Atmos. Meas. Tech. Discuss., 2, 1537–1573, 2009
www.atmos-meas-tech-discuss.net/2/1537/2009/

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Relationship between the NO_2 photolysis frequency and the solar global irradiance

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Received: 4 May 2009 – Accepted: 14 June 2009 – Published: 13 July 2009

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Representative values of the atmospheric NO_2 photolysis frequency, ($j(NO_2)$), are required for the adequate calculation and interpretation of NO and NO_2 concentrations and exchange fluxes near the surface. Direct measurements of $j(NO_2)$ at ground level are often not available in field studies. In most cases, modeling approaches involving complex radiative transfer calculations are used to estimate $j(NO_2)$ and other photolysis frequencies for air chemistry studies. However, important input parameters for accurate modeling are often missing, most importantly with regard to the radiative effects of clouds. On the other hand, solar global irradiance ("global radiation", G) is nowadays measured as a standard parameter in most field experiments and in many meteorological observation networks around the world. A linear relationship between $j(NO_2)$ and G was reported in previous studies and has been used to estimate $j(NO_2)$ from G in the past 30 years.

We have measured $j(NO_2)$ using spectro- or filter radiometers and G using pyranometers side-by-side at several field sites. Our results cover a solar zenith angle range of 0–90°, and are based on nine field campaigns in temperate, subtropical and tropical environments during the period 1994–2008. We show that a second-order polynomial function (intercept=0): $j(NO_2)=(1+\alpha)\times(B_1\times G+B_2\times G^2)$, with α defined as the site-dependent UV-A surface albedo and the polynomial coefficients (including uncertainty ranges): $B_1=(1.47\pm0.03)\times10^{-5}\,W^{-1}\,m^2\,s^{-1}$ and $B_2=(-4.84\pm0.31)\times10^{-9}\,W^{-2}\,m^4\,s^{-1}$ can be used to estimate ground-level $j(NO_2)$ directly from G, independent of solar zenith angle under all atmospheric conditions. The absolute $j(NO_2)\downarrow$ residual of the empirical function is $\pm6\times10^{-4}\,s^{-1}$ (95.45% confidence level). The relationship is valid for sites below 800 m a.s.l. and under low background albedo conditions. It is not valid in alpine regions, above snow or ice and sandy or dry soil surfaces. Our function can be applied to estimate chemical life times of the NO_2 molecule with respect to photolysis, and is useful for surface-atmosphere exchange and photochemistry studies close to the ground, e.g., above fields with short vegetation and above forest canopies.

1 Introduction

Solar ultraviolet (UV) radiation drives the photodissociation of tropospheric species and thus participates in chain-initiating reactions that play a key role for the chemistry of the troposphere. The fast photolysis of nitrogen dioxide (NO_2) largely controls tropospheric ozone (O_3) formation and, consequently, is important for the production of hydroxyl (OH) radicals, which are secondary products of ozone photolysis under tropospheric conditions (Crutzen and Lelieveld, 2001).

$$NO_2 + h\nu(\lambda < 420\,\text{nm}) \rightarrow NO + O(^3P) \tag{R1}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \tag{R2}$$

The first-order rate constant of Reaction (R1) is called the NO_2 photolysis frequency, $j(NO_2)$, which is a function of (a) the ability of the NO_2 molecule to absorb radiation (absorption cross section), (b) the probability that it is decomposed into NO and $O(^3P)$ (quantum yield), and (c) the actinic flux in the UV-A range (320–400 nm). The actinic flux is defined as the total radiative energy flux incident on a unit sphere, irrespective of the beam direction. The actinic flux relevant for Reaction (R1) in the troposphere is determined by the solar radiation entering the atmosphere and modifications by Rayleigh scattering and absorptions by gaseous constituents (e.g., stratospheric ozone), scattering and absorption by aerosols and clouds, and reflections from the ground (Seinfeld and Pandis, 2006). The value of $j(NO_2)$ is therefore dependent on the solar zenith angle (SZA), the altitude, and on specific local environmental conditions (e.g., Wiegand and Bofinger, 2000).

The photolysis of NO_2 may be an important parameter affecting the surface-atmosphere exchange of NO_2 and associated reactive species, such as nitric oxide (NO) and O_3. The application of the flux-gradient method (Dyer and Hicks, 1970) and resistance based inferential models (Hicks et al., 1987) presumes that vertical exchange fluxes of the so-called NO-NO_2-O_3 triad are constant with height within the atmospheric surface layer. This implies that the trace compounds are considered chemically non-reactive tracers (Trebs et al., 2006). However, if characteristic chemical time scales (τ_{chem}) of trace substances, such as NO_2, are shorter than the corresponding time scales of turbulent transport, this prerequisite is not met. The Damköhler theory has been introduced to evaluate whether or not chemical reactions violate the "constant flux layer assumption" (De Arellano and Duynkerke, 1992). In order to estimate τ_{chem} for the NO-NO_2-O_3 triad, $j(NO_2)$ must be known (Lenschow, 1982). Moreover, a simple tool to evaluate the photochemical steady state (PSS) assumption of NO_x (Leighton, 1961) in the absence of $j(NO_2)$ measurements is required, especially for examining the local peroxy radical photochemistry and the photochemical ozone tendency (e.g., Yang et al., 2004; Mannschreck et al., 2004).

Direct measurements of $j(NO_2)$ at ground level using spectroradiometers (SR) or filter radiometers (FR) are often not available from field experiments (e.g., during NitroEurope-IP, Sutton et al., 2007). Although several approaches exist to estimate $j(NO_2)$, most of them involve complex radiative transfer algorithms that depend on the knowledge of local atmospheric parameters such as aerosol optical thickness, ozone column concentration and cloud cover (Cotte et al., 1997; Madronich, 1987b; Ruggaber et al., 1993; Wiegand and Bofinger, 2000). Some studies also use parameterizations only involving SZA to calculate $j(NO_2)$ at ground level, which, however, is limited to clear-sky conditions (Dickerson et al., 1982; Parrish et al., 1983). For many sites this approach is rarely applicable, since high loadings of aerosols as well as clouds strongly influence $j(NO_2)$ (Monks et al., 2004; Thielmann et al., 2001).

Compared to $j(NO_2)$, measurements of the solar global irradiance (G) are more common because this quantity constitutes a fundamental meteorological parameter: the total solar radiant flux incident on a flat surface. While cloud observations by monitoring stations worldwide have decreased in the last decades, several surface radiation monitoring networks have been established (e.g., Baseline Surface Radiation Network, FLUXNET, World Radiation Data Centre as part of the WMO Global Atmospheric Watch Program) where G is measured as a standard parameter. G is also often measured as part of automated weather stations using pyranometers, which determine the total of direct plus diffuse solar irradiance between 300 nm and 3000 nm. Although there is a difference in (a) the wavelength range and (b) the receiver geometry for the reception of irradiance and actinic flux, near-linear relationships between $j(NO_2)$ and G were proposed (Bahe et al., 1980; Brauers and Hofzumahaus, 1992; Schere and Demerjian, 1978; Wratt et al., 1992). In other studies, a curvature in the relation between UV-A actinic flux and irradiance was implied (e.g., Madronich, 1987a; van Weele et al., 1995; Zafonte et al., 1977). McKenzie et al. (2002) and van Weele et al. (1995) suggested that $j(NO_2)$ may be estimated from measurements of G or spectral irradiances within an accuracy of 20%. In this study, we propose an empirical second-order polynomial function that can be used to accurately estimate $j(NO_2)$ solely from G. In contrast to previous studies, our results also include solar zenith angles smaller than 30° and are based on field observations in temperate, subtropical and tropical environments.

2 Experimental

2.1 Site descriptions

Table 1 provides an overview of the field sites and the sensors used for the radiation measurements. All of the measurements in Table 1 were obtained from ground-based stations under various environmental conditions (e.g., Earth-Sun distance, urban versus rural environments, elevation above sea level, cloud and haze conditions, overhead O_3 column, and regional surface albedo, cf. Madronich, 1987a).

