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Validation of SCIAMACHY tropospheric NO₂-columns with AMAXDOAS measurements

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Abstract. Tropospheric NO₂ vertical and slant columns from the new satellite instrument SCIAMACHY on ENVISAT are validated by measurements of the Airborne Multi AXis DOAS (AMAXDOAS) instrument on board the DLR Falcon. The results presented here were obtained in February 2003 on a flight over the Alps, the Po-Valley and the Mediterranean. The tropospheric vertical column measured by AMAXDOAS varied between 16.2 and 35.2*10¹⁵ molec/cm² over the Po-Valley where SCIAMACHY data resulted in 19.9 to 37*10¹⁵ molec/cm². Over less polluted areas a similarly good agreement was found. The linear correlation between the two datasets results in a slope of 0.93. The slight differences observed can be attributed to the different spatial resolution and the temporal mismatch between the measurements over the Po-Valley.

1 Introduction

The ENVISAT satellite was launched on 1 March 2002; apart from other instruments it contains the **SC**anning **I**maging **A**bsorption spectro**M**eter for **A**tmospheric **CH**artography (SCIAMACHY).

The SCIAMACHY instrument analyses the sunlight reflected from the earth or scattered in the atmosphere. This can be used to retrieve column densities of many tropospheric trace gases such as O₃, BrO, SO₂, NO₂, CO, CO₂, CH₄, H₂O and N₂O (Bovensmann et al., 1999 and Proceedings of ACVE2 May 2004 Frascati <http://envisat.esa.int/workshops/acve2/contents.html>). The results of several scientific groups can be found at the web-pages of their institutes e.g.: <http://satellite.iup.uni-heidelberg.de>, <http://www.doas-bremen.de>, <http://www.temis.nl>, <http://wdc.dlr.de>, <http://cfa-www.harvard.edu/saohome.html>. These observations help to improve our understanding of the physics and the

chemistry of the earth's atmosphere. With the global coverage of the satellite instruments it is in particular possible to study transport phenomena as well as regional variations in urban centres and in remote areas.

In the troposphere NO₂ is produced by both anthropogenic and natural sources such as bio mass burning or lightning. One major source is fossil fuel consumption. Many sources do not emit NO₂ but NO, which is rapidly oxidized to NO₂. Because of the fast interchange between the two species the sum of NO plus NO₂ is usually referred to as NO_x. In Europe the Po-Valley provides ideal opportunities for the NO₂ validation study because of its high tropospheric concentrations and the clean air in the high Alps nearby (Beirle et al., 2004).

The Airborne Multi Axis DOAS instrument was especially designed for the comparison with SCIAMACHY on ENVISAT. Like SCIAMACHY it was laid out to separate the stratospheric and the tropospheric column of several trace gases like BrO, NO₂ and O₃ (Wagner et al., 2001). As the conversion of the measured slant columns into vertical columns is known to be a major source of uncertainty (Boersma et al., 2004), the idea was to build an instrument which yields similar intermediate products – slant column densities. They can be compared without the additional uncertainties of the conversion to vertical columns.

For the comparison of the Tropospheric Slant Column Density (TSCD) it is necessary to subtract the stratospheric absorptions first. This of course adds errors to both SCIAMACHY and AMAXDOAS data. Several ways to separate the tropospheric from the stratospheric columns are introduced and compared. (see Sect. 3.3.1)

A comparison of the tropospheric vertical column is possible when the correct stratospheric correction is found and the AMF for both instruments are calculated. It is essential to use the same settings, to minimize the effect of the AMF uncertainties. The uncertainties of the conversion to VCD can be reduced by introducing independent observations for the AMF calculations.

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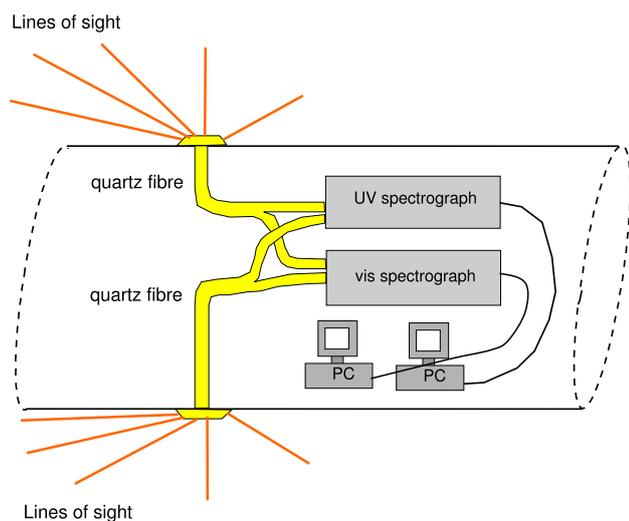


Fig. 1. Sketch of the instrumental setup. Here 2×5 lines of sight are shown. The scattered sunlight is observed using small telescopes and is led to two spectrographs via quartz fibres. Here it is analysed and the spectra are saved on a PC.

Here we compare both slant and vertical columns and we discuss the main sources of errors expected and quantify them where possible.

In the past a variety of DOAS-airborne-measurements were performed by different groups (Pfeilsticker and Platt, 1994; McElroy et al., 1999; Petritoli et al., 2002; Melamed et al., 2003) in different altitudes and regions. All these measurements had different aims varying from stratospheric chemistry studies to tropospheric point source emissions. We concentrate on tropospheric NO₂ for satellite validation.

2 Description of the instruments and data analysis

In this study the measurements of two different instruments SCIAMACHY and AMAXDOAS are compared to each other. Therefore a brief description of both instruments and the analysis is given. For SCIAMACHY the most relevant features of the instrument and the analysis of the tropospheric columns are given here. More details on the SCIAMACHY instrument and its mission objectives are described by Bovensmann et al. (1999).

The AMAXDOAS instrument observes scattered or reflected sunlight in different lines of sight above and below the aeroplane. For an aeroplane flying below the stratosphere all viewing directions will be influenced by the stratospheric absorptions, and therefore these absorptions will be detected in all viewing directions (Bruns et al., 2004). In addition light, received by the downward looking telescopes which is scattered in lower altitude or reflected at the ground contains the absorption structures of the tropospheric gases. Multiple scattering at higher altitudes might lead to tropospheric ab-

sorption in the other viewing directions as well. The concept of using different lines of sight enables us to derive partial VCDs for both the stratosphere and the troposphere (Wagner et al., 2001; Wang et al., 2003; Heue et al., 2003). In addition limited profile information can be derived (Bruns et al., 2004).

The tropospheric and stratospheric columns can be separated in a similar way from SCIAMACHY observations. In Nadir mode SCIAMACHY observes the total column. In limb mode, the stratospheric profile and thus the stratospheric column is measured. (Bovensmann et al., 1999).

