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Abstract

The trend in stratospheric NO₂ column at the NDACC (Network for the Detection of Atmospheric Composition Change) station of Jungfraujoch (46.5° N, 8.0° E) is assessed using ground-based FTIR and zenith-scattered visible sunlight SAOZ measurements over the period 1990 to 2009 as well as a composite satellite nadir data set constructed from ERS-2/GOME, ENVISAT/SCIAMACHY, and METOP-A/GOME-2 observations over the 1996–2009 period. To calculate the trends, a linear least squares regression model including explanatory variables for a linear trend, the mean annual cycle, the quasi-biennial oscillation (QBO), solar activity, and stratospheric aerosol loading is used. For the 1990–2009 period, statistically indistinguishable trends of -3.7 ± 1.1 %/decade and -3.6 ± 0.9 %/decade are derived for the SAOZ and FTIR NO₂ column time series, respectively. SAOZ, FTIR, and satellite nadir data sets show a similar decrease over the 1996–2009 period, with trends of -2.4 ± 1.1 %/decade, -4.3 ± 1.4 %/decade, and -3.6 ± 2.2 %/decade, respectively. The fact that these declines are opposite in sign to the globally observed $+2.5$ %/decade trend in N₂O, suggests that factors other than N₂O are driving the evolution of stratospheric NO₂ at northern mid-latitudes. Possible causes of the decrease in stratospheric NO₂ columns have been investigated. The most likely cause is a change in the NO₂/NO partitioning in favor of NO, due to a possible stratospheric cooling and a decrease in stratospheric chlorine content, the latter being further confirmed by the negative trend in the ClONO₂ column derived from FTIR observations at Jungfraujoch. Decreasing ClO concentrations slows the NO + ClO → NO₂ + Cl reaction and a stratospheric cooling slows the NO + O₃ → NO₂ + O₂ reaction, leaving more NO_x in the form of NO. The slightly positive trends in ozone estimated from ground- and satellite-based data sets are also consistent with the decrease of NO₂ through the NO₂ + O₃ → NO₃ + O₂ reaction. Finally, we cannot rule out the possibility that a strengthening of the Dobson-Brewer circulation, which reduces the time available for N₂O photolysis in the stratosphere, could also contribute to the observed decline in stratospheric NO₂ above Jungfraujoch.

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1 Introduction

Nitrogen dioxide (NO₂) plays an important role in controlling ozone abundances in the stratosphere (Solomon, 1999), either by destroying ozone through the NO_x (NO + NO₂) catalytic destruction cycles, or by mitigating ozone destruction by converting active chlorine, hydrogen, and bromine into their reservoir forms (ClONO₂, HNO₃, and BrONO₂, respectively). The primary source of NO_x is the oxidation of nitrous oxide (N₂O) in the middle stratosphere. N₂O is an important greenhouse gas and its emissions in the troposphere are known to be increasing by 2.5–3% per decade (Liley et al., 2000), mainly due to agricultural activity. Monitoring long-term changes in stratospheric NO₂ is essential for attributing observed changes in stratospheric ozone. However, few studies of the long-term evolution of stratospheric NO₂ have been published to date. Liley et al. (2000) reported an increase in stratospheric NO₂ of about 5%/decade from ground-based zenith-scattered visible sunlight measurements at Lauder, New Zealand (45° S, 170° E) between 1981 and 1999. Recently, Dirksen et al. (2011) further confirmed an increase of NO₂ of 5%/decade over this station for the 1981–2010 period also from ground-based UV-visible data. Using 3-D-Chemical Transport Model calculations, McLinden et al. (2001) suggested that the 5%/decade NO₂ trend from 1981 to 1999 results from a 2.5%/decade increase due to rising N₂O emissions and further 2.5%/decade increase resulting from a decrease in stratospheric ozone. The abundance of NO₂ in the stratosphere can be affected by ozone through the following reaction (Fish et al., 2000):



Gruzdev (2009) investigated the latitudinal structure of the stratospheric NO₂ trend using ground-based zenith-sky UV-visible and FTIR observations from a selection of 23 sites within the Network for the Detection of Atmospheric Composition Change (NDACC). This study, performed over different time periods between 1983 and 2007, showed that the NO₂ trend is predominantly positive at mid-latitudes in the Southern Hemisphere while negative trends are observed at most Northern Hemisphere mid-

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latitude sites. Cook and Roscoe (2009) inferred trends in stratospheric NO₂ from measurements obtained during the 1990–2007 period from a zenith-sky UV-visible spectrometer in the Antarctic. The NO₂ trend strongly depends on the period, with a positive trend of ~10%/decade from 1990 to 2000, a negative trend of ~20%/decade from 2000 to 2007, and no overall trend for the full time period. These studies show that the trend in stratospheric NO₂ has a complicated structure which does not always follow the evolution of its main source (N₂O) and displays a strong dependence on the location and time period considered for the trend analysis.

Trends in stratospheric NO₂ at the Jungfraujoch NDACC station in the Swiss Alps (46.5° N, 8.0° E) are quantified and interpreted below. Ground-based UV-visible SAOZ (Système d'Analyse par Observation Zénithale) and Fourier Transform Infra-Red (FTIR) spectrometers have been operating continuously at this station since 1990 and 1985, respectively, providing more than two decades of measurements. A combination of stratospheric NO₂ columns retrieved from the ERS-2/GOME (1996–2003), ENVISAT/SCIAMACHY (2003–2009), and METOP-A/ GOME-2 (2007–2009) satellite nadir instruments is also included in this study, permitting, for the first time, a thorough analysis of the long-term evolution of stratospheric NO₂ from three (two ground-based and one satellite) independent measurement techniques at this site. The paper is divided into 4 sections. Section 2 provides a description of the ground-based and satellite data sets. The consistency between the different data sets is investigated in Sect. 3 through comparisons between (1) ground-based FTIR and UV-visible NO₂ column time series, and (2) satellite and ground-based UV-visible observations. In Sect. 4, the linear least squares regression model used for the trend study is described and the results of the trend analyses are presented and discussed. Conclusions are given in Sect. 5.

2 Data sets

2.1 SAOZ observations

The SAOZ instrument is a broad-band (300–600 nm), medium resolution (~ 1 nm) diode-array spectrometer that measures zenith scattered sunlight (Pommereau and Goutail, 1988). Between 1990 and 2009 two different versions of the SAOZ instrument were used. The first (NMOS) described in Van Roozendaal et al. (1994) is based on a Jobin-Yvon spectrometer (model CP200) coupled to a 512 diode Hamamatsu NMOS detector. In December 1998, the system was upgraded to a 1024 diode Hamamatsu detector. This second version (SAM) provides low sun spectra with a better resolution and a higher signal to noise ratio than the NMOS version.

