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Measurement of Volcanic SO_2 Concentration in Miyakejima Using Differential Optical Absorption Spectroscopy (DOAS)

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ABSTRACT

Since the volcanic eruption in 2000, continuous monitoring of sulfur dioxide (SO_2) gas has been conducted with *in-situ* samplers located along the seashore road in Miyakejima, a volcano island around 180 km south of Tokyo. The purpose of these sampling measurements has been to issue warning on the hazardous air pollution to the local residents. Therefore, the resulting data do not provide direct information on pollution levels inside the restricted areas where high concentration of SO_2 still takes place frequently. From the ecological point of view, it is desirable to have pollution data covering wider regions of the island. In this paper we report on our differential optical absorption spectroscopy (DOAS) measurements carried out inside the highly-polluted, restricted areas in Miyakejima in December 2009 and September 2010. The system is based on continuous light emitted from a xenon light sources, while detector setups consisting of a telescope and a compact spectrometer detect the light after passing a nearly horizontal optical path of 460 m - 1300 m. By virtue of the portability of the DOAS observation systems, we achieved the measurement of the concentrations inside the restricted districts in the eastern and southwestern parts of the island. The DOAS results in both of these districts revealed the occurrence of pollution of volcanic gas even when no pollution was observed at nearby sampling stations. In addition, simultaneous measurements with two nearly orthogonal DOAS paths were conducted for examining the spatial distribution of the volcanic gas over the spatial range of several hundred meters. The result of this two paths measurement has indicated the importance of orography, in addition to the wind speed and wind direction, in determining the spatial concentration of SO_2 emitted from the volcano crater.

Keywords: Miyakejima; SO_2 Concentration; Air Pollution; Sampling Measurement; DOAS

1. Introduction

Mount Oyama in Miyakejima Island erupted in 2000 with the formation of a collapse caldera of around 500 m diameter. Since then, long-lasting emission of volcanic gas has damaged vegetation all around the island, accompanied with the acidification of the soil and ground water on a wide scale [1-3]. In the initial phase between 2000 and 2002, the emission of sulfur dioxide (SO_2), the major component of the volcanic gas, was as high as 4000 - 50,000 ton/day [4]. As of today, the SO_2 emission has reduced, but still a considerable amount of 900 - 1200 ton/day is emitted [5]. Entrance to some areas on the island is officially restricted due to the frequent coverage by volcanic plumes with high concentration of SO_2 depending on the wind speed and direction [6]. Although ground-based, *in-situ* sampling measurements have been conducted at 14 stations by the municipal government (Miyakejima Village), it is difficult to monitor the gas concentration in the restricted areas, since all of the sampling stations are placed along the peripheral (seashore) road of the island, and the measured values are not always representative of the concentration in nearby areas. The vegetation coverage of Miyakejima is on the way of recovering from the big eruption in 2000.

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Restoration of forest, however, is rather slow, since withering took place due to the continuous influence of the volcanic gas [7]. From such an ecological point of view, it is desirable to have pollution data covering wider regions of the island.

In the present work, we report the application of differential optical absorption measurement (DOAS) to the regional measurement of volcanic SO_2 concentrations inside high concentration districts in Miyakejima. The DOAS approach, in general, enables us to monitor the concentration of air pollution species such as NO_2 to an accuracy of a few ppb averaged over the optical path of several hundred meters to several kilometers [8-10]. The early form of active DOAS methodology based on artificial light sources was established in the 1970s [11-13]. For volcanic studies, the measurement of sulfur dioxide flux has been a focus of air pollution monitoring since the development of the correlation spectrometer (COSPEC) in the 1970s [14]. Intensive gas emissions from non-erupting volcanoes have been regarded as evidence of endogenous growth of volcanoes [15-17]. [4] reported the SO_2 emission rate of an extremely large volcanic gas emission in Miyakejima measured with the COSPEC instrument, and discussed its degassing mechanism. Also, a compact SO_2 monitoring instrument based on UV spectroscopy has been developed since the 2000s, with reports describing the application to volcanic measurements [18]. Passive measurement of SO_2 can be achieved using several ground-based instruments, such as mini-UV spectrometers employing either DOAS, correlation spectroscopy, or UV camera imagery [14,19-24]. The variation of SO_2 flux was successfully monitored using mini-UV spectrometers based on the DOAS principle [20,25,26].

The results described here are based on our campaigns performed during 19-23 December 2009 and 22-29 September 2010. In both cases, portable light sources based on xenon lamps were employed for the UV DOAS measurement of SO_2. The high luminosity of the lamps made it possible to detect the light from distant locations. Because of the compactness of our DOAS observation systems, we could achieve the measurement of the concentrations inside the restricted districts in the eastern and southwestern parts of the island. In order to obtain two-dimensional distribution information, we have also deployed two DOAS setups having light paths nearly perpendicular to each other. In spite of relatively limited time durations of our campaign measurements, our study has shown, for the first time to our knowledge, that considerable concentration of SO_2 is observed in the high concentration areas even when the values reported at nearby *in-situ* sampling stations were below the detection limit. The details of the study area will be described in Section 2, and the ground sampling and DOAS instruments will be explained in Section 3 together with the DOAS retrieval algorithm. The results and discussion will be given in Section 4, followed by conclusions given in Section 5.

2. Study Area

Miyakejima is a volcano island with a diameter of approximately 8 km and an area of 55.44 km^2 (**Figures 1(a)** and **(b)**). It is known that in the past 550 years, its volcano (Mount Oyama) erupted occasionally with low viscosity basaltic lava spilling from the flank fissure craters [27]. All the residents were evacuated after the eruption in 2000, because of the hazardous concentration of volcanic SO_2 emitted from the volcano crater. In February 2005, the evacuation order was finally removed. As of January 2012, the population on the island is around 2800, engaged mainly in agriculture, fishing, and tourism. The transportation from the mainland (Tokyo) to the island is available via either a ship (6.5 h) or an airplane (45 min), but the air flights are often cancelled due to the hindrance of volcanic plume.