2.1 Slant and Vertical columns

Both analysis methods described below result in tropospheric slant columns. They therefore depend on the light path through the atmosphere to the detector. The light path depends on many parameters like solar zenith angle, aerosol load, surface albedo, and the vertical distribution of the absorber. For a better comparison with other measurements usually the vertical column is calculated. It is defined as:

$$VCD = \int_0^H c(z) dz, \quad (1)$$

where z stands for the altitude above ground, and c again is the concentration of the trace gas. The upper limit H of the integral can be either the top of atmosphere if one is interested in total columns or the tropopause height, like in our case, when we study tropospheric trace gases. It is obvious that the vertical column density does not depend on the light path.

To convert a slant column to the corresponding vertical column the influence of the light path and according parameters is calculated and expressed as air mass factor (AMF)

$$AMF = SCD/VCD. \quad (2)$$

The air mass factors describe the sensitivity of the instrument for a trace gas under certain conditions in the atmosphere.

2.2 The AMAXDOAS-instrument

2.2.1 Instrumental setup

In Fig. 1 a sketch of the instrumental setup is shown. There are different lines of sight above and below the aeroplane. According to Bruns et al. (2004) the best vertical resolution in the Upper Troposphere and Lower Stratosphere region is achieved by using small elevation angles, therefore in addition to Nadir and Zenith two telescopes with $+2^\circ$ and -2° viewing direction relative to the horizon were installed.

Small telescopes with a diameter of 10 mm and 0.2° half aperture are used to observe the scattered sunlight. These telescopes are mounted inside housings outside the aeroplane. The light is led to spectrographs via quartz fibres.

Two different spectrographs are used for the ultra violet and visible wavelength region. The UV spectrograph has a spectral resolution of 0.5 nm FWHM whereas the resolution for the visible light is 1 nm. Together the instruments cover the wavelength interval from 300 nm to 550 nm. Two-dimensional CCD-cameras are used as detectors, so all the lines of sight are observed simultaneously. The lines of sight and the corresponding area on the CCD-chip of the “visible” spectrometer are shown in Figs. 2a and b.

The total integration time was 30 s for both spectrographs, and as the ground speed of the Falcon is about 760 km/h the horizontal resolution of the measurements is about 6.6 km. Perpendicular to the flight direction the horizontal resolution is given by the flight altitude (11 600 m) and the aperture and can be estimated to be around 80 m.

2.2.2 Data analysis of AMAXDOAS data

The measured spectra were analysed using the DOAS technique (Platt and Stutz, 2004). Several cross-sections of the trace gases which show structured absorptions in the respective wavelength regions are fitted to the logarithm of the measured spectrum $I(\lambda)$ divided by a solar reference spectrum $I_0(\lambda)$ using a non linear least squares algorithm.

$$\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = -\sum_i \sigma_i(\lambda) \int c_i(l)dl + P(\lambda) \quad (3)$$

$\sigma_i(\lambda)$ is the cross section of the specific trace gas (i) and $c_i(l)$ the corresponding concentration along the light path. A polynomial P is added to account for slowly varying extinction caused by Rayleigh- and Mie-scattering. The integral $\int c_i(l)dl$ is called **Slant Column Density (SCD)**.

In contrast to satellite observations where the solar reference spectrum I_0 (direct sun light) contains no atmospheric absorption structures, the AMAXDOAS analysis does not yield total atmospheric column density (SCD) but the difference in the slant column densities between the measurement and a reference spectrum. The reference spectrum is a measured spectrum, chosen according to the following conditions:

- Use of the same telescope (viewing direction) to minimise instrumental differences,
- Small solar zenith angle SZA – this will keep the influence of stratospheric absorptions as low as possible.
- No clouds – the light path inside a cloud is not known. Although normally a cloud leads to lower absorptions, there are also cases where higher absorptions are observed above clouds (Wang et al., 2005).
- High intensity – the noise of the data is ruled by the statistical photon noise, and thus the signal to noise ratio increases with increasing intensity.

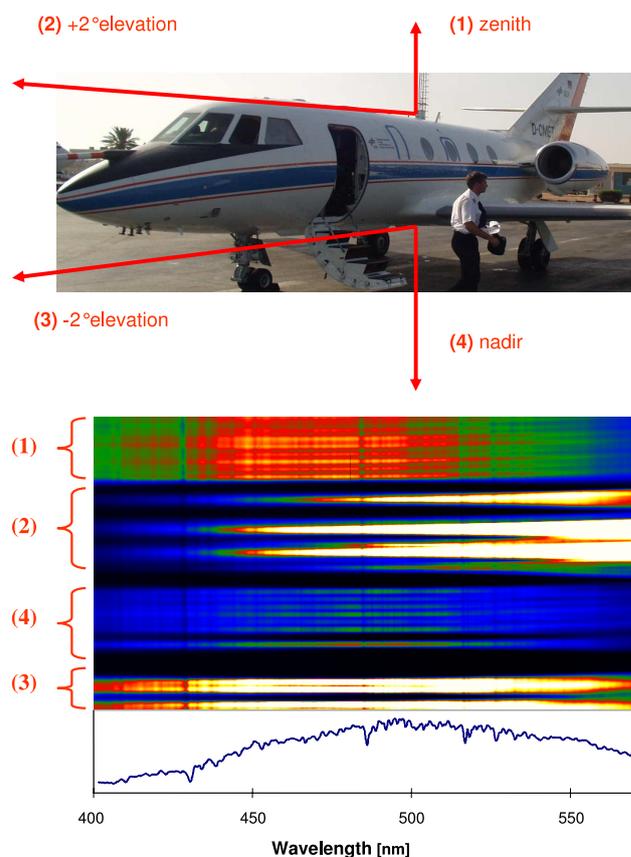


Fig. 2. (a) Upper panel: Pictures of the DLR-Falcon, including a sketch of the used lines of sights. (b) Lower panel: Typical image of vis CCD – the different viewing directions are separated from each other by dark lines. The numbers on the left side belong to the different LOS as marked in Fig. 2a. Usually the direction -2° was the brightest one and therefore only a small area on the chip is used for it.

- Clean air – as described below it is necessary to separate the stratospheric from the tropospheric signal, and this is easier if the SCD in the reference is small.

For the flight discussed (19/02/2003) here a spectrum taken at 8:30 GMT was used. At this time the Falcon crossed the Alps. According to our log no clouds were observed there. Due to the high albedo the intensity in the nadir spectrum is high. The Alps are known to be a clean air region. The solar zenith angle was about 70° , which is quite high, but the other criteria were well fulfilled, and the reference spectrum was taken close to the most important region, so the stratospheric absorption did not change too much until the southern Po-valley was reached. The SZA just north of the Apennine was 66° so the difference in the stratospheric absorption can be estimated: $dSCD = VCD[1/\cos(SZA_2) - 1/\cos(SZA_1)]$ to be in the order of $6 \cdot 10^{14}$ molec/cm², when a vertical column of $2.8 \cdot 10^{15}$ molec/cm² is assumed as retrieved from the SCIAMACHY data.

