with ozone to create NO\textsubscript{2} as indicated by reaction 2.12:

\begin{equation}
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
\end{equation}

(2.12)
Photolysis of nitrogen dioxide molecules with solar radiation in the near-UV and visible spectral range (sunlight with wavelengths shorter than 300 nm is absorbed by stratospheric ozone and does not reach the earth’s surface) produces excited oxygen as indicated by reaction (2.13):

$$\text{NO}_2 + h\nu (300 < \lambda < 420 \text{ nm}) \rightarrow \text{NO} + \text{O}(^3\text{P}) \quad (2.13)$$

This reaction is followed by reaction (2.14) that again produces ozone:

$$\text{O}(^3\text{P}) + \text{O}_2 (+\text{M}) \rightarrow \text{O}_3 (+\text{M}) \quad (2.14)$$

The above reactions 2.12-2.14 make up a null cycle where no net ozone production takes place. This state is known as the photostationary equilibrium state established within minutes. 

Levy (1971) pointed out the production of the hydroxyl radical through photolysis of the ozone molecule by the following mechanism:

$$\text{O}_3 + h\nu (\lambda \leq 320 \text{ nm}) \rightarrow \text{O}_2 + \text{O}(^1\text{D}) \quad (2.15)$$

$$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad (2.16)$$

The reactive OH radical oxidizes a multitude of compounds in the atmosphere (Fig. 2.2). For instance, the oxidation of carbon monoxide (CO) with the hydroxyl radical initiates the following reaction chain (Crutzen, 1973):

$$\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2 \quad (2.17)$$

$$\text{H} + \text{O}_2 \rightarrow \text{HO}_2 \quad (2.18)$$

$$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad (2.19)$$

$$\text{net} \quad \text{CO} + \text{O}_2 + \text{NO} \rightarrow \text{CO}_2 + \text{NO}_2 \quad (2.20)$$

The net reaction 2.20 oxidises NO to NO$_2$ without destroying an O$_3$ molecule (Fig. 2.2). Other (net) reactions arise from the decomposition of CH$_4$ (net reaction 2.21; Crutzen, 1973) and reactive organic compounds (ROCs; abbreviated as RCH$_3$ in net reaction 2.22 with R an organic fragment) which predominantly occur in the polluted boundary layer (Haagen-Smit and Fox, 1954):

$$\text{net} \quad \text{CH}_4 + 2\text{O}_2 + 2\text{NO} \rightarrow \text{HCHO} + \text{H}_2\text{O} + 2\text{NO}_2 \quad (2.21)$$

$$\text{net} \quad \text{RCH}_3 + \text{OH} + 2\text{O}_2 + \text{NO} \rightarrow \text{RCHO} + \text{H}_2\text{O} + \text{HO}_2 + \text{NO}_2 \quad (2.22)$$

The above (net) decomposition reactions of CO, CH$_4$ and ROCs alternatively oxidise NO to NO$_2$ instead of reaction 2.12. The nitrogen dioxide molecule again underlies photolysis through sunlight (reaction 2.13), produces excited oxygen and, subsequently, ozone (reaction 2.14) that accumulates. The NO$_x$ molecules therefore catalyse the ozone production in the polluted boundary layer and are – under
summertime radiative conditions – jointly responsible for summertime smog episodes.

![Figure 2.2. A simplified scheme of photochemical reactions where R denotes an organic fragment. (from Staehelin et al., 2000).](image)

Following Figure 2.2, the aldehydes (RCHO) formed in net reaction 2.22 further react with OH radicals and oxygen to acylperoxy radicals (RC[O]O2). These can either oxidise NO to NO2 or react with NO2 to form peroxyacetyl nitrate (PAN). The latter is a strongly temperature dependent equilibrium reaction leading to relatively short PAN lifetimes at warmer temperatures near the ground and longer lifetimes in low temperature regimes prevailing in the higher troposphere. This is of importance for the NOx abundance and the photochemical ozone production in remote areas: PAN molecules once lifted up to higher tropospheric levels, e.g. due to fronts, can subsequently be transported over large distances of several thousand km and, again arriving near the ground, release nitrogen oxides and peroxy radicals in regions far away from where they have been emitted (see Staehelin et al. (2000) and references therein).

Note that at very low NOx concentrations (lower than ~10 ppt), the reaction of HO2 radicals with O3 can dominate over reaction 2.19 and ozone is destroyed by photochemistry in the troposphere. However, this takes place at very remote regions on the globe and is not important for the conditions studied in this thesis.

2.1.4 Removal of NOx from the troposphere

There are a number of potential removal mechanisms for NOx in the troposphere, including photolysis of NO2 and reaction of the latter and NO with OH, O3, NO3, HO2,
RO₂ and RO (Finlayson-Pitts and Pitts, 1986). Most of these reactions, however, do not play a significant role for the removal of NOₓ: the photolysis of NO₂ (reaction 2.13) depends on parameters such as latitude, season, solar zenith angle and cloud cover. Typical summertime photolytic rate constants correspond to NO₂ lifetimes of only a few minutes. Similar lifetimes are found for the reactions with HO₂ and RO₂. However, the NO molecules formed through the photolysis of NO₂ are subsequently re-oxidised to NO₂ (reaction 2.12); and the products from the reactions of NO₂ with HO₂ and RO₂ similarly do not form significant sinks, but decompose back to the reactants (except for some special conditions in the upper troposphere). Thus, for the effective removal of NOₓ, these reactions do not play a major role. On the other hand, the reaction of NO₂ with RO leads to an NO₂ lifetime in the order of 2 months (Finlayson-Pitts and Pitts, 1986), which is too slow to be a significant sink for NO₂.

The mechanisms that mainly affect the NOₓ lifetime in the troposphere are the following: During daytime, the reaction 2.23 between the photolytically produced OH radical and NO₂ forms nitric acid (Fig. 2.2),

$$\text{OH} + \text{NO}_2(\pm \text{M}) \rightarrow \text{HNO}_3(\pm \text{M}) \quad (2.23)$$

With a typical OH concentration of $5 \times 10^6$ molecules cm$^{-3}$ occurring in the polluted boundary layer, the NO₂ lifetime with respect to reaction 2.23 is approximately 5 hours. Further lifetime estimates based on OH field measurements are discussed in section 5.

During nighttime, reaction (2.24) between NO₂ and ozone forms the nitrate radical,

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad (2.24)$$

(This reaction chain plays a minor role during daytime as the NO₃ molecule is quickly photolysed to NO₂ or NO). Subsequently, NO₂ and NO₃ react to dinitrogen pentoxide (N₂O₅). The latter decomposes back to the reactants, so that reaction 2.25 is an equilibrium reaction:

$$\text{NO}_2 + \text{NO}_3(\pm \text{M}) \leftrightarrow \text{N}_2\text{O}_5(\pm \text{M}) \quad (2.25)$$

A major loss process for N₂O₅ is the conversion with H₂O to HNO₃ on aerosol surfaces (Dentener and Crutzen, 1993). Finally, the HNO₃ molecule that is produced during both day- and nighttime can deposit (Kramm et al., 1995) and, thus, effectively remove the involved NOₓ molecules from the troposphere.

Due to the different NOₓ removal pathways taking place during night and day and changing meteorological conditions (affecting, e.g., the photolysis of NO₂ according to reaction 2.13), the diurnal variations of the NOₓ lifetime are considerable. The average boundary layer lifetime during the whole year is estimated to be in the order of one day (Warneck, 2000). However, during photochemically active summer days, it can be reduced to only a few hours (e.g. Spicer, 1982). An increasing lifetime of up to several days is found with increasing height in the troposphere (Jaeglé et al., 1998; Seinfeld and Pandis, 1998; Warneck, 2000) (see 2.1.5).

Further references to different studies investigating the NOₓ lifetime as well as lifetime estimates calculated in the present thesis are given in section 5.
2.1.5 Vertical distribution of NO\textsubscript{x} and NO\textsubscript{2} in the troposphere

The mainly near-ground emissions of nitrogen species (Tab. 2.1), their production and loss reactions and meteorological transport lead to a distinct vertical tropospheric profile of NO\textsubscript{x}. Over industrialised areas, it exhibits a C-shape with enhanced NO\textsubscript{x} mixing ratios in the polluted boundary layer, low concentrations in the free troposphere, and again increasing mixing ratios in the tropopause region due to stratosphere-troposphere exchange, lightning or deep convection (Ridley et al., 1994; Ziereis et al., 1999; Emmons et al., 2000; Jeker et al., 2000; Brunner et al., 2001).

The NO\textsubscript{2} profile is additionally affected by the partitioning of NO\textsubscript{x} into NO and NO\textsubscript{2}. This partitioning is determined by the competition between the reactions 2.12 and 2.13: Near the earth’s surface, the reaction constant from reaction 2.12 dominates the photolysis rate from reaction 2.13 and, thus, NO\textsubscript{x} is dominated by NO\textsubscript{2}. During the Transport and Chemical Evolution over the Pacific (TRACE-P) campaign between February and April 2001 (Jacob et al., 2003), the bulk of the NO\textsubscript{2}/NO ratios have been found to be around 4 at near-ground levels (Nakamura et al., 2003). Similar values from different campaigns can be found in Warneck (2000). With increasing altitude in the troposphere, the photolysis rate constant of reaction 2.13 slightly increases, whereas the temperature dependent reaction constant of reaction 2.12 is decreasing (e.g. Warneck, 2000). Thus, the partitioning of NO\textsubscript{x} is shifted towards NO, which is in agreement with mid tropospheric NO\textsubscript{2}/NO ratios of around 1 that have been found by Nakamura et al. (2003). Finally, over industrialised areas, this changing partitioning results in an NO\textsubscript{2} profile that exhibits a more pronounced profile than NO\textsubscript{x} with the bulk of the NO\textsubscript{2} residing in the planetary boundary layer (PBL) and a decreasing NO\textsubscript{2} mixing ratio with increasing altitude. This is a major reason for the increasing NO\textsubscript{x} lifetime with increasing altitude as the main removal pathways of NO\textsubscript{x} are connected to reactions with NO\textsubscript{2}.

2.1.6 Absorption spectrum of NO\textsubscript{2}

NO\textsubscript{2} absorbs radiation throughout the entire visible and near ultraviolet spectral region. Because radiation with wavelengths shorter than \sim 200 nm is absorbed already in the upper atmosphere above 50 km altitude (Brasseur and Solomon, 1986), Figure 2.3 denotes the absorption cross sections of NO\textsubscript{2} in the spectral range between 200 and 700 nm (Schneider, 1987). For wavelengths longer than 274 nm the absorption cross sections are temperature dependent. A parameterisation was given by, e.g., DeMore et al. (1997). An extended database of measured NO\textsubscript{2} absorption cross section data from different authors can be found on [www.atmosphere.mpg.de](http://www.atmosphere.mpg.de) (Photo-oxidation mechanisms and aerosols → Projects → Spectral atlas → Catalogue → Nitrogen oxides).

The retrieval of NO\textsubscript{2} from space-borne measurements is based on UV-visible absorption spectroscopy. Because of the large number of absorbing species in the atmosphere, NO\textsubscript{2} is usually measured using the Differential Optical Absorption Spectroscopy (DOAS) method (Platt, 1994). This means one uses the narrow band absorption structure (the “peak-to-valley” absorbance) which has been separated from the numerically fitted broadband structure rather than the total “peak-to-zero” absorbance. While reducing the temperature only slightly affects the peak absorption cross sections, it does decrease the minima in the spectrum, thus increasing the
peak-to-valley absorbance differences \((\text{Finlayson-Pitts and Pitts, 2000})\). This has to be taken into account in the DOAS retrieval of trace species. In addition to the temperature dependence, a pressure dependence of the absorption cross sections has been observed by \textit{Harder et al. (1997)}. This pressure dependence, however, is predominantly important for application in the upper atmosphere \((\text{Finlayson-Pitts and Pitts, 2000})\).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_3.png}
\caption{Absorption cross sections of \(\text{NO}_2\) in the ultraviolet and visible spectral region (200-700 nm) at 298 K with a resolution of 1 nm. Adapted from \textit{Schneider et al. (1987)}.}
\end{figure}

\section*{2.2 Space-borne measurement of nitrogen dioxide}

For roughly half a century humans are able to deliver artificial satellites into orbits around the Earth. In the 1970s, the American Nimbus satellites for the first time carried remote sensing devices to monitor ozone. The first satellite instrument that allowed the measurement of \(\text{NO}_2\) was the NASA’s Stratospheric Aerosol and Gas Experiment (SAGE) \((\text{Chu and McCormick, 1979})\) that measured in the solar occultation technique. More precisely, in the solar occultation mode, the instrument is pointed toward the horizon at sunrise and sunset and measures the attenuation due to stratospheric gases and particles along the light path from the sun through the atmosphere to the satellite.

It took many years, until the middle of the 1990s, when the Global Ozone Monitoring Experiment (GOME) spectrometer \((\text{Burrows et al., 1999})\) for the first time allowed the measurement of tropospheric \(\text{NO}_2\). This was enabled by the nadir-viewing geometry of the spectrometer. In the nadir mode, the instrument looks down to the nadir point (located perpendicularly below the satellite on the earth’s surface) and observes the
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atmospheric volume beneath the satellite. The nadir mirror scans across the satellite track and transmits the sunlight scattered back from the earth and the atmosphere to the spectrometer (Figs. 2.4 and 2.8). Table 2.2 gives a (non-complete) overview over space-borne instruments enabling the retrieval of NO₂.

Table 2.2. Selected space-borne instruments enabling the observation of nitrogen oxides.

<table>
<thead>
<tr>
<th>Instrument (mission)</th>
<th>Mission duration</th>
<th>Viewing geometry</th>
<th>Main focus</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAGE (AEM-2)</td>
<td>1979-1982</td>
<td>Solar occultation</td>
<td>Stratosphere</td>
</tr>
<tr>
<td>SAGE II (ERBS)</td>
<td>1984-</td>
<td>Solar occultation</td>
<td>Stratosphere</td>
</tr>
<tr>
<td>HALOE (UARS)</td>
<td>1991-</td>
<td>Limb</td>
<td>Stratosphere</td>
</tr>
<tr>
<td>CLAES (UARS)</td>
<td>1991-</td>
<td>Limb</td>
<td>Stratosphere</td>
</tr>
<tr>
<td>POAM II (SPOT-3)</td>
<td>1993-1996</td>
<td>Solar occultation</td>
<td>Stratosphere</td>
</tr>
<tr>
<td>GOME (ERS-2)</td>
<td>1995-2003</td>
<td>Nadir</td>
<td>Stratosphere, troposphere</td>
</tr>
<tr>
<td>POAM III (SPOT-4)</td>
<td>1998-</td>
<td>Solar occultation</td>
<td>Stratosphere</td>
</tr>
<tr>
<td>OSIRIS (ODIN)</td>
<td>2001-</td>
<td>Limb</td>
<td>Stratosphere</td>
</tr>
<tr>
<td>SCIAMACHY (ENVISAT)</td>
<td>2002-</td>
<td>Nadir/limb/occultation</td>
<td>Stratosphere, troposphere</td>
</tr>
<tr>
<td>MIPAS (ENVISAT)</td>
<td>2002-</td>
<td>Limb</td>
<td>Stratosphere</td>
</tr>
<tr>
<td>GOMOS (ENVISAT)</td>
<td>2002-</td>
<td>Stellar occultation</td>
<td>Stratosphere</td>
</tr>
<tr>
<td>OMI (EOS-AURA)</td>
<td>2004-</td>
<td>Nadir</td>
<td>Stratosphere, troposphere</td>
</tr>
<tr>
<td>HIRDLS (EOS-AURA)</td>
<td>2004-</td>
<td>Limb</td>
<td>Stratosphere, upper troposphere</td>
</tr>
<tr>
<td>TES (EOS-AURA)</td>
<td>2004-</td>
<td>Nadir/limb</td>
<td>Stratosphere, troposphere</td>
</tr>
<tr>
<td>GOME-2 (METOP)</td>
<td>2006-</td>
<td>Nadir</td>
<td>Stratosphere, troposphere</td>
</tr>
</tbody>
</table>

2.2.1 The GOME spectrometer

On April 21, 1995, the European Space Agency (ESA) launched the GOME spectrometer (Burrows, 1999) aboard the second European Remote Sensing satellite (ERS-2, Fig. 2.4). ERS-2 moves on a sun-synchronous, near polar orbit at a height of about 800 km around the Earth and crosses the equator at 10:30 hrs local time (LT). GOME is the first European passive remote sensing instrument operating in the ultraviolet, visible, and near infrared wavelength regions whose primary objective is the determination of the amounts and distributions of atmospheric trace constituents such as O₃, O₄, H₂O, SO₂, BrO, OCIO, HCHO and NO₂. The instrument was proposed as a small-scale version and as a precursor of the SCIAMACHY spectrometer (Bovensmann et al., 1999). It observes the atmosphere in the nadir viewing geometry and detects backscattered solar radiation in the wavelength range from 240 nm to 793 nm with a spectral resolution of 0.2 nm to 0.4 nm. The horizontal resolution of a single GOME NO₂ pixel is 40 (along track) × 320 (across track) km² (Fig. 2.6). With a total across track swath width of 960 km GOME reaches full coverage at the mid-latitudes within 2-3 days.

2.2.2 The SCIAMACHY spectrometer

SCIAMACHY is a Greek word which means chasing or hunting shadows and has the meaning of doing an impossible task. Nevertheless, SCIAMACHY (Bovensmann et
al., 1999) is also an innovative and novel earth observation experiment aboard ESA’s newest earth observation satellite ENVISAT (Environmental Satellite) launched in March 2002 (Fig. 2.5). ENVISAT, the largest environmental satellite ever built, flies in a sun-synchronous polar orbit in 800 km height, crosses the equator at 10:00 hrs LT and carries ten instruments that monitor the Earth’s environment from the surface to the mesosphere.

Figure 2.4. ESA’s ERS-2 satellite carrying the GOME spectrometer. The left picture illustrates the flight geometry (adapted from Deutsches Zentrum für Luft- und Raumfahrt (DLR, 1996)). Image on the right from European Aeronautic Defence and Space Company (EADS) Astrium.

Figure 2.5. ESA’s Ariane 5 rocket (during launch on 1st March 2002, left, photo: ESA/CNES/Arianespace – S. Corvaja) carries the ENVISAT satellite to its orbit around the globe (right, image: ESA/ Denmann production).

Within the ENVISAT mission the SCIAMACHY spectrometer aims to deliver relevant data about the changing composition of the atmosphere from the troposphere up to the mesosphere. It was first proposed to ESA in 1988 (Burrows et al., 1988) and is
designed to measure sunlight transmitted, reflected and scattered by the Earth’s atmosphere or surface in the ultraviolet, visible and near infrared wavelength region (214-2380 nm) at moderate spectral resolution of 0.2 nm to 1.5 nm. SCIAMACHY performs earthshine radiance measurements in three different viewing geometries: nadir, limb, and solar/lunar occultation. In the limb mode, SCIAMACHY measures the scattered sunlight for different viewing angles corresponding to different tangent heights. During one limb state, the atmosphere is scanned in ~3 km steps from the ground to 100 km altitude. This allows the retrieval of (stratospheric) trace gas profiles.

An orbit typically starts with a limb measurement of the twilight atmosphere, followed by the solar occultation measurement during sunrise over the North Pole and, subsequently, a limb-nadir sequence. Inversion of the SCIAMACHY measurements enables the determination of the amounts and distribution of the atmospheric constituents O₃, O₄, BrO, OCIO, ClO, SO₂, H₂CO, NO, NO₂, NO₃, CO, CO₂, CH₄, H₂O, N₂O and aerosol, as well as additional knowledge about the physical parameters pressure, temperature, radiation field, cloud cover, cloud top height and surface spectral reflectance to be determined. The resulting horizontal resolution of an NO₂ pixel is 30 × 60 km² (Fig. 2.6).

**Figure 2.6.** Example single day NO₂ vertical tropospheric column densities retrieved from GOME measurements taken on 17 July 1997 (left) and SCIAMACHY measurements taken on 13 March 2003. The GOME and SCIAMACHY horizontal pixel resolutions are 320 × 40 km² and 60 × 30 km², respectively.

### 2.2.3 Retrieval of tropospheric NO₂ columns

The NO₂ vertical tropospheric column density (VTC) data used in this thesis were processed and provided by the University of Bremen (GOME retrievals used in section 3) (Richter and Burrows, 2002) and by the Royal Netherlands Meteorological Institute (KNMI) (GOME and SCIAMACHY retrievals used in sections 4 and 5) (Boersma et al., 2004). The data from the latter are the result of a collaboration of
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KNMI with the Belgian Institute for Space Aeronomy (BIRA/IASB) and are available on a day-by-day basis via ESA's TEMIS project (www.temis.nl).

The retrieval of vertical tropospheric NO₂ columns from GOME and SCIAMACHY measurements is a 3-step process. It starts with quantifying the total slant column density of the NO₂, from which – in a second step – the stratospheric part is subtracted to provide the tropospheric slant column density. Finally, in the third and most challenging step, the tropospheric slant column is converted into a vertical NO₂ column by applying the tropospheric air mass factor. In the following, these three steps are described in more detail.

Retrieval of the slant column density

The first step of the retrieval is based on the DOAS method. This technique uses differential spectral features to determine the absorption optical thickness of the substance of interest and can be interpreted as an application of the Lambert-Beer law. The DOAS method has often been used to retrieve total column amounts of trace gases measured in the UV-visible spectral range from ground-based instruments (Platt, 1994). Since the launch of the GOME spectrometer in 1995, DOAS has also successfully been used for retrievals of atmospheric constituents from space-borne backscatter instruments such as GOME and SCIAMACHY.

When measuring in the nadir mode, both GOME and SCIAMACHY measure a spectrum of light scattered back from the earth and the atmosphere in the direction of the satellite. In addition, the spectrometers measure direct sunlight. The ratio of the backscattered radiance spectrum and the direct solar (irradiance) spectrum provides a reflectance spectrum. Figure 2.7 shows an example reflectance spectrum from GOME for a cloud free situation observed on 25 July above the Netherlands. The smooth variation of the spectrum with wavelength can be attributed to absorption by ozone (< 340 nm) and, towards longer wavelengths, scattering by molecules, clouds, aerosols and surface. Superimposed high resolution spectral features are additionally denoted. Such features are exploited for the retrieval of trace species and cloud characteristics.

For NO₂, the DOAS method consists of the (least square) fitting of a modelled spectrum to a GOME- or SCIAMACHY-measured reflectance spectrum in a narrow spectral window. The optimal wavelength range for the latter must have high sensitivity to the NO₂ absorption signature and minimal sensitivity to spectral features from other absorbers. The resulting wavelength region lies in the visible spectral range and can slightly vary: at University of Bremen, a spectral window from 425-450 nm is used (Richter and Burrows, 2002); at KNMI, NO₂ is retrieved from the 426.3-451.3 nm wavelength region (Boersma et al., 2004). The modelled reflectance spectrum is divided into two parts: a spectrally smooth part that describes the above mentioned broadband absorption by a low-order polynomial, and a differential part from which NO₂ information is retrieved (Richter and Burrows, 2002; Boersma et al., 2004).

The result of this first step is the so-called slant column density (SCD) of NO₂. This SCD is the column integral of absorbing NO₂ molecules along the effective photon path from the sun through the atmosphere to the space-borne spectrometer and consists of comparable stratospheric and tropospheric contributions over large parts of the globe. Note that the temperature dependence of the NO₂ absorption that has been pointed out in section 2.1.6 is usually corrected for *a posteriori*: the SCD fit uses an absorption cross section with a fixed temperature (243 and 241 K for the present
KNMI and University of Bremen retrievals, respectively). The temperature dependence is then corrected for by introducing an empirical correction term in the air mass factor (AMF) calculation (Boersma et al., 2004). Hereafter, this correction term is not shown in the formulas for the AMF calculation (sections 4 and 5).

**Figure 2.7.** Clear sky reflectance spectrum measured from the GOME spectrometer on 25 July 1995 over the Netherlands. Important scattering and absorption features are denoted at their wavelength of strongest impact (Courtesy of Piter and Stammes, 1996).

**Estimating the stratospheric background slant column density**

The second step of the retrieval is the separation of the stratospheric contribution from the total SCD. Different separation techniques to determine the stratospheric SCD are described in literature (Leue et al., 2001; Martin et al., 2002; Richter et al., 2002; Richter and Burrows, 2002; Eskes, 2003). For the data used in the present thesis, the following techniques have been applied:

1) For the NO$_2$ VTCs provided by the University of Bremen, the reference sector method is used (Richter and Burrows, 2002; Martin et al., 2002): The stratospheric column is approximated by taking the average total columns over a remote Pacific region with a very low tropospheric amount of NO$_2$. The approach assumes the stratospheric NO$_2$ to be longitudinally constant. This assumption is critical for higher latitudes and can lead to biases. A further drawback is the fact that a small amount of tropospheric NO$_2$ may still be present in the reference sector pixels. Martin et al. (2002) correct for this by subsequent subtraction of the tropospheric amount taken from a chemistry transport model (CTM).

2) For the KNMI retrieval, the stratospheric slant column is determined by a data-assimilation approach (Eskes, 2003). The values of the CTM stratosphere are made consistent with the observed slant columns over unpolluted areas. The
advantage of this method is that dynamical features in the stratospheric NO$_2$ – leading to a longitudinally inhomogeneous distribution of NO$_2$ – are taken into account.

Subsequently, the estimated stratospheric slant column density is subtracted from the total SCD to yield the tropospheric slant column density ($SCD_{trop}$).

**Retrieval of the NO$_2$ vertical tropospheric column density**

In the third step, the $SCD_{trop}$ is converted into a VTC by applying the tropospheric air mass factor ($AMF_{trop}$):

$$VTC = \frac{SCD_{trop}}{AMF_{trop}}$$

A more detailed description of the corresponding formulas for the $SCD_{trop}$-VTC conversion and the $AMF_{trop}$ calculation is given in section 4. Figure 2.8 illustrates the fundamental problem of the $SCD_{trop}$-VTC conversion: $SCD_{trop}$ is the tropospheric column integral of absorbing NO$_2$ molecules along the effective photon path in the troposphere. Therefore, on the one hand, information about the photon path is required. This is calculated with radiative transfer models – GOMETRAN (Rozanov et al., 1997) and Doubling Adding KNMI radiative transfer model (Stammes, 2001) for the Bremen and KNMI retrievals, respectively – yielding the best estimate of the length of the effective photon path for a particular retrieval scene. A further complication is that the radiative transfer (or scattering) becomes sensitive to the vertical distribution of the atmospheric species being retrieved, because the penetration of near UV-visible radiation to the lower atmosphere is increasingly inhibited by scattering. Thus, knowledge about the shape of the vertical profile of the species is additionally required. Because such vertical profiles are usually unknown, an a priori estimate has to be calculated with CTMs. For the present retrievals, a priori NO$_2$ profiles are calculated with MOZART (Model of Ozone and Related Tracers) (Horowitz et al., 2003) for Bremen retrievals and with the CTM TM4 (Dentener et al., 2003) for KNMI retrievals. The decoupling of the $AMF_{trop}$ calculation into i) the calculation of layer-specific “scattering weights” (calculated with the radiative transfer model for single tropospheric layers containing a unit quantity of the retrieved species) and ii) the calculation of the vertical distribution of the species has been proposed by Palmer et al. (2001). The resulting information can subsequently be combined to calculate the $AMF_{trop}$ as indicated in section 4. It becomes obvious that the height dependent sensitivity of the space-borne instrument to the tracer density results in a tracer profile dependence that may introduce large systematic errors in the retrieved columns. A proper comparison of retrieved trace gas columns with independent profile measurements therefore requires additional information given by the averaging kernel (Rodgers, 2000; Rodgers and Connor, 2003; Eskes and Boersma, 2003). This is further discussed in section 4.

