First comparison of tropospheric NO_2 column densities retrieved from GOME measurements and in situ aircraft profile measurements

Jörg Heland and Hans Schlager

Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institut für Physik der Atmosphäre, Oberpfaffenhofen, Germany

Andreas Richter and John P. Burrows

Universität Bremen, Institut für Umweltphysik, Bremen, Germany

Received 22 May 2002; revised 19 June 2002; accepted 20 June 2002; published 26 October 2002.

[1] For the first time tropospheric NO_2 columns from GOME were compared to tropospheric columns derived from in situ measurements with the DLR research aircraft Falcon on a clear day above Austria. Under these conditions the agreement between the two methods is very good. The in situ measurements yield a tropospheric NO_2 column of $(4.2 \pm 1.7)\cdot10^{15}$ molec./cm^2, whereas the GOME data result in columns of $(3.5 \pm 0.9)\cdot10^{15}$ molec./cm^2 and $(4.1 \pm 1.0)\cdot10^{15}$ molec./cm^2 for near-real-time and dedicated analyses, respectively. The most important uncertainty of the aircraft measurements is caused by the lack of data in the lower boundary layer. The GOME uncertainties in this particular case are dominated by the assumptions made for the airmass factor calculation. This work is the first independent validation of tropospheric NO_2 columns from satellite instrumentation. Further validation at other seasons, and regions, including a more comprehensive sampling of the boundary layer is needed. *INDEX TERMS:* 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques; 0933 Exploration Geophysics: Remote sensing. **Citation:** Heland, J., H. Schlager, A. Richter, and J. P. Burrows, First comparison of tropospheric NO_2 column densities retrieved from GOME measurements and in situ aircraft profile measurements, *Geophys. Res. Lett.*, *29*(20), 1983, doi:10.1029/2002GL015528, 2002.

1. Introduction

[2] Nitrogen dioxide (NO_2) is one of the most important species in tropospheric chemistry. It controls the ozone production and thus the tropospheric ozone budget. Its tropospheric abundance is highly variable and is mainly influenced by anthropogenic emissions, i.e. fossil fuel and biomass burning, and natural sources such as soil emissions, lightning, and biomass/forest fires [e.g. *Lee et al.*, 1997, *Bradshaw et al.*, 2000]. Recently, algorithms to retrieve the vertical tropospheric column densities (VCD) of NO_2 from measurements of the Global Ozone Monitoring Experiment (GOME) on the ESA European research satellite ERS-2 have become available [e.g. *Burrows et al.*, 1999; *Leue et al.*, 2001]. Such data has many scientific applications. For example it can be used to study the tropospheric NO_2 distribution and transport on large scales and the impact of various anthropogenic and natural sources on the tropospheric NO_x abundance accounting for regional and seasonal variability [*Richter and Burrows*, 2001; *Leue et al.*, 2001; *Velders et al.*, 2001; *Martin et al.*, 2002; *Lauer et al.*, 2002]. In addition, the satellite data can be used to validate global chemistry-climate models, to better understand global atmospheric processes, and to facilitate future research campaigns and environmental monitoring on regional and global scales. However, in order to fully exploit the GOME data, it is necessary to understand the strengths and limitations of both the measurements from orbiting satellites and the assumptions within the retrieval algorithms.

[3] Many potential uncertainties are involved in the determination of total and tropospheric column density data of NO_2 from GOME and experimental validation is still missing. Within the EUROTRAC-2/TROPOSAT project validation strategies have been developed which include radiosondes, FTIR measurements, and aircraft-based observations (http://troposat.iup.uni-heidelberg.de). The objective of this case study was to compare GOME tropospheric NO_2 vertical column densities with aircraft-based tropospheric profile measurements of NO_2 and thereby begin the process of independent validation of the satellite data products. Comparisons were performed for measurements taken under cloud free conditions close to the time of an overpass of the ERS-2 satellite / GOME instrument.