Zenith radiance spectra are analyzed using the DOAS (Differential Optical Absorption Spectroscopy) technique (Platt and Stutz, 2008). NO_2 is retrieved in the 425–490 nm wavelength range, taking into account the spectral signatures of NO_2 , O_3 , H_2O , O_4 , and the filling-in of the solar Fraunhofer bands by the Ring effect (Grainger and Ring, 1962). The NO_2 absorption cross-sections at 220 K are from Vandaele et al. (1997). A third-order polynomial is used to fit the low frequency spectral structure due to molecular and Mie scattering.

NO_2 vertical column densities are derived from vertical profiles retrieved by applying a profiling technique to sunrise and sunset NO_2 differential slant column densities (DSCDs) which are the direct product of the DOAS analysis. The profiling algorithm is based on the Optimal Estimation Method (OEM; Rodgers, 2000) and is described in Hendrick et al. (2004). In brief, a profile $\hat{\mathbf{x}}$ is retrieved given an a priori profile \mathbf{x}_a , the measurements \mathbf{y} (here, twilight NO_2 DSCDs as a function of solar zenith angle (SZA)), their respective uncertainty covariance matrices (\mathbf{S}_a and \mathbf{S}_ϵ), and the matrix \mathbf{K} of the weighting functions. Since NO_2 is an optically thin absorber, the OEM for the linear case can be considered:

$$\hat{\mathbf{x}} = \mathbf{x}_a + \mathbf{S}_a \mathbf{K}^T (\mathbf{K} \mathbf{S}_a \mathbf{K}^T + \mathbf{S}_\epsilon)^{-1} (\mathbf{y} - \mathbf{K} \mathbf{x}_a) \quad (1)$$

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with $\mathbf{K} = \frac{\partial \mathbf{y}}{\partial \mathbf{x}}$ and \mathbf{K}^T is the transpose of \mathbf{K} .

The weighting functions indicate the sensitivity of the measurements to a change in the vertical profile. The matrix \mathbf{K} is determined by consecutively perturbing each layer of the a priori profile and recalculating the set of measurements using the so-called forward model which describes the physics of the measurements. Here, the forward model consists of the stacked photochemical box model PSCBOX coupled to the radiative transfer model (RTM) UVSPEC/DISORT (see Hendrick et al., 2004, 2006 for further details about both models). The photochemical model, initialized daily with chemical and meteorological fields from the SLIMCAT 3-D-CTM (Chipperfield et al., 2006), is able to simulate the rapid variation of NO_2 at twilight. The model also provides a priori profiles to the profiling algorithm and is used to photochemically convert the retrieved profiles, which are representative of twilight conditions, to the mean SZA corresponding to the FTIR and satellite nadir observations. The DSCDs are analyzed using daily reference spectra and the effective residual amounts of NO_2 in the reference spectra are directly fitted by the profiling algorithm. Combining this with an a priori tropospheric NO_2 content close to zero leads to retrieved vertical profiles and corresponding vertical columns mainly representative of the stratosphere (Hendrick et al., 2004, 2008). Performing the DOAS analysis with daily reference spectra also minimizes the potential impact of any long-term degradation of the instrument on the NO_2 vertical column time series, which is important for calculating robust trends. NO_2 profile retrievals are quality-checked based on the retrieval fit residual (RMS of the difference between measured SCDs and those calculated using the retrieved profiles; see Hendrick et al., 2004). In practice, all retrievals with a residual larger than 3.5×10^{15} molec cm^{-2} are rejected. This method of selection excludes measurements contaminated by tropospheric NO_2 which usually display short-term variability inconsistent with the expected smooth variation of the stratospheric slant column during twilight. A detailed error budget can be found in Hendrick et al. (2004). Taking into account the smoothing error, the retrieval noise, and the forward model parameter error,

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the total relative uncertainty on the retrieved stratospheric NO₂ columns is about 8 % on average. High aerosol loading can also perturb UV-visible measurements by modifying the scattering geometry. During the period considered in this study (1990–2009), the Mount Pinatubo eruption in June 1991 injected large amounts of aerosols into the stratosphere. In the years immediately following this event (1991–1994), an extinction profile corresponding to a volcanic aerosol loading was selected from the aerosol model of Shettle (1989) and included in the UVSPEC/DISORT RTM for the calculation of the weighting functions needed for the OEM-based profile retrieval. Before and after the 1991–1994 period, a background aerosol extinction profile was used. Sensitivity tests have shown that the use of an aerosol extinction profile corresponding to volcanic conditions has an impact of up to 10 % on the retrieved stratospheric NO₂ columns. Aerosol loading changes due to the Mount Pinatubo eruption are also implemented in the SLIMCAT model through the use of monthly zonal mean time series of surface sulfate area density created from different satellite data sets (more details are available at http://homepages.see.leeds.ac.uk/~lecmc/sparc/Forcings/SPARC_Forcing_WMO2011.html).

2.2 Ground-based FTIR observations

In the early 1950s, M. Migeotte performed pioneering atmospheric infrared observations at the Jungfraujoch. Since then, the University of Liège has operated state-of-the-art instruments at that site to record high-resolution spectra allowing production of atlases of the solar spectrum and monitoring of the state of the Earth's atmosphere (Zander et al., 2008 and references therein). This long-term commitment has allowed the collection of a unique observational data base in terms of quality, time extension and measurement density. FTIR high-resolution solar absorption spectra have been recorded regularly under clear-sky conditions since 1985 with a homemade instrument, backed-up in the early 1990s by a commercial Bruker IFS-120HR. Over the time period of interest here, spectra were obtained on average on 115 days per year.

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For this study, all available observations since 1990 have been fitted with the V3.91 of the SFIT-2 algorithm, using pressure and temperature information provided by the National Centers for Environmental Prediction (NCEP, see <http://www.ncep.noaa.gov>) and assuming the HITRAN 2004 spectroscopic line parameter compilation, including the August 2006 updates (Rothmann et al., 2004, see also <http://www.cfa.harvard.edu/hitrان>). The SFIT-2 code also implements the OEM (Rodgers, 2000), enabling the derivation of the vertical distributions of most of the FTIR target gases (e.g., Pougatchev and Rinsland, 1995; Rinsland et al., 2003a). In the present case, two microwindows ranging from 2914.6 to 2914.7 cm⁻¹ and from 2915 to 2915.11 cm⁻¹ have been fitted; a priori vertical profiles for fitted (H₂O, CH₄ and O₃ scaled during the retrieval process) and simulated interferences (e.g. H₂CO) were based on predictions obtained with the version 5 of the WACCM model (Whole-Atmosphere Community Climate Model, see Chang et al., 2008). For NO₂, we used 12 monthly profiles based on the same PSCBOX/SLIMCAT modeled a priori profile data set as for the SAOZ profile retrieval (see Sect. 2.1). The forward model was characterized by a diagonal covariance of 40 % per km and, with extra-diagonal elements based on a Gaussian half-width for interlayer correlation of 4 km. Regarding the error budget, estimates reported in Table 2 of Rinsland et al. (2003a) remain valid (total random and systematic errors of 11 % and 36 %, respectively), although they can be considered as conservative.