[28] studied the seasonal and regional characteristics of SO_2 concentration on the island by analyzing the data from the *in-situ* station measurements from January 2001 to December 2007. High concentration of SO_2 occurs on the leeward when the volcanic emission gas is blown down by strong winds. As a result, the monthly averaged volume concentration becomes high in the eastern part of the island (Tsubota district, hereafter T district; see **Figures 1(b)** and **(d)**) in the winter; similarly, the value often exceeds the environmental standard (ca. 40 ppbv), especially in the southwestern part of the island (Usugi and Awabe district, hereafter UA district; (see **Figures 1(b)** and **(c)**) in the fall [6,28]. In both of these high-concentration districts, we conducted our DOAS campaign measurements by means of xenon lamps and UV telescopes, as described below.

3. Methods

3.1. *In-Situ* Sampling Data

First we analyze the changes of SO_2 concentrations in high-concentration districts in Miyakejima Island on the basis of ground sampling data taken in the years between 2006 and 2009, after the evacuation order was lifted in 2005. The data were obtained from point observation stations along the periphery road of the Miyakejima island (**Figure 1(b)**). The sampling observation at each station has been implemented by means of the fluorescence measurement with ultraviolet (UV) illumination, normally around 220 nm wavelength. The instruments are commercially available ones (e.g., Horiba, APSA-370), with typical resolution of 0.02 ppmv and accuracy of ±1% of the full scale. The data are recorded in every 5 min, and sent to a data accumulation server installed at

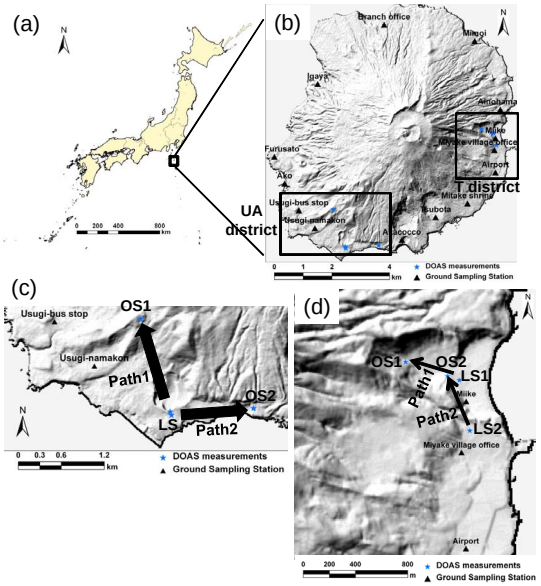


Figure 1. Location maps: (a) Miyakejima is a volcano island located in the Pacific Ocean, at around 180 km south of Tokyo. (b) Mt. Oyama is at the center of the island. The Tsubota district (T district) is on the eastern seashore, while the Usugi and Awabe district (UA district) on the south-western part of the island. Entrance to these two districts is still restricted due to the frequent occurrence of air pollution due to volcanic SO_2. (c) In the UA district, the DOAS observation was made along the light path (path 1, 1.3 km) from the light source (LS) to the observation site (OS1) from 20 to 23 December, 2009. The other observation path (path 2, 1.1 km) from the LS to OS2 was employed from 23 to 29 September, 2010. (d) In the T district, the observation path (path 1, 460 m) was used from 20 to 23 December 2009 and from 23 to 28 September 2010. The other path (path 2, 480 m) was additionally employed for the double path DOAS measurement conducted during 28 and 29 September 2010.

the Miyakejima Village Office via telephone lines. After appropriate data screening, the result is announced in an internet site [29].

3.2. DOAS Instrument

Figure 2 shows a schematic diagram of the experimental setup employed for the present open-path DOAS observation. Two highly stabilized xenon lamps were used as light sources: a 300 W lamp (Cermax, PE300BFM) at UA district and a 150 W lamp (Hamamatsu Photonics, L2273) at T district. Since these continuously emitting xenon lamps provide relatively smooth spectra in the UV region, they are more suitable for the present purpose when compared with the xenon flashlight sources (used for our former DOAS experiments in the visible wavelength), in which the existence of several sharp emission lines could deteriorate the gas absorption measurement. A parabolic mirror of 10 cm diameter, coupled with a beam expanding system consisting of a convex lens and a

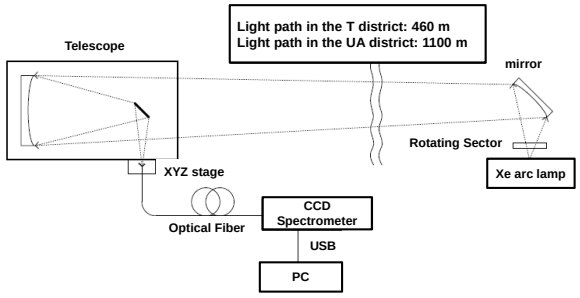


Figure 2. Open-path DOAS instrumentation for the observation of SO_2 concentration.

concave mirror, is used to produce a collimated light beam from each of the light sources. A rotating sector (30 rpm) was placed in front of each lamp in order to measure the background spectra arising from the outdoor natural light conditions. The difference between the spectrum with unobstructed DOAS light illumination (on-spectra) and the background spectra (off-spectra) yields the net spectra due only to the xenon light source after propagating the DOAS optical path length of around 460 m - 1300 m.

The detection system consists of an astronomical telescope (Vixen, R100M or RS200SS) and a compact charge-coupled device (CCD) spectrometer (Ocean Optics, USB2000 or HR4000). **Table 1** shows specifications of the CCD spectrometers. The point-like image of each light source located at a far distance is observed using a telescope of 100 (200) mm diameter, with the focal length of 400 (800) mm. The image formed near the eyepiece location is coupled to an optical fiber (400 μm core diameter), the other end of which is connected to the entrance slit (1 mm high and 5 μm wide) of the CCD spectrometer. The CCD spectrometers are composed of a fixed grating and a linear CCD array with a length range of 200 nm - 640 nm. The CCD gate duration was set at 300 ms in the experiment. Between successive gate periods, there exists a time lag of 7 ms, in which each spectral data set is sent to a personal computer (PC) through the universal serial bus.

