Atmos. Chem. Phys. Discuss., 10, 12827–12858, 2010
www.atmos-chem-phys-discuss.net/10/12827/2010/
doi:10.5194/acpd-10-12827-2010


Atmospheric Chemistry and Physics Discussions



# $NO_2$ photolysis frequencies in street canyons

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Received: 16 March 2010 – Accepted: 6 April 2010 – Published: 18 May 2010

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

## Abstract

Photolysis frequencies for $NO_2$ are modeled for the conditions in urban streets, which are taken into account as canyons with variable height and width. The effect of a street canyon is presented with absolute values and as a ratio RJ of the photolysis frequency within the street against those with free horizon, which allows further use of the existing photolysis parameterizations. Values are presented for variable solar elevation and azimuth angles, varying atmospheric conditions and different street properties. The $NO_2$ photolysis frequency in the street, averaged over atmospheric conditions and street orientation, is reduced to less than 20% for narrow streets, to about 40% for typical urban streets, and only to about 80% for garden streets, each with about ±5% uncertainty. A parameterization of RJ with the global solar irradiance is given for values that are averaged over the meteorological conditions and the street orientation.

## 1 Introduction

Nitrogen dioxide ($NO_2$) is a key component in the chemistry of the atmosphere. It links the reaction cycles of hydrogen and the halogen species by forming metastable constituents like $HO_2NO_2$ or $ClONO_2$. In the troposphere, $NO_2$ controls the concentrations of the peroxy radicals and, hence, the photochemical production of ozone.

In humans, $NO_2$ causes respiratory diseases and other ailments (Kirsch et al., 2002). As a toxic component of the air $NO_2$ is subject to regulations and it is monitored regularly. Licensing procedures (e.g. TA-Luft, 2002) as well as the prediction of the next day's $NO_2$ burden (Elbern et al., 2007) depend on model calculations of atmospheric photochemistry. For modeling purposes the exact knowledge of the actual $NO_2$ photolysis is essential.



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The photolysis frequency of a chemical substance is given by the equation

$$J = \int F(\lambda) \cdot \sigma(\lambda, T) \cdot \Phi(\lambda, T) \cdot d\lambda \quad (1)$$

where $F(\lambda)$ is the spectral actinic solar flux, $\sigma(\lambda,T)$ the wavelength and temperature dependent absorption cross section of the substance, and $\Phi(\lambda,T)$ the quantum yield of the specific reaction.

The actinic flux is determined as

$$F(\lambda) = \int_0^{2\pi} \int_{-1}^{+1} I(\lambda; \vartheta, \varphi) \cdot d(\cos\vartheta) \cdot d\varphi \quad (2)$$

with $I(\lambda;\vartheta,\varphi)$ being the spectral radiances of the sky, of the direct sun, and of the radiation that is reflected at the surface, from any direction of both hemispheres, defined by the zenith angle $\vartheta$ and the azimuth $\phi$.

For a given chemical reaction, the absorption cross-section and the quantum yield are fixed values, available from laboratory measurements (a compilation of measured spectra can be found in : Keller-Rudek and Moortgat, 2010, MPI-Mainz UV-VIS Spectral Atlas of Gaseous Molecules) and only slightly depending on temperature. The actinic flux, however, depends on the actual radiation conditions, the spectral field of direct, diffuse and reflected radiation. Thus the actinic flux depends on the solar zenith angle and on the scattering and absorption processes in the atmosphere, i.e. on the amount of the aerosol particles, the absorbing gases, the air molecules and the surface albedo. For the photolysis frequency of $NO_2$ the radiation in the range below 420 nm is of interest, with a relative large amount of diffuse radiation. Since the radiances from all directions participate in the actinic flux with equal importance, and with no cosine weighting as it is the case for the irradiance, also the radiances from large zenith angles contribute essentially.

In a street canyon, the radiances from the sky and the sun may be obstructed by the buildings at large zenith angles. Instead of the radiances from the sky, for these angles the radiation that is reflected at the walls of the buildings contributes to the actinic flux.





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These radiances in general are much lower than the obstructed radiation, since the albedo of the materials of the buildings is low in the spectral range of interest. Thus, the actinic flux in a street canyon, and consequently the $NO_2$ photolysis frequency, is strongly reduced compared to that for the same atmospheric conditions, but with a free horizon. Since the street canyon effect is a systematic one, the effect should be taken into account if the $NO_2$ photolysis frequency will be determined for urban conditions.

The $NO_2$ photolysis frequencies for the conditions in a street are modeled with respect to variable values of the solar zenith angle and of the sun's azimuth relative to the street. Additionally analyzed is the influence of aerosol amount and absorption, of total ozone, of clouds, and of the relative width of the street canyon.

In general, for simplification with respect to the short computation time that is available in photochemical models, the photolysis frequencies are given with simple parameterizations (Roeth, 2002; Trebs et al., 2009). Thus, for the present paper ratios are derived between the photolysis frequency in the street and its value for the same atmospheric conditions, but with free horizon. Using these ratios, the application of the existing parameterizations can easily be expanded to the photolysis rates in street canyons.

## 2 Model and data

### 2.1 Radiative transfer model

The photolysis frequencies in this study are modeled via spectral radiances, which are determined with the actual version of the System for Transfer of Atmospheric Radiation (STAR) (Koepke et al., 2006; Ruggaber at al., 1994). STAR is a one dimensional radiative transfer model for the UV spectral range that models photolysis frequencies for very different chemical reactions in a fast version (Ruggaber et al., 1994), but also spectral irradiances, actinic fluxes and radiances. The radiances depend on the solar elevation, the state of the atmosphere and the ground properties. The atmosphere is described



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by height-resolved fields of the radiative properties of air molecules, aerosols, ozone, and clouds. The high quality of the model was demonstrated in comparisons with measured and modeled data (Koepke et al., 1998; DeBacker et al., 2001).