2.3 Satellite nadir observations

GOME, SCIAMACHY, and GOME-2 stratospheric NO₂ columns are retrieved using the KNMI/BIRA TEMIS NO₂ algorithm (Boersma et al., 2004, 2007; Dirksen et al., 2011). For this study, we use versions TM4NO2A v1.04 for GOME and TM4NO2A v1.10 for SCIAMACHY and GOME-2, and the periods covered by the different instruments are 1995–2003, 2002–2009, and 2007–2009, respectively. The TEMIS algorithm is based on a two-step process including (1) the retrieval of NO₂ slant columns with the DOAS method, and (2) the estimation of the stratospheric component of the NO₂ slant columns through data assimilation in the TM4 chemistry transport model.

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The purpose of the assimilation is to regularly update the TM4 simulation with available measurements such that the model simulation of the stratospheric NO₂ column is closely constrained by the satellite measurements. In step 1, the DOAS analysis is performed in the following wavelength ranges: 425–450 nm for GOME and GOME-2 and 426.5–451.5 nm for SCIAMACHY. Absorption by NO₂, ozone, water vapor, the Ring effect, and a third-order polynomial that describes the residual broadband features due to Rayleigh and Mie scattering are taken into account. The NO₂ cross-sections set at 220 K from Vandaele et al. (1997) is used. A correction for the difference between 220 K and the effective temperature of NO₂ along the light path is applied to the NO₂ absorption cross-sections. The stratospheric NO₂ vertical columns are calculated by dividing the assimilated stratospheric slant columns by a simple geometrical airmass factor depending only on the SZA and viewing angle (Boersma et al., 2004). The estimated error on TEMIS stratospheric NO₂ columns is about 0.2–0.3 × 10¹⁵ molec cm⁻² (Boersma et al., 2004; Dirksen et al., 2011).

For this study, all pixels falling within a radius of 300 km around Jungfraujoch were selected and no filtering based on the cloud fraction was applied.

3 Evaluation of data consistency

3.1 FTIR and SAOZ data set comparison

First, we have compared the information content associated with both FTIR and SAOZ profile retrievals. As can be seen in Fig. 1, column averaging kernels are very similar for both techniques with no sensitivity to NO₂ in the troposphere and a maximum sensitivity between 20 and 35 km altitude where the NO₂ concentration in the stratosphere is the largest. Figure 1 also presents the eigenvector expansion of the averaging kernel matrix **A** corresponding to the two largest eigenvalues. The first eigenvalue, close to unity, implies an almost 100 % contribution of the measurements in this pattern (Hendrick et al., 2004). This pattern also indicates that the altitude range with high sensitivity

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to the NO₂ vertical distribution is ~13–40 km for both retrievals. The number of independent pieces of information, also called the degree of freedom for signal (DOFS), given by the trace of the matrix **A** (Rodgers, 2000), is about 1.2 in both cases. From this information content assessment, it can be concluded that both FTIR and SAOZ retrievals have similar vertical resolution and sensitivity to the vertical distribution of NO₂ and therefore retrieved NO₂ columns can be directly compared.

The consistency between ground-based FTIR and SAOZ data sets is evaluated by comparing the monthly mean stratospheric NO₂ columns for the 1990–2009 period (see Fig. 2). To ensure photochemical matching, i.e. comparison in the same photochemical conditions, the SAOZ profiles and corresponding columns, representative of twilight conditions, are converted on a daily basis to the mean FTIR measurement SZA using the PSCBOX photochemical model of the SAOZ profiling algorithm forward model (see Sect. 2.1). FTIR and SAOZ data sets are in good agreement, with FTIR measurements lower than SAOZ by $7.8 \pm 8.2\%$ on average.

Combining the facts that both retrievals used similar a priori profiles and have similar sensitivity to the vertical distribution of NO₂, the remaining differences between FTIR and SAOZ NO₂ columns are consistent with the uncertainties affecting the respective spectroscopic parameters.

3.2 SAOZ and satellite nadir data set comparison

SAOZ and satellite nadir (GOME, SCIAMACHY, and GOME-2) monthly mean stratospheric NO₂ columns are compared in Fig. 3. The retrieved SAOZ columns are photochemically converted to the satellite overpass SZA in order to perform comparisons under the same photochemical conditions. A good agreement is obtained with mean satellite minus SAOZ relative differences of $+0.9 \pm 8.8\%$ (GOME), $+1.9 \pm 11.5\%$ (SCIAMACHY), and $+2.3 \pm 11.6\%$ (GOME-2), i.e. not significant at the 1-sigma uncertainty level. Based on these results, the composite satellite data set of monthly mean NO₂ columns used for trend analysis is constructed as follows: GOME data for the March 1996–June 2003 period, SCIAMACHY data for the July 2003–March

2007 period, and a merging of the SCIAMACHY and GOME-2 data for the April 2007–December 2009 period, given the fact that the biases between both satellite data sets and SAOZ observations are similar.

4 Trend analysis

4.1 Statistical model description

To extract the linear trend in the stratospheric NO₂ vertical column time series, a linear least squares regression model is fitted to the data to account for any extraneous variability that might affect the trend or its uncertainty. A modified version of the regression model developed by Bodeker et al. (1998) is used. It includes terms for offset, linear trend, quasi-biennial oscillation (QBO), solar activity, and aerosols effect, i.e.:

$$\begin{aligned}
 m(t) = & A(N_A = 2) + \\
 & B(N_B = 2) \times t + \\
 & C(N_C = 2) \times \text{QBO}(t) + \\
 & D(N_D = 0) \times \text{Solar}(t) + \\
 & E(N_E = 1) \times \text{Aerosols}(t) + \\
 & U\delta
 \end{aligned} \tag{2}$$

where $m(t)$ is the statistically modeled monthly NO₂ vertical column at decimal year t and A – E are the model coefficients expanded as (for example):

$$A = A_0 + \sum_{k=1}^{N_A} [A_{2k-1} \sin(2\pi kt) + A_{2k} \cos(2\pi kt)] \tag{3}$$

to fit seasonality. The N_A to N_E coefficient values appear in Eq. (2). U accounts for a possible bias between the GOME and SCIAMACHY/GOME-2 columns (δ switches

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from 1 to 0 in July 2003). A similar approach is applied to the SAOZ data set to account for any bias after April 1998 resulting from the installation of the new version of the SAOZ instrument.