Besides the a priori estimate of the NO$_2$ profile, the radiative transfer in the troposphere – and, thus, the $AMF_{trop}$ – depends on further a priori knowledge on the state of the atmosphere, including surface albedo, aerosol load and cloud
characteristics (cloud fraction and cloud top height). The retrieval of cloud parameters is summarised in the following subsection.

The GOME data provided by the University of Bremen have been processed based on simply assuming a maritime aerosol and a surface albedo of 0.05 (Richter and Burrows, 2002). Note, however, that current data provided by this institute are retrieved based on more accurate estimates of these parameters. Furthermore, for the case study in section 3, these parameters are of minor importance, because GOME pixels containing a dense cloud cover are investigated.

![Figure 2.8](image)

**Figure 2.8.** The conversion from the NO$_2$ tropospheric slant column density (SCD$_\text{trop}$) to the NO$_2$ vertical tropospheric column density (VTC) requires knowledge about the radiative transfer and the vertical NO$_2$ distribution in the troposphere. Both radiative transfer and (a priori) NO$_2$ profile information is included in the tropospheric air mass factor used to convert the SCD$_\text{trop}$ to the VTC.

For estimating the surface albedo, the more recent GOME and SCIAMACHY retrievals provided by KNMI assume a Lambertian (or diffuse) surface, meaning that the surface reflects radiation equally in all directions. Thus, the Lambert-equivalent reflectivity (LER) is taken to be the surface albedo. Monthly averaged LER maps for 440 nm are constructed by multiplying the ratio between the Total Ozone Mapping Spectrometer (TOMS) 380 nm LER data set (Herman and Celarier, 1997) and the GOME 380 nm LER data set (Koelemeijer et al., 2002) for the month of March with the GOME 440 nm LER. Thus, the strengths of both data sets are combined: the long-term TOMS record (1978-1992) and the spectral information of the shorter GOME record.

The aerosol load is not included in the AMF$_\text{trop}$ calculation of the KNMI retrieval. The reason for this is given in section 2.2.4 describing the uncertainty of tropospheric NO$_2$ columns.

The resulting NO$_2$ VTCs are provided as number of NO$_2$ molecules per cm$^{-2}$, i.e., the number of molecules within a vertical tropospheric column with a base area of 1 cm$^{-2}$. Typical NO$_2$ VTC values can be seen in Figures 1.1, 1.4 and 2.6.
Retrieval of cloud parameters

The measurement of tropospheric NO2 in the UV-visible spectral range is hindered by the presence of clouds which shield the NO2 below from the satellites view. Important cloud parameters that are required to correct trace gas column density retrievals for the disturbing effects of clouds are the (effective) cloud fraction and cloud top pressure.

For the GOME data provided by the University of Bremen, the cloud fraction is derived from the Initial Cloud Fitting Algorithm (ICFA) \textit{(DLR, 1994)}. It consists of chi-square minimization of a measured and a simulated spectrum from 758 to 778 nm, thereby solving for the cloud fraction. The cloud top pressure, however, is assumed a priori and is taken from the International Satellite Cloud Climatology Project (ISCCP) database \textit{(Rossow and Garder, 1993)}. It is obvious that actual cloud top pressures can significantly differ from climatological mean values. However, due to the use of the GOME data from the University of Bremen for a case study only (including a reprocessing based on knowledge about the cloud top height, see section 3) this is not problematic for the present investigation.

For the KNMI GOME and SCIAMACHY retrievals that are mainly used in this work, cloud fraction and cloud top height are retrieved with the widely known Fast Retrieval Scheme for Clouds from the Oxygen A band (FRESCO) algorithm \textit{(Koelmeijer et al., 2001)}. The latter simultaneously retrieves cloud fraction and cloud top height by using reflectivities as measured by GOME inside and outside the O2 A band (758-766 nm; Fig. 2.7). The reflectivity of a cloudy scene is mainly determined by the cloud fraction, the cloud optical thickness (or cloud albedo) and the surface albedo. Within the O2 A band, the reflectivity further depends on the cloud top pressure because the clouds shield the oxygen below and, to a lesser extent, inside them. In FRESCO, three \~1 nm wide wavelength windows around the O2 A band are used (no absorption, strong absorption, moderate absorption). The FRESCO retrieval method is based on comparing the measured and simulated reflectivities in these wavelength windows. For the simulation of the spectrum of a partly cloudy GOME pixel, the latter is assumed to consist of a clear and a cloudy part, with a fractional area of \((1 – c)\) and \(c\), respectively, with \(c\) the cloud fraction. The contributions of the clear and the cloudy part of the pixel are further assumed to be the sum of the reflectivity of a completely clear and a completely cloudy pixel weighted with the cloud fractions. In other words: the AMF\textsubscript{trop} for a partly clouded scene is determined as a linear combination of a cloudy and a clear sky AMF\textsubscript{trop}. The retrieval is simplified by neglecting molecular scattering, scattering and absorption by aerosols and absorption by oxygen inside and below the cloud. Only absorption due to O2 above the cloud or ground surface, as well as reflection by the cloud top or surface is considered.

For the cloud fraction it is noteworthy that the latter is an effective cloud fraction determined by assuming an a priori chosen cloud albedo (usually 0.8). If a thin cloud layer with a lower albedo is detected, the effective cloud fraction may be smaller than the geometrical cloud fraction (known from meteorological observations).

In this thesis, the satellite pixel specific cloud fraction is used to distinguish between clear sky and overcast conditions. Usually, for clear sky conditions, \(c \leq 0.1\) is used (in section 5, the clear sky data set is extended to pixels with \(c \leq 0.2\)). Overcast conditions are defined to prevail for pixels with \(c \geq 0.75\) (section 4).
2.2.4 Uncertainty of tropospheric NO\textsubscript{2} columns

The errors of tropospheric NO\textsubscript{2} retrievals from space-borne measurements have been discussed in a general sense in Leue et al. (2001), Martin et al. (2002), Martin et al. (2003) and Richter and Burrows (2002). Furthermore, they have been extensively investigated and discussed on a quantitative pixel-to-pixel basis by Boersma et al. (2004). Here, a summary of the most important findings is given.

**Slant column density errors**

The first error source of space-borne trace gas retrievals is the slant column density. Errors in the latter are due to instrument noise, imperfect wavelength calibration, laboratory reference spectra errors, instrumental spectral features, interference with other absorbers and Ring effect. The Ring effect arises from the fact that, mostly, radiative transfer models assume the scattering to be elastic, i.e., there is no redistribution of the energy of a photon after a scattering event. In the real atmosphere, however, inelastic scattering by air molecules results in a redistribution of photons to other wavelengths, which scrambles the original small-scale features in the absorption spectra. This is called the scrambling or Ring effect. Conventionally, the Ring effect is corrected for by introducing a pseudo-absorber in the spectral fitting procedure (e.g. Chance et al., 2000). A further error in the slant column density is introduced by using an NO\textsubscript{2} absorption cross section with a fixed temperature for the slant column density fit. As already mentioned earlier, this error is corrected for a posteriori. The resulting total uncertainty of the SCD is difficult to quantify. For GOME NO\textsubscript{2} retrievals, Richter and Burrows (2002) estimated a conservative limit of $1 \times 10^{15}$ molec cm\textsuperscript{-2}. Boersma et al. (2004) reported on an estimated slant column error of $0.4 \times 10^{15}$ molec cm\textsuperscript{-2}.

**Uncertainty in the separation of the troposphere**

The second error source is the estimation of the stratospheric slant column that is required for the separation of the SCD\textsubscript{trop} from the SCD. The separation techniques used for the data in the present study have been described in section 2.2.3. For the Bremen retrieval using the reference sector method, the error in the determination of the stratospheric contribution to the SCD is estimated to be $<1 \times 10^{15}$ molec cm\textsuperscript{-2} for most of the cases (Richter and Burrows, 2002). However, due to the assumption of the stratospheric NO\textsubscript{2} being longitudinally constant, larger errors can be expected for higher latitudes. For the data-assimilation approach used in the KNMI retrieval, Boersma et al. (2004) give an uncertainty in the estimation of the stratospheric SCD of $<0.2 \times 10^{15}$ molec cm\textsuperscript{-2}.

**Errors in the tropospheric air mass factor**

The third and by far most critical error source for tropospheric retrievals over polluted continental areas is the AMF\textsubscript{trop}. The latter depends on the a priori assumed NO\textsubscript{2} profile shape, the cloud fraction, the cloud top height, the surface spectral reflectance (surface albedo) and the aerosol optical thickness profile. From section 2.2.3 and from Figure 2.8, it becomes obvious that the AMF\textsubscript{trop} depends further on parameters such as solar zenith and viewing zenith angle. However, the measurement geometry
is known with high accuracy and does, therefore, not contribute significantly to errors in the AMF\textsubscript{trop}. Boersma et al. (2004) have given a very precise description of the AMF\textsubscript{trop} sensitivities and errors due to the above mentioned parameters. This is summarised in Table 2.3. In order to have a significant tropospheric signal in the data, the uncertainties given in Table 2.3 have been estimated for pixels with a cloud reflectance fraction <50\%, which corresponds to a cloud fraction of 15-20\%. Furthermore, the data have been separated by the pollution regime. Obiously, the largest total uncertainties in the AMF\textsubscript{trop} can be expected for the most polluted pixels with an error of around 30\%.

As can be seen in Table 2.3, no error due to aerosol is given. Boersma et al. (2004) have argued that the presence of aerosol modifies the retrieval of cloud fraction and height with the FRESCO algorithm. A comparison of the expected aerosol correction factor versus the actual correction effect from the cloud retrieval has shown that even for a large aerosol optical thickness, the expected correction factor and actual correction effect agree to within 10\%. Boersma et al. (2004) therefore suggest that cloud algorithms implicitly correct for aerosol through their modified cloud fraction and height. Or in other words: correcting air mass factors for aerosols can not be decoupled from correcting cloud retrieval schemes for aerosols. These corrections have a comparable impact and nearly cancel. Martin et al. (2003) suggested the improvement of the NO\textsubscript{2} retrieval by directly accounting for the aerosol. However, Boersma et al. (2004) put this into question, since Martin et al. (2003) did not take into account the sensitivity of their cloud retrieval algorithm to aerosol.

Table 2.3. Estimated mean uncertainties of the AMF\textsubscript{trop} due to the model parameters cloud fraction $\sigma_{\text{AMF}(f_{cl})}$, cloud top height $\sigma_{\text{AMF}(z_{cl})}$, surface albedo $\sigma_{\text{AMF}(a_{sd})}$ and a priori NO\textsubscript{2} profile shape $\sigma_{\text{AMF}(x_{a})}$. Further denoted are the total mean uncertainties of both the AMF\textsubscript{trop} $\sigma_{\text{AMF}}$ and the NO\textsubscript{2} VTCs $\sigma_{\text{VTC}}$ (from Boersma et al., 2004).

<table>
<thead>
<tr>
<th>NO\textsubscript{2} VTC ($10^{15}$ molec cm\textsuperscript{-2})</th>
<th>$\sigma_{\text{AMF}(f_{cl})}$</th>
<th>$\sigma_{\text{AMF}(z_{cl})}$</th>
<th>$\sigma_{\text{AMF}(a_{sd})}$</th>
<th>$\sigma_{\text{AMF}(x_{a})}$</th>
<th>$\sigma_{\text{AMF}}$</th>
<th>$\sigma_{\text{VTC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.3</td>
<td>5%</td>
<td>2%</td>
<td>5%</td>
<td>10%</td>
<td>17%</td>
<td>&gt;100%</td>
</tr>
<tr>
<td>0.3-1.0</td>
<td>8%</td>
<td>3%</td>
<td>8%</td>
<td>11%</td>
<td>20%</td>
<td>55-125%</td>
</tr>
<tr>
<td>&gt;1.0</td>
<td>15%</td>
<td>2%</td>
<td>15%</td>
<td>9%</td>
<td>29%</td>
<td>35-60%</td>
</tr>
</tbody>
</table>

Total mean uncertainties in the AMF\textsubscript{trop} and the NO\textsubscript{2} VTCs

Finally, for estimating the total uncertainty of the NO\textsubscript{2} VTCs, one has to consider all errors including the uncertainties in the slant column density, the stratosphere-troposphere separation and the AMF\textsubscript{trop} calculation. For little polluted pixels over the oceans and remote continental regions, the overall NO\textsubscript{2} VTC retrieval uncertainty is dominated by errors in the spectral fitting and the stratospheric column estimate (because comparable stratospheric and tropospheric column contributions prevail over remote areas) and can exceed 100\%. This is in agreement with Richter and Burrows (2002) that estimated a total uncertainty for NO\textsubscript{2} VTCs of up to a factor of 2. For larger NO\textsubscript{2} VTCs over the continents, the relative uncertainty in the columns is
2 Scientific background

dominated by the uncertainty in the AMF\text{trop}. For such regions, Boersma et al. (2004) estimated a mean uncertainty in the NO\textsubscript{2} VTCs of 35-60%. Larger errors can be expected for pixels dominated by clouds.

2.3 Principle of ground-based in situ nitrogen oxide measurements

In the present work, space-borne observations of tropospheric nitrogen dioxide are related to ground-based in situ measurements of NO\textsubscript{2} carried out in Switzerland and adjacent areas. Details about the used ground-based measurement sites (location and measurement devices) are given in sections 3, 4 and 5. Therefore, the following section only introduces the principles of the ground-based in situ measurements.

At ground-based in situ sites, NO and NO\textsubscript{2} are measured with the chemiluminescence technique (Zellweger et al., 2003; Clemitshaw, 2004; Empa, 2005; FOEN, 2005). Chemiluminescence is the emission of ultraviolet, visible or infrared radiation from a molecule or atom as the result of the transition of an electronically excited state, having been produced as a consequence of a chemical reaction.

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2, \\
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2^*, \\
\text{NO}_2^* & \rightarrow \text{NO}_2 + h\nu \\
\text{NO}_x & = \text{NO} + \text{NO}_2
\end{align*}
\]

Figure 2.9. Principle of measuring NO\textsubscript{x} with the chemiluminescence technique.

For nitrogen oxide measurements, the most common technique is based upon the reaction between NO and O\textsubscript{3} (Fig. 2.9). A part of the formed NO\textsubscript{2} molecules exist in an electronically excited state. The detectable light that is emitted through the relaxation of the excited NO\textsubscript{2} to the ground state (visible-infrared spectral range; $\lambda = 590$-2800 nm) is proportional to the concentration of NO. The NO\textsubscript{2} concentration can additionally be measured by first reducing NO\textsubscript{2} to NO and then measuring the total NO\textsubscript{x} as NO. The NO\textsubscript{2} concentration results from the difference between the NO (without conversion) and the NO\textsubscript{x} measurement.

Most of the measurement sites are equipped with measurement devices that reduce NO\textsubscript{2} to NO with a molybdenum converter. This conversion is not specific for NO\textsubscript{2}, but other nitrogen species such as PAN, HNO\textsubscript{2}, HNO\textsubscript{3} and particulate nitrate are also
reduced to NO and act as interferences in the NO$_2$ measurement. (Clemishaw, 2004; Wendel et al., 1983). Only a minor part of the ground-based in situ measurement stations are equipped with photolysis converters allowing a selective measurement of NO$_2$. The overall NO$_2$ measurement uncertainty estimate for 1h-averages includes the precision of the chemiluminescence detector, the NO standard uncertainty and the conversion efficiencies. For the NO$_2$ measurement with the photolytic and molybdenum conversion technique, the 1σ uncertainty is estimated to be ±4% and ±6.1-9.4% (the latter depending on the instrument). Note, however, that the interference of the NO$_2$ measurement with the molybdenum conversion technique is not accounted for in the uncertainty estimate. Thus, in section 4, a correction factor for this interference is given together with an error estimate.
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3 Transboundary transport of NO\(_2\) as observed from GOME and its impact in the Alpine region

This section is based on

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Abstract

High tropospheric NO\(_2\) amounts are occasionally detected by space-borne spectrometers above cloudy scenes. For monitoring of near-ground air pollution such data are not directly applicable because clouds shield the highly polluted planetary boundary layer (PBL). We present a method based on trajectories which implicitly estimates the additional sub-cloud NO\(_2\) distribution in order to model concentrations at ground stations. The method is applied to a transboundary pollution transport episode which led to high NO\(_2\) vertical tropospheric column densities (VTCs) over middle Europe observed by the Global Ozone Monitoring Experiment (GOME) instrument above clouds on 17 February 2001. The case study shows that pollution originally residing near the ground in central Germany, the Ruhr area and adjacent parts of the Netherlands and Belgium has been advected to higher tropospheric levels by a passing weather front. Combining the above-cloud NO\(_2\) VTCs with trajectory information covering the GOME columns and including their sub-cloud part yields an estimate of the total NO\(_2\) distribution within the tropospheric columns. The highly polluted air masses are then traced by forward trajectories starting from the GOME columns to move further to the Alpine region and their impact there is assessed. Considering ground-based in situ measurements in the Alpine region, we conclude that for this episode, at least 50% of the NO\(_2\) concentration recorded at the sites can be attributed to transboundary transport during the frontal passage. This study demonstrates the potential of using NO\(_2\) VTCs from GOME detected above clouds when combined with transport modelling.
3.1 Introduction

Nitrogen dioxide (NO₂) plays a key role in photochemical air pollution. Its amount and distribution is of significance directly for air quality and human health and indirectly as an ozone precursor (e.g. Seinfeld and Pandis, 1998). Therefore, for air quality policy, accurate source attribution and impact assessment is required.

3.1.1 NO₂ chemistry

NO₂ is formed according to the photochemical equilibrium on a time scale of minutes from the primarily emitted nitrogen oxide (NO), the bulk of which is of anthropogenic origin (Brasseur, 2003). The NO₂ concentration at any time and place is determined by the emission of NOₓ (≡ NO + NO₂), its production and loss reactions as well as meteorological transport and dilution. Furthermore, the NO₂ concentration is affected by the partitioning of NOₓ into NO and NO₂ which depends on the meteorological conditions, the abundance of reactive organic compounds and the altitude in the troposphere. During the Transport and Chemical Evolution over the Pacific (TRACE-P) campaign between February and April 2001 (Jacob et al., 2003), the bulk of the NO/NO₂ ratios have been found to be around 0.25 at near-ground levels (Nakamura et al., 2003). Similar values from different campaigns can be found in Warneck (2000). Ratios of up to 1 are found in the middle troposphere (Nakamura et al., 2003).

NO₂ is removed from the troposphere through conversion to nitric acid (HNO₃) which deposits (Kramm et al., 1995). During daytime, HNO₃ emanates from the reaction of NO₂ with the OH radical. During night time, NO₂ reacts with ozone to form the NO₃ radical, the latter further reacting with NO₂ to N₂O₅. Nitrogen pentoxide subsequently reacts on surfaces and aerosol to HNO₃ (Dentener and Crutzen, 1993). Although diurnal variations of the NO₂ lifetime are considerable and may be only a few hours during photochemically active summer days, the average boundary layer lifetime during the whole year is estimated to be in the order of one day (Warneck, 2000).

Leue et al. (2001) used vertical tropospheric NO₂ column densities observed from GOME over the eastern coast of North America to estimate an NO₂ lifetime of 27 hours in the planetary boundary layer (PBL). Following the plume leaving the coast of India, Kunhikrishnan et al. (2004) estimated a lifetime of 18 hours. However, in the middle and upper troposphere, decreasing OH and aerosol concentrations lead to a longer NO₂ lifetime being of the order of several days to a week (Jaegle et al., 1998; Seinfeld and Pandis, 1998; Warneck, 2000). Thus, NO₂ may be transported over larger distances once it is lifted to higher tropospheric levels, for example by frontal systems.

3.1.2 Previous observations

For high-alpine sites, the importance of meteorological transport processes such as frontal advection on the variability of trace gases has been shown. For example, Forrer et al. (2000) investigated among others the variability of NOₓ at the high-alpine site Jungfraujoch and found that during such events, NOₓ concentrations can increase from below 1 ppb up to around 10 ppb. Such frontal episodes have been
found to significantly increase the monthly mean concentrations during the whole year, most pronounced during winter months. Further investigations at our institute have distinguished between background and polluted conditions at the high-alpine site Jungfraujoch based on classifying trajectories. It has been found that around one third of the days at this site are affected by synoptical lifting and frontal pollution transport causing an average NOx concentration increase in the order of 100%.

Numerical model results have shown synoptic-scale vertical advection to be a significant transport mechanism for nitrogen oxides (Hov and Flatoy, 1997). In agreement with this, more than 50% of a passive tracer released in the boundary layer was found to be transported to the free troposphere within 24 hours during a frontal passage (Donnell et al., 2001). Aircraft campaigns have verified that significant quantities of trace gases are lifted up from the PBL into the free troposphere by a warm conveyor belt associated with the frontal system (Bethan et al., 1998). The importance of synoptic uplift and subsequent long-range transport of trace gases for air pollution monitoring was shown by Stohl et al. (2002). The retrieval of the tropospheric NO2 column from space-borne instrumentation has become available since the launch of the GOME instrument (Burrows et al., 1999) aboard the European Space Agency (ESA) satellite ERS-2 (Earth Remote Sensing Satellite). GOME measurements were successfully used to observe intercontinental transport events of nitrogen dioxide (Spichtinger et al., 2001; Wenig et al., 2003; Stohl et al., 2003). Therefore, combining satellite and ground-based data with transport models is useful to observe transport phenomena influencing the NO2 distribution.

3.1.3 Present study

We present a method to quantify air pollution transport based on trajectory analysis by using tropospheric NO2 observed from GOME above clouds instead of emission inventories. The method is applicable for high NO2 columns observed from GOME above an extended cloud cover where lightning NOx can be excluded and, thus, a frontal transport episode is postulated to have advected near-ground pollution above the cloud cover. Because the trajectories cover the whole GOME column including its sub-cloud part, the method implicitly estimates the NO2 distribution within the whole column.

In this paper, an episode of “intracontinental” transport of nitrogen dioxide is investigated for a cloudy scene on 17 February 2001. First, the source region of the pollution detected from GOME is assessed with backward trajectories. Forward trajectories are used to estimate potential impact regions of the pollution transport. Employing a higher number of trajectories and the GOME NO2 VTCs the NO2 transport and its impact in the Alpine region is identified quantitatively and compared to ground-based in situ measurements.

3.2 Measurement data

3.2.1 GOME measurements

The GOME instrument aboard ESA’s ERS-2 satellite measures upwelling radiance from the atmosphere and extraterrestrial solar irradiance. The amount and
distribution of a variety of significant atmospheric trace constituents may be retrieved from these observations (Burrows et al., 1999). It was designed and optimised primarily to measure the global ozone distribution, but also the amounts of the trace gases BrO, OCIO, H2O, HCHO and NO2 can be obtained. The GOME instrument comprises a nadir-viewing spectrometer which observes simultaneously the entire spectral range between 240 and 793 nm at channel dependent spectral resolutions between 0.2 and 0.4 nm. From the spectral features of the trace gases, their vertical columns are retrieved (e.g. Richter and Burrows, 2002). Because of its sun-synchronous polar orbit, GOME measurements in middle latitudes are always taken in the late morning local time. With its swath width of 960 km (single ground pixel size is 320 km across track and 40 km along track) GOME reaches full coverage at the mid-latitudes within 2-3 days.

The NO2 vertical tropospheric column density (VTC) data used in this study were provided by the University of Bremen (Richter and Burrows, 2002). Uncertainties in the VTCs are due to the NO2 fitting algorithm, instrument characteristics, the method of the stratosphere-troposphere separation and atmospheric parameters such as the a priori NO2 profile shape, the surface spectral reflectance, the aerosol loading and the clouds. These atmospheric parameters account for the largest part of the uncertainties. Richter and Burrows (2002) and Boersma et al. (2004) carried out detailed error analysis for the NO2 VTCs and found a total uncertainty of up to a factor of 2. In order to reduce the uncertainty, the GOME data used in the present study were reprocessed with an adapted cloud top height (CTH) and an assumed location of the NO2 layer. Furthermore, different scenarios for the structure of the cloud cover (closed cloud cover and partly cloudy taking into account cloud mask data) are used.

3.2.2 Ground-based in situ measurements

The Swiss National Air Pollution Monitoring Network (NABEL) provides long-term ambient air measurements (EMPA, 2002; BUWAL, 2002). To investigate the impact of the mesoscale transport process, rural and remote sites located in the Swiss Plateau or elevated and north-exposed stations are suitable as the air mass inflow during this episode is from northern to north-eastern direction. Data from the following sites (Fig. 3.1) are used in this study:

- **A)** Rigi (47° 04' N, 8° 28' E, 1030 m asl): A rural site that is well suited for detection of events advected from northern direction, because it is situated on a north-exposed mountain slope. In winter, local influences arising from thermal transport are rare.

- **B)** Chaumont (47° 03' N, 6° 59' E, 1140 m asl): This site is also situated at an elevated location at some distance from cities and is surrounded by meadows and grassland. The nearest industrial enterprises are situated 5 to 10 kilometres away.

- **C)** Taenikon (47° 28' N, 8° 54' E, 540 m asl): A site that samples air from the Swiss Plateau. The surroundings are dominated by agriculture and forests, the highway A1 lies in north-eastern direction at a distance of 4 kilometres.
D) Zugspitze (47° 25' N, 10° 59' E, 2963 m asl):
This site is located at the northern rim of the Alps and, therefore, suitable for the detection of air masses advected from the North (Umweltbundesamt, 2002). It is used because no measurements from the high-alpine site Jungfraujoch (Switzerland) are available during the time of the case study.

Figure 3.1. The location of the three remote ground-based measurement stations operated by the Swiss National Air Pollution Monitoring Network (NABEL) and the Zugspitze station (Umweltbundesamt, 2002) which are used in this case study.

At these sites, nitrogen oxides are measured with the ozone chemiluminescence detectors Monitor Labs (ML) 8841 (Rigi), ML 9841 A (Chaumont), ECO Physics CLD 700 (Taenikon) and TE 42 Thermo Environmental Systems/TECAN (Zugspitze). All measurement devices are equipped with a molybdenum converter. It should be noted that these catalytic surface converters are sensitive not only to NO₂, but also to other nitrogen species such as PAN, HNO₂, HNO₃ and particulate nitrate to NO. Generally, the PAN mixing ratio can be expected to be small during winter conditions. Wunderli and Gehrig (1991) found a mean February PAN mixing ratio at Davos (Switzerland, 1640 meters asl) of 0.1 ppb. Under cold and clear weather conditions, however, elevated PAN mixing ratios were measured in winter with an evening maximum at Davos of 0.6 ppb. HNO₂ is rapidly transformed to OH and NO by photolysis and mixing ratios are normally below the detection limit during the day (Winer and Biermann, 1994). Maximum February/March HNO₃ concentrations were found to be in the order of 0.3 ppb at Jungfraujoch (Zellweger et al., 2003) and 0.8 ppb in Duebendorf (Zellweger et al., 1999) at 3580 m asl and 430 m asl, respectively. Particulate nitrate exhibits large temporal and spatial variations and might have the strongest influence on the interference. In March 1997, Zellweger et al. (1999)
measured nitrate concentrations of up to 5.5 ppb at the Swiss Plateau station Duebendorf. February measurements at the high-alpine site Jungfraujoch indicated maximum concentrations of 0.3 ppb during weak thermal transport events and much lower values when thermal transport is absent (Zellweger et al., 2003). As the NO$_2$ mixing ratios are between 5 (high-alpine) and 30 ppb (Swiss Plateau) in this case study, we consider the interference of the above discussed nitrogen species to have a minor influence.

