

Comparison of 7 years of satellite-borne and ground-based tropospheric NO₂ measurements around Milan, Italy

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[1] Tropospheric NO₂ vertical column densities (VCDs) over the Lombardy region were retrieved from measurements of the Global Ozone Monitoring Experiment (GOME) spectrometer for the period 1996–2002 using a differential optical absorption method. This data set was compared with in situ measurements of NO₂ at around 100 ground stations in the Lombardy region, northern Italy. The tropospheric NO₂ VCDs are reasonably well correlated with the near-surface measurements under cloud-free conditions. However, the slope of the tropospheric VCDs versus ground measurements is higher in autumn-winter than in spring-summer. This effect is clearly reduced when the peroxyacetyl nitrate and nitric acid (HNO₃) interferences of conventional NO_x analyzers are taken into account. For a more quantitative comparison, the NO₂ ground measurements were scaled to tropospheric VCDs using a seasonal NO₂ vertical profile over northern Italy calculated by the Model of Ozone and Related Tracers 2 (MOZART-2). The tropospheric VCDs retrieved from satellite and those determined from ground measurements agree well, with a correlation coefficient $R = 0.78$ and a slope close to 1 for slightly polluted stations. GOME cannot reproduce the high NO₂ amounts over the most polluted stations, mainly because of the large spatial variability in the distribution of pollution within the GOME footprint. The yearly and weekly cycles of the tropospheric NO₂ VCDs are similar for both data sets, with significantly lower values in the summer months and on Sundays, respectively. Considering the pollution level and high aerosol concentrations of this region, the agreement is very good. Furthermore, uncertainties in the ground-based measurements, including the extrapolation to NO₂ VCDs, might be as important as those of the NO₂ satellite retrieval itself.

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1. Introduction

[2] Nitrogen dioxide (NO₂) is one of the most important species in tropospheric chemistry. The photolysis of NO₂ leads to the photochemical formation of ozone (O₃) during daytime by a catalytic cycle involving organic peroxy radicals (RO₂), the hydroperoxy radical (HO₂), the hydroxyl radical (OH), volatile organic compounds (VOC) and carbon monoxide (CO). NO₂ can also react with O₃ to form the nitrate radical (NO₃), which is a strong oxidant and plays an important role in the nighttime chemistry. The main products of NO₂ in the troposphere are peroxyacetyl nitrate (PAN or CH₃C(O)OONO₂) and nitric acid (HNO₃). The

stability of PAN in the atmosphere is highly temperature dependent, and NO₂ is released with increasing temperature. Nitric acid is produced by daytime reaction of NO₂ with the OH radical or by nighttime formation of N₂O₅ followed by hydrolysis on aerosols [e.g., Dentener and Crutzen, 1993; Jacob, 2003]. More details on the chemistry of tropospheric NO₂ are given by Seinfeld and Pandis [1998] and Finlayson-Pitts and Pitts [2000].

[3] The abundance of NO₂ in the troposphere is highly variable and influenced by both anthropogenic and natural emissions. On a global scale, the major sources of nitrogen oxides (NO_x ≡ NO + NO₂) are fossil fuel combustion, biomass burning, lightning, and soil microbial production [Lee *et al.*, 1997]. Tropospheric NO_x has a relatively short lifetime, on the order of hours in the boundary layer and a few days in the upper troposphere [Jaeglé *et al.*, 1998], and is usually considered to be confined to polluted areas. NO₂ also contributes to radiative forcing [Solomon *et al.*, 1999] but, because of its short lifetime, mainly locally and not on a global scale. However, its atmospheric chemistry controls in part the oxidizing capacity of the troposphere, as well as the abundance of ozone. Therefore NO₂ can also modify the

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radiative balance of the Earth through its influence not only on the tropospheric ozone chemistry, but also on the lifetimes of methane (CH₄) and other greenhouse gases [Intergovernmental Panel on Climate Change, 2001]. In addition, nitrogen dioxide can act as an acidifying and eutrophying agent in terrestrial ecosystems through dry or wet deposition of its oxidation products.

[4] The Global Ozone Monitoring Experiment (GOME) aboard the Second European Remote Sensing Satellite (ERS-2), which was launched in April 1995, allows the retrieval of vertical column densities (VCDs) of NO₂ on a global scale [e.g., Burrows *et al.*, 1999]. The spatial resolution of a GOME ground pixel is 320 km across track and 40 km along track for the three forward scans and 960 km × 40 km for the back scan. Global coverage is achieved within three days (43 orbits) at the equator and faster at higher latitudes. Different algorithms to retrieve tropospheric NO₂ VCDs from GOME measurements have been developed [e.g., Leue *et al.*, 2001; Richter and Burrows, 2002; Martin *et al.*, 2002]. These data can be used for many scientific applications, as for example to study the emissions, distribution and abundance of tropospheric NO₂ accounting for regional and seasonal variability [e.g., Leue *et al.*, 2001; Richter and Burrows, 2002; Beirle *et al.*, 2003]. GOME NO₂ measurements have also been combined with other tools to successfully describe intercontinental or transboundary transport events of NO₂ and identification of sources [e.g., Spichtinger *et al.*, 2001; Stohl *et al.*, 2003; Wenig *et al.*, 2003; Schaub *et al.*, 2005]. In addition, GOME tropospheric NO₂ VCDs have been compared to results from global [Velders *et al.*, 2001; Lauer *et al.*, 2002; Martin *et al.*, 2002] and European [Kononov *et al.*, 2005] 3-D chemistry transport models (CTMs).

[5] The retrieval of the tropospheric NO₂ VCDs from GOME requires several steps. Measurement errors, the knowledge of reference spectra and assumptions in the retrieval algorithms limit the precision and accuracy of the NO₂ VCDs (e.g., see Richter and Burrows [2002], Boersma *et al.* [2004], or section 2.1 of this work), and validation of this data product under a variety of conditions is required. A first validation of tropospheric NO₂ VCDs from GOME was made by comparison with aircraft NO₂ profiles measured during a GOME overpass over Austria under cloud-free conditions [Heland *et al.*, 2002]. Petritoli *et al.* [2004] compared tropospheric NO₂ VCDs, derived from GOME by the approach used here, with ground-based tropospheric columns and in situ measurements of NO₂ in the Po basin, northern Italy. Martin *et al.* [2004] evaluated tropospheric measurements of NO₂ from GOME, using in situ measurements over eastern Texas and the southeast United States from two aircraft campaigns carried out in summer. These studies reported good agreement between GOME and in situ measurements of NO₂ under certain meteorological conditions. The different algorithms retrieving tropospheric NO₂ VCDs appear to have reasonable accuracy for the cases considered. However, more extensive validation of the tropospheric NO₂ retrievals from GOME measurements is needed for different regions, seasons and meteorological conditions. Furthermore, validation is needed using coincident in situ measurements that span the whole satellite footprint, especially in the planetary boundary layer (PBL).

