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NO$_2$ Profile Retrieval using airborne multi axis UV-visible skylight absorption measurements over central Europe

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Abstract

A recent development in ground-based remote sensing of atmospheric constituents by UV/visible absorption measurements of scattered light is the simultaneous use of several directions with small elevation angles in addition to the traditional zenith-sky pointing. The different light paths through the atmosphere enable the vertical distribution of some atmospheric absorbers such as NO$_2$, BrO or O$_3$ to be retrieved.

In this study, the amount of profile information that can be retrieved from such measurements on aircraft is investigated for the trace gas NO$_2$. A Sensitivity study on synthetic data is performed for a combination of four lines of sight (LOS) (0° (nadir), 88°, 92°, and 180° (zenith)) and three wavelength regions [center wavelengths: 362.5 nm, 437.5 nm, and 485.0 nm]. This investigation demonstrates the potential of this LOS/wavelengths setup to retrieve a significant amount of profile information from **a**irborne **m**ulti**ax**is **d**ifferential **o**ptical **a**bsorption **s**pectrometer (AMAXDOAS) measurements with a vertical resolution of 3.0 to 4.5 km in the lower troposphere and 2.0 to 3.5 km near flight altitude. Above 13 km the profile information content of AMAXDOAS measurements is sparse.

Further, retrieved profiles with a significant amount (up to 3.2 ppbv) of NO$_2$ in the boundary layer over the Po-valley (Italy) are presented. Airborne multiaxis measurements are thus a promising tool for atmospheric studies in the troposphere.

1. Introduction

In the troposphere Nitrogen Dioxide (NO$_2$) is an important trace gas since its photochemistry is involved in the production of tropospheric Ozone. In densely populated areas the most important source of NO$_2$ are anthropogenic emissions. Thus the monitoring of NO$_2$ concentrations in these areas is necessary because Ozone and NO$_2$ itself are harmful species effecting both human health and the growth of vegetation. Since all NO$_2$ emissions affect the planetary boundary layer directly the monitoring of the NO_2 levels in the boundary layer are getting more and more important. As can be seen below we present a novel tool consisting of a remote sensing instrument and a profile retrieval method to accomplish this task.

To understand the NOx chemistry in more detail an acquisition of the vertical distribution of trace gases is necessary. Thus an instrument being able to resolve the vertical profile information of trace gases is important. The use of airborne UV/visible spectrometers to study the tropospheric (McElroy et al., 1999; Melamed et al., 2003) and stratospheric (Pfeilsticker and Platt, 1994; Petritoli et al., 2002) composition is a well known technique. In recent years different groups (Petritoli et al., 2002; Melamed et al., 2003) presented interesting results of limited profile information using the DOAS method and different LOS observed from an airborne platform. The latest study presents a profile retrieval for Ozone using airborne multiaxis UV/visible measurements (Liu et al., 2005).

Here, we have used different lines of sight (LOS) in combination with different wavelength regions (4-3 setup) to maximize the content of profile information. The careful selection of the LOS and wavelength regions enables the retrieval of a significant amount of profile information from the AMAXDOAS measurements. Compared to the profile retrieval method using only a four LOS setup as presented in Bruns (2004) the 4-3 setup improves the retrieved profiles significantly. This new setup demonstrates even significant improvements compared to some LOS setups using ten LOS but only one wavelength region as shown in Bruns et al. (2004). A different method to derive vertical distributions for trace gases from AMAXDOAS data as described in this work and Bruns et al. (2004); Bruns (2004) was used by Wang et al. (2004). Wang et al. (2004) are using only the nadir and zenith LOS at three different wavelength regions. Their method enables the determination of boundary layer NO_2 only with the use of significant a priori information regarding the height of the planetary boundary layer and the profile shape. The profile retrieval method described in this work does not rely on any a priori information regarding the troposphere (i.e. boundary layer height and/or profile shape) since the a priori profile shows no NO_2 in the troposphere. The only a priori information the presented profile retrieval method uses is regarding the stratospheric NO_2 profile.

The **a**irborne **m**ulti**ax**is **d**ifferential **o**ptical **a**bsorption **s**pectrometer (AMAXDOAS) is a remote sensing instrument built to detect a number of different trace gases such as O_3, NO_2, BrO, OClO, and SO_2. AMAXDOAS was used to validate (Heue et al., 2004) measurements of the **sc**anning **i**maging **a**bsorption spectro**m**eter for **a**tmospheric **ch**artograph**y** (SCIAMACHY) (Bovensmann et al., 1999). The former has been flown in two major camgaigns (**SCIA**MACHY **val**idation **u**tilization **e**xperiment (SCIA-VALUE)) in September 2002 and February/March 2003 (Fix et al., 2004).

2. Experimental

2.1. Instrument

The AMAXDOAS instrument was designed to detect atmospheric abundances of different trace gases like Ozone, NO_2, BrO, OClO, SO_2, and Formaldehyde. It consists of two grating spectrometers one operating in the UV wavelength region (300 to 440 nm) and the other operating in the visible wavelength region (400 to 550 nm). The scattered skylight is collected by several telescopes (one per spectrometer and LOS) and directed into the spectrometers using a quartzfiber bundle. The spectral information is recorded by two CCD-detectors and passed on to two computers for data storage. A more detailed description of the AMAXDOAS experimental setup can be found in Bruns (2004). The AMAXDOAS instrument is simultaneously measuring in four different LOS (0° (nadir), 88°, 92°, and 180° (zenith)). The different measurement geometries resulting from this technique are described in Bruns et al. (2004); Bruns (2004). The novelty of the profile retrieval method described in this investigation is the combination of four LOS with three different wavelength regions (362.5, 437.5, and 485 nm) resulting in twelve virtual LOS. The additional information from the different wavelength regions improves the vertical resolution of the retrieved profiles significantly as can be seen in the sensitivity study below.

The wellknown differential optical absorption spectroscopy (DOAS) method was used to analyze the spectral information recorded by the AMAXDOAS instrument (Solomon et al., 1987; Platt, 1994).