To model the variation of the radiation field as an effect of a street canyon, the Sky Obstruction Program Skop (Hess and Koepke, 2008) is used. The modelling procedure is started with a STAR model run for the solar and atmospheric conditions in question. This model run yields a complete hemispheric spectrally resolved radiance field. Next, the properties of the objects, which are obstructing parts of the sky, are given with their size, shape, and position in terms of their angular dimensions in zenith and azimuth, as seen from the position of the volume for which the actinic flux is calculated. These objects are defined by an arbitrary number of zenith-azimuth angle combinations relative to the sun, under the assumption that the objects are flat. For buildings, the transparency, which could also be taken into account in the program, is zero. Thus the radiances from the sky behind the buildings are omitted and instead the radiation from sun and sky that is reflected at the buildings is taken into account. The spectral irradiances impinging on the walls are calculated by a computer code to get irradiances on arbitrarily oriented receivers (Mech and Koepke, 2004), using the first, undisturbed radiation field. The surfaces are assumed to have Lambertian reflectance with a given albedo, resulting in spectral radiances coming from the walls, which are included into the original radiance field by replacing those sky radiances that are obstructed by the objects. Finally the radiances are integrated to form the spectral actinic flux. Always the total ($4\pi$ sr) actinic flux is simulated.

It has to be noted that no interaction between the different objects are considered in the model. That means, there are no shadows from one object falling on the other, and there is also no reflection between such objects. These effects are considered to be of minor importance because of the usually low reflectance of the building material in the UV. For the purposes described in this paper, the complete hemispherical radiance fields have been calculated with a 1° resolution in zenith and azimuth angle and a spectral resolution of 10 nm.

To get the $NO_2$ photolysis frequencies, the spectral actinic flux values are multiplied with the relevant absorption cross-sections and quantum yields and spectrally integrated. The effects of the atmospheric conditions, the solar position and the street canyon influence the spectral values of the actinic flux, but not the absorption cross-sections and the quantum yields. However, the processes are strongly wavelength dependent, due to the variable spectral distributions of the radiances over the sky for different atmospheric conditions and solar elevation. Thus, the final effects have to be discussed on the basis of the photolysis frequencies

Not only the photolysis frequencies for the street canyon have been calculated, but also the values for the same conditions, but with free horizon. The results have been used to determine the ratios between street and free conditions. Such ratios depend only on the variable spectral actinic fluxes, i.e. the properties of atmosphere and of ground, and not on the chemical reactions of the photolytic processes. Thus these ratios offer the possibility to convert photolysis frequencies from available parameterizations, which in general are valid for undisturbed conditions, into photolysis frequencies for a street canyon.

## 2.2 Atmospheric properties

The solar irradiation of the earth is described with spectral data for the extraterrestrial sun (Woods et al., 1996), and a relative sun-earth distance which is fixed to 1 as average condition. The solar zenith angle (SZA) is varied with values between 1° and 85°. The photolysis is modelled under the assumption of an altitude of 200 m a.s.l. The regional albedo, which is used to model the undisturbed irradiance, is set to 3%, a typical value in the UV (Blumthaler and Ambach, 1988). The scattering air molecules are considered to be at a barometric pressure of 980 hPa, appropriate to the altitude. The total amount of ozone in the column in general is fixed at 320 DU. However, also 260 and 400 DU is tested to demonstrate that an effect due to ozone variation is negligible for $NO_2$ photolysis frequencies, which is a consequence of its spectral weighting (see Fig. 3).



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The aerosol properties are varied between clear, average and turbid conditions. With the turbidity not only the aerosol amount is changed, but also the aerosol type, which is a mixture of different components, and thus of its absorption properties (Hess et al., 1996). For the clear conditions, the aerosol optical depth (AOD) at 550 nm is set to 0.05 and for the aerosol in the boundary layer the type "clear continental" is used. For more polluted conditions, both the AOD and the type is changed: for average conditions the AOD at 550 nm is 0.2 and the type "continental average" and for turbid conditions the AOD is set to 0.4 and the type to "continental polluted" (Hess et al., 1996). With the aerosol type the spectral values of all optical aerosol properties change, not only the extinction coefficient, but also the single scattering albedo and the phase function. Since the aerosol particles influence the distribution of the sun and sky radiances, and as a consequence the effects of the street buildings, also aerosol absorption and aerosol optical depth are tested independently.

The aerosol amount and its properties are changed in the boundary layer, given as a layer with constant mixture up to 1 km over ground. Above the boundary layer background aerosol is used.

The effect of clouds is modeled for a stratus cloud layer with a geometrical extension of 1 km. The clouds obstruct the radiation of the direct sun completely. Thus, an effect of shadow of the buildings, which partly is responsible for the street effect, is negligible for these conditions.

For the calculation of the photolysis frequency according to Eq. (1) the $NO_2$ spectrum given by Mérienne et al. (1995) is applied. The temperature dependence of the $NO_2$ spectrum is accounted for by multiplying the data at 298 K with a series of Gaussian functions:

$$Fkt(T,\lambda)=1+.0023(T-298)\exp\left(-.005(\lambda-272)^2\right)+.0040(T-298)\exp\left(-.0003(\lambda-600)^2\right) \quad (3)$$

The coefficients of this formula were gained by analyzing the relative temperature dependence of the spectra published by Bogumil et al. (2003).





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For the photolysis reaction

$$NO_2 + h\upsilon \rightarrow NO + O \tag{R1}$$

the quantum yield can be expressed by a Fermi-function

$$\Phi(T,\lambda) = \frac{1}{1+\exp(0.35(\lambda-\lambda_0))} \tag{4}$$

with a temperature shift of $\lambda_0$ given by

$$\lambda_0 = 404[\text{nm}] + 0.2[\text{nm/K}](T-298)[\text{K}] \tag{5}$$

This function represents the data published by Troe (2000) within the error bars.

The temperature is fixed at 298 K in the present calculations and no temperature effect is considered, neither for the absorption spectrum nor for the quantum yield. The results are focused on the ratios between the photolysis in the street and that under undisturbed conditions and these ratios have a negligible temperature dependence.

### 2.3 Description of the street canyon

The street under consideration is assumed to have a total width $b$ and the bordering buildings the height $h$. The actinic flux, and hence the photolysis frequencies, are modeled for a position close to the surface in the middle of a street (Fig. 1). Consequently, the elevation angle of the buildings perpendicular to the street, i.e. the condition for maximum elevation, $\varepsilon_{max}$ is given by

$$\tan(\varepsilon_{max}) = 2h/b \tag{6}$$

The street is assumed to be endless. Thus, the equation for the elevation of the



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buildings for any direction shifts to

$$\tan(\varepsilon) = 2 \cdot h \cdot \sin\phi / b \quad (7)$$

with $\phi$ the azimuth angle against the orientation of the street ($\phi$=90° for the direction perpendicular to the street orientation).