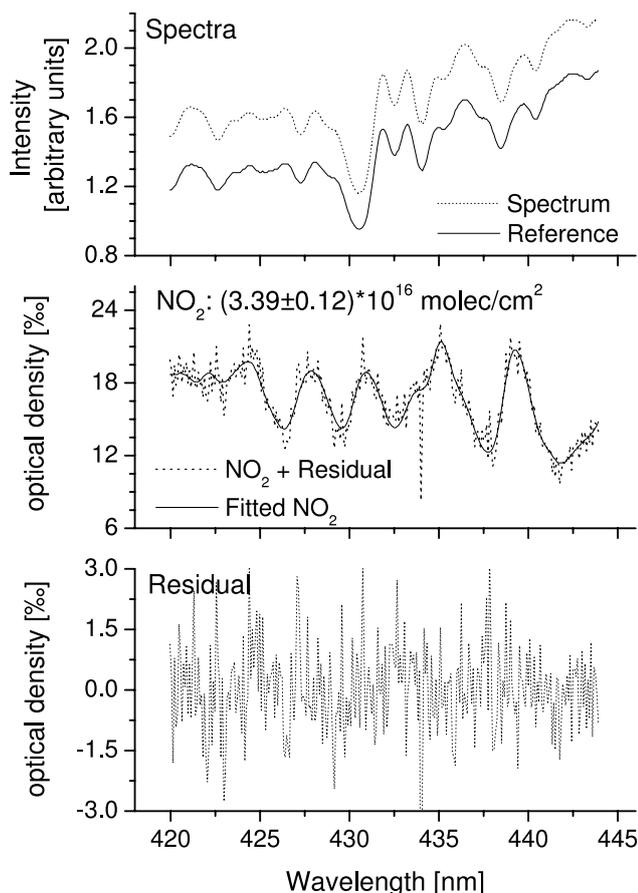


Fig. 3. NO₂-fit for a Nadir spectrum taken on the flight on 19/02/2003 from Basel to Tozeur at 8:14:30 close to Zürich, the reference was taken about 15 min later in the clean air of the Alps.

The WinDOAS-software (Fayt and Roozendaal, 2001) was used to analyse the AMAXDOAS data. The data presented here were all observed with the vis-spectrometer. For the NO₂ analysis, the wavelength region 420–444 nm was used. The cross sections for NO₂ (Burrows et al., 1998), O₃ (Burrows et al., 1999), O₄ (Hermans et al., 1999) and H₂O from HITRAN (Rothman, 1998) were included in the fit. The Ring effect was considered by using a Ring spectrum calculated with WinDOAS.

In Fig. 3 we show a typical DOAS-fit of the flight from Basel to Tozeur (Tunisia). The spectrum was taken at 8:14:30 UT close to Zürich.

To derive the tropospheric columns the stratospheric signal has to be subtracted from the total column. The stratospheric NO₂ is known to vary slowly in time and space, at least for the flight distance of 3000 km in mid-latitudes this can be assumed.

In the nadir view the tropospheric absorption is added to this slowly varying signal. In the troposphere most of the emissions originate, so the temporal and spatial variations are much larger. This means the general trend has to be

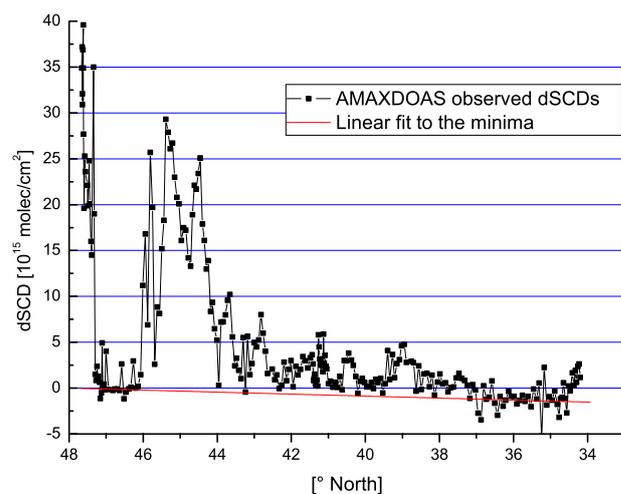


Fig. 4. The observed $dSCD$ from AMAXDOAS and the linear correction (red) for the stratospheric signal. The tropospheric signal was assumed to be negligible in the Alps (47° N) and over the Mediterranean south of Sardegna (36° N).

separated from these variations. The minimum of the tropospheric signal was assumed to be negligible over the Alps and the Mediterranean south of Sardinia. The result is called tropospheric slant column, and by dividing through the tropospheric Air Mass Factor (AMF) the tropospheric vertical column is determined. Two methods of correcting for stratospheric absorptions are compared:

- A linear fit to the minima was made, and subtracted.
- The geometrical approximation $\frac{1}{\cos(SZA)}$ for the stratospheric AMF is used. If we assume the latitudinal variations of the vertical column to be linear. So the stratospheric NO₂ column to be subtracted can be written as:

$$dSCD_{Strat} = (a + b\phi) * \left(\frac{1}{\cos(SZA)} \right) - (a + b\phi_{ref}) * \left(\frac{1}{\cos(SZA_{ref})} \right) \quad (4)$$

where ϕ represents the latitude. The first part of the sum is the SCD at any latitude ϕ and the second part is the slant column at the reference place. The parameters a and b were defined by using the same approach for the SCIAMACHY total $SCDs$, where the reference contains no stratospheric absorption. Thus the vertical column as a function of latitude is derived from SCIAMACHY measurements.

For the relevant cases both corrections are very similar and differ by less than $0.5 \cdot 10^{15}$ molec/cm². In Fig. 4 the observed $dSCD$ together with the linear correction for stratospheric absorptions are shown. To simplify the graph the second correction is not shown here.

More details concerning the AMAXDOAS instrument as well as a comparison to ground based data on another flight were described by Wang et al. (2005) and Bruns et al. (2004). The instrument was also used on board a smaller aeroplane a Partenavia 68 for emission measurements in the Po-basin (Wang et al., 2005(2) submitted to ACPD).

2.3 The SCIAMACHY instrument

2.3.1 Description of the instrument and its measurement characteristics

The ENVISAT satellite orbits the earth in about 800 km altitude in a sun-synchronous polar orbit, crossing the equator at 10:00 local time. The SCIAMACHY instrument is a 8 channel spectrometer designed for measuring the sunlight in the UV, visible and near infrared region (240–2380 nm). Depending on the channel the resolution varies between 0.22 and 1.48 nm. The NO₂-columns are retrieved in the wavelength region of 425 to 450 nm (channel 3) where the resolution of the instrument is 0.44 nm.

Measurements are performed alternatingly in nadir and limb direction, changing every 2 min. Within 7 min the same air mass is observed first in limb viewing mode and in the nadir mode afterwards. With this method the stratospheric column and the total column are measured independently.

At the beginning and the end of each orbit, solar and lunar occultation measurements are also performed.

The horizontal resolution of the instrument in the nadir is 30×60 km² in the region of interest. Global coverage is achieved after 6 days (Bovensmann et al., 1999).

2.3.2 Data Analysis for SCIAMACHY

Details on the spectral NO₂ analysis of SCIAMACHY data can be found in Richter et al. (2004).