2.1.1 Site 1: Marondera (Zimbabwe)

Measurements were performed at the Grasslands Research Station, Marondera, Zimbabwe. The site is located 8 km west of Marondera and about 60 km south-east of Harare on the central Zimbabwean plateau (Meixner et al., 1997). This region falls within the so-called broad-leaved savanna. The local climate is characterized by a long dry season (8 months) and a short wet/rainy season (October to January). Mean monthly temperatures range from 11.7°C (June) to 19.0°C (November), and more than 80% of the mean annual rainfall (846 mm) occurs between November and March (Meixner et al., 1997).

2.1.2 Site 2: Jarú (Brazil)

Measurements were done within the framework of the LBA-EUSTACH project (EUropean Studies on Trace gases and Atmospheric CHemistry as a contribution to Large-scale Biosphere-atmosphere experiment in Amazonia, Andreae et al., 2002). The experimental site was located in the Reserva Biológica Jarú, a forest reserve 90 km north of the city of Ji-Paraná in the state of Rondônia (Amazon Basin, Brazil). Our radiation measurements were performed at the end of the wet season (clean background conditions) from 19–21 May 1999, and at the end of the dry season, which is characterized by strong biomass burning activities, from 20–24 October 1999. The site is characterized by a humid tropical climate (Culf et al., 1996; Gash and Nobre, 1997) with a mean annual rainfall of about 2500 mm and a mean annual temperature of about 26°C. In 1999, the vegetation cover at the Jarú site consisted of primary (terra firme) open rain forest with a closed canopy of about 32 m height (Rummel et al., 2002, 2007).

2.1.3 Site 3: Jülich (Germany)

Measurements were performed within the framework of the ECHO 2002 campaign (Emission and chemical transformation of biogenic volatile organic compounds: investigations in and above a mixed forest stand) on top of a building close to the main forest measurement site. The region is dominated by agriculture and forests (Bohn, 2006). The climate is temperate with an average annual rainfall of 685 mm and a mean annual temperature of 9.7°C.

2.1.4 Site 4: Hohenpeißenberg (Germany)

The experimental site was a managed and fertilized meadow located at the WSW-slope (743 m a.s.l.) of the mountain Hoher Peißenberg (summit 988 m a.s.l., Hohenpeißenberg Meteorological Observatory of the German Weather Service), directly west of the village Hohenpeißenberg in Bavaria, Southern Germany (Winkler, 2006). The surrounding pre-alpine landscape is characterized by its glacially shaped, hilly relief and a patchy land use dominated by the alternation of cattle pastures, meadows, mainly coniferous forests and rural settlements. The climate is temperate, with a mean annual temperature of 6.4°C (record from 1781–2008) and an average annual precipitation of 1129 mm.

2.1.5 Site 5: Jungfraujoch (Switzerland)

Measurements were made at the Sphinx observatory that is located on a crest in the Bernese Alps between the mountains Jungfrau and Mönch at 3580 m altitude (cf. Fluckiger, 2002). Towards South-East the surrounding is mainly snow and ice covered rocks with glaciers, whereas towards North-West the Swiss midlands are usually snow-free, as they are more than 2000 m below the station. The average temperature is about −8°C.

2.1.6 Site 6: Guangzhou (China)

The radiation measurements at Guangzhou (capital city of Guangdong Province) were performed within the framework of the PRIDE-PRD2006 (Program of Regional Integrated Experiments on Air Quality over Pearl River Delta of China 2006) Campaign. Measurements were made at the site in Backgarden, a small village in a rural farming environment on the outskirts of the densely populated center of the PRD situated about 48 km northwest of Guangzhou (cf. Garland et al., 2008). The $j(\mathrm{NO_2})$ sensor was installed on the top of a 10 m high hotel building, while the G sensor was located at a nearby grassland site. The climate is tropical to subtropical; the mean annual precipitation is about 1500–2000 mm with a mean annual temperature of ~19°C.

2.1.7 Site 7: Oensingen (Switzerland)

The experimental site was located on the Central Swiss Plateau near the village of Oensingen in the north-western part of Switzerland. The region is characterized by a relatively small scale pattern of agricultural fields (grassland and arable crops). The measurement field is covered by a grass-clover mixture. The climate is temperate with an average annual rainfall of about 1100 mm and a mean annual temperature of 9.5°C (Ammann et al., 2007).

2.1.8 Site 8: Fichtelgebirge (Germany)

The site was located in the Fichtelgebirge mountains in Northeastern Bavaria. The arched, densely forested Fichtelgebirge (ca. 1000 km^2) lies in the northeastern part of Bavaria (district of Oberfranken; near the frontier to the Czech Republic). Measurements were done on a meteorological tower surrounded by hilly terrain with slopes of moderate steepness. The area is mainly covered by spruce forest with a mean canopy height of 23 m around the tower. The climate is temperate with an average annual rainfall of about 1200 mm and a mean annual temperature of 5.3°C.

2.1.9 Site 9: Mainz (Germany)

Measurements were conducted on the roof of the Max Planck Institute for Chemistry in Mainz, which is located at the western margin of the urban agglomeration of the Rhein-Main area. The climate is temperate with an average annual rainfall of about 585 mm and a mean annual temperature of 9.6°C.

2.2 Solar global irradiance measurements

The pyranometer sensors employed at sites 3, 4, 7 and 8 (see Table 1) were manufactured by Kipp & Zonen. They measure the total solar irradiance and have an accuracy of ±3%. The CM series from Kipp & Zonen provide a flat spectral response for the full solar spectrum range. The other type of pyranometer sensor, used for the measurements at sites 1, 2 and 9 (see Table 1), is manufactured by LI-COR and has an accuracy of ±5%. The spectral sensitivity of this sensor is less broad than that of the CM series from Kipp & Zonen and is also not constant over the solar spectrum. We have intercompared the Kipp & Zonen (CM14) and the LI-200SZ pyranometer sensor, e.g., at the Jarú rainforest site in Brazil 1999. The slope of the linear regression was ∼0.99 and r^2 was ∼0.99. Obviously, the different characteristics and spectral sensitivities of the global radiation sensors did not significantly influence the results. At the Jungfraujoch (site 5), an Eppley Pyranometer (Modell PSP) was used, which is a World Meteorological Organization First Class Radiometer with an accuracy of ±4%. In Guangzhou (site 6), a BT-1 global radiation sensor was used (accuracy ±5%), manufactured by the Institute of Atmospheric Sounding, Chinese Academy of Meteorological Science.

2.3 $j(NO_2)$ measurements

The spectral actinic flux was measured either integrated over a suitable wavelength range by $j(NO_2)$-filter radiometers, or spectrally resolved by spectroradiometers covering the whole UV range. Bohn et al. (2008) demonstrated that $j(NO_2)$-filter radiometers are reliable instruments for $j(NO_2)$ measurements, with excellent linearity, low detection limits and long-term stability of calibration factors (Bohn et al., 2008). The filter radiometers employed in this study at Marondera, Jarú, Hohenpeißenberg, Oensingen, Fichtelgebirge and Mainz (sites 1, 2, 4 and 7–9, see Table 1) are of the same type as examined by Bohn et al. (2008) (Meteorologie Consult GmbH, Königstein, Germany). Their setup and principle of operation follow that described by Volz-Thomas et al. (1996). The filter radiometer employed during the 1994 and 1999 campaigns (Marondera and Jarú, sites 1 and 2) was calibrated before the field experiments against a master $j(NO_2)$ radiometer by the manufacturer. The master radiometer was compared against the former chemical actinometric system at Forschungszentrum Jülich. Calibrations of the filter radiometers during the field campaigns (Hohenpeißenberg, Oensingen, Fichtelgebirge and Mainz, sites 4, 7–9) were made prior and/or after the installation of the instruments at the field sites using a spectroradiometer with absolute spectral calibration as a reference (Hofzumahaus et al., 1999). The spectral calibration is traceable to a primary irradiance standard (blackbody BB3200pg of the Physikalisch-Technische Bundesanstalt (PTB)). For the calculation of $j(NO_2)$ from the actinic flux spectra, the absorption cross section and quantum yield data of Merienne et al. (1995) and Troe (2000) were used. These molecular data were selected because they gave consistent results within 5–10% in comparisons with chemical actinometer measurements of $j(NO_2)$ (Kraus et al., 2000; Shetter et al., 2003). The same molecular data were used in the analysis of the data obtained at Jülich and Guangzhou (sites 3 and 6, Table 1), where double monochromator and single monochromator based spectroradiometers were employed, respectively. Spectroradiometer and filter radiometer measurements of $j(NO_2)$ are therefore based on the same molecular data of NO_2. More information on the spectroradiometer instruments is given elsewhere (Bohn et al., 2008).

