First comparison between ground-based and satellite-borne measurements of tropospheric nitrogen dioxide in the Po basin

Andrea Petritoli,[1] Paolo Bonasoni,[1] Giorgio Giovanelli,[1] Fabrizio Ravegnani,[1] Ivan Kostadinov,[1,2] Daniele Bortoli,[1] Andrea Weiss,[3] Daniel Schaub,[3] Andreas Richter,[4] and Francesco Fortezza[5]

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[1] In this paper we present in situ and tropospheric column measurements of NO_2 in the Po river basin (northern Italy). The aim of the work is to provide a quantitative comparison between ground-based and satellite measurements in order to assess the validity of spaceborne measurements for estimating NO_2 emissions and evaluate possible climatic effects. The study is carried out using in situ chemiluminescent instrumentation installed in the Po valley, a UV/Vis spectrometer installed at Mount Cimone (44.2°N, 10.7°E, 2165 m asl), and tropospheric column measurements obtained from the Global Ozone Monitoring Experiment (GOME) spectrometer. Results show that the annual cycle in surface concentrations and also some specific pollution periods observed by the air quality network are well reproduced by the GOME measurements. However, tropospheric columns derived from the surface measurements assuming a well-mixed planetary boundary layer (PBL) are much larger than the GOME columns and also have a different seasonal cycle. This is interpreted as indication of a smaller and less variable mixing height for NO_2 in the boundary layer. Under particular meteorological conditions the agreement between UV/Vis tropospheric column observations and GOME measurements in the Mount Cimone area is good ($R^2 = 0.9$) with the mixing properties of the atmosphere being the most important parameter for a valid comparison of the measurements. However, even when the atmospheric mixing properties are optimal for comparison, the ratio between GOME and ground-based tropospheric column data may not be unity. It is demonstrated that the values obtained (less than 1) are related to the fraction of the satellite ground pixel occupied by the NO_2 hot spot. *INDEX TERMS:* 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0360 Atmospheric Composition and Structure: Transmission and scattering of radiation; *KEYWORDS:* tropospheric NO_2, satellite validation, Po basin

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1. Introduction

[2] Atmospheric odd nitrogen ($NO_x = NO + NO_2$) is an important tropospheric constituent from both chemical and energetic points of view. It is produced by human activity through fossil fuel combustion and soil emission due to the use of fertilizers (through the oxidation of ammonia). The primary source of NO_x is NO which, in the troposphere, reacts rapidly with ozone to create NO_2 and reaches a photostationary equilibrium governed by the following reactions:

$$\text{(R1a)} \qquad NO + O_3 \rightarrow NO_2 + O_2$$

$$\text{(R1b)} \qquad NO_2 + h\nu \rightarrow NO + O \qquad \lambda \leq 420 \text{ nm}$$

$$\text{(R1c)} \qquad O + O_2 + M \rightarrow O_3 + M.$$

Reactions (1a)–(1c) make up a null cycle both for NO_x and ozone, but odd nitrogen can also participate in other chemical processes which determine the concentration of tropospheric O_3 such as all the possible cycles involving volatile organic compounds (VOCs). When formaldehyde,

[1]Institute of Atmospheric Science and Climate, ISAC-CNR, Bologna, Italy.
[2]Also at Bulgarian Academy of Science, BAS-STIL, Stara Zagora, Bulgaria.
[3]Swiss Federal Laboratories for Materials Testing and Research, EMPA, Dübendorf, Switzerland.
[4]Institute of Environmental Physics, University of Bremen, Bremen, Germany.
[5]Regional Agency for Environmental Protection, ARPA, Bologna, Italy.

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benzene and other VOCs are emitted in the planetary boundary layer (PBL) and transported into the free troposphere in the presence of solar radiation they can activate an oxidation cycle which results in the formation of ozone from the combustion of the VOCs. The role of the NO_x in such processes is mainly that of supplying the oxygen atom through reaction (1b). On the other hand, the main reservoir for the NO_2 species in the troposphere, HNO_3, is produced by the reaction of nitrogen dioxide with the hydroxyl radical (OH), one of the main compounds which start the ozone production cycle with VOCs [*Ridley and Atlas*, 1999]. The chemical role of NO_x can thus be ambivalent with respect to the ozone balance in the troposphere and its study is essential to understand tropospheric ozone measurements as well as the lifetimes of the primary pollutants.

[3] Recent studies have also investigated the potential of NO_2 in absorbing solar radiation. The nitrogen dioxide absorption cross section has in fact its maximum in the visible region. *Solomon et al.* [1999] have observed that, during particular days when combined effects of pollution and production in convective clouds create very high values of NO_2 concentration, the incoming solar radiation can be reduced at the ground by about 5–12%. This was estimated to produce a radiative forcing of 2–10 W/m^2 which is quite remarkable when compared, for instance, with the warming effect of the most important greenhouse gas, CO_2, estimated at 1.4 W/m^2 [*Intergovernmental Panel on Climate Change* (*IPCC*), 2001]. The reason for the limited scientific interest in the tropospheric NO_2 climatic role so far is the timescales and space scales of such phenomena, usually considered to be confined to industrialized areas and with relatively short lifetimes due mainly to dispersion and wet or dry removal by the troposphere.

[4] Recent developments in satellite-borne instrumentation and data retrieval techniques show the need for more detailed studies. The first tropospheric NO_2 column measurements on a global scale were provided by the Global Ozone Monitoring Experiment (GOME) spectrometer [*Burrows et al.*, 1999] on board the ESA ERS-2 platform by removing the stratospheric signal calculating the difference between total columns in polluted and unpolluted regions [*Richter and Burrows*, 2002; *Leue et al.*, 2001; *Martin et al.*, 2002]. The advantage of satellite measurements lies in the possibility of studying the horizontal distribution of pollution. "Pollution hot spots," i.e., relatively high NO_2 concentrations spreading over industrialized regions can be observed by satellites. Such observations are limited by the horizontal and temporal resolution (320 × 40 km^2 and global coverage in 3 days, respectively). The resolution has already partly been improved for the recently launched SCIAMACHY instrument on ENVISAT [*Bovensmann et al.*, 1999], future spaceborne missions such as OMI on AURA [*Stammes et al.*, 1999], and GOME-2 will provide even more detail.

[5] The two major results from these new measurements are as follows: (1) Tropospheric NO_2 hot spots can spread over large areas for several days [*Leue et al.*, 2001; *Velders et al.*, 2001]. (2) Transport over long distances has been reported [*Wenig et al.*, 2003] by measurements and confirmed also by back trajectory calculations [*Stohl et al.*, 2003; *Spichtinger et al.*, 2001].

[6] The information obtained from satellite measurements could then be used for chemical and climatic studies on a regional scale, quantifying in a more accurate way the extent of the hot spots. However, considering a recent comparison with chemical models [*Lauer et al.*, 2002] reporting differences from the observations of up to 300%, validation by independent measurements is required.

[7] In order to compare satellite and ground-based NO_2 data, one of the most interesting geographical areas is the Po valley region, in northern Italy. In this area, where the orographic characteristics (a basin delimited by the Alps to the north and west and by the Apennines to the south) favor the buildup of pollutants and the stagnation of air masses, the NO_x emission is among the highest worldwide due to both natural and anthropogenic sources. Besides the emissions from industry and traffic, there are also emissions from the ground in the rural areas of the Po basin due to fertilizers. *Kessel et al.* [1992] estimated this flux of NO to be of the order of 6.5 n mol m^{-2} s^{-1} corresponding to a concentration of the order of 10^3 n mol m^{-3} (about 10^{12} molec/cm^3 or 80 ppbv). Since 1992 the trend in NO_2 emissions started to decrease due, in part, to the Göteborg protocol, and there has been a net reduction of about 25% between 1992 and 1999 [*Bini et al.*, 2002], but concentrations still remain very high and the question to be answered is whether and in which ways such an excess of NO_2 can interact with the regional climate. The transport of polluted air masses away from their sources is the second issue on which satellite measurements can produce significant improvements in our knowledge. The tropospheric chemical equilibrium can be modified by transported pollutants, and this makes regional pollution an issue to be dealt with on a larger scale. Spaceborne observations are an interesting additional source of information especially for their large spatial coverage. The Po valley has been shown to be both a source and a sink of NO_x pollution with respect to central Europe. *Camuffo et al.* [1991] studied the cross boundary transport of pollutants across the eastern Alps stressing the relationships of their transport from and to the Po valley with the local meteorology and found a particularly NO_2-rich airflow from the south. A recent study by *Lelieveld et al.* [2002] has also shown the Mediterranean area as a sort of crossroads for pollution from other continents and that polluted air masses have been observed to reach the tropopause.

2. Data Set Used for the Comparison

[8] The ground-based data set used for the comparison is based on two different kinds of measurements performed during 2000 and 2001: remote sensing observations with a DOAS system installed at Mount Cimone (44.2°N, 10.7°E, 2165 m asl) and in situ sampling with a chemiluminescence analyzer installed in the Ferrara area (Gherardi station, see Figure 1) far from any urban area, which can be considered as a Po valley background site. The in situ sensor is located within the Po valley, while the Mount Cimone laboratory is located on the highest peak of the northern Apennines, usually above the PBL, on the southern boundary of the Po valley. These different data sets provide different information for the comparison. Generally, when polluted air masses from the Po valley reach the Mount Cimone area,

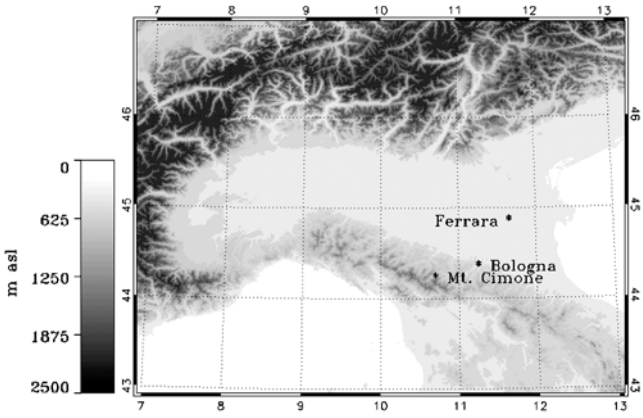

Figure 1. Geographical location of Mount Cimone (2165 m asl), Bologna, and Ferrara. Mount Cimone is the highest peak of the northern Apennines which mark the southern boundary of the Po valley. Ferrara is located in the middle of the Po valley.

mixing processes occurred during the transport (illustrated by the schematic drawing in Figure 2). Thus the transported air masses which are sampled by our UV/Vis spectrometer Gas Analyser Spectrometer Correlating Optical Differences (GASCOD) are expected to be more homogenous than near the source. On days with meteorological conditions where pollution is transported and mixed to remoter areas, we expect a larger and more homogeneous hot spot of the Po basin. Thus the effect due to the different field of view (FOV) of GASCOD and GOME should be reduced. On the other hand, sampling air masses within the PBL in the Po valley is expected to be sensitive to very local variations in chemical composition due mainly to the different intensities of pollutant sources. A remote site with minor local emissions in the vicinity and thus representative of a larger area (as that of Gherardi), could provide useful information for comparing measurements over the long term since it would provide, daily, reasonable background values for NO_2 concentrations.

