

UV attenuation in the cloudy atmosphere

Jianhui Bai

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Abstract Ultraviolet (UV) energy absorption plays a very important role in the Earth–atmosphere system. Based on observational data for Beijing, we suggest that some atmospheric constituents utilize or transfer UV energy in **chemical and photochemical (C&P)** reactions, in addition to those which absorb UV energy directly. These constituents are primarily volatile organic compounds (VOCs) emitted from both vegetative and anthropogenic sources. The total UV energy loss in the cloudy atmosphere for Beijing in 1990 was 78.9 Wm^{-2} . This attenuation was caused by ozone (48.3 Wm^{-2}), other compounds in the atmosphere (26.6 Wm^{-2}) and a scattering factor (4.0 Wm^{-2}). Our results for a cloudy atmosphere in the Beijing area show that the absorption due to these other compounds occurs largely through the mediation of water vapor. This fraction of energy loss has not been fully accounted for in previous models. Observations and previous models results suggest that 1) a cloudy atmosphere absorbs $25\sim 30 \text{ Wm}^{-2}$ more solar shortwave radiation than models predict; and 2) aerosols can significantly decrease the downward mean UV-visible radiation and the absorbed solar radiation at the surface by up to 28 and 23 Wm^{-2} , respectively. Thus, quantitative study of UV and visible absorption by atmospheric constituents involved in homogeneous and heterogeneous C&P reactions is important for atmospheric models.

Keywords UV radiation · Water vapor · Chemical and photochemical reaction · Scattering factor · Volatile organic compounds

1 Introduction

Discrepancies between radiative transfer model predictions and observations have persisted since Fritz (1951). Ackerman et al. (2003) suggested that the cloudy atmosphere absorbs

J. Bai (✉)

LAGEO, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029,
People's Republic of China
e-mail: jianhuibai@263.sina.com

more solar radiation than that predicted by the models used at that time (Valero et al. 2000). Cess et al. (1995, 1999), Ramanathan et al. (1995), and Pilewskie and Valero (1995) reported greater shortwave cloud absorption than that predicted by any model using current knowledge of cloud microphysical characteristics. However, Francis et al. (1997), Hayasaka et al. (1995), Stephens (1996), Li and Moreau (1996) do not support the view that the excess energy is absorbed by clouds and there is also debate about excess absorption in clear skies (Arking 1996; Kato et al. 1997; Halthore et al. 1998; Zender et al. 1997; Valero and Bush 1999; Charlock 1998).

Previous theory suggests that the atmosphere absorbs about 20% of the solar energy (Kiehl et al. 1995), but some later studies estimate that the average atmospheric absorption is closer to 28% and is greatly affected by clouds (Valero et al. 2000). The 8% energy difference is the largest uncertainty in the global climatic energy budget. It is therefore important to investigate how much solar energy is absorbed in the earth's atmosphere (Valero et al. 2000), and to identify all the sink(s) responsible for atmospheric energy absorption. Arking (1996) suggested that models underestimate the solar flux absorbed in the atmosphere by $25\text{--}30\text{ W m}^{-2}$, and that clouds do not have a strong effect on atmospheric absorption. However, observations indicate that there is a strong dependence of atmospheric absorption on total column water vapor. After analyzing the data from aircraft, satellite, and surface observation, Valero et al. (2000) provided strong evidence for UV absorption by the cloudy atmosphere. They concluded that absorbance in overcast conditions in the $0.224\text{--}0.68\text{ }\mu\text{m}$ spectral region and ranges between 0.04 ± 0.06 and 0.08 ± 0.06 , which were case studies that did not distinguish cloud and aerosol absorption. Later, significant progress has been made in understanding organic and inorganic aerosol forcing, especially with organic compounds, secondary organic compounds, and some aerosol types (Papayannis et al. 1998; Zerefos et al. 2000). Aerosol optical thickness (AOT) and other aerosol properties, and different levels of relative humidity (RH) have also been considered in the models. Model results indicate that aerosols can significantly decrease the downward mean UV-visible ($0.2\text{--}0.85\text{ }\mu\text{m}$) radiation and the absorbed solar radiation at the surface, by up to 28 and 23 W m^{-2} , respectively (Hatzianastassiou et al. 2004a). Hatzianastassiou et al. (2004b) used a series of sensitivity tests with a radiative transfer model to investigate the role of several key parameters of the Earth–atmosphere climate system on aerosol radiative forcings at the top of the atmosphere (TOA), within the atmosphere and at the Earth's surface. They reported that RH and aerosol single-scattering albedo are the most important climatic parameters which strongly affect aerosol forcing. Ming et al. (2005) also reported that hygroscopic growth considerably enhances the negative forcing. So the role played by RH and organic aerosols and the forcing mechanisms involved deserve further investigation.

Recently, a number of measurements and studies have been advances in quantifying both aerosols and clouds absorption have occurred (Valero et al. 2003; Pilewskie et al. 2005; Bergstrom et al. 2004; Feingold et al. 2006; Redemann et al. 2006; Dong et al. 2008), but, the models still underpredicted the measured instantaneous cloudy column absorption by amounts ranging from 17 to 61 W m^{-2} (Valero et al. 2003).

Based on re-analysis of previous observational data, it is hypothesized that the $25\text{--}30\text{ W m}^{-2}$ energy losses in the cloudy atmosphere may derive from the energy absorption by atmospheric gases, liquids, and particles (GLP). This energy absorption occurs in both clear and cloudy skies in Beijing megacity, as well as other sites in the world. This process affects the energy distribution of the atmospheric column and thus the thermal dynamics, further affecting the local climate. So, an accurate knowledge of atmospheric components including the anthropogenic and vegetative volatile organic

compounds (VOCs) budgets could help to parameterize the effects. Then, studies of the strong impact in Beijing could help reduce anomalous absorption errors in global models.