### 3.3 Methods

#### 3.3.1 Trajectory calculations

Backward and forward trajectories are used to investigate the origin of the detected air masses in the studied GOME columns and their further movement. The trajectories are based on analysed wind fields with a six hour temporal and $1^\circ \times 1^\circ$ geographical resolution provided by the model of the European Centre for Medium-Range Weather Forecast (ECMWF). Three dimensional kinematic backward and forward trajectories are calculated with the software package “Lagranjo” (Wernli and Davies, 1997). Their length is chosen to be long enough for source and impact analysis (several days). The NO$_2$ distribution within the GOME columns is unknown. Therefore, the backward/forward trajectory arrival/starting points cover the GOME columns both horizontally and vertically in order to account for its whole tropospheric volume ($320 \, \text{km} \times 40 \, \text{km} \times \text{tropopause height}$).

For a first assessment of the source regions and the further air mass movement (sections 3.4.3 and 3.4.4), each column is covered with 70 arrival/starting points; 10 levels from 900 hPa up to 400 hPa in 50 hPa steps, each level containing 7 points. For a quantitative transport assessment (sections 3.3.2 and 3.4.6), a much higher density of backward and forward trajectories is calculated for each GOME column with 128 (4 along track $\times$ 32 across track) arrival/starting points in the horizontal for 23 height levels between 950 hPa and 400 hPa in 25 hPa steps (resulting in a total of 2944 trajectories per column). The arrival/starting time point for the case study is chosen to be on 17 February, 2001, 9:00 UTC corresponding to the GOME overpass at around 10:15 local time.

#### 3.3.2 Transport model based on trajectories and GOME observations

A transport model based on backward and forward trajectories, GOME NO$_2$ VTCs above a cloudy scene, population distribution data, and an assumed average NO$_2$ lifetime is employed to estimate the amount of advected NO$_2$ at ground measurement sites. The method comprising three steps is discussed in detail in the following sections and is illustrated in Figure 3.2. Firstly, the population number is added up (as a proxy for NO$_2$ emissions), transported along the backward trajectories and corrected for the NO$_2$ lifetime. Secondly, the NO$_2$ proxy arriving in the GOME columns is summed vertically above different CTH. These proxy VTCs are compared to the GOME NO$_2$ VTCs in order to identify an effective CTH (CTH$_{\text{eff}}$) where the modelled above-cloud pollution best reproduces the detected pollution from GOME. Relating the proxy VTCs above CTH$_{\text{eff}}$ to the GOME NO$_2$ VTCs yields a conversion
Using the latter, the proxy is converted to number of NO$_2$ molecules. Thirdly, the NO$_2$ polluted air masses is traced with forward trajectories, corrected for the NO$_2$ lifetime and converted into NO$_2$ mixing ratios when trajectories reach near-ground levels.

**Pollution uptake and NO$_2$ lifetime correction**

The NO$_2$ uptake along the backward trajectories is simulated by passing the trajectories over a $1^\circ \times 1^\circ$ resolved population grid (UNEP: Global Population Distribution Database, http://grid2.cr.usgs.gov/globalpop, 1997) assuming the NO$_2$ emission to be proportional to the population in the respective grid cell. Following the trajectory forward in time, pollution is taken up when the trajectory reaches a near-ground level of less than an assumed PBL height above model ground. In this case, the number of the population in the respective grid cell is added up along the trajectory as a proxy for NO$_2$ emissions. In order to account for the enhanced NO$_x$ emissions during daytime, the night time uptake is weighted with a factor of 0.5, whereas the daytime uptake is multiplied with a factor of 1.5. Further, the NO$_2$ proxy transported along the trajectory is decreasing every time step according to an assumed average NO$_2$ lifetime.

It must be mentioned that the bulk of NO$_x$ is emitted as NO. Further, the partitioning of NO$_x$ into NO and NO$_2$ is dependent on the meteorological conditions (and therefore the season), the pollution situation and the abundance of reactive organic compounds shifting the photostationary steady state (Warneck, 2000, and references therein). Nevertheless, we henceforth allude to NO$_2$ (emissions), because the NO$_x$ partitioning is – due to the conversion described in the next paragraph - circumstantial for the further analysis shown here. Thus, the implicit assumptions are made that (i) emission sources are similar concerning the NO$_x$ partitioning and that (ii) the NO$_x$ partitioning during the investigated episode is similar within the transported air parcels.

**Conversion of NO$_2$ proxy to number of NO$_2$ molecules**

Each backward trajectory arrives in its appropriate GOME column containing a population number as a proxy for NO$_2$. This quantity is converted to a number of NO$_2$ molecules by applying a conversion factor. The latter is deduced from relating the sum of the considered GOME NO$_2$ VTCs detected above the clouds to the appropriate sum of the proxy VTCs above the cloud cover. As in this way also the NO$_2$ proxy below the clouds is converted, this step implicitly estimates the NO$_2$ distribution within the whole column including its sub-cloud part. However, two main issues complicate this approach:

1. The sensitivity of the GOME instrument for NO$_2$ within the column is not constant. For a cloudy pixel, the sensitivity is maximal at the CTH and decreases for NO$_2$ situated above or within the cloud (Hild et al., 2002).

2. Near-ground trajectories based on a $1^\circ \times 1^\circ$ resolved wind field might not properly reproduce the (frontal) air mass movement.
Figure 3.2. Flow chart illustrating the proposed method (section 3.3.2) to model NO\textsubscript{2} mixing ratios at ground, employing population numbers assigned to the trajectories and subsequent conversion with GOME NO\textsubscript{2} vertical tropospheric column densities (VTCs). (CTH\textsubscript{eff} = effective cloud top height, VMR = volume mixing ratio, VC = vertical column, pixel = GOME pixel).

This prevents the straightforward use of the real CTH above which the proxy VTCs can be calculated. To account for both, we define a CTH\textsubscript{eff} where the modelled above-cloud pollution (proxy VTCs) best reproduces the pollution pattern detected.
from GOME (NO₂ VTCs). Because GOME sees to some extent into the clouds, the CTH_{eff} is expected to be lower than the real CTH. The CTH is assumed to be constant across the considered GOME pixels (Fig. 3.3c). Linearly fitting the proxy VTCs above different CTHs with the real GOME NO₂ VTCs yields the adequate CTH_{eff} where the explained variance R² maximizes.

**Pollution propagation, NO₂ lifetime and conversion to NO₂ mixing ratios at ground stations**

The NO₂ is modelled to propagate further along the forward trajectories. Again, the NO₂ loading is decreasing every time step according to the assumed average NO₂ lifetime. As soon as the trajectories reach near-ground levels, the impact on the NO₂ concentration there can be assessed by assigning the NO₂ values of the trajectories to appropriate grid cells superimposed over the region of interest (for the investigated episode a 0.5° × 0.5° resolved grid is superimposed over the Alpine region). In a last step, the hourly resolved numbers of molecules in the grid cells corresponding to the measurement sites are recalculated to mixing ratios using temperature and pressure data and the vertical box extension. The vertical box extension (near-ground level) for the case study is defined in section 3.4.6.

**Errors of the method**

Main error sources of the described approach are (i) the assumption of an average lifetime of NO₂, (ii) the fact that a single air mass trajectory does not implicitly account for dilution, (iii) the error associated with the assumption of the population distribution being a representative proxy for NOₓ emissions, (iv) the assumption of a constant CTH and (v) the uncertainties in the GOME NO₂ VTCs.

(i) Assuming an average lifetime for NO₂ is a strong simplification given its complex atmospheric chemistry. Especially when transport occurs within a shorter time scale (within a few hours only), also differences between daytime and night time NO₂ chemistry have to be considered. For the present case study investigating a transport episode of several days an average NO₂ lifetime is assumed. In order to account for errors arising from this simplification, the sensitivity of the results with respect to the lifetime is tested (and no major impact is found, see section 3.4.6). A relatively long lifetime (24 hours) is chosen because the photolysis is relatively weak in winter due to the increased solar zenith angle (Dickerson et al., 1982; Parrish et al., 1983; Wiegand and Bofinger, 2000). Furthermore, the loss of NO₂ through conversion with OH to HNO₃ is slow because the amount of OH is low in winter (Seinfeld and Pandis, 1998). An average lifetime of one day can also be found in literature (Warneck, 2000) and is confirmed from assessments with tropospheric NO₂ columns from GOME (Leue et al., 2001; Kunhikrishnan et al., 2004).

(ii) The dilution is to some extent taken into account by the large number of trajectories and their divergence. Furthermore, the effect of dilution can be expected to be rather weak for the frontal transport as it lifts up an extended air mass having enhanced NO₂ concentrations and, thus, relatively small concentration gradients.
A basic assumption is that the population distribution constitutes a proxy for NO\textsubscript{x} emissions. This seems plausible taking into account the fact that NO\textsubscript{x} is mainly of anthropogenic origin (Brasseur et al., 2003). Although NO\textsubscript{x} emissions along highways also take place outside the population centres, this error is expected to be of minor influence because the population data are based on a relatively coarse resolved grid. This means that busy highways can be thought to be located around the population centres.

The CTH is essential for the described method and large inhomogeneities in the CTH must be considered. For the present study, the inspection of recent satellite data (KNMI, personal communication) indicates a rather uniform cloud cover over the considered GOME pixels and therefore, in this study, the assumption of a constant CTH is made.

The error of the GOME NO\textsubscript{2} VTCs can be reduced by reprocessing the data considering the occurrence of clouds.

### 3.4 Case study – results and discussion

#### 3.4.1 GOME observations on 17 February 2001

GOME recorded high NO\textsubscript{2} VTC values over central Europe on 17 February, 2001 (Fig. 3.3c). As can be seen in the Meteosat image (Fig. 3.3d), clouds shielded the ground. Therefore, a significant amount of nitrogen dioxide has to be located within and/or above the cloud cover. However, as pointed out by Richter and Burrows (2002), Leue et al. (2001) and Hild et al. (2002), the albedo effect of underlying clouds can increase the NO\textsubscript{2} signal. Therefore, a reprocessing of the GOME NO\textsubscript{2} VTCs is carried out using an assumed NO\textsubscript{2} layer, the CTH, and the structure of the cloud cover. A closed cloud cover is assumed in the reprocessing version A. In version B, cloud mask information is used and the total tropospheric column (where cloud free) and above-cloud columns are combined. On the basis of preliminary trajectory calculations, the NO\textsubscript{2} is assumed to occur in a layer between 4000 and 6000 meters asl, whereas for standard processing an a priori NO\textsubscript{2} profile with a constant mixing ratio in the lowermost 1.5 km of the troposphere is used (Richter and Burrows, 2002). For the underlying cloud cover, a height of 3000 metres is assumed (which is accordance with live cams in the Alps). In fact, both the real vertical NO\textsubscript{2} distribution and the CTH are not exactly known, but an inaccurate estimation of this heights turned out to be not very critical. The two reprocessing scenarios A and B yielded quite similar column values as shown in Table 3.1. Furthermore, the reprocessing results in distinctly lower values than the standard processing, which is due to the above mentioned albedo effect of the clouds (Richter and Burrows, 2002; Leue et al., 2001; Hild et al., 2002). For the further analysis, the overall cloudy case is used.
Table 3.1. GOME NO₂ vertical tropospheric column densities (VTCs) for the standard processing and the two reprocessing scenarios A and B. The NO₂ VTCs are the average values for the two pixel groups shown in Figure 3.3c.

<table>
<thead>
<tr>
<th></th>
<th>standard processing</th>
<th>reprocessing A</th>
<th>reprocessing B</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂ profile</td>
<td>standard a priori profile, constant mixing ratio in the lowermost 1.5 km ((Richter and Burrows, 2002))</td>
<td>NO₂ layer between 4000 and 6000 m asl</td>
<td>NO₂ layer between 4000 and 6000 m asl</td>
</tr>
<tr>
<td>cloud cover</td>
<td>-</td>
<td>closed cloud cover</td>
<td>partly cloudy</td>
</tr>
<tr>
<td>cloud top height</td>
<td>-</td>
<td>3000 m asl</td>
<td>3000 m asl</td>
</tr>
<tr>
<td>NO₂ VTCs ([\times 10^{15} \text{ molec cm}^{-2}])</td>
<td>38 (pixel group 1)</td>
<td>13 (pixel group 1)</td>
<td>12 (pixel group 1)</td>
</tr>
<tr>
<td></td>
<td>64 (pixel group 2)</td>
<td>17.5 (pixel group 2)</td>
<td>16.5 (pixel group 2)</td>
</tr>
</tbody>
</table>

Figure 3.3. GOME track on 16 February, 2001, indicating high NO₂ VTCs over France, Belgium, the Netherlands and Germany (a). Meteosat visible wavelength image detected at 9:30 am UCT on 16 February, 2001 (b). GOME track on 17 February, 2001, showing high NO₂ VTCs above clouds. For the highest values (pixel groups 1 and 2, each consisting of 2 GOME pixels) trajectories are discussed qualitatively. The transport model calculation is based on all of the 12 framed pixels found relevant for the investigated air mass (c). Meteosat visible wavelength image detected at 9:30 am UTC on 17 February, 2001, indicating the extended cloud cover over middle Europe (d).
3.4.2 Meteorological situation

After a frontal passage on 13 February, a high pressure system installed over southern England and moved slowly to the east, causing the inflow of dry continental polar air to Switzerland during 14-16 February (from Alpine Weather Statistics (MeteoSwiss, 1985)). The flat pressure distribution associated with the high pressure system led to stagnating air over middle Europe. On the 16th, a cold-front formed over north-eastern Europe (Figs. 3.3b and 3.4) and moved southward, developing to an occlusion during 17 February (Figs. 3.3d and 3.4).

Cold-fronts are often associated with lightning activity, the latter being known to be an in situ source of NOx in the free troposphere (e.g. Huntrieser et al., 2002). During the time of our case study, however, no lightning activity was recorded (www.wetterzentrale.de/topkarten/tkbeoblar.htm), and NO2 production by lightning can, therefore, be excluded.

![Weather maps showing the southward moving cold front on 16 February 2001 (left) developing into an occlusion on 17 February (right) approaching the Alpine region.](image)

3.4.3 Backward trajectories – NO2 source

The source region of the air pollution detected by the GOME instrument is analysed with backward trajectories (Fig. 3.5), focusing on the two NO2 pixel groups (each composed of two GOME pixels as defined in Figure 3.3c) over the border triangle of France, Germany and Switzerland (pixel group 1) and over south-eastern Germany (pixel group 2).

The trajectories indicate that the air masses arriving in the GOME columns are advected from western directions above the Northern Atlantic. They descend over Southern Scandinavia and the North Sea and subsequently turn clockwise over the region of the Netherlands, Belgium and Germany. This is a result of the presence of the high pressure system which installed over Europe before the frontal passage (Fig. 3.4). Near the ground, the vertical distribution of the trajectories is investigated in detail, because the residence time of an air parcel within the PBL allows the uptake of anthropogenic NO2.
Backward trajectories arriving on 17 February 2001, 9:00 UTC, in the two GOME pixel groups 1 (a) and 2 (b) defined in Figure 3.3c. The colored dots mark hourly trajectory time steps with a trajectory height above model ground of less than 150 hPa (blue), less than 100 hPa (green) and less than 50 hPa (red), respectively. For clarity, in the horizontal projections, only trajectories with a distance from ground of less than 100 hPa for at least one hourly time step are shown and trajectory points exceeding 150 hPa ground distances are omitted. The source regions of the detected NO\textsubscript{2} are likely to be located where the trajectories reside near the ground (red dots).

For better identification of the potential source regions, only trajectories residing at a ground distance of less than 100 hPa for at least one (hourly) time step are considered in Figure 3.5. Further, in the horizontal projections, time steps along these trajectories are omitted when their distance from ground exceeds 150 hPa. The potential source regions are most likely located where the trajectories travel near the ground, the latter indicated in Figure 3.5 by trajectory time steps below 50 hPa ground distance. Comparing these regions with the GOME NO\textsubscript{2} VTCs on 16 February (Fig. 3.3a) shows a convincing coincidence between the regions with high NO\textsubscript{2} VTCs and the potential source regions. For 15 February, no GOME track
covering the appropriate region is available. The narrow spatial distances of the hourly time steps (red dots in Figure 3.5) show that the air was rather stagnant during 15 and 16 February. As a result, the air parcels were exposed to NO\textsubscript{x} emissions for several hours in the highly populated region of the Netherlands, Belgium, Central Germany and the Ruhr area, the latter known to be one of the European hot spot regions concerning NO\textsubscript{2} pollution (Leue et al., 2001; Beirle et al., 2003; Konovalov, 2004).

![Figure 3.6.](image)

**Figure 3.6.** The forward trajectories of the two GOME pixel groups 1 and 2 (defined in Figure 3.3c) starting on 17 February 2001, 9:00 UTC, indicate the polluted air masses proceed to Switzerland and the Alpine region and further to south-west.

The air mass trajectories then exhibit a sudden movement to southern direction associated with frontal uplifting (Fig. 3.5). These air masses are highly likely to be responsible for the enhanced NO\textsubscript{2} in the pixel groups 1 and 2. The near-ground pollution reaches heights of up to 500 hPa above surface pressure (Fig. 3.5). This corresponds to lifting up to up to 5000 meters above model ground. Even higher
levels were reached by air formerly travelling at a ground distance of more than 100 hPa. Comparing the backward calculations for GOME pixel groups 1 and 2 indicates that the air from pixel group 2 over south-eastern Germany is more affected by polluted PBL air, because the density of the trajectories at less than 50 hPa is higher, and their uplifting takes place later. This explains the higher NO\textsubscript{2} VTCs in these GOME columns.

3.4.4 Forward trajectories – impact in the Alpine region

The forward trajectories show that the polluted air masses detected by GOME move to the Alpine region including Switzerland (Fig. 3.6). For both GOME pixel groups, the forward trajectories’ distance to the ground decreases again. This is explained by both an effective subsidence and the increasing altitude of the ground in southern direction. The air masses reach heights below 50 hPa over the Alpine region (Fig. 3.6). The forward trajectories from GOME pixel group 1 stay relatively bundled and reach Switzerland in its north-western part. The trajectories from GOME pixel group 2, however, show a much larger spread and the polluted air reaching Switzerland can therefore be expected to be more diluted.

![Figure 3.7. NO\textsubscript{2} mixing ratios measured at the NABEL ground stations Chaumont, Rigi and Taenikon and at the high-alpine site at Zugspitze in February 2001.](image)

3.4.5 In situ measurements in the Alpine region

The February 2001 time series of NO\textsubscript{2} measurements from the NABEL and Zugspitze stations indicate several events with high NO\textsubscript{2}, the two most outstanding ones around 7-8 and 17-18 February (Fig. 3.7). The highest NO\textsubscript{2} mixing ratio of this
month was measured in the evening on 17 February at the Rigi station with a value of 30 ppb. The \( \text{NO}_2 \) measurements at Chaumont and Zugspitze reached their maximum values at the same time with 27 ppb and 6 ppb, respectively. At the Taenikon station, the highest value was measured on 8 February (29 ppb), but the value on the evening of the 17\textsuperscript{th} is, nevertheless, a distinct event with 26 ppb \( \text{NO}_2 \). What makes the event on 17-18 February special is the fact that all four stations show an almost simultaneous and significant increase in their nitrogen dioxide mixing ratios. This is in contrast to the event on 7-8 February, when very high \( \text{NO}_2 \) values are limited to Taenikon. There, local pollution events are frequent due to the relatively near highway and the inversion layer above the Swiss Plateau which increases pollution concentrations especially in winter.

The simultaneous pollution event on 17\textsuperscript{th} and 18\textsuperscript{th} and the similar mixing ratios at the Swiss sites cannot be explained by local sources, because these are strongly different in the north of each of the considered measurement stations. Furthermore, thermal uplifting, which is typical for elevated sites, is not likely to occur during the night and early morning hours, when the maximum \( \text{NO}_2 \) mixing ratios were observed. Thus, the higher \( \text{NO}_2 \) amounts measured at the elevated stations must be caused by larger scale meteorological transport of pollution. It is noteworthy that the maximum \( \text{NO}_2 \) mixing ratios of 26 ppb measured in Taenikon, 27 ppb at Chaumont and 30 ppb at Rigi are quite similar, even though the annual mean \( \text{NO}_2 \) amounts show a pronounced decrease with increasing height (Taenikon: 7.0 ppb, Rigi: 4.8 ppb, Chaumont: 3.7 ppb \cite{BUWAL, 2002}). These similar mixing ratios indicate a rather well mixed and extended air mass, the latter additionally confirmed by the simultaneous increasing mixing ratio at Zugspitze which is located about 290 kilometres away from Rigi. These findings agree well with the above described air masses that have taken up pollution over an extended region and having been transported over mesoscale distances of several hundred kilometres.

3.4.6 Transport model

**Effective cloud top height and conversion with GOME observations**

Our method proposed in section 3.3.2 and illustrated in the flow chart of Figure 3.2 is used to model the transport of \( \text{NO}_2 \) for this case study. The core element of it is the conversion of population numbers assigned to the trajectories as a proxy for \( \text{NO}_2 \) to number of \( \text{NO}_2 \) molecules considering the GOME \( \text{NO}_2 \) VTCs and the CTH\textsubscript{eff}. As pointed out in section 3.3.2, the latter is defined to be the CTH for which the modelled above-cloud pollution (proxy VTCs) best reproduces the detected pollution from GOME (\( \text{NO}_2 \) VTCs). Figure 3.8 illustrates an intermediate step where the population numbers assigned to the trajectories are added up above different CTH ranging between 750 and 875 hPa. This results in a 2-dimensional proxy for the \( \text{NO}_2 \) distribution above the clouds. Especially when the CTH is in the range of 800 to 875 hPa (which is lower than the real CTH), the modelled \( \text{NO}_2 \) distribution resembles the GOME observation (Fig. 3.3c). The band structure of high \( \text{NO}_2 \) present in Figure 3.8 agrees with the shape of the occlusion in Figure 3.4 and indicates the uplift of previously ground-near pollution. Summing the population numbers from Figure 3.8 for each of the 12 considered GOME pixel locations (Fig. 3.3c) yields the \( \text{NO}_2 \) proxy VTCs. They are related to the appropriate \( \text{NO}_2 \) VTCs from GOME in order to determine the adequate CTH\textsubscript{eff} for the further calculation. Figure 3.8 already indicates
that the CTH$_{eff}$ must be located at a lower altitude because the pollution distribution detected from GOME (Fig. 3.3c) seems to be better reproduced at these CTHs. For a CTH of, e.g., 750 hPa, a poor linear fit between the two quantities can be expected: for some GOME pixel locations, no NO$_2$ proxy is found above the clouds although the appropriate GOME columns show an enhanced NO$_2$ amount (Figs. 3.8 and 3.3c).

![Figure 3.8](image.png)

**Figure 3.8.** Population numbers (assigned to the backward trajectories as a proxy for NO$_x$ emissions) added up above different cloud top heights (CTH) between 750 hPa and 875 hPa to a 2-dimensional proxy for the NO$_2$ distribution above the clouds.

Figure 3.9 shows the scatter plot between the two quantities for the CTH located at 850 hPa. For this CTH, a relatively good correlation and no offset is found between the proxy VTCs and the GOME NO$_2$ VTCs although a constant CTH has been assumed. This indicates the latter assumption to be not too far away from reality.
This is also confirmed by an inspection of more recent satellite data *(KNMI, personal communication)* indicating that all the CTHs of the individual pixels lie in a range of within 8% around the mean CTH over the 12 considered GOME column locations of 693.5 hPa, the latter being very close to the assumption made in section 3.4.1. Figure 3.10 summarises the explained variances $R^2$ of the linear fits for different CTHs. As the $R^2$-curve culminates at about 840 hPa, we use this CTH$_{\text{eff}}$ as the relevant level for our further calculation and use the 825 and 850 hPa levels as the confidence interval.

![Figure 3.9](image)

**Figure 3.9.** Scatter plot and linear fit between vertical column proxy (population numbers) and appropriate GOME NO$_2$ VTCs for a CTH of 850 hPa.

The conversion factor is the ratio between the sum of the 12 GOME NO$_2$ VTCs (Fig. 3.3c) and the sum of the respective 12 proxy VTCs (calculated above CTH$_{\text{eff}}$). The conversion function showing the conversion factor for different CTHs (Fig. 3.10) indicates that small changes around 840 hPa do not have a large impact on the results. With the conversion factor associated with 840 hPa, the population number of every trajectory is converted to an NO$_2$ amount, which further propagates along the forward trajectory.

**Comparing in situ measurements and modelled impact**

Below, the modelled NO$_2$ concentrations are compared with the actual measurements at the ground stations. As pointed out in section 3.3.2 the trajectories are defined to reach a ground measurement site as soon as they travel near the ground. The definition of the near-ground level, however, is not straightforward. The representation of the complex topography in the Alpine region can be thought to be relatively poor in the coarse resolved ECMWF model. Generally, trajectory modelling
requires a height of a station to be not too far from the model topography for realistic results. For the present episode, the ECMWF model ground has been 960, 947, 906 and 875 hPa for Taenikon (real surface pressure in winter around 950 hPa), Chaumont (890 hPa), Rigi (900 hPa) and Zugspitze (700 hPa), respectively. For the first three stations, the box extension in which the trajectories are taken into account is defined to be up to 50 hPa distance from model ground. For the Zugspitze, however, the model ground differs much more from the real height. Taking the real height of the site could thus lead to errors, because trajectories representing the free troposphere would be regarded as being representative for the Zugspitze. Therefore, the box representing the Zugspitze station is chosen to be located in distance of between 50 hPa and 100 hPa from model ground.

![Figure 3.10. Explained variance $R^2$ of the linear fit between the proxy vertical column densities and the GOME NO$_2$ VTCs (solid line) and the respective conversion factors (dashed line) for different CTHs.](image)

The model results for Zugspitze are shown, together with the measured time series of NO$_2$, in Figure 3.11. The modelled NO$_2$ mixing ratios match the measured series surprisingly well (Fig. 3.11a). The measured variations in the NO$_2$ mixing ratio are reproduced and the modelled maximum value of about 4 ppb is in the order of the measured value of 6 ppb. Assuming that no local pollution occurred at this high-alpine site, the bulk of the 6 ppb NO$_2$ can be considered as being due to frontal transport. This implies, that the model approach somewhat underestimates the transported NO$_2$. The time shift of the modelled relative to the measured time series of about 1 to 2 hours is most likely explained by inaccuracies in the near-ground trajectories.
Figure 3.11. NO$_2$ mixing ratios measured at the Zugspitze station during the investigated episode (black) and model results for the advected additional NO$_2$ for an NO$_2$ lifetime of 24 hours (red) and of 12 hours (green) (a). Measured NO$_2$ mixing ratios (black) and model results for different assumptions on the planetary boundary layer (PBL) height. In order to simplify the visual assessment of the figure, the time shift of the modelled curves is neglected (b).

Sensitivity studies concerning the average NO$_2$ lifetime and the PBL height have been performed. Figure 3.11a includes the time series modelled for an average NO$_2$ lifetime of 12 and of 24 hours for Zugspitze. The comparison shows that this quantity has not a major impact on the results. Further calculations (not shown) indicated that for the other investigated sites, the differences due to different lifetimes are even smaller. Following the arguments pointed out in section 3.3.2, an average lifetime of 24 hours is chosen for the further calculation.
Figure 3.12. Scatter plot and linear fit between the NO$_2$ concentration measured at the ground station Zugspitze and the respective modelled NO$_2$ mixing ratios for an assumed PBL height of 50 hPa (and an NO$_2$ lifetime of 24 hours).

