

Influence of volcanic sulfur dioxide on spectral UV irradiance as measured by Brewer spectrophotometers

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Abstract. Spectra of UV irradiance measured by Brewer spectrophotometers at 13 stations in Japan and Canada have been examined to determine the effect of absorption by sulfur dioxide (SO_2). A simple algorithm to estimate the total column amount of SO_2 from global UV irradiance measurements has been developed. The algorithm which overestimates SO_2 amounts at low altitudes is useful for identifying large SO_2 absorption and for establishing upper limits of the SO_2 values. Except at one station, the overall occurrence of days with SO_2 amounts greater than 10 Dobson Units (DU) was about 0.22%. The exception was the Kagoshima observatory located 10 km from the volcano, Sakurajima. Volcanic activity resulted in frequent observation of column SO_2 amounts of more than 20 DU over Kagoshima and in extreme cases up to 100 DU. The reduction in the long-term erythemally weighted UV irradiation due to absorption by SO_2 is between one and two percent at Kagoshima and negligible at the twelve other stations.

Introduction

The two atmospheric gases that affect UV-B irradiance at the Earth's surface most strongly are ozone (O_3) and SO_2 . Molecular absorption in the wavelength range 300-325 nm by sulfur dioxide is about 2.5 times that of ozone, but attenuation by SO_2 in the atmosphere is normally much less than by ozone due to much lower column amount. It is typically 1-2 DU (1 DU is the amount contained in a 10-micrometre thick layer of pure gas at standard pressure and temperature) and rises to 4-6 DU in polluted air [Evans *et al.*, 1980; Josefsson, 1986] and up to 10-20 DU in rare cases of extremely high pollution [De Backer and De Muer, 1991]. Normally, ozone variability dominates the UV-B radiation changes, contributing at least one order of magnitude more than the variability caused by SO_2 [Bais *et al.*, 1993].

Very high total SO_2 amounts that may substantially affect UV irradiance have been observed in volcanic plumes [Josefsson, 1986]. Values of more than 600 DU were found in the Pinatubo plume immediately after the eruption in 1991 [Krueger *et al.*, 1995]. These high values were seen for a few days following major eruptions in the data from the Total Ozone Mapping Spectrometer (TOMS). However, TOMS normally does not detect small volcanic events and diffuse, non-explosive emissions [Bluth *et al.*, 1993] that can be important for local UV conditions at the Earth's surface.

For this study global UV irradiance spectra, measured by Brewer spectrophotometers and available from the World Ozone and Ultraviolet radiation Data Centre (WOUDC),

have been analyzed for the effects of SO_2 absorption. An algorithm for the estimation of total SO_2 amounts from these spectra is discussed and its results, which span more than 50 station-years, are described.

Data and Algorithm

Brewer instruments measure the spectrum of UV radiation falling on a horizontal surface, i.e. the global spectral irradiance. In the present study, data from 4 Japanese and 9 Canadian stations have been analyzed. Stations and their observation periods are given in Table 1. The wavelength range for these data is 290-325 nm; the resolution is approximately 0.55 nm, full width at half maximum, and the sampling interval is 0.5 nm. At most stations, spectra are recorded between once and twice per hour throughout the day. At the Canadian stations, direct-sun measurements of ozone and SO_2 are made between the spectral scans if the sun is unobscured, but there are no such measurements from the Japanese stations.

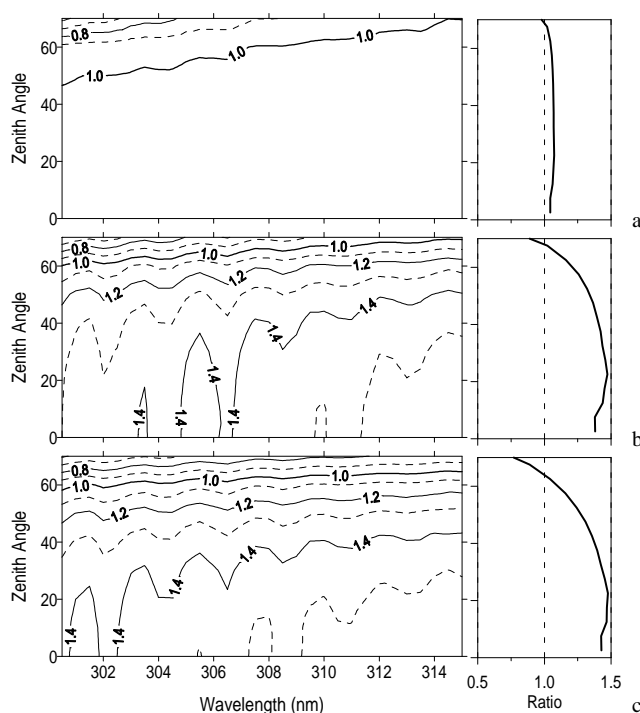


Figure 1. The ratio $h_{mod}(\lambda, z)/h_{abs}(\lambda, z)$ between the modeled function of SO_2 absorption and the similar function for a purely absorbing atmosphere (left) and the associated ratios in SO_2 results when using these functions in the whole spectrum algorithm (right) for the three scenarios each with 10 DU of SO_2 contained in 15-16 km (a), 3-5 km (b), and 0-2 km (c) layers.