2.2. Measurements

The measurements were gathered during two major campaigns (SCIA-VALUE) in September 2002 and February/March 2003 (Fix et al., 2004) in the context of validation of the SCIAMACHY instrument onboard ESA's ENVISAT. The flight routes for both campaigns have been chosen to cover latitudes from the arctic to the tropics as well as a significant longitudinal cross section.

In this study measurements from the flight on 19 February 2003 have been analyzed to retrieve profile information for the trace gas NO_2. This flight started in Basel, Switzerland, and headed for Tozeur, Tunesia, crossing the Alps and Italy. Figure 1 shows the flight track and the meteorological situation for this flight. The MODIS satellite image acquired on the same day at 10:26 UTC shows no clouds for the first part of the flight. Over the Alps the cloud situation is hard to evaluate from Fig. 1 because of the snow covered mountains. The observations made by the operator onboard the aircraft stated a cloud free situation over the Alps and haze over the Po valley.

3. The profile retrieval

3.1. Method

The profile retrieval method used in this work is the same as presented in Bruns et al. (2004); Bruns (2004) giving a detailed description. It is based on the Optimal Estimation Method described by Rodgers (2000). A set of measurements $\boldsymbol{y}$ can be related to a vertical profile $\boldsymbol{x}$ by a forward model F:

$$\boldsymbol{y} = F(\boldsymbol{x}, \boldsymbol{b}) + \boldsymbol{\epsilon} \tag{1}$$

where $\boldsymbol{b}$ is the vector of the forward model parameters and ϵ is the sum of the measurement error and the model error. In our case, $\boldsymbol{y}$ is a vector of slant columns as a function of LOS and wavelength, and $\boldsymbol{x}$ is the vertical profile of the trace gas of interest. The profile $\boldsymbol{x}$ – a continuous function in the real atmosphere – has to be sampled discretely by the retrieval algorithm and is therefore presented as a vector. Equation (1) can be rewritten in a linearized form:

$$\Delta\boldsymbol{y} = \mathbf{K}\Delta\boldsymbol{x} \tag{2}$$

where

$$\mathbf{K} = \frac{d\boldsymbol{y}}{d\boldsymbol{x}} \tag{3}$$

The rows of the $\mathbf{K}$ matrix represent the weighting functions, and each row corresponds to a different measurement taken at a specific LOS and a specific wavelength region. The weighting functions characterize the sensitivity of the measured slant columns $\boldsymbol{y}$ depending on the variation of the vertical profile $\boldsymbol{x}$. The forward model used in this study to calculate the weighting functions is the radiative transfer model SCIATRAN (Rozanov et al., 2001).

SCIATRAN calculates the weighting functions by solving the linearized radiative transfer equation. For a more detailed description of how SCIATRAN is actually calculating weighting functions see Rozanov et al. (1998). Weighting functions give the absolute change in intensity for a relative change of 100% of a parameter, for example NO_2 in a specific layer. However, for AMAXDOAS one is more interested in a weighting function that indicates the change in slant column depending on the variation of NO_2 at a specific altitude. Fortunately, for an optically thin atmosphere, the weighting functions as calculated by SCIATRAN can easily be converted into weighting functions regarding the change in slant columns.

$$WF_{SC}(h,\lambda) = \frac{-WF_I(h,\lambda)\cdot\Delta VMR}{I_0(\lambda)\cdot\sigma(\lambda)\cdot VMR(h)}, \tag{4}$$

where WF_{SC} are the weighting functions regarding the change in slant columns, h is the altitude, λ is the wavelength, WF_I are the weighting functions regarding the change in intensity (output of the SCIATRAN model), ΔVMR is the difference in volume mixing ratio in each layer, I_0 is the absolute intensity at the top of atmosphere, σ is the wavelength dependent absorption cross section of the considered trace gas, and VMR is the profile of the considered trace gas in volume mixing ratio. The units of WF_{SC} depend on the units of ΔVMR and the step size in the retrieval grid used in the profile retrieval run. E.g. ΔVMR is given in ppbv, and the step size of the retrieval grid is 2 km. Thus the unit of WF_{SC} is molec·cm^{-2}·ppbv^{-1}·2 km^{-1}.

In this study the Maximum a Posteriori (MAP) solution is chosen (Rodgers, 2000). This method calculates the retrieved profile as follows:

$$\hat{\boldsymbol{x}} = \left(\mathbf{K}^{\mathrm{T}}\mathbf{S}_{\epsilon}^{-1}\mathbf{K} + \mathbf{S}_a^{-1}\right)^{-1}\left(\mathbf{K}^{\mathrm{T}}\mathbf{S}_{\epsilon}^{-1}\boldsymbol{y} + \mathbf{S}_a^{-1}\boldsymbol{x}_a\right) \tag{5}$$

where $\mathbf{K}$ is the weighting function matrix, $\mathbf{S}_{\epsilon}$ is measurement error covariance matrix, $\mathbf{S}_a$ is the error covariance matrix of the a priori error, $\boldsymbol{y}$ is the measurement vector, and $\boldsymbol{x}_a$ is the a priori profile information.

To characterize the retrieved profile more precisely, the averaging kernel matrix $\mathbf{A}$ is introduced:

$$\mathbf{A} = \mathbf{DK}; \qquad \mathbf{D} \equiv \mathbf{S}_a\mathbf{K}^{\mathrm{T}}\left(\mathbf{K}\mathbf{S}_a\mathbf{K}^{\mathrm{T}} + \mathbf{S}_{\epsilon}\right)^{-1} \tag{6}$$

where $\mathbf{D}$ are the so-called contribution functions. The averaging kernel describes the sensitivity of each layer of the retrieved profile on the variation of the true vertical profile.

3.2. Error analysis

The total error of the retrieved profile can be separated into three components. According to Rodgers (2000) the total error of the profile retrieval is the difference between the retrieved and the true profile. According to error propagation the error covariance matrix of the total error can be written as:

$$\mathbf{S}_{\text{tot}} = \mathbf{S}_n + \mathbf{S}_m + \mathbf{S}_f \tag{7}$$

$\mathbf{S}_n$ is the smoothing error covariance matrix, $\mathbf{S}_m$ is the retrieval noise covariance matrix, and $\mathbf{S}_f$ is the forward model error covariance matrix. The last error component will not be considered in this work because the error produced by the forward model SCIATRAN is less than 2% for LOS with tangent heights up to 30 km (Rozanov et al., 2001).