2.1. Tropospheric NO_2 Column From GASCOD Spectrometer

[9] The GASCOD UV/Vis spectrometer, operational at Mount Cimone (44.2°N, 10.7°E, 2165 m asl; see Figure 1) since August 1993 [*Evangelisti et al.*, 1996], measures zenith scattered solar radiation with a narrow FOV (<1°) to retrieve nitrogen dioxide slant column values during sunrise and sunset by means of Differential Optical Absorption Spectroscopy (DOAS) techniques [*Platt*, 1999, and references therein]. Here we used an inversion method based on the weighted Chahine algorithm [*Chaine*, 1972] to retrieve nitrogen dioxide concentration profiles from the slant column measurements performed during sunrise and sunset. The method was first used by *McKenzie et al.* [1991], who also demonstrated its ability to detect tropospheric pollution. Nitrogen dioxide vertical profiles from ground-based DOAS measurements have also been previously calculated [*Preston et al.*, 1997; *Elokhov and Gruzdev*, 2000; *Petritoli et al.*, 2002a; *Petritoli*, 2003] in different kinds of studies and were also used to analyze pollution transport from the Po valley to Mount Cimone [*Petritoli et al.*, 2002a]. Within this work the inversion

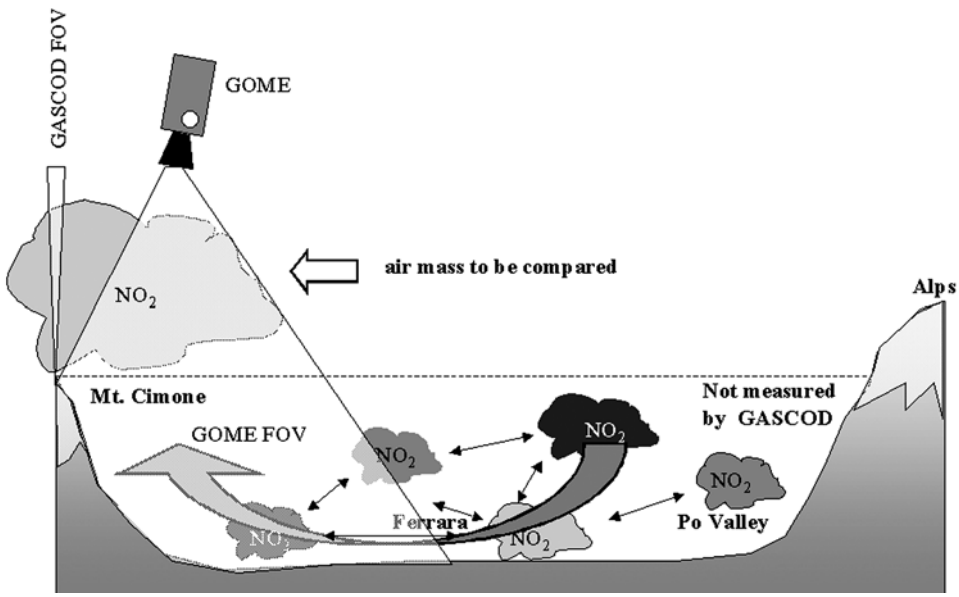

Figure 2. Schematic drawing of the measurement set up for GASCOD, GOME, and in situ instruments in the Po valley region. In the realistic model assumption that the pollution "cloud" is made up of different sources of different concentrations (different grey tones in the figure), comparing values measured with a large field of view (FOV) and narrow FOV can be misleading. If, however, polluted air masses are transported toward a normally nonpolluted site (e.g., Mount Cimone), mixing processes are expected to dilute the NO_2 "cloud" resulting in a more homogeneous NO_2 distribution. Measurements performed within the Po valley using in situ instruments are suitable for comparing long-term trends if the observation site is opportunely chosen to be representative of a large area.

method was used to retrieve NO_2 vertical profiles of concentrations in 2000 to 2001. Slant column measurements performed at solar zenith angles (SZA) between 82° and 92° in the 436–464 nm spectral range were considered for the inversion. The tropospheric column was then calculated by integrating the profile values between 2.5 and 12.5 km. The theoretical approach to error calculation in inversion techniques has been dealt with in detail by *Rodgers* [2000]. Given the true profile of the nitrogen dioxide in the atmosphere, $\vec{x}$, the a priori profile used for the inversion, $\vec{x}_a$, the vector of measurements, $\vec{y}$, the forward model F and the inverse model R, the error, i.e., the difference between the retrieved state $\hat{\vec{x}}$ and real atmospheric state $\vec{x}$, can be expressed as

$$\hat{\vec{x}} - \vec{x} = (\mathbf{A} - \mathbf{I}_n)(\vec{x} - \vec{x}_a) + \mathbf{G}_y \mathbf{K}_b \left(\vec{b} - \hat{\vec{b}}\right) + \mathbf{G}_y \Delta\vec{F} + \mathbf{G}_y \vec{\varepsilon}, \quad (1)$$

where $\mathbf{A}$ and $\mathbf{G}_y$ are the matrices of averaging kernels and contribution function respectively, $\mathbf{I}_n$ is the n-dimensional unit matrix, $\Delta\vec{F}$ is the error we have when the real atmosphere is approximated by our Radiative Transfer Model (RTM), $\vec{\varepsilon}$ is the vector of measurement errors, $\vec{b}$ and $\hat{\vec{b}}$ are, respectively, the vector with parameters (other than the NO_2 profile) describing the real and the guessed atmospheric status, and $\mathbf{K}_b$ is the sensitivity of the forward model to the $\vec{b}$ parameters. Our forward model is a single scattering radiative transfer model, Atmospheric Model for Enhancement Factor Calculation (AMEFCO) [*Petritoli et al.*, 2002b], based on the Intensity Weighted Optical Path (IWOP) [*Slusser et al.*, 1996] approach. The sensitivity, $\mathbf{K}_b$, of the simulated measurement (NO_2 slant column) to other parameters $\vec{b}$, except the NO_2 profile, can be considered to be less than 5% within the physical range of variation of such parameters [*Petritoli*, 1998]. The Chahine algorithm inversion model used in our calculation is the modified version where only a few measurement points are used to calculate the real solution from the a priori profile but where the whole set is used to check the consistency of the solution in a least squares manner [*McKenzie et al.*, 1991]. This latter aspect makes the calculation very stable with respect to oscillations in measurements and also tends to give higher weight to the shape of the measured slant column which contains the real physical information on the NO_2 vertical distribution. Measurement errors (from the DOAS processing) and the forward model errors (by comparison with other RTM models [*Hendrick et al.*, 2003]) can be estimated to be of the order of 3–10% and 2–5%, respectively, within the SZA range used for profile retrieval. Such error estimation also includes tests performed with medium pollution level NO_2 profiles (ground concentration of the order of 5×10^9 molec/cm^3) corresponding to the cases dealt with in this work (see below). This is due to the fact that Mount Cimone is relatively far from pollution sources and high NO_2 levels in the Po valley are diluted during transport. Maximum values observed so far at the ground are of the order of 1 ppbv [*Fischer et al.*, 2003].

[10] Another effect to be addressed is the possible contribution of NO_2 absorption occurring below Mount Cimone (in the Po valley) to the measured slant columns. Photons which interact via scattering processes would require a high order of scattering to reach the instrumental FOV after going through the lowest layers and this significantly reduces their weight in the measured signal. Ground albedo can, however, reflect photons, from direct Sun, up to the instrument field of view. Only part of the reflected radiation will reach the instrument because of further interactions between the ground and 2165 m asl (altitude of Mount Cimone), and the measurements (slant columns) show no clear evidence of this contribution. In fact the Po valley experiences high NO_2 levels during the great part of the year as found from both in situ and satellite observations. Nevertheless, analyzing NO_2 slant column measurements at Mount Cimone showed only about 30 days/yr (normalized to the available observations at Mount Cimone during 2000 and 2001) probably affected by pollution. The contribution of this effect to our retrieval (expected to be low for the reasons above) is thus difficult to model because a reasonable estimation of the NO_2 vertical and horizontal distribution below 2165 m in the Po valley must be known. The approach we have followed is thus to estimate in our retrieval the error due to albedo. At 436–464 nm and in absence of snow cover a reasonable value for albedo in the Po valley lies within the range of 4–6%. Such a value, according to *Perliski and Solomon* [1993], will alter the zenith sky observation of a purely tropospheric gas only by few percent (~10%). On the basis of this result we have assigned an error in the range of 5–10% in our forward model $\vec{F}$. This error propagates into our retrieval as described by equation (1), i.e., it is weighted by the contribution function.

[11] The averaging kernels of our inversion model are shown in Figure 3 with the estimated percentage errors on the retrieved vertical profiles calculated using a mid-latitude climatological NO_2 profile. Sensitivity for altitudes higher than 32.5 km is very low and errors can reach values of up to 80%. Accurate a priori information is then necessary for these altitudes to give further stability to the solution. In the troposphere and the middle-low stratosphere, where the nitrogen dioxide variability is higher, the method is reasonably accurate with errors in the range of 12–38%. Full width at half maximum (FWHM) of the averaging kernel rows gives a possible estimation of the vertical resolution in the retrieved profile. From 2.5 up to 32.5 km the FWHM varies from 10 to 15 km so that a vertical step of 5 km is required at least to reproduce the retrieved signal without losing information.