For the separation of stratospheric and tropospheric slant columns, three approaches were compared:

In addition to the two methods used for the AMAXDOAS, “linear fit” and “1/cos(SZA)” a third way is possible here: to subtract a stratospheric reference sector measured by SCIAMACHY on the same day at the same latitude over clean regions like the Pacific ocean. This last method is usually applied for the retrieval of tropospheric columns from satellite observations.

Dividing the tropospheric slant column by a tropospheric AMF one yields the tropospheric vertical columns (Richter and Burrows, 2002). For the vertical columns (version 0.5) available through the internet (<http://www.DOAS-Bremen.de>) a standard AMF is used. It is calculated using a 1 km grid, a constant NO₂ value in the lowest 1 km and a linear decrease to 0 in the layer between 1 km and 2 km. In addition to these standard AMFs, we calculated specific AMF for the Po-Valley based on independent information here.

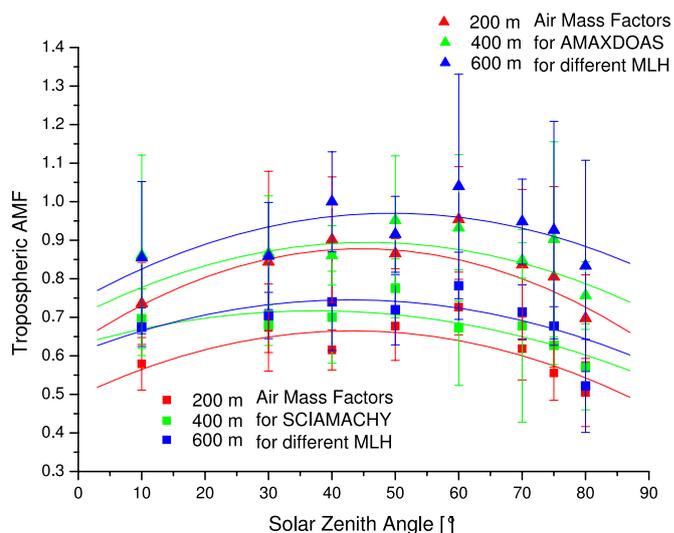


Fig. 5. The AMF for both instruments SCIAMACHY and AMAXDOAS. In general AMAXDOAS is more sensitive to tropospheric pollution than SCIAMACHY. The NO₂ was assumed to be well mixed within the mixing layer and 0 above. Different heights of the ML were assumed and the total aerosol optical thickness was assumed to be constant. The sensitivity decreases slightly from 600 m MLH to 200 m.

The SCIAMACHY data used for this comparison have been retrieved at the University of Bremen from raw radiances and they are referred to as “scientific products”. As already mentioned there are several groups retrieving tropospheric NO₂ columns, but an official product of tropospheric vertical NO₂-columns is currently not planned.

The validation of operational and scientific total NO₂-data is also still in progress (Lambert et al., 2004).

2.4 The specific AMFs for the Po basin

The tropospheric AMFs for both AMAXDOAS and SCIAMACHY were calculated using the Monte Carlo based ray tracing program TRACY. The program and its main features are described in Friedeburg (2003) and Hönninger et al. (2004).

It is very important that the AMFs for both instruments are calculated with comparable settings. Of course the detector’s altitude and the field of view must be set according to the instruments characteristics. The important values for the AMF-calculations that should be the same are:

- The aerosol extinction profile and the corresponding single scattering albedo,
- the NO₂ – profile in the troposphere,
- the surface albedo.

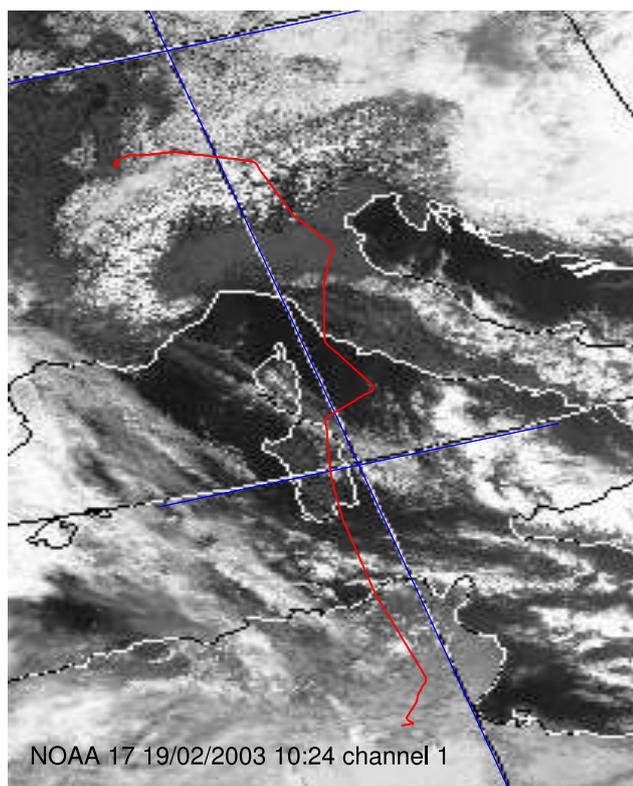


Fig. 6. NOAA-17 Satellite image as published by the University of Dundee in 2004 on (www.sat.dundee.ac.uk/auth.html). The image shows the cloud coverage over southern Europe and the Mediterranean on 19/02/2003. The flight track is shown in red.

For the calculation of the AMFs, an urban aerosol type was used and a constant visibility in the mixing layer was assumed. The mixing layer height (MLH) in this region and time of the year varies between 200 m and 600 m above ground (AGL) (Petritoli et al., 2004). The vertical aerosol optical thickness was set 0.3 which is in agreement with the AERONET data in Ispra (Zibordi, 2004; <http://aeronet.gsfc.nasa.gov>). A typical background aerosol-load was used for the higher altitudes.

The NO₂ – concentration was assumed to be constant within the mixing layer and above this altitude the concentration was set to 0.

In our calculation the albedo was set to 5% which is a value typical of winter fields (Feister and Grewe, 1995).

In Fig. 5 the AMFs for both AMAXDOAS and SCIAMACHY are shown. The AMFs for the AMAXDOAS are generally higher than those for the SCIAMACHY instrument. For the satellite observations, more light scattered in higher altitudes contributes, to the signal and the measurement therefore is less sensitive to tropospheric absorbers than the airborne measurements. One has to keep in mind that about 20% of the atmosphere is still above the flight altitude (11 600 m) of the Falcon.

The AMF were calculated for different heights of the mixing layer, 200 m, 400 m and 600 m. As expected, the sensitivity decrease with a decreasing MLH, because the signal is more influenced by the light scattered in altitudes above the mixing layer. However the influence of the mixing layer height is very small. The difference between the AMFs for 200 m and 600 m MLH is about 11%. The main reason for this small influence is the high aerosol load and the fact that the aerosol and the NO₂ mixing heights are the same. From our experience with low aerosol load we expected to find a stronger dependency. The small change in the AMF leads to only slightly varying TVCDs (Fig. 9).