Table 1. List of Stations, Periods of Observation, and Number of Days with $\text{SO}_2 \geq 10\text{DU}$

Station	Period	Number of Days
Kagoshima (32°N, 131°E)	1991-1995	236 (13.04)
Toronto (44°N, 79°W)	1989-1995	26 (1.08)
Saturna (49°N, 123°W)	1991-1995	5 (0.28)
Montreal (50°N, 74°W)	1993-1995	3 (0.32)
Naha (26°N, 128°E)	1991-1995	2 (0.11)
Churchill (58°N, 94°W)	1992-1995	1 (0.09)
Winnipeg (50°N, 97°W)	1992-1995	1 (0.08)
Edmonton (54°N, 114°W)	1992-1995	1 (0.08)
Saskatoon (52°N, 107°W)	1990-1995	1 (0.05)
Sapporo (43°N, 141°E)	1991-1995	0 (0.00)
Tateno (36°N, 140°E)	1991-1995	0 (0.00)
Halifax (45°N, 64°W)	1992-1995	0 (0.00)
Regina (50°N, 105°W)	1994-1995	0 (0.00)

*Percent of total number of days with UV observations are shown in brackets.

The method used here to derive the column SO_2 from Brewer UV irradiance spectra is an extension of that described for ozone estimation by [Fioletov et al., 1997]. It is based on the following model:

$$\log \frac{E(\lambda, z)}{E(324, z)} = M(\lambda, z) - g(\lambda, z)(O_3 - 300) - h(\lambda, z)SO_2 + \epsilon(\lambda, z) \quad (1)$$

where $E(\lambda, z)/E(324, z)$ is the ratio of irradiances at wavelength λ and 324 nm at the solar zenith angle z , O_3 and SO_2 are the total ozone and sulfur dioxide amounts, $\epsilon(\lambda, z)$ is an error with standard deviation $\sigma(\lambda, z)$, $M(\lambda, z)$ is the mean value of $\log(E(\lambda, z)/E(324, z))$ when the ozone is 300 DU, and $g(\lambda, z)$ and $h(\lambda, z)$ are functions that express the absorption by ozone and by SO_2 respectively. If M , g , σ and h are known, the O_3 and SO_2 amounts can be derived from the full spectrum using equation (1) and the least squares method with weighting $\sigma^{-2}(\lambda, z)$. In practice, the retrieved values are little sensitive to the spectrum outside the 300-315 nm range.

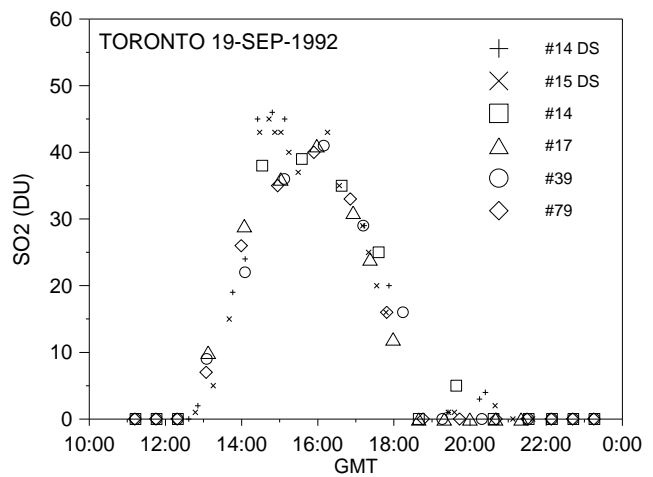
The functions M , g , σ were estimated empirically as described by [Fioletov et al., 1997]. This empirical method is impractical for the function $h(\lambda, z)$ because there are too few direct observations of high SO_2 values. The approach that has been taken here for calculating SO_2 amounts is to use, in place of $h(\lambda, z)$, the function $h_{abs}(\lambda, z) = (\Omega(\lambda) - \Omega(324))/\cos(z)$, where $\Omega(\lambda)$ is the SO_2 absorption coefficient at wavelength λ and to investigate the errors introduced by this approximation. The function $h_{abs}(\lambda, z)$ exactly describes the absorption that would occur in a non-scattering atmosphere. The errors are examined by radiative transfer modeling and by comparing results with direct-sun observations on the single day for which simultaneous measurements of $\text{SO}_2 \geq 20$ DU are available. Spectra with solar elevations less than 20° have not been used in this study because of the higher fractional measurement errors in the spectra.