2 Instruments and observation

Solar spectral radiation was measured every day from January 1 to December 31, 1990 at Xianghe station. Xianghe station is situated at 39°46'N, 116°58'E, 70 km southeast of Beijing, associated with the Institute of Atmospheric Physics, Chinese Academy of Sciences (IAP, CAS). All radiation sensors were placed on the top of the building (about 15 m above the ground). The instrument system (322 Institute of Jinzhou, China) consisted of three radiation sensors (model TBQ-4-1) and a recorder with accuracy of 5% (Bai and Wang 1994, 2003). These radiation sensors were commonly deployed in China, their wavelength sensing ranges were 270~3,200, 400~3,200 and 700~3,200 nm, respectively. Solar global irradiance (Q) was obtained from the measurement of the 270~3,200 nm sensor. UV irradiance (UVI) (290~400 nm) was derived by subtraction of radiation over 400~3,200 nm from 270 to 3,200 nm. The yearly stability of the three sensors was $<\pm 2\%$, temperature dependence is 0.05%/degree, the cosine response error was $\leq \pm 3\%$ for solar zenith angle $< 70^\circ$. The desiccant of all sensors was changed regularly or when their color changed, to ensure dry condition. Routine cleaning of all sensors was done every morning before sunrise. All sensors were covered after sunset. The instrument system was calibrated at regular intervals (1 or 2 years) in the dry season and under “clear sky” conditions. UVI was obtained from two spectral radiation readings, using sharp cut-off filters (at 280 nm and 400 nm) carefully selected in the factory. They were calibrated before this campaign by using Eppler radiometers (Model PSP) with WG 295, 395 filters, respectively, under clear sky conditions. Direct solar irradiance (D) was measured with a radiometer (TBS model), its yearly stability was $<\pm 1\%$, tracing accuracy was $<\pm 1^\circ/24$ h, ambient temperature range was $<\pm 45^\circ\text{C}$. The solar scattered irradiance (S) was derived from the global and direct irradiance measurements, $S = Q - D$. The broadband scattered and direct solar radiation were measured from 0.3 to 3.0 μm . The working reference of calibration related to global radiation and direct irradiance is traceable to the Chinese national radiometric reference. The estimated maximum observational error of UVI was about 10%, accounts for the influence of sensitivity change and other factors, including Eppler uncertainties. In order to decrease the influence of observational error, the data collected during the early morning and late afternoon were eliminated in the reanalysis, i.e. the data with solar zenith angle higher than about 80° were discarded. The cloudiness (by eye survey) and weather parameters were recorded every day, and total ozone amount was also measured by a Dobson instrument at Xianghe station (IAP, CAS).

All parameters described above were measured at Xianghe station (Bai et al. 2003), except D and S (i.e., S/D) and water vapor pressure (e) at the ground were obtained from Beijing meteorological observatory (39°56'N, 116°17'E).

3 Factors affecting UV attenuation and generating an empirical model

3.1 Model development

When UV radiation passes through the atmosphere, it is usually attenuated or influenced by several factors: (1) The “ozone term”, which describes ozone selective absorption, and is

calculated using $e^{-k_1 O_3 m}$, where $k_1 = 3.30 \times 10^5 (\text{Pa} - \text{cm})^{-1}$ and is the averaged absorption coefficient in the UV band (290.2~400.0 nm), O_3 is the total column ozone amount (unit of DU, 1 atm-cm=1,000 DU), m is air mass; (2) The “water vapor” or “photochemical” term, which represents UV energy absorption by diverse GLP, and the utilization/transfer of UV energy during their chemical and photochemical (C&P) activities. This term is highly related to the concentrations of OH radicals, H_2O , all substances in the atmosphere, and O_3 UV photolysis. Because it is impractical to describe all energy absorptions by all atmospheric constituents, this term is obtained empirically. It is expressed as $Ae^{-k_2 wm}$ (Bai and Wang 1995a), where k_2 is the averaged absorption coefficient of water vapor in the wavelength range of 0.70~2.845 μm , A is an empirical coefficient determined by analyzing observational data, w is the total water vapor content in the atmospheric column (unit of cm), and is obtained from an empirical formula using the value of water vapor pressure (E) at the ground:

$$w = 0.21E \quad (1)$$

The averaged relative bias of this method compared to radiosonde data is less than 18% (Yang and Qiu 2002). The basic idea is that total UV energy absorption by various substances should have a quantitative relationship with their absorption of solar global radiation, because water and water vapor play a vital role in energy transfer and utilization, as well acting as important mediums in C&P reactions. $Ae^{-k_2 wm}$ is calculated empirically as follows: The fraction of solar global radiation absorbed by water vapor is expressed as $\Delta S = 0.172 (mw)^{0.303}$ (Kondratyev 1962). If only water vapor is considered, and if the atmosphere is presumed to be plane-parallel, then the solar radiation on the horizontal surface can be expressed as:

$$I_s = I_0 \cos Z - \Delta S = I_0 e^{-k_2 wm} \cos Z \quad (2)$$

$$\text{i.e., } e^{-k_2 wm} = 1 - \Delta S / (I_0 \cos Z) \quad (3)$$

Here Z is solar zenith angle and I_0 is solar constant.

(3) The “scattering term”, which describes multiple scattering by various gases, liquids (including water droplets, cloud drops etc), and aerosol particles, and also includes the reflection between the earth’s surface and aerosols, clouds (when present), etc. It is expressed by $e^{-S/D}$, S/D being a term reflecting the integrated scattering roles of gases, liquids, and aerosol particles for UVI, as S and D contain the information of scattering and absorption of all substances in the atmosphere. There is roughly 60 km between Xianghe station and Beijing meteorological observatory, S , D , and Q were different, but the ratio S/D was used for describing the relative column amount of all substances or their scattering roles, which should be closer for daily and especially monthly averages within this distance, and can be selected as a substitute to make up the shortage of S/D measurements at Xianghe station.

Using a statistical regression on monthly “clear skies” data (cloudiness $\leq 20\%$) for Beijing (1990), an empirical model was obtained for UVI at the Earth’s surface:

$$Q_{uv} = A_1 e^{-k_1 O_3 m} + A_2 e^{-k_2 wm} + A_3 e^{-S/D} + A_0 \quad (4)$$

where Q_{uv} is monthly mean daily sum (MMDS) of UVI at the ground, O_3 , w , S , D are MMDS, m is the air mass at the noon on the 15th, S/D is the ratio of MMDS of S to MMDS of D . A_1 , A_2 , and A_3 are coefficients, A_0 is also a coefficient. The coefficients and constant were determined by statistical analysis of observational data (Bai and Wang

1995a). The correlation coefficient (R) between Q_{uv} and the three terms is 0.973, and the standard error (σ) is 0.072. The F -test values for ozone, water vapor, and the scattering term are 67.2, 10.8 and 0.86, respectively. This means that the ozone term is highly correlated with Q_{uv} at the confidence level $\alpha=0.01$, which is consistent with our knowledge about the relationship of O_3 and UVI. The water vapor term is significantly correlated with Q_{uv} at confidence level $\alpha=0.05$. As described above, scattering term describes the total UVI scattering roles by all atmospheric constituents (GLP). Though the scattering term is not significantly correlated with Q_{uv} at confidence level $\alpha=0.10$, it is an important factor influencing UVI, and should be considered in the formula.