The reduction of the actinic flux due to the shadowing in the street, and thus the reduction of photolysis frequency, of course depends on the width of the street canyon relative to the height of the buildings. To take the variability into account, the street-effects are determined for different street types: urban street, skyscraper street and garden street.

Urban streets in general have a total width that is in same order of magnitude as the height of the buildings, e.g. with values of about 18 m as shown in Fig. 2 for a typical street in Munich. From h = b, for the urban street, the angular elevation of the buildings as function of the azimuth Φ is given by

$$\varepsilon = \arctan(2 \cdot \sin\phi), \quad \text{with} \quad \varepsilon_{max} = 63° \quad (8)$$

For a street in an area with skyscrapers $h$=4·$b$ is assumed as ratio, resulting in $\varepsilon_{max}$=83°.

In a typical suburban street the houses are lower and standing in gardens, resulting in a larger width of the street. These conditions are expressed as $h$=$b$/4, resulting in $\varepsilon_{max}$=27°.

The albedo of the street surface and of the walls of the buildings is set to a mean value of 8%, independent of the wavelength. Different material types show some variation of the albedo, but the values are always low in the UV (Feister and Grewe, 1995; Bucars, 2006). Moreover, the structure of the walls often produces a certain amount of shady areas, which reduce the average reflection of the buildings.





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## 3 Results

### 3.1 $NO_2$ photolysis frequencies

Figure 3 shows on a logarithmic scale the wavelength dependence of the quantities entering the $NO_2$ photolysis frequency $J_{NO_2}$. To use only one axis in the figure, the values of all quantities are multiplied by an individual factor which brings the maximum into the range between 0.1 and 1. The $NO_2$ photolysis (red) has its maximum between 360 and 410 nm, resulting from the actinic flux (blue), which increases with wavelength, and the quantum yield (black), which is strongly decreasing around 420 nm. Additionally shown is the absorption cross section (yellow), which, however, is not varying very strongly with wavelength.

Spectrally integrated values of the $NO_2$ photolysis frequencies $J_{NO_2}$ (in 1/s) are the final result of the sensitivity study. Such values are depicted in the following figures as a function of the solar zenith angle (SZA). The modeled data are given by the symbols, the connecting lines in between are given only as a guidance for the eye. In general, values are given for conditions with a free horizon and for a position at the bottom of the street canyon. These values are shown both for the sun shining parallel ($\phi$=0, long dashed lines) and perpendicular to the street ($\phi$=90, short dashed lines), with the sun's azimuth modeled independent of the solar zenith angle.

Figure 4 shows the $NO_2$ photolysis frequency $J_{NO_2}$ for average cloud-free atmospheric conditions both for free horizon and for the three types of street canyons, which are taken into consideration, each with the sun shining parallel and perpendicular to the street.

The values $J_{NO_2}$ for undisturbed conditions become smaller with increasing SZA, due to the reduced actinic flux for lower solar elevation. The photolysis frequency in the street canyons also decreases with increasing SZA, but $J_{NO_2}^{street}$ is always additionally reduced, since a part of the sky is obstructed by the buildings. Thus the reduction of the $J_{NO_2}$ increases with the deepness of the street canyons, from garden to skyscraper streets. In the case of shadow, which is given for a SZA where the solar elevation is too





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low to the illuminate the bottom of the street, the direct sun no longer contributes to the actinic flux. Thus, for the conditions with the sun shining perpendicular to the street, a strong decrease of the photolysis frequencies occurs between 5° and 10° SZA for the skyscraper street, between 25° and 30° for the urban street, and between 60° and 65° for the garden street case. For small SZA the sun always illuminates the whole street canyon, with the consequence that the differences between the two azimuth directions are very low. Here $J_{NO_2}^{street}$ can be even slightly larger for the sun shining perpendicular to the street, resulting from the radiation reflected at the houses, which are stronger illuminated under these conditions.

The spectral radiances of sun and sky, and their distribution over the hemisphere, depend on the properties of the atmospheric parameters. Thus, also the spectral actinic fluxes and the photolysis frequencies depend on these parameters, and, moreover, their variation due to a street canyon likewise. Figure 5 shows $J_{NO_2}^{street}$ as a function of the solar zenith angle for clean and turbid, cloud-free atmospheres and for an atmosphere with average turbidity and an additional cloud layer of 1 km thickness. For the conditions with a free horizon, i.e. above a street canyon, in the figure again the reduction of $J_{NO_2}$ with increasing SZA is to be seen and additionally its reduction with increasing aerosol turbidity. The decrease of the actinic flux due to the assumed cloud layer causes a reduction of $J_{NO_2}$ to about one third of the value for clean, cloud-free conditions. Both the turbidity and the cloud effects are increasing with increasing SZA, as a consequence of the increasing path length of the radiation through the atmosphere.

Additionally shown in Fig. 5 are the related $J_{NO_2}^{street}$ for an urban street canyon with parallel and perpendicular illumination. As in Fig. 4, the effect of shadow is evident for cloud-free conditions. The reduction for shadow conditions is less pronounced for high turbidity than for low turbidity, due to the sky radiation increasing with turbidity. For the conditions with the cloud layer both azimuth directions of the street result in the same values, since only diffuse radiation exists and thus no shadow due to the buildings occurs.



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### 3.2 Street canyon ratios of $NO_2$ photolysis frequencies

For an uncomplicated use of photolysis frequencies in chemical models often parameterizations are applied (Röth, 2002). Generally, this is a good approximation when detailed actual conditions are not known. These parameterized photolysis frequencies in general are valid for undisturbed conditions with free horizon, since they are based on values of the global solar radiation, which are measured for such conditions (Trebs et al., 2009).

$$J_{NO_2}^{\mathrm{freehorizon}} = f\,(\text{solar global irradiance}G)$$

With the help of the ratio RJ of the photolysis frequency in the street canyon $J_{NO_2}^{\mathrm{street}}$ and the corresponding values for undisturbed conditions $J_{NO_2}^{\mathrm{freehorizon}}$

$$\mathrm{RJ}(\text{street properties}, \mathrm{SZA}, \phi, \text{turbidity}) = \frac{J_{NO_2}^{\mathrm{street}}(\text{street properties}, \mathrm{SZA}, \phi, \text{turbidity})}{J_{NO_2}^{\mathrm{freehorizon}}(\mathrm{SZA}, \text{turbidity})} \quad (9)$$

it is possible to determine $J_{NO_2}^{\mathrm{street}}$ for conditions where the frequencies for undisturbed conditions $J_{NO_2}^{\mathrm{freehorizon}}$ are known. Since the effect is a systematic one, it is possible to use furthermore the existing parameterizations for undisturbed conditions.

$$J_{NO_2}^{\mathrm{street}} = \mathrm{RJ} \cdot J_{NO_2}^{\mathrm{freehorizon}} = \mathrm{RJ} \cdot f\,(\text{solar global irradiance G}) \quad (10)$$

Of course, these ratios RJ depend on the properties of the street, on the atmospheric conditions and on the sun's position relative to the street. Thus, in the following figures their variability is displayed, namely the values that finally are used to determine averaged RJ values. Moreover, the variability gives the opportunity to discuss the range of uncertainty for such a general consideration of street canyon effects in the $NO_2$ photolysis frequencies.