Measurement of SO_2 concentration by the DOAS technique requires the knowledge of the absorption cross-section with a resolution of the order of 1 nm in the UV region of the spectrum, typically from 250 to 350 nm [30-33]. **Figure 3** shows an example of optical thickness of atmospheric extinction (absorption and scattering) simulated for an optical path length of 500 m with SO_2 concentration of 0.2 ppmv. In this example, the absorption of SO_2 gas species gives a structure that has the optical thickness variation of approximately 0.2 (non-dimensional). In order to extract the SO_2 concentration, contributions from molecules (Rayleigh scattering) and aerosol particles (Mie scattering) must be subtracted, as explained below. Below, we employ the wavelength

Table 1. CCD Detector Specifications.

Spectrometer	USB2000	HR4000
Linear CCD Array	SONY ILX511	TOSHIBA TCD1304AP
Slit width (μm)	5	5
Integration time (ms)	3 - 65000	0.01 - 65000
Wavelength range (nm)	200 - 800	200 - 640
Nominal resolution (nm)	0.3	0.23
A/D resolution	12 bit	14 bit
Signal to noise ratio	250: 1 (at full signal)	300: 1 (at full signal)
Observations	UA district (20-23 Dec. 2009, path 1) UA district (23-28 Sep. 2010, path 2) T district (28-29 Sep. 2010, path 2)	T district (20-23 Dec. 2009, path 1) T district (23-29 Sep. 2010, path 1)

range from 300 to 310 nm for analyzing the DOAS observation data in consideration of the lower sensitivity of the spectrometers at wavelengths shorter than 300 nm.

3.3. Analysis of DOAS Spectra

Theoretically the observed light intensity can be expressed as

$$I_{\text{obs}}(\lambda) = k(\lambda) I_0(\lambda) T_{\text{m}}(\lambda) T_{\text{a}}(\lambda) T_{\text{SO}_2}(\lambda). \quad (1)$$

Here, λ is the wavelength, $k(\lambda)$ is an instrumental coefficient including the detector sensitivity, $I_0(\lambda)$ is the spectrum of light source observed at a location close to the light source, $T_{\text{m}}(\lambda)$ is the transmittance of air molecules due to Rayleigh scattering, $T_{\text{a}}(\lambda)$ is the transmittance of aerosols due to Mie scattering, and $T_{\text{SO}_2}(\lambda)$ is the transmittance representing the SO_2 absorption. The molecular (Rayleigh) and aerosol transmittance factors can be expressed as

$$T_{\text{m}}(\lambda) = \exp\left[-\tau_{\text{m}}(\lambda)\right] \quad (2)$$

and

$$T_{\text{a}}(\lambda) = \exp\left[-\tau_{\text{a}}(\lambda)\right], \quad (3)$$

respectively, where $\tau_{\text{m}}(\lambda)$ and $\tau_{\text{a}}(\lambda)$ are the molecular and aerosol optical thickness, respectively. The transmission due to SO_2, on the other hand, can be given as

$$T_{\text{SO}_2}(\lambda) = \exp\left[-\sigma(\lambda) NL\right], \quad (4)$$

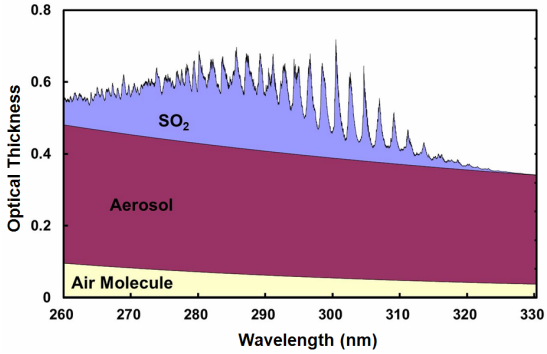


Figure 3. Wavelength dependence of each optical thickness component simulated for the wavelength range of 260 nm - 330 nm. It is noted that SO_2 absorption exhibits notable spectral features, whereas aerosol and air-molecule extinction show less prominent wavelength dependence.

where $\sigma(\lambda)$ is the wavelength-dependent absorption cross-section, N is the number density of SO_2 molecule averaged over the path length, L. Combining Equations (1)-(4), we obtain

$$\ln\frac{I_0(\lambda)}{I_{\text{obs}}(\lambda)} + \ln k(\lambda) = (NL)\sigma(\lambda) + \tau_{\text{m}}(\lambda) + \tau_{\text{a}}(\lambda). \quad (5)$$

Since $\ln k(\lambda), \tau_{\text{m}}(\lambda)$ and $\tau_{\text{a}}(\lambda)$ are slowly varying functions of wavelength, it is possible to extract the information of SO_2 absorption by subtracting an appropriate polynomial of wavelength λ from the quantity given by the left-hand side of equation (5). In other words, the differential optical thickness, $\Delta\tau$, can be derived by applying "high-pass filtering" to $\ln[I_0(\lambda)k(\lambda)/I_{\text{obs}}(\lambda)]$. Thus, the value of $\Delta\tau$ is related to the differential cross-section, $\Delta\sigma$ as

$$\Delta\tau(\lambda) = (NL)\Delta\sigma(\lambda) + r(\lambda), \quad (6)$$

where $r(\lambda)$ indicates the residual of this fitting procedure. The column amount NL, of SO_2 molecule can be derived so as to minimize $r(\lambda)$.

Before applying this spectral analysis, background subtraction is attained by discriminating the on-spectra (with light source) and off-spectra (no light source) events caused by the influence of the rotating sector placed in front of the xenon lamp. For this purpose, threshold intensities are appropriately chosen for both the on-spectra (95% value) and off-spectra (the lowest value). The spectral range chosen for this procedure is 350 nm - 450 nm because of the better sensitivity of the spectrometer as compared with shorter wavelengths. **Figure 4** summarizes this preprocessing for a DOAS spectrum observed around 17:00 Japan Standard Time (JST) on 20 December 2009. By averaging 201 on-spectra (above the intensity of 7254) and 119 off-spectra (with the lowest intensity of 615) (**Figure 4(a)**), we obtain a pair of on-

and off-spectra, as shown in **Figure 4(b)**. A good contrast is seen between the on- and off-events, since the scene behind the light source was a mountain region covered with vegetation, not the bright sky. Then, the spectral analysis based on Equations (5) and (6) is applied in the wavelength region of 300 and 310 nm using the differential absorption cross-section, $\Delta\sigma$, derived from a laboratory spectrum [33], as shown in **Figure 4(c)**. The resulting concentration of SO_2 is 230 ± 10 ppbv in this example. The residual spectrum, $r(\lambda)$, is obtained as shown in **Figure 4(d)**. The detection limit of DOAS analysis can be estimated from this residual spectrum to be of the order of 10 ppbv.