[12] Figure 4 gives the nitrogen dioxide concentration profiles during 2000 and 2001 as well as the tropospheric column amounts retrieved from the profiles. Several episodes of high NO_2 concentrations in the lowest troposphere both in the morning and evening measurements are evident. The respective tropospheric columns reach maximum values of the order of 10×10^{15} molec/cm^2 and 15×10^{15} molec/cm^2. Missing profiles in the plot are due to both missing and rejected data. The rejection criterion is based on the shape of the slant column that is expected to increase monotonically within the solar zenith angle range used for profile retrieval. The two main phenomena causing the slant column to diverge from monotonic changes are a strong variation of the NO_2 concentration over a short time period in the field of view (FOV) of the instrument (due, for instance, to transport of pollutants from nearby areas) or to clouds entering, for a fraction of the sunset or sunrise

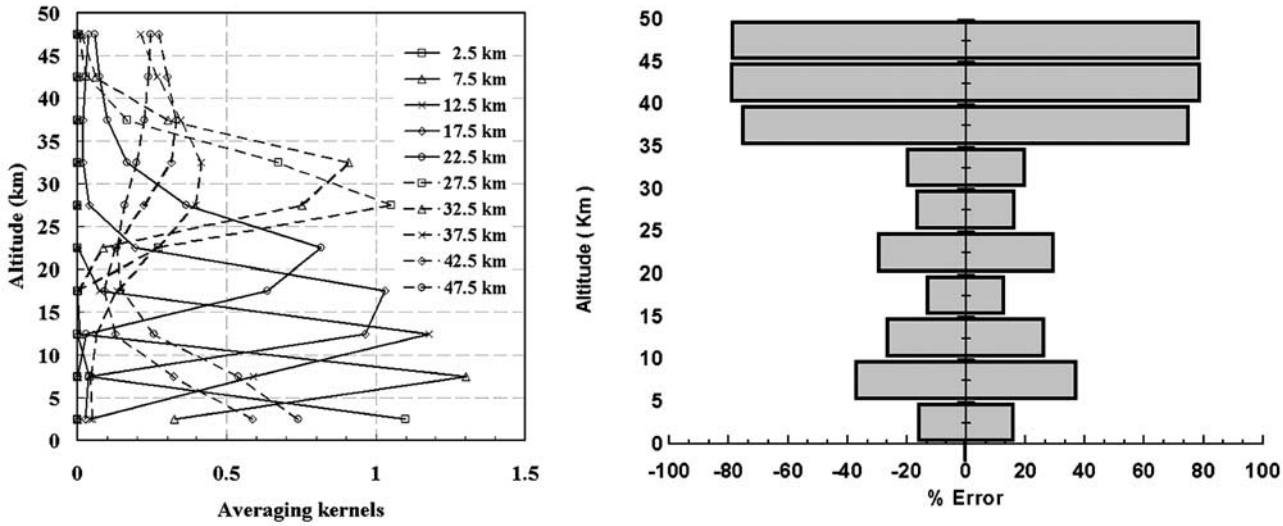

Figure 3. (left) Averaging kernels of the inversion model used for nitrogen dioxide vertical profile retrieval from slant column measurements. (right) Estimated percentage error on the retrieval (see text for more details). The model can retrieve useful information on the vertical distribution of the gas up to 32.5 km with errors ranging between 12% and 38%.

period, the instrumental FOV. Actually the latter can lead to nonmonotonic NO_2 slant column changes only if a large amount of NO_2 is already present in the troposphere since it is enhanced (in optical depth units) by the multiple scattering induced by clouds. If clouds are within the instrumental FOV during the entire measurement time the slant column could still increase monotonically even when an extra NO_2 burden is present in the troposphere. Such cases will produce slant column amounts higher than the real one [*Erle et al.*, 1995], and other criteria such as the color index parameter, O_4 slant column, or satellite images can be used to remove these days from the analysis. It is worthwhile stressing the fact that the physical events we have explained are removed from the analysis only because the forward and inverse calculations are unable to model them in a proper way. In fact one profile is retrieved using measurements performed over about 2 hours during sunrise and sunset. This means that our results should be representative of the atmospheric status during this time interval. Real (sudden increases due to transport) or nonreal (cloud effects) modifications of the NO_2 profile during the measurement period are not compatible with our model. The chemical variation of the tropospheric NO_2 could be another physical phenomenon modifying the NO_2 measurements. But taking into account that the NO_2 lifetime in the free troposphere is of the order of one day considering it as constant for 2 hours is an acceptable approximation.

2.2. In Situ Concentration From the ARPA Network

[13] Po valley in situ measurements were carried out by the Regional Agency for Environmental Protection (ARPA) of Emilia Romagna using a DASIBI chemiluminescent analyzer. Measurements are performed with a sampling time of 1 min and (within the range of 20–200 $\mu g/m^3$) an error of a few percent. For this study we used various data sets. For the comparison with satellite data on an annual basis the station of Gherardi (near Jolanda di Savoia 44.9°N, 12°E, Ferrara area) was used. From this station

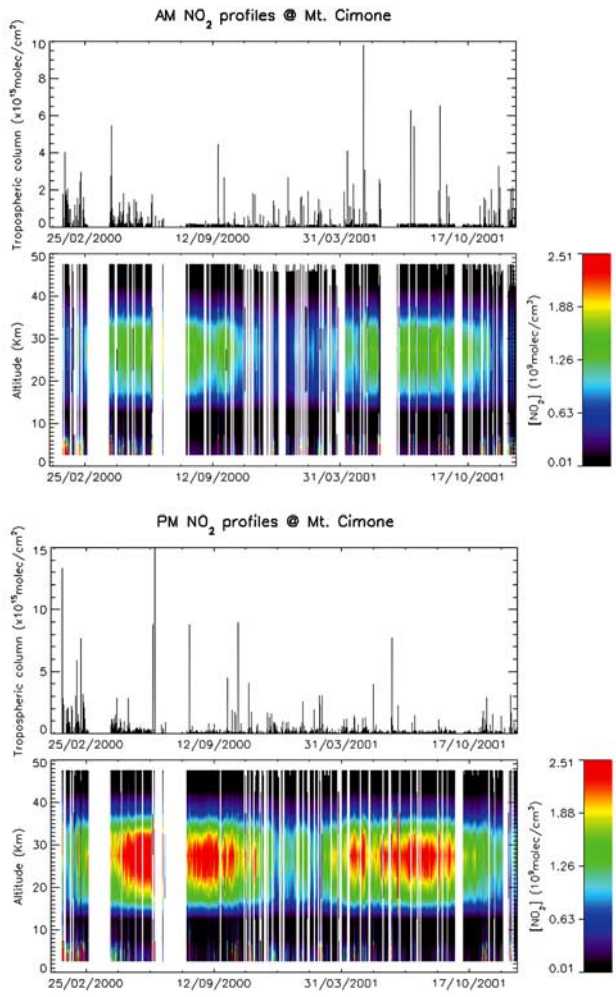

Figure 4. NO_2 profiles and tropospheric column amounts retrieved at Mount Cimone during 2000 and 2001 (morning values above and evening values below).

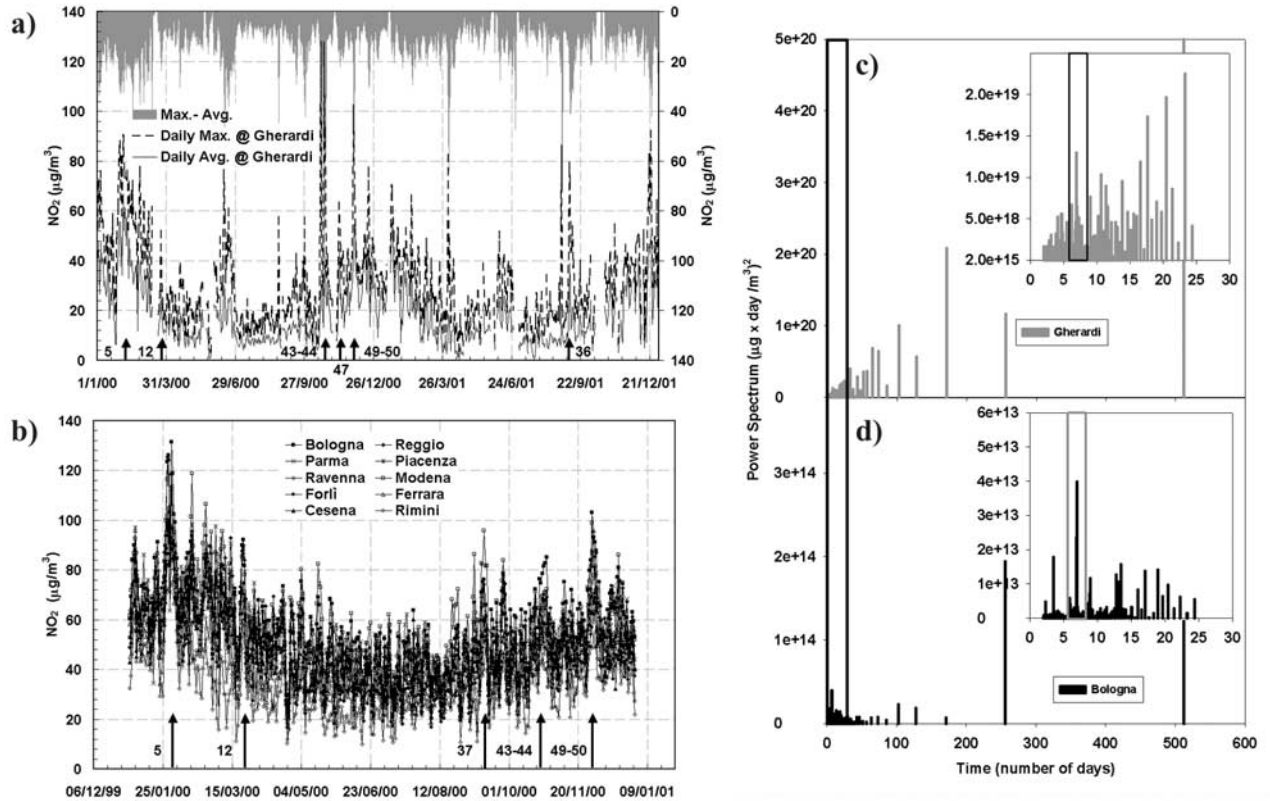

Figure 5. Daily averages of NO_2 concentration at (a) the Gherardi station near Ferrara for 2000 and 2001 and (b) for all other stations of ARPA Emilia Romagna for 2000. The latter are averages of several stations within each city area. In Figure 5a the daily maximum is also plotted as well as the difference to the daily average (grey area). Arrows and numbers mark the weeks with particularly high NO_2 concentrations. The calculated spectrum using an FFT algorithm is shown for the daily averages at (c) Gherardi and (d) Bologna. The zooms (relative to the area of the plot marked by the black rectangle) enlarge the high frequency part of the spectrum to highlight the weight of the weekly frequency (grey rectangle) in the respective data set. In the Gherardi data the 7-day frequency has a relatively low contribution, and this supports the hypothesis on the Gherardi data for the comparison (see text for more details).

we considered 2 years of data (2000 and 2001), and the daily maxima and daily averages of NO_2 concentrations are shown in Figure 5a. Other stations in Emilia Romagna were used to characterize the possible horizontal extension of the Po basin hot spots. Table 1 lists the stations with their respective geographical coordinates. The daily averages during 2000 of each station, in their respective areas, are shown in Figure 5b. All measurements from the various cities show very similar values all year-round. The maximum deviation from the mean occurred in the Ravenna area with a root mean square difference of about 16 $\mu g/m^3$. In particular, similar high NO_2 concentration values (indicated in the figure by the arrows and the week number) characterized each station time series.

[14] As mentioned above, the Gherardi station, located in the polluted Po basin area but not affected directly by local pollution sources, has been chosen because it can be considered as a representative rural station and is expected to give a correct estimation of the background NO_2 concentration. A check on this expected behavior was made by applying an FFT algorithm [*Press et al.*, 1992] on the measurements to observe the relative "weight" of the weekly frequency connected to human activity. The power spectrum for Gherardi and Bologna (chosen as an example of an urban station) data are shown in Figures 5c and 5d. In the respective zoom insets the 7-day signal is a factor of 2 higher than

Table 1. Geographical Location of the Cities Where in Situ NO_2 Measurements From the ARPA Network Are Performed

City	Latitude	Longitude
Bologna	44.3	11.2
Cesena	44.1	12.1
Ferrara	44.5	11.4
Forlì	44.1	12
Modena	44.4	10.5
Parma	44.5	10.2
Piacenza	45	9.4
Ravenna	44.2	12.1
Reggio Emilia	44.7	10.4
Rimini	44	12.3

adjacent frequencies in the Bologna data, while being less distinguishable from other frequencies in the Gherardi data as expected.