The smoothing error covariance matrix $\mathbf{S}_n$ can be calculated as:

$$\mathbf{S}_n = \left(\mathbf{A} - \mathbf{I}\right)\mathbf{S}_a\left(\mathbf{A} - \mathbf{I}\right)^{\mathrm{T}} \tag{8}$$

where $\mathbf{S}_a$ is the error covariance matrix of the a priori profile. The diagonal elements of $\mathbf{S}_a$ have been determined empirically. The following values for the elements of $\mathbf{S}_a$ have been used for the retrieval grid (1 km, 4 km, 7 km, 9 km, 11 km, 13 km, ..., 39 km): 2.8, 0.4, 0.1, 0.1, 0.1, 0.1, and 0.01 above 13 km altitude. $\mathbf{S}_a$ also contains extra-diagonal elements to take into account correlations between NO_2 values at different altitude levels. The extra diagonal elements of $\mathbf{S}_a$ are calculated using a Gaussian function as follows (Barret et al., 2002):

$$S_{a_{ij}} = \sqrt{S_{a_{ii}} S_{a_{jj}} \exp(-\ln(2)((z_i - z_j)/\gamma)^2)} \tag{9}$$

where z_i and z_j are the altitudes of levels i and j. γ is the correlations length represented as half width at half maximum (HWHM). In this work γ was set to 1.5 km which translates to a correlation length of 3 km.

Rodgers (2000) refers to $\mathbf{S}_n$ as smoothing error covariance matrix, due to the fact that this covariance matrix corresponds to portions of profile space the measurements cannot see. In our case those portions are the higher altitudes in the stratosphere, and small scale variations obscured by the limited altitude resolution of the profile retrieval.

The retrieval noise covariance matrix $\mathbf{S}_m$ can be calculated as:

$$\mathbf{S}_m = \mathbf{D}\mathbf{S}_\epsilon\mathbf{D}^\mathrm{T} \tag{10}$$

where $\mathbf{S}_\epsilon$ is the covariance matrix of the measurement error and $\mathbf{D}$ is the contribution function matrix. This error component is caused by noise in the measurements propagating into the retrieval. The contribution function matrix maps the measurement error into the profile space since the dimension of the measurement error covariance matrix is different compared to the dimension of the a priori covariance matrix and Eq. (7) is used to add up all error components to result in a total retrieval error. $\mathbf{S}_\epsilon$ is a diagonal matrix with the diagonal elements being the squares of the individual measurement errors of each LOS.

4. Sensitivity study

Before discussing the results involving real AMAXDOAS data a sensitivity study dealing with the four LOS and three wavelengths setup (4-3 setup) is presented. This study is intended to demonstrate the potential of the 4-3 setup to retrieve profile information since this retrieval method using different LOS in combination with three different wavelength regions is new. The general assumptions made for this sensitivity study are:

- flight altitude 10 km
- surface albedo of 0.1
- solar zenith angle (SZA) is 51.6°

- no clouds
- trace gas NO_2
- retrieval grid: 1, 4, 7, 9, 11, . . . , 39 km
- a priori error of 4 ppbv at 1 and 4 km, 1 ppbv otherwise
- measurement error of 10^{15} molec/cm^2
- urban aerosol profile (see Table 1 and Fig. 3)

The 4-3 setup proved to be the optimum of LOS setups for the AMAXDOAS instrument. The main reason the number of different LOS was set to four is the increase of the signal-to-noise ratio. Since all LOS are recorded simultaneously on the CCD-chip fewer LOS result in more lines of the CCD-chip per LOS. The increased signal-to-noise ratio produces smaller retrieval errors. Figure 2 shows the results of a profile retrieval using the 4-3 setup. Plot (a) presents the weighting functions indicating additional profile information when taking into account three wavelength regions. For example the weighting functions for the 88° LOS indicate the largest sensitivity of the measured slant columns considering variations of the vertical profile in 9 km altitude at 362.5 nm and 437.5 nm. The increasing width of the 88° LOS weighting function at 485.0 nm demonstrates the additional profile information as a result of the wavelength dependant Rayleigh scattering. Figure 2b displays the averaging kernels. For example the 9 km averaging kernel demonstrates the sensitivity of the layer in 9 km altitude of the retrieved profile being the largest when changing the true vertical profile in 9 km altitude. This is the optimum behavior of an averaging kernel which is shown in altitudes where the measurements have sufficient profile information. The results of this sensitivity study show a similar or even better quality of the retrieved profiles compared to most setups consisting of ten LOS and only one wavelength region (350 or 500 nm) shown in Bruns et al. (2004) and Bruns (2004). For example the retrieved profiles of the 10 LOS setup at 350 nm (model 1) in Bruns et al. (2004) have a poorer quality in the lower troposphere than those of the 4-3 setup shown in this work. Other examples include the 4 LOS setup at 350 and 500 nm presented in Bruns (2004). These retrieved profiles have a much poorer quality in the lower troposphere and a poorer vertical resolution. The conclusion of the retrieved profiles from the 4-3 setup having a good quality is supported by Fig. 2c showing the total retrieval error of the retrieved profiles. A larger total retrieval error indicates a poorer quality of the retrieved profiles.

Figure 4 represents the vertical resolution of the retrieved profiles of the 4-3 setup. The FWHM of the averaging kernels is taken as a measure for vertical resolution as suggested in Rodgers (2000). In the lower troposphere a vertical resolution of 3.0 to 4.5 km is to be expected and 2.0 to 3.5 km near flight altitude.