The assumed PBL height in the NO$_2$ source region has been varied between 25 and 50 hPa. In Figure 3.11b, the time shift is adjusted for better visualisation. The absolute values depend somewhat on the assumed height of the PBL and also on the vertical resolution of the trajectory model (in our case 25 hPa). The time series calculated for a 40 hPa PBL indicate higher concentrations at the Zugspitze compared to the 50 hPa PBL run. This is expected because a lower number of polluted trajectories arrive in the GOME columns at an altitude above the CTH$_{eff}$. Thus, the conversion factor increases. Further decreasing the PBL height leads to lower pollution also below the clouds which explains the decrease in the modelled concentrations for an assumed PBL of 30 hPa compared to the 40 hPa run. The best estimate for the PBL height is chosen via correlating the different resulting time series with the measured concentrations with the time shift adjusted. The best correlation is found for a PBL height of 50 hPa (Fig. 3.12). Defining a near-ground layer of 50 hPa corresponds to a PBL height of about 500 metres. This is rather high for winter conditions investigated in this episode. However, near the ground, trajectories are less accurate than at higher levels. This might be a reason for the best result emanating from modelling with a rather high PBL. Furthermore, mixing processes during the frontal movement associated with the southward transport described here complicates the proper definition of a PBL height.

Altogether, changing parameters such as the average NO$_2$ lifetime and the PBL height does not change the results strongly (also valid for the other stations, not shown) because the conversion in the GOME columns compensates to some extent for different starting conditions. Thus, the results are relatively stable and indicate a successful use of the suggested method for this transport episode.
Figure 3.13 illustrates the measured (black) and modelled (red) NO$_2$ time series for all the stations investigated in this study. Besides the result for the CTH$_{eff}$ located at 840 hPa, the modelled concentrations for the two neighbouring levels with trajectory calculations in 850 and 825 hPa are additionally shown as a confidence interval. The model output for Taenikon is less correlated with the measurement than seen for the Zugspitze station. At the beginning of the episode, the increasing mixing ratios are well shown by the model results, but the nearly constant values during the night are somewhat overestimated. However, the time range of the overall event is reproduced well and the order of magnitude of the NO$_2$ mixing ratio is matched. For the two elevated sites at Rigi and Chaumont, the time series modelled for the grid cells corresponding to the sites did not explain the measured NO$_2$ time series adequately. Taking into account adjacent grid cells, the time series found there match the measured mixing ratios much better, which might be due to uncertainties in the near-ground trajectories. The latter explanation is additionally supported by the fact that for both stations, the corresponding adjacent grid cells are found to be shifted towards the Swiss Plateau. This favours the following explanation: the air mass flow is approximately parallel to the mountain ridges on which the two stations are located (the Jura Mountains for Chaumont and the foothills of the Alps for Rigi, Figs. 3.1 and 3.6). However, the complex Swiss topography strongly affecting the flow is not properly resolved in the ECMWF model with a resolution of $1\degree \times 1\degree$, displacing the near-ground trajectories somewhat. The modelled NO$_2$ in the appropriate adjacent grid cells explain the shapes of the measured NO$_2$ time series at Rigi and Chaumont quite reasonable although for the Chaumont station, the modelled mixing ratios are distinctly lower than the measured values. A reason for that could be that the Chaumont station is most affected by air masses from pixel group 1 (Figs. 3.1, 3.3c and 3.6). Figure 3.6 indicates that the air from pixel group 2 has to cover a larger distance to reach this most western station and can, therefore, be expected to have a minor influence. The colours of pixel group 1 in Figure 3.8 further show that the NO$_2$ proxy for these two pixels might be somewhat underestimated by our method, because for this pixel group with the second highest column values (Fig. 3.3c), we would expect higher population numbers. This underestimation is probably due to the assumption of a cloud cover with a uniform height.

During the investigated episode, roughly 50 to 90% of the measured NO$_2$ are found to be caused by transboundary transport. This seems plausible taking into account that the mean NO$_2$ mixing ratios are much lower. The latter are determined by averaging the NO$_2$ mixing ratios over the February months of the years 1999 to 2001 for the four stations (with the investigated period from 17 February, 0:00 MET, to 18 February, 12:00 MET, excluded). Typical night time NO$_2$ mixing ratios from 0.5 ppb at Zugspitze to about 5 ppb for the elevated sites at Rigi and Chaumont are found. Only the Swiss Plateau station Taenikon shows evening mixing ratios exceeding 10 ppb.

Altogether we conclude from the comparison of the measured with the modelled NO$_2$ mixing ratios that the GOME NO$_2$ VTCs combined with our model can explain the exceptional events with high mixing ratios measured at the four sites and that the proposed method using above-cloud NO$_2$ detected from space can successfully be applied.
3 Transboundary transport of nitrogen dioxide observed from GOME

Figure 3.13. NO₂ mixing ratios measured during the investigated episode (black) and results of the model assessment of the advected additional NO₂ (red). The thick red curve corresponds to the optimal CTH_{eff} at 840 hPa, the thin curves from the adjacent (trajectory) levels in 825 (upper curve) and 850 hPa (lower curve) are shown as a confidence interval. For the Zugspitze and Taenikon stations, the time series from the grid cells containing the measurement sites are used, whereas for Rigi and Chaumont, adjacent grid cells show more reliable results (see text).

3.5 Summary and conclusions

A method is presented to exploit enhanced tropospheric GOME NO₂ measurements above extended cloud covers together with a trajectory based analysis to quantitatively assess air pollution transport. A NO₂ proxy is assumed to be proportional to the population distribution in the source region and is accumulated along ground-near trajectories considering an assumed average NO₂ lifetime. After arriving at the locations of the GOME columns, the proxy vertical tropospheric column densities (VTCs) are calculated above different cloud top heights (CTHs). Comparing the latter with the GOME NO₂ VTCs allows choosing the most appropriate effective cloud top height (CTH_{eff}) where the pollution distribution from GOME is best reproduced by the model. Relating the proxy VTCs with the GOME NO₂ VTCs yields a factor for converting the proxy to number of NO₂ molecules. Because the transport model covers the whole tropospheric columns, this results in an implicit estimate of the NO₂ distribution including its sub-cloud part. Further tracing the air masses with forward trajectories allows the estimation of pollution transport to other areas.

In a case study, the origin and impact of air pollution observed from the GOME instrument on 17 February 2001 above a cloud cover is investigated. Trajectory studies reveal that polluted boundary layer air was lifted up by a frontal system. This
led to nitrogen dioxide being located within and/or above an extended cloud cover and therefore being detectable by the GOME instrument. The source region of the NO\textsubscript{2} pollution is identified as the central part of Germany, the Ruhr area, and adjacent regions in the Netherlands and Belgium. Forward trajectory calculations indicate the subsequent movement of the polluted air masses to the Alpine region and predict that measurement stations in Switzerland and southern Germany are affected by the frontal transported NO\textsubscript{2}. Rural in situ measurements of enhanced NO\textsubscript{2} mixing ratios during the night confirm the prediction.

The NO\textsubscript{2} transport to the Alpine area is modelled using the proposed method and compared with the ground-based measurements. The model successfully reproduced the measured time series and shows that at least 50 \% of the NO\textsubscript{2} peak mixing ratios measured at the stations during the frontal passage can be attributed to transboundary transport. It is further demonstrated that the suggested method to convert the NO\textsubscript{2} proxy into NO\textsubscript{2} concentrations using CTH\textsubscript{eff} and the appropriate above-cloud NO\textsubscript{2} VTCs from GOME is stable in terms of changing parameters such as the average NO\textsubscript{2} lifetime and the assumed boundary layer height.

The study shows the potential of pollution detected from space-borne spectrometers above cloudy scenes. For compounds measured in the visible spectral range (as, e.g., NO\textsubscript{2} from GOME) this means that the lowest and often most polluted part of the troposphere is shielded from view. However, retrievals above clouds might be of better quality because of the enhanced sensitivity of satellite measurements above a strong reflector. The synergistic use of pollution detected above clouds and transport models in order to model pollution transport to ground stations is demonstrated in this study. The method can be improved by applying individual CTHs for every pixel (recently provided with satellite data). The enhanced spatial resolution of instruments such as SCIAMACHY further allows accounting for inhomogeneities in the CTH.

**Acknowledgements**

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4 Comparison of GOME tropospheric NO$_2$ columns with NO$_2$ profiles deduced from ground-based in situ measurements

This section is based on


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Abstract

Nitrogen dioxide (NO$_2$) vertical tropospheric column densities (VTCs) retrieved from the Global Ozone Monitoring Experiment (GOME) are compared to coincident ground-based tropospheric NO$_2$ columns. The ground-based columns are deduced from in situ measurements at different altitudes in the Alps for 1997 to June 2003, yielding a unique long-term comparison of GOME NO$_2$ VTC data retrieved by a collaboration of KNMI (Royal Netherlands Meteorological Institute) and BIRA/IASB (Belgian Institute for Space Aeronomy) with independently derived tropospheric NO$_2$ profiles. A first comparison relates the GOME retrieved tropospheric columns to the tropospheric columns obtained by integrating the ground-based NO$_2$ measurements. For a second comparison, the tropospheric profiles constructed from the ground-based measurements are first multiplied with the averaging kernel (AK) of the GOME retrieval. This allows splitting the total difference between the column data sets into two contributions: one that is due to differences between the a priori and the ground-based NO$_2$ profile shapes, and another that can be attributed to uncertainties in both the remaining retrieval parameters (such as, e.g., surface albedo or aerosol concentration) and the ground-based in situ NO$_2$ profiles. For anticyclonic clear sky conditions the comparison indicates a good agreement between the columns ($n=157$, $R=0.70/0.74$ for the first/second comparison approach, respectively). The mean relative difference (with respect to the ground-based columns) is -7% with a standard deviation of 40% and GOME on average slightly underestimating the ground-based columns. Further analysis
indicates small GOME columns being systematically smaller than the ground-based ones. The influence of different shapes in the a priori and the ground-based NO2 profile is analysed by considering AK information. It is moderate and indicates similar shapes of the profiles for clear sky conditions. Only for large GOME columns, differences between the profile shapes explain the larger part of the relative difference. In contrast, the other error sources give rise to the larger relative differences found towards smaller columns. Further, for the clear sky cases, errors from different sources are found to compensate each other partially. The comparison for cloudy cases indicates a poorer agreement between the columns (n=60, R=0.61). The mean relative difference between the columns is 60% with a standard deviation of 118% and GOME on average overestimating the ground-based columns. The clear improvement after inclusion of AK information (n=60, R=0.87) suggests larger errors in the a priori NO2 profiles under cloudy conditions and demonstrates the importance of using accurate profile information for (partially) clouded scenes.

4.1 Introduction

Nitrogen dioxide (NO2) is one of the most important air pollutants in the troposphere. It directly affects human health and plays a major role in the production of ground-level ozone (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000). Furthermore, Solomon et al. (1999) pointed out the climatic effect of NO2 as an absorber of solar radiation.

The bulk of the emitted NOx (≡ NO + NO2) is of anthropogenic origin (Brasseur, 2003). The primarily emitted nitrogen oxide (NO) oxidises to NO2 within seconds to minutes. The latter is removed from the troposphere after being converted to nitric acid (HNO3) which deposits (Kramm et al., 1995). During daytime, HNO3 is formed through the reaction of NO2 with the OH radical. During night time, a two step reaction chain forms nitrogen pentoxide (N2O5). The latter further reacts on surfaces and aerosol to HNO3 (Dentener and Crutzen, 1993). The resulting NOx lifetime is highly variable with an annual average boundary layer lifetime in the order of one day (Warneck, 2000). During photochemically active summer days, the lifetime can be reduced to only a few hours (e.g. Spicer, 1982). An increasing lifetime up to several days is found with increasing height in the troposphere (Jaeglé et al., 1998; Seinfeld and Pandis, 1998; Warneck, 2000). The mainly near-ground emissions of nitrogen species over industrialised areas, their production and loss reactions and meteorological transport lead to a distinct vertical tropospheric profile of NO2 with enhanced mixing ratios in the polluted boundary layer.

In terms of air quality in Switzerland, the NOx pollution situation has been improved during the last 15 years, but the annual limit values are still exceeded in polluted areas (BUWAL, 2004). Therefore, monitoring of nitrogen oxides still plays an important role in order to examine reduction measures. In addition to the monitoring networks around the globe, which provide ground-based in situ NO2 measurements, space-borne spectrometers such as GOME (Burrows et al., 1999) provide area-wide information about the NO2 vertical tropospheric column densities (VTCs) with a global coverage within only a few days.
4.1.1 Previous validation or comparison studies with space-borne NO$_2$ VTCs

Typically, for validation purposes, space-borne trace gas columns are compared to ground-based or airborne column measurements. Some recent works on validation of NO$_2$ VTCs are summarised in Table 4.1. The comparison of GOME NO$_2$ VTCs with ground-based DOAS measurements carried out at Mount Cimone (Italy) yielded a good agreement for situations with horizontally homogeneous distribution of the pollution distribution (Petritoli et al., 2004). Heue et al. (2005) used the Airborne Multi Axis DOAS (AMAXDOAS) instrument on board the DLR Falcon to validate SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric Chartography; Bovensmann et al., 1999). NO$_2$ VTCs over Italy in February 2003 and found SCIAMACHY values to be systematically higher than AMAXDOAS by approximately 7%.

Few comparisons including in situ data can be found in literature. The fundamental problem when comparing in situ measurements with column quantities arises from the fact that the latter integrate both horizontally and vertically, whereas in situ measurements provide point (ground-based site) or line (aircraft profile) information only. Petritoli et al. (2004) compared boundary layer in situ measurements from the Po-valley with GOME NO$_2$ VTCs and found a good qualitative correlation in the annual trend for high pollution episodes. Ordóñez et al. (2006) used 3-monthly averaged profile shapes from the chemistry transport model (CTM) MOZART-2 (Horowitz et al., 2003) that are scaled with ground-based in situ measurements for comparison with GOME NO$_2$ VTCs in the Lombardy region (Italy). Because the GOME NO$_2$ VTCs used in that study were retrieved based on a priori profiles from the same CTM, the focus has been on finding the best average boundary layer pollution level that scales the CTM column to best fit the GOME measurements. The best agreement has been found for average polluted situations.

In a case study, one in situ NO$_2$ profile measured from the DLR Falcon on a clear sky day above Austria has been used by Heland et al. (2002) for a comparison with GOME. They found a very small difference of $-0.1 \times 10^{15}$ molec cm$^{-2}$ between the GOME and the in situ column. Martin et al. (2004) evaluated the consistency between GOME tropospheric NO$_2$ columns and averaged aircraft profile measurements not coinciding with the GOME observation. The latter two comparisons are the only published comparisons of tropospheric GOME NO$_2$ observations with independent tropospheric in situ profile measurements known to the authors. Furthermore, the comparison case study by Heland et al. (2002) is the only study that validates an individual GOME retrieval with a coincident aircraft profile.

Shortcomings of the validations/comparisons mentioned above arise from their necessary focus on very limited numbers of coincident pixels (or even single pixels) or their use of CTM derived NO$_2$ profile shapes. Furthermore, no study so far discussed the inclusion of averaging kernels for the comparison of space-borne NO$_2$ VTCs with independently derived NO$_2$ columns.
Table 4.1. Recent works on validation and/or intercomparison of space-borne NO$_2$ vertical tropospheric column densities with independent measurement data.

<table>
<thead>
<tr>
<th>Author</th>
<th>Data: instrument (data provider)</th>
<th>Method (location)</th>
<th>Investigated period</th>
<th>Main result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petritoli et al. (2004)</td>
<td>GOME (IUP Bremen)</td>
<td>Ground-based DOAS (Mt. Cimone, Italy)</td>
<td>2000-2001</td>
<td>GOME smaller by 14%</td>
</tr>
<tr>
<td>Petritoli et al. (2004)</td>
<td>GOME (IUP Bremen)</td>
<td>In situ measurements (Ferrara, Po-Valley)</td>
<td>2000-2001</td>
<td>Annual cycle reproduced by GOME</td>
</tr>
<tr>
<td>Heue et al. (2005)</td>
<td>SCIAMACHY (IUP Bremen)</td>
<td>AMAXDOAS (Alps, Po-Valley, Mediterranean)</td>
<td>Feb 2003</td>
<td>SCIAMACHY higher by 7%</td>
</tr>
<tr>
<td>Ordóñez et al. (submitted 2005)</td>
<td>GOME (IUP Bremen)</td>
<td>Surface (PBL) measurements combined with CTM-NO$_2$ profile shape (Lombardy)</td>
<td>1996-2002</td>
<td>GOME best agrees for slightly polluted stations</td>
</tr>
<tr>
<td>Heland et al. (2002)</td>
<td>GOME (IUP Bremen)</td>
<td>In situ aircraft NO$_2$ profile (Austria)</td>
<td>2 May 2001</td>
<td>GOME smaller by 3%</td>
</tr>
<tr>
<td>Martin et al. (2004)</td>
<td>GOME (CfA Cambridge, MA)</td>
<td>In situ aircraft NO$_2$ profiles (Texas, Tennessee)</td>
<td>Jun/Jul 1999 Aug/Sep 2000</td>
<td>GOME smaller by 8%</td>
</tr>
</tbody>
</table>

4.1.2 Present study

The present study compares GOME NO$_2$ VTCs from 1997 to June 2003 with a set of NO$_2$ columns derived from in situ NO$_2$ measurements in Switzerland. Ground-based in situ sites continuously measuring NO$_2$ at different altitudes in the Alpine region are used to obtain tropospheric NO$_2$ profile information. New aspects of the present work are

- the first long-term comparison of GOME NO$_2$ VTC data retrieved by KNMI/BIRA (available at the Tropospheric Emission Monitoring Internet Service (TEMIS) web site www.temis.nl) with independently derived tropospheric NO$_2$ profiles,
- the NO$_2$ profile/column construction from ground-based in situ measurements,
- the comparison through inclusion of averaging kernel information,
- the first investigation of tropospheric NO$_2$ retrieval errors under cloudy situations.
4 Comparing GOME NO2 columns to ground-based NO2 profiles

Both the space-borne and the ground-based in situ measurement data are described in Sect. 4.2. The detailed method of deducing the tropospheric NO2 column from ground-based in situ measurements is introduced in Sect. 4.3. Sections 4.4 and 4.5 discuss the ground-based in situ columns (hereafter called ground-based columns) and the comparison between the latter and GOME NO2 VTCs for anticyclonic clear sky and for cloudy conditions, respectively.

4.2 Measurement data

4.2.1 KNMI/BIRA GOME tropospheric NO2 observations

The Global Ozone Monitoring Experiment (GOME) instrument on board ESA's ERS-2 satellite is a nadir-viewing spectrometer that measures upwelling radiance from the atmosphere and solar irradiance. The satellite instrument takes observation at approximately 10:30 hrs local time and individual pixels cover an area of 320 × 40 km². The GOME principles are described by Burrows et al. (1999).

The GOME NO2 VTCs studied in this work are the result of a collaboration of KNMI (Royal Dutch Meteorological Institute) and BIRA/IASB (Belgian Institute for Space Aeronomy). GOME NO2 data are publicly available on a day-by-day basis from 1 April 1996 until 30 June 2003 via ESA's TEMIS project (www.temis.nl).

The first step of the retrieval is taken by BIRA/IASB based on the Differential Optical Absorption Spectroscopy (DOAS) technique (Vandaele et al., 2005). It consists of the fitting of a modelled spectrum to a GOME-measured reflectance spectrum in the spectral window from 426.3-451.3 nm. This modelled spectrum takes into account the spectral features of absorption by NO2, O3, O2-O2, and H2O, and describes scattering on clouds, aerosols and air molecules by a low-order polynomial. The result of this first step is the so-called slant column density (SCD) of NO2. This SCD should be interpreted as the column integral of absorbing NO2 molecules along the effective photon path from the sun through the atmosphere to the GOME spectrometer.

The second step of the retrieval is the separation of the stratospheric contribution from the total SCD (Boersma et al., 2004). This is achieved with a data-assimilation approach. In the data-assimilation step, NO2 in TM4 (Dentener et al., 2003) is made consistent with observed SCDs over unpolluted areas. Subsequently, the stratospheric estimate is subtracted from the total SCD. Note that the residual tropospheric slant column (SCD trop) is insensitive to calibration errors, as any offsets in the total and stratospheric SCDs will cancel in the subtraction.

Finally, the SCD trop is converted into a VTC by applying the tropospheric air mass factor. The latter is calculated with the Doubling Adding KNMI (DAK) radiative transfer model (Stammes, 2001) and represents the best estimate of the length of the effective photon path for a particular retrieval scene. The tropospheric air mass factor depends on a priori assumptions on the state of the atmosphere, including surface albedo, cloud fraction, cloud height and the vertical distribution of NO2. For KNMI retrievals, a priori NO2 profiles for every location and all times are obtained from the TM4 CTM. Cloud parameters are taken from the Fast Retrieval Scheme for Clouds from the Oxygen A band (FRESCO) algorithm (Koelemeijer et al., 2001).

During the above mentioned steps, a number of error sources can lead to inaccurate retrieval results. The error budget of the tropospheric vertical columns has been
studied extensively in Boersma et al. (2004). Over polluted regions as considered in the present study, errors in the SCD (e.g. due to instrument noise, laboratory, reference spectra errors, interference with other absorbers and Ring effect) and in the separation of the stratospheric contribution from the total SCD play a minor role. For such regions, the most critical error source is the calculation of the tropospheric air mass factor. The latter depends on the a priori assumed NO2 profile shape, the cloud fraction, the cloud top height, the surface spectral reflectance (surface albedo, e.g. near land-snow boundaries) and the aerosol optical thickness profile. Based on theoretical error sources and for cloud free conditions, Boersma et al. (2004) estimated mean tropospheric air mass factor uncertainties for polluted regions (>1.0 × 10^{15} \text{ molec cm}^{-2}) of 15%, 2%, 15% and 9% due to the model parameters cloud fraction, cloud top height, surface albedo and a priori NO2 profile shape, respectively. The total mean uncertainty for the tropospheric air mass factor is estimated to be 29%, resulting in a total mean uncertainty for the NO2 VTCs of 35-60%. No error due to aerosol is included for the KNMI NO2 retrievals. Boersma et al. (2004) have argued that the presence of aerosol modifies the retrieval of cloud fraction and height with the FRESCO algorithm. A comparison of the expected aerosol correction factor versus the actual correction effect from the cloud retrieval has shown that even for a large aerosol optical thickness, the expected correction factor and actual correction effect agree to within 10%. Boersma et al. (2004) therefore suggest that cloud algorithms implicitly correct for aerosol through their modified cloud fraction and height.

Due to the cloud parameters that can be affected by uncertainties and the simplifying assumption that the cloud can be approximated as a Lambertian reflector with an effective cloud top height, larger errors are expected for the retrieval of cloudy scenes. The DAK radiative transfer model (Stammes, 2001) accounts for multiple scattering, but a detailed quantitative error analysis has so far not been carried out for these issues. Preliminary simulations with the DAK showed that light penetrates quite far into the cloud and the NO2 signal can originate from the upper half of the cloud. The FRESCO effective cloud top height represents this by putting the effective reflective surface below the real cloud top. However, the above mentioned small error due to uncertainties in the cloud top height for clear sky conditions can be thought to increase when the clouds are associated with, e.g., frontal activity. The vertical mixing of near ground pollution can then lead to a higher NO2 abundance near the cloud top, which induces a larger error compared to the clear sky situation with the bulk of the NO2 residing well below the cloud height. An explicit quantification of the error of cloudy NO2 VTCs has so far not been given in literature, but we estimate it to be in the order of 100%.

4.2.2 Ground-based in situ measurements

The Swiss National Air Pollution Monitoring Network (NABEL) provides long-term ground-based in situ measurements. Planetary boundary layer (PBL) stations representative for different pollution levels as well as stations located at different altitudes are included in this study (Fig. 4.1). In order to get more information about higher levels in the lower troposphere, two Alpine stations operated by the Umweltbundesamt (Germany) are further taken into account (Fig. 4.1). Details about measurement devices and locations can be found in Umweltbundesamt (2003), BUWAL (2004) and Empa (2005).
4 Comparing GOME NO2 columns to ground-based NO2 profiles

Figure 4.1. Ground-based in situ measurement stations in the PBL and at elevated sites used in the present study. GOME pixels with its centre coordinates located within the rectangular frame above northern Switzerland are used for the comparison. The resulting region covered by the GOME pixels of interest is additionally denoted.

NO2 is measured with the chemiluminescence technique (Navas et al., 1997; Clemitshaw, 2004) that includes the conversion of NO2 to NO. While the Jungfraujoch and the Hohenpeissenberg stations are equipped with photolysis converters that allow a selective measurement of NO2, the other stations are measuring with the molybdenum conversion technique. It is known that these catalytic surface converters are sensitive not only to NO2, but also to other nitrogen species such as PAN, HNO2, HNO3 and particulate nitrate (Zellweger et al., 2003; Clemitshaw, 2004). In order to account for this non-selective NO2 measurements at most of the stations used in this study, campaign results of simultaneous measurements based on both the photolysis and the molybdenum conversion technique at a PBL station (Taenikon) and an elevated station (Rigi) are used to determine correction factors (Sect. 4.3.1). A similar approach has been used in Ordóñez et al. (2006).

4.3 Methods

4.3.1 Column calculation from ground-based in situ measurements
The mountainous terrain in the Alpine region allows operating ground-based in situ measurement sites at different altitudes. These stations are assumed to detect NO2 concentrations that are approximately representative for the appropriate height in the
Comparing GOME NO₂ columns to ground-based NO₂ profiles

(free) troposphere over flat terrain. These measurements, together with boundary layer in situ measurements and an assumed mixing ratio at 8 km, are used to construct NO₂ profiles. The latter can subsequently be integrated to tropospheric NO₂ columns. Deducing tropospheric profile and column information from ground-based in situ measurements is not straightforward because the issue of representativeness has to be taken into account carefully. The following subsection alludes to the principle method of constructing the NO₂ profile from the in situ measurements. Afterwards, issues of representativeness and errors are discussed.

Deducing the NO₂ profile/column

The stations shown in Fig. 4.1 are used to deduce the tropospheric NO₂ profile. Every station provides a 3-hour NO₂ average concentration calculated around the GOME overpass from 9:00 to 12:00 UTC (i.e. around the GOME overpass at 10:30 hrs local time). Concentrations not measured with a photolysis converter are corrected with correction factors accounting for the interference in the NO₂ measurement. Because we are going to use averaging kernel (AK) information with a higher vertical resolution than covered by the various stations, the ground-based profile is divided into partial subcolumns to match the vertical resolution of the AK. The NO₂ in the upper troposphere is neglected because, due to the generally smaller mixing ratios and decreasing pressure with height, the effective NO₂ molecule number concentration at these levels is small compared to the NO₂ in the lower troposphere. The elevated stations (above 900 m asl) together with a near-zero NO₂ mixing ratio of 0.02 ppb at 8 km are first used for a curve fit, which can be regarded as an average profile given by the elevated stations. The curve fit is based on a power law equation resulting in a hyperbolic profile shape. Subsequently, the in situ measurements are assigned to the appropriate height intervals in the following way: Above 900 m asl (i.e. for the elevated part of the profile), the partial subcolumns are given as either the mean NO₂ concentration from the stations within the height interval, or the NO₂ concentration from the curve fit if no elevated station is available. Subcolumns for height intervals below 900 m asl are obtained from linear interpolation between the 900 m NO₂ concentration (resulting from the curve fit) and the remote and elevated PBL station Laegeren, as well as between the latter and the average PBL NO₂ concentration at the mean Swiss Plateau ground height of 400 m asl.