2. Experimental

[4] The second European research satellite ERS-2 was launched on 20 April 1995 into a sun-synchronous near polar orbit with an equator crossing time of 10:30 LT in the descending node. The GOME instrument scans by means of a moving mirror across track. For the majority of GOME data the swath covers 960 km divided in three scans. Each of these scans has a ground-pixel size of 320 km across track and 40 km along track. With 14 orbits per day, global coverage at the equator is achieved after three days [*Burrows et al.*, 1999]. On approximately 3 days per month a smaller swath is used.

[5] The GOME instrument is a 4-channel double monochromator covering the wavelength range from 280 to 790 nm with a spectral resolution of 0.2 – 0.4 nm. GOME observes the light scattered by the atmosphere and reflected on the ground in near nadir view. Once per day, the

0094-8276/02/2002GL015528$05.00

extraterrestrial solar irradiance is measured and can be used as an absorption free background in the data analysis. The main target of the GOME instrument are global ozone measurements, but in addition, column amounts of other absorbers such as NO_2, BrO, OClO, SO_2, HCHO, and H_2O can be retrieved as well using the Differential Optical Absorption Spectroscopy (DOAS) technique [*Burrows et al.*, 1999].

[6] In this study the tropospheric NO_2 columns were derived from GOME spectra using the Tropospheric Excess Method (TEM) as described in *Richter and Burrows* [2001, *and references therein*]. Briefly, the data analysis consists of three steps: (a) determination of the total NO_2 column amount in the measurement, (b) subtraction of the estimated stratospheric contribution using measurements over regions with very clean tropospheric air and assuming that stratospheric NO_2 is not varying with longitude, and (c) correction for the light path through application of the so-called airmass factor (AMF).

[7] The AMF is defined as the ratio between the observed column density (slant column) and the vertically integrated column through the troposphere. AMF for tropospheric NO_2 columns were computed using the radiative transfer model GOMETRAN [*Rozanov et al.*, 1997]. Several assumptions are used in the calculation that have an impact on the results. The most important include the assumed shape of the vertical profile of the absorber, the surface albedo and the tropospheric aerosol loading. For this study, a surface albedo of 5% and an aerosol parameterisation based on the LOWTRAN aerosol model [*Shettle and Fenn*, 1976] are used. The error of the GOME columns is dominated by the uncertainties in the correction of the stratosphere and a number of input parameters used for the airmass factor calculation. A detailed discussion of the error budget is given in *Richter and Burrows* [2001]. Briefly, the main error sources are inhomogeneities in the stratospheric NO_2 field, uncertainties in cloud cover, the assumed vertical profile of NO_2, surface albedo and aerosol loading. An overview of the different error sources and their contribution to the total uncertainty is given in Table 1. The overall error of the near-real-time analyses is estimated to be in the order of $1.5 \cdot 10^{15}$ molec./cm^2.

[8] For comparison with the in situ measurements, three different GOME analyses have been considered: (a) The near-real-time data as described in *Richter and Burrows* [2001] and available on the internet (http://www.doas-bremen.de), (b) a dedicated analysis using the measured profile shape and urban aerosols in the radiative transfer calculations for the determination of the airmass factors and (c) a third analysis assuming different boundary layer profiles of NO_2 based on the minimum and maximum values of the ground-based measurements.

[9] In situ NO_2 profiles were measured with the research aircraft Falcon of Deutsches Zentrum für Luft- und Raumfahrt (DLR) over the Donau valley in Austria between Steyr and Mistelbach across two cloud free pixels of GOME (48.1–48.6°N, 14.3–16.5°E) between 12 and 13 UTC on 2 May 2001. The GOME overpass in this region was at 10 UTC.

[10] Simultaneous in situ measurements of NO, NO_2, O_3, CO, and meteorological parameters were performed with the Falcon aircraft. The details of the equipment are reported elsewhere [*Ziereis et al.*, 1999; 2000; *Huntrieser et al.*, 2002]. Briefly, NO is measured with a well characterized chemiluminescence detector (CLD). NO_2 is measured with a second CLD in combination with a photolysis cell in which the light from a broad-band 500 W UV Xe-lamp selectively converts a large fraction of NO_2 into NO. In order to minimize artifact response due to thermal dissociation of other reactive nitrogen species - which may become an important error source in the upper troposphere where the NO_2 mixing ratio is low - [*Gao et al.*, 1994; *Ziereis et al.*, 1999; *Ryerson et al.*, 2000; *Bradshaw et al.*, 2000] the temperature of the cell walls is kept constant at about 9°C. Calibration of the CLDs is performed before the flights using a diluted mixture of 3.11 ppmV ± 1% NO in N_2 (Messer Griesheim) with purified air. The pressure dependent efficiency of the NO_2 photolysis is determined with a known amount of NO_2 generated from gas phase titration of NO with O_3 and is 0.75–0.90 the altitudes discussed in this study. The detection limits of the instruments are 5 pptV for NO, and 10 pptV for NO_2. The nominal accuracies of the measurements are 10% and 15% for NO and NO_2, respectively [*Ziereis et al.*, 1999].