The atmospheric conditions during the measurement varied quite often. Over the Alps there was snow, and clear visibility, whereas in the Po-valley it was quite hazy during the overpass of AMAXDOAS and the albedo was lower than over the mountains. It is impossible to get detailed information on the visibility, the aerosol concentration and optical properties, the ground albedo and the NO₂ profile. Therefore we used the AMF described above for the complete dataset. These settings should be realistic for the Po-Valley, where the highest column densities were observed.

3 Results and discussion

In this section we first present the AMAXDOAS results and discuss them briefly for the whole flight on 19/02/2003. The focus however is on the comparison with collocated measurements of SCIAMACHY in the Alps, northern Italy and the southern Mediterranean and northern Africa.

3.1 The AMAXDOAS flight from Basel to Tozeur on 19/02/2003

Within the SCIAVALUES project, two major campaigns consisting of 28 flights were flown in September 2002 and February/March 2003. Measurements were performed in Polar Regions e.g. Greenland and the tropics en route to the Seychelles. Details on both campaigns are given by Fix et al., (2004). Here we concentrate on the flight from Basel to Tozeur on 19 February for several reasons:

- The weather conditions were very good.
- We overflew both clean and heavily polluted areas.
- SCIAMACHY data are available for the same day and time.

In Fig. 6 the flight track is shown, in the background a satellite image showing the clouds over Italy and the Mediterranean. After a short stop in Basel the Falcon headed south-east crossing the Alps and the Po-Valley and continued along the Italian coast over Sardinia to Tozeur in central Tunisia.

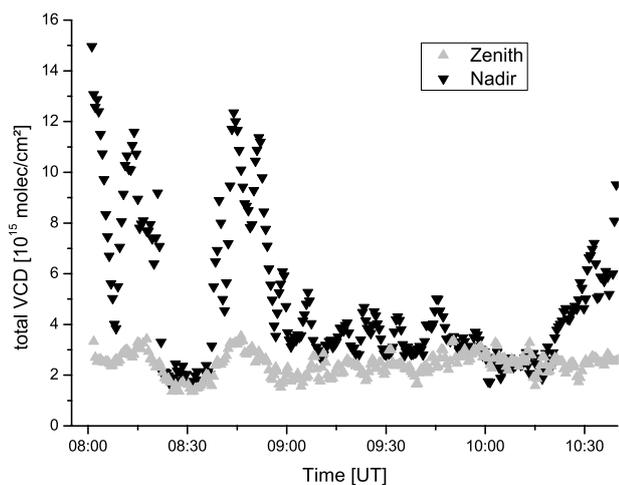


Fig. 7. Time series of the vertical NO₂ columns for AMAXDOAS Nadir and Zenith observations. In Nadir a strong enhancement is observed from 8:40 until 8:55. Here stratospheric AMFs were used, to show the slowly varying stratospheric signal and the influence of tropospheric pollution on the telescope directed to the zenith.

The Alps were still covered with snow. There was no cloud over the southern Alps, the Po-Valley and from the Apennine to the Italian coast. During the first part of the flight from Basel to the mountains there was fog below the aeroplane. Additional cloudy regions were observed east of Sardinia and north of Tunisia.

In the southern Alps the large Adige-Valley can be recognized. One of the few highways crossing the mountains runs through this valley.

The distribution of clouds and snow was also confirmed by simultaneous O₄ measurements and the observed intensity in the nadir viewing telescope. The retrieval of cloud information from O₄-SCDs is described by Wagner et al. (2002) and Wittrock et al. (2003).

The Po-Valley is known to be one of the most polluted areas in Europe (Beirle et al., 2004), and is therefore a region well suited for a comparison of tropospheric NO₂. The geographical conditions and the Italian industrial centres concentrated in this plain cause the pollution observed.

3.2 Discussion of the AMAXDOAS results

As expected, a strong enhancement in the total vertical column of the nadir telescope was observed over the Po-valley (Fig. 7, 8:44). Over the heavily polluted regions, we measured a slightly increased NO₂-signal in the zenith as well. Simulations with a ray tracing model can reproduce this effect caused by multiple scattering and tropospheric pollution. A small part of the light observed in the zenith telescope was scattered in lower altitudes or even reflected on the surface and is therefore influenced by tropospheric absorbers. So the observed variations in the Zenith telescope do not conflict

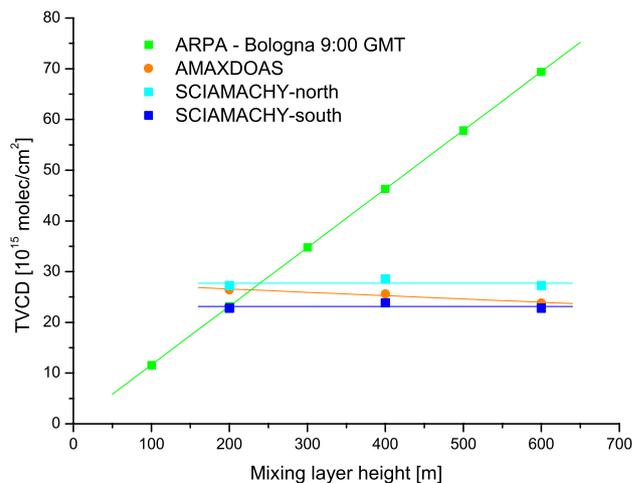


Fig. 8. The tropospheric vertical column calculated for different mixing layer heights. The in situ measurements are shown in green, the AMAXDOAS TSCDs in orange and SCIAMACHY data in blue. As the position of the measurement stations is close to the border between two SCIAMACHY pixels, the data of both pixels are shown here. The southern pixel (dark blue) partly covers the Apennine Mountains.

with the assumptions of a slowly varying stratospheric NO₂ signal.

The total vertical column densities of both viewing directions showed a similar effect just north of the Alps at about 8:11 GMT. At this time the aeroplane was passing the region of Zürich. As this area was not covered by SCIAMACHY pixels on this day (Fig. 9), we do not discuss this enhancement in detail here. However, the observed NO₂ enhancement is in good agreement with a smog event reported for Zürich on these days (NZZ, 2003).

From now on only the tropospheric NO₂ shall be discussed in a more detailed comparison.

3.2.1 Comparison to ground based data

From the ARPA-Bologna (Agenzia Regionale per la Protezione dell' Ambiente <http://www.arpa.emr.it>) ground based data were available via personal communications. In addition the aerosol optical thickness from AERONET Ispra (Zibordi, 2004; <http://aeronet.gsfc.nasa.gov>) and the soundings from Linate and San Pietro (available at the University of Wyoming <http://weather.uwyo.edu/upperair/sounding.html>) were used. The mixing layer height in Linate and San Pietro can be assumed to be 160 m AGL at minimum in the morning hours, the aerosol optical thickness was 0.3 and stayed constant for most of the day. This information was used to calculate the AMFs for AMAXDOAS.