In the formula (4), the estimated uncertainties of UVI were less than 1%, 5%, and 5%, respectively, which were caused by the uncertainty of O_3 , water vapor pressure, and S/D of 2%, 18%, and 5%. Then, the maximum uncertainty of UVI was about 11%.

Monthly observation data in 1990 and 1991 for Beijing shows no strong correlation between water vapor concentration and S/D (total UVI scattering), nor any correlation between the water term and the scattering term. So, there is no redundancy of parameterization in Eq. 4.

3.2 The factors contributing to Q_{uv}

Three different algorithms were used to investigate the contribution of the three main factors to Q_{uv} :

$$Q_{uv} = A'_1 e^{-k_1 o_3 m} + A'_0 \quad (4a)$$

$$Q_{uv} = A''_1 e^{-k_1 o_3 m} + A''_2 e^{-k_2 w m} + A''_0 \quad (4b)$$

$$Q_{uv} = A_1 e^{-k_1 o_3 m} + A_2 e^{-k_2 w m} + A_3 e^{-S/D} + A_0 \quad (4c)$$

Using these formulae, **MMDS** of UVI at the ground were calculated for “clear skies” in 1990 at Xianghe station. The resulting values of Q_{uv} and the relative bias (δ) between calculated and observed values, R (the correlation coefficient), and σ (the standard error) are presented in Table 1.

When ozone was considered alone (algorithm 4a), the average of absolute relative bias ($\bar{\delta}$) for 12 months was 5.8%, maximum relative bias (δ_{\max}) was 13.1%, σ was 0.10, and R was 0.93. After including the water vapor term (algorithm 4b), δ_{\max} , $\bar{\delta}$ and σ were reduced. The best results were obtained, and $\bar{\delta}$, δ_{\max} , σ , and R were, 3.6%, 8.8%, 0.07, 0.97, respectively, when all three factors contributed to the formulation of Q_{uv} (algorithm 4c), where $A_1=5.0$, $A_2=1.4$, $A_3=0.3$, $A_0=-5.4$. There was no big systematic bias between calculated and observed Q_{uv} for 1990, because the yearly averaged relative bias in clear sky was 0.22%, and the yearly average of the absolute relative bias was 3.62%. In detail, the relative bias between calculated and observed annual average Q_{uv} for 1990 was 3.36×10^{-14} .

This analyzing method was then applied to “all sky” conditions (i.e. all days for which observations were made) for 1990, and a formula similar to (4) and new coefficients were obtained which yielded comparable results (Table 2). In this case $R=0.99$ and $\sigma=0.04$ for the correlation between Q_{uv} and all three factors. The F -test values for ozone, water vapor, and the scattering term were 116.4, 13.6 and 2.0, respectively. So both the ozone term and water term were highly correlated with Q_{uv} at the confidence level $\alpha=0.01$.

Table 1 Observed and calculated MMDS of UVI (MJm^{-2}) and their relative biases δ (%) in “clear skies”

Month	UVI obs.	Algorithm a		Algorithm b		Algorithm c	
		UVI cal.	δ	UVI cal.	δ	UVI cal.	δ
1	0.95	0.92	−2.38	0.97	1.94	0.98	2.99
2	1.27	1.10	−13.10	1.18	−7.18	1.16	−8.78
3	1.37	1.33	−2.57	1.42	3.92	1.43	4.60
4	1.48	1.44	−2.76	1.53	3.38	1.53	3.54
5	1.54	1.54	−0.42	1.58	2.19	1.56	1.29
6	1.65	1.49	−9.96	1.53	−7.08	1.55	−6.19
7	1.52	1.61	5.60	1.55	2.28	1.52	0.15
8	1.48	1.58	6.38	1.51	1.70	1.49	0.75
9	1.44	1.48	2.17	1.44	−0.09	1.47	1.81
10	1.36	1.36	0.19	1.27	−6.84	1.30	−4.34
11	0.98	1.11	13.02	1.06	8.02	1.06	7.93
12	0.82	0.92	11.45	0.83	0.92	0.81	−1.07
Average			5.83		3.79		3.62
<i>R</i>		0.933		0.970		0.973	
σ		0.100		0.071		0.072	

In “all sky” conditions, when ozone was considered alone (similar to algorithm 4a), $\delta_{\text{max}} = 16.6\%$, $\delta = 4.8\%$, $\sigma = 0.06$, and $R = 0.96$, and these values were improved after the water vapor term was included (similar to algorithm 4b). As for the clear and cloudy sky conditions, the best results were obtained when all three factors contributed to the formulation of Q_{uv}

Table 2 Observed and calculated MMDS of UVI (MJm^{-2}), and their relative biases δ (%) in “all skies”

Month	UVI obs.	Algorithm a		Algorithm b		Algorithm c	
		UVI cal.	δ	UVI cal.	δ	UVI cal.	δ
1	0.72	0.70	−2.56	0.73	1.27	0.73	0.88
2	0.92	0.86	−6.15	0.90	−2.20	0.89	−3.45
3	1.05	1.04	−0.91	1.09	3.95	1.08	3.29
4	1.17	1.13	−3.39	1.20	2.36	1.20	2.75
5	1.27	1.20	−5.77	1.24	−2.67	1.26	−0.76
6	1.26	1.19	−5.61	1.22	−3.27	1.23	−2.85
7	1.22	1.26	3.07	1.24	1.22	1.20	−1.93
8	1.22	1.25	2.09	1.21	−0.73	1.21	−1.23
9	1.10	1.18	7.41	1.14	3.93	1.15	4.80
10	1.06	1.08	1.51	1.01	−4.97	1.03	−2.65
11	0.75	0.87	16.55	0.81	8.05	0.80	6.89
12	0.71	0.69	−2.22	0.67	−5.57	0.67	−4.71
Average			4.77		3.35		3.02
<i>R</i>		0.960		0.984		0.987	
σ		0.063		0.042		0.040	

(algorithm 4c). No large systematic bias existed between calculated and observed Q_{uv} for 1990 in “all skies”, with a yearly averaged relative bias of 0.09%, and a yearly average of the absolute relative bias of 3.02%. The relative bias between calculated and observed annual average Q_{uv} for 1990 was 3.36×10^{-14} (similar to algorithm 4c). Therefore, the calculated and measured UVI were in good agreement for both clear and all sky conditions. It is reasonable that there were positive and negative estimation errors of monthly UVI due to the observational and calculation uncertainties, but the empirical Eq. 4 can insure the minimum errors of annual averaged UVI under two sky conditions, especially for a longer dataset, which can be seen from the monthly and annual estimation biases of Q_{uv} in all skies, comparing with clear skies.