4. Results and Discussion

4.1. Seasonal Changes in the High-Concentration Districts

First we describe the seasonal changes of SO_2 concentration in the residential districts on the periphery of the island. For this purpose, we have analyzed the data of *in-situ* sampling stations to obtain the monthly variation of SO_2 during five years between 2006 and 2010. **Figures 5(a)** and **(b)** show the monthly average values derived from 5 min average SO_2 data observed in the T-district and UA-district, respectively. High concentration of SO_2 was often observed in winter at observation points of Miike, Miyake Village Office, and Airport, all located in the T district. In the UA district, on the other hand, the concentrations seen at the Usugi-Namakon and Usugi-Busstop stations (UA district) were high not only in winter but also in September and October. The long-term trend shown in **Figure 5** indicates that the influence of SO_2 has gradually decreased year by year, which is consistent with the similar analysis based on the sampling data between 2001 and 2007 [30]. Nevertheless, air pollution at hazardous levels still occurs in both the T and UA districts, thus entering these districts has been restricted even after the evacuation order was lifted in 2005. This implies that there had been no means to monitor the SO_2 concentration inside each of these districts before our DOAS campaigns were conducted in 2009 and 2010 with the special permission from the village office. The results of our campaigns are described in the following subsections.

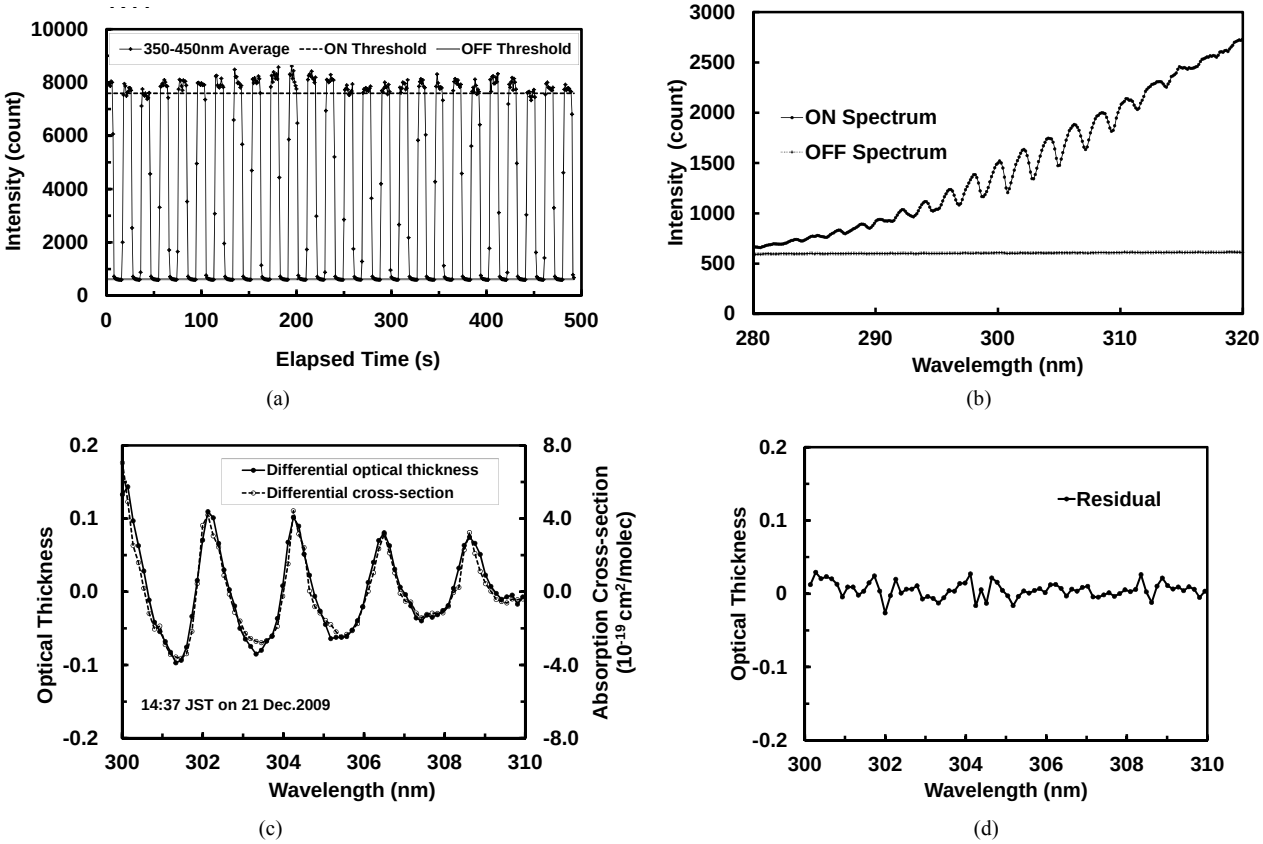


Figure 4. Analysis of observed DOAS spectra: (a) intensity variation observed during 500 s with a light path length of 460 m, (b) wavelength dependence of the resulting spectra for both off and on conditions, (c) comparison between the differential optical thickness ($\Delta\tau$) of the DOAS spectrum and differential absorption cross-section ($\Delta\sigma$) from reference Vandaele *et al.* (1994), and (d) the residual optical thickness after the fitting procedure.