<table>
<thead>
<tr>
<th>Pollution class (c)</th>
<th>Population density [km⁻²]</th>
<th>Representative measurement station</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very remote</td>
<td>&lt; 30</td>
<td>None (0.5 × remote)</td>
</tr>
<tr>
<td>Remote</td>
<td>30-499</td>
<td>Taenikon, Payerne</td>
</tr>
<tr>
<td>Polluted</td>
<td>500-999</td>
<td>Duebendorf, Basel</td>
</tr>
<tr>
<td>Highly polluted</td>
<td>&gt; 1000</td>
<td>Berne, Zurich</td>
</tr>
</tbody>
</table>

Table 4.2. NO₂ pollution classes represented by population density ranges and associated representative Swiss Plateau (boundary layer) ground measurement stations.
To determine the average PBL NO\textsubscript{2} concentration within an individual GOME pixel, spatial inhomogeneities of the NO\textsubscript{x} emissions must be taken into account. To do this, we assume that the NO\textsubscript{x} emissions are proportional to the population density distribution. This assumption has previously been proven to be useful (Schaub et al., 2005). For the GOME pixel under consideration, the 0.25° × 0.25° population density grid elements enclosed in the pixel are sorted into four different (arbitrarily chosen) pollution classes \( c \) (Table 4.2). Each class is described by a population density range and appropriate measurement stations representative for the pollution level (Empa, 2005). From the numbers \( p_c \) of population density grid elements in each class, the average PBL NO\textsubscript{2} concentration within the GOME pixel is calculated as a weighted mean concentration using the appropriate stations representative for the pollution class:

\[
[NO_2]_{pbl} = \frac{\sum_{c=1}^{4} [NO_2]_c \cdot p_c}{\sum_{c=1}^{4} p_c}
\] (4.1)

Measurement gaps at the ground measurement sites occasionally prevent the use of all 15 stations from Fig. 4.1 for the NO\textsubscript{2} profile construction. On average, 13 stations are available for deducing a profile.

The ground-based columns described so far are derived for an NO\textsubscript{2} profile starting at ground-height (Swiss Plateau). The Alpine terrain is excluded as far as possible (Fig. 4.1). Nevertheless, the GOME pixels always cover a non-flat terrain in the present study area and the signal can be seen as a superposition of signals associated with columns of different vertical extension. To reproduce this in the ground-based columns, the topography of the Alpine Local Model (aLMo, operational numerical weather forecast model of MeteoSwiss) with a resolution of 7 km × 7 km is used to calculate a mean (or effective) surface height within the GOME pixel. The part of the ground-based NO\textsubscript{2} VTC located above this height is finally used as the representative ground-based column for the further comparison.

Representativeness of the constructed profiles

The representativity of the constructed profiles for the true atmospheric NO\textsubscript{2} profile over Northern Switzerland may be limited as a consequence of the following:

A) The vertical distribution of NO\textsubscript{2} within the PBL may not be well captured.

B) Inhomogeneities of NO\textsubscript{2} over the size of a GOME pixel may not be well captured.

C) Elevated stations may not be representative for the NO\textsubscript{2} at corresponding heights.
Here we shortly discuss each of these issues and their possible impact on the representativity of our constructed profile.

A) Vertical NO$_2$ distributions within the PBL are variable. For instance, Pisano et al. (1997) have shown NO$_2$ to be homogeneously distributed within the well-mixed convective boundary layer (CBL) in summer. On the other hand, Herwehe et al. (2000) modelled the boundary layer NO$_2$ vertical distribution and found that also within a summertime well-mixed boundary layer, the NO$_2$ can exhibit a strong decrease with height because the NO$_2$ lifetime can be shorter than the typical mixing time scale in the CBL (Spicer, 1982; Herwehe et al., 2000). Therefore, in situ measurements from an additional PBL station that is located on a mountain ridge about 250 metres above the ground height of the Swiss Plateau (Laegeren, Fig. 4.1) are used.

B) Due to the distances between the elevated stations (Fig. 4.1) and the relatively short chemical lifetime of NO$_2$ it is obvious that small-scale structures of the 3-dimensional NO$_2$ distribution in the free troposphere are difficult to catch by our comparison approach. Furthermore, neglecting the upper troposphere NO$_2$ above 8 km might not apply for columns affected by lightning or deep convection where NO$_2$ column enhancements of up to $1.0 \times 10^{15}$ molec cm$^{-2}$ were reported (Boersma et al., 2005; Choi et al., 2005). However, such events occur only occasionally and are not expected during anticyclonic clear sky days. During such conditions, Ridley et al. (1998) conducted simultaneous flights measuring NO$_x$ profiles up to 5000 metres asl representative locally (flight patterns with sides of 15-20 km) and regionally (horizontal flight distances of around 200 km) and qualitatively described a good agreement between the two profiles. Although these measurements were carried out at lower latitudes (30°-34° N), we suggest that the focus on anticyclonic conditions supports our assumption of the NO$_2$ being homogeneously distributed on clear sky high pressure days also in mid latitudes. It can be expected that larger inhomogeneities occur under cloudy conditions when frontal transport takes place. However, such conditions can also lead to spatially extended air masses, which are relatively well-mixed (Schaub et al., 2005). We furthermore note the large GOME footprint, which averages over a large area. Finally, the averaging time window for the ground-based measurements from 9:00 – 12:00 UTC to a certain extent averages out horizontal inhomogeneities.

C) Measurements from elevated stations may not be representative for the NO$_2$ at corresponding heights over flat terrain. It is known that, mainly during summertime convective conditions in the Alpine region, even high-alpine stations often detect pollution that reaches the site due to thermally induced upslope transport in the afternoon (Forrer et al., 2000; Lugauer et al., 2000; Nyeki et al., 2000; Zellweger et al., 2003). However, because of the GOME overpass around 10:30 hrs local time in the morning with an averaging time window for the ground-based in situ NO$_2$ measurements from 9:00 – 12:00 UTC, this is not expected to be a major issue for the present comparison. During the winter season, high-alpine sites have shown to be decoupled from the boundary layer during anticyclonic conditions, and thus representing the undisturbed free troposphere (Lugauer et al., 2000). Hence, we expect the high-alpine measurements taken during the GOME overpass time to be representative for free tropospheric NO$_2$ levels. Stations located around 1000 metres asl, on the other hand, are affected by polluted air masses already before noon. Nevertheless, we suggest these stations to be representative. Three cases can be distinguished:
1) On clear sky summer days, the boundary layer height grows very fast and can reach heights of 1000 m above ground already before noon (Nyeki et al., 2000; Seibert et al., 2000). Because in Switzerland a station located at 1000 m asl lies around 500 m above the ground (Swiss Plateau) effectively, the site can be thought to represent the PBL NO$_2$ levels.

2) During wintertime, the PBL often does not reach a height of 500 metres above ground (e.g. Seibert et al., 2000). In fact, the stations around 1000 m asl used in this study often measure low concentrations during clear sky winter days. Therefore, in winter, measurements at 1000 m asl are thought to be representative for free tropospheric NO$_2$ levels.

3) In spring, the upslope pollution transport could lead to pollution located above the PBL height over flat terrain, and one might argue that a station is no longer representative for the corresponding height level over the flat terrain. On the other hand, GOME measurements over the northern part of Switzerland should detect such events to a certain extent. The region is surrounded by mountainous areas with the Alps and the foothills of the Alps in the south/east and the Jura/Black Forest mountains in the north. Lugauer et al. (1998) argued that pollution once lifted can reside in the free troposphere. A measurement site affected by thermal upslope pollution transport can therefore be regarded to be representative for the “disturbed” free troposphere on a regional scale at least. Thus, with the five measurement sites around 1000 m asl and situated at five different locations within the region of interest and with different slope expositions and surroundings included in this study, the overall pollution situation should – on average – be captured. Nevertheless, NO$_2$ concentration differences between these five measurements are taken as a measure for inhomogeneities and thermally induced upslope transport.

**Interference in ground-based in situ NO$_2$ measurements**

Ground measurement stations equipped with molybdenum converters overestimate the NO$_2$ concentration due to non-selective conversion of nitrogen species (Clemitshaw, 2004). Due to the complex chemistry of nitrogen species, the difference between the selective and the non-selective NO$_2$ measurement strongly depends on meteorological conditions and the distance of the station from major emission sources. Campaign results of two stations that simultaneously measured with both the photolysis (selective NO$_2$ measurement) and the molybdenum conversion technique (non-selective NO$_2$ measurement) are used to compute a correction factor: a boundary layer station (Taenikon, 540 m asl) and an elevated site (Rigi, 1030 m asl) for the correction of measurements from boundary layer and elevated stations, respectively. The correction factor is calculated as

$$cf = \frac{[NO_2]_{\text{photolysis}}}{[NO_2]_{\text{molybdenum}}} \quad (4.2)$$

The elevated stations at Jungfraujoch and Hohenpeissenberg are equipped with selective (photolysis) converters and are, therefore, not corrected. Due to the seasonal variation in the photochemical activity monthly averaged correction factors are calculated for NO$_2$ measurements from 9:00 to 12:00 UTC (Fig. 4.2).
Figure 4.2. Monthly mean ratios (and standard deviations) between NO$_2$ concentrations measured from 9:00 to 12:00 UTC on clear sky days with photolysis and with molybdenum conversion technique for the elevated station Rigi (a) and the PBL station Taenikon (b).

Error estimation for ground-based NO$_2$ VTCs

This section discusses the main error sources in the ground-based columns and suggests a simple 'worst case' error estimate.

1) The error due to the selected pollution classes for determining the average PBL NO$_2$ concentration is very small. This is because the weak impact due to changing pollution classes is further decreased by the use of an effective surface height at the GOME pixel location. The effective surface height does not reach down to the Swiss Plateau height. Based on different choices for the pollution classes, relative uncertainties in the resulting ground-based NO$_2$ VTCs of only a few percent are found. This error is very small compared to the other errors and is therefore neglected.

2) Errors in the vertical NO$_2$ distribution in the PBL, the representativity of elevated stations for the free troposphere, and the assumption of horizontal homogeneity of
NO$_2$ in the free troposphere can be thought to be a major error source for the estimated ground-based columns. A crude overall estimation of this error is based on the five measurement sites located at altitudes of between 920 m asl and 1205 m asl (Fig. 4.1). On the one hand, these sites strongly affect the NO$_2$ profile deduced from the ground stations. On the other hand, the stations are located in an altitude range of only 285 m. Therefore, the standard deviation of their NO$_2$ concentrations is taken as an indicator for horizontal inhomogeneities and the non-representativeness of certain stations due to, e.g., thermal upslope transport of pollution. The resulting uncertainty of the ground-based column is determined with a sensitivity test, where the five concentrations are enhanced simultaneously by the calculated standard deviation. This can be seen as a ‘worst case’ scenario. The average resulting uncertainty is in the order of 20%, with an upper limit of approximately 50%.

3) Another significant error arises from the non-selective NO$_2$ measurement techniques used at most of the ground stations. Correction factors calculated for a selected station might not be representative for another station. Furthermore, meteorological conditions affect the correction factor, as indicated by the large standard deviations in the monthly correction factors (Fig. 4.2). For the error estimation, the change in the ground-based columns is calculated with monthly correction factors that are simultaneously changed by their standard deviations (‘worst case’ scenario). The average resulting error is in the order of 30%, with an upper limit of approximately 35%.

Finally, because dependence between these errors cannot be excluded, the error is assumed to be additive and is calculated as the sum of the two main error contributions, amounting to a conservative estimate of the average error of around 50%. This error will consist of both systematic error contributions – which will amount to a bias – and random contributions. The same holds for the GOME retrievals.

4.3.2 Space-borne to ground-based comparison methods

Following Palmer et al. (2001) and Boersma et al. (2004), the retrieved GOME NO$_2$ VTC (VTC$_{GOME}$) is calculated as

$$VTC_{GOME} = \frac{SCD_{trop}}{AMF_{trop}(x_a, \hat{b})} = \frac{SCD_{trop} \cdot \sum_l x_{a,l}}{\sum_l m_l(\hat{b}) \cdot x_{a,l}}$$  \hspace{1cm} (4.3)

SCD$_{trop}$ denotes the tropospheric slant column density, which is the difference between the total SCD resulting from fitting the reflectance spectrum measured from the satellite and a stratospheric SCD. For KNMI retrievals, the latter is determined by data assimilation of observed SCDs in a chemistry-transport model (Eskes, 2003). AMF$_{trop}$ is the tropospheric air mass factor, which is defined as the ratio between SCD and VTC. $x_{a,l}$ are the layer specific subcolumns from the a priori profile $x_a$, and $m_l$ are the altitude-dependent scattering weights. The latter are calculated with a radiative transfer model and best estimates for forward model parameters $b$, describing surface albedo, cloud parameters (fraction, cloud top pressure) and GOME pixel surface pressure.
If independently measured tropospheric NO\textsubscript{2} profile information \(x_{\text{ind}}\) is available, there are different possibilities for comparison, each having its own meaning.

**First comparison approach**

The straightforward first comparison approach (hereafter called first comparison) uses the independently measured NO\textsubscript{2} profiles that are directly integrated to tropospheric columns (\(VTC_{\text{ind}}\)):

\[
VTC_{\text{ind}} = \sum_l x_{\text{ind},l}
\]  

(4.4)

with \(x_{\text{ind}}\) the ground-based NO\textsubscript{2} profile and \(l\) the tropospheric layers. The relative difference between the two columns with respect to the ground-based column is calculated as

\[
\Delta_0 = \frac{VTC_{\text{GOME}} - VTC_{\text{ind}}}{VTC_{\text{ind}}} = f(SCD_{\text{trop}}, m_l(\hat{b}), x_a, x_{\text{ind}})
\]  

(4.5)

\(\Delta_0\) is a measure that will be comparable to other validation studies where, typically, relative differences are calculated with respect to the ‘true’ columns. \(\Delta_0\) depends on all parameters affecting the retrieval and the ground-based column calculation, including differences in the shapes of the a priori profile \(x_a\) and the ground-based profile \(x_{\text{ind}}\).

A second relative difference is calculated with respect to the GOME column (and the latter therefore being the denominator in Eq. 4.6):

\[
\Delta_1 = \frac{VTC_{\text{GOME}} - VTC_{\text{ind}}}{VTC_{\text{GOME}}} = f(SCD_{\text{trop}}, m_l(\hat{b}), x_a, x_{\text{ind}})
\]  

(4.6)

The reason for defining \(\Delta_1\) will become obvious in the next section (where \(\Delta_1\) is further divided into two contributions).

**Second comparison approach**

Eskes and Boersma (2003) applied the general formalism developed by Rodgers (2000) for the case of DOAS retrievals that are typically done for weak absorbers (\(\tau < 1\)) and generally give column integrals of the concentration species only. The averaging kernel (AK) vector describes the relation between the true vertical distribution of a species and the retrieved vertical column. Multiplying the ground-based NO\textsubscript{2} profile with the AK yields \(VTC_{\text{ind,AK}}\):
Comparing GOME NO₂ columns to ground-based NO₂ profiles

\[ VTC_{\text{ind\_AK}} = \sum_l a_l(x_a, \hat{b}) \cdot x_{\text{ind},l} \]  

(4.7)

with \( a_l \) the AK element for layer \( l \). Following Boersma et al. (2004) the relative difference between \( VTC_{\text{ind\_AK}} \) and the GOME column is

\[ \Delta_2 = \frac{VTC_{\text{GOME}} - VTC_{\text{ind\_AK}}}{VTC_{\text{GOME}}} = f(SCD_{\text{trop}}, m_l(\hat{b}), x_{\text{ind}}) \]  

(4.8)

Unlike \( \Delta_1 \), \( \Delta_2 \) is no longer influenced by the a priori NO₂ profile \( x_a \) (Eskes and Boersma, 2003). For the interpretation of the second comparison approach (hereafter called second comparison), it is helpful to reformulate Eq. 4.8. Following Eskes and Boersma (2003), the expression for \( a_l \) can be written as

\[ a_l = \frac{m_l(\hat{b})}{AMF_{\text{trop}}(x_a, \hat{b})} \]  

(4.9)

Including Eqs. 4.3, 4.7 and 4.9 in Eq. 4.8 and reformulating yields

\[ \Delta_2 = \frac{SCD_{\text{trop}} - \sum_l m_l(\hat{b}) \cdot x_{\text{ind},l}}{SCD_{\text{trop}}} = f(SCD_{\text{trop}}, m_l(\hat{b}), x_{\text{ind}}) \]  

(4.10)

Equation 4.10 demonstrates that the second comparison amounts to a comparison of slant column densities. Because the \( AMF_{\text{trop}} \) divides out, the a priori NO₂ profile \( x_a \) no longer contributes to \( \Delta_2 \). Further, the second term of the numerator in Eq. 4.10 indicates the slant column to be a linear sum of signal contributions from all individual layers, which is a valid approximation for weak absorbers (Eskes and Boersma, 2003; Boersma et al., 2004). Therefore, the above equation can be interpreted as how well the ground-based NO₂ profile together with the scattering weights \( m_l \) can describe \( SCD_{\text{trop}} \).

In the previous section, we introduced \( \Delta_1 \), which depends on all parameters affecting the comparison. Because the same denominator appears in both \( \Delta_1 \) and \( \Delta_2 \), we can write
Therefore, $\Delta_f$ can be split into two contributions: $\Delta_3$ that depends on differences between the shapes of the a priori and the ground-based NO\textsubscript{2} profile, and $\Delta_2$ that is due to uncertainties in both the remaining retrieval parameters and the ground-based NO\textsubscript{2} profile. In the following, $\Delta_1$ and $\Delta_2$ are calculated from the first and the second comparison, respectively. $\Delta_3$ is calculated as the difference between $\Delta_1$ and $\Delta_2$.

4.4 Results for clear sky (anticyclonic) conditions

4.4.1 NO\textsubscript{2} VTCs from ground-based in situ measurements

From 1997 to June 2003, ground-based NO\textsubscript{2} VTCs are calculated for 335 days with both clear sky conditions (MeteoSwiss, 1985) and GOME NO\textsubscript{2} VTC data above northern Switzerland (Fig. 4.1) available. Figure 4.3 shows two example NO\textsubscript{2} profiles deduced from ground-based in situ measurements for 3 December 1999 and for 22 July 2002. The December example shows a typical anticyclonic winter case where an inversion prevents vertical mixing and the NO\textsubscript{2} is concentrated in the narrow PBL. The more effective mixing in the July example and the reduced chemical lifetime of NO\textsubscript{2} during the warm season leads to a boundary layer concentration being a factor of 10 lower than for the winter case.

![Figure 4.3. Example NO2 profiles for 3 December 1999 (a) and for 22 July 2002 (b). Note the different x-axis. The two PBL values (filled and open black circles) are derived from the PBL ground and elevated stations in Fig. 4.1. The red data points are derived from the elevated stations located in Southern Germany and Switzerland (Fig. 4.1). Occasionally, measurement gaps prevent the use of all available measurement sites for the profile determination.](image-url)
Employing 12:00 UTC radio soundings from Payerne (Switzerland; e.g. Beyrich et al., 1998), PBL heights are calculated with the parcel method (Troen and Mahrt, 1986; Holtslag et al., 1990) and the Richardson number method (Vogelezang and Holtslag, 1996). With these PBL heights, the annual mean fractions of NO$_2$ located within and above the PBL are calculated to be 69% and 31%, respectively, for the ground-based NO$_2$ profiles reaching down to the Swiss Plateau height. For comparison, Martin et al. (2004) reported a summertime fraction of nearly 75% of the tropospheric NO$_2$ below 1500 m in Houston and Nashville, USA. Ordóñez et al. (2006) found an average NO$_2$ fraction below 1000 m in the northern Italy region of more than 80%. The reason for the lower PBL column fraction in the area of northern Switzerland and surroundings is the lower NO$_2$ pollution compared to northern Italy.

The GOME nadir UV-VIS sensor exhibits a higher sensitivity towards NO$_2$ located in higher atmospheric layers. To check the “satellite’s view”, the layer-specific NO$_2$ ($x_{\text{ind}, l}$) is multiplied with the altitude-dependent scattering weight $m_l$ to get the within/above PBL NO$_2$ SCDs as seen from satellite. Employing averaging kernel information and the AMF$_{\text{trop}}$ and following Eq. 4.9 the NO$_2$ SCD above the PBL is

$$SCD_{\text{NO}_2, \text{abovePBL}} = \sum_{\text{abovePBL}} x_{\text{ind}, l} \cdot m_l(b) = AMF_{\text{trop}} \cdot \sum_{\text{abovePBL}} x_{\text{ind}, l} \cdot a_l$$

(4.12)

Similarly the total tropospheric NO$_2$ SCD, the PBL NO$_2$ SCD and, subsequently, the fractions within and above the PBL are calculated. Table 4.3 indicates that, on average, 55% of the signal measured by the space-borne instrument in the present study area originates from above the PBL, although only 31% of the NO$_2$ resides there in reality. The PBL contribution is 45%. Because the following comparison employs the part of the ground-based profile located above the mean topography height within a GOME pixel, the importance of the PBL contribution is further reduced. This emphasises the importance of the elevated stations for the present comparison.

Table 4.3. Fraction of NO$_2$ vertical column density (VTC) above and within the planetary boundary layer (PBL) calculated from the ground-based NO$_2$ VTC alone and multiplied with averaging kernel (AK) information. The whole ground-based NO$_2$ columns are considered (i.e. reaching down to the height of the Swiss Plateau).

<table>
<thead>
<tr>
<th></th>
<th>Ground-based NO$_2$ VTC</th>
<th>Ground-based NO$_2$ VTC × AK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction of NO$_2$ above PBL</td>
<td>31 ± 14%</td>
<td>55 ± 16%</td>
</tr>
<tr>
<td>Fraction of PBL NO$_2$</td>
<td>69 ± 14%</td>
<td>45 ± 16%</td>
</tr>
</tbody>
</table>
4.4.2 Comparison for clear sky conditions

For the clear sky comparison between the GOME and the ground-based NO\textsubscript{2} VTCs, we have used the following criteria:

- GOME pixel location above northern Switzerland (Fig. 4.1),
- Alpine weather statistics parameters (MeteoSwiss, 1985) indicate anticyclonic conditions and the absence of clouds,
- GOME pixel cloud fraction from FRESCO algorithm (Koelemeijer et al., 2001) ≤ 0.1,
- SCD\textsubscript{trop}/SCD > 10%.

The last condition is enforced because for some cases unrealistically small GOME NO\textsubscript{2} VTCs are retrieved when the total SCD and the (assimilated) stratospheric SCD are very similar. For such cases, uncertainties in the stratospheric SCD generate a strong change in the tropospheric VTC, although the error of the stratospheric SCD is small and estimated to not exceed 0.2 × 10\textsuperscript{15} molec cm\textsuperscript{-2} (Boersma et al., 2004). This criterion rejects 20 GOME pixels from the comparison.

Based on GOME NO\textsubscript{2} VTCs from 1997 to June 2003 and following the above conditions a data set of 157 clear sky columns is extracted for the subsequent comparison.

First comparison

Figure 4.4a shows the scatter plot for the first comparison between $VTC_{GOME}$ and $VTC_{ind}$. A weighted orthogonal regression is used instead of a simple linear regression, because both data sets are affected by errors (York, 1966). GOME NO\textsubscript{2} VTCs 1-sigma errors are taken from the TEMIS data file where, for each individual pixel, an error estimate is given (Boersma et al., 2004). The error assessment for each of the ground-based VTCs follows Sect. 4.3.1. Interestingly, the independently calculated error estimates for the two data sets are very similar: the mean GOME 1-sigma error and the mean ground-based VTC error are determined to be 56% and 49%, respectively. The slope and the intercept (with their standard deviations) are calculated to be 1.15 (±0.22) and -1.23 (±0.90), respectively, with a correlation coefficient R=0.70. Although there is a good general agreement between the two column data sets, the regression indicates a tendency of small GOME columns slightly underestimating the corresponding ground-based columns. This is further discussed in Sect. 4.4.3.

The seasonal behaviour is very similar (Fig. 4.4b). The small summertime NO\textsubscript{2} VTCs mirror the shorter chemical lifetime of NO\textsubscript{2} during photochemically active summer days (Spicer, 1982; Warneck, 2000). Furthermore, both column data sets independently detect the largest NO\textsubscript{2} VTCs during the spring season. Moxim et al. (1996) simulated the global tropospheric chemistry of peroxyacetyl nitrate (PAN) and NO\textsubscript{x} and found regional NO\textsubscript{x} spring maxima in the lower troposphere of the northern hemisphere. This is consistent with Penkett and Brice (1986) who suggested the measured PAN maximum in spring to be due to the accumulation of precursor substances (such as NO\textsubscript{x}) during the cold season and subsequent photochemistry in
spring leading to enhanced photooxidants such as PAN and ozone. Note, however, that the latter studies focused on a larger region than middle Europe. Nevertheless, due to their vertical extension, the GOME columns investigated here could be affected by air masses representative for a larger spatial scale similarly to elevated measurement sites in the Alpine region. At such sites, the NO2 concentration also shows a spring maximum (Staehelin et al., 2000; BUWAL, 2004). The good agreement for the spring NO2 VTCs can be seen as a crude validation of both NO2 column data sets.

The qualitative comparison between the GOME NO2 VTCs and the PBL NO2 concentrations (derived following Sect. 4.3.1, Fig. 4.4c) shows that a proper comparison requires information on the vertical NO2 distribution. As expected, the near-ground NO2 concentrations are highest in winter, mainly due to near-ground inversions that often occur during this season. In summer, the near-ground NO2 concentrations are lowest because of stronger photochemical activity and vertical mixing leading to dilution. The NO2 VTC spring maximum is not mirrored in the average PBL NO2 concentration.

Second comparison

The second comparison is shown in Fig. 4.5. Again, a weighted orthogonal regression is calculated based on both the GOME NO2 VTC 1-sigma errors and the ground-based NO2 VTC errors estimated following Sect. 4.3.1. The mean errors for both data sets are again similar, with a mean GOME 1-sigma error of 48% and a mean error for the ground-based VTCs of 45%. The resulting slope and intercept (with their standard deviations) are calculated to be 1.01 (±0.16) and -0.83 (±0.70), respectively, with a correlation coefficient R=0.74. The inclusion of AK information tends to improve the comparison. Nevertheless, the offset still gives evidence for small GOME columns slightly underestimating the corresponding ground-based columns.

It should, however, be noted that the orthogonal regression depends on the errors attributed to the data sets. These errors are estimates that also have their uncertainties. Tests performed with varying errors indicated somewhat changing results for slopes and offsets. However, independent from changes in the errors, the slopes of the orthogonal regression together with their standard deviations indicate, that the multiplication with the AK has a relatively weak impact. This is due to - on average - similar shapes of the a priori and the ground-based NO2 profiles. Thus, the a priori profile shapes calculated with the CTM reproduce the tropospheric NO2 distribution seen from the ground-based measurements well for clear sky cases. This can also be seen in the scatter plot between $VTC_{ind}$ and $VTC_{ind,AK}$ (Fig. 4.6). Although the latter is slightly higher, the relatively small difference between the two columns can be attributed to the small difference in the two NO2 profile shapes (it will be shown that this difference is much larger for cloudy cases). Martin et al. (2004) similarly found a good agreement between CTM NO2 profiles and profile information from aircraft campaigns, although a different model was used to generate a priori profile shapes for the retrieval.
Figure 4.4. Clear sky first comparison between GOME NO$_2$ and the (directly integrated) ground-based NO$_2$ VTCs including orthogonal regression output (a). The same comparison showing the four seasons MAM, JJA, SON and DJF (b). Qualitative comparison between GOME NO$_2$ VTCs and PBL NO$_2$ concentrations (c).
4 Comparing GOME NO$_2$ columns to ground-based NO$_2$ profiles

![Graph showing comparisons between GOME NO$_2$ VTCs and ground-based NO$_2$ columns.](image)

**Figure 4.5.** Clear sky comparisons between GOME NO$_2$ VTCs and ground-based NO$_2$ columns with orthogonal regression output for the second comparison (ground-based profiles multiplied with the averaging kernel).