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In Fig. 6 the ratios RJ are depicted as a function of the SZA for the same conditions as in Fig. 4, i.e. illuminated street canyons of different type under average atmospheric conditions, in each case both for the sun shining parallel and perpendicular to the street. As mentioned for Fig. 4, for zenith angles, which are so small that the sun is shining into the street in both cases, the ratios for both directions are equal. These conditions shift to larger SZA with increasing width of the street compared to the height of the houses.

The reduction of RJ with reduced width of the street canyon is evident, since larger parts of the radiation of sun and sky is omitted. For typical urban streets, the ratio is between 0.7 and 0.4 for sunny conditions and between 0.2 and 0.3 in the case of shadow. For the skyscraper streets the radiation reduction due to the buildings is stronger, with RJ between 0.55 and 0.2 in the sun and about 0.15 in the shade. Contrary, for the garden streets the reduction of is only small, with RJ about 0.85 for sunny and between 0.5 and 0.7 for shadow conditions. Figure 6 again shows the effect that shadow in the street occurs often for small streets and is shifted to conditions with increased SZA, to conditions with lower sun, with increasing width of the streets. For sunny conditions, a slight decrease of RJ with increasing SZA can be seen for all street types. This results from the fact that the diffuse radiation increases relative to the direct sun's. Thus, the obstruction of the diffuse radiation becomes more important at larger SZA. For conditions with shadow in the street, RJ is slightly increasing with SZA, since for undisturbed conditions the total actinic flux decreases more strongly than the diffuse radiation only. For very large SZA the contribution of the direct sun is very low, with the effect that the sky's radiation dominates totally and thus the RJ values become similar for both, the sun shining parallel and perpendicular to the street.

The photolysis frequency ratio for different atmospheric conditions is shown in Fig. 7 as a function of SZA for an urban street, analog to Fig. 5. For cloud-free conditions, the effects of sun and shadow become obvious again. As mentioned, the aerosol absorption is assumed to increase with increasing AOD, resulting in larger absorption for high then for low turbidity. In the actinic flux for free horizon, for small SZA the





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effect of absorption is dominant while for large SZA the extinction and thus the aerosol optical depth is of higher relevance. The trend of RJ with SZA can be explained by combination of the different contributions of sun and sky to $J_{NO_2}^{freehorizon}$ and to $J_{NO_2}^{street}$. In case of shadow the diffuse radiation dominates, and, hence, RJ increases with turbidity, and for sunny conditions the opposite is the case. In comparison to the conditions with average turbidity (Fig. 6) it can be seen that the variation of the aerosol properties produces an uncertainty of RJ in the order of less than ±0.05.

Clouds in front of the sun reduce the actinic flux in general. If the cloud has such a large optical thickness that the direct sun is no longer of relevance, as modeled, the values are the same for the two azimuths between sun and street and nearly independent of SZA. The data are results for overcast conditions, but the effect of missing building shadows would be similar also for a single thick cloud in front of the sun. As shown in Fig. 7, RJ for the condition with a cloud obscuring the sun is between that for sunny and for shadow conditions, since the buildings do not cast a shadow. RJ is about 0.4 for conditions without direct sun for a typical European street canyon. A slight increase of RJ with SZA results from the fact that the total irradiance is more strongly reduced due to solar elevation than the irradiance from the zenith region.

The photolysis frequencies under cloudy conditions and the corresponding RJ are not shown for the other street types as they are nearly constant for different SZA and street azimuth. The values are about 0.8 for garden streets and about 0.17 for the skyscraper streets.

The effects of the aerosol amount and absorption, as independent variables, and of the total ozone amount in the atmosphere are analyzed, but not displayed. Their effect on $J_{NO_2}^{street}$ is negligible in comparison to the other effects. The RJ are determined with fixed average AOD, but variable aerosol absorption, on the one hand, and with fixed average absorption but variable AOD, on the other hand. The effect on RJ is a bit different for the conditions in sun and those with shadow, but in any case the variation in RJ is much less than that between a clean and a turbid atmosphere.





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Variations in total atmospheric ozone influence the UV actinic flux, but this effect can be neglected in the spectral range relevant for the $NO_2$ photolysis frequencies (see Fig. 3). Thus the values RJ do not depend on the total ozone. Of course, this effect has to be separated from the chemical reactions in the street, which form $NO_2$, and which directly depend on the local ozone concentration.

## 4 Parameterization with global irradiance

Parameterized photolysis frequencies (Röth, 2002) in general are valid for undisturbed conditions with free horizon, since they are based on values of the global solar irradiance $G$, measured for such conditions (Trebs et al., 2009).

Using adequate ratios RJ, the $J_{NO_2}^{street}$ values for a street canyon can be determined from the values for undisturbed conditions $J_{NO_2}^{freehorizon}$ derived with the existing parameterization schemes. To make the corresponding RJ easily available, they also should be parameterized versus the global solar irradiance $G$, which already is used to get $J_{NO_2}^{freehorizon}$. Such a correlation, of course, can only take into account the variability of the atmospheric and solar conditions. The individual width and orientation of a street canyon has to be considered independently.

In general, neither the atmospheric conditions nor the street properties are known. Thus, average RJ are determined, which are valid for average conditions, and connected with the global solar irradiance. The average ratios RJ are derived from the values for the three different conditions that have to be taken into account. These are atmospheric conditions with no cloud obscuring the sun, i.e. with free sun, either with the street in the sun, $RJ_{freessun}$, or in the shadow, $RJ_{freeshad}$, and conditions where the sun is obscured by a cloud, $RJ_{cloud}$. These data are available for the different street types, as discussed above.