Table 1. Contribution of Possible Error Sources in GOME Analyses to the Uncertainty of the Retrieved Tropospheric NO_2 Column

Error Source	Uncertainty
fitting error	5%
stratospheric subtraction	$0.5 \cdot 10^{15}$ molec./cm^2
NO_2 vertical profile assumption (AMF)	50%[a]
aerosol assumption (AMF)	35%
surface albedo assumption (AMF)	max. 50% [a,b]
Cloud effects	30%[a]

[a] Error sources minimised in this study.
[b] In case of snow.

[11] The tropospheric NO_2 columns from the in situ measurements were calculated from the sum of the mean NO_2 number densities in bins of 100 m thickness. The error bars were derived from the standard deviations of the data in the 100 m bins and the measurement uncertainties. The aircraft data set was extrapolated to the tropopause at 11500 m and to the ground at 200 m because the aircraft measurement altitudes were limited to the range of 900 to 11300 m. The error bars on the extrapolated data were estimated to include the spread and the error bars of the experimental data above and - if possible - below the respective altitudes.

[12] Data from the nearest radiosonde launch from Hohe Warte Wien at 12 UTC, 2 May 2001, show that the planetary boundary layer (PBL) on this day was well mixed. As indicated on the right side of Figure 1 the measured water vapor mixing ratio was (1.1 ± 0.1) % by volume and the potential temperature was (296 ± 1) K from ground level to the top of the boundary layer at 1500 m. The aircraft data between 900 and 1500 m altitude also show fairly constant O_3- and CO-mixing ratios of 60 ppbV and 160 ppbV, respectively. Additionally, close to the area of interest, routine ground-based NO_2 measurements are performed in Illmitz (16.76°E, 47.77°N), Pillersdorf (15.94°E, 48.72°N), and Zöbelboden (14.44°E, 47.84°N), Austria [*Federal Environmental Agency, Austria*, 2001]. On 2 May 2001 between 10 and 13 UTC the measurements at these stations yielded an average value of (1.02 ± 0.81) ppbv of NO_2

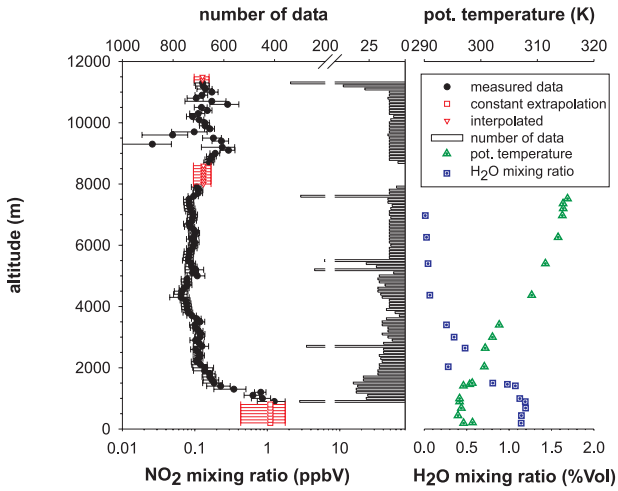

Figure 1. NO_2 profile from Falcon measurements and number of single measurements in the altitude bins. The tropospheric NO_2 column derived from the data amounts to $(4.2 \pm 1.7)\cdot10^{15}$ molec./cm^2. The radiosonde H_2O data and the potential temperature on the right hand side indicate that the PBL was well mixed.