[6] In contrast to previous studies, this paper presents a comparison of NO₂ measurements derived from GOME and from ground-based instruments in a climatological perspective. Tropospheric NO₂ VCDs over the Lombardy region were retrieved from GOME measurements for the period 1996–2002 using a differential optical absorption method [Burrows *et al.*, 1999; Richter and Burrows, 2002]. This data set was compared with simultaneous near-surface measurements of NO₂ from 99 ground stations in the Lombardy region in northern Italy. Section 2 describes the GOME and ground-based measurements used in this study. The ground-based measurements of NO₂ are first corrected for interferences and then scaled to vertical column densities, and both data sets are compared in section 3. Section 4 discusses some of the limitations of both data sets and identifies the most important error sources in this comparison. Finally, section 5 summarizes the main results.

2. Space-Based and In Situ Measurements of NO₂

2.1. GOME Satellite Retrieval

[7] The NO₂ retrieval from GOME is based on the Differential Optical Absorption Spectroscopy (DOAS) method. This technique determines the NO₂ slant column density (SCD) along the light path through the atmosphere in a given spectral window between 425 and 450 nm. For that purpose, the reflectance spectrum is divided into a spectrally smooth part (broadband absorption and scattering), modeled by a polynomial, and a differential part from which NO₂ information is retrieved [Burrows *et al.*, 1999; Richter and Burrows, 2002; Boersma *et al.*, 2004]. The NO₂ SCD is interpreted as the NO₂ column density along the average photon path from the Sun through the atmosphere to the satellite instrument. This absolute column contains both stratospheric and tropospheric contributions. The stratospheric NO₂ SCD can be estimated from NO₂ columns over the remote Pacific Ocean with very low contamination from tropospheric NO₂, and is subtracted from the total NO₂ SCD assuming that stratospheric NO₂ does not vary with longitude. This technique is known as tropospheric excess or reference sector method [Richter and Burrows, 2002]. The resulting tropospheric NO₂ SCD can be converted to a tropospheric NO₂ vertical column density (VCD) through the application of the so-called air mass factor (AMF). The AMF corrects for the different sensitivity of the measurements to absorption in different altitudes, which is of particular importance for absorbers located close to the surface. As explained in detail by Richter and Burrows [2002] and summarized by Heland *et al.* [2002], the main sources of error in the AMF calculation are the assumptions made on the NO₂ vertical profile, the surface albedo and the aerosol loading. The calculation of AMF has been undertaken with the radiative transfer model SCIATRAN [Ročanov *et al.*, 1997], assuming a seasonally varying surface albedo [Koelemeijer *et al.*, 2003], urban aerosols, and vertical NO₂ profiles from a Model of Ozone and Related Tracers (MOZART) run [Horowitz *et al.*, 2003], with a spatial resolution of 2.8° × 2.8°. Monthly averaged AMF during 1997 are finally used for the retrieval of tropospheric NO₂ VCDs. Other sources of error in the NO₂ GOME retrieval are the uncertainties in cloud cover, which will be discussed later, and inhomogeneities in the

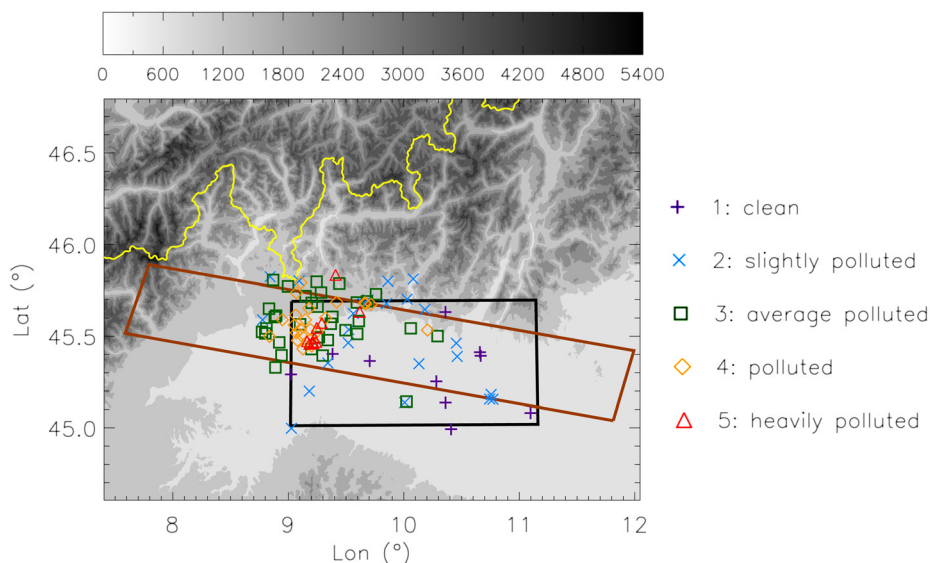


Figure 1. Location of the Lombardy ground stations used in the analysis. These stations have been grouped into five classes according to their mean NO₂ levels (see Table 1). The GOME pixels used in this analysis are centered in the area covered by the rectangle 45°–45.7°N, 9°–11.2°E (solid black lines). Brown lines show an example of a GOME footprint. The yellow line denotes the border between Switzerland and Italy. Grey scale represents altitude (m a.s.l.). The geographical coordinates of Milan are 45.47°N, 9.17°E.

stratospheric NO₂ field. For the retrieval of NO₂ VCDs over the Po basin, northern Italy, the most probable error sources or difference with the ground-based measurements averaged over the GOME scene are the large aerosol optical depth and fog frequently observed in the region, as well as the horizontal inhomogeneity within the area of a GOME pixel [Petritoli *et al.*, 2004]. More details of the retrieval of tropospheric NO₂ VCDs from GOME are given by Burrows *et al.* [1999] and Richter and Burrows [2002].

2.2. Surface Measurements

[8] Hourly average near-surface concentrations of NO₂ at around 150 sites of the Regional Agency for Environmental Protection (ARPA), Lombardy (<http://www.ambiente.regione.lombardia.it>), were used in this study. At these sites, nitrogen oxides (NO_x ≡ NO + NO₂) are measured using commercial instruments with molybdenum converters. NO₂ is catalytically converted to NO on a heated molybdenum surface and then measured as NO by chemiluminescence after reaction with ozone. The drawback of this technique is that other oxidized nitrogen compounds such as nitric acid (HNO₃), peroxyacetyl nitrate (PAN) and a variety of other organic nitrates are also partly converted [e.g., Winer *et al.*, 1974; Grosjean and Harrison, 1985; M. Steinbacher *et al.*, Nitrogen oxides measurements at rural sites in Switzerland: Bias of conventional measurement techniques, manuscript in preparation, 2006]. Therefore NO₂ measurements are often overestimated because of interferences, especially when measuring photochemically aged air masses. The correction of this effect will be discussed in section 3.1. One-hour average ground measurements during 1000–1100 UTC on days with a GOME overpass (~1030 UTC)

were used for the comparison with the tropospheric NO₂ VCDs retrieved from GOME.