The QBO basis function is based on the 30 and 50 hPa Singapore monthly mean zonal winds (<http://www.geo.fu-berlin.de/met/ag/strat/produkte/qbo/index.html>). Using these two pressure levels separately allows a covering of the altitude range of the stratospheric NO₂ profile and an automatic fitting of the phase of the QBO. For the solar cycle basis function, the radio-frequency F10.7 cm solar flux (ftp://ftp.ngdc.noaa.gov/STP/SOLAR_DATA/SOLAR_RADIO/FLUX) is used. The aerosols basis function is based on the stratospheric aerosol optical depth (AOD) climatology of Vernier et al. (2011) created from SAGE II, CALIPSO, and ENVISAT/GOMOS observational data sets. The AOD time series corresponding to the 20° N–50° N latitude band was extracted for this study. This climatology includes the large changes in aerosol loading related to the Mount Pinatubo eruption as well as smaller changes due to a series of moderate volcanic eruptions, primarily at tropical latitudes, causing an increase in the stratospheric aerosol loading since 2002 (Vernier et al., 2011).

The standard deviation σ_B on a trend B can be calculated using the standard deviation σ_N of the fit residuals (differences between modelled and observed NO₂ columns) and their autocorrelation coefficient ϕ (Weatherhead et al., 1998; van der A et al., 2006):

$$\sigma_B = \frac{\sigma_N}{n^{3/2}} \sqrt{\frac{1 + \phi}{1 - \phi}} \quad (4)$$

where n is the length of the time series.

A test of the significance of the trend B can be computed as the ratio between the trend and its standard deviation:

$$t_B = |B/\sigma_B| \quad (5)$$

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A commonly applied decision rule for trend detection is that a trend is real at a 95 % confidence level when $t_B > 2$ (Weatherhead et al., 1998; Santer et al., 2000).

4.2 Results and discussion

Figure 4 shows the regression fits to the SAOZ and FTIR monthly mean time series and the derived trends over the period 1990–2009. The SAOZ-based trend (-3.7 ± 1.1 %/decade; 1-sigma uncertainty) agrees with the FTIR-based trend (-3.6 ± 0.9 %/decade). The contributions of the QBO, solar cycle, and aerosols basis functions to the signal are presented in Fig. 5. An examination of the regression fit coefficients and their respective standard deviations indicates that only the aerosols basis function makes a statistically significant contribution to the FTIR and SAOZ signals. The fact that QBO and solar cycle do not contribute significantly is consistent with what Dirksen et al. (2011) found using OMI data at 50° N. We find also that the contributions of the QBO and solar cycle basis functions are larger for the SAOZ time series than for the FTIR time series. Sensitivity tests show that this results from the greater number of gaps in the SAOZ data set. The above mentioned trend values are significant at the 95 % confidence level. The uncertainty on the fit coefficients is based on the premise that the fit residuals are normally distributed. Figure 6 shows that this assumption is justified for both FTIR and SAOZ with fit residuals randomly scattered around zero and normally distributed.

A similar trend analysis is performed for the 1996–2009 period using ground-based SAOZ, FTIR, and satellite nadir data sets (see Fig. 7). For SAOZ, the trend is estimated using two data sets corresponding to the twilight NO_2 columns converted daily to the mean SZA of the FTIR and satellite nadir observations, respectively. Declines in NO_2 are seen consistently across all data sets, viz.: -3.6 ± 2.2 %/decade for satellites, -2.4 ± 1.1 %/decade for SAOZ at satellite SZA, -4.3 ± 1.4 %/decade for FTIR, and -2.7 ± 1.2 %/decade for SAOZ at FTIR SZA. It should be noted that the trend value estimated from the satellite data is not statistically significant at the 95 % confidence level. The uncertainty on the fit coefficients for the QBO, solar cycle, and aerosols basis

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functions indicates that none of these forcing mechanisms make a statistically significant contribution to the NO₂ time series measured by satellite, SAOZ, and FTIR for the 1996–2009 period.

All trend analysis results are summarized in Table 1. A good agreement is found between SAOZ, FTIR, and satellite nadir observations with a decline in the stratospheric NO₂ column reaching 3%/decade for both the 1990–2009 and 1996–2009 periods. This decrease is not consistent with the increase in N₂O of about +2.5%/decade reported globally (WMO, 2007) and in particular from FTIR observations at the Jungfraujoch station (Angelbratt et al., 2011). Since in the NO_y chemistry, N₂O is the source of NO_y and then NO_y is subsequently partitioned into family members, opposite NO₂ and N₂O trends suggest a change in the NO_y partitioning. In the second part of this Section, we discuss possible explanations for the observed decline of NO₂ related or not to a NO_y partitioning change.

First, ClONO₂ and HNO₃, which are two major NO_y species (Brohede et al., 2008) and important chlorine and hydrogen reservoirs in the stratosphere, can be useful indicators of the abundance of NO₂. They are formed by the following termolecular reactions:



The main loss reactions for these species are photolysis, which releases NO₂, as well as reactions with OH (for HNO₃) and dissociation on aerosols and ice particles (for ClONO₂). HNO₃ and ClONO₂ have been measured routinely at the Jungfraujoch station since the early 1980s using the FTIR technique (Rinsland et al., 2003b; Vigouroux et al., 2007; Wolff et al., 2008; Kohlhepp et al., 2011). This permits a trend analysis over the same time periods as was done for NO₂. Trend values are derived by applying the least squares regression model, described in Sect. 4.1, to the FTIR ClONO₂ and HNO₃ total column time series. Results are presented in Fig. 8. For ClONO₂, negative trends of -5.8 ± 1.0 %/decade and -8.2 ± 1.4 %/decade are found

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for the 1990–2009 and 1996–2009 periods, respectively. The latter value is more negative by about 3%/decade with respect to the trend in total tropospheric chlorine of -6.0 ± 0.5 %/decade observed over the same 1996–2009 period (WMO, 2011a). In the light of Reaction (R2), this larger decline of ClONO_2 is consistent with a decrease of stratospheric NO_2 of about 3%/decade as observed since 1996 from SAOZ, FTIR, and satellite nadir NO_2 data sets, suggesting that NO_2 could control the trend of ClONO_2 together with total chlorine. Moreover, chlorine may also play an important role in the partitioning of NO_x into NO and NO_2 through the following reaction (Crutzen, 1979):



Given (R4), if ClO would be decreasing, more NO_x could stay in the NO form.