The $j(NO_2)$ measurements at Jungfraujoch (site 5) were also made with a spectroradiometer. The spectroradiometer was regularly calibrated against a 1000 W standard lamp, traceable to PTB. Photolysis frequencies were initially calculated according to the NASA-JPL recommendation of 1997 (DeMore et al., 1997). These recommendations resulted in $j(NO_2)$ values that were 10.5% lower compared to the use of cross-sections from Merienne et al. (1995) and quantum yields from Troe (2000), virtually independent of external conditions. Thus, the Jungfraujoch data were scaled accordingly. The overall accuracy of the radiometric $j(NO_2)$ measurements using spectroradiometers or calibrated filter radiometers was estimated to 13% (Hofzumahaus et al., 1999).

The $j(NO_2)$ and G values measured at each site were synchronized to half-hourly averages. Outliers were identified and removed manually due to repeated occurrence at the same time of the day potentially caused by temporary shadowing effects from adjacent objects, e.g., masts. The number of outliers in the data sets was less than 1% of the total number of data points.

3 Results

In principle, $j(NO_2)$ results from the integral UV radiation from all directions. However, like for the total shortwave radiation, the contribution from the lower hemisphere (reflected by the surface) is generally much smaller than from the upper hemisphere. Thus in many field experiments, only the downwelling (upper hemisphere 2π sr) contribution to $j(NO_2)$ was measured (henceforth abbreviated as $j(NO_2)\downarrow$). In addition, different measurement heights, local surface properties (albedo), and topographic conditions at the field sites make a comparison of reflected (upwelling) radiation very difficult.

We plotted the half-hourly averaged $j(NO_2)\downarrow$ values versus respective G values observed for all nine measurement sites (Fig. 1). The results generally show a non-linear dependence between $j(NO_2)\downarrow$ and G. While the lower part of the graphs up to a value of $G \approx 450\,\mathrm{W\,m^{-2}}$ appears to be linear, the overall relationship shows a clear curvature with reduced slopes in the high G range. Most measurements were made during the summer, except those at Mainz (Germany), which were made during winter and show a near-linear dependency (G is always below $450\,\mathrm{W\,m^{-2}}$).

As a first approach, Table 2 presents results for second-order polynomial curve fittings of the data for the different sites according to:

$$j(NO_2)\downarrow = B_1 \times G + B_2 \times G^2 \tag{1}$$

The coefficients B_1 and B_2 were obtained by an unweighted Levenberg-Marquardt least-squares minimization. The polynomials were forced through the origin, because co-fitted intercepts B_0 were always close to zero and both quantities are zero at night. The coefficients B_1 and B_2 are very similar for most sites, except for those which are located higher than 800 m a.s.l. (Marondera and Jungfraujoch). Because of the good agreement of the relationships between $j(NO_2)\downarrow$ and G for all sites below 800 m a.s.l., we pooled the respective data for further analysis. These data are shown in Fig. 2a, where a consistent, site-independent behavior is evident, which disagrees with previous parameterizations found by Bahe et al. (1980) and Wratt et al. (1992).

A prerequisite for accurate fitting of the parameters B_1 and B_2 to the data in Fig. 2a is an adequate weighting of data points with random and/or systematic measurement errors. These may consist of, e.g., radiometric measurement uncertainties and calibration errors, respectively. However, these errors are hard to estimate and cannot be assigned to either $j(NO_2)\downarrow$ or G values, because our data scatter is partly caused by synchronization problems of the different measurements. To account for the varying density of data points and their scatter, we binned the $j(NO_2)\downarrow$ data into 10 $W\,m^{-2}$–G intervals and calculated mean $j(NO_2)\downarrow$ values and the corresponding standard deviations. These data are plotted in Fig. 2b. We then made a least-squares minimization where the data points were weighted with the $j(NO_2)\downarrow$ standard deviations. The resulting polynomial coefficients B_1 and B_2 were determined to: $B_1=(1.47\pm0.03)\times10^{-5}\,W^{-1}\,m^2\,s^{-1}$ and $B_2=(-4.8\pm0.3)\times10^{-9}\,W^{-2}\,m^4\,s^{-1}$. It should be noted that the parameters B_1 and B_2 are highly correlated and that the relationship in Eq. (1) is empirical, i.e., there is no obvious physical reason why a second-order polynomial is appropriate. However, Fig. 3a shows that the $j(NO_2)\downarrow$ residuals are nearly normally distributed. Figure 3b shows the absolute $j(NO_2)\downarrow$ residuals versus G along with the $\pm2\sigma$ (95.45%) confidence band of $\pm6\times10^{-4}\,s^{-1}$. The $j(NO_2)$ residuals vary randomly around zero and the spread of the residuals is about the same throughout the plot, indicating that the $j(NO_2)\downarrow$ residual variance exhibits no dependence on G, which justifies our fitting approach. Figure 3c illustrates a substantial decrease of the relative $j(NO_2)\downarrow$ residual towards higher G values. For $G<100\,W\,m^{-2}$ the relative deviation of the measured values (half-hourly averages) from the fitted function is often considerably higher than 40%. For G between 100 and 500 W m^{-2} the relative deviation of the measured values from the fitted function ranges from 10 to 40% and for G>500 W m^{-2} the deviation is lower than 10% (95.45% confidence level). Since the distribution of relative residuals of individual sites was comparable to that in Fig. 3c, we did not find an indication that measurements at one or more sites deviated systematically from the overall fitted relationship. For test purposes we also binned the G data into 10^{-4} s^{-1}–$j(NO_2)\downarrow$ intervals and fitted the reverse function to obtain the parameters B_1 and B_2. The obtained parameters were similar within their error limits, namely $B_1=(1.44\pm0.02)\times10^{-5}$W^{-1}m^{2}s^{-1}, $B_2=(-4.24\pm0.29)\times10^{-9}$ W^{-2} m^4 s^{-1}. The corresponding parameterisation is hard to distinguish from that shown in Fig. 2b.

In order to check whether the empirically found relationship between $j(NO_2)\downarrow$ and G can be reproduced by theoretical calculations, we applied a radiative transfer model, using sites 2 and 4 as examples, under clear-sky conditions. The Tropospheric Ultraviolet Visible (TUV) model (http://cprm.acd.ucar.edu/Models/TUV/) (version 4.4) was used to calculate clear-sky $j(NO_2)\downarrow$ for a simple model atmosphere. The molecular data used in the TUV model were consistent with those used above (Merienne et al., 1995; Troe, 2000). The model was set up with the following parameters: UV-A surface albedo α=0.03 (cf. Feister and Grewe, 1995), O_3 column=300 DU, NO_2 column=0.3 DU, no clouds, AOT (550 nm)=0.235 (scaled to different wavelengths using an Angstrom exponent of 1.0), single scattering albedo ω_0=0.99. Since our measurements of G include wavelengths of up to 3000 nm and the TUV model code stops at 1000 nm (absorption by water vapor is not treated), the TUV model could not be used to calculate clear-sky G. Hence, we used a parameterization of Schmetz and Raschke (1978) to estimate potential clear-sky G. The predicted clear-sky $j(NO_2)\downarrow$ is plotted versus estimated clear-sky G for the two selected sites in Fig. 4a, b. It shows that the model results reproduce the non-linear relationship relatively well, with fitted polynomial coefficients that are comparable to those in Table 2.