This retrieval method is able to retrieve vertical profile information of trace gases because it involves LOS pointing close to the horizon. These LOS provide information on an enhanced light path through layers of the atmosphere between the aircraft and the point of the last scattering incident. When the LOS is pointing closer towards the horizon the light path is getting longer and the observed layer is getting thinner. Therefore these measurements are very sensitive to absorptions near flight altitude. Another physical effect that is used in this retrieval method is the λ^{-4} dependance of the Rayleigh scattering. Using this effect the amount of profile information to be retrieved from this kind of measurements is increasing significantly because measurements in the UV are only sensitive to layers close to flight altitude and measurements in the visible wavelength region are sensitive to layers close to the surface. Thus a combination of a clever chosen set of LOS and different wavelength regions provide the optimum amount of profile information to be retrieved from AMAXDOAS measurements.

5. Results and discussion

In this section the retrieved profiles from AMAXDOAS data will be discussed using meteorological and geographical data. This discussion also includes the comparison of vertical columns calculated from profiles retrieved by APROVAL and vertical columns retrieved from SCIAMACHY data. This comparison was done by Heue et al. (2004) for the same flight. The SCIAMACHY tropospheric vertical columns used in Heue et al. (2004) were calculated by the Excess-method (Richter and Burrows, 2002) where the slant columns retrieved from SCIAMACHY data over a clean air region (Pacific Ocean) at the same latitude are subtracted from the slant columns retrieved over polluted areas to yield tropospheric slant columns. Division by a tropospheric air mass factor obtains the tropospheric vertical columns.

Figure 5 presents the retrieved profiles of a part of the flight from 19 February 2003 between 8.350 UTC and 9.305 UTC (see black dots in Fig. 1). The upper panel (plot a) shows all profiles retrieved from the measurements taken during this period of time as a contour plot where the x-axis represents the time of the day in UTC and the y-axis represents the altitude in km. The color code indicates the NO_2 VMR in ppbv. The lower panel (plots b through e) shows four examples of retrieved profiles taken from interesting parts of the flight (see colored marks in plot a) where the x-axis represents the NO_2 VMR in ppbv and the y-axis again indicates the altitude in km.

Figure 5a shows tropospheric NO_2 on four occasions. The first tropospheric NO_2 plume occurs at 8.350 UTC (08:21:00 UTC). A second event appears at 8.660 UTC (08:39:36 UTC), another event shows up at 8.660 UTC (08:43:30 UTC), and the last event appears at 8.860 UTC (08:51:36 UTC). The first observation of tropospheric NO_2 is still north of the Alps (see Fig. 6a). The footprint of the first measurement (8.350 UTC) is covering part of the Rhine valley containing two major Highways – the Swiss N13 and the Austrian A14. The daily averaged volume of traffic on the Swiss Highway N13 is 23 625 (ASTRA, 2003) vehicles for February 2003 on weekdays (19 February 2003 is a Wednesday). The time of crossing the Rhine valley and the Swiss highway N13 was 08:21:00 UTC (09:21:00 local time) shortly after the morning rush hour. Figure 5b shows the plot of the measurement at 8.350 UTC. It can be seen that the tropospheric NO_2 value of 2.9 ppbv at 8.350 UTC is coinciding with crossing the Rhine valley and the Swiss highway N13 (see Fig. 6a). Pundt et al. (2005) have shown that major highways are a large source for NO_2 emissions (Pundt et al., 2005). Figure 7 shows the temperature soundings (Oolman, 2005) of five stations covering a large area including Munich (Germany), Payerne (Switzerland), Milano, Udine, and San Pietro (all Italy). The last three location do cover the Po valley quite perfectly since Milano is situated on the north western rim, Udine is situated on the north eastern rim and San Pietro on the southern rim of the Po valley only 30 km north east of Bologna. This plot indicates that large parts of Europe and especially the Po valley were subject to a stationary temperature inversion caused by the very stable high pressure system “Helga” situated over southern Scandinavia. This weather situation explains the accumulation of the enhanced NO_2 values observed in the Rhine valley due to the morning rush hour. Since the atmosphere during those weather conditions is very calm, transport will only play a minor role.

The second tropospheric NO_2 event is observed at 8.660 UTC crossing the valley hosting the major transit route for crossing the Alps – the Italian highway A22 (see Fig. 6b). Figure 5c presents the corresponding profile revealing an enhanced NO_2 value of 2.8 ppbv. Since this measurement was done over a valley as well, a large amount of NO_2 was accumulated because of the stationary temperature inversion. It has to be mentioned that the next measurement which is crossing the highway A22 directly shows a similar value of enhanced NO_2 (2.3 ppbv).

The third observation of tropospheric NO_2 is just south of the Alps near the city of Verona (Italy, population: 260 000; Wikipedia, 2005) (see Fig. 6c). It can be seen that in this incident the footprint of the measurement shown in this figure is again very close to the Italian highway A4. It was not possible to find any statistical data on traffic for highway A4. Figure 5d shows the retrieved profile for the measurement at 8.725 UTC with 3.2 ppbv of tropospheric NO_2. The prior measurement shows a similar enhanced tropospheric NO_2 value of 2.3 ppbv. Converting the profile measured at 8.725 UTC into a tropospheric NO_2 vertical column (0–2.5 km) results in a vertical column density of $2.2 \cdot 10^{16}$ molecules/cm^2. Heue et al. (2004) present tropospheric NO_2 vertical columns measured by the SCIAMACHY instrument on 19 February 2003. The results of the SCIAMACHY data analysis identified a tropospheric NO_2 vertical column of $2.8 \cdot 10^{16}$ molecules/cm^2 at the geolocation of the measured profile shown in Fig. 5d. Compared to the AMAXDOAS value it is 27% larger which is not very unusual since the footprints of the SCIAMACHY measurements (60 km×30 km) are much larger than the footprints of the AMAXDOAS measurements (6.6 km×0.1 km). The larger footprint of the SCIAMACHY measurements result in a higher degree of averaging over a large area, because the AMAXDOAS measurements show a large variability in boundary layer NO_2 values even in the highly polluted Po valley. This implies that there are much higher values of tropospheric NO_2 outside the AMAXDOAS flight track for example the city of Verona which is included in this particular SCIAMACHY footprint.