3. Data Analysis and Results

[9] A careful analysis of the sensitivity of the satellite measurements to latitude and longitude in the Po basin revealed low NO₂ VCDs north of 45.7°N, and the influence of the orography (proximity of the Alps). In addition, seasonal changes in surface albedo in the Alpine areas (due to the presence or absence of snow) might influence the NO₂ retrieval at those latitudes. No significant dependence of the NO₂ VCDs on the longitude was observed. All GOME pixels centered in the area (45°–45.7°N, 9°–11.2°E) (see rectangle in Figure 1) were used in the analysis. For data analysis of the period 1996–2002, only stations with data coverage of more than 60% at the time of the GOME overpass were considered, totaling 99 stations.

[10] Data from a regional NO₂ network such as that of Lombardy needs to address adequately the spatial variability of the NO₂ field. A balance between interpretation, simplicity of approach, and incorporation of regional-scale information for increased statistical power is required. The mean or the median of the NO₂ concentrations from the ensemble of 99 stations can be compared with the tropospheric NO₂ VCDs from GOME. However, the horizontal heterogeneities in the distribution of pollution in the area are known to be significant [e.g., Dommen *et al.*, 2002; Andreani-Aksoyoglu *et al.*, 2004; Petritoli *et al.*, 2004]. In addition, many stations are located close to streets and are exposed to fresh emissions, so they are only representative of a small fraction of the GOME ground scene. For these reasons, we decided to group the 99 stations used in the

Table 1. Classification of the 99 Lombardy Stations Used in the Analysis^a

Class	Pollution Level	Number of Stations	Percentile Range	Average NO ₂ , ppb
1	clean	10	<10th	<18.58
2	slightly polluted	23	10th to 33rd	18.58–25.16
3	average polluted	33	33rd to 66th	25.16–34.80
4	polluted	23	66th to 90th	34.80–42.56
5	heavily polluted	10	>90th	>42.56

^aThese stations are grouped into five classes according to the percentiles of the distribution of the mean NO₂ levels from all stations between 1000 and 1100 UTC (the GOME overpass is at around 1030 UTC) during 1996–2002. See location of the stations in Figure 1.

analysis into 5 different pollution levels, class 1 (clean), class 2 (slightly polluted), class 3 (average polluted), class 4 (polluted) and class 5 (heavily polluted), according to the distribution of their mean NO₂ hourly levels between 1000 and 1100 UTC during the period of study, expecting not the average polluted stations but those with NO₂ levels in the low percentiles to be most representative for the whole GOME pixel. The range of NO₂ levels and locations of these stations are summarized in Table 1 and Figure 1. It should be noted that Lombardy is a rather polluted region where the NO₂ levels can be high even at the stations defined in this analysis as “clean.”

3.1. Comparison Between Tropospheric NO₂ VCDs From GOME Measurements and Ground-Based NO₂ Mixing Ratios

[11] Clouds limit the observation of trace gases below cloud top. In this analysis, we therefore focus on GOME measurements under cloud-free conditions. Cloud fraction was derived from GOME measurements with the Fast Retrieval Scheme for Clouds from the Oxygen A Band (FRESCO) algorithm [Koelemeijer *et al.*, 2001, 2002]. On average, for each day with a GOME overpass over the area of study, there were 2 GOME ground scenes in the rectangle of Figure 1. We selected the days on which the average cloud cover for those pixels was lower than a certain threshold. The tropospheric NO₂ VCDs of those ground scenes were averaged and compared to the median of the NO₂ concentrations for every group of stations at that time. The median rather than the mean of the NO₂ concentrations was chosen because it is less sensitive to concentration outliers, arising from local pollution events, that can occur at any station and at any time. The selection of the mean or the median of the measurements does not impact significantly on the results of the comparison and the subsequent conclusions (see section 3.2).

[12] Figure 2 shows a comparison of tropospheric NO₂ VCDs (molecules/cm²) from GOME with NO₂ mixing ratios (ppb) from in situ measurements at the ensemble of 99 stations. In general, less scatter in the data is observed when only measurements with a low cloud fraction (e.g., lower than 0.2, open triangles in Figure 2) are considered. The GOME signal is usually low in the presence of clouds (see some very low NO₂ VCDs for cloud fractions higher than 0.2, grey crosses in Figure 2), as the pollution below the clouds is shielded from the view of satellites (cloud shielding effect). However, low clouds or fog can also enhance the GOME sensitivity toward trace gases (cloud

albedo effect), as it will be explained in more detail in section 4.

[13] The tropospheric NO₂ VCDs are reasonably well correlated with the near-surface measurements under cloud-free conditions. However, the slope of the tropospheric NO₂ VCDs versus ground measurements is higher in autumn-winter than in spring-summer (see left panel of Figure 3). These slopes seem to be unreasonable since the low mixing heights in winter would be expected to possibly yield lower tropospheric columns versus ground measurements in comparison to summer. As already mentioned in section 2.2, the NO₂ ground measurements were performed with standard molybdenum converter instruments. These instruments are sensitive to other products of the NO_x oxidation such as PAN and HNO₃. As a consequence, the NO₂ measurements from these instruments represent an upper limit for the real NO₂ concentrations [Winer *et al.*, 1974; Grosjean and Harrison, 1985]. Although the thermal decomposition of PAN is strongly temperature dependent, during the warm season, overall the photochemistry leads to higher production of secondary pollutants than in autumn-winter, and consequently to a more pronounced overestimation of the NO₂ surface concentrations by ground measurements. This explains the lower slope of NO₂ VCDs versus NO₂ ground measurements observed in those months. Therefore, for a proper comparison, the interference of conventional NO_x analyzers toward other species needs to be taken into account.

[14] In this work the surface concentrations were corrected by using simultaneous measurements of NO₂ performed with a photolytic converter (highly specific technique for NO₂) and a molybdenum converter (sensitive

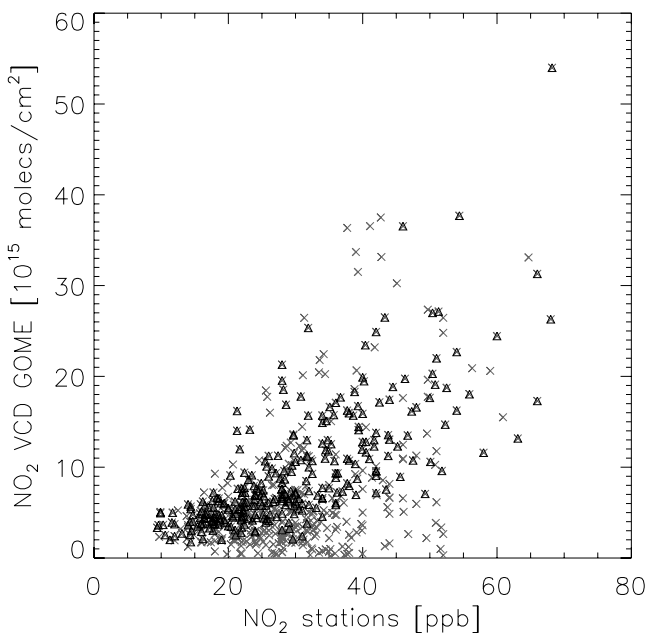


Figure 2. Tropospheric NO₂ VCDs (10¹⁵ molecules/cm²) from GOME versus the median of the NO₂ mixing ratios (ppb) from uncorrected in situ measurements at the ensemble of 99 stations. Open triangles represent the data points for days with cloud fraction lower than 0.2, while grey crosses are used for the rest of the days.