2.3. NO_2 Tropospheric Column Measurements From GOME

[15] The GOME spectrometer was launched on board ERS-2 in 1995 [*Burrows et al.*, 1999]. Although it was designed for total ozone column measurements using DOAS in the UV and visible part of the spectrum, several methods and models have been developed to retrieve from the acquired spectra information on other trace gases (NO_2, BrO, OClO, H_2O, etc.) and aerosol content in the atmosphere. One of these methods, developed by *Richter and Burrows* [2002], makes it possible to retrieve the tropospheric nitrogen dioxide column by comparing total column measurements performed at the same latitude over a polluted area with one performed over a nonpolluted area, e.g., the Pacific Ocean. The method is still in the development stage, and as demonstrated by *Martin et al.* [2002, 2003], there are some aspects of the retrieval that could be further improved in order to reduce the errors. One of the advantages of the method is that the tropospheric column is obtained by the difference between two measurements performed from the same instrument. Therefore it is "self calibrating" in the sense that many systematic errors due to the DOAS methodology or to the instrument itself are removed. Nevertheless, there are several other sources of error explained in detail by *Richter and Burrows* [2002] and summarized by *Heland et al.* [2002] which indicate that the error estimation of the tropospheric column retrieval depends upon the atmospheric status of the column sampled by the GOME spectrometer (e.g., the cloud cover, NO_2 profile assumption for air mass factor calculation, etc.). In the case of measurements over the Po valley, the most important error sources are large aerosols optical depth and fog which are frequently observed in the area and are not properly taken into account in the analysis, but influence the GOME NO_2 estimation. An additional problem arises from the horizontal inhomogeneity within the area of one GOME measurement (320×40 km^2), which will be discussed later in this paper. A quantitative discussion of errors will have to be based on an extensive analysis mainly based on model results [*Boersma et al.*, 2004]. For this reason, error bars will not be considered in the present study except for specific discussions on daily data.

3. Long-Term Comparison

[16] The comparison between ground-based in situ measurements and GOME tropospheric column measurements of NO_2 is structured in two parts. We first compared the annual cycle of NO_2 as measured by both instruments. As mentioned above, tropospheric NO_2 is mainly produced by human activity such as fuel combustion related to traffic and heating systems and thus a winter maximum value is expected. Figure 6 shows the GOME tropospheric column of NO_2 over the Ferrara area and the in situ measurements at the Gherardi station during 2000 and 2001. The GOME overpass was selected by defining a square region of about 50×70 km^2 around the ground-based station and considering valid for the comparison all the pixels covering more than 22% of the target area. Although in situ measurements were performed about every minute, a 24-hour average was chosen for the analysis. Such criteria consider the ground-based NO_2 values to be representative of a larger area. In fact, the NO_2 value around 10:30 am (roughly the time of satellite overpass) corresponds to a good approximation, to the daily average value of the NO_2 photochemical cycle. On the other hand, any possible variations during the day due to air masses dynamics (captured by the satellite because of the extended cover of the ground pixel) could be added to the in situ measurement by taking its daily average and it has been verified, by comparing the overpass measurements and the daily averages at Gherardi station, how such variations are larger than the discrepancy between the daily average and the 10:30 am concentrations. As shown in Figure 5, considering the daily average does not affect the annual cycle. In fact the grey shaded area in Figure 5a shows the difference between the NO_2 daily maximum (expected to contain the maximum information related to pollution induced by human activities) and the daily average. The absence of any clear annual frequency confirms the fact that both measurements contain the same information on the annual cycle.

[17] The agreement between the two measured annual cycles (plotted in Figure 6) is good during both years of investigation. As expected, during winter, the NO_2 concentrations and tropospheric columns reach their highest values of about 550×10^9 molec/cm^3 and 12×10^{15} molec/cm^2, respectively. During summer, NO_2 values of around 100×10^9 molec/cm^3 and 2.5×10^{15} molec/cm^2 were found while a local maximum was measured in June by in situ instrument but not by GOME (probably due to a local phenomena perhaps connected to the use of fertilizers). Also several short timescale features were observed by both instruments such as the local maxima indicated by the arrows in the figure. The absolute maximum around week 5 of 2000 was also observed at Mount Cimone where tropospheric column values remained around 2×10^{15} molec/cm^2 for several days (see Figure 4).

[18] Such a trend was observed by GOME over the entire Po valley area. In order to estimate the horizontal extension of the hot spot, seasonal averages of NO_2 tropospheric columns were calculated for 2000 and 2001 and plotted in Figure 7. During the whole year the polluted area seems to cover the entire Po valley with a maximum average value ranging from 4×10^{15} molec/cm^2 (spring) to 8×10^{15} molec/cm^2 (winter). As mentioned above, the tropospheric columns were obtained from the difference between two slant column values obtained at the same latitude. In order to fulfil this requirement the GOME ground pixel is divided, before subtraction, into several subpixels along the north-south direction. This procedure provides the tropospheric column data with an "unreal" higher spatial resolution as visible in the maps in Figure 7. The average seasonal values were calculated using these subpixel values (see the POLPO project handbook available from the ISAC Web server http://www.isac.cnr.it/~trasfene/POLPO_WEB/HomePage.html).

[19] This also helps to smooth the boundaries of the selected geographical region which would have otherwise shown stronger evidence of the 320×40 km^2 area of the real GOME pixel. However, this procedure does not alter

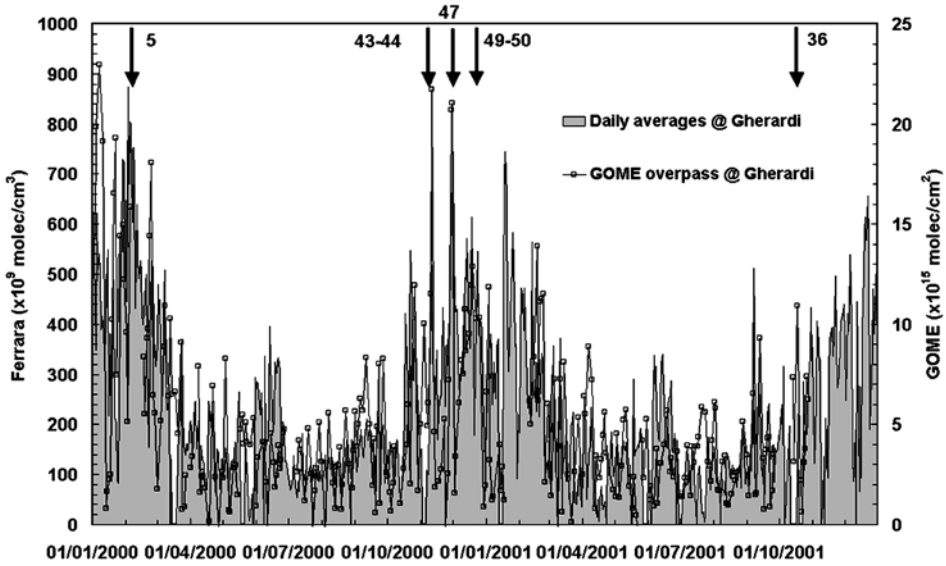

Figure 6. Comparison between Gherardi in situ measurements of NO_2 and NO_2 tropospheric columns from GOME. As in Figure 5, arrows and numbers mark periods of relatively high NO_2 concentration observed both by GOME and Gherardi. The annual cycle is well reproduced with winter maximum and summer minimum. The relative summer (around June) maximum observed in Gherardi measurements for both years is not evident in GOME measurements.

the information provided by the satellite measurement. The northern, southern, and western boundaries of the hot spot agree well with the real physical extension of the Po basin (note also the NW-SE tilt in the southern boundary due to the orography of the Apennines) but the eastern limit extends well into the Adriatic Sea (for about 150 km). Even though, as shown by *Leue et al.* [2001], the NO_2 lifetime in the lowest troposphere could be long enough to allow NO_2 transportation over the sea far from its original sources (in our case there is a possible correlation with the sea breeze

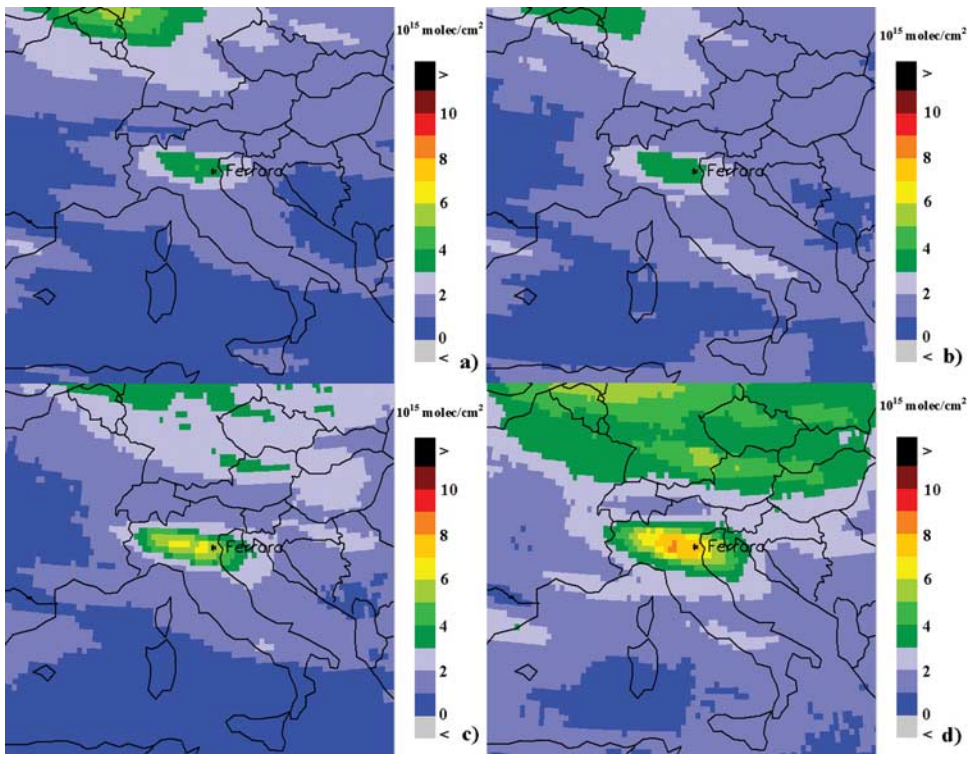

Figure 7. Average NO_2 tropospheric column as measured by GOME during the years 2000 and 2001: (a) spring, (b) summer, (c) autumn, and (d) winter.