The relationship between calculated and observed Q_{uv} was found to be $Q_{uvcal} = 0.998Q_{uvobs}$ ($R^2 = 0.944$) and $Q_{uvcal} = 0.999Q_{uvobs}$ ($R^2 = 0.976$) for clear and all skies, respectively. The observed versus modeled agreement is strong, the more data are considered in the establishment of empirical model, the better estimation can be determined (compared δ , δ_{max} , σ , and R between all sky and clear sky conditions), which can help us to understand the effect of empirical Eq. 4.

3.3 Interpretation of the water vapor term

It is evident from the above results that water vapor plays a very important role in the loss of UVI as it travels to the earth's surface. But according to current theory, water and water vapor do not absorb directly in the UV band, then, direct absorption by water or water vapor cannot be the real interpretation of this term in the algorithm. A reasonable interpretation of the water vapor term is direct absorption of UV energy by the various and diverse substances (GLP) found in the real atmosphere and indirect absorption/utilization by other substances (including GLP) when they are going through various C&P reactions with OH radicals. In short, many substances absorb UV energy directly, including large numbers of VOCs, secondary organic aerosols (SOA) and absorbing particles (i.e. Black Carbon (BC) produced by incomplete combustion of carbonaceous fuels) (Crowley et al. 1994; Atkinson 2000; Atkinson and Arey 2003; Dickerson et al. 1997; Jacobson 2004, 2006; Koch and Hansen 2005). BC is also an absorber in the visible band. Many other GLP that are not direct UV absorbers can consume or transfer UV energy when they are participating in C&P reactions in the atmosphere, especially in reactions involving OH, HO₂ radicals, and O₃. For example, these GLP substances include organic and inorganic compounds, such as NO₂, SO₂, VOCs (such as alkanes, alkenes, alkynes, aromatic, alcohols, aldehydes, ketones, esters, ethers, sesquiterpenes), peroxides, acids, nitrates, and aerosols (including SOA) and fine particles such as BC (Atkinson 2000; Fuentes et al. 2001; Karl et al. 2008; Brasseur et al. 1999). These reactions include homogeneous and heterogeneous reactions, both in the atmosphere and on the surface of aerosols. Energy absorption by some materials, such as NO₂ (Solomon et al. 1999) and nitrated and aromatic and nitrated aromatic gases (Jacobson 1999), have been determined quantitatively, but, there are still large quantities that have to be studied and quantified in the laboratory in the future. Another important task is to add these new data into the models (such as Bruhl and Crutzen 1989; Zerefos 2002), to improve predictions and simulations of the changing atmosphere. In this complex system of atmospheric chemistry and photochemistry, OH radicals play a very significant role, as they can take part in almost all C&P reactions, and are often rapidly recycled (Atkinson 2000; Aschmann et al. 2002; Atkinson and Arey 2003; Hofzumahaus et al. 2009). Their production is highly related to O₃ UV photolysis, UV energy, and water or water vapor. Because water or water vapor is a vital component of OH

generation, it is used as a surrogate for OH in the formulae in this study. As the concentrations of gases, including VOCs and oxygenated VOCs, and fine particles, including BC, are very low; their integrated UV energy consumption is easily ignored before. It is the time to consider them quantitatively. In addition, C&P reactions in the atmosphere are dynamic processes, so UV energy consumption continues and constantly varies with the changes of GLP.

Relative humidity (**RH**) is the single most important parameter that determines direct aerosol forcing, since the increase in aerosol mass as a result of water uptake is the most important driving process (Pruppacher and Klett 1997). RH significantly affects aerosol optical thickness, single-scattering albedo, micro-physical, micro-chemical, optical and radiative properties by modifying the aerosol liquid water content, size and hence extinction coefficient and refractive indices. Yang et al. (1999), in experiments in Chongqing, China, found that RH increasing from 65% to 95% affected the aerosol shortwave radiation properties in a manner similar to the effect of multiple change of aerosol particles total number. Hatzianastassiou et al. (2004b) computed that the changes in aerosol forcings due to a change in RH of 10% in relative terms would reach 300% on a local scale and 40% on global scale. Increasing the RH generally increases the magnitude of aerosol forcing, and in a non-linear way. This appears to reflect the important roles of water alone, but in fact, it reflects the important role of all the constituents (gases, other fine particles) in the water layer coating the aerosol nuclei. The higher the RH, the more water can condense on the aerosol nuclei and its surface, and the more substances can mix in the water layer and nuclei, consequently producing more UV energy consumption.

3.4 Estimating the UV energy absorbed by atmospheric constituents

In view of the difficulties in accurately estimating the concentration of OH in the atmosphere and also the total amount of reactions and concentration of each gas (as well as substantial amounts of unknown/unmeasured VOCs, Di Carlo et al. 2004; Goldstein and Galbally 2007; Kim et al. 2009), liquid and aerosol, formulating an expression to describe UV energy absorption by all OH-reactive atmospheric components is challenging. The ratio of UVI to solar shortwave global irradiance (Q_{uv}/Q) arriving at the ground is approximately a constant, its average is about $5.5\% \pm 0.4\%$ for eight stations over China (Zhou 1986), and close to the value we obtained in Beijing. It is hypothesized that Q'_{uv}/Q' is also approximately a constant, where Q'_{uv} is UVI absorption by various atmospheric GLP directly and indirectly when they are taking part in C&P reactions, Q' is solar shortwave ($\lambda = 0.70 \sim 2.845 \mu\text{m}$) absorption by water vapor, and $Q'_{uv}/Q' = A$. The ratio of Q'_{uv}/Q' should have characteristics similar to Q_{uv}/Q , i.e. basically a constant. Using formula (4) and observational data (Beijing 1990, 1991), $A=1.41$ and 1.50 , respectively, were obtained for “clear skies”, and $A=1.69$ and 1.79 , respectively, were obtained for “all skies”. As far as we know, Q_{uv} and Q are expected to vary in a similar way, and the ratio of Q_{uv}/Q and Q'_{uv}/Q' vary little monthly and yearly, which can be seen from the A value in different years under two sky conditions, it implies energy absorption ratios vary (about 6%) with the change of GLP in the atmosphere, and A values in all skies in both 1990 and 1991 were bigger than that in clear skies indicated the energy consumption ratios in all skies were about 20% bigger than clear skies. It indicated the GLP substances influence the UV energy consumption under different sky conditions and their annual variations. These ratios are affected by the variations of the several factors already described (total concentration of all atmospheric constituents, concentration of water vapor and total ozone amount). “ A ” was determined objectively by analyzing observational data under different sky conditions in