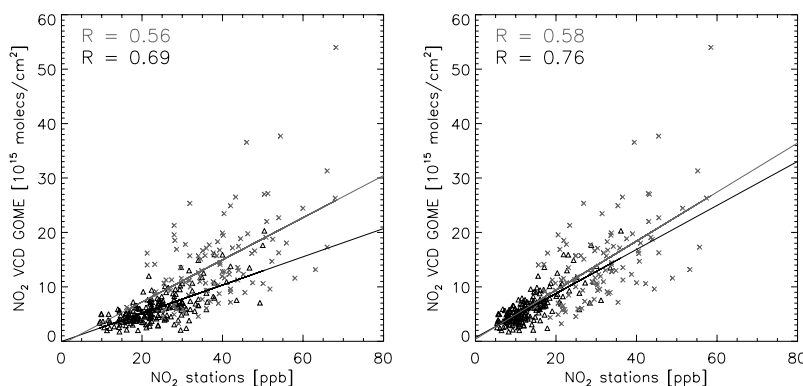


Figure 3. (left) Same as Figure 2 for cloud fraction lower than 0.2 (i.e., triangles from Figure 2). Data during winter-autumn are represented by grey crosses, while open triangles are used for the spring-summer months. (right) Same as left panel after correcting the ground-based NO₂ measurements for the interference of conventional NO_x analyzers toward PAN, HNO₃, and other interfering species.

to other species) at the rural site Tännikon (47.47°N, 8.90°E, 540 m a.s.l.), Switzerland, during the period 1995–2001. The ratio

$$r = \frac{NO_2(\text{photolytic})}{NO_2(\text{molybdenum})} \quad (1)$$

was calculated under cloud-free conditions at the time of the GOME overpass. Only hourly NO₂ concentrations between 1000 and 1100 UTC with a sunshine duration of at least 0.8 (80% of the time with direct solar radiation exceeding the level of 120 W/m²) at the ANETZ (network of automatic stations of MeteoSwiss) station in Tännikon were considered to calculate correction ratios. The monthly medians of r (see Table 2) are lower during the warm season compared to autumn-winter, as expected. Although there is a lack of measurements of NO₂ with photolytic converters in Lombardy, simultaneous measurements of NO_x and total reactive nitrogen, NO_y (sum of NO_x and its oxidation products), from a field campaign in the Lombardy region [Thielmann *et al.*, 2002] indicate that this factor might be somewhat underestimated in the spring-summer months. However, those measurements were conducted only from May to July 1998 and cannot be considered representative enough. Therefore we decided to use the ratios calculated for Tännikon to estimate corrected NO₂ concentrations at the Lombardy stations. The potential errors resulting from this assumption will be further discussed in section 4. The NO₂ mixing ratios at the ground stations in Lombardy were multiplied by the corresponding monthly median of r , which reduced the difference in the slopes of tropospheric NO₂ VCDs from GOME versus ground measurements between autumn-winter and spring-summer (see right panel of Figure 3). The correlation between the two data sets was also improved by the use of corrected NO₂ concentrations.

3.2. Calculation of Tropospheric NO₂ VCDs From Ground Measurements and Comparison With Tropospheric NO₂ VCDs From GOME

[15] For a more quantitative comparison of ground based data with the tropospheric VCDs from GOME, NO₂ mixing ratios measured at the surface have to be scaled to NO₂

VCDs by assuming the vertical profiles of NO₂ in the region. In this work daily NO₂ vertical profiles up to ~10,300 m a.s.l. from the chemical transport model MOZART-2, which has a spatial resolution of 2.8° × 2.8°, were used. The profiles were calculated for ~1000 UTC in 1997. Although the MOZART NO₂ vertical profiles with their center at (46.41°N, 9.84°E) are the closest ones to the area considered in this study, those profiles start at an altitude of ~1080 m a.s.l., considerably higher than the Po basin, because of the presence of the Alps in the pixel. As a consequence, MOZART profiles centered at (43.59°N, 9.84°E) were used for this study.

[16] Daily NO₂ VCDs from the surface to 20 tropospheric levels (up to ~10,300 m a.s.l.) were first calculated from MOZART data. Those VCDs were then normalized by dividing them by the NO₂ concentration given by the model for the lowest level (30 m a.s.l.). Figure 4 (left panel) shows a normalized cumulative profile of NO₂ VCDs under cloud-free conditions (average of all days in 1997 with sunshine duration higher than 0.80 at Stabio, southern Switzerland, 45.85°N, 8.93°E, 353 m a.s.l.). More than 80% of the NO₂ amounts within the tropospheric VCDs are found in the lowest 1000 m on average for the whole year, while Martin *et al.* [2004] found that during summer nearly 75% of the

Table 2. Monthly Medians of the Ratio of NO₂ Measurements Performed With Photolytic and Molybdenum Converters at Tännikon, Switzerland, Under Clear-Sky Conditions (Sunshine Duration of at Least 0.8) From 1000 to 1100 UTC During the Period January 1995 to Mid-August 2001

Month	Median Ratio
January	0.858
February	0.844
March	0.734
April	0.576
May	0.500
June	0.485
July	0.507
August	0.573
September	0.717
October	0.779
November	0.843
December	0.837

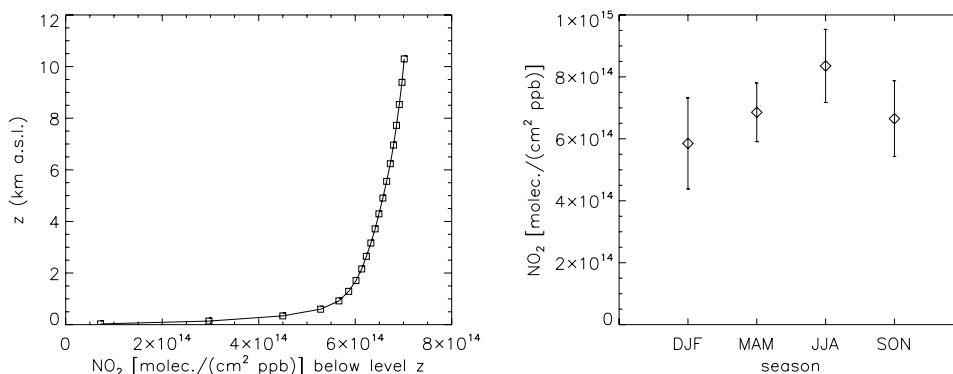


Figure 4. (left) Average cumulative profile of NO₂ VCDs (molecules/cm²) from the ground up to ~10,300 m a.s.l., normalized by the NO₂ mixing ratio (ppb) on the ground, as calculated by the MOZART-2 model for ~1000 UTC of all days in 1997 under cloud-free conditions (sunshine duration higher than 0.8 at Stabio, southern Switzerland). (right) Seasonal averages of the normalized NO₂ VCDs (molecules/(cm² ppb)) below ~10,300 m a.s.l. from MOZART under cloud-free conditions in 1997. The seasons are defined as follows: winter (DJF), spring (MAM), summer (JJA), and autumn (SON). Uncertainty estimates represent 95% confidence intervals. The NO₂ value given in the left panel for ~10,300 m a.s.l. and the four NO₂ values (rhombuses) from the right panel respectively correspond to the yearly and seasonal averages of the NO₂ VCDs (molecules/cm²) below 10,300 m a.s.l. calculated from a MOZART-2 run, divided by the NO₂ mixing ratios (ppb) given by the model for the lowest level. These so-called normalized NO₂ VCDs (molecules/(cm² ppb)) can therefore be multiplied by the NO₂ mixing ratios (ppb) measured at the Lombardy stations to calculate the final tropospheric NO₂ VCDs (molecules/cm²) from ground-based measurements.