($\pm 1\sigma$) with minimum and maximum values of 0.1 ppbv and 2.4 ppbv, respectively. These data indicate the range of the surface concentrations of NO_2 during this study, and are — together with the radiosonde observations — consistent with the assumption of a constant NO_2 mixing ratio of (1.1 ± 0.7) ppbv in the boundary layer as estimated from the aircraft data. The extreme values found at these stations are used for a sensitivity study (see below).

3. Results and Discussion

[13] Table 2 summarizes the results of the GOME analyses and the in situ measurements discussed in this study.

[14] Using the assumption of a well mixed boundary layer, as indicated in Figure 1, the in situ aircraft data yield a tropospheric NO_2 column of $(4.2 \pm 1.7)\cdot10^{15}$ molec./cm^2. The uncertainty of the aircraft column is about 40%, mainly due to the lack of data in the lower planetary boundary layer and the uncertainty associated with the extrapolation of the data at these altitudes.

[15] Figure 2 shows the near-real-time results of the GOME data in the vicinity of the aircraft flight track of this study. For comparison with the in situ measurements, the NO_2 columns from the two GOME pixels, which were covered by the aircraft flight-track, were averaged. As given in Table 2 the NO_2 column using the near-real-time GOME data amounts to $(3.5 \pm 0.9)\cdot10^{15}$ molec./cm^2, which is in good agreement with the in situ measurements. As discussed

Table 2. Summary of the Results of the Tropospheric NO_2 Column Densities for the Different Analysis Methods of GOME Spectra and the In Situ Aircraft Measurements, See Text for Details

	GOME NO_2 column (10^{15} molec./cm^2)	In situ NO_2 column (10^{15} molec./cm^2)
Near-real-time	3.5 ± 0.9	–
Dedicated analysis[a]	4.1 ± 1.0	4.2 ± 1.7

[a] In situ profile used for the GOME radiative transfer calculation.

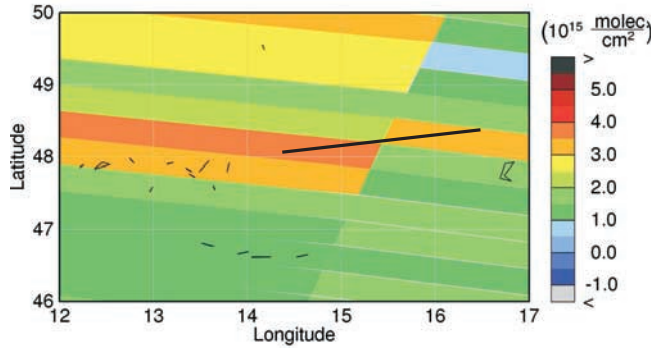

Figure 2. Near-real-time evaluation of the GOME tropospheric NO_2 column on 2 May 2001 including the aircraft flight track. The average value across the flight track is $(3.5 \pm 0.9)\cdot10^{15}$ molec./cm^2.

above, the NO_2 column derived from GOME measurements depends on the assumptions on vertical profile shape and aerosol loading made for the airmass factor calculation. If the shape of the vertical NO_2 distribution from the in situ measurements is used and an urban aerosol loading with 23 km visibility in the PBL is applied, as appropriate for the measurement location, the value increases to $(4.1 \pm 1.0)\cdot10^{15}$ molec./cm^2. This further improves the agreement with the DLR Falcon results.

[16] In general, the uncertainty of the GOME measurements arises primarily from uncertainties concerning cloud cover and airmass factors [*Richter and Burrows*, 2001] (see Table 1). As cloud free conditions prevailed on 2 May 2001, aerosol parameterisation and the uncertainty in the lowest part of the vertical NO_2 profile dominate the error budget for this particular case. Assuming the shape of the vertical profile as measured from the Falcon further reduces the errors. From a series of sensitivity studies, the remaining uncertainty in the GOME NO_2 columns in this study is estimated to be 25%, which is much lower than the values given in *Richter and Burrows* [2001].