To get an average value of RJ, the RJ for the three possible conditions mentioned abvove have to be weighted with their relative contribution. This is done by factors





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called $F_{\text{freessun}}$, $F_{\text{freeshad}}$, and $F_{\text{cloud}}$, which depend on the atmospheric conditions and the street azimuth, resulting in a final RJ by

$$\text{RJ} = F^{*}_{\text{freessun}}\text{RJ}_{\text{freessun}} + F^{*}_{\text{freeshad}}\text{RJ}_{\text{freeshad}} + F^{*}_{\text{cloud}}\text{RJ}_{\text{cloud}} \tag{11}$$

Of course, the weighting factors sum up to 100 %

$$F_{\text{freessun}} + F_{\text{freeshad}} + F_{\text{cloud}} = 1 \tag{12}$$

Since $G$ will be used for the parameterization, but the RJ are available for SZA, in a first step, $G$ is correlated to SZA for average conditions. Figure 8 shows $G$ as a function of SZA for cloud-free conditions for average turbidity (after Schulze, 1976; Iqbal, 1983). For conditions with clouds obscuring the sun, $G$ is assumed on an average to be reduces to 40% compared to cloud-free conditions. To get the SZA, which are needed for the correlation of RJ and $G$, $G$ is investigated in steps of 50 W/m$^2$.

Global irradiance with $G$>450 W/m$^2$ is assumed to occur only for cloud-free conditions. Thus, for these conditions always $F_{\text{cloud}}$ equals 0 and only conditions with the street in the sun or in the shadow of the buildings have to be separated, resulting in $F_{\text{freessun}} + F_{\text{freeshad}}$=1. The sun shines into the street if SZA is less than $(90^\circ - \varepsilon)$. This condition is used to get the appropiate values of the azimuth $\phi_{\text{sun}}$ according to Eq. (7). For all $\phi < \phi_{\text{sun}}$ the street is illuminated by the sun. Since in general the orientation of the street is not known, the assumption is made that it is random. Thus, the probability for the street in the sun is given by $\phi_{\text{sun}}$ divided by the total possibility of relevant orientation of 90°, resulting in

$$F_{\text{freessun}} = \phi_{\text{sun}}/90 \tag{13}$$

and, as a consequence,

$$F_{\text{freeshad}} = 1 - F_{\text{freessun}} \tag{14}$$

Of course $\phi_{\text{sun}}$ depends on the SZA, which for the parameterization is correlated to $G$. For high sun, i.e. small values of SZA, the sun may shine always into the street,





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resulting in $F_{freessun}$=1, and for low sun the conditions with a sunny street are reduced to a small range of $\phi$ values close to 0°, resulting in low values of $F_{freessun}$. Since $\phi_{sun}$ also depends on $\varepsilon$, $F_{freessun}$ and $F_{freeshad}$ are determined individually for the three different street types considered.

For conditions with $G$<450 W/m$^2$ it can not be decided without additional information whether the irradiance is valid for cloud-free conditions with large SZA or for those with a smaller SZA, but a cloud obscuring the sun. Since the desired parameterization uses only $G$ as information, an assumption is made with respect to the probability that clouds obscure the direct sun. With respect to the fact that in a layer with broken cloudiness from the sun's perspective the gaps between the clouds become smaller with increasing SZA, $F_{cloud}$ is varied between 0.5 for vertical sun and 1 for the sun at the horizon, taking into account the increasing length of the path through the atmosphere with increasing SZA.

Averaged RJ as a function of $G$ are determined for the three street types by Eq. (11), using the derived F-values as function of SZA and the related $RJ_{freessun}$ , $RJ_{freeshad}$ and $RJ_{cloud}$ for atmospheric conditions with average turbidity, as shown in Fig. 6. These averaged RJ are presented in Fig. 9 as function of the solar global irradiance. The RJ values are large, i.e. the reduction of the photolysis frequency is low, for the garden street. RJ becomes lower for the urban and for the sky scraper street, caused by the increasing reduction of sky radiation and the increased probability of shadow in the street. For all street types RJ has high values for large values of $G$, since the large values of global irradiance only occur for cloud-free conditions at small SZA. The probability for such conditions is shifted to lower values of $G$ with increasing street width. For decreasing values of $G$, but cloud-free conditions, the averaged RJ are reduced due to the increasing probability of shadow. For values of $G$ less than 450 W/m$^2$, where clouds are assumed to be of relevance, the RJ values increase a bit for the smaller streets, since the relative contribution of the visible part of the sky increase for cloudy conditions. For the wide garden street the effect of shadow is low, with the consequence that the possibility of a cloud further reduces RJ. With decreasing $G$ the probability of



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clouds obstructing the sun increases, with the effect that for $G<100\,\mathrm{W/m^2}$ the averaged RJ equal the values for cloudy conditions. The RJ for clouds obscuring the sun is nearly independent of SZA and thus independent of $G$. As a consequence, the relative minimum in the averaged RJ in Fig. 9 results from conditions with increased probability for shadow in the street, but without clouds.

For the conditions at mid latitudes, like in Europe, only solar zenith angles larger than 25° are of relevance. Since this results in general in $G<900\,\mathrm{W/m^2}$, the large values of averaged RJ, as shown in the right part of Fig. 9, are of no relevance for mid latitudes.

The averaged RJ are uncertain with respect to different reasons. The RJ values are influenced by the actual atmospheric conditions. Here, the optical thickness of the clouds has only a negligible effect, whenever the cloud is thick enough to block out the direct sunlight. The effect of aerosol type and amount is to be seen in Fig. 7. For the averaged RJ in Fig. 9, however, the uncertainty range is reduced since increasing aerosol optical depth has a converse effect on the direct sun and on sky irradiance, which thus partly cancel out each other. Thus, the averaged RJ values will be uncertain with respect to unknown atmospheric conditions in a range better than ±0.05.

The RJ values further are uncertain for an individual street due to its azimuth orientation, which is not considered and in general not known. This effect could be taken into account if conditions for a specific street are of interest, for example to check measured data. Moreover, it should be borne in mind that the street orientation is fix and thus the relative azimuth of the sun changes during the day. In general, the azimuth orientation of a street can not be incorporated into chemical models and thus the effect is accounted for by averaging in the averaged RJ shown in Fig. 9.

Of course, RJ varies strongly with the individual width of the street, the height of the buildings and its properties. Therefore, these effects are varied in a realistic range, considering three street types, and may be taken into account by a user.