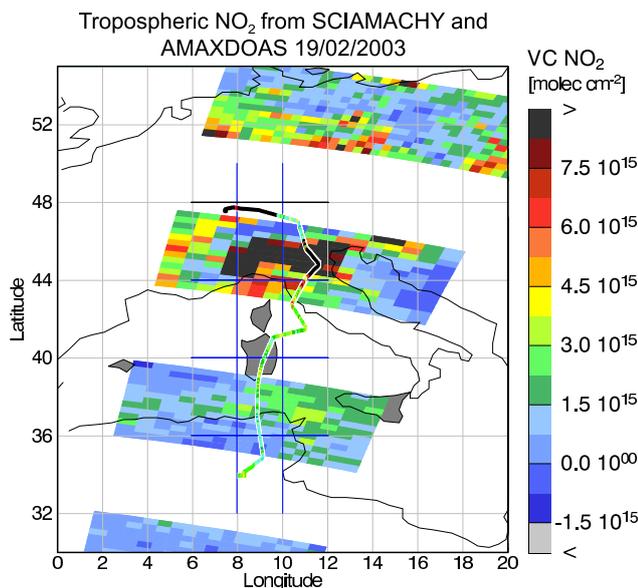


Fig. 9. Tropospheric vertical NO₂ column measured by AMAXDOAS and SCIAMACHY. The AMAXDOAS data were overlaid over SCIAMACHY's pixel in the same scale using very similar colours. Zürich is not covered by SCIAMACHY's pixel on this day.

The ground based in situ data closest to the flight track were used to calculate the vertical column:

$$TVCD = \int_0^{MLH} c(z) dz.$$

The mixing ratio (42 ± 22 ppb) was assumed to be constant in the mixing layer. For a mixing layer of 200 m this resulted in a tropospheric vertical column of $(23 \pm 12) \cdot 10^{15}$ molec/cm² and in $(34 \pm 18) \cdot 10^{15}$ molec/cm² for 300 m, here the error is given by the standard deviation.

In Fig. 8 the TVCD for the ground based in situ data, AMAXDOAS and SCIAMACHY is shown. We studied different MLHs and good agreement can be found for a MLH between 200 m and 300 m above ground.

3.3 Comparison between AMAXDOAS and SCIAMACHY

For a first comparison the reader may have a closer look at Fig. 9, where the tropospheric vertical columns of NO₂ are shown using the same colour scale for both datasets. The two measurements show the same horizontal distribution, in regard to the sparsely populated Alps, the heavily polluted Po-valley, the Apennine and the Italian coast. Also south of Sardinia and in northern Africa, a good agreement can be observed.

As can be seen from Fig. 9, SCIAMACHY observes a large variability in both north south and east west direction.

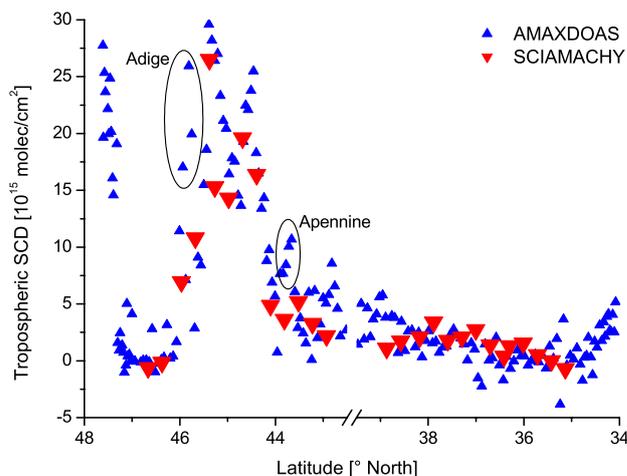


Fig. 10. Slant NO₂ columns measured by SCIAMACHY and AMAXDOAS. In the gaps between two SCIAMACHY Nadir scans no data are shown.

Therefore for the comparison only those SCIAMACHY data were taken into account where AMAXDOAS data are available. The flight track was laid over the SCIAMACHY pixels and only those SCIAMACHY data were used where at least one AMAXDOAS measurement was inside. As pointed out above the AMAXDOAS pixels (6.6×0.08 km²) are small compared to those of SCIAMACHY.

3.3.1 Validation of tropospheric slant columns

As the AMFs have a large influence on the results, the comparison of both slant and vertical column is shown here. This allows us to separate the influences of the slant column and the AMF calculations. According to Boersma et al. (2004) and Heland et al. (2002) the errors introduced by the uncertainties of the AMF are up to 50%.

The slant columns can well be compared as the measurement principle and viewing geometry of both participating instruments is nearly the same. Compared to validation efforts using in situ measurements (Heland et al., 2002), this is a big advantage of the AMAXDOAS instrument.

In Fig. 10 the tropospheric slant columns for both instruments are plotted as a function of latitude. The standard methods for the separation were used here, i.e. reference sector for SCIAMACHY and linear fit for AMAXDOAS. Both measurements show similar results for the Po-valley ($45^{\circ}30' \text{ N} - 44^{\circ}20' \text{ N}$) and the region south of Sardinia ($38^{\circ} \text{ N} - 36^{\circ} \text{ N}$). Over the southern Alps ($\sim 46^{\circ} \text{ N}$) and the southern Apennine ($\sim 43^{\circ}40' \text{ N}$) a difference can be made out, which might be due to a different response of the instruments to some NO₂ in the valleys (e.g. Adige) between the snow capped mountains. As a result of the higher spatial resolution, the AMAXDOAS is able to detect the NO₂ in the valley, whereas SCIAMACHY's signal is mainly influenced