[17] In order to obtain a better understanding of the effect of different profile assumptions in the lower part of the troposphere on the NO_2 column, both the in situ and the GOME data have been recalculated for 2 extreme scenarios. These calculations are based on the linear extrapolation of the in situ profile towards the minimum and maximum NO_2 concentrations, namely 0.1 and 2.4 ppbV, as measured by the ground-based systems during the experiment. The respective in situ columns amount to $3.4\cdot10^{15}$ and $5.6\cdot10^{15}$ molec./cm^2. Using the shape of these two extreme NO_2 profiles for the calculation of the GOME columns results in a variation of the retrieved NO_2 column between $3.6\cdot10^{15}$ and $4.5\cdot10^{15}$ molec./cm^2. It is important to note, that this relatively small variation is primarily due to the decreasing sensitivity of GOME towards the ground-layers and not the change in NO_2 column. However, even for these extreme scenarios, the in situ results changed by less than ±35%, and the GOME calculations by less than ±15%, showing that the comparison in this study does not depend critically on the assumptions made for the PBL.

[18] An additional and more fundamental uncertainty is introduced by the limited coverage of the two GOME pixels by the aircraft measurements. Comparing satellite and air-

borne results relies on a horizontally well mixed PBL over a scale of more than one hundred kilometres. As the meteorological situation on the day of the measurements was rather stable, this assumption seems acceptable. However, as seen in Figure 2, there are some spatial variations in the tropospheric NO_2 as measured from GOME, and on a different flight track the comparison between the two data sets might have been less favourable. The results presented in this study should therefore be regarded as a first attempt of validation by comparison, not as a rigorous validation of GOME measurements of tropospheric NO_2.

4. Summary

[19] Clear sky GOME measurements of tropospheric NO_2 columns above Austria have been compared to simultaneous measurements of the vertical distribution of tropospheric NO_2 by in situ instruments on board of the DLR Falcon. Based on radiosonde and ground-based measurements a well mixed planetary boundary layer with constant NO_2 mixing ratios was assumed, which lead to excellent agreement between tropospheric GOME columns and the columns derived from the in situ measurements.

[20] One of the difficulties of this study is the lack of in situ measurements in the lower boundary layer. In order to test the sensitivity of the results on the assumptions made for the PBL, the values have been varied within the range of concentrations found at three surface stations. Even for this extreme variation, the in situ measurements changed by less than ±35%, and the GOME measurements by less than ±15%, showing that the conclusions drawn do not depend critically on the assumptions made for the PBL.

[21] While the overall conditions of this validation exercise, i.e. cloud free GOME pixels, are favourable for UV/visible satellite observations of tropospheric species, the good agreement shows, that GOME measurements probe the troposphere and the algorithms yielding tropospheric columns are reasonably accurate at least for this particular case study. Clearly, more extensive validation of tropospheric measurements from space is required, including other regions, seasons, meteorological conditions and species.

[22] **Acknowledgments.** The authors thank U. Schumann, H. Ziereis, and P. Stock (DLR) for discussions the Falcon crew for good cooperation and the staff of the Austrian Federal Environmental Agency for fast provision of the ground-based data. This work benefited from the comments of two anonymous reviewers and discussions with T. Wagner (U. Heidelberg). GOME lv1-data were provided by ESA through DLR/DFD in Oberpfaffenhofen. Part of this study were funded by the University of Bremen and the EU through contract EVK2-CT-1999-00011.

References

Bradshaw, J., D. Davis, G. Grodzinsky, S. Smyth, R. Newell, S. Sandholm, and S. Liu, Observed distributions of nitrogen oxides in the remote free troposphere from NASA global tropospheric experiment programs, *Rev. Geophys.*, *38*, 61–116, 2000.

Burrows, J. P., M. Weber, M. Buchwitz, V. Rozanov, A. Ladstätter-Weißenmayer, A. Richter, R. DeBeek, R. Hoogen, K. Bramstedt, K.-U. Eichmann, M. Eisinger, and D. Perner, The global ozone monitoring experiment (GOME): Mission concept and first scientific results, *J. Atm. Sci.*, *56*, 151–175, 1999.

Federal Environmental Agency, Austria, Monatsbericht der an den Luftgütestellen des Umweltbundesamtes gemessenen Immissionsdaten - Mai 2001, Umweltbundesamt, Spittelauer Lände 5, A-1090 Wien, Austria, 2001.