tropospheric NO₂ VCD is below 1500 m over Houston and Nashville, USA. Seasonally averaged normalized profiles of NO₂ VCDs below ~10,300 m a.s.l. (see right panel of Figure 4) were used to scale near-surface NO₂ mixing ratios to tropospheric NO₂ VCDs. For each GOME overpass, the median of the NO₂ mixing ratios at each group of stations (corrected by the factor r from equation (1)) was multiplied by the corresponding seasonal factor from Figure 4 (right panel). Although there is high variability in the daily NO₂ VCDs below ~10,300 m a.s.l. (see high uncertainty estimates for the seasonally averages of the normalized NO₂ VCDs in the figure), the results suggest that the highest values of the VCDs versus ground mixing ratios occur in summer and the lowest in winter. This was expected since significant amounts of NO₂ can be found at high levels in summer as a result of the enhanced vertical mixing during the warm season, while NO₂ is usually confined to the lowest levels in winter because of the suppressed vertical mixing in that season.

[17] Calculations using MOZART profiles centered at (46.41°N, 9.84°E) reveal that on average these profiles have a very similar shape to that of the profiles with the center at (43.59°N, 9.84°E) which have been used in this analysis. The relative difference between the contributions of both profiles to the total column varies from 4% to 9% depending on the season. As NO₂ is produced mainly close to the surface, the differences in the vertical profiles for cloud-free scenes are determined by the vertical transport and chemical lifetime. In summary, the profiles with center at (43.59°N, 9.84°E) can be considered as representative for the area of analysis.

[18] For the final comparison of tropospheric NO₂ VCDs from GOME and from ground-based measurements at the five groups of stations, a stringent approach was chosen that

considered only days with average cloud fraction (derived from FRESCO) lower than 0.1 in the area of study, similarly to *Petritoli et al.* [2004]. The sunshine duration from 1000 to 1100 UTC at Stabio, which was used in this study to select cloud-free days in 1997 for the calculation of the normalized cumulative vertical profiles of NO₂, is 0.88 hours on average for cloud fractions lower than 0.1. The regression line of NO₂ VCDs from satellite versus NO₂ VCDs from ground measurements was calculated for the five groups of stations. Since both data sets have measurement uncertainties, ordinary least squares is not appropriate because it only minimizes the vertical distances of the data points to the linear regression line (y direction) and underestimates the true slope of the regression line [*Riggs et al.*, 1978]. A weighted orthogonal regression [*York, 1966*], which considers the error in both measurements and minimizes the distance in both y and x directions, was used instead. As the individual errors in the measurements were unknown, the error variances (needed in the orthogonal regression analysis) were estimated by the sample variances of both variables; that is, we assumed that the variability in the measured variables is also the variability in their errors. This is the most common approach used in orthogonal regression analysis when the individual errors in all the data points (and therefore the error variances) are not known. These estimated uncertainties were accounted for by a weighted line fit described by *Press et al.* [1992], and were used to calculate the uncertainty of the regression slopes and intercepts.

[19] The results from the regression analysis can be seen in Figure 5. In addition, Table 3 summarizes the average difference of tropospheric NO₂ VCDs calculated from near-surface measurements ($VCD_i^{stations}$) with respect to NO₂ VCDs retrieved from GOME measurements (VCD_i^{GOME})

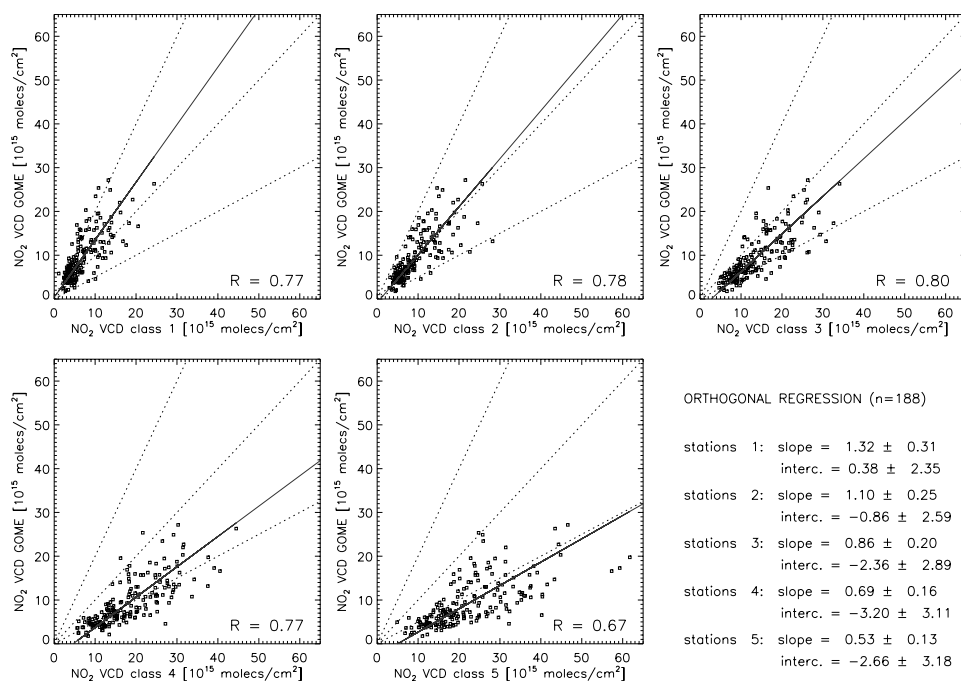


Figure 5. Tropospheric NO₂ VCDs from GOME versus tropospheric NO₂ VCDs from near-surface measurements (at the five groups of stations defined in Table 1) for 188 days under cloud-free conditions (cloud fraction lower than 0.1) during 1996–2002. Dotted lines represent the 1:2, 1:1, and 2:1 lines. The slopes and intercepts of the orthogonal regression lines are given together with their 95% confidence intervals.

under different conditions, which will be described in the text:

$$\bar{d} = \text{mean}(VCD_i^{\text{stations}} - VCD_i^{\text{GOME}}) \quad (2)$$

Most of the data points fall within the 1:2 line and the 2:1 line for the first, second and third group of stations, defined as “clean,” “slightly polluted” and “average polluted.” As expected, the best quantitative correspondence is not found for the average polluted stations but for the slightly polluted stations, with a slope close to 1, a high correlation ($R = 0.78$) and small average deviation with respect to NO₂ VCDs from GOME (see values of \bar{d}_1 in Table 3). Lower slopes and higher \bar{d}_1 values are observed for the most polluted stations. As a result of the spatial inhomogeneity in the distribution of pollution within the GOME footprint ($320 \times 40 \text{ km}^2$), it was expected that the satellite-retrieved NO₂ VCDs will not reproduce the high tropospheric NO₂ VCDs calculated from those polluted sites. In general, there is also an offset for low VCDs. In most of the cases intercepts are negative and relatively high (in absolute value), although the large 95% confidence intervals indicate high uncertainties in the calculation of these intercepts.