Simulations were first done for an aerosol and cloud free atmosphere in the range 300-324 nm using the radiative transfer code, discussed by [McLinden et al., 1997]. The effects of 10 DU SO_2 layers at 0-2 km, at 3-5 km or at 15-16 km were modeled. These layers were chosen to represent respectively, a highly polluted lower troposphere, an SO_2 plume from a local volcanic eruption and similarly for a large volcanic eruption with upward transport. The function of

sulfur dioxide absorption $h_{mod}(\lambda, z)$ was evaluated for each layer by comparing results with those from an equivalent model run without SO_2 . The ratios $h_{mod}(\lambda, z)/h_{abs}(\lambda, z)$ are plotted in Figure 1 for each layer. The ratios describe the fractional errors when using equation (1) with $h_{abs}(\lambda, z)$ in the estimation of the SO_2 from perfect measurements at individual wavelengths in an aerosol free atmosphere. The error for the whole spectrum method is shown in the right-hand panels.

Figure 1 shows the errors ranging from about 8% with the SO_2 at 15km up to as much as 50% with the SO_2 in the lower troposphere and with $z \leq 20^\circ$. The ratios decrease by about 20% with decreasing wavelength which reflects the suppression of multiple scattering by the stronger absorption by SO_2 and O_3 at shorter wavelengths. Model runs made for 50 DU layers gave slightly lower values of $h_{mod}(\lambda, z)$ than the 10 DU cases; the biggest change was to reduce the overestimation in the 0-2 km layer from 50% to 40%. The conclusion drawn from these aerosol-free simulations is that the method always overestimates the SO_2 amount for $z \leq 60^\circ$. The overestimation can be as much as 50% with 10 DU of SO_2 in the lower troposphere but it is smaller for higher altitudes and larger amounts of SO_2 . With the albedo set to 0.9, which is typical of fresh snow, there is a further overestimation of up to 40%.

The effects on the estimation of a 0-2 km SO_2 layer of two dense distributions of urban aerosols, which are considered to represent extreme cases, have been modeled using the Henyey-Greenstein phase function. The first, which is strongly scattering, is from [d'Almeida et al., 1991] (optical depth=1.5, asymmetry factor=0.671 and single scattering albedo=0.92, distributed over 0-2 km); the other is identical except that the single scattering albedo is 0.67, which is strongly absorbing. At $z \leq 60^\circ$, the d'Almeida aerosol causes an extra overestimation up to 15% while the absorbing aerosol decreased the retrieved value by up to 20%. Since aerosol optical depths are usually less than 1.5, these values roughly indicate the limits of possible aerosol interference. However, it is to be expected that dense clouds or fog can produce large enhancements of the scattering path length and therefore of the SO_2 values as is sometimes observed with ozone. The dependence of SO_2 absorption on temper-

**Figure 2.** Total column sulfur dioxide amount from Brewer direct sun measurements (pluses and asterisks) and from UV spectra (squares, triangles, circles, and diamonds) for September 19, 1992 at Toronto. Brewer instrument numbers are shown in the legend.

ature is a source of uncertainty unless the temperature is known. The absorption spectrum measured by [McGee and Burris, 1987] at room temperature (295°K) was adopted for normal use in the estimation algorithm. Based on the range 295°K to 210°K for the possible average temperature of the SO₂, using the 295°K spectrum could cause an overestimation from zero up to 20%.

Figure 2 shows results, for September 19, 1992 in Toronto, of SO₂ values retrieved from UV spectra from four instruments and direct-sun SO₂ measurements, which are not sensitive to multiple scattering, from two instruments. The occasion was the passage of the plume from the September 17 eruption of Mount Spurr in Alaska [Krueger et al., 1995]. The absorption spectrum for 210°K was used in both methods because the plume was known to be near the tropopause. Both methods show the same pattern in SO₂ variation and the difference between direct sun and global UV spectra methods is less than 20% at the time when the largest values of SO₂ were observed.