The fourth event of tropospheric NO_2 occurs over the city of Bologna at the southern rim of the Po valley. Figure 5e shows the profile actually retrieved over Bologna with an enhanced tropospheric NO_2 value of 3.0 ppbv. Figure 6d demonstrates the geographical situation of the AMAXDOAS footprint. It can be seen that large parts of the footprint are observing Bologna city area. Bologna is a city with a population of 370 000 (Wikipedia, 2005). Due to the stationary temperature inversion on this day in the Po valley the NO_2 emitted by the city could accumulate to result in the observed enhanced tropospheric NO_2 value. The measurement following the one shown in Fig. 5 d) shows an enhanced tropospheric NO_2 value of almost the same size (2.7 ppbv) since part of this footprint is also covering Bologna city area.

6. Conclusions

The AMAXDOAS instrument is the first to be able to measure tropospheric NO_2 profiles using a remote sensing technique. This investigation and Bruns et al. (2004) have shown that the combination of four lines of sight and three different wavelength regions is the ideal setup to retrieve NO_2 profile information from airborne multiaxis UV/visible scattered skylight measurements using the AMAXDOAS Profile Retrieval Algorithm (APROVAL). This has been demonstrated by a sensitivity study focussing on the combination of four lines of sight and three wavelength regions (4-3 setup). The sensitivity study has shown that a significant amount of profile information can be retrieved from those measurements using the 4-3 setup. The retrieved profiles have a vertical resolution of 3.0 to 4.5 km in the lower troposphere and 2.0 to 3.5 km near flight altitude. The profile information above 13 km altitude is sparse.

In this study the retrieved profiles of a part of the flight on 19 February 2003 have been analyzed. The flight took off in Basel (Switzerland) and headed for Tozeur (Tunesia) crossing the Po-valley in Italy which is notorious for significant anthropogenic pollution. Boundary layer values for NO_2 of up to 3.2 ppbv have been detected in this area and were compared to SCIAMACHY tropospheric NO_2 vertical columns from the same day. The comparison of both vertical columns is quite good considering the differences in the size of the footprints of the AMAXDOAS and SCIAMACHY measurements. All major events of tropospheric NO_2 shown in Fig. 5 could be assigned to anthropogenic sources. The weather situation of a stationary temperature inversion over large parts of Europe especially the Po valley is a very reasonable cause for the enhanced tropospheric NO_2 values found nearby the respective footprints of the AMAXDOAS measurements since transport is very unlikely during such a stable weather condition.

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References

ASTRA: Monatsmittel des 24-stündigen Verkehrs der automatischen Strassenverkehrszählung, Swiss Federal Roads Authority, http://www.verkehrsdaten.ch/e/home.html, 2003. 504

Barret, B., De Maziere, M., and Demoulin, P.: Retrieval and characterization of ozone profiles from solar infrared spectra at the Jungfraujoch, J. Geophys. Res., 107, doi:10.1029/2001JD001298, 2002. 500

Bovensmann, H., Burrows, J. P., Buchwitz, M., Frerick, J., Noel, S., and Rozanov, V. V.: SCIAMACHY: Mission Objectives and Measurement Modes, J. Atmos. Sci., 2, 127–150, 1999. 496

Bruns, M.: NO_2 Profile Retrieval using airborne multiaxis differential optical absorption spectrometer (AMAXDOAS) data, PhD thesis, University of Bremen, Germany, http://elib.suub.uni-bremen.de/publications/dissertations/E-Diss1124_mbruns.pdf, 2004. 495, 496, 497, 502, 503

Bruns, M., Buehler, S. A., Burrows, J. P., Heue, K.-P., Platt, U., Pundt, I., Richter, A., Rozanov, A., Wagner, T., and Wang, P.: Retrieval of Profile Information from Airborne Multi Axis UV/visible Skylight Absorption Measurements, Appl. Opt., 43, 22, 4415–4426, 2004. 495, 496, 497, 502, 506

Fix, A., Ehret, G., Flentje, H., Poberaj, G., Finkenzeller, H., Bremer, H., Bruns, M., Burrows, J. P., Kleinböhl, A., Küllmann, H., Kuttippurath, J., Richter, A., Wang, P., Heue, K.-P., Platt, U., and Wagner, T.: SCIAMACHY validation by aircraft remote measurements: Design, execution, and first results of the SCIA-VALUE mission, Atmos. Chem. Phys., 5, 1273–1289, 2005, SRef-ID: 1680-7324/acp/2005-5-1273. 496, 497

Heue, K.-P., Bruns, M., Burrows, J. P., von Friedeburg, C., Lee, W.-D., Platt, U., Pundt, I., Richter, A., Wagner, T., and Wang, P.: Validation of scientific NO_2-SCIAMACHY data using the AMAXDOAS instrument, Atmos. Chem. Phys., 5, 1039–1051, 2005, SRef-ID: 1680-7324/acp/2005-5-1039. 496, 504, 505

Hübler, G., Fahey, D. W., Ridley, B. A., Gregory, G. L., and Fehsenfeld, F. C.: Airborne measurments of total reactive odd nitrogen (NO_y), J. Geophys. Res., 97(D9), 9833–9850, 1992.

Liu, X., Sioris, C. E., Chance, K., Kurosu, T. P., Newchurch, M. J., Martin, R. V., and Palmer, P. I.: Mapping tropospheric ozone profiles from an airborne ultraviolet-visible spectrometer, Appl. Opt., 44(16), 3312–3319, 2005. 495

McElroy, C. T., McLinden, C. A., and McConnell, J. C.: Evidence for bromine monoxide in the free troposphere during the Arctic polar sunrise, Nature, 397, 338–341, 1999. 495

Melamed, M. L., Solomon, S., Daniel, J. S., Langford, A. O., Portmann, R. W., Ryerson, T. B., Nicks Jr., D. K., and McKeen, S. A.: Measuring reactive nitrogen emissions from point sources using visible spectroscopy from aircraft, J. Environ. Monit., 5, 29–34, 2003. 495

Oolman, L.: http://weather.uwyo.edu/upperair/sounding.html, ldoolman@uwyo.edu, University of Wyoming, Department of Atmospheric Science, 2005. 505, 517