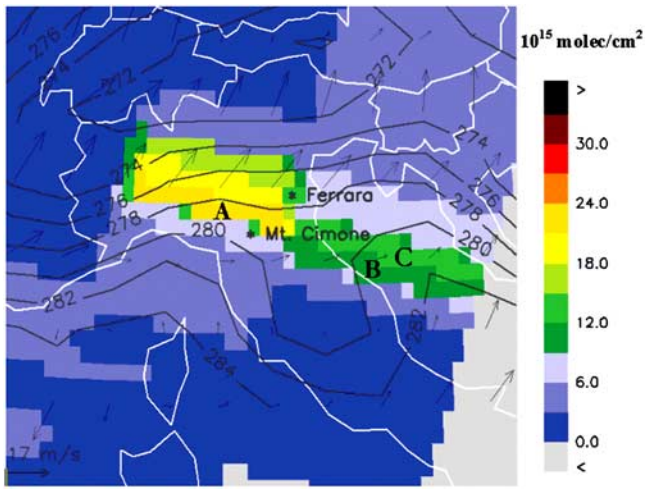

Figure 8. NO_2 tropospheric column from GOME on 29 January 2000. During this day, GOME observed very high values (up to 15×10^{15} molec/cm^2) of tropospheric NO_2 even over the Adriatic Sea (pixels B and C in the picture). As argued in section 5, these high column values are probably due to a hot spot covering only a fraction of the GOME pixel. The meteorological situation (the figure shows temperature and wind field at 1004 hPa from ECMWF analysis for the same day at 12:00 UTC) with relative low wind intensity (about 10 m/s) does not, in fact, justify a transport of pollutants across the Adriatic Sea to Croatia.

regime), such structure is also probably due to the partial coverage of the instrumental FOV by pollution ''cloud''. In fact this extension beyond the eastern coast of northern Italy derives from measurements such as that shown in Figure 8 relative to 29 January 2000 when although the winds (at 1004 hPa level) were not intense (about 10 m/s) and not exactly in the right direction to create the observed extension, very high values of NO_2 seemed to be transported across the Adriatic down to Croatia. As will be discussed in more detail in section 5, this was probably due to the hot spot that occupied only a small portion of the GOME FOV but the final effect was that a large amount of tropospheric NO_2 is assigned to a region where it was probably not present in such high concentrations while the values in the hot spot are underestimated.

[20] As we may expect if we assume that NO_2 is uniformly distributed within a certain vertical layer, the ratios between respective maxima and minima are very similar: 5.5 and 4.8 for in situ (Gherardi) and GOME and thus the tropospheric column is proportional to the measurement at ground level. One conclusion from this proportionality is that NO_2 cannot be distributed uniformly over the entire PBL throughout the year. In fact, assuming that this were true we calculated a tropospheric column amount of NO_2 using the in situ measurements from the Gherardi station and the mixing layer (ML) height calculated with the CALMET model [*Scire et al.*, 1990] as a function of day of the year and of the time of the day. The ML variation at 10:30 LT is from about 100 m (winter) to 2000 m (summer). Assuming a uniform distribution of NO_2 mixing ratios within the ML, we calculated the integral of the NO_2 number density from the ground up to the top of the ML assuming a vertical hydrostatic scale length of 9 km. Any possible NO_2 in the free and high troposphere was ignored for this calculation. Errors associated to these tropospheric column estimations are mainly due to the fact that NO_2 ML height may not coincide with the PBL height. The GOME columns are plotted versus the calculated columns from the Gherardi data in Figure 9, revealing a monthly linear relationship. It turns out that there is a clear dependence on the day of the year as shown by the color scale.

[21] Data are scattered over three main areas of the plot according to the season. Late autumn and middle winter days remain closer to the best relationship (dashed bold line) with angular coefficients ranging from 0.89 (February) to 1.2 (November and December), late winter and early autumn days (excluding the month of June) occupy the central part of the plot with angular coefficients ranging from 0.25 (August) to 0.42 (October). June has the greatest difference between the two data sets with an angular coefficient of 0.1. This last case is likely due to the local maximum in the Gherardi data mentioned above. The hypothesis of uniformly distributed NO_2 mixing ratios within the entire PBL can be thus discarded as it would result in a reversed annual cycle than observed in Gherardi.

[22] It is discussed below whether the obvious disagreement between the columns measured by GOME and the columns estimated from a well-mixed PBL could be the result of systematic errors in the GOME data analysis. The main reason for the increase of the calculated tropospheric columns is the increase in PBL height in summer which increases the volume filled up with high NO_2 mixing ratios. If this were in fact the case, the relative sensitivity of GOME measurements toward the NO_2 (which decreases toward the surface) should increase in summer, leading to an overestimation of summer values relative to winter columns. However, the opposite is observed. During winter and autumn we expect a high number of days with larger errors on GOME data retrieval with respect to spring and summer due to the presence of clouds and fog within the GOME FOV. The GOME data set used for this study was obtained considering only pixels where the cloud fraction was lower than about 0.1. It has, however, been demonstrated [*Richter and Burrows*, 2002] that even such a low fraction of clouds can produce an underestimation of the

Figure 9. Monthly correlation between tropospheric columns of nitrogen dioxide as measured by GOME and estimated from Gherardi in situ measurements. Using the PBL height to calculate the NO_2 column in the vertical uniform mixing ratio hypothesis leads to the unexpected conclusion that the tropospheric NO_2 column is maximum in summer and not in winter. This led us to assume a different mixing layer for NO_2 varying between 50 m and 300 m throughout the year (see text). The dashed line is the reference for the best correlation. The solid line is the linear regression analysis (the relative equation is written in each plot), and the crosses are the data points used month by month for the regression analysis, while the entire data set plotted in the color scale as a function of the day of the year is in the background of the January plot.

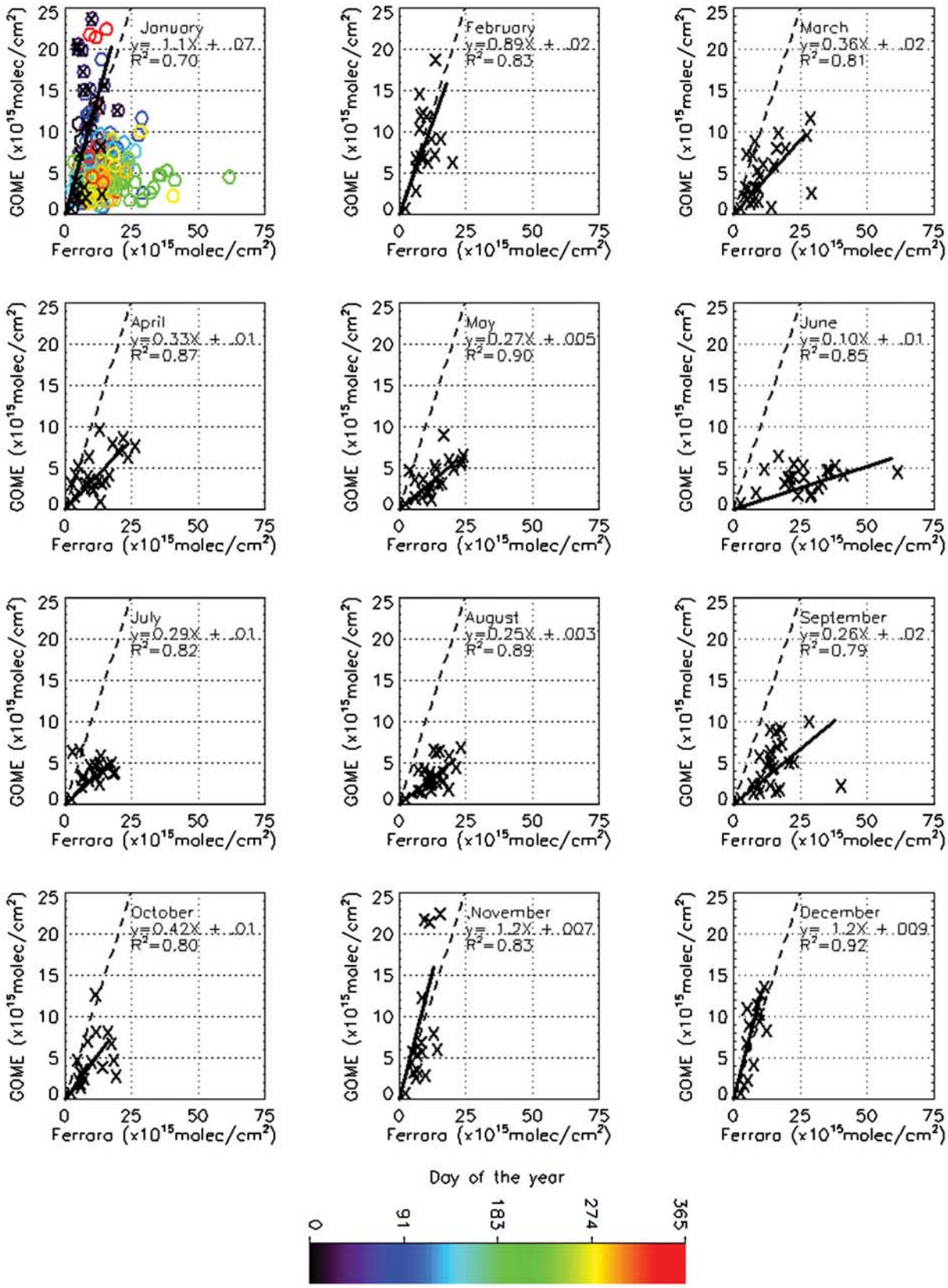
January
y= 1.1X + .07
R²=0.70
February
y=0.89X + .02
R²=0.83
March
y=0.36X + .02
R²=0.81
April
y=0.33X + .01
R²=0.87
May
y=0.27X + .005
R²=0.90
June
y=0.10X + .01
R²=0.85
July
y=0.29X + .01
R²=0.82
August
y=0.25X + .003
R²=0.89
September
y=0.26X + .02
R²=0.79
October
y=0.42X + .01
R²=0.80
November
y= 1.2X + .007
R²=0.83
December
y= 1.2X + .009
R²=0.92
GOME (x10¹⁵molec/cm²)
Ferrara (x10¹⁵molec/cm²)
0
25
50
75
Day of the year
0
91
183
274
365

Figure 9

Table 2. Summary of the Supplementary Information Available for the Ensemble of Days Selected for Comparison Between Tropospheric Column Measured by GASCOD and GOME[a]