![Graph showing comparisons between ground-based NO$_2$ VTCs and the corresponding column after multiplication with the averaging kernel.](image)

**Figure 4.6.** Clear sky comparison between the directly integrated ground-based NO$_2$ column ($VTC_{ind}$) and the corresponding column after multiplication with the averaging kernel ($VTC_{ind,AK}$). Additionally, the resulting orthogonal regression calculation is shown.

4.4.3 Quantifying differences between the NO$_2$ VTCs

In this section, relative differences between the two column data sets are analysed in more detail. The errors in both the GOME and the ground-based NO$_2$ columns are
Comparing GOME NO$_2$ columns to ground-based NO$_2$ profiles

not taken into account. First, for the whole data set, the mean and median relative difference with respect to the ground-based columns ($\Delta_0$), as well as the mean absolute difference between the columns is compared to results from other studies. This is followed by a detailed analysis of relative differences with respect to the GOME columns ($\Delta_{1-3}$, Sect. 4.3.2).

VTC differences relative to ground-based NO$_2$ VTCs

For the whole clear sky column data set, the mean, standard deviation and median of $\Delta_0$ are calculated to be -7%, 40% and -13% (Table 4.4). The standard deviation suggests that the a priori estimates of 50% errors on clear sky GOME and ground-based columns are too conservative, and errors of the order of 30% would be more consistent with the intercomparison results. The mean $\Delta_0$ indicates that on average, the GOME NO$_2$ VTCs are slightly smaller than the corresponding ground-based columns. This result is consistent with findings from other authors (Table 4.1) that found GOME columns being smaller than independently measured columns by 14% (Petritoli et al., 2004), 8% (Martin et al., 2004) and 3% (Heland et al., 2002). The mean and median absolute difference between GOME and the directly integrated ground-based columns ($VTC_{ind}$) are $0.51 \times 10^{15}$ molec cm$^{-2}$ (with a standard deviation of $1.9 \times 10^{15}$ molec cm$^{-2}$) and $0.66 \times 10^{15}$ molec cm$^{-2}$, which is comparable to the mean absolute difference of $0.49 \times 10^{15}$ molec cm$^{-2}$ reported by Martin et al. (2004). Note, however, that there are also considerable differences between the Bremen, Harvard and KNMI/BIRA retrievals (van Noije, 2006).

VTC differences relative to GOME NO$_2$ VTCs: detailed analysis

Unlike $\Delta_0$, $\Delta_{1-3}$ are relative differences calculated with respect to the GOME columns. These differences allow splitting the total relative difference ($\Delta_1$) into two contributions,

- $\Delta_2$, which is due to errors in the ground-based NO$_2$ profile, retrieval errors such as the estimate of the stratospheric background and/or the scattering weights $m_l$ (including estimated forward model parameters such as, e.g., surface albedo),

- $\Delta_3$, which depends on differences between the shapes of the a priori and the ground-based NO$_2$ profiles.

The mean, standard deviation and median of $\Delta_{1-3}$ are calculated for the whole clear sky data set (157 cases) as well as for 3 subclasses equally proportioned: GOME NO$_2$ VTC < 3.5, 3.5 - 5.0 and > 5.0 $\times 10^{15}$ molec cm$^{-2}$ (Table 4.4). In the following, we allude to the means, because this allows to write $\Delta_1$ as the sum of $\Delta_2$ and $\Delta_3$. For the whole clear sky data set, the mean $\Delta_{1-3}$ are calculated to be -26%, -34% and 8%, respectively. As $\Delta_0$ before, $\Delta_1$ indicates an underestimation of GOME with respect to the ground-based columns. The mean $\Delta_2$ dominates over $\Delta_3$ with the two contributions compensating each other to a certain extent. As $\Delta_2$ is independent of a priori profile errors in the retrieval, the large contribution indicates that the ground-based NO$_2$ profiles together with the scattering weights are, on average, higher than SC$_{D trop}$. The small contribution from $\Delta_3$ on the total $\Delta_1$ can be attributed to similar shapes of the a priori and the ground-based NO$_2$ profiles. This is consistent with the
relatively weak impact after inclusion of AK information as discussed in the previous section. The positive value of \( \Delta_3 \) indicates that the TM4 a priori NO2 profile shapes are, on average, slightly biased towards higher NO2 abundances at lower altitudes or smaller NO2 abundances at higher altitudes. I.e., TM4 profiles tend to peak more towards the surface than the observed profiles.

For the subclass with GOME NO2 VTCs > 5.0 \( \times 10^{15} \) molec cm\(^{-2} \), the mean \( \Delta_{1-3} \) are calculated to be 7\%, -5\% and 12\%, respectively. Thus, for this data subset, the positive \( \Delta_1 \) is consistent with GOME columns that are on average exceeding the ground-based columns. This explains the steeper slope for the first comparison (Fig. 4.4a). The small \( \Delta_2 \) of -5\% indicates that the ground-based NO2 profiles together with the scattering weights reliably reproduce \( SCD_{\text{trop}} \). The remaining \( \Delta_3 \) of 12\% shows that differences in the two NO2 profile shapes play a major role for this data subset. Therefore, the multiplication of the ground-based profiles with the AK has a larger impact in this data subset and explains to large parts the changing slope between the first and the second comparison (Figs. 4.4a and 4.5). The positive value again indicates TM4 a priori NO2 profile shapes that are, on average, biased towards higher NO2 abundances at lower altitudes or smaller NO2 abundances at higher altitudes. The reasons for that are manifold and could be uncertainties in the NO\(_x\) emission inventories, uncertainties arising from the CTM, uncertainties in the meteorological fields (e.g. an underestimation of vertical transport in the alpine region), but also errors in the ground-based NO2 profile. Which of the uncertainties is dominant is not clear.

Table 4.4. Mean, standard deviation and median of the relative differences \( \Delta_0 \) and \( \Delta_{1-3} \) between GOME and ground-based NO2 VTCs. \( \Delta_0 \) is the relative difference calculated with respect to the ground-based columns and is, therefore, comparable to the quantities given in Table 4.1. \( \Delta_{1-3} \) are calculated with respect to the GOME columns. This allows to split the total relative difference (\( \Delta_1 \)) into two contributions: one that is due to differences in the shapes of the a priori and the ground-based NO2 profile (\( \Delta_3 \)), and another that is due to the remaining retrieval parameters and uncertainties in the ground-based profile (\( \Delta_2 \)). For the subclass with GOME NO2 VTCs < 3.5 \( \times 10^{15} \) molec cm\(^{-2} \) a second scenario is calculated with ground-based NO2 columns deduced from ground-based in situ measurements averaged from 6:00 – 9:00 UTC (instead of 9:00 – 12:00 UTC).
For the subclasses with GOME NO₂ VTCs between $3.5 \times 10^{15}$ molec cm$^{-2}$ and < $3.5 \times 10^{15}$ molec cm$^{-2}$, $\Delta_{1,3}$ are calculated to be -22%, -30% and 8% and -61%, -65% and 4%, respectively (Table 4.4). Thus, for lower GOME NO₂ column values,

- $\Delta_1$ is increasing with GOME columns underestimating the ground-based columns,
- $\Delta_2$ is increasing as well, indicating that $SCD_{trop}$ underestimates the slant column given by the ground-based profile together with the scattering weights,
- the profile shapes are more similar than for situations with high GOME NO₂ column values.

The increasing $\Delta_1$ towards smaller GOME columns is mainly explained by $\Delta_2$. This is the main reason for the offsets found in the orthogonal regression calculations (Figs. 4.4a and 4.5). Therefore, $\Delta_1$ can no longer be explained by different NO₂ profile shapes, but by uncertainties in the ground-based NO₂ profiles, retrieval errors such as the estimate of the stratospheric background and/or the scattering weights. Smaller NO₂ columns in both data sets often occur in the summer season (Fig. 4.4b). Therefore, one might argue that the increase in $\Delta_2$ towards smaller columns is mainly due to thermal upslope transport of NO₂ that leads to a systematic overestimation of the NO₂ located at elevated levels in the ground-based profiles. To check this, we changed the averaging time window (for calculating the average NO₂ concentration for the ground stations; see Sect. 4.3.1) from 9:00 – 12:00 to 6:00 – 9:00 UTC. For this time window, the influence from thermal upslope transport at the elevated stations can be expected to be small. For GOME NO₂ VTCs < $3.5 \times 10^{15}$ molec cm$^{-2}$ the resulting $\Delta_{1,3}$ are -42%, -49% and 7%, respectively (Table 4.4). Although $\Delta_1$ and $\Delta_2$ now indicate a smaller relative difference between the column data sets, thermal upslope transport of pollution only explains 1/3 (1/2 if the median is considered) of the relative difference. It therefore seems likely that, towards smaller NO₂ columns, GOME retrievals over the study area indeed underestimate the true NO₂ column. This would be consistent with some unrealistically small GOME NO₂ VTCs that have been found (and that have been excluded from the comparison by the criterion $SCD_{trop}$/SCD, as pointed out at the beginning of Sect. 4.4.2). For instance, the smallest clear sky GOME column of $0.05 \times 10^{15}$ molec cm$^{-2}$ was detected over an area covering the most polluted part of the Swiss Plateau including the largest Swiss cities Zurich and Basel. The total and the stratospheric SCD are very similar in this case ($7.74 \times 10^{15}$ molec cm$^{-2}$ and $7.71 \times 10^{15}$ molec cm$^{-2}$, respectively), and uncertainty in the latter can at least partially explain the small GOME NO₂ VTC value. The investigation described above should be refined further in the future. Particularly for cases with $\Delta_2$ explaining the major part of $\Delta_1$, independent knowledge of non-profile retrieval parameters, such as surface albedo, would shed further light on the reason for column differences. The results presented here should be seen as tendencies, because averaged differences with large standard deviations are discussed. This means that for single day-to-day cases, parameters such as the a priori NO₂ profile shape can have a much larger (but also lower) impact than averaged over the whole data set. Moreover, the investigated GOME pixels exhibit a large extension always detecting a somewhat changing mix of remote and polluted areas in the study area. For future work with smaller pixels from SCIAMACHY ($60 \times 30$ km$^2$) or the Ozone Monitoring Instrument (OMI, $13 \times 24$ km$^2$), the pixel-to-pixel
NO$_2$ VTC differences can be expected to be much larger with remote and polluted pixels lying close to each other and probably being retrieved with similar or even the same a priori profile shapes (due to significant spatial undersampling with coarser resolved CTMs). We would therefore expect that the tendencies found in the present study will come out clearer for satellite pixels with a lower extension.

### 4.5 Results for cloudy conditions

A detailed comparison for cloudy GOME pixels has so far not been carried out. The potential retrieval errors under cloudy conditions can, however, be thought to be much larger than for clear sky conditions. This is mainly due to inaccurate knowledge of cloud characteristics (e.g. cloud top height, cloud fraction, optical thickness) and difficulties in the radiative transfer modelling (multiple scattering).

For the comparison under cloudy conditions the following has to be fulfilled:

- **GOME pixel location above northern Switzerland (Fig. 4.1),**
- **GOME pixel cloud fraction from FRESCO (Koelemeijer et al., 2001) $\geq 0.75$,**
- **$\text{SCD}_{\text{trop}}/\text{SCD} > 10\%$.**

Figure 4.7a shows the first and the second comparison between the GOME and the ground-based NO$_2$ VTCs for 76 cloudy cases. Obviously, there are a number of cases with a very poor agreement, with GOME columns being up to a factor of 20 higher than the ground-based columns. The reason for the strong disagreement for these cases is discussed qualitatively at the example of the most extreme case on 17 February 2001.

Based on GOME NO$_2$ measurements, Schaub et al. (2005) have shown that, during 16 and 17 February 2001, frontal activity over Central Europe caused vertical transport of polluted near-ground air masses to up to approximately 4000 m asl. No lightning activity was detected during that episode (www.wetterzentrale.de/topkarten/tkbeoblar.htm), but the vertical transport led to a significant amount of NO$_2$ being located within and above a dense cloud cover with a top height of approximately 700 hPa. Because of the high sensitivity of the space-borne instrument above reflecting clouds, this is consistent with a large $\text{SCD}_{\text{trop}}$ of $57 \times 10^{15}$ molec cm$^{-2}$ (which is nearly 90% of the total SCD of $64 \times 10^{15}$ molec cm$^{-2}$) given by the KNMI/BIRA data set. From this, an unrealistically high GOME NO$_2$ VTC value of $489.5 \times 10^{15}$ molec cm$^{-2}$ is retrieved.

The corresponding ground-based NO$_2$ VTCs are calculated to be $22.4 \times 10^{15}$ molec cm$^{-2}$ (directly integrated) and $38.3 \times 10^{15}$ molec cm$^{-2}$ (AK included). The strong disagreement between the latter and the GOME column indicates that the ground-based profile together with the scattering weights is much smaller than $\text{SCD}_{\text{trop}}$. Thus, two main reasons could explain the strong disagreement: on the one hand, the scattering weights could be wrong due to errors in the radiative transfer modelling resulting from uncertainties in the cloud parameters. It has been mentioned in section 4.2.1 that errors induced by uncertainties in the cloud top height are increasing for situations with enhanced NO$_2$ concentrations close to the cloud top height (which is the case here).
On the other hand, the disagreement can just as well be attributed to the ground-based profile: first, no NO$_2$ measurements from the high-alpine site Jungfraujoch are available for this episode (such data gaps can be neglected when calculating a clear sky column with typically very low NO$_2$ concentrations at Jungfraujoch; however, they become important when polluted air masses reach the station and the latter additionally being located above a reflecting cloud cover). Second, the peak NO$_2$ concentrations measured at the ground stations occurred rather in the evening of the 17 February, and not during the time of the GOME overpass. This shows that the assumption of a homogeneous NO$_2$ distribution at elevated levels may not be valid for this case. Therefore, a new scenario is calculated based on the following
assumptions: a) the Jungfraujoch station measures the same NO$_2$ concentration as the Zugspitze station, and b) every ground station contributes to the ground-based column with its maximum NO$_2$ concentration measured during the frontal passage (i.e. during 17 and the first half of 18 February). This yields ground-based columns of 46.7 × 10$^{15}$ molec cm$^{-2}$ (directly integrated, $VTC_{\text{ind}}$) and 304.8 × 10$^{15}$ molec cm$^{-2}$ after multiplication with the AK ($VTC_{\text{ind,AK}}$).

$VTC_{\text{ind}}$ still strongly underestimates the GOME NO$_2$ VTC, although the lower ground stations contributed with high concentrations in the order of 30 ppb to the column. Remarkably, for this new scenario, $VTC_{\text{ind,AK}}$ results in a value that is at least of the same order as the GOME column of 489.5 × 10$^{15}$ molec cm$^{-2}$. The distinct change in the ground-based column after multiplication with the AK indicates that the shapes of the ground-based and the a priori NO$_2$ profile are strongly differing. The increase of the column after multiplication with the AK is consistent with a TM4 a priori NO$_2$ profile shape that is biased towards higher NO$_2$ abundances at lower altitudes or smaller NO$_2$ abundances at higher altitudes. The latter point gives evidence for the following additional explanation of the large GOME column during this episode (besides uncertain cloud parameters): the frontal transport event results in complex air mass mixing together with horizontal and vertical movement which may not be properly reproduced by the coarsely resolved global CTM. The CTM might therefore calculate an a priori NO$_2$ profile that underestimates the enhanced NO$_2$ amount within and above the clouds. This further leads to an underestimation of the $AMF_{\text{trop}}$. The latter, together with the very high $SCD_{\text{trop}}$ value, results in a strong overestimation of the NO$_2$ VTC. The AK convoluted surface measurement, however, shows a reasonable agreement with the GOME retrieval. This indicates the GOME measurement to be consistent within error bars with the ground-based column amount for this special case.

It becomes obvious from Fig. 4.7a, that there are other cases with very high GOME NO$_2$ VTC values that, also after multiplication with the AK, do not agree with the ground-based columns. These cases are similar to the case from 17 February 2001 described above. Figure 4.7b shows that the $\Delta_0$ between the GOME NO$_2$ VTCs and the corresponding ground-based columns are increasing for increasing $SCD_{\text{trop}}/SCD$ ratios. This indicates that (frontal) transport events that lead to NO$_2$ pollution at elevated levels, and thus high $SCD_{\text{trop}}$ values, are difficult to handle for both the retrieval but also for the comparison with ground-based NO$_2$ profiles (due to representativity errors in the latter).

For the further investigation, the most extreme cases with $SCD_{\text{trop}}/SCD > 50\%$ are rejected from the data set. This $SCD_{\text{trop}}/SCD$ criterion is chosen arbitrarily. For the first comparison of the remaining 60 cases (Fig. 4.8a), the orthogonal regression calculates a slope of 2.99 (± 0.91), an intercept of -7.71 (± 4.18) and a correlation coefficient $R=0.61$. In consistency with a mean $\Delta_0$ of 60% (with a standard deviation of 118%) this indicates GOME columns on average clearly overestimating the ground-based columns. The second comparison leads to a much better agreement for the average of the cloudy cases (Fig. 4.8b) with slope, intercept and correlation coefficient changing to 1.17 (± 0.16), -0.51 (± 0.78) and $R=0.87$, respectively. Thus, differences between the two NO$_2$ profile shapes play a more important role under cloudy conditions.
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Figure 4.8. First comparison between GOME NO₂ VTCs and tropospheric columns derived from ground-based in situ measurements (a) and second comparison after multiplying the ground-based profile with the averaging kernel (b) together with orthogonal regression output for cloudy conditions. Columns with SCDₜrop/SCD > 50% are rejected.

This is further supported by mean $\Delta_1-3$ that are calculated to be 10%, 3% and 7%, respectively, with $\Delta_3$ explaining the major part of the total relative difference. Moreover, this is mirrored in a poorer agreement between $VTC_{ind}$ and $VTC_{ind, AK}$ (Fig. 4.9) than found for the clear sky cases (Fig. 4.6). This supports the conclusion that for the average of the cloudy cases, the retrieval error due to uncertainties in the a priori profile shapes becomes more important. As pointed out in the above case example, a positive value for $\Delta_3$ would be consistent with an underestimation of
upward transport of NO$_2$ in the CTM. As a consequence, the AMF$_{trop}$ would be under-
and the corresponding GOME NO$_2$ VTCs overestimated.

![Figure 4.9. Directly integrated ground-based NO$_2$ column (VTC$_{ind}$) and the corresponding column multiplied with the averaging kernel (VTC$_{ind}$,AK) for cloudy conditions.](image)

Note that the clear improvement after multiplication with the AK can also be found for other choices of the above rejection criterion SCD$_{trop}$/SCD (not shown). Only towards low SCD$_{trop}$/SCD values, the impact of AK is decreasing and comparable to the impact found for the clear sky cases. This becomes obvious from Fig. 4.8, where the comparison with larger GOME NO$_2$ columns is stronger affected by the multiplication with the AK than the comparison with smaller columns. If the impact of AK information is taken as a measure for the uncertainty of a priori NO$_2$ profiles (and the resulting GOME NO$_2$ columns) under cloudy conditions, we qualitatively estimate from Fig. 4.8, that for the study region, already GOME columns exceeding $10 \times 10^{15}$ molec cm$^{-2}$ should be handled with care before being further used for air pollution monitoring or as input parameters for models. Or in other words: for such cases, the proper use of averaging kernel information is a matter of special importance and the absolute value of the retrieval should be interpreted carefully.

### 4.6 Summary and conclusions

A long-term comparison of GOME NO$_2$ VTC data retrieved from KNMI/BIRA with independently derived NO$_2$ columns was carried out. The study compared GOME NO$_2$ VTCs over Northern Switzerland with coincident ground-based tropospheric columns for both anticyclonic clear sky (GOME pixel cloud fraction $\leq 0.1$) and cloudy conditions (cloud fraction $\geq 0.75$).

Ground-based in situ NO$_2$ profiles/columns were deduced from ground stations located at different altitudes in the Alps and Swiss Plateau (PBL) stations representative for different pollution levels. An error estimate for these ground-based NO$_2$ columns took into account the non-selective NO$_2$ measurements with molybdenum converters and inhomogeneities at stations located at around 1000 m
4 Comparing GOME NO$_2$ columns to ground-based NO$_2$ profiles

Asl (e.g. due to thermal transport). The resulting error in the ground-based columns is in the order of 50%, which is comparable to the 1-sigma errors estimated for the GOME NO$_2$ VTCs.

A first comparison related the GOME columns to the ground-based NO$_2$ profiles that are directly integrated to tropospheric columns. For a second comparison, the ground-based profiles are multiplied with the averaging kernel (AK). This makes the comparison independent from the a priori NO$_2$ profile used in the GOME retrieval. Thus, the total relative difference between the column data sets can be split into two contributions: one that depends on the differences between the a priori and the ground-based NO$_2$ profile shapes, and another which is no longer affected by the a priori NO$_2$ profile, but depends on errors in both the remaining retrieval parameters and the ground-based NO$_2$ profiles.

The clear sky comparison (157 cases) showed a good agreement between the two columns types. The seasonal behaviour is very similar, with smallest NO$_2$ VTCs during summertime and largest columns in the spring season. An orthogonal regression taking into account error estimates for both column types yielded a slope and an intercept of 1.15 (std. dev. 0.22) and -1.23 (std. dev. 0.90), respectively, with a correlation coefficient $R=0.70$. After AK inclusion, the slope and intercept changed to 1.01 (std. dev. 0.16) and -0.83 (std. dev. 0.70), respectively, with $R=0.74$. The multiplication of the ground-based profile with the AK has a relatively weak impact. This can be attributed to similar shapes of the ground-based and the a priori NO$_2$ profile for the average of the anticyclonic clear sky cases.

A detailed analysis of relative differences between the two data sets was carried out. For the whole clear sky data set a mean relative difference (with respect to the ground-based columns) of -7% with a standard deviation of 40% is found, with GOME NO$_2$ VTCs slightly underestimating the ground-based columns. The standard deviation result suggests that the a priori estimates of 50% errors on GOME and ground-based columns are too conservative, and errors of the order of 30% would be more consistent with the intercomparison results.

The further analysis showed that the above mentioned contributions to the total relative compensate each other to a certain extent for clear sky cases. This should be taken into account in detailed validation studies of space-borne data that are affected by uncertainties in a number of parameters. Further, the following evidences were found (with relative differences calculated with respect to the GOME columns):

- For large GOME NO$_2$ VTCs ($> 5.0 \times 10^{15}$ molec cm$^{-2}$), the GOME product is slightly larger (7%) than the ground-based columns. This is mainly caused by differences between the ground-based and the a priori NO$_2$ profile shapes.

- For smaller GOME NO$_2$ VTCs ($< 3.5$ and $3.5 - 5.0 \times 10^{15}$ molec cm$^{-2}$), the GOME product is smaller than the ground-based one (with a mean relative difference of up to -61%) due to other error sources than the a priori NO$_2$ profile assumptions (i.e., remaining retrieval parameters and/or ground-based NO$_2$ profiles).

The comparison for cloudy conditions generally yielded a poorer agreement between the columns. This can be expected due to additional error sources arising from inaccurate knowledge of cloud characteristics (e.g. cloud top height, cloud fraction, optical thickness) and difficulties in the radiative transfer modelling (multiple scattering). Unrealistically large GOME NO$_2$ VTCs have been found, e.g. for 17
February 2001, with a tropospheric GOME column of $490 \times 10^{15} \text{ molec cm}^{-2}$. Evidences are discussed that such high column values are likely due to an underestimation of the elevated NO$_2$ in the a priori profile in combination with retrieval errors due to inaccurate cloud parameters which lead to a strong magnification of above-cloud NO$_2$ concentrations. Also after excluding extremely large GOME columns, the remaining GOME NO$_2$ VTCs (60 cases) still overestimate the ground-based columns. The mean relative difference (with respect to the ground-based columns) is 60% with a standard deviation of 118%.

For the first comparison, the orthogonal regression yielded a slope and an intercept of 2.99 (std. dev. 0.91) and -7.71 (std. dev. 4.18), respectively, with a correlation coefficient $R=0.61$. For the second comparison, the slope and intercept changed to 1.17 (std. dev. 0.16) and -0.51 (std. dev. 0.78), respectively, with $R=0.87$. The multiplication with the AK clearly improved the comparison. This is consistent with a larger difference between the ground-based and the a priori NO$_2$ profile shapes and gives evidence for uncertainties in the a priori NO$_2$ profiles playing a more important role for the retrieval of cloudy scenes than for clear sky cases. This mainly applies for high GOME NO$_2$ column values (> $10 \times 10^{15} \text{ molec cm}^{-2}$ for the study area).

The good agreement between GOME and ground-based NO$_2$ VTCs found in the present study for clear sky conditions encourages the use of space-borne trace gas columns for air pollution modelling and monitoring also on a regional scale. The good agreement is remarkable taking into account both the complex topography at the foothills of the Alps and the uncertainties in both column data sets. The study further showed that comparison or validation studies of space-borne trace gas columns with independently derived profiles should include averaging kernel information in order to distinguish between different error sources. We expect this to become even more important for future comparisons with higher resolved pixels from SCIAMACHY and OMI (particularly with regard to a possible undersampling when calculating a priori NO$_2$ profiles with coarsely resolved global CTMs). However, this is a first step towards a more detailed comparison. A further improvement of comparison or validation studies can be reached by including independent knowledge of retrieval parameters such as surface albedo, satellite pixel surface pressure, and, for comparisons under cloudy conditions, cloud parameters. Moreover, the present study investigated absolutely cloud-free (GOME pixel cloud fraction ≤ 0.1) and clearly cloudy scenes (cloud fraction ≥ 0.75). Hence, work remains to be done on retrievals in situations of moderate cloudiness.

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References


Comparing GOME NO₂ columns to ground-based NO₂ profiles


5 SCIAMACHY tropospheric NO\textsubscript{2} over the Alpine region and importance of pixel surface pressure

This section is based on

D. Schaub\textsuperscript{1}, K. F. Boersma\textsuperscript{2}, J. Keller\textsuperscript{3}, D. Folini\textsuperscript{1}, D. Brunner\textsuperscript{1}, B. Buchmann\textsuperscript{1}, H. Berresheim\textsuperscript{4}, and J. Staehelin\textsuperscript{5}: SCIAMACHY tropospheric NO\textsubscript{2} over the Alpine region and importance of pixel surface pressure for the column retrieval, submitted to *Atmospheric Chemistry and Physics Discussions*, 2006.