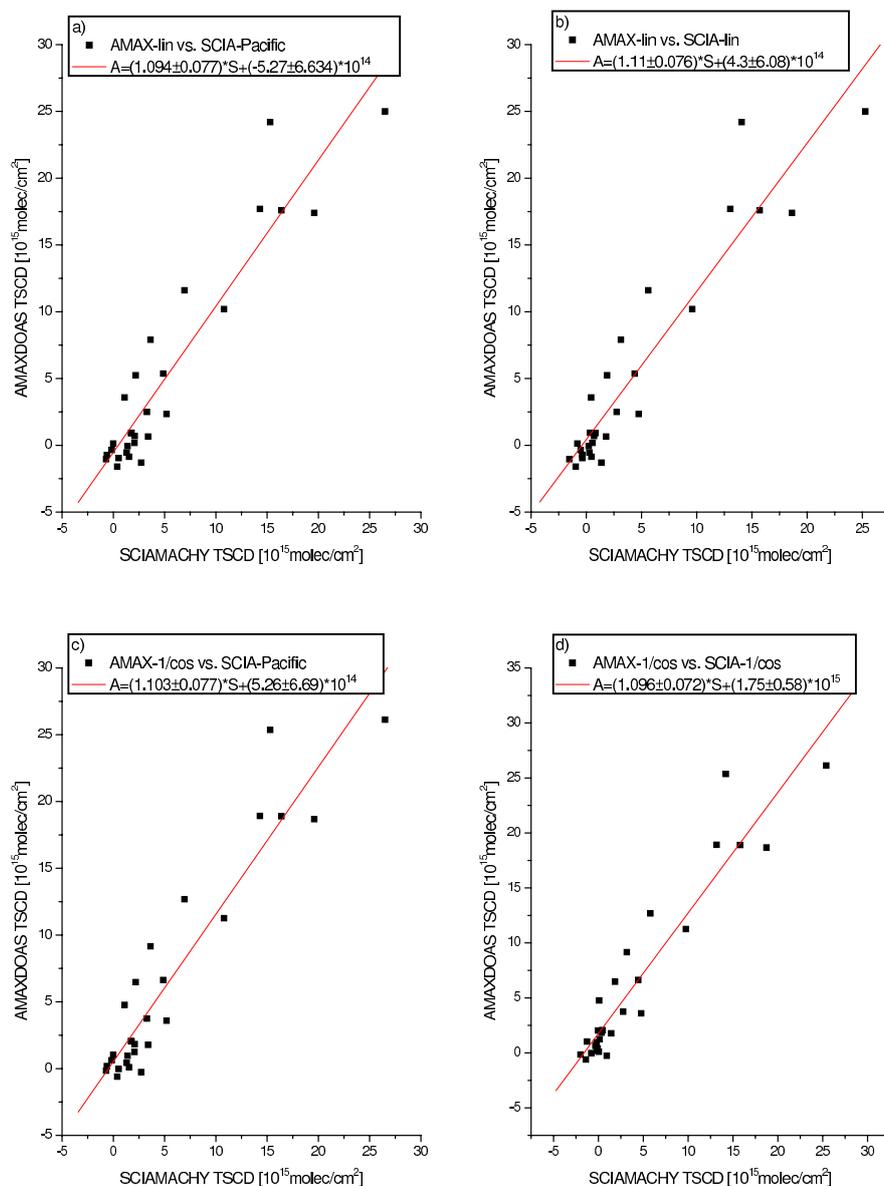


Fig. 11. Correlation between the tropospheric slant column densities measured by SCIAMACHY and AMAXDOAS for different methods of separation between stratospheric and tropospheric absorption. Upper left panel: Reference for SCIAMACHY and linear fit for AMAXDOAS. Upper right panel: For both instruments a linear fit was used. Lower left panel: reference for SCIAMACHY and $1/\cos(SZA)$ for AMAXDOAS. Lower right panel: $1/\cos(SZA)$ was used for both.

by the clean air over the snow capped mountains. Especially in the region of the southern Alps a high variability in the AMAXDOAS data can be observed, which also indicates the influence of the mountains and the valleys.

For the correlation analysis between both datasets the AMAXDOAS data covered by one SCIAMACHY pixel were averaged. Due to the flight direction from north to south, only the smaller expansion (30 km) of SCIAMACHY's pixel was taken into account. The gradients covered by one pixel within the 60 km east west expansion obviously influence the comparison. The different

spatial resolution is most probably the main reason for the differences observed.

One example of this effect was observed on the northern edge of the Po-Valley. AMAXDOAS measured about 10 km east of Verona and the same town was covered by the SCIAMACHY pixel. Therefore the emission of its about 250'000 inhabitants were observed by SCIAMACHY but not by AMAXDOAS. Nevertheless this data was used for the comparison as a similar effect was observed over Bologna, where the Falcon flew over the town and SCIAMACHY was more influenced by the background than AMAXDOAS.

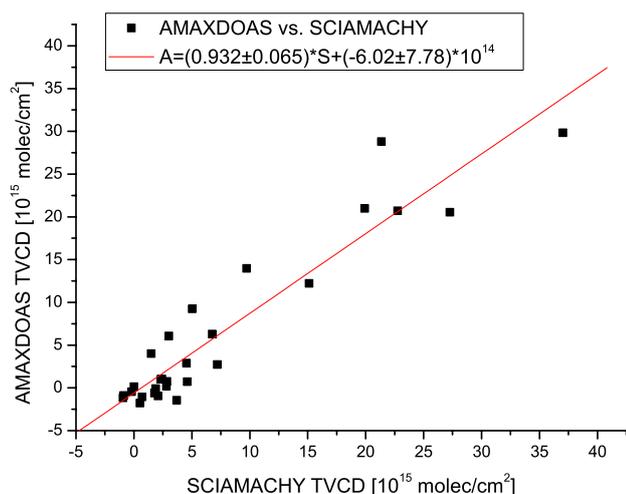


Fig. 12. Correlation of the tropospheric vertical columns. The reference method was used for SCIAMACHY and the linear fit for AMAXDOAS. The AMF was calculated assuming a MLH of 200 m and a total aerosol optical thickness of 0.3.

Figures 11a to d show correlation plots of the SCIAMACHY slant columns with the ones measured by AMAXDOAS. As can be seen, the correlations between the data sets are good. Four combinations of different background corrections are shown:

- the standard combination where the linear correction for the AMAXDOAS and the reference method for SCIAMACHY is used, (e.g. Fig. 10)
- both AMAXDOAS and SCIAMACHY were corrected with the linear fit method,
- the stratosphere was estimated using Eq. (2) for AMAXDOAS and the reference sector method for SCIAMACHY,
- the stratospheric SCD calculated via $VCD/\cos(SZA)$ as in Eq. (2) was applied to both datasets.

The two missing combinations (linear for AMAXDOAS versus $VCD/\cos(SZA)$ for SCIAMACHY and vice versa) are not shown here as they do not contain further information.

As can be seen the influence on the slope of the correlation is very small, within the error, all the slopes equal 1.1. The intercept of the fits are zero within the error, except for the combination d). The axis intercept can mostly be attributed to the separation of stratospheric and tropospheric columns. Method d) seems to introduce an offset to the SCIAMACHY data in the order of $-1 \cdot 10^{15}$ molec/cm². A comparison to Fig. 11c excludes an offset in the AMAXDOAS data here.

From the discussion of the AMF we would expect AMAXDOAS to be more sensitive to the tropospheric NO₂ than SCIAMACHY, so a slope larger than 1 can be expected.

3.3.2 Comparison of the vertical columns

For the comparison the standard tropospheric slant columns i.e. linear interpolation for AMAXDOAS and reference method for SCIAMACHY were used.

As already mentioned, the tropospheric slant columns of AMAXDOAS are about 10% higher than those observed by SCIAMACHY. The AMF were calculated for three different heights of the mixing layer. According to Fig. 5 the sensitivity of both instruments increases with an increasing thickness of the mixing layer height.

The correlation between SCIAMACHY and AMAXDOAS tropospheric vertical columns is shown in Fig. 12. Here the AMF with a 200 m MLH was used, for both SCIAMACHY and AMAXDOAS. The correlation is quite good, the slope equals 0.93 ± 0.06 and the intercept is zero within the error. The divergence between AMAXDOAS's and SCIAMACHY's TVCD was calculated:

$$\langle S - A \rangle = \sqrt{\frac{\sum_{i=1}^n (S_i - A_i)^2}{n}}. \quad (5)$$

Here S represents the SCIAMACHY data and A is the average of the AMAXDOAS measurements covered by one SCIAMACHY pixel. All collocated measurements were taken into account.

In Table 1 an overview over the slopes and intercepts of the linear fits and divergence for the three studied mixing layer heights is given. The best results in the slope and divergence are achieved assuming a MLH of 200 m.