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## 5 Conclusion and discussion

Street canyons reduce the $NO_2$ photolysis frequency compared to that for undisturbed conditions with free horizon. The reduction is low for sunny conditions, and quite large for a volume in the shadow of the buildings. In case of overcast sky, or with a cloud that obstructs the sun, the shadow of buildings is of no relevance and the canyon effect reduces the photolysis frequency in general to values between that for shadow and sun. The $J_{NO_2}$ reduction is strong for narrow streets and high buildings and less pronounced for wider streets and lower buildings, due to the relative amount of radiation that is obstructed by the buildings. The variability of the effect at different atmospheric conditions can be reduced, if not the absolute $NO_2$ photolysis frequency but the ratio RJ is considered. RJ is the quotient of the photolysis frequency in the street and that under the same atmospheric conditions, but with a free horizon.

For an easy handling in chemistry models, in general a parameterization of the $NO_2$ photolysis frequency with global solar irradiance $G$ is used. Therefore, such a parameterization is also derived for the RJ, with averaged values that take into account all aspects of the variability besides the street type.

For regions with solar zenith angles less than 25°, like in Europe, the global solar irradiance $G$ in general is less than 900 W/m$^2$. Thus, the averaged RJ values show only a small variability, as depicted in Fig. 9. These average values are given in Table 1 for the street types under consideration.

As shown, the relative width of the street strongly changes the actinic flux in the street and thus the photolysis frequency and the RJ values. Here, a more precise statistical analysis of the streets in the area of investigation would be helpful, together with the actual reflection properties of the buildings and the relevant atmospheric conditions like cloudiness and turbidity. For values of the global irradiance where cloud effects are possible ($G$<450 W/m$^2$), additional knowledge of SZA would allow for the decision whether a cloud is obscuring the sun or not. Of course, also the sunshine duration could be used for this purpose. And if the azimuth of a street is known, it could easily



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be used to determine individual RJ and the change during the day. However, all these aspects are far beyond the idea of this paper, and such additional information is most likely not applicable for routine conditions.

On the contrary, a further reduction of the possible variability of averaged RJ is suggested for practical use. Since in general even the street type is not available, a general reduction factor RJ=0.4 is suggested to shift the $NO_2$ photolysis frequency for conditions with a free horizon to the related values for a street canyon.

*Acknowledgements.* Financial support by the German Umweltbundesamt under UFO-Plan Grant 3709 42 207 is gratefully acknowledged.

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**Table 1.** Averaged reduction factors RJ for different street types.

| street type | building height/ street width | range of RJ for $G<900\,\mathrm{W/m^2}$ | Average RJ |
|---|---|---|---|
| free horizon | 0 | 1 | 1 |
| garden street | 0.25 | 0.75–0.9 | 0.8 |
| urban street | 1 | 0.3–0.45 | 0.4 |
| sky scarper street | 4 | 0.15–0.2 | 0.17 |

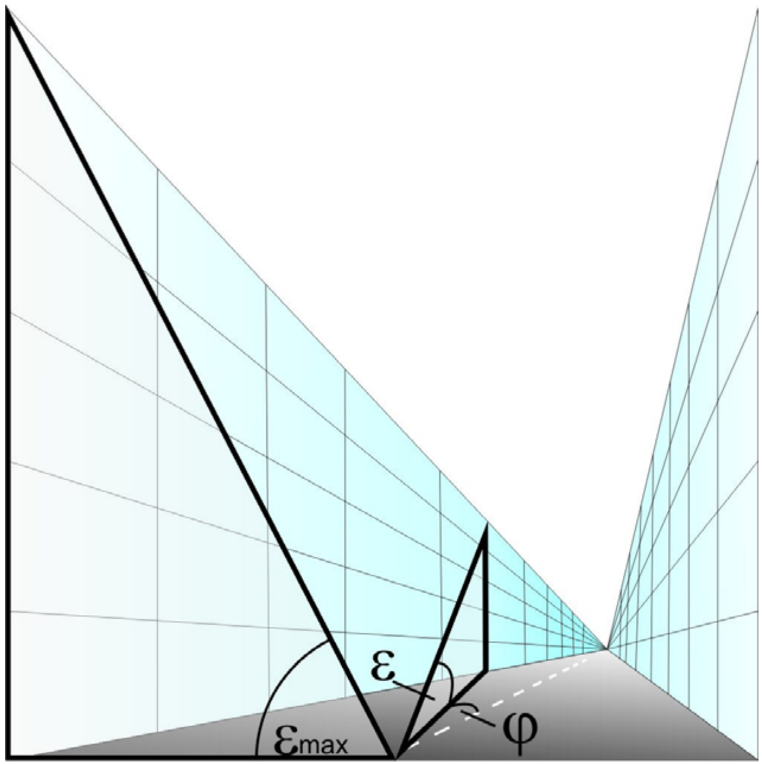


**Fig. 1.** Angles used to describe the illumination in a street canyon.





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**Fig. 2.** A typical urban street (Munich): the height of the buildings equals the width of the street.





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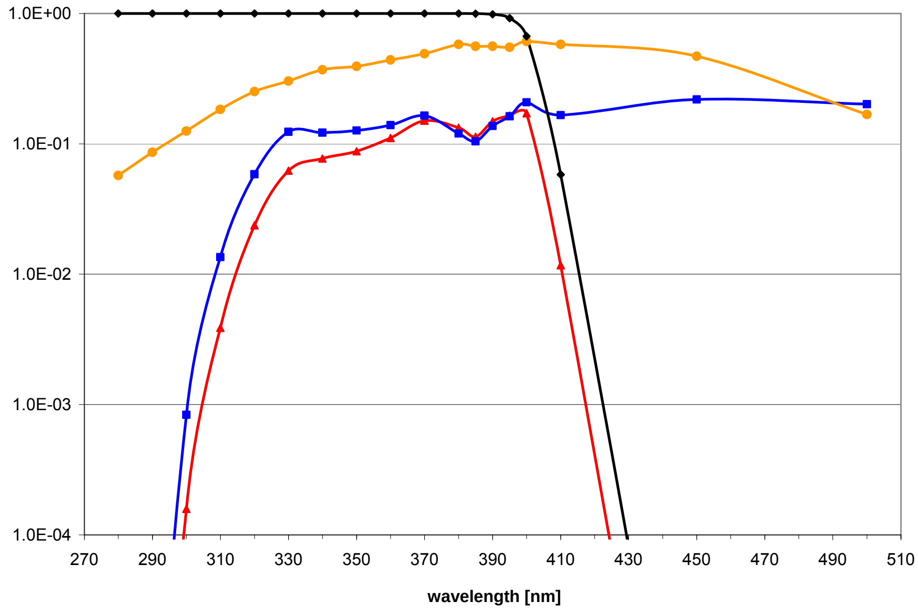