Group of Data	Date	AM/PM	$\Delta NO_{2\ tropocolumn}$, $\times 10^{15}$ molecule cm^{-2}	Wind Direction and Intensity, m s^{-1}	Temperature Profiles	Mixing Coefficient	Other Information
Triangles	18/02/2000	AM	2.3	no data	no inversion	0.7	/
	11/04/2000	PM	0.5	SW $\sim$ 10	1.2°/100 m 1116 m	0.0	lighting + clouds
	20/10/2000	PM	4.6	E $\ll$ 20	no inversion	0.7	clouds
	02/03/2001	AM	1.8	SW $\sim$ 20	1.9°/100 m 374 m	0.3	lighting + clouds
	02/03/2001	PM	4.0	SW $\sim$ 30	1.9°/100 m 374 m	0.3	lighting + clouds
	20/07/2001	AM	3.6	NE $\sim$ 10	0.8°/100 m 582 m	0.3	lighting + clouds
Squares	19/01/2000	PM	4.2	NE $\sim$ 20	no inversion Linate	1.0	✓ cloud-free
	17/02/2000	PM	3.5	NE $\sim$ 20	no inversion	1.0	✓ cloud-free
	30/04/2000	PM	−0.5	E $\sim$ 10	no inversion	1.0	✓ cloud-free
	21/09/2000	AM	−0.3	NW $\sim$ 30	no inversion	1.0	✓ cloud-free
	30/09/2000	AM	0.3	SE $\sim$ 30	no inversion	0.9	clouds → rejected
	03/10/2000	PM	1.1	NE $\sim$ 20	no inversion	1.0	clouds → rejected
	02/06/2001	AM	0.5	E $\ll$ 20	no inversion	0.9	clouds → rejected
	02/09/2001	AM	0.1	NE $\sim$ 20	no inversion Linate	1.0	✓ cloud-free
	15/09/2001	AM	0.4	N $\ll$ 20	no inversion Linate	0.9	✓ cloud-free
Diamonds	20/01/2000	PM	−5.8	W $\sim$ 20	1.5°/100 m 388 m	0.0	strong gradient
	22/01/2000	AM	−3.0	W $\ll$ 20	no data	0.0	/
	26/01/2000	AM	−5.1	NE $\sim$ 10	2.5°/100 m 456 m	0.3	strong gradient
	29/01/2000	AM	−4.4	W $\ll$ 20	no inversion	0.7	/
	02/02/2000	AM	−2.3	W $\sim$ 10	0.8°/100 m 570 m	0.0	/
	02/02/2000	PM	−1.1	W $\sim$ 20	0.8°/100 m 570 m	0.0	/
	18/02/2000	AM	−5.0	no data	no inversion	0.7	/
	20/02/2000	PM	−3.2	no data	no inversion	0.7	strong gradient
	21/02/2000	PM	−5.4	no data	0.4°/100 m 783 m	0.0	strong gradient
	23/02/2000	AM	−8.1	no data	no inversion	0.7	strong gradient
	23/02/2000	PM	−8.7	no data	no inversion	0.7	strong gradient
	20/04/2000	AM	−1.1	NE $\sim$ 10	2.5°/100 m 1004 m	0.3	/
	04/09/2000	PM	−1.5	NE $\sim$ 10	no data	0.3	/
	10/11/2000	PM	−3.7	SW $\sim$ 10	0.8°/100 m 511 m	0.7	strong gradient
	17/11/2000	AM	−0.6	S $\sim$ 20	no inversion	0.7	/
	16/12/2000	AM	−2.4	no data	0.7°/100 m 339 m	0.0	strong gradient
	16/12/2000	PM	−3.2	no data	0.7°/100 m 339 m	0.0	strong gradient
	18/12/2000	AM	−4.3	no data	1.0°/100 m 313 m	0.0	strong gradient
	25/12/2000	AM	−3.7	SW $\sim$ 30	no data	0.0	strong gradient
	10/02/2001	AM	−3.5	no data	no inversion	0.7	strong gradient
	17/02/2001	PM	−1.9	no data	0.8°/100 m 332 m	0.0	strong gradient
	20/02/2001	AM	−7.7	no data	0.4°/100 m 926 m	0.0	/
	27/02/2001	AM	−3.2	no data	no inversion	0.7	/
	01/03/2001	AM	−5.5	W $\sim$ 20	1.6°/100 m 783 m	0.0	/
	01/03/2001	PM	−3.4	W $\sim$ 20	1.6°/100 m 783 m	0.0	/
	27/03/2001	AM	−2.1	SW $\sim$ 10	no inversion	0.7	strong gradient
	27/03/2001	PM	−2.0	SW $\sim$ 10	no inversion	0.7	strong gradient
	21/04/2001	PM	−3.6	SW $\sim$ 30	0.6°/100 m 2155 m	0.0	/
	22/04/2001	PM	−2.1	NE $\ll$ 20	no data	0.2	/
	22/04/2001	AM	−0.5	N $\sim$ 10	no data	0.3	/
	11/05/2001	AM	−2.1	no data	no inversion	0.7	/
	31/08/2001	PM	−2.4	W $\sim$ 20	no inversion Linate	0.7	/
	18/09/2001	AM	−3.4	W $\ll$ 20	no inversion Linate	0.7	/
	19/09/2001	AM	−1.9	SW $\sim$ 10	no inversion Linate	0.7	/

[a]The three subgroups are divided according to value of the mixing coefficient (MC, see text for more details) and the difference between GASCOD and GOME tropospheric NO_2 columns ($\Delta NO_{2\ tropocolumn}$). Wind direction and intensity is referred to the 850-hPa level in the Mount Cimone area. The temperature profiles column reported the status of the vertical trends in temperature between ground and 2200 m asl at 12:00 UTC. All the information not marked with Linate come from balloon soundings in S. Pietro Capofiume. When temperature inversion is present, the gradient (°C/m) and the altitude of the first inversion is reported. For the MC calculation, missing data imply a value of 0 for the relative coefficient.

NO_2 tropospheric column of up to 40%. This can be explained as the sum of two effects: first the cloud hides to the sensor the NO_2 that is located between the cloud bottom and the ground and second, the higher albedo due to the same cloud tends to give higher weight to the radiances coming from that part of the pixel where the NO_2 signal is attenuated. On the other hand, the Po valley is particularly prone to fog which is present for many days per year especially in autumn and winter. The fog has a vertical extension of several hundred metres from the ground. From the above consideration it turns out that this is also the layer where NO_2 is distributed and such a combination, due to multiple scattering, causes an overestimation of the tropospheric column signal measured by GOME [*Richter and Burrows*, 2002] by up to a factor of 2. Such results (combination of clouds underestimation and fog overestimation) may in part account for the observed variances of data around the linear regression lines in Figure 9.

[23] However, this demonstrative exercise is useful to conclude that satisfactory agreement is obtained by comparing in situ ARPA and GOME column measurements even on a shorter timescale ($R^2 \geq 0.7$ for each month of

both 2000 and 2001). During winter even the comparison between column values (measured by GOME and estimated from ARPA measurements) looks good and allows the assumption that the PBL height (~100 m at 10:30 LT) in this period is probably coincident with the NO_2 vertical mixing length. This is not the case during the other seasons where an NO_2 ML variation between 100 and 200 m would be required for a reasonable slope. In the limiting cases of a systematic overestimation in GOME retrieval by a factor 2 (more reasonable in winter months than in summer ones) and a systematic underestimation of 40% due to clouds, we obtain the lower and upper limits of the annual excursion of the NO_2 ML that are about 50 m and 300 m.

4. Single Day Comparison

[24] The goal of the comparison based on a few cases of high pollution episodes measured at Mount Cimone is to assess the accuracy of the GOME tropospheric column measurements. The discussions of the previous section strengthen our working hypothesis that this task can give significant results only if homogenous measurements are compared. The NO_2 concentration vertical profiles retrieved at Mount Cimone are the only dataset in the Po valley that can provide tropospheric NO_2 column amount for several days of the year. As shown in section 2.1, this comparison concerns values of tropospheric NO_2 column much lower than those observed in the Po valley near pollution sources and the major part of NO_2 can be assumed to be located in the free troposphere. These are the boundary conditions within which our results must be considered. We have discussed in the same section 2.1 the errors in the retrieval of NO_2 profiles from the ground-based measurements. Another source of error could be introduced by the nonsimultaneity between GOME (about 10:30 LT) and GASCOD (as discussed above, profiles are obtained during sunrise and sunset only). The difference is a function of the day of the year and of the morning or evening measurements. The Mount Cimone morning profiles precede GOME measurements with a $\Delta T \sim 2h$ during winter and $\Delta T \sim 4h$ during summer, while the evening profiles are later with a $\Delta T \sim 5h$ during winter and $\Delta T \sim 9h$ during summer. Our working hypothesis is to consider the tropospheric column to be constant within these time intervals. Indeed, such an approximation is physically reasonable if we consider that most of the pollution episodes are due to transport from the surrounding areas and not to an unlikely vertical extension of the PBL up to 2165 m. Then, the polluted air masses can be considered as being in the free troposphere where the NO_2 lifetime is of the order of several days. The main source of variation within the ΔT interval between the two measurements is thus displacement of the polluted air masses. On the basis of the hypothesis of well mixed air masses we discussed earlier, and from the fact that pollution is detected in AM or PM profiles over a remote site such as Mount Cimone and is stable during the 2 hours of ground-based slant column measurements (which is a retrieval criterion), it can be assumed that the same air masses were within the GOME FOV a few hours later or earlier.

[25] An area of about 50×50 km^2 around the Mount Cimone station was selected to extract the GOME overpass values. The area is smaller than that used for the Gherardi station and is shifted toward the southwest (that is, Mount Cimone is in the higher right corner of the area) in order to select pixels covering mountainous areas and reduce as much as possible any possible offset due to the altitude of Mount Cimone. The similar latitudinal-longitudinal inclination of the GOME pixel and of the Apennines helps to reduce such an offset. The first criterion to build up the data set for the intercomparison was to select those days classified as polluted by both GASCOD and GOME. The ensemble is illustrated in Table 2. The subdivision into three subgroups has been performed using auxiliary information to characterize the status of the lower troposphere at the time of the measurement. For this purpose, data from several sources were used; wind fields were provided by the BOlogna Limited Area Model (BOLAM) (available on the Web at http://www.cmirl.ge.infn.it/archivio06.asp), cloud coverage information came from Meteosat images (from the British Atmospheric Data Centre (BADC) at http://badc.nerc.ac.uk/home/), temperature profiles of the Po valley area were obtained by balloon soundings at S. Pietro Capofiume (44.65N, 11.61E, 11 m asl) and Linate (45.43N, 9.28E, 103 m asl) (available from Wyoming University at http://weather.uwyo.edu/upperair/europe.html), and information on lightning events and intensity was provided by Wetterzentrale Karlsruhe http://www.wetterzentrale.de/). The idea was to select from these polluted days those with suitable characteristics for close correspondence between GOME and GASCOD measurements, that is, well-mixed sampled air masses and exclude situations with clouds, fog, and changing albedo in the ground pixels. In order to quantify the degree of mixing we define a mixing coefficient (MC) that is calculated using the following formula:

$$\mathrm{MC} = \frac{c_T T + c_W W}{c_T + c_W} \text{ with } W = \frac{b_D D + b_I I}{b_D + b_I}, \qquad (2)$$

where T, D, and I are flags that can be either 0 or 1, respectively, depending upon whether or not there is a temperature inversion below 2.1 km in the temperature profile (T), if there is not or there is a wind direction which transports air masses from possible polluted regions toward Mount Cimone (D), and if there is or there is not a wind intensity $\leq$20 m/s (I), and c_i and b_i are weighting coefficients that normalize the MC parameter between 0 and 1 and which give priority, respectively, to the temperature inversion flag ($c_T > c_W$) and to the wind direction flag ($b_D > b_I$). This MC parameter was calculated for each day of the selected data set, and the results are shown in Table 2. A MC close to 1 thus means well-mixed air was transported from possibly polluted sites to Mount Cimone, whereas MC $\ll$ 1 suggests possible nonhomogeneous air masses sampled by GOME and GASCOD. An MC threshold value of 0.9 was adopted to select the group of best candidates (marked with the square black symbol) for the comparison, that is the only flag that is allowed to be 0 is the wind intensity, I. The other two subgroups were defined according to the criteria GASCOD > GOME (triangles) and GASCOD < GOME (diamonds). Among the squares group the clouds selection caused 3 days, 30 September 2000, 3 October 2000, and 2 June 2001, to be