The divergence for all the situations studied here is in the order of $3.5 \cdot 10^{15}$ molec/cm², and is therefore about a factor of two higher than the average measurement error for AMAXDOAS, which is about $1.5 \cdot 10^{15}$ molec/cm².

The different spatial resolution is one of the main causes for different results, this systematic effect can only be minimized to a certain degree by averaging the AMAXDOAS measurements.

The NO₂ cross sections used for the analysis were very similar, both analysis used cross sections for temperatures in the stratospheric range – 223K for AMAXDOAS and 243K for SCIAMACHY. The error introduced by using the wrong temperature for the cross section can be up to 20% (Boersma et al., 2004) in our case however, this effect would influence both instruments in this comparison in the same way. The correlation would be very similar except that both instruments would observe larger slant columns.

The time difference between the AMAXDOAS and the SCIAMACHY overpass, of course also influences the observed columns. AMAXDOAS crossed the Po-basin between 8:40 and 8:50 GMT whereas SCIAMACHY scanned this region at 9:49 GMT. Ground based data in Bologna showed the local mixing ratio decreased from 42 ppb to 35 ppb (average of 4 points close to the flight track) between 9:00 GMT and 10:00 GMT. If the MLH increased (in

Table 1. For different mixing layer heights (MLH) the vertical columns were calculated for both instruments. Here an overview on the correlation between the according datasets is shown. The correlation is best for the mixing layer height of 200 m.

MLH	Slope of the linear fit	Axis intercept [10^{14} molec/cm ²]	Divergence [10^{15}]
200 m	0.932 ± 0.065	-6.02 ± 7.78	3.40
400 m	0.859 ± 0.059	-5.8 ± 7.54	3.74
600 m	0.834 ± 0.058	-5.33 ± 6.99	3.68

the same way) the vertical column would still be the same, and according to the time of the day we would expect the latter to be the reason for the observed decrease rather than transport or NO₂ destruction. The wind speed on this day was about 3 m/s from north-west, so the transport is maximum 10 km and the same air mass would still be covered by the same SCIAMACHY pixel.

Also the Solar Zenith Angle changes in the time between the two observations, for AMAXDOAS the average SZA was 67.5°, and for SCIAMACHY it was 61°. From Fig. 5 the difference in the AMF can be estimated to be below 5%.

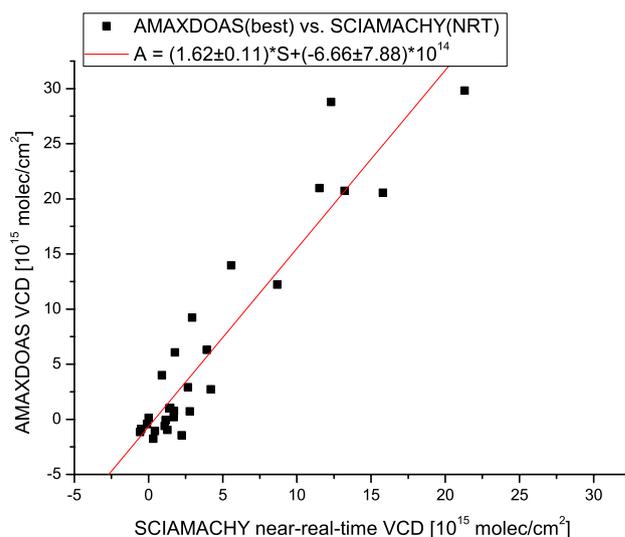
According to the AMF a difference in the slant columns can be expected in the way we observed it. Other reasons like different cross-sections, temporal variations or transport of air masses are unlikely but can not be excluded.

3.3.3 Comparison to the near-real-time product

Several versions exist of the SCIAMACHY tropospheric columns which mainly differ in the assumptions made for the air mass factor calculations. In the last sections, the AMF was determined using external information for the time and location studied, and very good agreement was found between satellite and AMAXDOAS measurements. However, the near-real-time images of tropospheric vertical NO₂ columns posted on <http://www.doas-bremen.de> (as used for Figs. 9 and 13) use a simplified air mass factor where the NO₂ is constant in the lowest 1000 m and decreases linearly up to 2000 m and a maritime aerosol is used (Richter and Burrows, 2002). Here we compare the AMAXDOAS measurements with the results from the near-real-time products.

The results are shown in Fig. 13. The linear fit now has a slope of 1.62 but the intercept is still close to 0 ($-6.66 \pm 7.88 \cdot 10^{14}$). This can be explained by the difference between the two sets of AMFs. The standard SCIAMACHY AMFs are about 60% higher than those calculated here for the Po-Valley, which in this case leads to a divergence of $5.04 \cdot 10^{14}$.

Although the error of 60% in the AMF is large it is within the range quoted in previous papers (e.g. 50%, Heland et al., 2002). The reason is that the specific atmospheric conditions in the Po-Valley (high aerosol load and low mixing layer height) are very different from the assumptions made for calculating the standard AMF.

**Fig. 13.** Correlation between the SCIAMACHY near-real-time data set and the AMAXDOAS data validated with the ground based in situ data.

This comparison highlights the importance of appropriate AMFs in the retrieval – only with reasonable assumptions good agreement with independent measurements can be achieved. For global data sets, such information is often not available, and model predicted profiles for NO₂ and sometimes also aerosol loading have to be used.

4 Conclusions

Tropospheric NO₂ slant and vertical columns measured by the AMAXDOAS were presented and compared to tropospheric NO₂ columns derived from SCIAMACHY. Measurements of the same day and region were used for the comparison and no trajectory calculations were necessary here.

To measure in different regions within a short time period is a big advantage of airborne measurements. The data shown here were observed on the flight on 19/02/2003 between Basel and Tozeur including the highly polluted Po-Valley.

Before the tropospheric columns can be computed the stratospheric and the tropospheric absorptions have to be

separated. Different separation methods were investigated for both instruments. For AMAXDOAS a linear interpolation and a $1/\cos(SZA)$ approach were compared. For SCIAMACHY also the reference sector method was included. We found that the influence of the separation method was small. The agreement between the slant columns of both instrument was in the expected range i.e. AMAXDOAS measured slightly higher slant columns according to the lower flight altitude it is more sensitive to tropospheric absorbers.

Three different profiles for NO₂ and the aerosols were used to calculate the AMFs, for the specific conditions over the Po-Valley in the observation period. The agreement between AMAXDOAS and SCIAMACHY was found to be best for the lowest profile, which is in good agreement also with ground based data.

The observed differences of the measurements e.g. at the edge of the Alps and the Apennine seem to be attributable to the different spatial resolutions of AMAXDOAS and SCIAMACHY. Also the temporal difference of one hour in the most interesting region causes some systematical difference.

As expected the agreement between AMAXDOAS and the SCIAMACHY near-real-time product is worse (slope 1.6). This finding demonstrates the importance of independent information like MLH for the calculation of appropriate AMFs.

Although only results from nadir and zenith are presented here, additional information from the other lines of sight can be retrieved especially for the upper troposphere lower stratosphere and will be discussed in Bruns et al 2005 “NO₂ Profile retrieval using airborne multi axis UV-visible skylight absorption measurements over central Europe”.

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