different years. Therefore Q'_{uv} can be defined as the photochemical term expressing total UV absorption by atmospheric constituents (most of which can react with OH radicals), and it can be calculated indirectly and empirically. Firstly, it includes the direct UV absorption by various GLP UV absorbers, which make use of UV energy in C&P reactions. Numerous studies indicate that there are numerous UV absorbers, for example, nitrated and aromatic aerosols and nitrated aromatic gases (Jacobson 1999; Volkamer et al. 2005), fine particles, including BC and SOA (Martin et al. 2003; Clarke et al. 2004; Bergstrom et al. 2004; Schwarz et al. 2008). It also includes a large amount of VOCs (Staffelbach et al. 1995; Neeb et al. 1997; Bauerle and Moortgat 1999; Mu and Mellouki 2000; Horowitz et al. 2001; Lanza et al. 2008; Matsunaga et al. 2008; Xiang et al. 2009). Secondly, it includes UV energy utilization by GLP components in the atmosphere, which don't absorb UV energy directly, but use UV energy in the processes of C&P reactivity with OH radicals, O₃, NO_x, etc.

For obtaining a more accurate estimation of UVI, another formula is introduced. The most important factor affecting the variability in the ratio Q_{uv}/Q is dynamic solar geometry, which can be expressed by the cosine of solar zenith angle (Z). In addition, Q_{uv}/Q is also modulated/influenced by ozone, water vapor, and scattering factors. Another advantage of this method is that the higher accuracy of observed Q gives a higher accuracy for the estimation of Q_{uv} . So, a better formula for estimating UVI at ground level is suggested (Bai and Wang 1993, 1995b):

$$Q_{uv}/Q = A \cos Z + B \quad (5)$$

where

$$\begin{aligned} A &= A_1 e^{-k_1 o_3 m} + A_2 e^{-k_2 w m} + A_3 e^{-S/D} \\ B &= B_1 e^{-k_1 o_3 m} + B_2 e^{-k_2 w m} + B_3 e^{-S/D} \end{aligned}$$

Here, Q_{uv} , Q , S , and D are MMDS of radiation exposure. Z is the solar zenith angle at noon on the 15th for every month and other terms are the same as before. The terms $e^{-k_1 o_3 m}$, $e^{-k_2 w m}$ and $e^{-S/D}$ are the ozone, water vapor, and scattering factors' roles, and modulate A and B (cf. Eq. 4). Using formula (5), it is easier to calculate the contribution of each factor to Q_{uv} . A high correlation was found between Q_{uv}/Q and $\cos Z$ using observational data for "clear skies" for Beijing, 1990 ($\alpha=0.01$, F value=1,103.5, $R=0.996$, $\sigma=0.137$), and the values for the coefficients A_1 , A_2 , A_3 , B_1 , B_2 and B_3 were -1.8 , -6.0 , -1.0 , 3.3 , 10.7 , 1.9 , respectively, which were determined by statistical analysis of observational data in clear skies. This analyzing method of estimating Q_{uv}/Q was applied to "all skies" data for 1990, and again, a high correlation between Q_{uv}/Q and $\cos Z$ at the confidence level of $\alpha=0.01$ was obtained (F value=428.8, $R=0.989$, $\sigma=0.192$). The coefficients A_1 , A_2 , A_3 , B_1 , B_2 and B_3 were -2.4 , -4.8 , -0.8 , 4.6 , 9.0 , 1.5 , respectively.

The uncertainty of O₃, water vapor pressure, S/D, and Q were 2%, 18%, 5%, and 2%, respectively, resulting in the estimated maximum uncertainty of UVI using formula (5) was about 13%.

MMDS of UVI in "clear sky" and "all sky" conditions in 1990 was calculated using formula (5). Figure 1 shows the observed and calculated MMDS of UVI for Beijing, 1990.

The calculated values agreed well with observations for "clear sky" and "all sky" conditions, and the averages of absolute biases δ were 3.18% and 3.95% for "clear sky" and "all sky", respectively. In addition, the averages of relative biases were 1.158% and 1.156% (in Fig. 1) for "clear skies" and "all skies", respectively, which means that there was no obvious system error when calculating the difference of UVI between "clear sky"

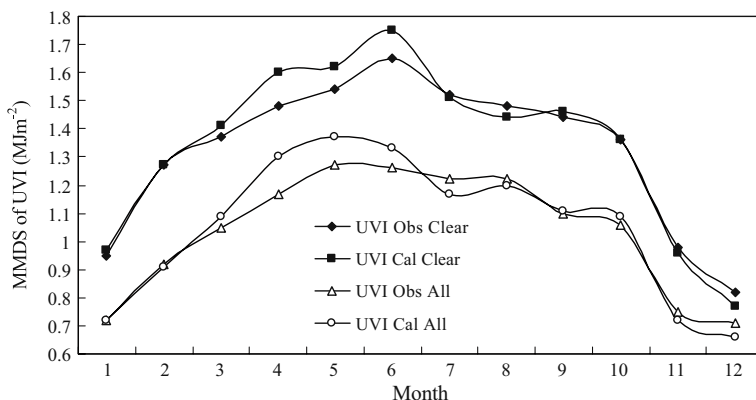


Fig. 1 Observed and calculated MMDS of UVI in clear sky and all sky in Beijing

and “all sky” conditions. The maximum bias for the two skies was less than 10%, with a single exception in April (11.20% for “all skies”). It suggests that we are justified in presenting this method as a practical tool for estimating UVI in different sky conditions.