4 Discussion

4.1 Shape of the relationship between $j(NO_2)\downarrow$ and G

In Sect. 3 we have established an empirical relationship between the irradiance integrated over the short-wave solar spectrum and the downwelling photolysis frequency $j(NO_2)\downarrow$, a quantity that is proportional to the upper hemispheric UV-A actinic flux. The fundamental difference between irradiance and actinic flux is that irradiance is describing a photon (or energy) flux density on a unit horizontal surface by weighting the radiance with the cosine of the SZA upon integration over the solid angle field of view (e.g., Schallhart et al., 2004; Webb, 2003; Webb et al., 2002a). The horizontal surface produces a cosine response to the directions of the incoming radiation due to the reduced projected area of the surface for angles of incidence other than 0° (cf. Zafonte et al., 1977). In contrast, the actinic flux is the unweighted radiance integrated over a sphere. It was demonstrated previously (e.g., Harvey et al., 1977; Madronich, 1987a; Nader and White, 1969; Zafonte et al., 1977) that a curved relationship between actinic flux and irradiance results from the cosine response of the irradiance sensors. For example van Weele et al. (1995) and Webb et al. (2002b) have shown that the ratio of actinic flux and the downward irradiance depends on α, SZA and the ratio of direct to total downward irradiance and also on the amount and isotropy of scattering in the atmosphere. Typically, spectral irradiance is decomposed in direct and diffuse components to convert into spectral actinic flux (cf. Kylling et al., 2003). The direct part of the actinic flux can be obtained by dividing the direct part of the irradiance by the cosine of the SZA. However, no simple relationship is available to accurately calculate the angular distributed diffuse part of the spectral actinic flux from the spectral irradiance under realistic conditions in the troposphere (Ruggaber et al., 1993). The situation is even more complex with regard to the broadband quantities $j(NO_2)$ and G considered in this work.

The curvature of the relationships plotted in Figs. 1 and 2a, b increases with decreasing SZAs (increasing G), when the proportion of direct incident radiation becomes larger because of the lower atmospheric scattering at small SZAs. It is evident that G and $j(NO_2)\downarrow$ do not have the same diel variation (cf. van Weele et al., 1995). Generally, the actinic flux varies more slowly in time than the spectral irradiance (see also Kazadzis et al., 2000; Kylling et al., 2003; McKenzie et al., 2002; Webb et al., 2002b). This implies that the curvature in Figs. 1 and 2a, b represents an almost vanishing $j(NO_2)\downarrow$ increase at small SZAs, while G is still benefiting from the increase of the cosine weighting factor. Correlating $j(NO_2)$ with the UV irradiance also results in a curvature with increasingly higher values of the UV irradiance (Madronich, 1987a). As found in many experimental studies, the relationship between UV-A irradiance and G can be described by a near-linear dependency (Canada et al., 2003; Jacovides et al., 2006; Kudish and Evseev, 2000; Ogunjobi and Kim, 2004).

However, some previous studies also found near-linear relationships between $j(NO_2)$ and G (e.g., Bahe et al., 1980; Brauers and Hofzumahaus, 1992; Schere and Demerjian, 1978; Wratt et al., 1992) (cf. Fig. 2a). Some of these previous studies rely on measurements using chemical actinometers. Brauers and Hofzumahaus (1992) made a linear fit though their data collected over the Atlantic, although a curvature was evident from their plot. Bahe et al's measurements in Bonn, Germany (70 m a.s.l.) did not include SZAs smaller than 30° and a substantial data scatter was observed. Although Bahe et al.'s measurements covered periods of dawn and sunset until darkness; they state that their linear function contains an intercept that has no physical significance (cf. Fig. 2a). It should be noted that the model predictions in Fig. 4a and b also reveal an intercept (i.e., $j(NO_2)\downarrow>0$ at clear-sky $G=0$, $SZA=90°$) that is even slightly higher than the one determined by Bahe et al. (1980). Van der Hage (1992) proposes that the actinic flux exceeds G at dawn and at sunset, resulting in an effective day length that is longer according to the actinic flux sensor than it would be according to the G sensor. Our measurements did not suggest an intercept between the relationship of $j(NO_2)\downarrow$ and G, but it should be kept in mind that the radiation sensors approach the limit of detection at dawn and sunset, and thus the sensor accuracy is low under these conditions.

Reuder (1999) has also shown previously for four sites in Germany and France that the relationship between $j(NO_2)\downarrow$ and G can be described by a second-order polynomial function with a $j(NO_2)\downarrow$ intercept=0. He found similar coefficients B_1 and B_2 as presented in Table 2. Madronich (1987a) argued that expressing $j(NO_2)$ as a polynomial function of the irradiance may only work for individual days, but the seasonal variation of $j(NO_2)$ cannot be reproduced accurately. The reason is the variation of the Sun-Earth distance affecting $j(NO_2)$ and G differently, because of the cosine weighting included in G. However, we consider this a minor effect that is not evident in our data within experimental errors and variations caused by atmospheric effects, e.g. clouds.

Blumthaler et al. (1994) and Dickerson et al. (1982) state that clouds attenuate total solar irradiance by about 20% more than UV radiation in the region of NO_2 photolysis. Moreover, UV radiation and $j(NO_2)$ are not attenuated by clouds in the same manner (Parrish et al., 1983). In Fig. 5a we plotted measured $j(NO_2)\downarrow$ versus SZA including clear-sky and cloudy conditions together with the empirical functions of Dickerson et al. (1982) and Parrish et al. (1983). Obviously, the functions involving SZA as the independent variable cannot be used to predict $j(NO_2)$ for cloudy conditions. Even the application of complex modeling approaches to predict $j(NO_2)$ are often hampered by the unavailability of exact cloud information. In contrast, our empirical function to estimate $j(NO_2)\downarrow$ is comparably valid for cloudy and clear-sky conditions (cf. Figs. 2a, b and 4). In Fig. 5b the effect of clouds has been removed. For clear-sky conditions, the empirical functions of Dickerson et al. (1982) and Parrish et al. (1983), which allow $j(NO_2)$ to be calculated from SZA for zero albedo and low-albedo background, respectively, fit relatively well to our experimental values for SZA<70°. Wiegand and Bofinger (2000) showed that these empirical functions also compare within 15% with the TUV model under clear-sky conditions. Figure 5c shows that the ratio $j(NO_2)\downarrow/G$ increases with increasing SZA under clear sky conditions (see also Webb et al., 2002b) and exhibits the same behavior for all sites up to SZA values of 60°. At large SZA, the scatter increases substantially, which is most likely due to the fact that at large SZA atmospheric scattering redirects some of the upward radiation flux back downward and the uncertainty of the sensors increases under these conditions.

4.2 Effect of aerosol load, elevation and surrounding terrain

Our measurements reveal that $j(NO_2)\downarrow/G$ is apparently not significantly dependent on the pollution state of the atmosphere, as, e.g., expressed by the aerosol optical thickness (AOT). Results from Brazil during the wet season and the dry (biomass burning) season show nearly the same ratio $j(NO_2)\downarrow/G$ (Table 3) at the same SZA, hence we did not find a significant dependence of the ratio $j(NO_2)\downarrow/G$ on AOT. Also the polluted atmosphere in Guangzhou (China) vs. the relatively unpolluted atmosphere in Hohenpeißenberg (Germany) reveal a comparable relationship between $j(NO_2)\downarrow$ and G (B_2 is nearly the same, see Table 2) and the ratio $j(NO_2)\downarrow/G$ is not substantially different (Table 3).