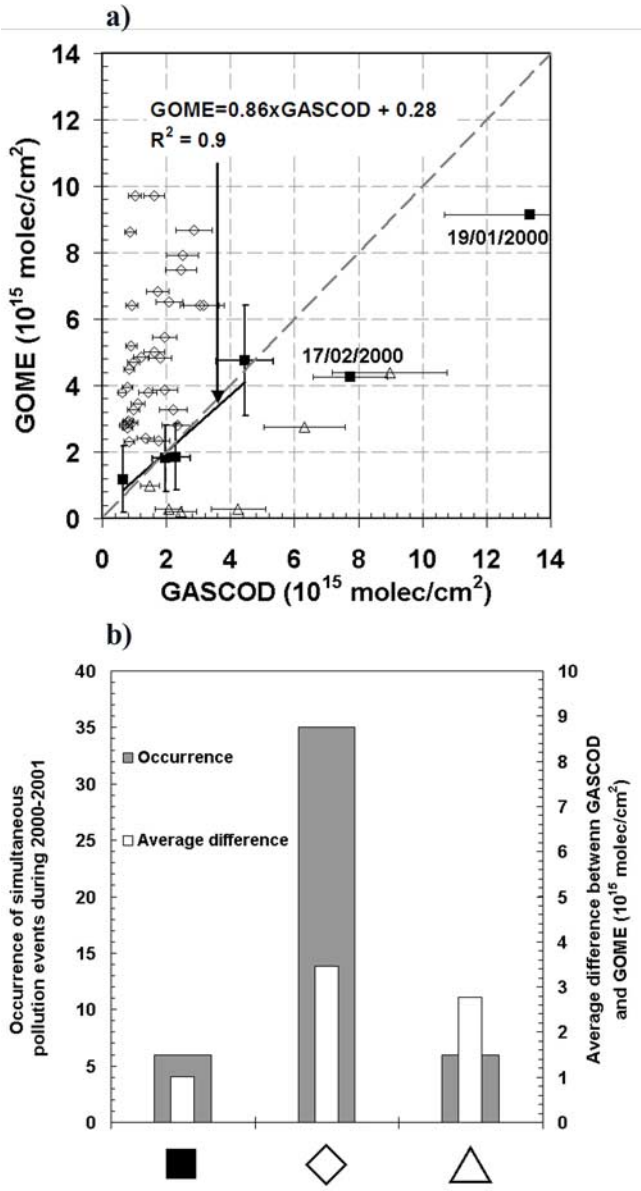

Figure 10. (a) Scatterplot between GOME and GASCOD tropospheric NO_2 columns in the Mount Cimone area. Different symbols are connected to the MC parameter as discussed in the text and in Table 2. The linear regression shown in the plot is calculated on the black solid squares excluding 19 January 2000, 17 February 2000, and the 3 cloudy days that are not included in the plot and in the analysis. (b) Statistical summary of the pollution events analyzed and the absolute average difference between GOME and GASCOD tropospheric NO_2 columns.

rejected (they are not included in the subsequent analysis and plots).

[26] In Figure 10a all the data are plotted in a scatterplot, and Figure 10b shows the statistics on the population of each group and the average difference between two measurements. The average difference for the squares group is about 4×10^{15} molec/cm^2 which is greater than the error on GOME retrieval which for this optimal situation, can estimated to be of the order of 1×10^{15} molec/cm^2. This rather large difference can be considered as being mainly due to the 19 January 2000 and 17 February 2000 measurements for which we have GOME/GASCOD values of 0.68 and 0.55, respectively. The linear regression analysis performed on the four remaining days of the square group gives excellent results with $R^2 = 0.9$, the angular coefficient (GOME/GASCOD) is 0.86, the average percentage difference between the two instruments is 15% and the offset of 0.28×10^{15}molec/cm^2 is far below the estimated errors. The ensemble of days on which the regression is performed (30 April 2000, 21 September 2000, 2 September 2001, and 15 September 2001) belongs to seasons when the snow cover at Mount Cimone and over the surrounding areas, has already melted (late spring) or not yet occurred (late summer). Thus the consequent low albedo excursion is expected to yield a GOME error within 1×10^{15} molec/cm^2. The rapid variations of surface elevation in the Mount Cimone region is not expected to introduce further errors in GOME retrieval because of the choice of the overpass pixel (Po valley is excluded in the GOME FOV) and because most of the NO_2 is not produced locally in valleys but transported from surrounding areas so that the lower surface of NO_2 iso-concentration is likely to lie on a plane at constant altitude above mountain tops.

[27] Another possible source of error in GOME retrieval is the unknown vertical and horizontal distribution of aerosols during the observations. No auxiliary simultaneous measurements are available on aerosol concentrations so that the largest values between 1×10^{15} molec/cm^2 and 35% [*Heland et al.*, 2002] of the measurements can be assumed to be the upper limit of error for the GOME retrieval and the error bars in plot 10a were calculated on this basis.

[28] The subgroups of diamonds and triangles defined above with arbitrary criteria have indeed days with common characteristics. In the last column of Table 2 we have reported supplementary information or comments on the atmospheric status relating mainly to the nitrogen dioxide and/or the troposphere. More than 80% of the triangle days show the presence of clouds in the GOME FOV and for about 66% of them there is a high probability that lightning occurred in the surrounding area causing high local increases in the NO_2 concentration. Clouds can explain the underestimation of the GOME NO_2 column which on average is about 2.9×10^{15} molec/cm^2, in percentage units ranging from 34% (on 11 April 2000) up to 93% (on 2 March 2001) as discussed above. Thus it was observed in our comparison that in most cases the effect of clouds was to hide the tropospheric NO_2 from the GOME instrument. Lightning effects on the comparison are, however, more difficult to identify because the NO_2 increase, due to diffuse or isolated thunderstorms, may have affected either only the GOME signal or also the GASCOD signal if transport processes had moved such an air mass into the Mount Cimone area. Part of these differences between GASCOD and GOME NO_2 tropospheric column values can be due to nonsimultaneity of the measurements (as discussed above), but we have no information to quantify this contribution.

[29] The diamond group has the largest average difference between the two measurements which is $3.4 \times$

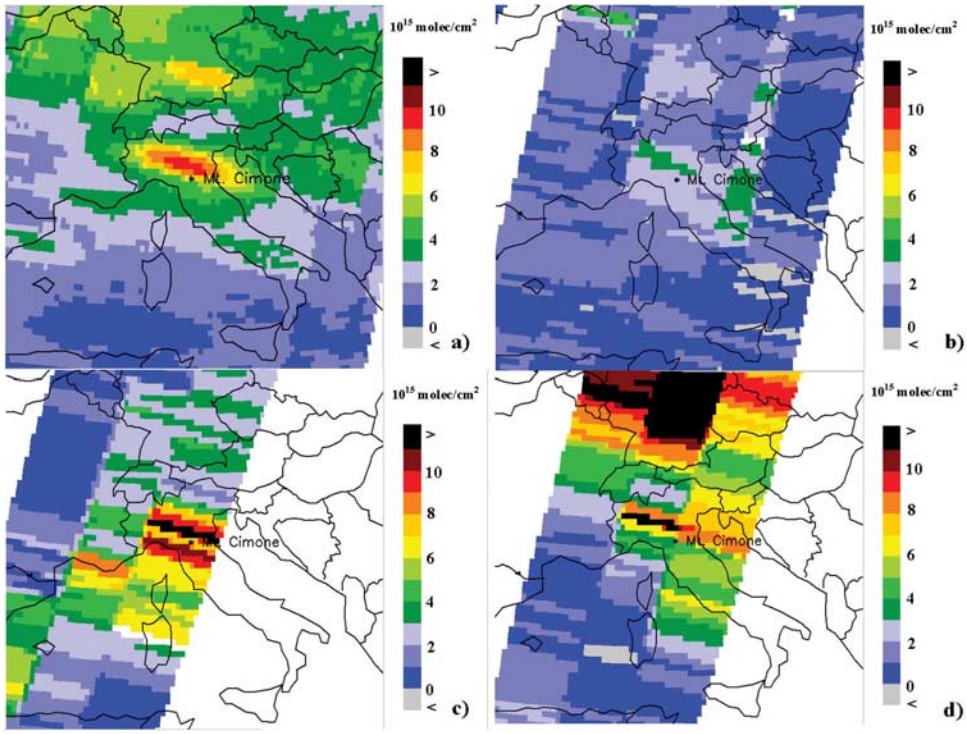

Figure 11. Daily averages of GOME tropospheric NO_2 column observations for (a) the diamonds group and (b) the squares group, excluding (c) 19 January 2000, (d) 17 February 2000, and the 3 cloudy days.

10^{15} molec/cm^2. About 43% of the group days present a strong NO_2 tropospheric column gradient along the Apennines on the boundary of the Po valley and for 51% we have incomplete supplementary information. The average gradient measured by GOME during these days, shown in Figure 11a, was about 0.12×10^{15}molec/cm^2/km in the direction perpendicular to the Po valley-Apennine boundary, and Mount Cimone is just in the area where this gradient has its maximum. This is a very high value when compared with the 4 days of the squares group chosen for the linear regression (Figure 11b). Here in the Mount Cimone area the gradient is 0.02×10^{15}molec/cm^2/km and the entire region around looks more homogenous. This means the MC parameter describes in a proper way the mixing of the atmosphere in the Mount Cimone area. The only two exceptions are 19 January 2000 and 17 February 2000 which even with MC = 1 gave GOME measurements much lower than the GASCOD ones. GOME measurements for these two days are shown in Figure 11c and 11d. Their peculiarity is that on 19 January 2000 there were high NO_2 levels also to the south of Mount Cimone and on 17 February 2000 Mount Cimone was on the boundary of the GOME pixel, and there was a significant gradient with respect to other neighboring pixels.