[20] Very similar results from the comparisons are obtained if the mean instead of the median (base case) of the NO₂ surface concentrations is used to represent the ground-based network data, the relative difference (in absolute value) in their slopes and correlation coefficients being on average lower than 1% and 1.4%, respectively, and the average deviations with respect to GOME (\bar{d}_2) slightly different from those of the base case (compare values of \bar{d}_2 and \bar{d}_1 in Table 3).

3.3. Yearly and Weekly Cycles of Tropospheric NO₂ VCDs

[21] We used both the GOME measurements and the in situ measurements at the second group of stations (slightly polluted, i.e., sites which showed the best agreement with GOME in terms of absolute tropospheric NO₂ VCDs) to

Table 3. Average Difference \bar{d} of the Tropospheric NO₂ VCDs Calculated From Near-Surface Measurements VCD_i^{stations} With Respect to the Tropospheric NO₂ VCDs Retrieved From GOME Measurements $VCD_i^{\text{GOME a}}$

Class	Pollution Level	Number of Stations	\bar{d}_1^b	\bar{d}_2^c	\bar{d}_3^d	\bar{d}_4^e
1	clean	10	-2.50	-2.50	-3.20	-2.60
2	slightly polluted	23	0.00	0.35	-1.00	-0.20
3	average polluted	33	4.25	4.64	2.72	3.95
4	polluted	23	8.72	9.09	6.65	8.31
5	heavily polluted	10	13.1	12.9	10.40	12.60
All stations		99	4.27	5.14	2.72	3.96

^aData from 188 days ($i = 1, 2, \dots, 188$) under cloud-free conditions (cloud fraction lower than 0.1) during 1996–2002 have been used for the calculation of \bar{d} . Units are 10^{15} molecules/cm².

^bThe base case. The median of the NO₂ mixing ratios at the different stations has been used to calculate tropospheric NO₂ VCDs from ground-based measurements. The correction factor r has been calculated from measurements at Tänikon, Switzerland (see values of r in Table 2). The NO₂ vertical profiles correspond to MOZART-2 outputs with center at (43.59°N, 9.84°E).

^cVariation with respect to the base case \bar{d}_1 in which the mean instead of the median of the NO₂ mixing ratios was used.

^dVariation with respect to the base case \bar{d}_1 using a value of r linearly varying with the month (see section 4).

^eVariation with respect to the base case \bar{d}_1 using MOZART NO₂ vertical profiles with center at (46.41°N, 9.84°E).

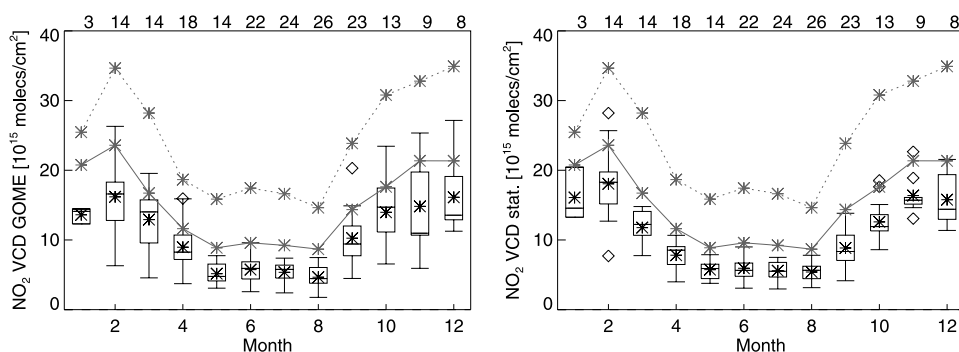


Figure 6. Yearly evolution of (left) tropospheric NO₂ VCDs from GOME and (right) tropospheric NO₂ VCDs from near-surface measurements at the second group of stations, under cloud-free conditions (cloud fraction lower than 0.1) for days with GOME overpass over Lombardy during 1996–2002. Each box depicts the central half of the data between the lower quartile ($q_{0.25}$) and the upper quartile ($q_{0.75}$). The line across the box displays the median value ($q_{0.5}$), and the star represents the mean. The whiskers extend from the top and the bottom of the box to depict the extent of the main body of the data. Extreme data values are plotted with rhombuses. The average annual cycles of the tropospheric NO₂ VCDs calculated from the measurements both at the ensemble of 99 stations and at the heavily polluted stations (class 5) are also plotted as solid grey lines and dotted grey lines, respectively. The numbers in the upper part of the plots refer to the number of cloud-free days considered for each month in the whole period.

examine the yearly and weekly variation in tropospheric NO₂ over Lombardy.

[22] The tropospheric NO₂ VCDs retrieved from both satellite and ground-based measurements show the expected annual evolution, with low NO₂ in warm summer conditions compared to the colder months (see Figure 6). This seasonality is mainly linked to the chemistry of the hydroxyl radical (OH) and the photolysis frequency of NO₂. The primary source of OH radicals is the photolysis of O₃ and other species like nitrous acid (HONO) and aldehydes. At midlatitudes the strongest actinic fluxes are found in summer, leading to both high OH production rates [e.g., Wang *et al.*, 1998; Jacob, 2003] and high NO₂ loss by photolysis, and consequently to a reduced NO₂ lifetime. The increase in emissions during the cold months (~14% more NO_x emitted in Lombardy during winter than during summer, according to the emission inventory), caused by residential heating, can also contribute to the high tropospheric NO₂ amounts observed for those months.

[23] Comparing tropospheric NO₂ VCDs in August with data from the other summer months (June–July), a general decrease during August can also be noted for the GOME data set. Although that decrease is significant at the 98% confidence level, no significant decrease (at 95%) in August is found for NO₂ VCDs calculated from ground-based data. Nonetheless, the NO₂ mixing ratios in August are significantly lower than those from June–July for all the groups of stations except for group 1 (“clean”). The correction factor r calculated from measurements at Tänikon is higher in August than in June–July (see Table 2) and compensates for the low NO₂ levels measured in August. As a consequence, the “vacation effect” is not so evident when considering tropospheric NO₂ VCDs calculated from ground-based data (Figure 6, right panel).

[24] The low tropospheric NO₂ amounts retrieved from GOME and the low NO₂ mixing ratios measured at most stations in August are attributed to the decrease in traffic and industrial activities during the summertime holidays, which in Italy are traditionally taken in August. Vecchi *et al.*

[2004] already observed a decrease in the PM₁ and PM_{2.5} concentrations as well as a strong reduction in some elements such as Fe, Zn and Pb (tracers of both industrial processes and traffic) in the greater urban area of Milan during August, and attributed it to the “vacation effect.”