For HNO_3 , positive trends of $+1.0 \pm 0.8$ %/decade and $+1.9 \pm 1.2$ %/decade are found for the 1990–2009 and 1996–2009 periods, respectively (see Fig. 8). Even if not statistically significant at the 95% confidence level, this increase in HNO_3 is not surprising and not necessarily inconsistent with the observed decline of NO_2 : HNO_3 being the most abundant NO_y species in terms of column, an increase of N_2O should result in a positive trend in NO_y and therefore in HNO_3 .

As discussed in the introduction, ozone can also influence the abundance of NO_2 in the stratosphere: a decrease in ozone leads to an increase in NO_2 and vice versa through the (R1) reaction. We have inferred the trend in the ozone column at Jungfraujoch by applying our least squares regression model to two total ozone column data sets. The first one is based on measurements from the Dobson spectrophotometer instrument No. 101 operating at Arosa (46.8°N , 9.7°E), close to the Jungfraujoch station. The second data set combines satellite-based measurements from TOMS (Total Ozone Mapping Spectrometer), SBUV (Solar Backscattered Ultra-Violet), and OMI (Ozone Monitoring Instrument), and GOME instruments (Bodeker et al., 2005). A very good consistency is obtained between Dobson and satellite trend values (see Fig. 8): $+0.6 \pm 0.6$ %/decade (Dobson) and $+0.3 \pm 0.6$ %/decade (satellite) for 1990–2009 and $+1.6 \pm 0.8$ %/decade (Dobson) and $+1.1 \pm 0.8$ %/decade (satellite) for 1996–2009. It should be noted that the two latter values are also reasonably consistent with the O_3

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trend of $+0.6 \pm 0.9$ %/decade estimated from FTIR observations at Jungfraujoch during the 1996–2009 period (Vigouroux et al., 2008; WMO, 2011b). Given the Reaction (R1), these slight increases in ozone could at least partly contribute to the observed negative trend in NO_2 , even if not statistically significant at the 95 % confidence level.

5 A change in the Dobson–Brewer circulation could also affect the evolution of stratospheric NO_2 (Fish et al., 2000). Cook and Roscoe (2009) recently reported a small, though not significant, increase in the stratospheric circulation of $+1.4 \pm 3.5$ %/decade derived from SAOZ NO_2 observations in Antarctic summer. A strengthening speed up of the Dobson-Brewer circulation would lead to less time in the stratosphere for the conversion of N_2O to reactive nitrogen, resulting in a downwards trend of the NO_2 vertical column.

10 Finally, Revell et al. (2012) recently investigated the links between N_2O and NO_x concentrations using chemistry-climate model simulations in order to study the past and future effectiveness of N_2O in depleting stratospheric ozone. Their findings are consistent with our observations at Jungfraujoch: they showed that the NO_2/NO partitioning is currently changing with time to favor NO , due to stratospheric cooling, which slows the $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ reaction, and decreasing ClO concentrations, which slows the $\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$ reaction. It should be noted that a stratospheric cooling can also decrease the amount of NO_y in the stratosphere from N_2O (Rosenfield and Douglass, 1998).

5 Summary and conclusions

We have presented consolidated time series of stratospheric NO_2 vertical columns at the NDACC station of Jungfraujoch retrieved from ground-based FTIR and SAOZ observations as well as from GOME, SCIAMACHY, and GOME-2 satellite nadir measurements. The time period covered by the FTIR and SAOZ observations is 1990–2009 while combining the three satellite data sets covers the 1996–2009 period. We have first performed a cross-verification of the different data sets through the comparison

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of FTIR and SAOZ NO₂ columns on one hand, and the comparison between satellite nadir and SAOZ observations on the other hand. FTIR NO₂ columns agree well with SAOZ columns with a bias of $-7.8 \pm 8.2\%$ on average over the 1990–2009 period. A good agreement is also found between satellite nadir and SAOZ data sets with mean relative differences of $+0.9 \pm 8.8\%$ (GOME), $+1.9 \pm 11.5\%$ (SCIAMACHY), and $+2.3 \pm 11.6\%$ (GOME-2). It should be noted that it is the first time that stratospheric NO₂ products from these satellite nadir instruments are validated for such an extended period.

The trend of the stratospheric NO₂ column has been estimated by applying a least squares regression model to the different ground-based and satellite data sets. For the analysis of trends in satellite observations, a composite data set covering the period 1996–2009 was constructed based on the comparison between the satellite and SAOZ measurements. A good consistency is found between the trends based on satellite and SAOZ measurements i.e. $-3.6 \pm 2.2\%/decade$ for satellite and $-2.4 \pm 1.1\%/decade$ for SAOZ. Similar trend values are obtained for the 1990–2009 period using SAOZ and FTIR observations ($-3.7 \pm 1.1\%/decade$ and $-3.6 \pm 0.9\%/decade$, respectively). This decline of stratospheric NO₂ of about 3%/decade, obtained from three independent measurement techniques, provides further evidence that, at least for northern mid-latitudes, the trend in stratospheric NO₂ does not necessarily reflect the evolution of N₂O, considered as the main source of NO_x in the stratosphere. The most reasonable explanation for this feature is a change in the NO_x partitioning in favor of NO, due to possible stratospheric cooling (not investigated here) and the decline of chlorine content in the stratosphere, the latter being further confirmed by the observed decrease in ClONO₂ at the Jungfraujoch station. Since previous studies have shown that ozone can affect significantly the trend in NO₂, we have derived the trend of this species at Jungfraujoch using ground- and satellite-based O₃ measurements. The slightly positive trends obtained for the 1990–2009 and 1996–2009 periods are consistent with a decrease of NO₂ through the NO₂ + O₃ → NO₃ + O₂ reaction. Although not investigated here, possible changes in the strength of the stratospheric circulation could also

contribute to the negative trend in stratospheric NO₂. A strengthening of the Brewer-Dobson circulation would allow less time in the stratosphere for the conversion of N₂O into reactive nitrogen, and therefore would lead to a decrease in stratospheric NO₂.

Similar trend analyses are needed at other locations using FTIR, UV-visible, and satellite observations to augment the interpretation of our findings by improving the statistics of such a trend study. This also suggests that more effort should be put into consolidating the different ground-based and satellite observational data sets, which is one of the major tasks of the NDACC.