In the troposphere, the downward component of the actinic flux increases with increasing elevation due to diminishing absorption and backscattering by ozone and aerosols (Wiegand and Bofinger, 2000). Thus, the measured $j(NO_2)\downarrow$ values are higher for sites with higher altitude (Marondera and Jungfraujoch, see Fig. 1) due to the decreasing optical thickness of the scattering air masses. According to Pfeifer et al. (2006) and Schmucki and Philipona (2002) the altitude effect on surface UV irradiance is in the range of 5–20% km^{-1}. In the Swiss Alps, an annual mean G gradient of 13 $W\,m^{-2}\,km^{-1}$ (equal to about 1–3% km^{-1}) was observed (Marty et al., 2002). Obviously, the increase of UV irradiance with decreasing optical thickness is much more substantial than that observed for G, increasing the ratio $j(NO_2)\downarrow/G$ with surface elevation (cf. Blumthaler et al., 1997). Reuder (1999) also showed that the ratio $j(NO_2)\downarrow/G$ is enhanced for sites with an elevation higher than 800 m a.s.l. The spring measurements at Jungfraujoch in 2001 reveal higher $j(NO_2)\downarrow$ values than the summer measurements, which is most likely caused by the higher surface albedo of the snow during spring and subsequent atmospheric backscatter. The mountains around Jungfraujoch and particularly the snow cover during spring increase atmospheric backscatter, i.e., the downward-propagating diffuse radiation will be larger thus increasing $j(\mathrm{NO_2})\downarrow$ in the lower troposphere. The empirically found dependencies could be reproduced with the TUV model for each site under clear-sky conditions (exemplarily shown for sites Jarú and Hohenpeißenberg in Fig. 4a, b), except in the cases of Jungfraujoch and Marondera. The Jungfraujoch site is characterized by a complex albedo effect related to distinct topographical patterns, which cannot be reproduced by the TUV model. An addition, the measurement site is substantially higher than the surrounding terrain. The measurements at Marondera were made at the end of the dry season when the grass was almost completely withered, such that bare soil (alfisols of granitic origin) was dominating the surface properties. We presume that this dry surface had a much higher albedo in the UV-A range (~0.1) than typical for grassland (~0.03) (cf. Feister and Grewe, 1995). The high $j(\mathrm{NO_2})\downarrow$ values at Jungfraujoch and Marondera were probably caused by a combination of surface albedo (backscattering) and elevation effects. According to the TUV model an increase of the surface albedo by 10% raises $j(\mathrm{NO_2})\downarrow$ on average by about 4% (under clear-sky conditions). We have also simulated the surface elevation effect on the predicted $j(\mathrm{NO_2})\downarrow$ with the TUV model for the Marondera site using the same input parameters as in section 3 for $\mathrm{SZA}=20^\circ$ and an UV-A surface albedo of 0.1. The model calculated a gradient of only $1.5\%\,\mathrm{km}^{-1}$, which is much smaller than revealed by the measurements in this study and also in Pfeifer et al. (2006) and Schmucki and Philipona (2002) (see above). This calculation was for relatively non-absorbing aerosols ($\omega_0=0.99$, for example sulfate). If we set $\omega_0=0.85$, (rather representing biomass burning aerosols), then the altitude gradient increases only slightly to $2.2\%\,\mathrm{km}^{-1}$. Thus we were unable to reproduce the measured data by this modeling approach. In order to reproduce the measured $j(\mathrm{NO_2})$ values at Marondera with the input values from Sect. 3, we would have to set the UV-A surface albedo to an unrealistic value of 0.4.

4.3 Contribution of upwelling $j(\mathrm{NO_2})$

Although $j(\mathrm{NO_2})\downarrow$ can be estimated from G for all sites below 800 m a.s.l. using the polynomial function presented in Sect. 3, it is obvious that upwelling $j(\mathrm{NO_2})$ ($j(\mathrm{NO_2})\uparrow$) would vary substantially from site to site due to the local surface albedo effects. We made measurements of $j(\mathrm{NO_2})\uparrow$ for the sites Jarú (tropical rain forest), Hohenpeißenberg (temperate productive grassland), and Fichtelgebirge (temperate spruce forest). We estimated $j(\mathrm{NO_2})\uparrow$ from our measurements for SZA<50° in Jarú to 6–8%, in Hohenpeißenberg to 6–8%, and in the Fichtelgebirge to 2–3% of $j(\mathrm{NO_2})\downarrow$. These data should be considered upper limits, because there is typically an unavoidable, slight crosstalk between upper and lower hemispheric measurements. Moreover, local surface effects at the site can influence these measurements. Consequently, the measured upwelling components for Jarú and Hohenpeißenberg are somewhat higher than expected for a typical albedo over vegetation of about 3% in the UV-A range (Feister and Grewe, 1995). The surface albedo effect increases $j(\mathrm{NO_2})/G$ (see van der Hage, 1992) and should be considered when the total $j(\mathrm{NO_2})$ (up- and downwelling) are estimated from G. We recommend expanding our empirical function to:

$$j(\mathrm{NO_2}) = (1 + \alpha)\times(B_1\times G + B_2\times G^2) \qquad (2)$$

where α is the site-dependent UV-A surface albedo. It should be noted that for our sites below 800 m a.s.l., the effect of surface albedo on $j(\mathrm{NO_2})$ is within the uncertainty of the polynomial fit (see Fig. 3c).

4.4 Implications for chemical reactions and lifetimes

As previously mentioned, our empirical parameterization is a useful tool to calculate the chemical lifetime of $\mathrm{NO_2}$ with respect to photolysis in the absence of $j(\mathrm{NO_2})$ measurements. Our empirical can also be applied for the estimation of the $\mathrm{HNO_2}$ photolysis frequency, $j(\mathrm{HNO_2})$, which can be calculated from $j(\mathrm{NO_2})$ with a simple scaling factor. At the Jülich site, a linear relationship between $j(\mathrm{HNO_2})$ and $j(\mathrm{NO_2})$ was found with a slope of 0.17 (data not shown), and at the Hohenpeißenberg Meteorological Observatory during the SALSA measurement period, a linear relationship was found with a slope of 0.18 (data not shown), both values being comparable to a previous parameterization of Kraus and Hofzumahaus (1998). A small discrepancy can be attributed to the updated molecular data compared to the older NASA-JPL recommendation of 1997 used by Kraus and Hofzumahaus (1998) (see Sect. 2.3). Interestingly, the correlation between $j(\mathrm{O^1D})$ and $j(\mathrm{NO_2})$ in Kraus and Hofzumahaus (1998) is worse than the one between G and $j(\mathrm{NO_2})\downarrow$ found in this study, although wavelength ranges and sensor geometries are more different for G and $j(\mathrm{NO_2})$. This can be attributed to the strong influence of stratospheric ozone on $j(\mathrm{O^1D})$. If only G measurements are available we suggest that $j(\mathrm{HNO_2})$ can be approximated using Eq. (2) with $B_1=2.95\times10^{-6}\,\mathrm{W^{-1}\,m^2\,s^{-1}}$ and $B_2=-1.14\times10^{-9}\,\mathrm{W^{-2}\,m^4\,s^{-1}}$ (polynomial fit of $j(\mathrm{HNO_2})$ vs. G based on data from Hohenpeißenberg). In the absence of photolysis frequency measurements, this is a reasonable approach to estimate, for example, the contribution of $\mathrm{HNO_2}$ photolysis to the OH radical production.

Figure 6 shows that for G values higher than $100\,\mathrm{W\,m^{-2}}$, our second-order polynomial function predicts chemical lifetimes of the $\mathrm{NO_2}$ molecule with respect to photolysis Reaction (R1) of 12–48% shorter than the linear expression by Bahe et al. (1980), which has been used most frequently in the past 30 years. The deviations are largest for G values between 100 and $600\,\mathrm{W\,m^{-2}}$.