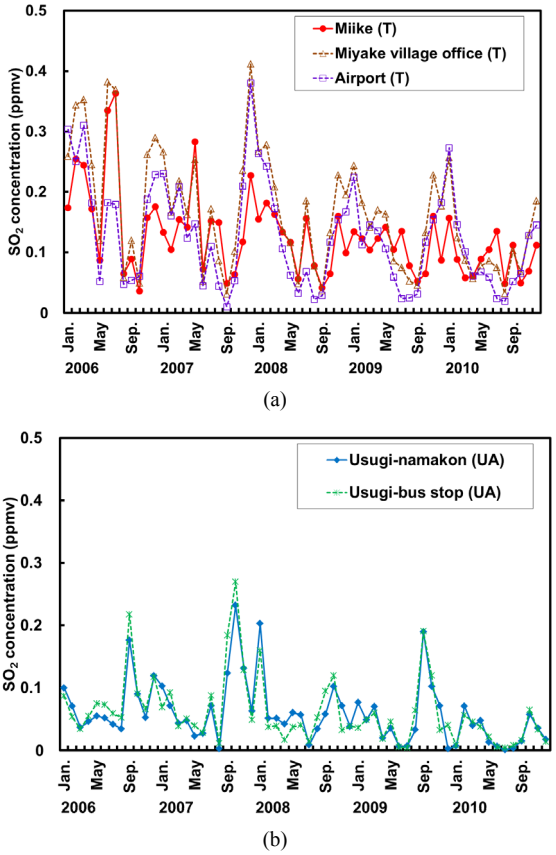


Figure 5. Monthly averaged of SO_2 concentrations during 2006-2010 for each of the volcanic gas monitoring stations of (a) T district and (b) UA district.

4.2. Air Pollution in December 2009

In **Figure 6(a)**, DOAS data of the T district are plotted in comparison with the sampling data obtained at the Miike ground sampling station for a time period between 12:00 on December 20 and 0:00 on December 23, 2009. The DOAS observation was made along an optical path length of about 460 m (path 1 in **Figure 1(d)**). The plotted data represent the values for 1 h, obtained by averageing 60 datasets of 1 min measurement. The similarity between the DOAS and sampling data indicates that during this observation period, the point sampling data are representative of the SO_2 concentration in the area that has a scale of several hundred meters. From 20 to 23 December, persistent presence of volcanic gas was detected in the T district, with some peaks reaching as high as 0.57 ppmv. In the UA district on the southwestern part of the island, on the contrary, no occurrence of highly polluted plumes was seen during the same time period.

Figure 6(b) shows the wind data during the same time period as **Figure 6(a)**. The wind data were taken every 10 min at a Japan Meteorological Agency (JMA) weather monitor station located at the Miyakejima Airport in the T district. The weather was mostly fine, with the dominance of westerly winds having the speed in the range of 4-12 m/s. Thus, it has been confirmed that when the T district was on the leeward of the crater, lingering pollution was indeed observed in both the DOAS and sampling measurements. **Figure 6(c)** shows the correlation of the SO_2 concentration between the ground sampling and DOAS measurements. In this case, each data point indicates the average over 5 min. From **Figure 6(c)**, it is seen that a reasonable correlation is found between the

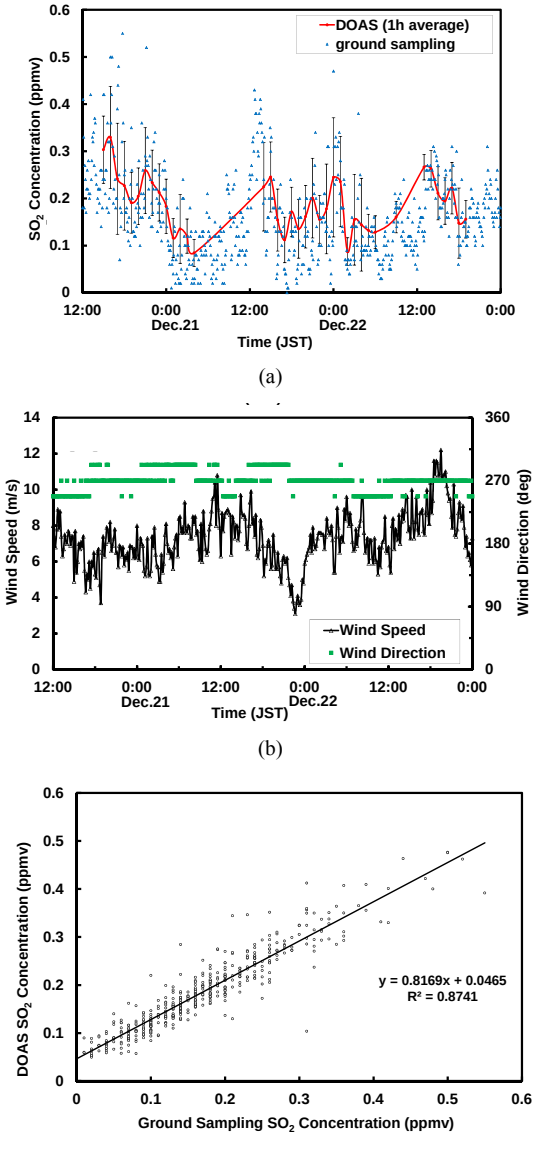


Figure 6. Temporal variations of air pollution and wind field in the T district during 20-23 December 2009: (a) SO_2 concentration from the DOAS and sampling measurements. Error bars show the variation range of DOAS concentration values during 1 h. (b) wind speed and wind direction, and (c) correlation between the results of the DOAS (5 min average) and ground sampling measurements (442 data points).

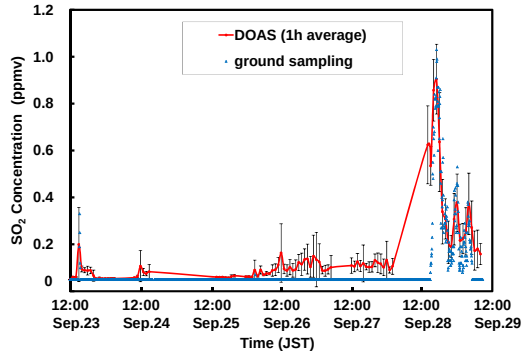
result of the long-path measurement and the ground sampling data at the Miike station when the west wind was dominant.