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Table 1. Trend values in %/decade derived from FTIR, SAOZ, and satellite NO₂ column data sets for the 1990–2009 and 1996–2009 periods.

	1990–2009 (%/decade)	1996–2009 (%/decade)
FTIR	-3.6 ± 0.9	-4.3 ± 1.4
SAOZ at FTIR SZA	-3.7 ± 1.1	-2.7 ± 1.2
Satellites	–	-3.6 ± 2.2
SAOZ at satellite SZA	–	-2.4 ± 1.1

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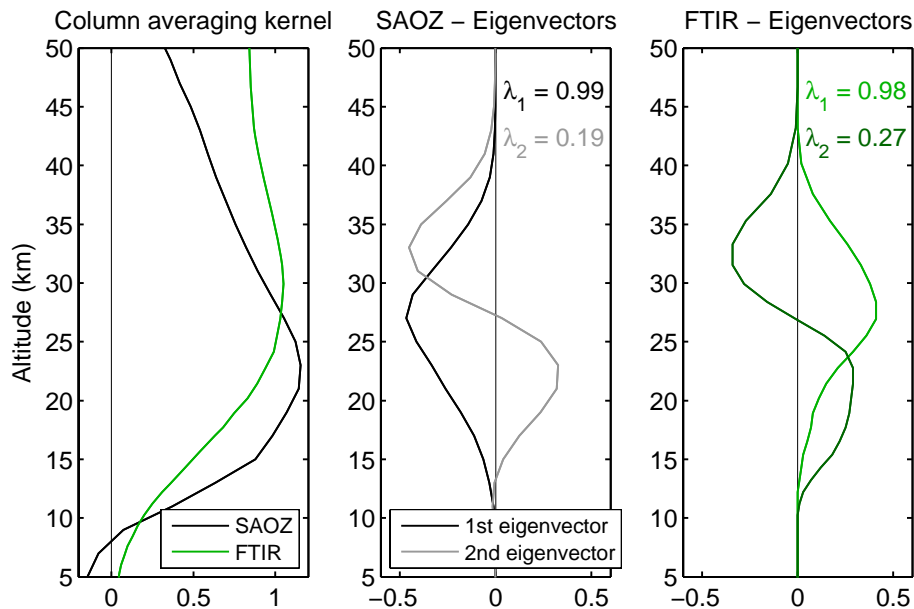


Fig. 1. Typical FTIR and SAOZ column averaging kernels (left plot) and leading eigenvectors and corresponding eigenvalues (middle plot: SAOZ; right plot: FTIR). The sum of the latter gives the DOFS.

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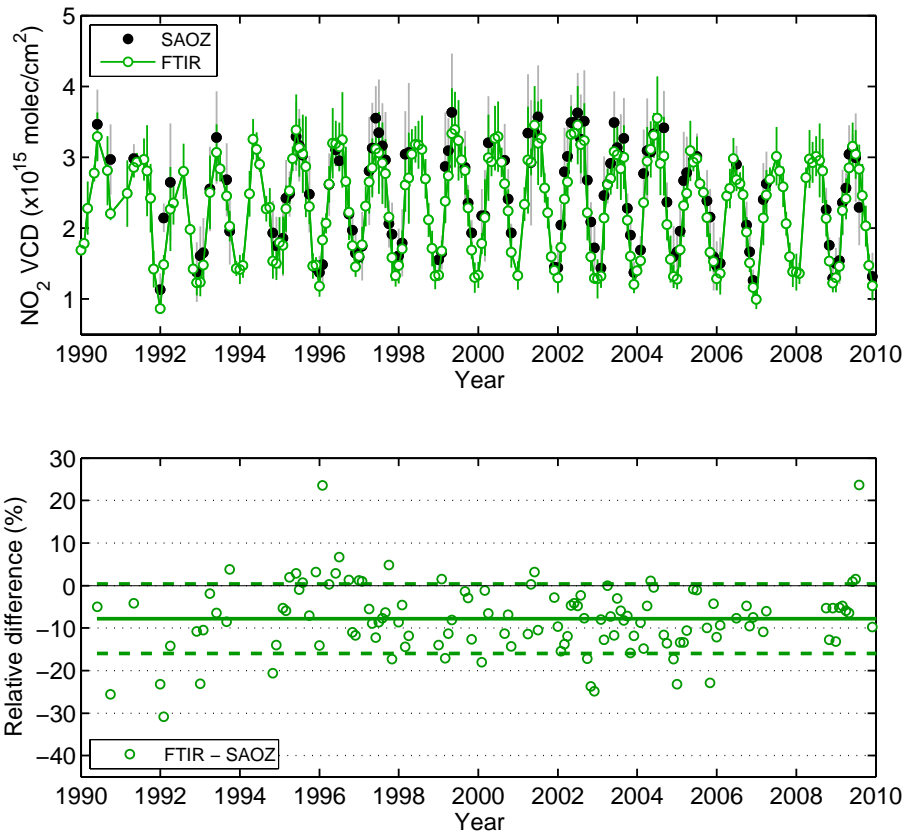


Fig. 2. Comparison between FTIR and SAOZ monthly mean stratospheric NO₂ columns at Jungfraujoch (46.5° N, 8° E) for the 1990–2009 period. The error bars correspond to the 1-sigma standard deviation (natural variability). The relative differences appear on the lower plot with solid and dashed green lines corresponding to the mean FTIR – SAOZ difference and its 1-sigma standard deviation, respectively, which is $-7.8 \pm 8.2\%$.