[25] Low tropospheric NO₂ VCDs on Sundays with respect to the rest of the days of the week can be seen in both data sets (see Figure 7) although only 6 cloud-free Sundays were selected in the analysis. As 4 out of those 6 days are summer days, those low VCDs on Sundays might be biased by the fact that the VCDs are also low in summer. Nevertheless, the same result, i.e., low NO₂ VCDs on Sundays compared to other days, is observed when cloud fractions higher than 0.1 are considered in the analysis, yielding more Sundays which are evenly distributed throughout the year (not shown). The reduced industrial activity and traffic in western countries during weekends, leading to lower levels of emitted pollutants (“weekend effect”), have been widely described in the literature, with especial attention to the influence on the surface ozone formation [e.g., Cleveland and McRae, 1978; Brönnimann and Neu, 1997; Jenkin *et al.*, 2002]. Moreover, Beirle *et al.* [2003] already used tropospheric NO₂ VCDs from GOME measurements to show a clear weekly cycle with a noticeable Sunday minimum in western industrialized areas, including Milan. Overall, the results of our analysis are also consistent with the findings of Steinbacher *et al.* [2005] for the same region. They found low toluene concentrations as well as low toluene to benzene ratios on weekends compared to weekdays and during August compared to July and September, as a consequence of lower anthropogenic emissions due to less traffic and reduced industrial activities.

4. Error Discussion

[26] In general, the most important sources of error in the tropospheric NO₂ retrieval from GOME data result from the assumptions in the calculation of the AMF (i.e., assumed

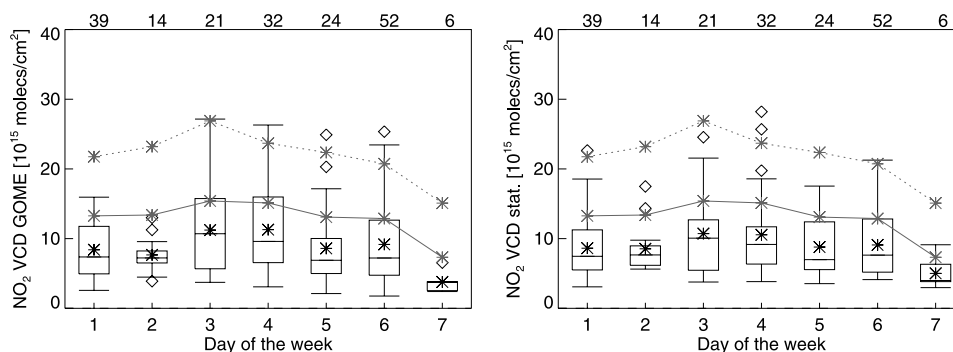


Figure 7. Weekly evolution of (left) tropospheric NO₂ VCDs from GOME and (right) tropospheric NO₂ VCDs from near-surface measurements at the second group of stations, under cloud-free conditions (cloud fraction lower than 0.1) for days with GOME overpass over Lombardy during 1996–2002. Same symbols are used as in Figure 6. The average weekly cycles of the tropospheric NO₂ VCDs calculated from the measurements both at the ensemble of 99 stations and at the heavily polluted stations (class 5) are also plotted as solid grey lines and dotted grey lines, respectively.

vertical profile of the absorber, surface albedo and aerosol loading) and uncertainties in cloud cover. For a detailed analysis of errors, we refer to *Boersma et al.* [2004]. As already mentioned by *Petritoli et al.* [2004], for GOME measurements over the Po valley, two of the most important error sources are the large aerosol optical depth and fog, which are frequently observed in the area and are not properly taken into account in the analysis. In order to investigate possible bias due to aerosols, we investigated the influence of two aerosol parameters on GOME measurements: namely the aerosol optical thickness (AOT) at 440 nm, measured at the AERONET station in Ispra (45.8°N, 8.6°E), and the median of the total suspended particulate (TSP) concentrations measured at a group of average polluted stations from the ARPA network of the Lombardy region. Again, only measurements of the aerosol parameters at around the time of the GOME overpass (1000–1100 UTC) and under cloud-free conditions (FRESCO cloud fraction lower than 0.1 or 0.2) were used. The AOT data at Ispra did not allow us to draw any conclusion on the influence of aerosols on GOME measurements, partly because of the lack of enough simultaneous measurements of AOT and GOME. In addition, Ispra is located in the northwest of the studied area and is not necessarily a representative site for the Lombardy region.

TSP data were not very enlightening either. High tropospheric NO₂ VCDs (both from GOME and from the Lombardy stations) and high NO₂ mixing ratios (at the Lombardy stations) were observed for high values of TSP. This is due to the fact that NO₂ and TSP are correlated: high (low) levels of both TSP and NO₂ are usually registered under polluted (clean) situations. Moreover, the uncertainties in both the GOME and the surface measurements as well as in the calculation of VCDs make it difficult to assess the influence of those aerosol parameters in our analysis.

[27] As mentioned in section 3.1, cloud fraction selection is also important for a proper comparison between satellite-borne and ground-based data. In the presence of clouds, normally a low GOME signal occurs as the pollution below the clouds is shielded from the view of satellites (cloud shielding effect). However, there is also a systematic overestimation at small and intermediate cloud fractions. Clouds are bright and enhance the sensitivity toward trace gases directly above the cloud compared to that for a clear sky scene with a low ground albedo (cloud albedo effect). As an example, Figure 8 depicts the relationship between tropospheric NO₂ VCDs from GOME and from slightly polluted stations for different cloud fractions, CF. The optimal situation takes place for low cloud fractions (CF < 0.1, Figure 8, left panel). Some enhanced GOME measurements

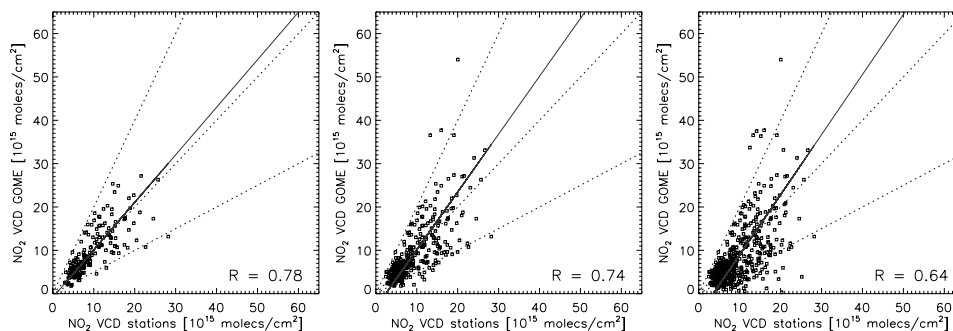


Figure 8. Tropospheric NO₂ VCDs from GOME versus tropospheric NO₂ VCDs from near-surface measurements at slightly polluted stations (class 2) during 1996–2002 under different cloud fractions: (left) CF < 0.1, (middle) CF < 0.25, and (right) CF < 0.6. The orthogonal regression fits are depicted by solid lines. Dotted lines represent the 1:2, 1:1, and 2:1 lines.

are already observed for $CF < 0.25$ (see some data points close to the 2:1 line in Figure 8, middle panel, cloud albedo effect), while the underestimation in GOME measurements occurs more often when high cloud fractions are included in the analysis (e.g., $CF < 0.6$, see data points below the 1:2 line in Figure 8, right panel, cloud shielding effect). Both effects have already been discussed in the literature [e.g., Richter and Burrows, 2002; Wagner *et al.*, 2003].