Gao, R. S., E. R. Keim, E. L. Woodbridge, S. J. Ciciora, M. H. Proffitt, T. L. Thomson, R. J. Mclaughlin, and D. W. Fahey, New photolysis system for NO_2 measurements in the lower stratosphere, *J. Geophys. Res.*, *99*, 20,673–20,681, 1994.

Huntrieser, H., C. Feigl, H. Schlager, F. Schröder, C. Gerbig, P. v. Velthoven, F. Flatoy, C. Thery, A. Petzold, H. Höller, and U. Schumann, Airborne measurements of NO_x, tracer species and small particles during the European Lightning Nitrogen Oxides Experiment, *J. Geophys. Res.*, in press, June 2002.

Lauer, A., M. Dameris, A. Richter, and J. P. Burrows, Tropospheric NO_2 columns: a comparison between model and retrieved data from GOME measurements, *Atmos. Chem. Phys.*, *2*, 67–78, 2002.

Lee, D. S., I. Köhler, E. Grobler, F. Rohrer, R. Sausen, L. Gallardo-Klenner, J. G. J. Olivier, F. J. Dentener, and A. F. Bouwman, Estimation of global NO_x emissions and their uncertainties, *Atmos. Environ.*, *31*, 1735–1749, 1997.

Leue, C., M. Wenig, T. Wagner, O. Klimm, U. Platt, and B. Jaehne, Quantitative analysis of NO_x emissions from Global Ozone Monitoring Experiment satellite image sequences, *J. Geophys. Res.*, *106*, 5493–5505, 2001.

Martin, R. V., K. Chance, D. J. Jacob, T. P. Kurosu, R. J. D. Spurr, E. Bucsela, J. F. Gleason, P. I. Palmer, I. Bey, A. M. Fiore, Q. Li, and R. M. Yantosca, An improved retrieval of tropospheric nitrogen dioxide from GOME, accepted for publication in *J. Geophys. Res.*, 2002.

Richter, A., and J. P. Burrows, Retrieval of tropospheric NO_2 from GOME measurements, *Adv. Space Res.*, in press, 2001.

Rozanov, V., D. Diebel, R. J. D. Spurr, and J. P. Burrows, GOMETRAN: A radiative transfer model for the satellite project GOME - the plane parallel version, *J. Geophys. Res.*, *102*, 16,683–16,695, 1997.

Ryerson, T. B., E. J. Williams, and F. C. Fehsenfeld, An efficient photolysis system for fast-response NO_2 measurements, *J. Geophys. Res.*, *105*, 26,447–26,461, 2000.

Shettle, E. P., and R. W. Fenn, Models of the atmospheric aerosols and their optical properties, in AGARD Conference Proceedings No. 183, ADA028-615, 1976.

Velders, G. J. M., C. Granier, R. W. Portmann, K. Pfeilsticker, M. Wenig, T. Wagner, U. Platt, A. Richter, and J. P. Burrows, Global tropospheric NO_2 column distributions: Comparing 3-D model calculations with GOME measurements, *J. Geophys. Res.*, *106*, 12,643–12,660, 2001.

Ziereis, H., H. Schlager, P. Schulte, I. Köhler, R. Marquardt, and C. Feigl, In situ measurements of the NO_x distribution and variability over the eastern North Atlantic, *J. Geophys. Res.*, *104*, 16,021–16,032, 1999.

Ziereis, H., H. Schlager, P. Schulte, P. F. J. v. Velthoven, and F. Slemr, Distributions of NO, NO_x, and NO_y in the upper troposphere and lower stratosphere between 28° and 61°N during POLINAT 2, *J. Geophys. Res.*, *105*, 3653–3664, 2000.

J. Heland and H. Schlager, Deutsches Zentrum für Luft- und Raumfahrt, Institut für Physik der Atmosphäre, 82234 Wessling, Germany. (joerg.heland@dlr.de; hans.schlager@dlr.de)

A. Richter and J. P. Burrows, Universität Bremen, Institut für Umweltphysik, 28359 Bremen, Germany. (andreas.richter@iup.physik.uni-bremen.de; john.burrows@iup.physik.uni-bremen.de)