Petritoli, A., Ravegnani, F., Giovanelli, G., Bortoli, D., Bonaf, U., Kostadinov, I., and Oulanovsky, A.: Off-Axis Measurements of Atmospheric Trace Gases by Use of an Airborne Ultraviolet-Visible Spectrometer, Appl. Opt., 27, 5593–5599, 2002. 495

Pfeilsticker, K. and Platt, U.: Airborne measurements during the European Arctic Stratospheric Ozone Experiment: Observation of O_3 and NO_2, Geophys. Res. Lett., 21, 1375–1378, 1994. 495

Platt, U.: Differential optical absorption spectroscopy (DOAS), in: Air Monitoring by Spectroscopic Techniques, edited by: Sigrist, M. W., Chem. Anal. Ser., John Wiley, New York, 127, 27–84, 1994. 497

Pundt, I., Mettendorf, K.-U., Laepple, T., Knab, V., Xie, P., Lösch, J., von Friedeburg, C., Platt, U., and Wagner, T.: Measurements of trace gas distributions using Long-path DOAS-Tomography during the motorway campaign BAB II: experimental setup and results for NO_2, Atmos. Environ., 39, 967–975, 2005. 504

Richter, A. and Burrows, J. P.: Retrieval of Tropospheric NO_2 from GOME Measurements, Adv. Space Res., 29(11), 1673–1683, 2002. 504

Rodgers, C. D.: Inverse Methods for atmospheric sounding: Theory and Practice, Series on Atmospheric, Oceanic and Planetary Physics, Vol. 2, World Scientific Publishing, London, 2000. 497, 499, 500, 503

Rozanov, V. V., Kurosu, T., and Burrows, J. P.: Retrieval of atmospheric constituents in the UV-visible: A new quasi-analytical approach for the calculation of weighting functions, J. Quant. Spectrosc. Radiat. Transfer, 60, 277–299, 1998. 498

Rozanov, A., Rozanov, V. V., and Burrows, J. P.: A numerical radiative transfer model for a spherical planetary atmosphere: combined differential integral approach involving the Picard iterative approximation, J. Quant. Spectrosc. Radiat. Transfer, 69, 491–512, 2001. 498, 500

Solomon, S., Schmeltekopf, A. L., and Sanders, R. W.: On the interpretation of zenith sky absorption measurements, J. Geophys. Res., 92, 8311–8319, 1987. 497

Wang, P., Richter, A., Bruns, M., Burrows, J. P., Heue, K.-P., Pundt, I., Wagner, T., and Platt, U.: Measurements of tropospheric $NO_2$with an airborne multi-axis DOAS instrument, Atmos. Chem. Phys., 5, 337–343, 2005,
SRef-ID: 1680-7324/acp/2005-5-337. 495

Wikipedia: http://en.wikipedia.org, 2005. 505, 506

Table 1. Urban aerosol setting.

layer	rel. humidity [%]	aerosol component	relative mixing ratio
0–2 km	80	water soluble	0.31399
		insoluble (dust)	0.00001
		soot	0.68600
2–10 km	70	water soluble	0.45790
		insoluble (dust)	0.00010
		soot	0.54200
10–30 km	0	sulfate	1.00000
30–60 km	0	meteoric dust	1.00000

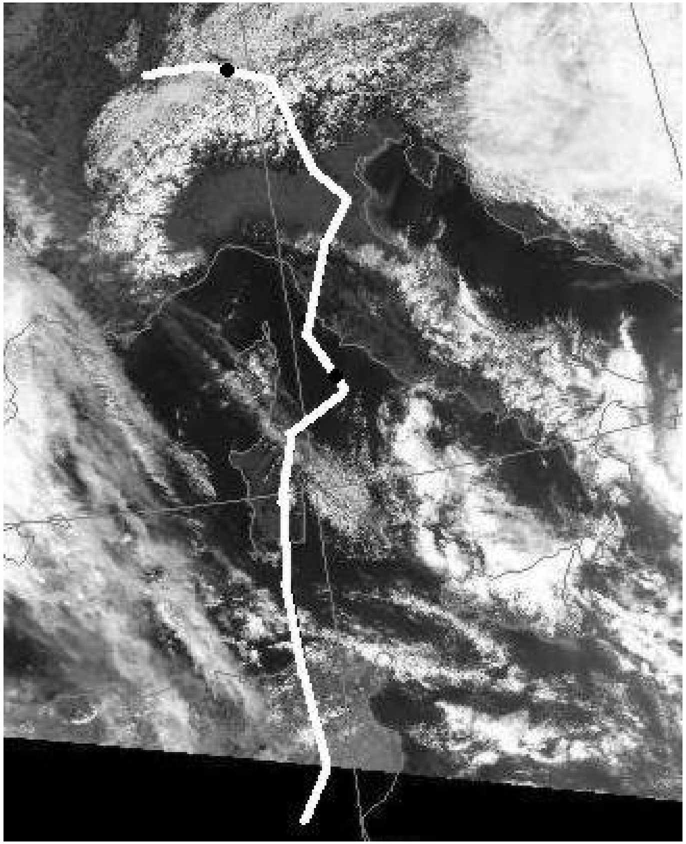

Fig. 1. Flight track of flight 030219 and meteorological situation. The satellite image is from the MODIS instrument onboard the TERRA satellite (source: http://www.sat.dundee.ac.uk). The data was acquired on 19 February 2003 at 10:26 UTC. The black dots mark the part of the flight track for which results will be presented in this work.