[28] The NO₂ ground measurements used in this study, performed with molybdenum converter, have been corrected for cross-sensitivity toward PAN and other species. For that purpose we have used simultaneous molybdenum and photolytic converter measurements at Tänikon, northern Switzerland. Tänikon is located in a different area, with lower NO₂ levels and different photochemical conditions than those in Lombardy. Continuous measurements of NO_x and NO_y at Verzago, a rural site in Lombardy, during the PIPAPO field campaign in spring-summer 1998 [Thielmann *et al.*, 2002], suggest values of the ratio r lower than those derived from Tänikon data. The NO₂/(NO_y - NO) ratio measured during PIPAPO was ~ 0.35 , while the value of r used in our analysis for the same months is close to 0.5. Nonetheless, NO₂ measurements performed with molybdenum converter might have lower values than the (NO_y - NO) measured in that campaign, yielding ratios higher than 0.35. We have performed several sensitivity analyses of the influence of r on this comparison. As an example, we used a value of 0.35 for both June and July (similar to the mentioned results from the PIPAPO field campaign), a value of 0.9 in December and January (higher than the corresponding values calculated from Tänikon data), and interpolations between these values of r linearly decreasing between January and June as well as linearly increasing between July and December. In this particularly extreme case, the second group of stations still yields the best comparison with the tropospheric NO₂ VCDs retrieved from GOME (see values of \bar{a}_3 in Table 3). On average for the five groups of stations, the new slopes and correlation coefficients calculated with this method differ (in absolute value) from those ones of the base case by around 1%.

[29] The uncertainty due to the correction of the ground-based measurements is less important than the possible errors due to the assumed seasonal NO₂ vertical profile from MOZART (see high uncertainties in right panel of Figure 4) that was used in the calculation of VCDs from ground-based data. As a result of the high variability in the daily and monthly NO₂ profiles from MOZART (not shown), seasonally averaged modeled vertical profiles of NO₂ were selected. Although in the base case we used the vertical profiles centered at (43.59°N, 9.84°E), we also repeated the analysis using profiles with the center at (46.41°N, 9.84°E), with an altitude of ~ 1080 m a.s.l., including a major fraction of the Alps. No significant differences in the results when using the northern profile were observed, the second group of stations having the best agreement with GOME VCDs (see values of \bar{a}_4 in Table 3). The differences (in absolute value) in slopes and correlation coefficients with respect to those of the base case are on average lower than 5% and 1%, respectively. The contribution to the total NO₂ column given by the northern profile is in general a bit lower than that one of the southern profile, yielding somewhat lower tropospheric NO₂ VCDs than in

the base case, except in spring. It is difficult to assess whether the errors of the calculated vertical columns are larger or smaller in the GOME retrieval of tropospheric NO₂ VCDs or in the extrapolation of the ground measurements to tropospheric VCDs. The resolution of MOZART is rather coarse ($2.8^\circ \times 2.8^\circ$) and as such models improve one source of systematic error will be reduced in the future. The day-to-day variability in the NO₂ vertical profiles and the horizontal inhomogeneity in the distribution of pollution within the GOME footprint (320×40 km²) remain as systematic sources of difference between the two data sets.

5. Conclusions

[30] GOME measurements of tropospheric NO₂ have been compared to simultaneous near-surface measurements of NO₂ in the Lombardy region, northern Italy, during the period 1996–2002. The in situ measurements, which partly span the satellite footprint at surface level, were corrected for the interference of the NO₂ monitors (equipped with molybdenum converter) to other species. The majority of the networks that have been established for air pollution monitoring also measure NO₂ using commercial molybdenum converter instruments. Measurements of these networks may become valid ancillary information for the validation of spaceborne measurements of NO₂ and other species. This study has shown for NO₂ that the influence of interfering compounds on ground-based measurements is an important issue for a proper validation of satellite data.

[31] The surface measurements have been scaled to tropospheric NO₂ VCDs by using NO₂ vertical profiles from the MOZART-2 model. The modeled profile yields tropospheric NO₂ VCDs with more than 80% of the NO₂ amounts accumulated within the lowest 1000 m, on average for the whole year. Good agreement is found between the tropospheric NO₂ VCDs retrieved from satellite and those determined from ground-based measurements under cloud-free conditions. The agreement is good both in correlation and in the magnitude of the tropospheric NO₂ VCDs, with a slope close to 1 when slightly polluted stations (class 2) are considered. The best comparison is not found for the average polluted stations (class 3) but it is shifted to the slightly polluted stations. A possible explanation for this might be that most of the Lombardy stations are located in polluted places and thus do not represent the average pollution in the area. As a result of the large horizontal variability of NO₂ within the GOME footprint (320 km \times 40 km), GOME measurements cannot reproduce the high NO₂ VCDs calculated from the most polluted stations (class 5). In addition, the modeled vertical profile of NO₂ and aerosols, used for the AMF calculations in the GOME retrieval, averages over a large area and might not be appropriate over the most polluted part of the area. The fact that most of the NO₂ amounts are accumulated in the lowest levels, as seen from the MOZART vertical profile of NO₂, and that there is good agreement between the NO₂ measurements from GOME and from ground-based stations, demonstrates well the ability of GOME to detect pollution within the PBL.

[32] We have compared the yearly and weekly cycles of the tropospheric NO₂ VCDs retrieved from GOME measurements with those determined from surface measure-

ments. Similar temporal evolution is found for both data sets, the lowest tropospheric NO₂ VCDs being in summer and on Sundays, respectively. This shows the reliability of tropospheric NO₂ VCDs obtained by measurements from space.

[33] Despite the uncertainties discussed in section 4, this study has shown that GOME is able to detect tropospheric NO₂ with reasonable accuracy over a polluted area such as the Lombardy region under cloud-free conditions. This justifies the use of tropospheric NO₂ data from GOME, the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY), and subsequently GOME-2 for analyses of changing concentrations and also for comparison between different source regions. The spatial resolution of satellite-derived NO₂ VCDs has improved with the mentioned SCIAMACHY instrument (60 × 30 km² spatial resolution) on board the ENVISAT satellite [Burrows *et al.*, 1995; Bovensmann *et al.*, 1999; Richter *et al.*, 2004], and OMI (24 × 13 km²) on AURA [Levelt *et al.*, 2000]. In this sense, the spatial variability of NO₂ can now be better resolved, increasing the potential for similar comparisons of satellite-derived NO₂ VCDs with in situ (ground-based or aircraft-borne) measurements of NO₂ over polluted areas such as Lombardy or over areas with rougher topography than this region. This will also allow for a larger fraction of cloud-free pixels available for the analysis of the spatial distribution of tropospheric NO₂ and the estimation of emissions both in polluted and remote areas.

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