It should be stated that ozone, water vapor, and scattering terms in formulae (4) and (5) represent the role of total ozone in the whole column (most ozone occurs in the stratosphere with approximately 10% of total ozone in the troposphere), the absorption/attenuation role by other substances (apart from ozone) in the whole column (including most substances stay in the troposphere), and the scattering roles by all substances in the whole column, respectively. Thus, all complicated and dynamic interaction and quantitative relationship can be determined objectively and accurately by analyzing the observational data, and formulas (4) and (5) can give good estimations of UVI for both sky conditions, respectively.

A sensitivity study was done for “clear sky” by using monthly data for 1990, when one factor of UVI was changed to some extent and the others kept at their original values. In general, the changing rates of UVI caused by the three factors (O_3 , water vapor pressure-E, S/D) presented different characteristics in different months, then the annual averages of changing rates can be obtained (Table 3). Similarly, Table 4 shows the UVI sensitivity results for “all sky” conditions.

It can be seen that 1) UVI is more sensitive to the changes of S/D than the other factors in “clear” and “all skies”; 2) when O_3 , E and S/D were increased 10%, UV decreased 1.65%, 0.52%, and 3.68% in clear skies, respectively, and 1.64%, 0.56%, and 7.69% in all skies, respectively, which means that more UV energy was absorbed and/or consumed by O_3 , atmospheric constituents and aerosols. The response of UVI to the change of O_3 was almost the same in both skies, which means the total O_3 (mainly stratospheric O_3) played the same role in UV transmission. The response of UVI to the change of E was about 10%

Table 3 Annual averages of changing rates (%) of MMDS of UVI to its factors in clear skies, when one factor was changed to varying extents and the others kept at their original values

	+5%	−5%	+10%	−10%	+20%	−20%
O_3	−0.83	0.84	−1.65	1.68	−3.27	3.39
E	−0.26	0.27	−0.52	0.55	−1.00	1.15
S/D	−1.86	1.90	−3.68	3.83	−7.21	7.82

Table 4 Annual averages of changing rates (%) of MMDS of UVI to its factors in all skies, when one factor was changed to varying extents and the others kept at their original values

	+5%	−5%	+10%	−10%	+20%	−20%
O ₃	−0.82	0.83	−1.64	1.67	−3.25	3.37
E	−0.29	0.30	−0.56	0.61	−1.09	1.26
S/D	−3.93	4.10	−7.69	8.39	−14.74	17.56

higher in all skies than clear skies, which means more UV energy was consumed by GLP during C&P reactions. The response of UVI to the change of S/D was about 114% higher in all skies than clear skies, which means more UV was attenuated (mostly scattered) by all GLP substances in all skies. We can also infer from Table 3 that annual averages of relative error of UVI estimation in clear skies are less than 6.10% (from column 5) or 12.40% (from column 7) when the uncertainties of O₃, E and S/D are each $\pm 10\%$ or each $\pm 20\%$, respectively.

4 UV energy loss in the cloudy atmosphere

4.1 UVI attenuation in the cloudy atmosphere

As described above, when UVI passes through the atmosphere, it is attenuated by ozone, photochemical and scattering factors to different degrees. When the ozone factor is considered alone, attenuation of UVI can be expressed by the ratio of

$$\eta_1 = Q_{uv1}/Q_{uv0} = (A_1 e^{-k_1 o_3 m} \cdot \cos Z + B_1 e^{-k_1 o_3 m})/Q_{uvo} \quad (6a)$$

and can be calculated by using Eq. 5, where Q_{uv0} is the calculated value of Q_{uv} at ground level. In the same way,

$$\eta_2 = Q_{uv2}/Q_{uv0} = (A_2 e^{-k_2 wm} \cdot \cos Z + B_2 e^{-k_2 wm})/Q_{uvo} \quad (6b)$$

and

$$\eta_3 = Q_{uv3}/Q_{uv0} = (A_3 e^{-S/D} \cdot \cos Z + B_3 e^{-S/D})/Q_{uvo} \quad (6c)$$

can also be obtained for the photochemical and scattering factors, respectively. Table 5 shows the calculated values of η_1 , η_2 and η_3 for “clear sky” and “all sky” conditions for Beijing, 1990.

The terms η_1 , η_2 and η_3 show no evident seasonal variations in “clear sky” and “all sky” conditions. This indicates that η_1 , η_2 and η_3 are relatively stable in the same sky condition. However, the UVI attenuation rate by each factor varies depending on the sky condition. The yearly averaged η_1 , η_2 and η_3 in Beijing, 1990, for “clear sky” and “all sky” conditions were estimated to be 66.4%, 25.5%, 8.2%; and 61.2%, 33.7%, 5.1%, respectively. Compared to “clear sky”, yearly averaged η_1 and η_3 were lower, and η_2 was greater in “all sky” conditions.

Generally, the total amount of ozone in “all sky” conditions is less than that in “clear sky” conditions in Beijing, resulting in a lower η_1 for “all sky” conditions. In “all sky” conditions, gases and aerosol particles accumulate easily, and more and larger aerosol particles are produced, which causes a decrease in UVI (or UVI loss in the atmosphere),

Table 5 The calculated contributions (%) η_1 , η_2 and η_3 for ozone, photochemical and scattering factors to Q_{uv0} for “clear sky” and “all sky” in 1990

Ratio month	“clear sky”			“all sky”		
	η_1	η_2	η_3	η_1	η_2	η_3
1	66.46	24.80	8.74	62.21	32.20	5.59
2	66.62	24.69	7.69	62.50	32.66	4.84
3	66.22	25.40	8.38	62.10	33.09	4.80
4	66.35	25.54	8.11	61.59	33.20	5.21
5	66.56	25.88	7.56	60.26	33.76	5.99
6	65.58	25.98	8.44	61.02	33.86	5.12
7	66.69	26.39	6.92	62.50	34.86	2.64
8	65.88	26.60	7.52	60.70	34.90	4.40
9	64.66	26.51	8.83	60.02	34.67	5.30
10	64.17	26.70	9.14	59.11	34.70	6.19
11	66.11	25.59	8.29	61.11	33.97	4.92
12	66.80	25.22	7.97	61.17	32.81	6.02
average	66.35	25.46	8.18	61.18	33.71	5.11