4.3. DOAS Measurement in September 2010

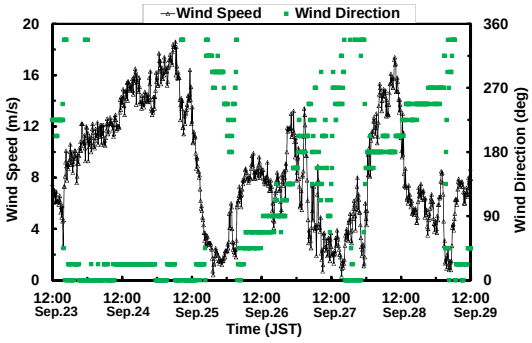
Figure 7(a) shows the DOAS data obtained at the T district (path 1 in **Figure 1(d)**; averaged over 1 h, *i.e.*, 60 datasets of 1 min measurement) for a time period between 12:00 on September 23 and 12:00 on September 29, 2010. The ground sampling data obtained at the Miike station are also shown in **Figure 7(a)**. **Figure 7(b)** shows the wind data during the same time period. The wind data are the 10-min data provided from the Airport Observatory of JMA. On the afternoon on 23 September, a maximum concentration of 0.52 ppmv was observed in the DOAS (1 min) measurement under the influence of strong wind from the southwest direction. After that day, the DOAS measurement was interrupted because of the strong wind and rain due to a typhoon. After the typhoon went past, some increase in SO_2 concentration was observed on 26 and 27 September 2010. On the morning of 28 September, no concentration was observed, due presumably to the dominance of southern winds. In the afternoon, however, western winds became noticeable, and a high concentration around 1 ppmv was observed in the DOAS (1 min) measurement in the T district. The highest value of 1.12 ppmv was observed around 17:00 JST, and both the DOAS and sampling data in **Figure 7(a)** indicate that this situation lasted until the morning of the next day.

Figure 7(c) shows the correlation plot between the ground sampling and DOAS data during the one week period of 23-29 September 2010. During this period, we obtained 291 data points (here, one data point corresponds to 5 min average) for which meaningful concentration of SO_2 gas was seen in the DOAS data, while no concentration (0 ppb) was recorded in the sampling measurement. This data number (291) amounts to 63% of the total data points (462) observed in the T district. As manifested in this example, our observation has shown that low-level to mid-level concentration was often seen in the DOAS data even when no concentration was recorded in the ground sampling data. This suggests that the orography effect plays an important role in the transport of the hazardous gas from the crater to the residence areas located on the periphery of the island. The location of the Miike sampling station is at approximately 200 m away from the valley path, as indicated in the relief map in **Figure 1(d)**. Thus, such a local effect can only be detected with the DOAS approach having an optical path length of several hundred meters.

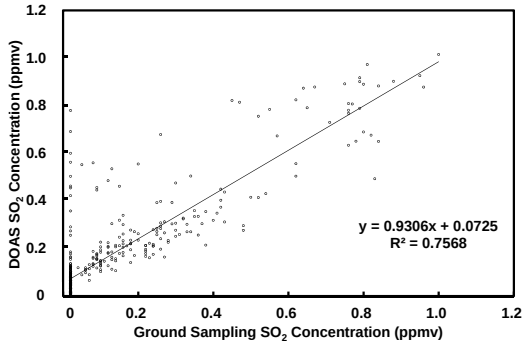
Figure 8(a) shows the DOAS data obtained at the UA district (averaged over 1 h, *i.e.*, 60 dataset of 1 min



(a)



(b)

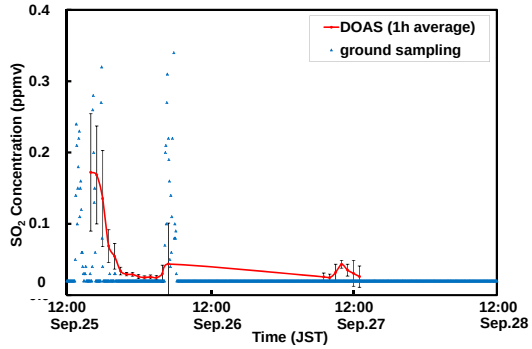


(c)

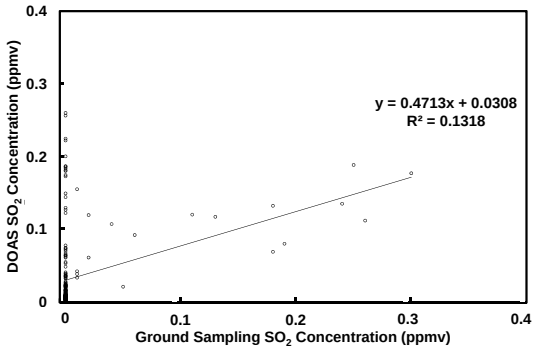
Figure 7. Temporal variations of air pollution and wind field in the T district during 23-29 September 2010: (a) SO_2 concentration from the DOAS and sampling measurements, (b) wind speed and wind direction: the high wind speed on 24 September is due to a typhoon, and (c) correlation between the results of the DOAS (5 min average) and ground sampling measurements (462 data points). In panels (a) and (c), it is often seen that meaningful values are observed in the DOAS data while the values were below the detection limit in the ground sampling measurement.

measurements) in comparison with the ground sampling data obtained at the Usugi-Namakon station for a time period between 12:00 on September 25 and 12:00 on September 28, 2010. The measurement was interrupted also due to the approach of the typhoon during 23-24 September. No wind data were measured at the southwestern part of the island. Thus, if we assume that Air-