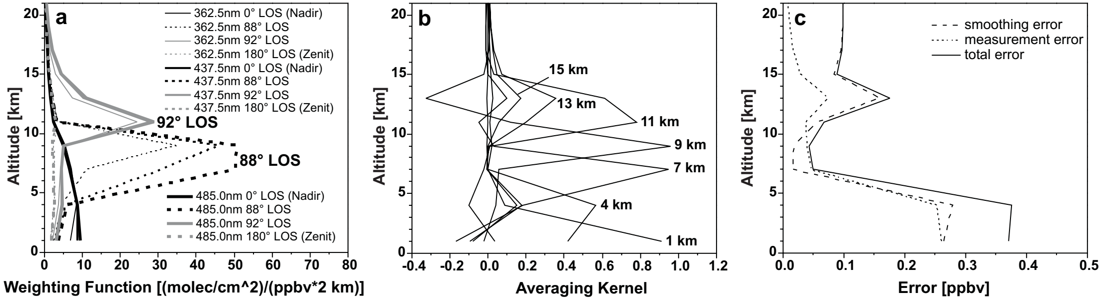

Fig. 2. This plots shows the weighting functions **(a)**, averaging kernels **(b)**, and errors **(c)** for the combination of four LOS and three wavelengths.

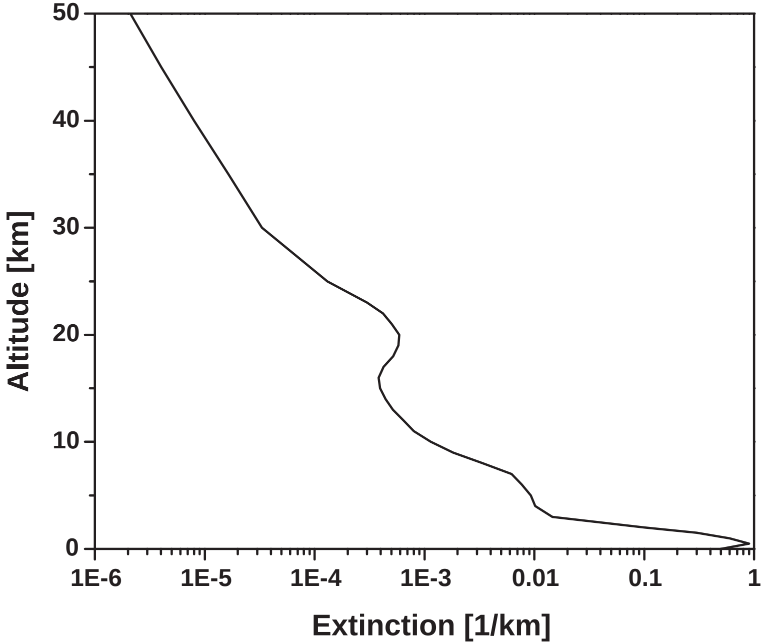

Fig. 3. This plot shows the vertical extinction profile of the urban aerosol setting.

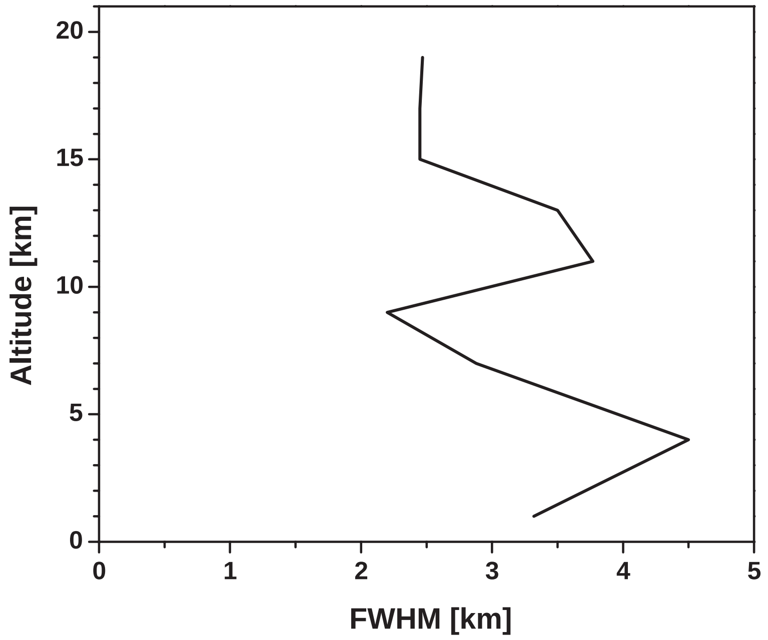

Fig. 4. This plot shows the vertical resolution (FWHM of the averaging kernels) of profiles retrieved from data using the 4-3 setup.