5. Discussion

[30] Comparing measurements obtained with strongly different approaches requires a deeper knowledge of sensitivities of the various systems to the crucial measurement parameters. One of the most important parameters which has not been quantified so far is the extremely different FOV of the two systems. We saw in the previous section that where dynamical atmospheric processes created uniform sampled air masses (MC $\geq$ 0.9, Figure 11b), comparison between the two data sets is satisfactory (R^2 = 0.9 and angular coefficient = 0.86). On the other hand, if nonhomogenous air masses are sampled the agreement is not as close. This happens in the case of strong gradients (Figure 11a) or complex situations with two different sources of pollutants contributing to the signal (Figure 11c) or simply due to geometrical considerations of the GOME pixel which, having the Mount Cimone area on its border, also receives signals from areas quite far from the region studied, (Figure 11d). What we need to model is then the response of GOME to nonhomogenous distributions of NO_2 in the sampled volume. Figure 12 shows a simplified outline of the situation modeled. We assumed two different values for the NO_2 tropospheric column, one being the clean tropospheric column, TC_1, occupying the area α within the pixel and the other the polluted value due to the hot spot coming from the Po valley, TC_2, and occupying the area β. Dividing the pixel into several small equal areas as much as necessary to closely reproduce the boundary between β and α, we can write the GOME measured radiance as:

$$I_{measured} = \sum_{k=1}^{N} I_k. \quad (3)$$

The fixed integration time of 6 s, divided into four subscans (east, center, west, and back), each of which is 1.5 s long, gives all the values of I_k the same weight in the sum. Assuming the NO_2 column in the hot spot to be horizontally homogenous and equal to TC_2 ($\Delta TC = TC_2 - TC_1$) greater than that in the remaining area of the pixel, TC_1, and that no

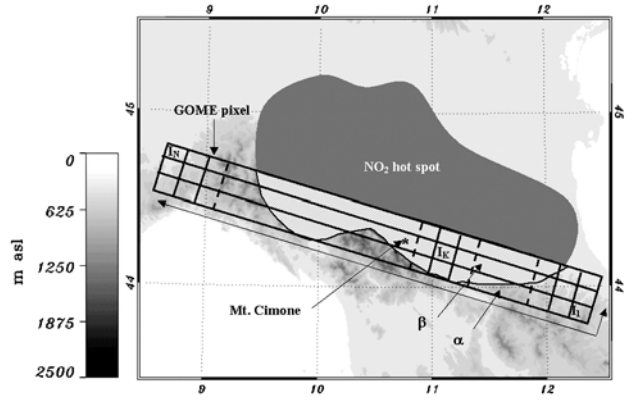

Figure 12. Schematic view of the GOME pixel for an overpass in the Mount Cimone area. In this situation we have modeled (see text for further details) the NO_2 hot spot as occupying only a part of the GOME pixel area (β), while the remaining area (α) is supposed to be free from any pollution. The pixel surface is divided into as many smaller areas (I_k) as required to reproduce accurately the boundary between β and α and model the signal measured by GOME (see equation (3)).

other atmospheric parameters (including albedo and cloud coverage) have significant gradients in the whole pixel area, when the DOAS methodology is applied we obtain a tropospheric column proportional to ln ($I_{measured}$):

$$\ln\left(I'_{measured}\right) = \ln\left\{I'_{\rho_1}\left[\alpha + \beta\frac{I'_{\rho_2}}{I'_{\rho_1}}\right]\right\} \cong \ln I'_{\rho_1} + \beta\xi(\ldots, \rho_2 - \rho_1, \ldots), \quad (4)$$

where the apex means only that we have divided by the reference spectrum, and ρ_1 and ρ_2 are the NO_2 profiles giving, respectively, the TC_1 and TC_2 tropospheric columns. ξ is the total atmospheric extinction, and the first-order approximations used are justified because $\xi(\ldots, \rho_2 - \rho_1, \ldots) < 1$ at the visible wavelengths (NO_2 is retrieved in the 425–450 nm spectral window; note also that we have considered normalized area units so that $\alpha + \beta = 1$). When differentiation (DOAS) is applied, the result obtained is equal to $TC_1 + \beta\,\Delta TC$ which is less than TC_2 (the case $\alpha = 0$, of course, will give TC_2). What GOME measures is then $TC_1 + \beta\,\Delta TC$, while GASCOD measures (on selected polluted days) $TC_1 + \Delta TC$. In the approximation that $TC_2 \gg TC_1$, i.e., TC_1 is the background tropospheric NO_2 column (this is not thus a strong limitation) the ratio between the two measurements gives:

$$\frac{\text{GOME}}{\text{GASCOD}} = \frac{TC_1 + \beta\Delta TC}{TC_1 + \Delta TC} \xrightarrow{TC_2 \gg TC_1} \beta. \quad (5)$$

In cases where well-mixed air masses reach the Mount Cimone area, the ratio between the measurements performed by GOME and GASCOD is proportional to the area occupied by the NO_2 "cloud" within the GOME pixel. Such results can be applied to the case of 17 February 2000 for example (the case of 19 January 2000 is slightly more complicated because we probably have two different pollution sources and the approximation $TC_2 \gg TC_1$ may not be valid). We get $\beta = 0.55$, i.e., the GOME pixel was almost half occupied by the polluted hot spot, for which, looking at the map in Figure 11d, the tropospheric column values of the nearby pixels in the Po valley were between 7 and 8×10^{15}molec/cm^2, in good agreement with the GASCOD measurement of 7.7×10^{15}molec/cm^2.

[31] Formula (5) helps us to understand some of the results of the comparison with measurements from the Gherardi station. In fact, we saw in section 3 that the average of GOME observations on a seasonal scale showed a clear extension of the hot spot toward the Adriatic Sea. Nevertheless, the case illustrated in Figure 8 demonstrated that part of this extension can be an artifact of the limited spatial resolution leading to the hot spot not covering the entire GOME pixel. Using the GOME measurements in the surrounding area and assuming other parameters (like aerosols, albedo, clouds) to be homogeneous throughout the ground pixel, equation (5) can be used to estimate the real extension of the hot spot and overcome in part the low spatial resolution. On 29 January 2000, for example, we can guess that the hot spot, assumed to be homogeneous, occupying pixel B and C had, for continuity reasons, a NO_2 tropospheric column the same as that of pixel A which covered the entire Po valley. It should be noted that in the Po valley a certain homogeneity in NO_2 concentration values during high pollution events can be guaranteed even over a horizontal scale of the order of hundreds of kilometres as suggested by measurements made by the ARPA stations (see Figure 5b and comments, considering that the distance between Rimini and Piacenza is about 280 km). What we obtain is thus $\beta_B = 0.42$ and $\beta_C = 0.57$, respectively. This means that, considering the position of the pixels with respect to the coast, the hot spot extended out from coast by about 100 km at the most.

6. Conclusions

[32] In this paper we have presented the first comparison between spaceborne and ground-based tropospheric column and in situ measurements of NO_2. Nitrogen dioxide is an important constituent for tropospheric chemistry and its monitoring from space could provide significant improvements in quantifying its emission in polluted areas and its transport across countries and continents. Nevertheless, the new methods developed to obtain tropospheric column amounts need to be compared with independent measurements to understand the nature of the information that can be used for scientific studies. Here we have used in situ and remote sensing measurements carried out in different places to allow such a comparison. In situ measurements from the Gherardi rural station give acceptable estimates of NO_2 concentrations in the Po valley from a mixture of natural and anthropogenic emission. The comparison of surface concentrations with satellite column measurements shows a good correlation in the annual trend and, in particular, for the presence of high level of pollution episodes. Although aerosol loading, fog, and clouds also may have an important influence on the comparison, our analysis was based on the effect of mixing lengths. It was found that when the surface measurements are converted to tropospheric columns assuming a well mixed PBL and

compared to GOME measurements, the correlation is acceptable on a monthly basis. There remained a difference in the seasonality of the two data sets with the computed columns much larger than the satellite measurements in summer. The linear correlation with estimated tropospheric columns retrieved from in situ measurements leads to the conclusion that the NO_2 mixing layer is probably different from the modeled PBL and ranges from 50 m up to 300 m from winter to summer. A presumably local phenomenon of high NO_2 observed during June from ground measurements is not reported by GOME measurements and this, as discussed in section 5, could be connected to the very limited area that such local hot spots occupy in the GOME pixel. The seasonal averages of the GOME measurements show a hot spot covering the entire Po valley region all the year-round. A clear extension eastward over the Adriatic Sea is also present throughout the year, but this feature is in part a result of the low spatial resolution of GOME.

[33] The comparison of satellite columns with profiles retrieved by DOAS ground-based measurements carried out at Mount Cimone (2165 m asl) provided good agreement when the troposphere was horizontally homogeneous enough to make the two measurements compatible. The strict selection criteria allowed only a selection of very few observations to be compared quantitatively. A set of nine episodes from the polluted days ensemble was selected according to the mixing coefficient (MC) parameter calculated using supplementary information on the tropospheric status, and three of them were rejected because of clouds in the GOME FOV. Four of the remaining episodes showed a good linear correlation between GOME and GASCOD NO_2 tropospheric columns with $R^2 = 0.9$ and the angular coefficient 0.86, while two cases (19 January 2000 and 17 February 2000) had a GOME/GASCOD ratio of 0.68 and 0.55. The model illustrated in section 5 and the pattern of GOME measurements in the area lead to the conclusion that two different pollution sources were sampled by the satellite on 19 January 2000 and only one half of the GOME pixel was covered by the hot spot on 17 February 2000. The data group with $MC \ll 1$ has also been discussed, and a reasonable interpretation of the discrepancy between the two instruments was found in cloud cover, lightning, and strong gradients in the NO_2 column amounts in the Mount Cimone area reflecting incomplete mixture of air masses sampled by GOME and GASCOD. Such results must be considered valid only in the range of variations in the NO_2 tropospheric column used for this study and for NO_2 located in the free troposphere.

[34] Our conclusion is thus that GOME NO_2 tropospheric column measurements can be used for nitrogen dioxide monitoring only if supported by auxiliary measurements and/or model calculations on the status of the troposphere with particular attention being paid to its mixing properties and cloud cover. The cloud cover limits the application of GOME for air quality studies, as already a small fraction of cloud cover influences the GOME measurement. For a cloud-free, homogeneous troposphere, GOME was found to compare well with other observations, although confidence is somewhat restricted as the selection criteria resulted in very few comparable days. The model developed on the GOME response to nonhomogenous distribution of the hot spot in the ground pixel also helps to give a proper interpretation to days with $MC \ll 1$ and to estimate the hot spot extension within the pixel. The examples provided and the methods used to allow a valid interpretation of the measurements could present a first guideline to the use of NO_2 tropospheric column measurements from GOME in atmospheric studies.

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P. Bonasoni, D. Bortoli, G. Giovanelli, I. Kostadinov, A. Petritoli, and F. Ravegnani, Institute of Atmospheric Science and Climate, ISAC-CNR, I-40129 Bologna, Italy. (a.petritoli@isac.cnr.it)

F. Fortezza, Regional Agency for Environmental Protection, ARPA, I-40139 Bologna, Italy.

A. Richter, Institute of Environmental Physics, University of Bremen, D-28334 Bremen, Germany.

D. Schaub and A. Weiss, Swiss Federal Laboratories for Materials Testing and Research, EMPA, CH-8600 Dübendorf, Switzerland.