port Observatory data in the T district (see **Figure 7(b)**) can also be employed here, northern or northeastern winds were dominant on the afternoon of 25 September, and consequently, similar temporal variations were found between the DOAS and ground sampling data in **Figure 8(a)**. The maximum concentration was 0.48 ppmv observed in the 1 min DOAS measurement at 15:33 JST. At the sampling station inside the UA district, the increase in SO_2 concentration was observed on the early morning (after 03:30 JST) of 26 September 2010, which is consistent with the increase in the northeastern winds. A maximum concentration of 0.20 ppmv was also observed in the DOAS (1 min) measurement at 04:33 on the same day. Then, the DOAS measurement was interrupted for a while due to the strong winds of more than 10 m/s, which resulted in the degradation of optical alignment of the DOAS instrument. During 07:00 - 13:00 JST on the next day (27 September 2010), however, the DOAS data revealed a slight increase in SO_2 concentration, but no such increase was detected in the sampling measurement. The optical path in the UA district (1.1 km; path 2 in **Figure 1(c)**) was nearly perpendicular to the slope of the Mount Oyama. The dominant wind direction was SSE-SW from 7:00 to 10:30 JST, while that was ENE-E from 10:30 to 11:30 JST. Therefore, it is likely that the polluted air was observed along the DOAS path after diffusion and advection effects. **Figure 8(b)** shows that from the afternoon on 25 September to the evening on 28 September 2010, we have obtained 212 data points (one data point corresponds to 5 min average) for which meaningful concentration of SO_2 gas was seen in the DOAS data, while the sampling data recorded no concentration (0 ppb). The corresponding data number (212) amounts to 92% of the total data points (230) observed in the UA district. Thus, as in the case of the T-district data mentioned above, it often happens that meaningful concentration can be seen in the DOAS data even when no increase is observed in the station measurement.



(a)



(b)

Figure 8. Temporal variation of SO_2 concentration from DOAS and ground sampling measurements in the UA district during 25-28 September 2010, and (b) correlation between the results of the DOAS (5 min average) and ground sampling measurements (230 data points).

4.4. Double-Path DOAS Measurement

After 28 September 2010, highly polluted air mass was observed in the T district under the influence of prominent westerly winds. Thus, we moved the DOAS setup (*i.e.*, the light source and detector) used for the UA district to the T district to conduct the double-path DOAS observation. As shown in **Figure 1(d)**, the path length was 460 m for the original DOAS path (path 1) along the down slope of Mount Oyama, while that was 480 m for the new path (path 2) along the periphery road.

Figures 9(a) and **(b)** show the 1-min average SO_2 concentration observed along the two DOAS paths and 10-min wind data observed at the JMA weather station, respectively, from 21:00 JST on 28 September to 03:00 JST on 29 September 2010. Although both path-1 and path-2 results exhibit temporal variations of SO_2 concentration similar to that of the ground sampling, it is seen that the path-1 values are always larger than the values from path-2, with a maximum difference of approximately 0.20 ppmv. Thus, the plume from the crater tends to spread along the slope of the mountain, and the path along the slope (path-1) shows higher concentration as compared with path-2. Nevertheless, noticeable concentration was also seen along path-2, because of the diffusion and advection effects on the scale of larger than a few hundred meters.

The correlation between the two DOAS paths is plotted in **Figure 9(c)** in order to examine the homogeneity of SO_2 distribution. As seen from this figure, the correlation between the two paths is fairly high, though generally the concentration of path 1 is higher than that of path 2, as already explained above.

5. Conclusions

The present paper has described the results of our DOAS observation in Miyakejima conducted in December 2009 and September 2010. During these observation periods, noticeable concentration of volcanic gas (SO_2) was seen in the T district in the eastern part of the island. In De-

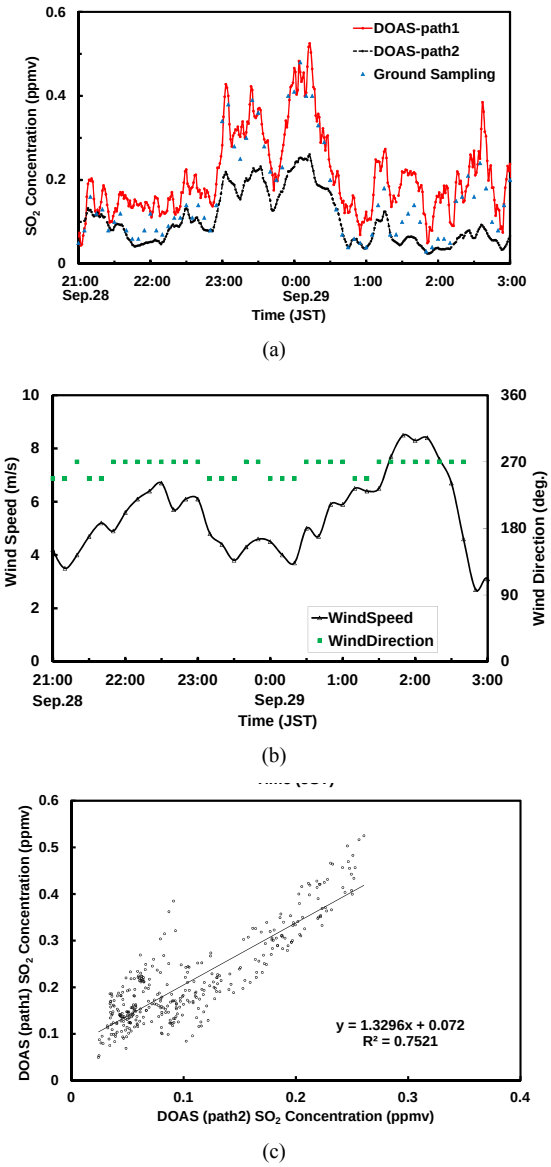


Figure 9. Result of the double-path DOAS observation conducted in the T district during 28-29 September 2010: (a) SO_2 concentration from the double-path DOAS and sampling measurements, (b) wind speed and wind direction, and (c) correlation between the two DOAS paths: one data point indicates the 5 min average for both paths.

cember 2009, a reasonable correlation was found between the result of the long-path measurement and the ground sampling data at the Miike station when the west wind was dominant. As such, high concentration of volcanic gas (SO_2) generally occurs leeward when strong winds blow from the volcano crater. The highest concentration of more than 1 ppmv, far exceeding the environmental standard of around 0.04 ppmv, was observed in the DOAS observation conducted in September 2010. In addition, our present observation has shown that low-level to mid-level concentration was often seen in the DOAS data even when no concentration was recorded in the ground sampling data. Since the DOAS data represent the concentration averaged over the corresponding light path length (460 m - 1300 m), it is likely that when the volcanic gas is conveyed along particular routes, it can happen that the DOAS method can detect the resulting pollution, though the pollution level is under the detection limit at a nearby sampling station. The result of the double-path DOAS observation has indicated that generally higher concentration was observed with the DOAS path along the slope of Mt. Oyama, also suggesting the orographic transport and diffusion of the volcanic gas.