5 Conclusions

This paper evaluates side-by-side measurements of downwelling $j(\mathrm{NO_2})$ and solar global irradiance G at nine different field sites. It was found that the relationships are generally non-linear, but very similar for all sites at low to medium altitudes. We thus propose that ground-level $j(\mathrm{NO_2})$ below 800 m a.s.l. can be estimated directly from measured G using an empirical second-order polynomial function, independent of latitude and longitude, solar zenith angle, aerosol optical thickness, and cloud cover. The absolute $j(NO_2)\downarrow$ residual of the empirical function is $\pm 6\times10^{-4}\,s^{-1}$ (95.45% confidence level), which corresponds to relative values of $>40\%$ for $G<100\,W\,m^{-2}$, 10–40% for $G=100–500\,W\,m^{-2}$ and $\leq 10\%$ for $G>500\,W\,m^{-2}$. The difference of our estimated $j(NO_2)$ values to previous studies, which proposed a linear relationship between $j(NO_2)$ and G, is up to 48%.

The empirical relationship can be applied to calculate chemical timescales of the $NO-NO_2-O_3$ triad in order to evaluate the potential influence of chemical reactions on surface-atmosphere exchange fluxes. Furthermore, the relationship represents a simple tool to evaluate the photochemical steady state (PSS) assumption of NO_x in the absence of $j(NO_2)$ measurements, subsequently being useful for examining the local photochemistry.

Acknowledgements. The authors gratefully acknowledge financial support by the European Commission (NitroEurope-IP, project 017841), the German Research Foundation (DFG project EGER, ME 2100/4-1) and by the Max Planck Society. The global radiation data in the Pearl River Delta were collected within the framework of the China National Basic Research and Development Program-2002CB410801. We are indebted to S. Madronich for assistance in using the TUV model. The authors wish to thank K. Staudt and T. Foken from the University of Bayreuth, Micrometeorology Dept. (Germany) for providing solar global irradiance data from the SALSA campaign 2005 and the EGER campaign 2007. We thank the German weather service (staff of the Meteorological Observatory Hohenpeißenberg, especially C. Plass-Dülmer) for providing HNO_2 photolysis frequency data. We are grateful to K. Hens, M. Kortner, M. Ermel and V. Wolff for helping with some of the measurements in Germany and Switzerland. We thank X. Li and T. Brauers for supervising a spectroradiometer during the PRD 2006 campaign.

The service charges for this open access publication
have been covered by the Max Planck Society.

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Table 1. Overview of the field sites and the sensors used for the radiation measurements.

site	Marondera Central Zimbabwean Plateau, Zimbabwe (site 1)	Jarú Amazon Basin, Rondônia Brazil (site 2)	Jülich Research Center Germany (site 3)	Hohenpeißenberg Bavaria Germany (site 4)	Jungfraujoch High Altitude Research Station Switzerland (site 5)	Guangzhou Backgarden Pearl River Delta China (site 6)	Oensingen Central Swiss Plaetau Switzerland (site 7)	Fichtelgebirge Bavaria Germany (site 8)	Mainz Max Planck Institute for Chemistry Germany (site 9)
measurement periods	10 Oct–1 Dec 1994	19–21 May 1999 20–24 Oct 1999	16 Jun–29 Jul 2002	7–20 Sep 2005	22 Jul–29 Aug 2001 8 Mar–17 Apr 2002 7 Apr–10 May 2005	30 Jun–29 Jul 2006	21 Jul–5 Sep 2006	7–30 Sep 2007	25 Jan–25 Feb 2008
campaign	–	LBA-EUSTACH	ECHO	SALSA	–	Pearl River Delta Campaign	NitroEurope	EGER	–
Lat/ Lon	18°11′ S 31°28′ E	10°05′ S 61°56′ W	50°54′ N 6°25′ E	47°47′ N 10°59′ E	46°33′ N 7°59′ E	23°29′ N 113°02′ E	47°17′ N 7°44′ E	50°09′ N 11°52′ E	49°59′ N 8°14′ E
elevation (a.s.l.)	1630 m	147 m	91 m	735 m	3580 m	13 m	450 m	775 m	131 m
vegetation/site	savanna	rain forest	decidous forest/ building	grassland	None (Research station)	grassland	grassland	spruce forest	None (roof of building)
climate	subtropical	tropical	temperate	temperate	temperate	tropical/ subtropical	temperate	temperate	temperate
measurement height (a.g.l.)	1 m ($j(NO_2)$) 2 m (G)	51.7 m	105 m ($j(NO_2)$) 100 m (G)	2 m	200–2000 m	11 m ($j(NO_2)$) 1 m (G)	1.5 m ($j(NO_2)$) 3 m (G)	28 m ($j(NO_2)$) 30 m (G)	25 m
$j(NO_2)$ sensor	filter radiometer	filter radiometer	spectroradiometer	filter radiometer	spectroradiometer	spectroradiometer	filter radiometer	filter radiometer	filter radiometer
G sensor	pyranometer LI-200SZ, (LI-COR)	pyranometer LI-200SZ, (LI-COR)	pyranometer CM 7 (Kipp & Zonen B.V.)	pyranometer CM21 (Kipp & Zonen B.V.)	Eppley Pyranometer (Modell PSP)	BT-1(Chinese Academy of Meteorological Science)	pyranometer CM3 (Kipp & Zonen B.V.)	pyranometer CM14 (Kipp & Zonen B.V.)	pyranometer LI-200SZ, (LI-COR)
reference	(Meixner et al., 1997)	(Andreae et al., 2002)	(Bohn, 2006)	(Acker et al., 2006)	(Fluckiger, 2002)	(Garland et al., 2008)	(Ammann et al., 2007)	(Gockede et al., 2007)	–

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Table 2. Results for unweighted polynomial curve fitting $j(NO_2)\downarrow = B_1 \times G + B_2 \times G^2$ (with $j(NO_2)$ intercept=0) of the measured downwelling NO_2 photolysis frequency versus solar global irradiance for all sites (data for cloudy and clear-sky conditions were used for curve fitting, for details see text).

site	Marondera Zimbabwe (site 1)	Jarú Brazil (site 2)	Jülich Germany (site 3)	Hohenpeißenberg Germany (site 4)	Jungfraujoch Switzerland (site 5)		Guangzhou China (site 6)	Oensingen Switzerland (site 7)	Fichtelgebirge Germany (site 8)	Mainz Germany (site 9)
	1994	1999	2002	2005	2001	2002/2005 (summer)	2006 (spring)	2006	2007	2008
Number of data points (N)	681	125	1366	495	848	539	684	1294	342	509
B_1, $W^{-1}\,m^2\,s^{-1}$	1.78×10^{-5}	1.47×10^{-5}	1.44×10^{-5}	1.47×10^{-5}	1.72×10^{-5}	1.91×10^{-5}	1.53×10^{-5}	1.52×10^{-5}	1.51×10^{-5}	1.53×10^{-5}
B_2, $W^{-2}\,m^4\,s^{-1}$	-7.11×10^{-9}	-5.32×10^{-9}	-4.62×10^{-9}	-5.26×10^{-9}	-7.82×10^{-9}	-7.47×10^{-9}	-5.42×10^{-9}	-6.08×10^{-9}	-5.18×10^{-9}	-5.00×10^{-9}

Table 3. Comparison of AOT and the ratio $j(\mathrm{NO_2})\!\downarrow\!/G$ for the Jarú site (wet season compared to dry season, AOT measurements using a sun photometer were made at the Abracos Hill site that is located approximately 90 km NE of the Jarú site) and for the Hohenpeißenberg site compared to the Guangzhou site for selected times when AOT and $j(\mathrm{NO_2})$ data were available. AOT data (Level 2.0, cloud screened and quality-assured) were obtained from the AERONET (AErosol RObotic NETwork) website (http://aeronet.gsfc.nasa.gov/index.html).