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Abstract

This study evaluates NO\textsubscript{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. A clear relationship between a spatially and temporally highly resolved Swiss NO\textsubscript{x} emission inventory and SCIAMACHY NO\textsubscript{2} columns under anticyclonic meteorological conditions supports the general ability of SCIAMACHY to detect sources of NO\textsubscript{x} pollution in Switzerland. Summertime NO\textsubscript{x} lifetime estimates derived from this relation agree reasonably with values from literature. A further evaluation of the SCIAMACHY data is based on the comparison with NO\textsubscript{2} VTCs retrieved from the Global Ozone Monitoring Experiment (GOME). The annual mean NO\textsubscript{2} VTCs calculated from both data sets clearly show the advantage of the improved SCIAMACHY pixel resolution for qualitatively estimating the NO\textsubscript{x} pollution distribution in a small country such as Switzerland. However, a more quantitative comparison of seasonally averaged NO\textsubscript{2} VTCs gives evidence for SCIAMACHY NO\textsubscript{2} VTCs being systematically underestimated over the Swiss Plateau during winter. A possible explanation for this problem (not reported in earlier literature) is the use of inaccurate satellite pixel surface pressures derived from coarsely resolved global models in the retrieval. The marked topography in the Alpine region can lead to deviations of several hundred meters between the assumed and the real mean surface height over
a pixel. A sensitivity study based on selected clear sky SCIAMACHY NO2 VTCs over the Swiss Plateau and two fixed a priori NO2 profile shapes indicates that inaccurate pixel surface pressures have a considerable effect of up to 40% on the retrieved NO2 columns. 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 NO2 resides close to the ground, which occurs most pronounced during the winter season.

5.1 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 NOx 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 NOx is directly injected into the troposphere by lightning and aircraft emissions (IPCC, 2001).

NOx is primarily emitted as NO which oxidises to NO2 within a few minutes. The NO2 concentration is affected by the partitioning of NOx into NO and NO2 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. NOx is removed from the troposphere mainly by conversion to nitric acid (HNO3). During daytime, HNO3 is formed through the reaction of NO2 with the OH radical. At night, a two step reaction mechanism forms nitrogen pentoxide (N2O5) which further reacts on surfaces and aerosol to HNO3 (Dentener and Crutzen, 1993). HNO3 is finally removed by dry and wet deposition (Kramm et al., 1995). The resulting NOx lifetime is highly variable with an annual average boundary layer lifetime of about one day (Warneck, 2000). However, due to the higher summertime abundance of OH, much shorter lifetimes of a few hours prevail during photochemically active summer days. In this study, we infer NOx lifetimes from the combination of SCIAMACHY NO2 VTCs with a high-quality NOx emission inventory to check the reliability of SCIAMACHY data. Generally, NOx lifetimes are essential to determine emissions from space-borne data (e.g. Martin et al., 2003).

Although the NOx (≡ NO + NO2) concentration in Switzerland decreased during the last 15 years the Swiss NO2 annual ambient air quality standard of 30 μgm-3 (≈ 16 ppb) is still exceeded in polluted areas (FOEN, 2005). 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 NO2 vertical tropospheric column densities (VTCs) with global coverage within a few days. The improved resolution of space-borne NO2 VTCs (GOME pixel size: 320 × 40 km2, SCIAMACHY: 60 × 30 km2, Ozone Monitoring Instrument (OMI): 13 × 24 km2) increasingly allows to detect NO2 pollution features on a regional scale. However, these space-borne data and their complex retrieval are emerging techniques and validation is needed. Schaub et al. (2006) summarised different validation campaigns of GOME and SCIAMACHY NO2 data and carried out a detailed comparison of
GOME NO₂ VTCs retrieved by KNMI (Royal Dutch Meteorological Institute) and BIRA/IASB (Belgian Institute for Space Aeronomy) with NO₂ profiles derived from ground-based in situ measurements at different altitudes in the Alpine region. In this paper we evaluate SCIAMACHY NO₂ VTCs over Switzerland and the Alpine region with regard to their use for air quality monitoring and modelling on a regional scale. For the first time, the focus is on the size of a small country such as Switzerland. The above mentioned GOME validation approach presented in Schaub et al. (2006) can not be adopted for SCIAMACHY here. In that approach in situ measurements from a number of widely separated stations located at different altitudes in Switzerland and Southern Germany have been used to estimate vertical NO₂ columns. The size of SCIAMACHY pixels, however, is too small to justify the combination of measurements that are spatially separated (the latter are only used for a qualitative comparison in this study). We therefore first perform a qualitative evaluation by relating SCIAMACHY NO₂ VTCs to a spatially and temporally highly resolved NOₓ emission inventory available for Switzerland, showing the general ability of SCIAMACHY data to detect the NO₂ pollution distribution on the scale of a small country. This comparison is then used to infer seasonal mean daytime NOₓ lifetimes that are subsequently compared to values from literature. Further, the SCIAMACHY NO₂ VTCs are evaluated by a comparison with GOME NO₂ columns over Switzerland and a qualitative comparison with the seasonal variation of NO₂ columns deduced from ground-based in situ measurements carried out at different altitudes. Evidence is found for SCIAMACHY NO₂ VTCs being systematically underestimated over the Swiss Plateau during the winter season. We will present a plausible reason contributing to this problem which is related to an inadequate representation of the surface topography in the NO₂ retrieval. This problem potentially affects any region on the globe with a marked topography and becomes increasingly important with improving pixel resolution when the retrieval is based on coarsely resolved input parameters, e.g. derived from global models.

5.2 Data

5.2.1 KNMI/BIRA GOME and SCIAMACHY tropospheric NO₂ 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. The GOME and SCIAMACHY observations are obtained at approximately 10:30 and 10:00 local time and individual pixels cover an area of 320 × 40 km² and 60 × 30 km², respectively. The GOME and SCIAMACHY measurement principles are described in Burrows et al. (1999) and Bovensmann et al. (1999), respectively. The NO₂ VTCs studied in this work are the product of a collaboration between KNMI and BIRA/IASB. Both GOME and SCIAMACHY NO₂ 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 (Vandaele et al., 2005): a modelled spectrum is fitted to the measured reflectance spectrum in the spectral window from 426.3-451.3 nm. The modelled spectrum accounts for spectral absorption features of NO₂, O₃, O₂-O₂ and H₂O. 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$_2$, which can be interpreted as the column integral of absorbing NO$_2$ 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 global TM4 chemistry transport model (CTM) (Dentener et al., 2003). The tropospheric SCD (SCD$_\text{trop}$) results from the subtraction of the stratospheric estimate from the total SCD.

In the third retrieval step, the SCD$_\text{trop}$ is converted into a VTC by applying the tropospheric air mass factor (AMF$_\text{trop}$). Following Palmer et al. (2001) and Boersma et al. (2004), the retrieved SCIAMACHY NO$_2$ VTC ($X_{\text{SCIA}}$) is calculated as

$$X_{\text{SCIA}} = \frac{N_{\text{trop}}}{M_{\text{trop}}(x_a,b)} = \frac{N_{\text{trop}} \cdot \sum_l x_{a,l}}{\sum_l m_l(b) \cdot x_{a,l}}$$

(5.1)

where $N_{\text{trop}}$ denotes the tropospheric slant column density, $M_{\text{trop}}$ 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. The latter are calculated with the Doubling Adding KNMI (DAK) radiative transfer model (Stammes, 2001) and best estimates for forward model parameters $b$, describing surface albedo, cloud parameters (fraction, height) and pixel surface pressure. The a priori NO$_2$ profiles for every location and all times are obtained from the TM4 CTM. Cloud fraction and height are taken from the Fast 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 $2^\circ \times 3^\circ$ 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).

Errors of GOME tropospheric NO$_2$ retrievals have extensively been discussed in Boersma et al. (2004). Based on this work, errors for both GOME and SCIAMACHY NO$_2$ VTCs are estimated on a pixel-to-pixel basis and additionally provided in the TEMIS data sets. Error propagation studies have shown SCIAMACHY NO$_2$ VTC errors to be similar to GOME errors. However, these studies have not included the effect of surface pressure. The present work will show that, over a complex topography, this parameter can be expected to lead to larger errors for the higher resolved SCIAMACHY data.

### 5.2.2 Swiss NO$_x$ emissions

Swiss NO$_x$ emissions mount up to 33.2 kt N/year 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$_x$ emission inventory for Switzerland available on a $3 \times 3$ km$^2$ grid. It combines the following basic data sets:
• Road traffic emissions of NO$_x$ for the reference year 2000 with a spatial resolution of 250 m were prepared by the consulting company INFRAS, Switzerland. An average diurnal variation is provided as well. Long-term trends of annual totals recently published in Keller and Zbinden (2004) were used to interpolate the emissions between 2000 and 2005.

• NO$_x$ 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 were prepared by the Meteotest company, 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. Kühlwein and Friedrich, 2000). For the 3 × 3 km$^2$ Swiss NO$_x$ emission inventory an accuracy of ± 15–20% is estimated in FOEN (1995). Kühlwein (2004) further pointed out increasing errors in emission inventories for increasing spatial resolutions. Thus, due to integration of the 3 × 3 km$^2$ resolved emission data over the SCIAMACHY pixel size of 60 × 30 km$^2$ in the present work, the above given error of 20% is considered as a reasonable upper limit, which will be assumed in this study.

5.3 Methods

5.3.1 Comparison of SCIAMACHY NO$_2$ VTCs with a high resolution emission inventory and estimation of mean NO$_x$ lifetimes

SCIAMACHY NO$_2$ VTCs located entirely within the Swiss boundaries are related to the high resolution Swiss NO$_x$ emission inventory presented in Sect. 5.2.2. NO$_x$ emission rates between 9:00 and 10:00 (alternatively between 6:00 and 10:00) UTC are summed up over the individual pixel footprints.

First, the qualitative relation between NO$_2$ VTCs and collocated NO$_x$ emissions is discussed. Then, neglecting any transport into or out of the column enclosed by the satellite pixel, seasonal NO$_x$ lifetimes are estimated simply as the ratio between the observed column (in N-equivalents: g(N) km$^{-2}$) and the emission rate (g(N) km$^{-2}$ hr$^{-1}$). In order to account for inaccuracies in both the observed columns and the emission rates, the lifetime estimates are based on the calculation of a weighted orthogonal regression (York, 1966). SCIAMACHY NO$_2$ 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). For the NO$_x$ emission rates added up over the individual SCIAMACHY pixels an error of 20% is assumed (Sect. 5.2.2).

SCIAMACHY NO$_2$ VTCs are converted to NO$_x$ VTCs by employing representative values for the seasonal mean NO$_2$/NO ratio. The latter depends on the abundance of ozone and reactive organic compounds as well as on solar light intensity 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 operated since 1999 at a rural site at the edge of the Swiss Plateau (Rigi, 47° 04’ N, 8° 28’ E, 1030 m asl) using a standard chemiluminescence detector for the measurement of NO and a photolytic converter for the selective conversion of NO2 to NO indicates a seasonal variation of monthly mean NO2/NO 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). Because the location of the measurement site on a mountain ridge roughly 500 m above the Swiss Plateau can lead to a decoupling from the near-ground Swiss Plateau air masses during winter and the NO2/NO ratio is decreasing with height (e.g. Nakamura et al., 2003), we suppose that the wintertime ratio given above is rather low. Thus, for the present work, we assume seasonal mean NO2/NO ratios of 3, 4, 3 and 2 for the spring (MAM), summer (JJA), fall (SON) and winter (DJF) season, respectively. Due to the bulk of NOx residing near the ground in polluted regions we further assume these NO2/NO ratios to be representative for the whole tropospheric column.

The NOx emissions taking place at the location of the column are considered as the main flux of NOx 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

\[ \frac{dM}{dt} = E - k \cdot M = 0 \]  
(5.2)

and hence

\[ M = \frac{1}{k} \cdot E = \tau \cdot E \]  
(5.3)

with \( M \) the amount of NOx in the column, \( E \) the NOx emission rate (both converted to N-equivalents) and \( \tau \) the lifetime. The basic assumption of steady state has also been made by Leue et al. (2001), Beirle et al. (2003) and Kunhikrishnan et al. (2004). It disregards the horizontal NOx transport into and out of the column. This transport, however, leads to a smearing effect that is depending on the distribution of the NOx emissions, 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 NOx lifetimes in the order of hours to one day, this length scale is \(~100\) km (Martin et al., 2003). This might be problematic regarding the SCIAMACHY pixel size of \(60 \times 30\) km\(^2\). However, anticyclonic clear sky conditions (which are the present focus) are known to be associated with low wind speeds, i.e. rather stagnant air, and fast photochemistry, which reduces 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 considered to be unimportant for the anticyclonic days investigated here.
5.3.2 Sensitivity of SCIAMACHY NO$_2$ VTCs to varying pixel surface pressure

Following Sect. 5.2.1 the mean pixel surface pressure is one of the parameters used in the column retrieval. For both GOME and SCIAMACHY pixels with centre coordinates within the region of interest ROI$_{CH}$ (Fig. 5.1) covering the whole Switzerland (6° E – 10.5° E, 45.75° N – 47.75° N) the deviations between the ECMWF/TM4 mean surface pressures used in the retrieval ($p_{surf}$) and the corresponding effective mean surface pressures ($p_{eff}$) are determined and compared to each other. $p_{eff}$ over the pixel extension is determined from the aLMo (Alpine Model, the MeteoSwiss numerical weather prediction model) topography which better represents the real topography as the aLMo resolution of 7 × 7 km$^2$ is much finer than the TM4 model grid (2° × 3°, ~220 × 240 km$^2$).

![Figure 5.1. Regions of interest used in this study covering the whole Switzerland (6° E – 10.5° E, 45.75° N – 47.75° N, ROI$_{CH}$) and the polluted Swiss Plateau (7° E – 9.5° E, 47° N – 47.75° N, ROI$_{SP}$). (Topographic map of Switzerland: © 2005 swisstopo).](image)

An estimate of the effect of inaccurate pixel surface pressure used in the retrieval is carried out for a subset of clear sky SCIAMACHY pixels. The AMFs$_{rop}$ and NO$_2$ VTCs are first calculated for $p_{surf}$ as in the retrieval and then recalculated for the better surface pressure estimate $p_{eff}$. The criteria for the pixel subset are i) anticyclonic clear sky meteorological conditions (Alpine Weather Statistics; MeteoSwiss, 1985), ii) pixel cloud fraction ≤ 0.1, and iii) a small standard deviation <65 m of the aLMo 7 x 7 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 over the complex Alpine topography. The resulting SCIAMACHY pixels are located above the north-eastern Swiss Plateau (Fig. 5.2). The sensitivity test is based on two characteristic (and fixed) CTM a priori NO$_2$ profile shapes (Fig. 5.3). In a first profile (A), the bulk of the NO$_2$ is residing near the ground. Such profile shapes are expected to occur over polluted regions and most pronounced during the winter months when vertical mixing is generally weak or non-
existing. A second profile (B) shows a much lower NO₂ abundance near the ground and can be expected to represent either a remote profile or a summertime profile shape resulting from vertical mixing. As shown in Fig. 5.3 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.

Figure 5.2. Topographic map of Switzerland (© 2005 swisstopo) with the location of the SCIAMACHY pixels used for the pixel surface pressure sensitivity calculation.

Figure 5.3. CTM a priori NO₂ profiles A (poor vertical mixing/polluted) and B (strong vertical mixing/remote) given as layer-specific sub columns. The black profiles are associated with the ECMWF/TM4 surface pressure at the location of the SCIAMACHY pixel. The red profiles are reaching down to the effective surface pressure calculated from the aLMo model with a 7 × 7 km² resolution. For the examples shown here, surface pressures are taken from 10 March 2004 (profile A) and from 21 July 2001 (profile B).
5.4 Results and discussion

5.4.1 SCIAMACHY NO$_2$ VTCs and NO$_x$ emissions in Switzerland

Qualitative comparison

Figure 5.4a shows the comparison between SCIAMACHY NO$_2$ VTCs and the corresponding NO$_x$ emission rates for anticyclonic clear sky (pixel cloud fraction $\leq 0.1$) meteorological conditions together with a simple linear regression ($n=243$). Anticyclonic conditions are deduced from the Alpine Weather Statistics (MeteoSwiss, 1985). Although (i) the present comparison does not include any vertical profile information, (ii) the smearing effect is not taken into account and (iii) different meteorological conditions can be expected to lead to different relations between the NO$_2$ VTCs and the corresponding emissions (due to different NO$_2$/NO ratios and different NO$_x$ lifetimes), 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. Thus, SCIAMACHY seems to observe the sources of air pollution from space although its sensitivity is strongly decreasing towards the earth’s surface.

Figure 5.4. Comparison between SCIAMACHY NO$_2$ VTCs (from 2003-2005) and collocated NO$_x$ emission rates for pixels located entirely within the Swiss boundaries and anticyclonic clear sky meteorological conditions (pixel cloud fraction $\leq 0.1$, $n=243$) (a). Correlation coefficients of the present comparison for different upper limits of cloud fraction (b).

Figure 5.4b shows the correlation coefficient vs. the upper limit for the SCIAMACHY cloud fraction; i.e., SCIAMACHY pixels with cloud fractions lower than or equal to this limit have been taken into account. The comparison is carried out for all meteorological conditions as well as for anticyclonic conditions only. We suppose that the better correlations under anticyclonic conditions are due to low wind speeds and rather homogeneous air masses often prevailing during such conditions. Thus, the NO$_2$ columns are more directly related to the collocated NO$_x$ emissions. Note that the stable values of the correlation coefficients for higher upper cloud fraction limits in Fig. 5.4b are 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). The
decreasing correlation coefficients with increasing cloud fraction limits can be understood from clouds screening the NO$_2$ below. In such situations, the retrieved column is strongly affected by the a priori assumption on the vertical NO$_2$ distribution (Schaub et al., 2006).

![Figure 5.5](image)

**Figure 5.5.** Clear sky (cloud fraction ≤ 0.2) SCIAMACHY NO$_x$ VTCs located entirely within the Swiss boundaries vs. NO$_x$ emission rates (both given in N-equivalents). NO$_2$ VTCs are converted to NO$_x$ VTCs using assumed values for the seasonal mean NO$_2$/NO ratios. The resulting NO$_x$ VTCs are compared to NO$_x$ emission rates enclosed within the individual pixels for the four seasons spring (a), summer (b), fall (c) and winter (d). The examples shown here are based on NO$_x$ emission rates taking place between 9:00 and 10:00 UTC. Additionally, the orthogonal regression calculation output (based on data errors as described in Sect. 5.3.1) is given (see also Tab. 5.1).

### Near-ground NO$_x$ lifetime under anticyclonic clear sky conditions

For estimating seasonal NO$_x$ lifetimes we define clear sky conditions to prevail for SCIAMACHY pixels with a cloud fraction ≤ 0.2 (still yielding a correlation coefficient R > 0.5 in Fig. 5.4b). In this way the analysis can be based on a larger data set than available for a limit of 0.1. SCIAMACHY NO$_2$ VTCs are converted to NO$_x$ VTCs as described in Sect. 5.3.1.

Figure 5.5 shows for each season the relationship between individual SCIAMACHY NO$_x$ columns located entirely within the Swiss boundaries and the corresponding NO$_x$ emission rates between 9:00 and 10:00 UTC. Additionally, the weighted orthogonal regression output is given. The relatively small intercepts suggest that
under anticyclonic conditions the background NO\textsubscript{x} plays a rather marginal role and the SCIAMACHY observations are dominated by the local NO\textsubscript{x} emissions. From the slopes the corresponding column-average NO\textsubscript{x} lifetimes for the spring, summer, fall and winter season are calculated as 5.00 ± 0.87, 3.36 ± 0.55, 5.27 ± 0.60 and 11.21 ± 2.13 hours, respectively. An additional estimate is calculated using a different time window between 6:00 and 10:00 UTC for summing up the NO\textsubscript{x} emission rates. The resulting NO\textsubscript{x} lifetimes are summarised in Tab. 5.1 and Fig. 5.6. The alternative time window used to derive the NO\textsubscript{x} emission rates (6:00-10:00 UTC instead of 9:00-10:00 UTC) has only a very small impact on the results even though NO\textsubscript{x} emission peaks due to morning traffic are included in this case.

Table 5.1. Seasonal NO\textsubscript{x} lifetime estimates based on a weighted orthogonal regression for two different time windows for averaging the emission rates over the SCIAMACHY pixels. The standard deviations are given by the standard deviations of the slopes of the regression lines.

<table>
<thead>
<tr>
<th>emission rates (time window)</th>
<th>( \tau_{\text{NOx}} ) (hrs) MAM (± std. dev.)</th>
<th>( \tau_{\text{NOx}} ) (hrs) JJA (± std. dev.)</th>
<th>( \tau_{\text{NOx}} ) (hrs) SON (± std. dev.)</th>
<th>( \tau_{\text{NOx}} ) (hrs) DJF (± std. dev.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n=57</td>
<td>n=116</td>
<td>n=149</td>
<td>n=42</td>
</tr>
<tr>
<td>9-10 UTC</td>
<td>5.00 (±0.87)</td>
<td>3.36 (±0.55)</td>
<td>5.27 (±0.60)</td>
<td>11.21 (±2.13)</td>
</tr>
<tr>
<td>6-10 UTC</td>
<td>4.90 (±0.86)</td>
<td>3.22 (±0.53)</td>
<td>5.23 (±0.59)</td>
<td>11.53 (±2.19)</td>
</tr>
</tbody>
</table>

Besides the NO\textsubscript{x} lifetimes estimated here, Fig. 5.6 denotes additional summertime lifetime estimates from literature:

- from measurements in power plant plumes: 5 hours (Ryerson et al., 1998), 2.8 and 4.2 hours (Nunnermacker et al., 2000) and 6.4 hours (Sillman, 2000),

- from measurements in urban plumes: Boston: 5.5 hours (Spicer, 1982), Nashville: 2.0 hours (Nunnermacker et al., 2000), Zurich: 3.2 hours (Dommen et al., 1999),

- from GOME NO\textsubscript{2} VTCs above Germany: 6.0 hours (Beirle et al., 2003) and

- zonal mean in the boundary layer (0-2 km) from the GEOS-CHEM CTM: 3.0 hours (Martin et al., 2003).

For spring, Martin et al. (2003) calculated a mid-latitude NO\textsubscript{x} lifetime from the GEOS-CHEM model of 8 hours. For the winter season, Martin et al. (2003) and Beirle et al. (2003) reported on NO\textsubscript{x} lifetimes of 19 and 21 hours, respectively. Additional NO\textsubscript{x} lifetimes are estimated here for the main NO\textsubscript{x} loss mechanism which is the oxidation of NO\textsubscript{2} with OH to HNO\textsubscript{3}. These estimates are based on typical Swiss Plateau values of pressure (960 hPa) and temperature 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 asl. From a pollution point of view, all regions are similar to the Swiss Plateau and surroundings. For an assumed temperature of 298 K and based on OH concentrations taken from the BERLIOZ and the SLOPE96 campaigns with noontime values of \((4-8) \times 10^6 \text{ cm}^{-3}\) \((\text{Volz-Thomas et al., 2003; Mihelcic et al., 2003})\) and \((7-10) \times 10^6 \text{ cm}^{-3}\) \((\text{Volz-Thomas and Kolahgar, 2000})\), respectively, the resulting mean daytime NOx lifetimes in summer are estimated to be 4.6 hours and 3.0 hours. Seasonally averaged 9:00-10:00 UTC OH concentrations determined from clear sky OH measurements at Hohenpeissenberg carried out between 1999 and 2005 \((\text{Rohrer and Berresheim, 2006; Berresheim, unpublished data, 2006})\) are used together with assumed temperatures for the summer, spring/fall and winter seasons of 298 K, 288 K and 278 K, respectively, to estimate NOx lifetimes of 6.1, 3.9, 8.2 and 21.0 hours for the MAM, JJA, SON and DJF seasons, respectively (Fig. 5.6).

![Figure 5.6. Seasonal NOx 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; Dommen et al., 2000; Stillman, 2000) and in the Swiss Plateau (Dommen et al., 1999), from GOME NO2 VTCs over Germany (Beirle et al., 2003) and from the GEOS-CHEM model (Martin et al., 2003). Additionally, mean NOx lifetimes against oxidation to HNO3 are calculated for (i) 960 hPa and 298 K with OH concentrations of \((4-8) \times 10^6 \text{ cm}^{-3}\) measured during the BERLIOZ campaign \((\text{Volz-Thomas et al., 2003; Mihelcic et al., 2003})\) and of \((7-10) \times 10^6 \text{ cm}^{-3}\) measured during the SLOPE96 campaign \((\text{Volz-Thomas and Kolahgar, 2000})\) as well as for (ii) seasonally averaged OH concentrations measured by \((\text{Rohrer and Berresheim, 2006; Berresheim, unpublished data, 2006})\) with 960 hPa and assumed temperatures for the summer, spring/fall and winter seasons of 298 K, 288 K and 278 K, respectively.](image-url)
The comparison of our NO$_x$ lifetimes with estimates from literature shows that the summertime values obtained here are reasonable. Our estimate is near the lower end of the range of published values, but it is noteworthy that our values of 3.4 and 3.2 hours (depending on the emission time window) perfectly agree with another study carried out in Switzerland by Dommen et al. (1999) yielding a lifetime of 3.2 hours (Fig. 5.6). For spring and fall only few published values are available for comparison (Fig. 5.6). However, our result is still similar to these values for spring. For the fall season our estimate can only be compared to a lifetime value deduced from Hohenpeissenberg OH measurements and a conclusive statement can not be given. A stronger disagreement is found for winter where our mean NO$_x$ lifetime values are nearly a factor of two smaller than the literature values shown in Fig. 5.6.

Our wintertime estimate could differ (i) due to the focus on a rather polluted region (in contrast to the zonal mean value given by Martin et al. (2003)), (ii) due to additional wintertime NO$_x$ loss mechanisms besides the oxidation to HNO$_3$ (which was the only loss considered by Martin et al. (2003) and for calculating the NO$_x$ lifetime from the Hohenpeissenberg OH data) or (iii) due to our approach focusing directly on the location of the NO$_x$ emissions (in contrast to Beirle et al. (2003) who estimated the NO$_x$ lifetime from GOME NO$_2$ VTCs downwind of emitting regions in Germany). However, based on the fact that the very similar wintertime NO$_x$ lifetime estimates given by Martin et al. (2003) and Beirle et al. (2003) and calculated from the Hohenpeissenberg OH measurements have been derived with independent methods, one could also argue that our wintertime NO$_x$ lifetime estimate (and, possibly, less pronounced also the spring and fall estimates) are too low. The disregard of the horizontal transport (smearing effect) could partly explain our lower values. However, due to the focus on anticyclonic clear sky conditions with enhanced photochemical activity and generally low wind speeds the importance of the smearing effect decreases and we suppose that other reasons could additionally play a role.

In our approach, a higher lifetime is associated with a steeper slope in Fig. 5.5, i.e. higher space-borne NO$_2$ VTCs over highly emitting regions. We therefore explore whether, most pronounced in winter, SCIAMACHY retrievals might underestimate the NO$_2$ VTCs over the polluted Swiss Plateau.

![Figure 5.7](image)

**Figure 5.7.** Mean clear sky (satellite pixel cloud fraction $\leq 0.1$) NO$_2$ tropospheric columns over the Central Alps and Switzerland deduced from GOME (1996–2003) (a) and SCIAMACHY (2003-2005) (b) retrievals. In contrast to the GOME picture, specific features such as the Alpine chain, the Jura Mountains, the Swiss Plateau and the areas of Greater Zurich and Basel clearly show up in the SCIAMACHY data.
5.4.2 Comparing GOME and SCIAMACHY NO\textsubscript{2} VTCs over the Swiss Plateau

For a qualitative comparison of clear sky (pixel cloud fraction ≤ 0.1) GOME and SCIAMACHY NO\textsubscript{2} VTCs, the data are mapped onto a fine 0.125° × 0.125° grid covering Switzerland and surroundings. For each cell a mean VTC is computed by averaging over all SCIAMACHY (2003-2005) (Fig. 5.7a) or GOME (1996-2003) (Fig. 5.7b) pixels covering the given cell. In contrast to the picture derived from the GOME columns, the higher resolved SCIAMACHY data clearly indicate individual population/industry centres such as the areas of Zurich and Basel as well as the Alpine chain and the Jura Mountains.