The precision of the SO₂ retrieval is typically 2-3 DU (1 σ) and therefore the method is not suitable for detecting SO₂ amounts below 5 DU. The method is suitable for identifying large SO₂ amounts and, because the systematic errors are all those of possible overestimation, it can be used effectively to put upper bounds on SO₂ amounts. It may be noted that knowledge of the temperature and especially of the vertical profile of the SO₂ can improve the estimation of the amount. From a different perspective, the retrieved value may be seen as the SO₂ amount that, if located above most of the atmosphere, would cause the observed degree of absorption. In this sense the retrieved value is an unbiased descriptor of the absorption.

Survey of Results

SO₂ was calculated from all available spectra using the algorithm described above. The summary of all days with SO₂ more than 10 DU is shown in Table 1. The criterion for being counted in this list is that a day must have at least two observations of SO₂ ≥ 10 DU. As mentioned, the method overestimates tropospheric SO₂ so the actual SO₂ values would usually be even lower. The high SO₂ amounts over Kagoshima will be discussed below. For all other stations, the SO₂ was above 20 DU only on one day which was when the Mount Spurr plume was over Toronto. For the stations other than Kagoshima, the most frequent occurrence of days with SO₂ ≥ 10 DU was 1.1%, observed at Toronto, and the

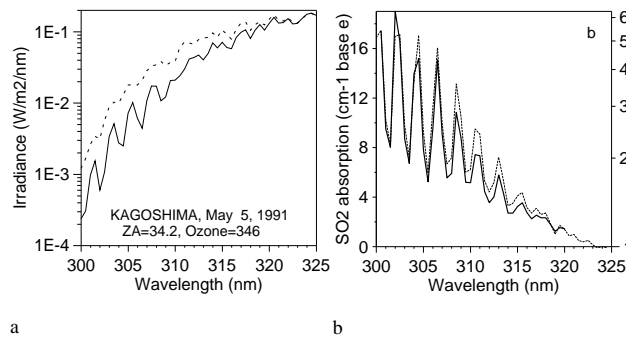


Figure 3. Measured spectrum (solid line) at Kagoshima, May 5, 1991, and calculated spectrum (dotted line) for the same conditions (O₃, z) but without SO₂. Ratio between the two spectra (dotted line) and absorption spectrum (solid line) (right).

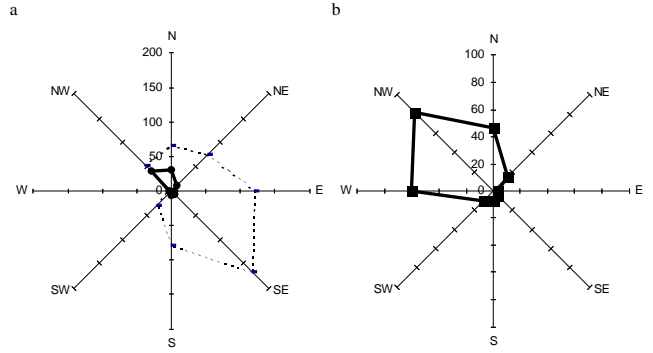


Figure 4. (a) Number of days with volcanic activity for the period 1991-1992. The dotted line shows the number of days for different directions of the volcanic plume movement; the solid line indicates the number of days when high (≥ 10 DU) SO₂ content was observed over Kagoshima. (b) Percentage of days with high SO₂ events over Kagoshima when volcanic activity was reported for different directions of the volcanic plume movement.

combined mean occurrence for all these stations was 0.22%. With SO₂ values between 10 and 20 DU, the reduction of erythemally weighted UV irradiance by sulfur dioxide is only a few percent. The overall effect of SO₂ absorption on UV climate is therefore negligible for all stations in this study except Kagoshima.

The relatively large number of cases with SO₂ above 10 DU in Toronto can be explained by local pollution sources. Also the measurement frequency at Toronto which is usually about five per hour, is about twice that at most other stations which may cause short-term SO₂ increases to affect daily statistics more than at other stations.

For the 5-year observation period at Kagoshima, SO₂ amounts above 20 DU were observed on 126 days. A spectrum observed on May 5, 1991, and one calculated for the same zenith angle and O₃ amount are shown in Figure 3a. The absorption spectrum of SO₂ smoothed to the resolution of Brewer instrument is clearly visible in the ratio of these two spectra (Figure 3b). The SO₂ value retrieved from the observed spectrum, as discussed in section 2, is 106 DU.

The high SO₂ amounts observed over Kagoshima are related to Sakurajima, one of a few active volcanoes in Japan. The meteorological observatory in 1991-1993 was located in the northern part of Kagoshima. The observatory was then 10 km to the northwest of the volcano. In February 1994, the observatory was moved to a new location in the southern part of city and it is now 10 km west-northwest of the volcano.