	SZA, deg	AOT (340 nm)	ratio $j(\mathrm{NO_2})\!\downarrow\!/G$, m^2 W^{-1} s^{-1}
Jarú, wet season (13:30 p.m. (LT) 20 May 1999)	~23	0.2	1.07×10^{-5}
Jarú, dry season (11:30 a.m. (LT) 23 Oct 1999)	~23	2.5	1.02×10^{-5}
Hohenpeißenberg (13:30 a.m. (LT) 7 Sep 2005)	~42	0.2	1.03×10^{-5}
Guangzhou (09:30 a.m. (LT) 5 Jul 2006)	~42	0.6	1.21×10^{-5}

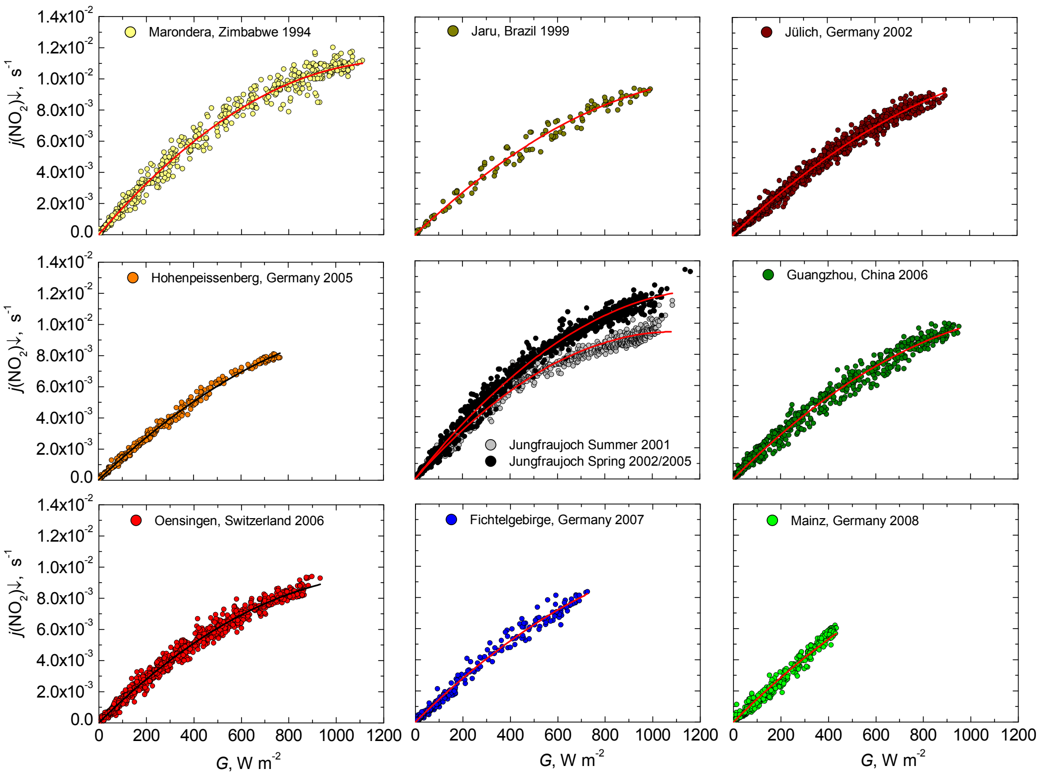

Fig. 1. Scatter plots of $j(NO_2)\downarrow$ vs. G (half-hourly averages) measured at the nine field sites listed in Table 1 (including cloudy and clear-sky conditions) and corresponding unweighted second-order polynomial fit curves (for details see Table 2).

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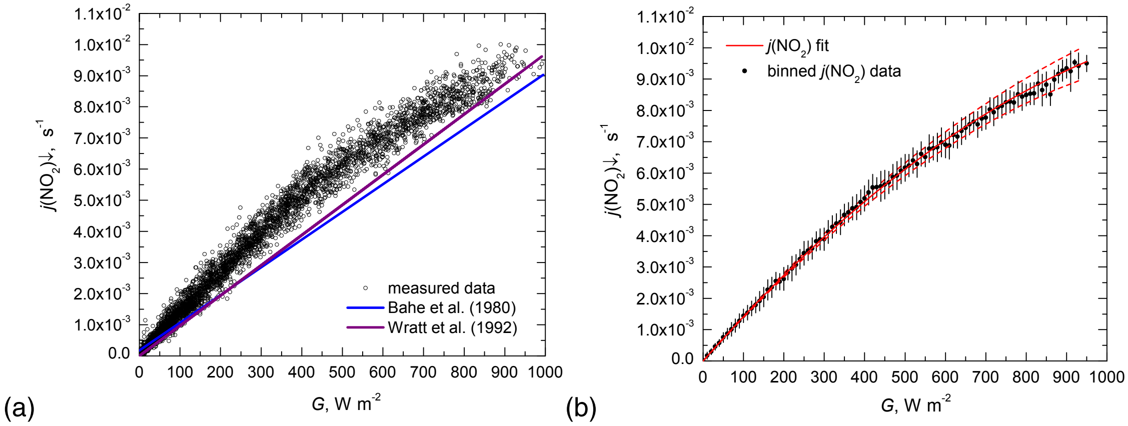

Fig. 2. **(a)** Scatter plot of $j(NO_2)\downarrow$ vs. G (half-hourly averages) for all data from sites located below 800 m a.s.l. (cloudy and clear-sky conditions are included, N=4815). For comparison, previously published linear parameterizations are also displayed. **(b)** Mean $j(NO_2)\downarrow$ values (black filled circles) and corresponding standard deviations (error bars) versus $10\,\mathrm{W\,m^{-2}}-G$ intervals (N=95) with weighted second-order polynomial fit (red line, $r^2=0.99$), uncertainty range of the fitted function calculated from the errors of B_1 and B_2 is shown as red dashed lines. For further explanations see text.

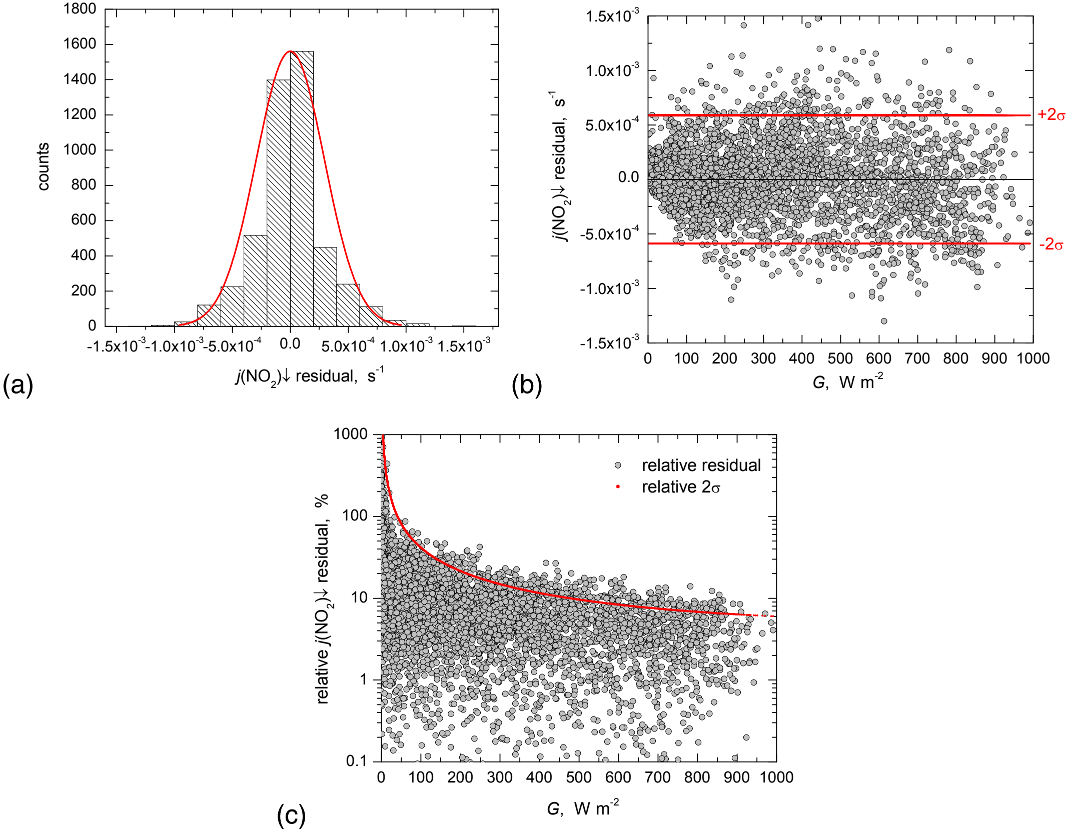

Fig. 3. Residual analysis for polynomial fit shown in Fig. 2b including **(a)** histogram of the $j(NO_2)\downarrow$ residuals with Gaussian probability distribution (red line) **(b)** plot of absolute $j(NO_2)\downarrow$ residuals versus G with ±2σ (95.45%) confidence bands (red lines) and **(c)** relative $j(NO_2)\downarrow$ residual versus G with relative 2σ (95.45%) confidence band (red line).