For a more quantitative comparison seasonally averaged GOME and SCIAMACHY NO\textsubscript{2} VTCs are calculated from all clear sky pixels with centre coordinates located within the region ROI\textsubscript{SP} (Fig. 5.1) covering the polluted regions of the Swiss Plateau (7° E – 9.5° E, 47° N – 47.75° N) only. Similar to Schaub et al. (2006), the ROI\textsubscript{SP} excludes the complex Alpine terrain as far as possible. In Fig. 5.8a the resulting SCIAMACHY NO\textsubscript{2} VTCs are on average higher than the GOME columns in spring, summer and autumn. This can be understood because the extended GOME pixels always include less polluted regions outside of the Swiss Plateau. Surprisingly, the wintertime SCIAMACHY NO\textsubscript{2} VTC values are lower than the ones from GOME.

Figure 5.8. Seasonal mean and median NO\textsubscript{2} VTCs from GOME and SCIAMACHY over the ROI\textsubscript{SP} (Fig. 5.1) for clear sky conditions (cloud fraction ≤ 0.1). For the four seasons MAM, JJA, SON and DJF, SCIAMACHY and GOME contributed with 76, 175, 129 and 86 and 52, 95, 33 and 7 NO\textsubscript{2} VTCs, respectively (a). Seasonal mean and median NO\textsubscript{2} columns from GOME, SCIAMACHY and derived from ground-based in situ NO\textsubscript{2} measurements normalised to the spring (MAM) season. The ground-based in situ columns were calculated following the method and data set described in Schaub et al. (2006) and for a Swiss Plateau ground height of 450 m asl. For the four seasons MAM, JJA, SON and DJF, 139, 165, 69 and 78 columns contribute to the seasonal values (b).

Figure 5.8b shows the same comparison with the seasonal mean columns normalised to the spring (MAM) season. Additionally, seasonally averaged NO\textsubscript{2} columns estimated from NO\textsubscript{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 shown. The elevated sites are assumed to detect NO\textsubscript{2} concentrations that are approximately 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 NO₂ profiles. The latter are subsequently integrated to tropospheric NO₂ columns. Details on the data set and method of deriving vertical NO₂ profiles/columns can be found in Schaub et al. (2006). For the present study, the ground-based in situ data set is restricted to all clear sky days as indicated by the sunshine and high fog parameters from the Alpine Weather Statistics (MeteoSwiss, 1985) and the columns reach down to an assumed mean Swiss Plateau height of 450 m asl. The normalised seasonal variation of the ground-based data again indicates the highest NO₂ columns over the Swiss Plateau to occur during the winter season, which is better reflected by the GOME columns and expected due to the higher NOₓ lifetime in winter. Moreover, the seasonal variation of space-borne NO₂ VTCs over industrialised regions with a distinct wintertime maximum has also been described by Petritoli et al. (2004), Richter et al. (2005), van der A et al. (2006) and Uno et al. (2006). Although in Fig. 5.8a SCIAMACHY and GOME have been sampled differently in space and time and, thus, a perfect agreement is not expected, it seems likely that SCIAMACHY values over the Swiss Plateau are underestimated in this season. A possible reason for this is discussed in the following section.

![Figure 5.9. A simplified 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.]

5.4.3 Inaccurate pixel surface pressure as a possible reason for too low wintertime SCIAMACHY NO₂ VTC retrievals over the Swiss Plateau

**GOME and SCIAMACHY pixel surface pressures**

Richter and Burrows (2002) and Boersma et al. (2004) discussed errors of GOME NO₂ VTC retrievals which in principle also apply to SCIAMACHY retrievals. 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 of SCIAMACHY NO$_2$ VTCs over the Swiss Plateau: 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. Note that for large parts of the world, the mean surface pressures taken from global models are accurate enough. Over the Alpine topography, however, mean surface pressures taken from a coarsely resolved model could be problematic, particularly for higher resolved satellite pixels. Figure 5.9 illustrates the situation over the Alpine region: in a coarsely resolved model (e.g. global CTM used for the retrieval), the topography is averaged over extended grid elements, typically leading to an underestimation of the effective elevation of mountains and an overestimation of the effective ground height in the vicinity of the mountains. Due to the different horizontal extensions of GOME and SCIAMACHY pixels, it can be expected that the mean model heights calculated over the smaller SCIAMACHY pixels show a larger deviation from the averaged real surface heights than the mean model heights calculated over the extension of a GOME pixel.

Figure 5.10. Histogram distribution of the differences between pixel surface heights used in the retrieval and effective surface heights averaged over the pixels ($\Delta$surf) for all GOME (1996-2003) (a) and SCIAMACHY (2003-2005) (b) pixels with centre coordinates above ROI$_{CH}$ (Fig. 5.1).

Figure 5.11. Differences between pixel surface heights used in the retrieval and effective surface heights averaged over the respective pixels ($\Delta$surf) for all GOME (1996-2003) (a) and SCIAMACHY (2003-2005) (b) pixels located over ROI$_{CH}$ (Fig. 5.1). The $\Delta$surf value for a pixel is indicated at its corresponding centre coordinate.
For each GOME (1996-2003) and SCIAMACHY (2003-2005) pixel above ROI\textsubscript{CH} (Fig. 5.1) the original mean pixel surface pressure $p_{\text{surf}}$ derived from ECMWF/TM4 and $p_{\text{eff}}$ determined from the aLMo topography (Sect. 5.3.2) are converted to m asl based on pressure profiles derived from measurements at different altitudes in Switzerland. Figure 5.10 shows the resulting histogram distribution of $\Delta_{\text{surf}} = h_{\text{surf}} - h_{\text{eff}}$ for the GOME (Fig. 5.10a) and SCIAMACHY (Fig. 5.10b) pixels and Fig. 5.11 indicates the pixel centre locations and corresponding values of $\Delta_{\text{surf}}$. 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. 5.11).

- Lower minimum and higher maximum for $\Delta_{\text{surf}}$ are found for SCIAMACHY pixels (Figs. 5.10 and 5.11). This can be expected due to the smaller pixel size of SCIAMACHY compared to GOME (Fig. 5.9).

The above points confirm our expectation that certain parameters, such as the mean pixel surface pressure, can become increasingly inaccurate for better resolved satellite data if the spatial resolution of the forward model parameters is not improved accordingly. In the following section, the effect of an inaccurate pixel surface pressure on the resulting NO\textsubscript{2} VTC is investigated for selected SCIAMACHY columns.

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{figure5_12.png}
\caption{Possible reason for too low SCIAMACHY NO\textsubscript{2} VTCs over the polluted Swiss Plateau: retrieval errors due to inaccurate pixel surface heights in regions with a marked topography.}
\end{figure}
5 SCIAMACHY nitrogen dioxide over the Alpine region

Table 5.2. Date, orbit/pixel number, cloud fraction, mean pixel specific ECMWF/TM4 surface pressure $\rho_{\text{surf}}$, mean pixel specific aLMo surface pressure $\rho_{\text{eff}}$, AMF$_{\text{trop}}$ based on $\rho_{\text{surf}}$ and AMF$_{\text{trop}}$ based on $\rho_{\text{eff}}$ for the selected SCIAMACHY pixels. Further denoted are the resulting relative changes in both the AMFs$_{\text{trop}}$ and the NO$_2$ VTCs.

<table>
<thead>
<tr>
<th>Date</th>
<th>Orbit, pixel number</th>
<th>Cloud fraction</th>
<th>$\rho_{\text{surf}}$ from ECMWF/TM4 [hPa]</th>
<th>$\rho_{\text{eff}}$ from aLMo [hPa]</th>
<th>AMF$<em>{\text{trop}}$ calc. for $\rho</em>{\text{surf}}$</th>
<th>AMF$<em>{\text{trop}}$ calc. for $\rho</em>{\text{eff}}$</th>
<th>relative change AMF$_{\text{trop}}$ [%]</th>
<th>relative change NO$_2$ VTC [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Profile A (Fig. 5.3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>10 Mar 04</td>
<td>7, 1117</td>
<td>0.024</td>
<td>912.22</td>
<td>964.22</td>
<td>1.023</td>
<td>0.776</td>
<td>-24.1</td>
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<tr>
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<td>6, 574</td>
<td>0.011</td>
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<td>0.033</td>
<td>911.71</td>
<td>963.08</td>
<td>1.359</td>
<td>0.982</td>
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<td>1.315</td>
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<tr>
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<td>0.074</td>
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<td>912.22</td>
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Effect of inaccurate pixel surface pressure on SCIAMACHY retrievals

Figure 5.12 illustrates the situation over the Swiss Plateau where $h_{\text{surf}} > h_{\text{eff}}$ (for the Alps the situation is reversed with $h_{\text{surf}} < h_{\text{eff}}$). Following equation (5.1) (Sect. 5.2.1) and the formulation for the AMF$_{\text{trop}}$ given there, the following systematic errors due to inaccurate surface heights are expected:
For positive $\Delta_{\text{surf}} (h_{\text{surf}} > h_{\text{eff}})$, e.g. over the Swiss Plateau, Figs. 5.11 and 5.12) the near-ground NO$_2$ pollution is in reality located at a lower level than assumed in the data retrieval. The retrieval therefore associates the high near-ground pollution with a too high sensitivity. This leads to an overestimated AMF$_{\text{trop}}$ and, thus, to an underestimated NO$_2$ VTC.

For negative $\Delta_{\text{surf}} (h_{\text{surf}} < h_{\text{eff}})$, e.g. over the Alps, Fig. 5.11) we expect a tendency towards overestimation of the NO$_2$ VTCs.

The effect of inaccurate pixel surface pressures is investigated following the method described in Sect. 5.3.2. Clear sky SCIAMACHY NO$_2$ VTCs are selected over the north-eastern Swiss Plateau with a smooth topography (Fig. 5.2). Table 5.2 presents an overview over the SCIAMACHY pixel parameters and the (re-)processed AMF$_{\text{trop}}$. The comparison of the surface pressures $p_{\text{surf}}$ and $p_{\text{eff}}$ shows that in the region of the north-eastern Swiss Plateau the surface pressures differ by about 50 hPa, which corresponds to ~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. 5.3), 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 changes in the AMF$_{\text{trop}}$ and the NO$_2$ VTCs due to changes in the pixel surface pressure are strongly dependent on the NO$_2$ profile shape. Given the distinctly different shapes A and B, the 13-38% NO$_2$ VTC error range is a reasonable first estimate of the effect of errors in the pixel surface pressure over a non-trivial topography.

The present sensitivity study is a first-order estimate of the effect of changing pixel surface pressure for a limited subset of SCIAMACHY pixels and based on assumed a priori profile shapes. Depending on the NO$_x$ emissions taking place at the pixel location, photochemical activity and prevailing meteorological conditions, real NO$_2$ profile shapes can differ from the shapes A and B used here. Nevertheless, we suggest that inaccurate pixel surface pressures used for the NO$_2$ retrieval over regions with a marked topography can have a considerable effect on the resulting columns. For retrievals in the UV-visible spectral range with a significant decrease of the sensitivity towards the earth’s surface, this effect is of major importance when the NO$_2$ resides close to the ground. This situation is most pronounced in winter. Thus, the tendency for underestimated wintertime SCIAMACHY NO$_2$ VTCs over the Swiss Plateau described earlier could at least partly be explained by inaccuracies in the mean pixel surface pressure.

For GOME NO$_2$ VTCs over heavily polluted regions (NO$_2$ VTC > $1.0 \times 10^{15}$ molec cm$^{-2}$), Boersma et al. (2004) estimated mean AMF$_{\text{trop}}$ uncertainties of 15%, 2%, 15% and 9% due to inaccuracies in the cloud fraction, the cloud top height, the surface albedo and the a priori NO$_2$ profile shape, respectively. Even though GOME uncertainties can not directly be transferred to SCIAMACHY retrievals, the orders of magnitude let us assume that the effect of an inaccurate pixel surface pressure on the AMF$_{\text{trop}}$ of 12-27% is of equal importance as other types of errors for tropospheric retrievals over regions with a marked topography such as Switzerland.
5.5 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 derived. Summertime NO$_x$ lifetimes have been found to be 3.2 – 3.4 hours. These values agree well with lifetime estimates from literature. The plausibility of the NO$_x$ lifetimes estimated for winter is difficult to assess because of the lack of such data in literature. The values found from two studies and calculated here based on OH concentration data are not necessarily representative for the study region. 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 improvement of better resolved space-borne data with regard to monitoring the NO$_2$ pollution distribution on a regional scale. However, the quantitative comparison of seasonally averaged SCIAMACHY and GOME NO$_2$ VTCs provides evidence for SCIAMACHY NO$_2$ VTCs tending to systematically underestimate the tropospheric NO$_2$ columns over the Swiss Plateau during winter. This is further supported by the seasonal variation of NO$_2$ measured at ground-based in situ sites that is better reflected in the GOME columns.

A possible explanation for underestimated SCIAMACHY NO$_2$ VTCs over the Swiss Plateau is the use of inaccurate satellite pixel surface pressures derived from coarsely resolved global models in the retrieval. It has been found that the marked topography in the Alpine region can lead to deviations of several hundred meters between the assumed and the real mean surface height over a pixel, particularly pronounced for the smaller sized SCIAMACHY pixels. The resulting effect has been estimated based on selected clear sky SCIAMACHY NO$_2$ VTCs over the Swiss Plateau and two fixed a priori NO$_2$ profile shapes. An effect in the 10-40% range has been found for different profile shapes. Although real NO$_2$ profile shapes can differ from the fixed profiles used for the sensitivity study, the result suggests that inaccurate pixel surface pressures have a considerable effect on the NO$_2$ column retrieval.

In general, for the air pollution monitoring on a regional scale, higher resolved space-borne data are strongly required and very useful. SCIAMACHY NO$_2$ VTCs have shown to be sensitive to the near-ground NO$_2$ pollution in Switzerland. However, we further conclude from this study that in order to fully exploit the potential of such data, the retrieval should be done on a scale that better fits the satellite pixel size. This is of increasing importance with regard to the decreasing pixel sizes from 320 × 40 km$^2$ (GOME) to 60 × 30 km$^2$ (SCIAMACHY) to 13 × 24 km$^2$ (OMI).

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References


6 Conclusions and outlook

Anthropogenic air pollution, mainly caused by the increasing exploitation of coal, has already been documented in the 19th century. In the 20th century, the growing use of high temperature combustion led to increasing emissions of nitrogen oxides, which are important precursors of photosmog. In order to evaluate air pollution and respective reduction measures, air pollution monitoring has been introduced in many countries around the globe. In Switzerland, the Swiss National Air Pollution Monitoring Network (NABEL) operates ground-based in situ measurement sites providing concentration data of numerous atmospheric species – among them nitrogen oxides – for more than 25 years. Monitoring from space offers interesting complementary means to study air pollution. While space-borne monitoring of stratospheric NO₂ already began in 1979, tropospheric NO₂ pollution monitoring from space is more complex and only started a decade ago with NO₂ retrievals from GOME measurements. Satellite NO₂ vertical tropospheric column densities (VTCs) have been used successfully in a vast number of studies. As an example, Richter et al. (2005) and van der A et al. (2006) analysed GOME and SCIAMACHY time series to show the strongly increasing emissions of nitrogen oxides over China. However, a similar analysis of trends over Switzerland is more difficult because emission changes have been rather moderate since the launch of GOME. Thus, the relatively large uncertainties in space-borne NO₂ VTCs become more important. An additional complication for data analysis over Switzerland is the small sample size which is due to the limited usability of NO₂ VTCs under cloudy conditions and the limited spatial and temporal coverage of the satellite observations. And finally, the complex topography in the Alpine region further complicates the use of space-borne data.

In this thesis, NO₂ VTCs retrieved from GOME and SCIAMACHY measurements by the University of Bremen and the Royal Netherlands Meteorological Institute (KNMI) were investigated with regard to their use for air pollution monitoring and modelling in Switzerland. The following main results and conclusions were obtained.

1. A major problem of space-borne tropospheric NO₂ retrievals is the presence of clouds, because they hinder to a large extent the penetration of solar UV and visible radiation into the lower troposphere. The satellite instrument is not able to “see” the pollution in the planetary boundary layer under such conditions. A case study was carried out for a frontal transport episode on 17 February 2001 that led to very high NO₂ columns detected from GOME above a dense cloud cover. Combining the above-cloud NO₂ column with a trajectory transport model allowed to estimate the transport of the polluted air masses to the Alpine region. It was estimated that at least 50% of the measured NO₂ concentrations at the ground-based measurement sites originate from transboundary (cross-border) transport with a cold front. To answer the question about the usability of space-borne NO₂ columns associated with clouds, it is noteworthy that the GOME above-cloud NO₂ columns have been reprocessed at the University of Bremen using additional knowledge about the cloud top height and an assumed NO₂ layer located above the clouds. Thus, due to the plausible results of the case study, one can conclude that the original column values...
were wrong. A general conclusion on the usability of space-borne retrievals under cloudy conditions is still difficult to give, as most studies focus on clear sky satellite data. One reason for the usability of the 17 February 2001 case was surely its relatively large NO₂ abundance at higher altitude (within and above the cloud cover). This allowed to accurately estimate the additional sub-cloud NO₂ by combining the above cloud NO₂ column with air masses originating near the ground, taking up emissions and arriving at the pixel location above and below the cloud cover. For most of the cloudy cases, however, the above cloud NO₂ column is small and the method would lead to larger errors. In general, the quality of cloudy NO₂ VTCs calculated for the whole troposphere (including the sub-cloud part) is depending on the quality of the models used in the data retrieval. The models largely determine the sub-cloud part of the column not seen by the space-borne spectrometer.

2. A detailed comparison/validation of clear sky and cloudy NO₂ tropospheric columns retrieved from GOME measurements with coincident ground-based tropospheric NO₂ columns was carried out in a second study. The ground-based NO₂ profiles were determined from in situ measurements operated at different altitudes in the Alps. The inclusion of averaging kernel (AK) information as suggested by Eskes and Boersma (2003) allowed separating the influence of the difference in shape between the a priori and ground-based NO₂ profiles from other contributions to the total difference between the column data sets.

A good agreement was found for anticyclonic clear sky conditions (pixel cloud fraction ≤ 0.1) with a mean relative difference (with respect to the ground-based columns) of -7(±40)% and GOME retrievals on average slightly underestimating the ground-based data. This result agrees with other validation studies that found an underestimation of clear sky GOME data with respect to independently derived NO₂ columns of -3%, -8% and -14% published by Heland et al. (2002), Martin et al. (2004) and Petritoli et al. (2004), respectively. For most of the investigated clear sky GOME retrievals, the shapes of the a priori and the ground-based NO₂ profiles were similar. Thus, assuming the ground-based profiles to describe the state in the troposphere accurately, uncertain CTM (TM4) a priori NO₂ profile shapes are not a major issue for clear sky GOME retrievals. A minor tendency of the a priori profiles to peak more towards the surface than the observed profiles could be due to the coarsely resolved topography in the global TM4 which, for instance, can not resolve thermal upslope transport in mountainous terrain. The good agreement between GOME and the ground-based observations under clear sky conditions was, however, partly due to compensating errors. This shows that detailed validation studies require the inclusion of AK information because the error related to the application of a given a priori profile can be eliminated in this way.

A poorer agreement was found for the cloudy cases (pixel cloud fraction ≥ 0.75) with a mean relative difference between the independent NO₂ column data sets of 60 (±118)% and GOME retrievals on average overestimating the ground-based columns. A clearly improved agreement was obtained when the ground-based profiles were first multiplied by the AK. This suggests that a significant part of the difference is due to uncertainties in the a priori NO₂ profile shapes. The results further indicated that the TM4 profile shapes tend towards an overestimation of the near-ground NO₂ (or an underestimation of the NO₂ at higher layers in the troposphere) under cloudy situations. From this, it is suggested that vertical transport phenomena often associated with dense cloud covers (e.g. frontal lifting) are not reproduced accurately enough in the coarsely resolved global CTM.
6 Conclusions and outlook

The good agreement between GOME and ground-based observations for clear sky conditions encourages the use of space-borne trace gas columns for air pollution modelling and monitoring also on a regional scale. However, the comparison study was carried out for the large (320 × 40 km²) GOME pixels and the findings can not readily be transferred to SCIAMACHY. Due to the increased resolution of SCIAMACHY (60 × 30 km²) it is presumed that retrieval uncertainties associated with a priori NO₂ profiles could play a larger role, in particular as the latter are usually obtained from coarsely resolved global CTMs.

3. In a third study, the effect of an increasing resolution of space-borne NO₂ columns retrieved with a priori knowledge from coarsely resolved CTMs was investigated using SCIAMACHY and GOME observations. In a first analysis SCIAMACHY NO₂ column retrievals were combined with a temporally and spatially highly resolved Swiss NOₓ emission inventory to estimate seasonal mean NOₓ lifetimes in Switzerland. These lifetimes were compared to other estimates given in literature. In a second analysis seasonally averaged NO₂ columns from SCIAMACHY and GOME were compared to each other. Both investigations provided evidence for a systematic underestimation of wintertime SCIAMACHY NO₂ VTCs over the Swiss Plateau.

An explanation not yet discussed in literature is suggested to be the use of inaccurate pixel surface heights derived from coarsely resolved global models in the retrieval. In such models, the pronounced Alpine topography is highly smoothed and deviations of several hundred meters between the assumed and the real surface height averaged over the extension of a pixel was found. As expected, these deviations are much larger for SCIAMACHY than for GOME pixels.

The effect of erroneous surface height assumptions was estimated based on selected clear sky SCIAMACHY NO₂ column retrievals over the Swiss Plateau and two fixed CTM a priori NO₂ profile shapes. For a profile with the bulk of NO₂ residing near the earth’s surface, the mean relative changes in the tropospheric air mass factor and the resulting NO₂ column were approximately -30% and +40%, respectively. This suggests that over regions with a marked topography, uncertainties in the pixel specific mean surface height can be among the most important error sources. 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 NO₂ resides close to the ground, which occurs most prominently during the winter season.

The most important conclusion summarising the findings from the three different studies is the requirement for retrievals on a regional scale. The models used in the data retrieval should improve in resolution simultaneously to the increasing resolution of the space-borne trace gas products. This would allow to obtain more accurate a priori information – e.g. on a priori NO₂ profiles or pixel specific surface pressure. This is crucial for the quantitative use of single data pixels.

In order to prove both the state-of-the-art retrievals and the expected improvement of regional retrieval products, the validation should be intensified. In their conclusions of published papers, authors working in the field of tropospheric NO₂ retrievals repeatedly mentioned the “lack of direct validation of tropospheric NO₂ column products” (Martin et al., 2003) and the need for “a thorough validation campaign of tropospheric NO₂ profiles and columns over polluted regions” (Boersma et al., 2004). This remains an issue. Aircraft- and balloon-borne NO₂ profile measurements and subsequent comparison with space-borne NO₂ retrievals is highly encouraged, particularly over the complex Alpine region.
A conclusion and outlook concerning the suitability of space-borne NO\textsubscript{2} columns for air pollution monitoring can only be given with regard to the specific requirements. For example, NO\textsubscript{2} pollution maps have widely been used to show – on a qualitative base – the global and regional distribution of nitrogen oxide pollution. Such maps can be an important tool for policy makers and the general public. In the Netherlands, for instance, the publication of averaged space-borne NO\textsubscript{2} maps highlighting the outstanding pollution hot spot above the Benelux countries contributed to an increased public awareness and political priority given to the air quality issue (Boersma, personal communication.). Also for determining perennial pollution trends based on monthly or seasonal mean columns over regions with a distinct change in emissions, the present-day tropospheric NO\textsubscript{2} products have been used successfully (Richter et al., 2005; van der A et al., 2006).

![NO\textsubscript{2} Vertical Tropospheric Columns Retrieved from OMI Measurements Taken on 27 October 2005](http://www.temis.nl)

For the detailed investigation of local or regional pollution episodes with space-borne data alone or for air pollution trend studies combining data sets of different instruments, an improved quality of space-borne NO\textsubscript{2} retrievals is highly desirable. Martin et al. (2002) concluded in their study that “future satellite instruments with smaller fields of view such as SCIAMACHY and OMI should further improve the potential to retrieve tropospheric NO\textsubscript{2} columns from solar backscatter measurements”. It is indisputable that an increased resolution is an important step towards higher quality maps of the air pollution distribution. Retrievals in the UV-visible spectral range are strongly affected by clouds and a higher spatial resolution enhances the chance for finding cloud free pixels. Furthermore, additional small scale pollution features become visible. Especially for a small country such as Switzerland, the applicability of NO\textsubscript{2} data retrieved from GOME (with a 320 × 40 km\textsuperscript{2} pixel resolution) and SCIAMACHY (with a 60 × 30 km\textsuperscript{2} pixel resolution) remains
limited (Figs. 2.5 and 5.1). An improved detection of smaller scale pollution features can be expected from the OMI instrument (13 × 24 km² pixel resolution; Levelt et al., 2006) aboard the NASA’s EOS-AURA satellite launched in 2004. Figure 6.1 shows a single day NO₂ column retrieval of OMI measurements taken above Switzerland and surroundings. Obviously, pollution features induced by Greater Zurich, Basel and Geneva as well as the Swiss Plateau and the Alpine chain become visible. In contrast, for SCIAMACHY retrievals, such features show up in average maps only (Fig. 5.1). Besides OMI, the Tropospheric Emission Spectrometer (TES) instrument aboard the EOS-AURA satellite enables the retrieval of NO₂ profiles. A further mission scheduled for launch on 7 October 2006 is the polar-orbiting Meteorological Operational Satellite Programme (MetOp). MetOp carries the GOME-2 spectrometer (Callies et al., 2000) that will provide measurements for the retrieval of NO₂. However, with a pixel size of 40 × 40 km² or 80 × 40 km², depending on the swath widths of 960 (global coverage within 3 days) or 1920 km (global coverage within one day), respectively, the GOME-2 data will not reach the spatial resolution of OMI retrievals.

A further and major issue is the improvement of the temporal resolution of space-borne data. Again, this may play a minor role for qualitative seasonal or annual mean pollution maps over the continental or global scale. On such scales, a sufficient number of satellite pixels exist, even when rejecting erroneous cloudy columns. For the focus on regional or local air pollution, however, the temporal resolution is still far away from being ideal. For a fixed point on the earth’s surface, the NO₂ retrievals studied in the present work provide data every 3 (GOME) and every 6 (SCIAMACHY) days. An improvement will be the OMI NO₂ retrievals providing data every day. Nevertheless, for short-lived substances such as nitrogen oxides, this temporal resolution still does not allow to trace pollution clouds or to investigate daily variations. An improvement could be expected from the TRAQ (Tropospheric Composition and Air Quality) mission proposed to ESA by a collaboration of Dutch and French institutions. A non-sun synchronous low earth orbiting satellite in combination with a swath width of 2000-2600 km enables the detection of air pollution at mid-latitude up to 5 times a day with 90 minute intervals. GeoTROPE (Geostationary Tropospheric Explorer; Burrows et al., 2004), another mission proposed to ESA by a collaboration of German, French and UK institutions, suggests a geostationary satellite orbit. Due to the geosynchronous orbit in a distance from the earth of roughly 36000 km, the field of view of the satellite remains stationary with regard to the detected region. Thus, an even better temporal resolution of 30-60 minutes is proposed (with the disadvantage of not providing global coverage).
6 Conclusions and outlook

References


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