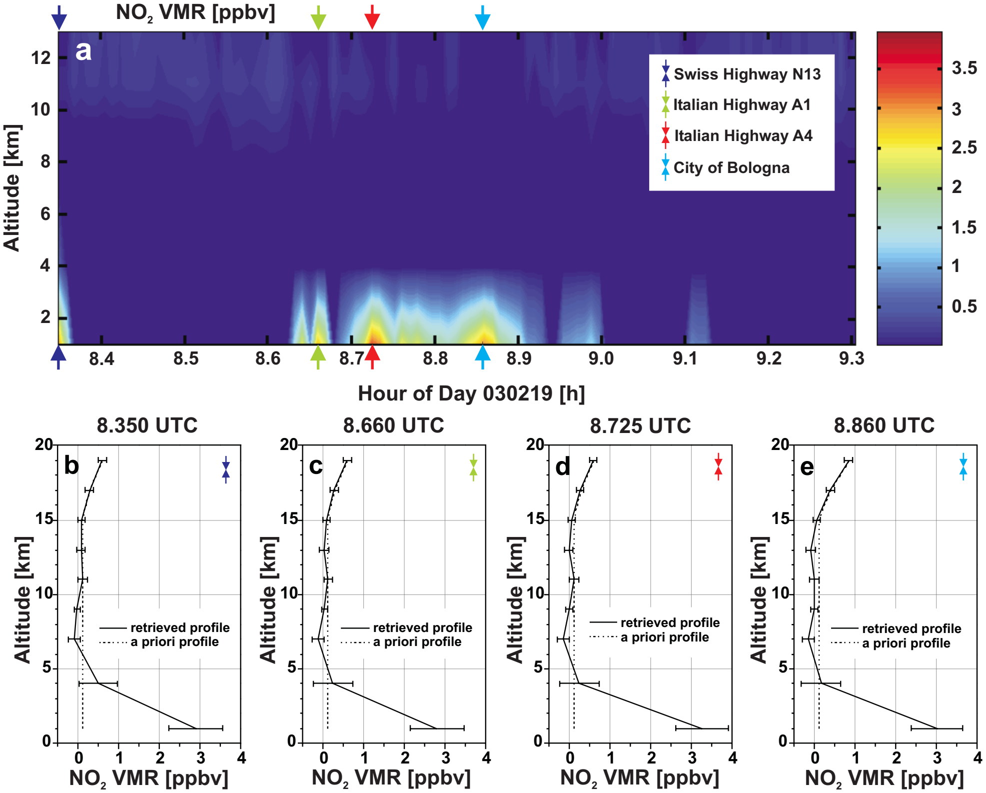

Fig. 5. Retrieved profiles of flight 030219. Plot **(a)** represents a contour of all retrieved profiles of flight 030219. Plot **(b)** shows the retrieved profile of tropospheric NO$_2$ at 8.350 UTC, plot **(c)** depicts the retrieved profile of NO$_2$ in the UTLS region at 8.350 UTC, plot **(d)** indicates the retrieved profile of tropospheric NO$_2$ at 8.725 UTC, and plot **(e)** shows the retrieved profile of NO$_2$ in the UTLS region at 8.725 UTC. The dark blue and green arrows mark the positions of the profiles shown in plots (b) and (c) and the red and light blue arrows mark the positions of the profiles represented by plots (d) and (e).

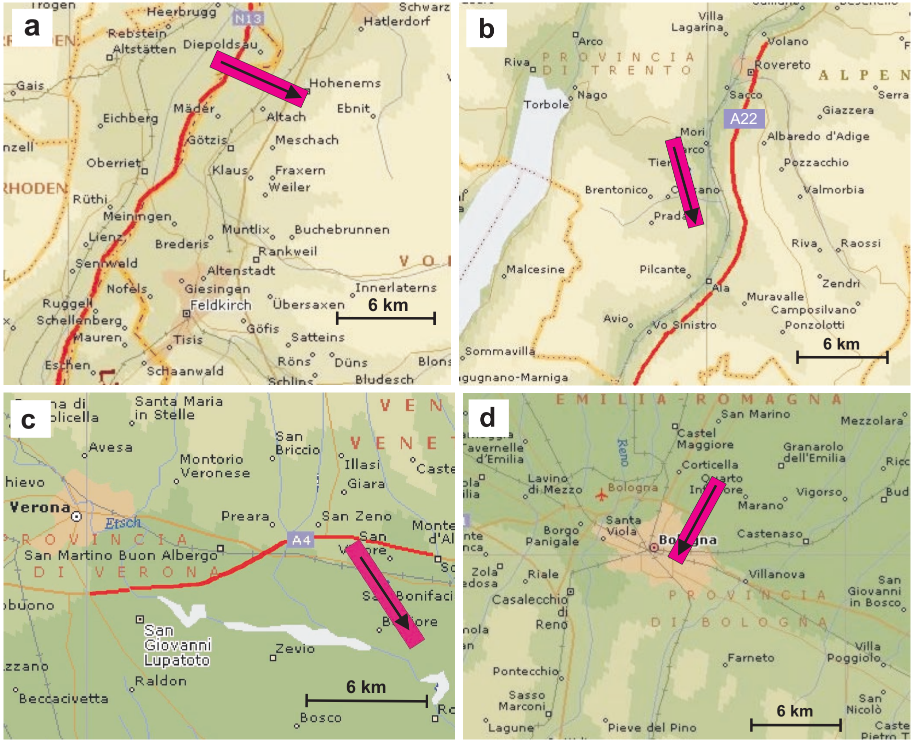

Fig. 6. Maps demonstrating the footprints of the AMAXDOAS measurements shown in Fig. 5. Map **(a)** depicts the footprint of the measurement taken at 8.350 UTC. This footprint crosses the Swiss major highway N13 (marked in red). Map **(b)** is a schematic of the footprint measured at 8.660 UTC crossing the Italian major highway A22 (marked in red) which is a major route for crossing the Alps. Map **(c)** is a schematic of the footprint measured at 8.725 UTC crossing the Italian major highway A4 (marked in red) east of Verona and Map **(d)** is a schematic of a footprint measured at 8.860 UTC crossing the city of Bologna. These maps have been created using Microsoft Encarta 2001.

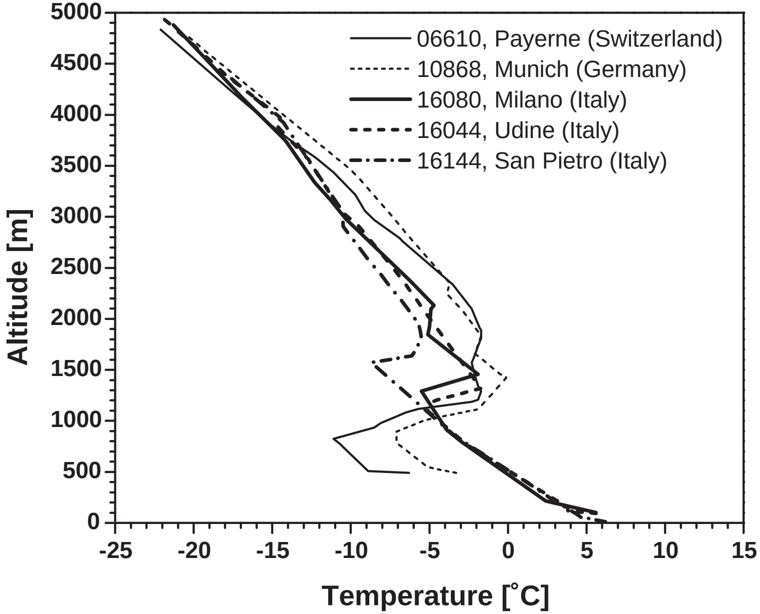

Fig. 7. This plot shows the stationary temperature inversion caused by the high pressure system "Helga" which was present over large parts of central Europe on 19 February 2003, 12:00 UTC. The data is taken from the website of the University of Wyoming, Department of atmospheric scienes (Oolman, 2005).