**Fig. 3.** Spectral values of $NO_2$ photolysis frequency: red, and of its contributors in relative values (see text).





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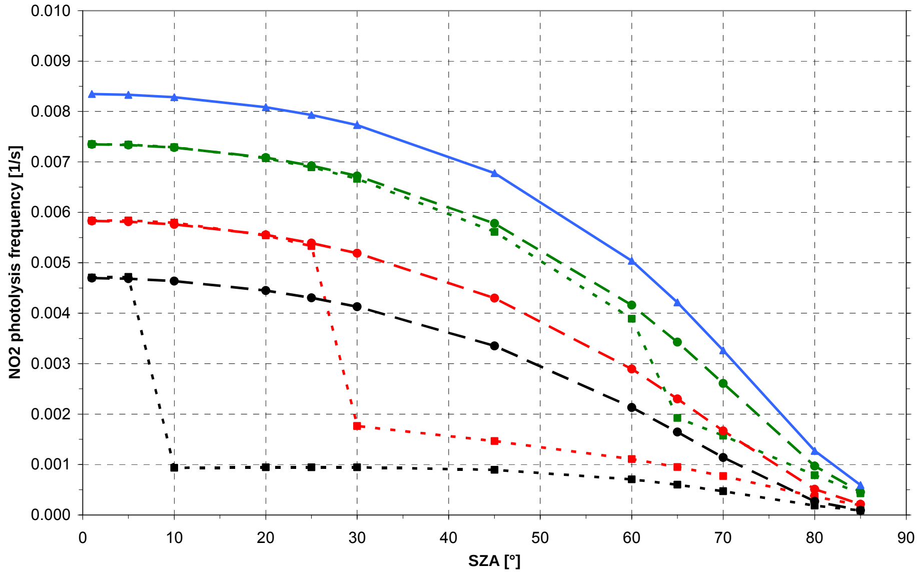


**Fig. 4.** $J_{NO_2}$ as function of solar zenith angle for average turbidity and cloud-free conditions

- undisturbed conditions with free horizon: blue,
- garden street: green,
- urban street: red,
- skyscraper street: black,
- street orientation parallel to the sun ($\phi$=0°): long dashed,
- street orientation perpendicular to the sun ($\phi$=90°): short dashed.





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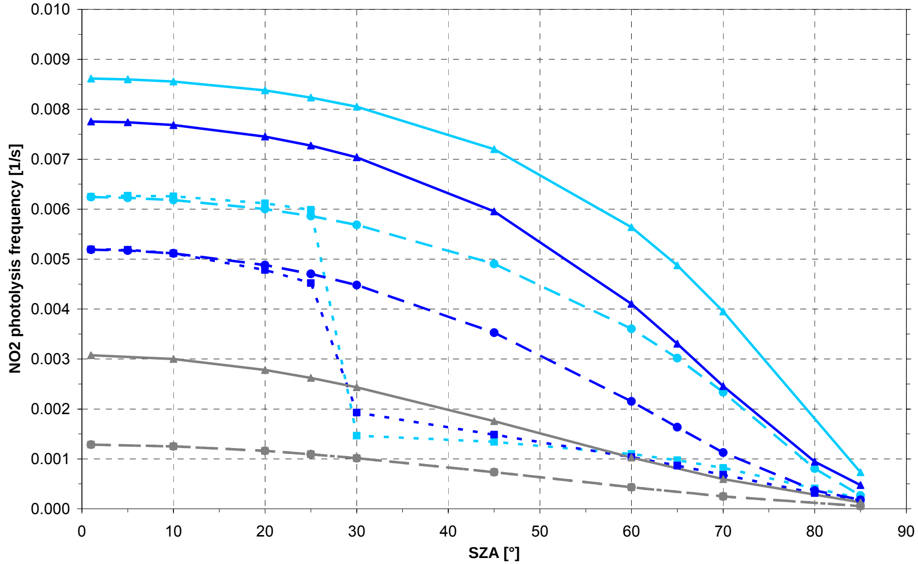


**Fig. 5.** $J_{NO_2}$ as function of solar zenith angle for

- conditions with a free horizon: solid lines,
- urban street with orientation parallel to the sun ($\phi$=0°): long dashed,
- urban street with orientation perpendicular to the sun ($\phi$=90°): short dashed,

for an atmosphere with

- low turbidity, but cloud-free: light blue,
- high turbidity, but cloud-free: dark blue,
- thick cloud and average turbidity: grey.





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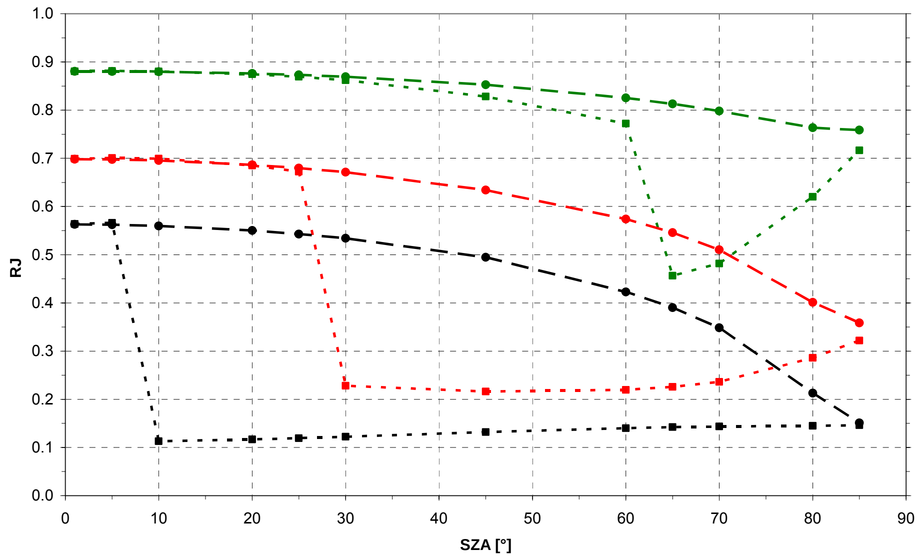


**Fig. 6.** Ratio RJ between $NO_2$ photolysis frequency in a street canyon and for undisturbed conditions as function of solar zenith angle for average turbidity

- garden street: green,
- urban street: red,
- skyscraper street: black,
- street orientation parallel to the sun ($\phi$=0°): long dashed,
- street orientation perpendicular to the sun ($\phi$=90°): short dashed.