Information about volcanic activity and gas plume motion is published by the Japan Meteorological Agency (JMA) [e.g., JMA, 1995]. At the time of writing, data for 1991-1992 are available. These data have been examined in relation to the observed SO₂ amounts. Eruptions occurred on most days (635 days of 731). The number of days as a function of the heading of the volcanic plume are plotted as the dashed line in the radial diagram (Figure 4a). In most cases the plume moved to the east or southeast with the prevailing winds and did not pass over the station. However, on 51 days the flow was toward the northwest, i.e. toward the observatory, and SO₂ amounts above 10 DU were registered by the Brewer on 42 of these days. The number of days

when SO_2 above 10 DU was measured over the observatory as a function of flow direction is shown in Figure 4a by a solid line. Figure 4b shows the percentage of days when $\text{SO}_2 \geq 10$ DU was measured at the observatory for different flow directions. For an additional 50 days the flow direction was reported as "just above the vent" and, for 21 of these, $\text{SO}_2 \geq 10$ DU was observed over the station including a few cases with extremely high SO_2 (80–100 DU). These days with little or no flow likely resulted in the accumulation of large SO_2 amounts near the volcano.

Diagram 4b gives some information about the angular extent of the plume that can be used to estimate the total volcanic emission. The average SO_2 over Kagoshima during eruptions was about 20 DU. SO_2 was detected over the observatory in about 50% of the cases when the plume flow direction was north or west. This information with the crude assumption that, when there was a defined wind direction, the wind speed was always 10 km per hour, leads to an estimate of 60–70 tons per hour for the total emission from the volcano. This is in reasonable agreement with direct estimates of emissions using ordinary methods; i.e. a few hundreds to a few thousands tons per day (K. Ishihara personal communication, 1996).

The observed levels of SO_2 can substantially reduce the level of biologically active ultraviolet radiation. For an SO_2 amount of 50 DU the energy of the UV-B spectrum weighted by the erythral (skin-reddening) action function is about 25% less than its level for the same atmosphere without SO_2 . Similarly, the reduction for the biologically damaging action spectrum [Wester, 1981] is about 40% (both weighted integrals are described in and available from WOUDC data files). This comparison is between measurements made with the same total ozone amount (330 DU), the same zenith angle (40°) and the same level of irradiance at 324 nm (i.e., outside ozone and SO_2 major absorption bands). Other components of volcanic plume such as aerosol and dust also attenuate solar radiation, so the overall reduction of UV irradiance due to volcanic eruption will be greater than that due only to SO_2 absorption. However, SO_2 is the major factor in many cases. During the 5-year period, 65 observations with $\text{SO}_2 \geq 50$ DU were found. In 23 cases (35%), the UV irradiance at 324 nm was $\geq 60\%$ of the clear sky level. For these cases the effect of SO_2 absorption on the biologically damaging weighted UV irradiance is stronger than the attenuation by other constituents of the volcanic plume and any cloud that might have been present.

Multiplying the number of days with high SO_2 by the reduction of UV irradiance due to SO_2 , provides an estimate of the long-term effect of volcanic SO_2 absorption on the UV climate at the surface. At Kagoshima it is in the range 1–2%. The total effect of the volcano on UV irradiance is likely even higher because of the other volcanic plume components that absorb and scatter solar radiation. The effect would be at least twice as strong if the observatory was located in the prevailing downwind direction from the volcano. Since no other Japanese stations reported SO_2 values more than 20 DU, it is likely that the effects of this volcano are not widespread.

Conclusions

In an analysis of UV-B spectral data from 13 stations in Canada and Japan, values of SO_2 more than 20 DU were registered at only 2 stations (Toronto and Kagoshima). In

both cases the high values are associated with volcanic activity. The Toronto event is related to Mount Spurr volcanic eruption when SO_2 was observed to be about 50 DU. The occurrence of days with SO_2 more than 10 DU is less than 1.1% at all the stations except Kagoshima, even though several of them are in urban areas. The overall effect of SO_2 pollution on UV climate at these stations is negligible.

At Kagoshima, high SO_2 amounts are seen regularly due to the Sakurajima volcano which is about 10 km from the station. Amounts of $\text{SO}_2 \geq 20$ DU were observed on about 7% of all days. The presence of volcanic SO_2 reduces the mean level of UV irradiance over Kagoshima by about 1–2%; however it can be much higher for individual days and is likely higher on average in the direction of the prevailing winds. Absorption of UV radiation by volcanic SO_2 is a local effect that should be considered when local levels of UV irradiance are assessed or forecasted.

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