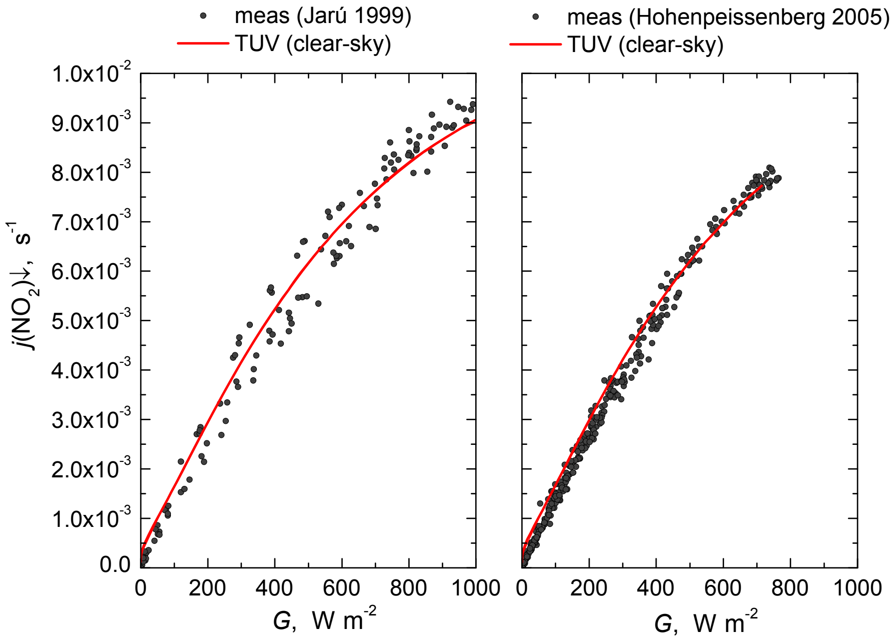

Fig. 4. Clear-sky $j(NO_2)\downarrow$ for a simple model atmosphere as predicted with the Tropospheric Ultraviolet Visible (TUV) model (http://cprm.acd.ucar.edu/Models/TUV/) versus G (for explanation see text) exemplarily for **(a)** 21 May 1999 at the Jarú site in Brazil (site 2) and **(b)** 9 September 2005 at the Hohenpeißenberg site in Germany (site 4).

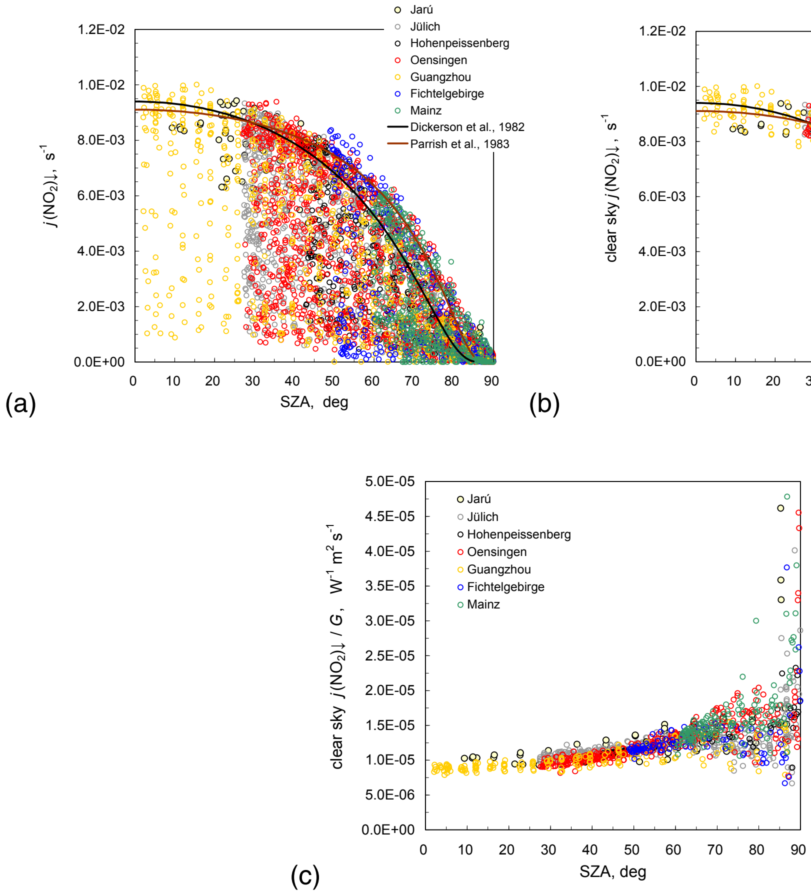

Fig. 5. Plots of **(a)** $j(NO_2)\downarrow$ versus SZA under clear-sky and cloudy conditions, **(b)** $j(NO_2)\downarrow$ and **(c)** ratio $j(NO_2)\downarrow/G$ versus SZA under clear-sky conditions for seven field sites below 800 m a.s.l. In (a) and (b) the empirical functions of Dickerson et al. (1982) and Parrish et al. (1983) are also shown.

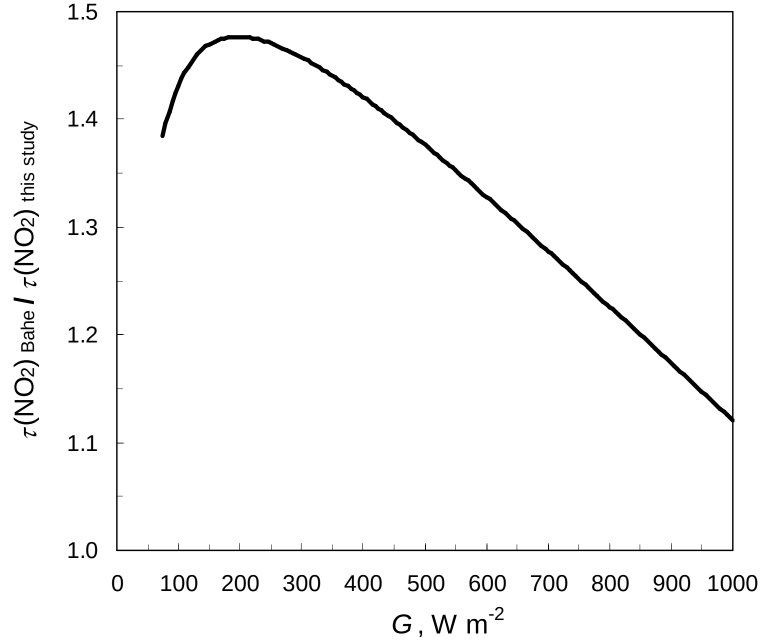

Fig. 6. Ratio of chemical lifetimes for the NO_2 molecule with respect to photolysis ($\tau(NO_2)=j(NO_2)^{-1}$) according to the empirical function from Bahe et al. (1980) and from this study (with $\alpha=0.03$) as a function of G. Bahe et al. (1980) recommended to use their function only for G values >70 W m^{-2}.