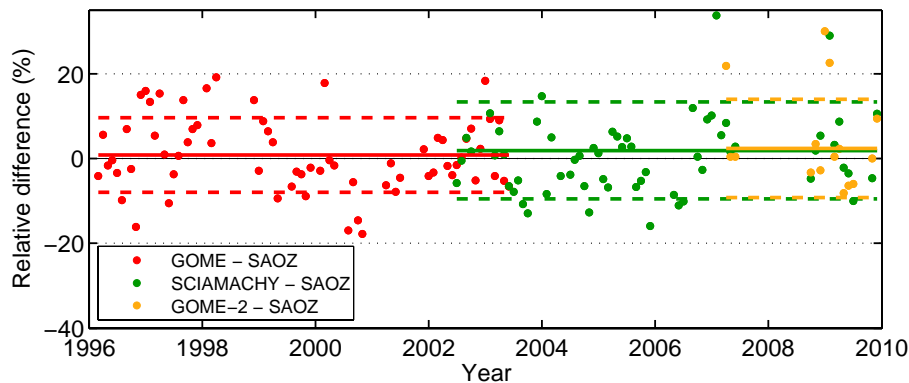
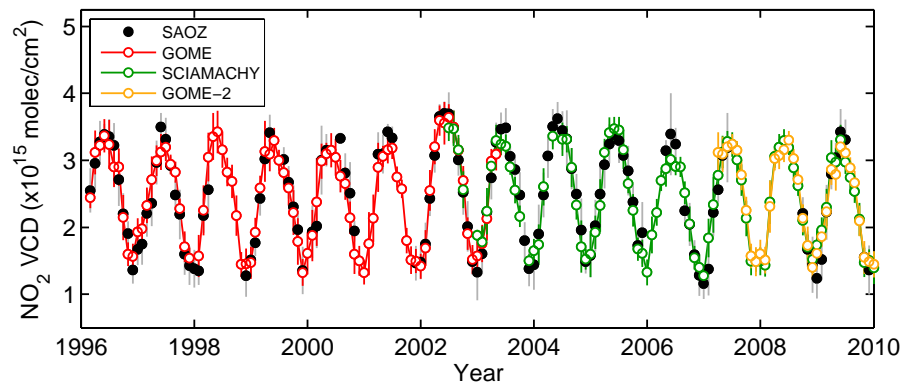


Fig. 3. Comparison between SAOZ and satellite nadir (GOME, SCIAMACHY, and GOME-2) monthly mean stratospheric NO_2 columns at Jungfraujoch (46.5°N , 8°E) for the 1996–2009 period. The error bars correspond to the 1-sigma standard deviation (natural variability). The relative differences appear on the lower plot with solid and dashed colored lines corresponding to the mean satellite – SAOZ differences and their one-sigma standard deviation, respectively, which are $+0.9 \pm 8.8\%$ (GOME), $+1.9 \pm 11.5\%$ (SCIAMACHY), and $+2.3 \pm 11.6\%$ (GOME-2).

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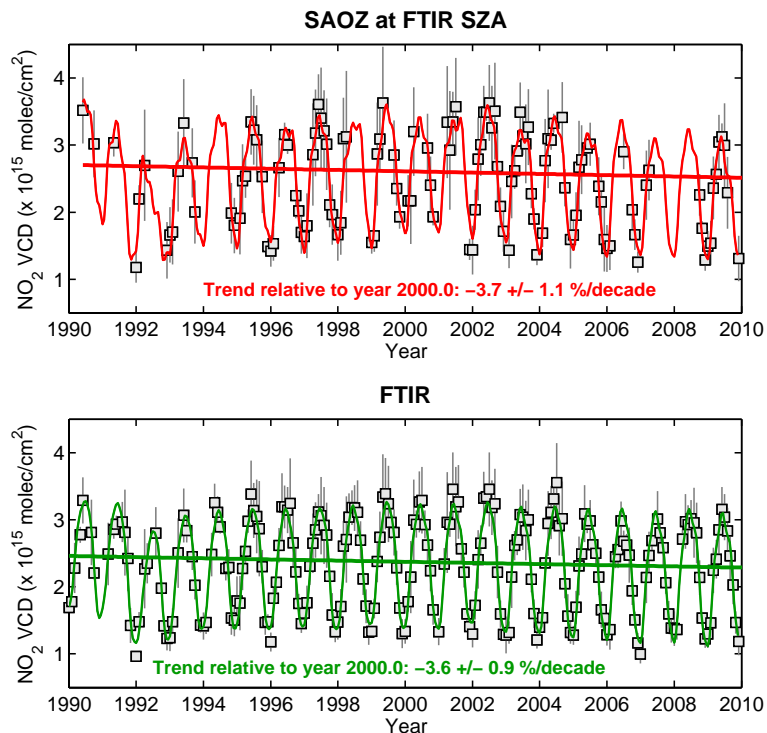


Fig. 4. Results of the trend analysis over the 1990–2009 period using the ground-based UV-visible SAOZ and FTIR monthly mean NO₂ vertical column densities (VCD; grey squares). Twilight SAOZ columns are photochemically converted to the mean SZA of the FTIR measurements. Colored lines correspond to the linear trend (thick line) and to the NO₂ columns recalculated using the multiple linear regression model (thin line). The error bars correspond to the 1-sigma standard deviation.

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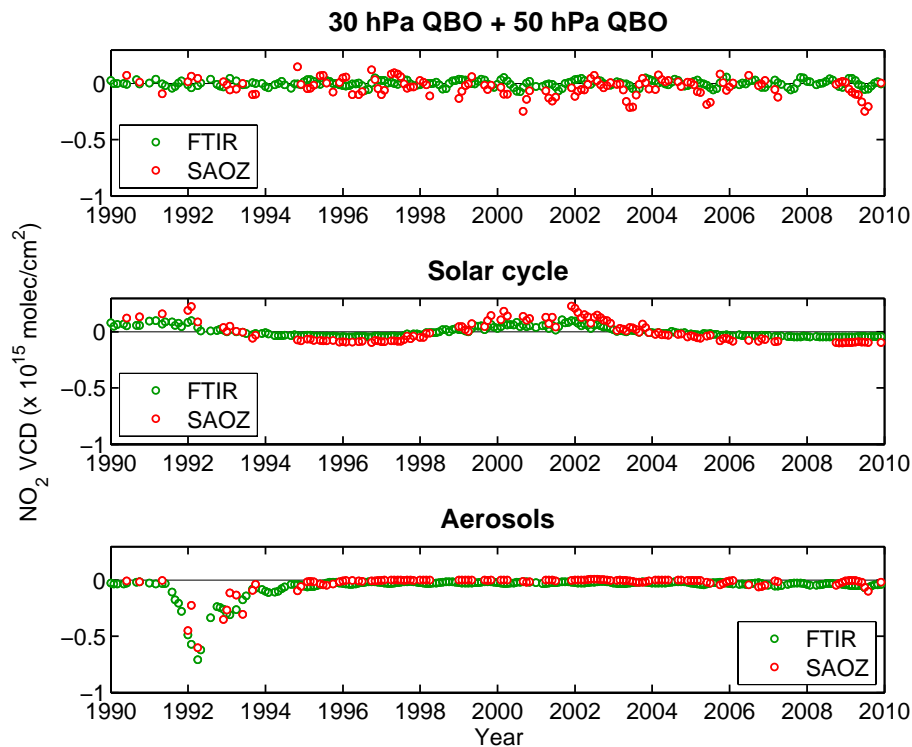


Fig. 5. Contributions of the QBO (upper plot), solar cycle (middle plot), and aerosols (lower plot) basis functions to the FTIR and SAOZ signals.