resulting in a smaller value for η_3 for “all sky” conditions compared to “clear sky” conditions. One reason for the difference in η_2 for the two sky types could be that there is more water vapor in “all sky” conditions compared to “clear skies”. This was observed in the measurements for 1990 and 1991 in Beijing, and the 24 monthly mean water vapor pressure (E) at the ground was greater by 31.5% for “all sky” conditions than for “clear skies”. The higher concentration of water vapor in “all sky” conditions results in higher concentrations of OH and HO₂ radicals which are produced from UV absorption. Another reason for the difference in η_2 for the two sky types could be that the synoptic system is controlled by low pressure in a cloudy atmosphere, which is associated with the converging movement and then rising air flow, resulting in higher column concentrations of all substances. For example, our observational data from the Dinghushan Biosphere Reserve, Guangdong province, China (August to December 1998) showed that all monthly averaged concentrations of NO, NO₂ in “all sky” conditions were higher than that in “clear sky” conditions by 53.2% and 36.2%, respectively. In addition, the monthly averages of S/D were higher in “all sky” conditions than that in “clear sky” conditions in 1990 and 1991 over the Beijing area, and 2-year averages of S/D were 0.33 and 0.92 for “clear sky” and “all sky” conditions, respectively. So more OH radicals can be produced through ozone photolysis in the troposphere under “all skies”, and these can react with a wide range of pollutants and non-pollutants, resulting in more UV energy loss in the atmosphere. This is probably the real reason hidden for the strong dependence of atmospheric absorption on total column water vapor (Arking 1996). The subtraction of the annual UVI loss in the atmosphere (“all sky”–“clear sky”) caused by the individual ozone, water vapor, and scattering factors was calculated and 0.92, 7.82, and -1.66 Wm^{-2} , respectively. In all sky conditions, the bigger size particles and the higher S/D result in a smaller UV attenuation (compared to clear sky conditions), which corresponds to that UV is more sensitive to the small particles.

If we plot η_2 vs E for “clear sky” and “all sky” conditions, the linear relationship between η_2 and E can be found, $\eta_2 = 0.007E + 25.2$ with $R^2=0.58$, and $\eta_2 =$

$0.010E + 32.7$ with $R^2=0.72$, respectively, which indicated there were evident correlations between η_2 and E at confidential level $\alpha=0.01$ and 0.001 for clear and all skies. In fact, it would be better to find a direct relationship between the UV consumption and the concentration of absorbing GLP, but, it is a challenge at present.

4.2 The relative importance of the different factors contributing to attenuation of UV in cloudy sky condition

For each month, total UVI losses in the cloudy atmosphere can be expressed as the difference of MMDS of UVI between “all sky” and “clear sky” conditions divided by the sunshine duration. This was estimated using the Beijing 1990 data, where the cloudy day atmosphere was defined as having cloud cover $\geq 30\%$. Using the values of η_1 , η_2 and η_3 for “all sky” and “clear sky” conditions (Table 4), UVI losses in cloudy atmosphere in the Beijing caused by the attenuation of ozone, photochemical and scattering factors were estimated by subtraction (Fig. 2).

In Fig. 2, L_1 , L_2 and L_3 are UVI losses caused by ozone, photochemical and scattering factors respectively in the cloudy atmosphere, and L ($L = L_1 + L_2 + L_3$) is the total UVI loss. Excluding December (its L_1 , L_2 , L_3 are much smaller than that in other months), the total loss of UVI in the cloudy atmosphere (“all sky” minus “clear sky”) in Beijing, 1990 was estimated to be between 64 and 108 Wm^{-2} . This loss was caused by the three factors whose contributions to total loss were estimated to be $39.1\sim 66.3$, $21.5\sim 36.5$ and $3.2\sim 5.5 \text{ Wm}^{-2}$, respectively. The yearly averaged estimations of UVI loss caused by the three contributing factors in 1990 were 48.3 , 26.6 and 4.0 Wm^{-2} respectively for a total of 78.9 Wm^{-2} . According to the computation of Hatzianastassiou et al. (2004a), aerosols decreased the downward and the absorbed solar radiation by up to 28 and 23 Wm^{-2} , respectively. Then, the recalculated absorbing and scattering contributions from aerosols were 89.3% and 10.7% , respectively; the corresponding values in this paper are 86.9% and 13.1% , respectively. The relatively small differences in these two results may be due to the differences in studied regions, wavebands, and parameters in the models.

In addition, there are some uncertainties in estimating the aerosol forcing in different models (Ming et al. 2005). Current models do not completely account for the scattering role of aerosol particles. One reason is our incomplete understanding of the complex physical and chemical properties of aerosols. For example, it is still not known whether BC is mixed

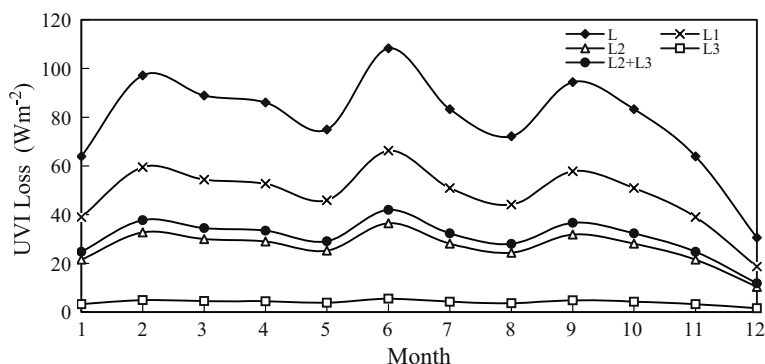


Fig. 2 Monthly averaged UVI losses caused by the attenuation of ozone (L_1), photochemical (L_2) and scattering factors (L_3) in the cloudy atmosphere in 1990

internally or externally with other aerosol constituents (Jacobson 2001), though progress on BC mixing and absorption has been made (Schwarz et al. 2008). In fact, there are many uncertainties concerning UVI scattering loss in the various gas, gas–aerosol, gas–liquid, liquid–aerosol, and gas–liquid–aerosol matrices (Jacobson 2002). It is better to attempt to describe their integrated scattering role in the real atmosphere, which can be described by using the S/D term or the other scattering term. The S/D term is more easily calculated, and perhaps the most reliable estimation, because it does not rely on any assumptions to express total (including GLP) scattering. Therefore, L_3 partially estimates UVI scattering loss by all atmospheric constituents, which are not accounted for in current models. Both L_2 and parts of L_3 represent the actual UVI loss for unaccounted UV absorption/attenuation, so this component should be considered in models. Comparing L_3 and L_2 (Fig. 2), energy loss due to absorption by atmospheric constituents is more important than losses due to scattering.