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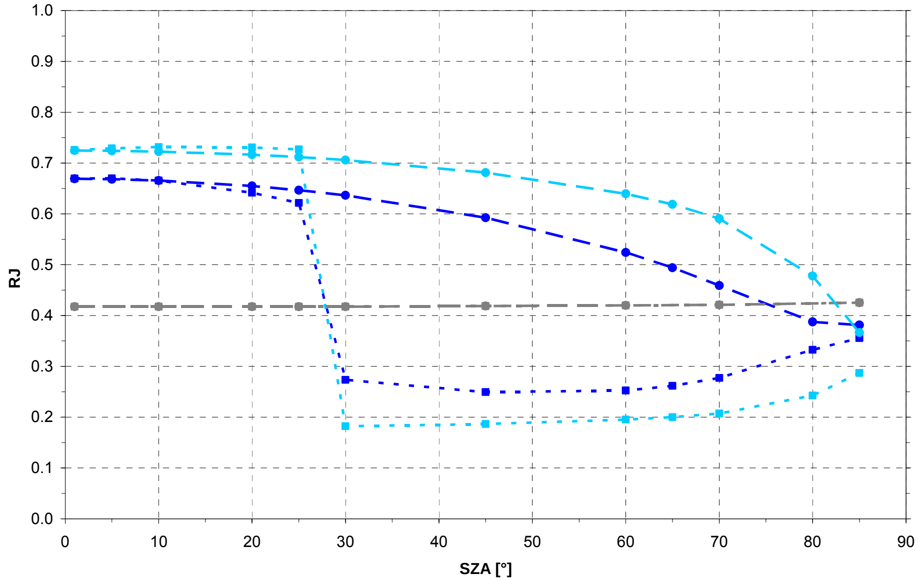


**Fig. 7.** Ratio RJ of $NO_2$ photolysis frequency between urban street and undisturbed conditions as function of solar zenith angle

- low turbidity, but cloud-free: light blue,
- high turbidity, but cloud-free: dark blue,
- thick cloud and average turbidity: grey,
- street orientation parallel to the sun ($\phi$=0°): long dashed,
- street orientation perpendicular to the sun ($\phi$=90°): short dashed.





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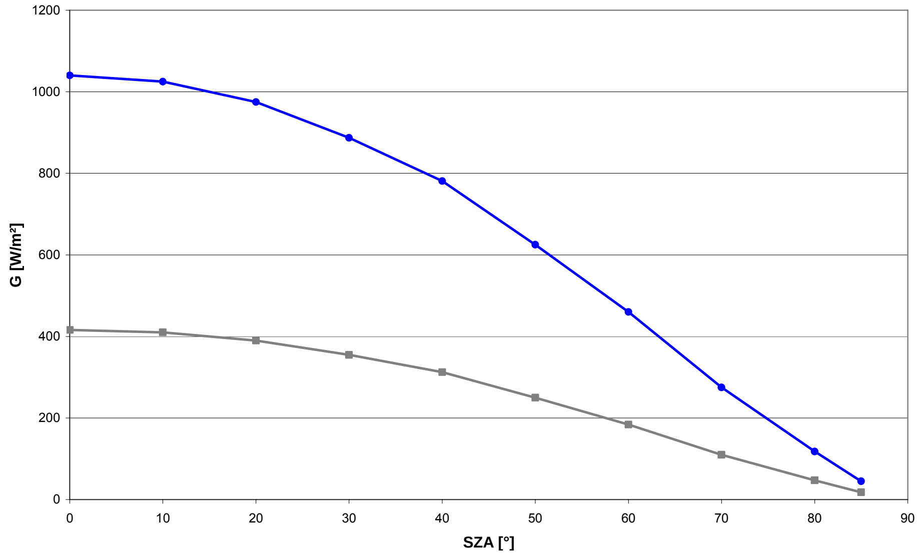


**Fig. 8.** Global solar irradiance as function of solar zenith angle for average conditions

- cloud-free conditions: blue,
- clouds obscuring the sun: grey.



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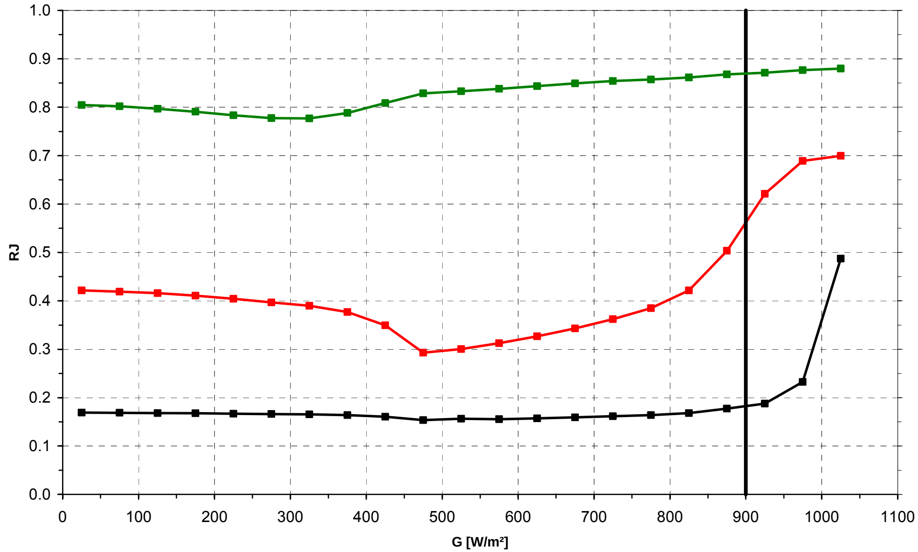


**Fig. 9.** Averaged RJ as function of solar global irradiance *G* for

- garden street: green,
- urban street canyon: red,
- skyscraper street: black.

The vertical line at 900 W/m$^2$ cuts out conditions with *G*, which, in general, do not occur for mid latitudes.



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