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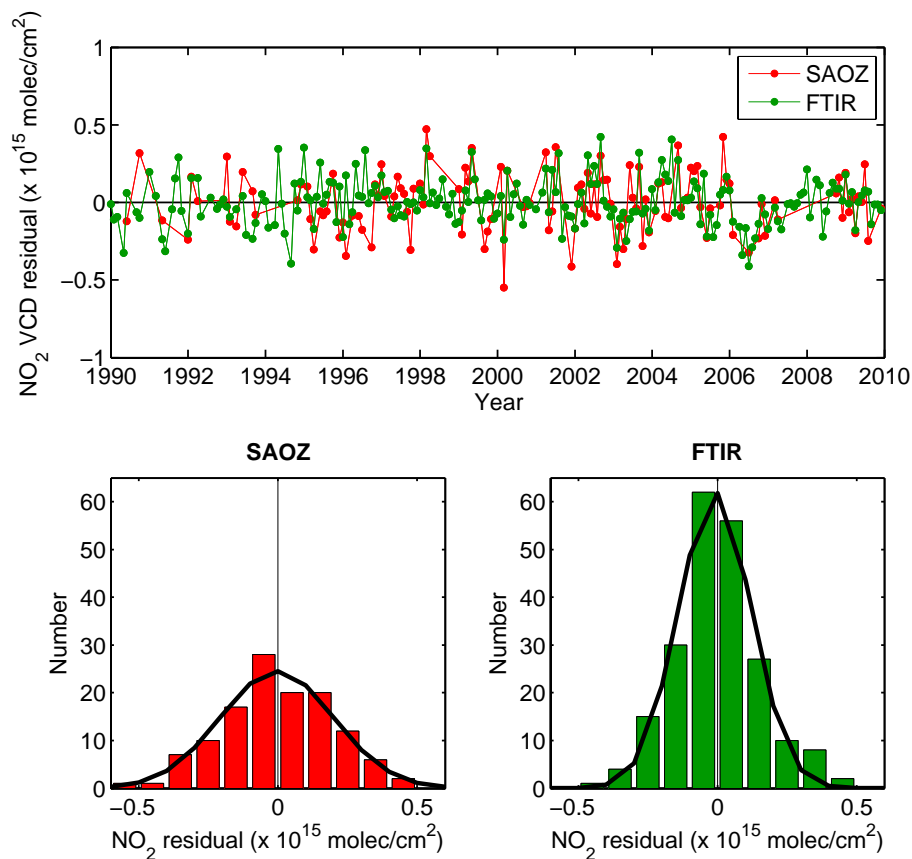


Fig. 6. SAOZ and FTIR fit residuals (upper plot) and their distributions (lower plots). Black lines correspond to Gaussian functions fitted on residuals distribution.

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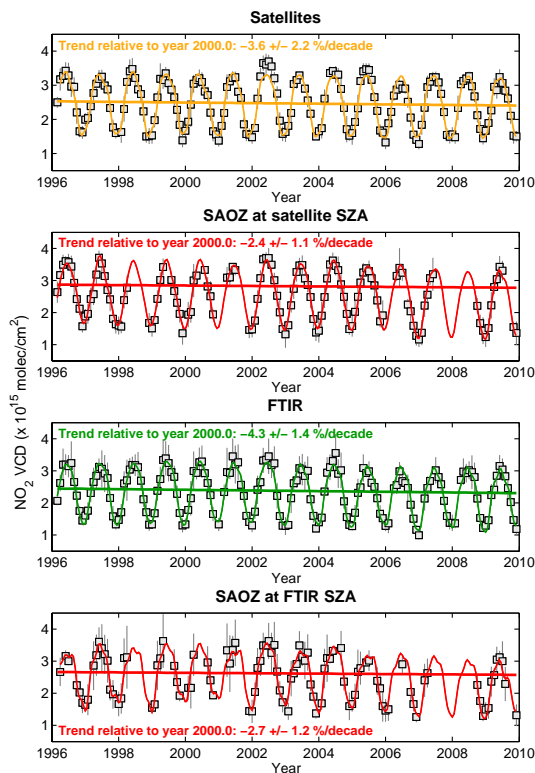


Fig. 7. Results of the trend analysis over the 1996–2009 period using the satellites, SAOZ, and FTIR monthly mean NO₂ vertical column densities (VCD; grey squares). Twilight SAOZ columns are photochemically converted to the mean SZAs of the FTIR and satellite measurements. Colored lines correspond to the linear trend (thick line) and to the NO₂ columns recalculated using the multiple linear regression model (thin line). The error bars correspond to 1-sigma standard deviation.

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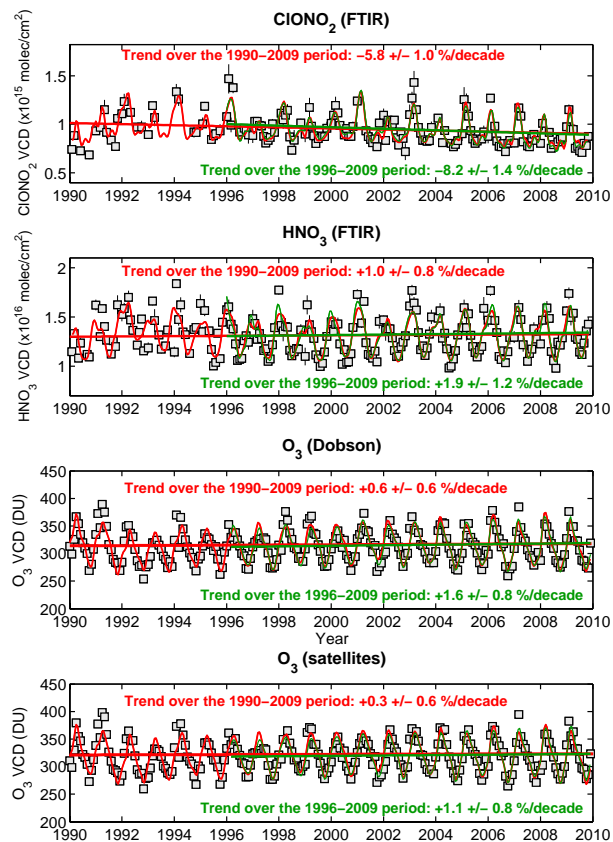


Fig. 8. Results of the trend analysis of the CIONO_2 , HNO_3 , and O_3 total columns measured above Jungfraujoch (above the Arosa station for Dobson measurements). Trend values are relative to year 2000.

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