The ratios of observed MMDS of UVI in all sky to that in clear sky range from 72.4% to 86.6% (from Table 2), its average is 78.6%. So, monthly UVI loss in the atmosphere in 1990 varies from 13.4% to 27.6%, and annual UVI loss is 21.4%.

The highest absorption of UVI by the photochemical factor occurred in June, which coincided with higher VOCs emissions from trees during June to August in Beijing in 1998 (Wang et al. 2003), and similar emission patterns during June to August in 2002 and 2003 in the Inner Mongolia Grassland (Bai and Baker 2005). This also implies that VOCs emitted from vegetation play an important role in UV absorption in the atmosphere.

The observed maximums for UVI in July and August 1990 were about 50 Wm^{-2} . The instrument error of 10% results in a maximum observational error of about 5 Wm^{-2} . According to this result and the analysis in 3.3 and 3.4, errors from the instruments and the calculations were not significant.

4.3 The contributions of gases and aerosols to UVI losses in the atmosphere

O_3 , NO_x and SO_2 concentrations in the troposphere in many cities and rural areas around the world are increasing. With the fast development of agriculture and industry, and major regional and global land-use change, more and more gases (NO_x , SO_2 , biogenic and anthropogenic VOCs), organic and inorganic compounds, and aerosols are being emitted into the atmosphere. Black carbon (BC), an important absorber in UV and visible wavelength bands, showed an increasing trend in Beijing, and the averaged concentrations in autumn under “all skies” in 1992, 1996, 1997, 1998 were 3.2, 20.4, 25.7, 24.9 μgm^{-3} , respectively (Wang et al. 2002).

Ming et al. (2005) also reported that anthropogenic burning of fossil fuels and biomass considerably elevates the atmospheric concentrations of organic aerosol. The emissions from the industrial areas of the northern hemisphere (NH), including East Asia, have increased regional organic carbon (OC) burdens by approximately a factor of ten relative to pre-industrial times. The seasonal pattern of present-day burdens is largely determined by that of OC emissions, and the global mean present-day burden in July is 40% higher than in January. Therefore, gases, compounds, and very fine particles (SOA, BC) that were unimportant in the past may gradually become significant. Great attention should be paid to above substances and their UV absorptions (Bruhl and Crutzen 1989; Bais et al. 1993; Papayannis et al. 1998; Zerefos et al. 2000). These issues are not likely unique to Beijing and should arise in other locations. Adding carbonaceous aerosols to the models improves the simulations (Pope and Valero, 2000, 2002; Valero and Bush 1999; Valero et al. 2000). It should be mentioned that because of the small size of these substances, their scattering role was not as easily identified by the S/D factor as coarse particles. A better scattering factor

needs to be developed to distinguish UVI scattering roles of coarse and fine particles. Their concentrations are usually very low, but their integrated and dynamic energy absorptions are important, and should be considered in the models.

Pilewskie and Valero (1995) observed that cloud forcing C_S/C_T (C_S is the cloud forcing beneath the cloud layer, C_T is cloud forcing above the cloud layer) are 1.58, 1.54 and 1.50 for three conditions, 10–20 km, surface to 20 km, and surface to the top of the atmosphere (TOA). With the increase of height, the concentrations of water vapor and all kinds of gases and aerosols decrease, and UVI absorption by all GLP substances decreases. All substances from 10 to 20 km, surface to 20 km, and surface to TOA gradually increases, C_S/C_S decreases (see above values), i.e. cloud forcing decreases with the increase of the thickness of atmospheric layer. This is the main reason for the strong dependence of atmospheric absorption on total column water vapor, and the discrepancy between model and observations increase with increasing water vapor (Arking 1996). In fact, with increasing substances in the atmosphere, this is consistent with the assumption of UVI absorption.

UV energy absorption by the GLP substances exists not only in the cloudy atmosphere, but also in the clear atmosphere. The energy absorption by the substances happens not only in UV band, but also in visible band, i.e. in the actinic radiation band (290–700 nm), and it should be bigger than 26.6 Wm^{-2} on a yearly average. UV and visible energy absorption by the GLP substances in the atmosphere exists in the natural world, and more accurate energy absorption measurements using more accurate UV and visible sensors are needed in the future. The accuracy and precision should be better than $\pm 3\%$ or $\pm 4\%$ and $\pm 1\%$, respectively, and stability better than $\pm 2\%$ per year. In addition, improvements in the cosine response error will greatly enhance the value to the models. Further measurement studies need to be conducted to determine the quantitative effect on the anomalous absorption of the issues suggested by this paper.

5 Conclusions

Based on reanalyzing observational UVI under clear and all sky conditions in Beijing, two empirical models of UVI were introduced, producing accurate estimations and similar variation patterns of calculated UVI. The first was used to evaluate the roles of ozone, scattering and photochemistry on atmospheric absorption. The second was used to examine the impact of those factors on UVI and provided accurate calculations of total UVI. Monthly UVI loss in the cloudy atmosphere in 1990 varies from 13.4% to 27.6%, and annual UVI loss is 21.4%. Using observation data and calculations of UVI attenuation under “all sky” and “clear sky” conditions, we estimated an annual UVI loss of 78.9 Wm^{-2} in the cloudy atmosphere. Of this, an attenuation of 26.6 Wm^{-2} was contributed by various atmospheric constituents (GLP). Water is vital component of the attenuation primarily due to its role in OH radical production. UV energy is consumed and transferred in the processes of OH radical formation and in OH radical reactions with atmospheric constituents (GLP) (including VOCs, SOA, BC, etc). The latter processes merit further attention. The observations and models contain significant uncertainties, but the results of this study reflect important natural phenomena and issues. Solar radiation provides the energy to drive the atmosphere, the ocean and their interactions. Accurately quantifying this energy and its components is therefore very important for the entire atmosphere–ocean–land system. Further laboratory, field experiment, and model studies are necessary to determine energy absorption in UV and visible bands by the substances in the atmosphere. With more first-hand and reliable data, chemical, radiative transfer and climate models can

be improved, which will ultimately improve our understanding of the global and regional energy budget, especially in the context of current and future climate and climate change.

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