The ground sampling stations are deployed on the periphery of the island for protecting the inhabitants from hazardous exposure to highly concentrated volcanic SO_2. For studying the possibility of restoration of the vegetation coverage, however, it would be required to monitor the spatial extent of the air pollution including the pasture, agriculture, and forest areas. The present work has shown that the methodology of DOAS can be useful as a sensitive method for implementing this latter type of continuous monitoring.

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REFERENCES

[1] T. Kamijo and K. Hashiba, "Island Ecosystem and Vegetation Dynamics before and after the 2000-Year Eruption on Miyakejima Island, Japan with Implications for Conservation of Island's Ecosystem," *Global Environmental Research*, Vol. 7, No. 1, 2003, pp. 69-78.

[2] A. Yamanishi, T. Kamijo, A. Tsunekawa and H. Higuchi, "Monitoring of Vegetation Damage Caused by the 2000 Miyake Island Volcanic Eruption Using Satellite Remote Sensing and Field Surveys," *Journal of Agricultural Meteorology*, Vol. 60, No. 6, 2005, pp. 1183-1188.

[3] I. Machida and S. Lee, "Delayed Impact of New Volcanic Ejecta on Ground Water Quality," *Ground Water*, Vol. 46, No. 4, 2005, pp. 532-538. doi:10.1111/j.1745-6584.2008.00452.x

[4] K. Kazahaya, H. Shinohara, K. Uto, M. Odai, Y. Naka-

hori, H. Mori, H. Iino, M. Miyashita and J. Hirabayashi, "Gigantic SO_2 Emission from Miyakejima Volcano, Japan, Caused by Caldera Collapse," *Geology*, Vol. 32, No. 5, 2004, pp. 425-428.

[5] Japan Meteorological Agency, "Monthly Volcanic Activity Report (January, 2012)," 2012. http://www.seisvol.kishou.go.jp/tokyo/eng/volcano_activity/2012/2012_01_monthly.pdf

[6] N. Iino, K. Kinoshita and T. Yano, "Regional Characteristics of High Concentration Events of Volcanic Gas at Miyakejima," *Japan Society for Natural Disaster Science*, Vol. 23, No. 4, 2005, pp. 505-520.

[7] T. Kamijo, M. Kawagoe, T. Kato, Y. Kiyohara, M. Matsuda, K. Hashiba and K. Shimada, "Destruction and Recovery of Vegetation Caused by the 2000-Year Eruption on Miyakejima Island, Japan," *Journal of Disaster Research*, Vol. 3, No. 3, 2008, pp. 226-235.

[8] Y. Yoshii, H. Kuze and N. Takeuchi, "Long-Path Measurement of Atmospheric NO_2 with an Obstruction Flash0-light and a Charge Coupled Device Spectrometer," *Applied Optics*, Vol. 42, No. 21, 2003, pp. 4362-4368. doi:10.1364/AO.42.004362

[9] F. Si, H. Kuze, Y. Yoshii, M. Nemoto, N. Takeuchi, T. Kimura, T. Umekawa, T. Yoshida, T. Hioki, T. Tsutsui and M. Kawasaki, "Measurement of Regional Distribution of Atmospheric NO_2 and Aerosol Particles with Flashlight Long-Path Optical Monitoring," *Atmospheric Environment*, Vol. 39, No. 27, 2005, pp. 4959-4968.

[10] K. Kuriyama, Y. Kaba, Y. Yoshii, S. Miyazawa, N. Manago, I. Harada and H. Kuze, "Pulsed Differential Optical Absorption Spectroscopy Applied to Air Pollution Measurement in Urban Troposphere," *Journal of Quantitative Spectroscopy & Radiative Transfer*, Vol. 112, No. 2, 2011, pp. 277-284. doi:10.1016/j.jqsrt.2010.06.010

[11] D. Perner, D. H. Ehhalt, H. W. Patz, U. Platt, E. P. Roth and A. Volz, "OH Radicals in the Lower Troposphere," *Geophysical Research Letters*, Vol. 3, No. 8, 1976, pp. 466-468. doi:10.1029/GL003i008p00466

[12] D. Perner and U. Platt, "Detection of Nitrous Acid in the Atmosphere by Differential Optical Absorption," *Geophysical Research Letters*, Vol. 6, No. 12, 1979, pp. 917-920. doi:10.1029/GL006i012p00917

[13] U. Platt and D. Perner, "Direct Measurements of Atmospheric CH_2O, HNO_2, O_3, NO_2 and SO_2 by Differential Optical Absorption in the Near UV," *Journal of Geophysical Research*, Vol. 85, No. C12, 1980, pp.7453-7458. doi:10.1029/JC085iC12p07453

[14] R. E. Stoiber, L. L. Malinconico and S. N. Williams, "Use of the Correlation Spectrometer at Volcanoes," In: H. Tazieff and H, J. C. Sabroux, Eds., *Forecasting volcanic events*. Elsevier, Amsterdam, 1983, pp. 425-444.

[15] P. Francis, C. Oppenheimer and D. Stevenson, "Endogenous Growth of Persistently Active Volcanoes," *Nature*, Vol. 366, No. 6455, 1993, pp. 554-557. doi:10.1038/366554a0

[16] K. Kazahaya, H. Shinohara and G. Saito, "Excessive Degassing of Izu-Oshima Volcano: Magma Convection in a Conduit," *Bulletin of Volcanology*, Vol. 56, No. 3, 1994, pp. 207-216. doi:10.1007/BF00279605

[17] P. Allard, "Endogenous Magma Degassing and Storage at Mount Etna," *Geophysical Research Letters*, Vol. 24, No. 17, 1997, pp. 2219-2222. doi:10.1029/97GL02101

[18] A. J. S. McGonigle, A. Aiuppa, M. Ripepe, E. P. Kantzas and G. Tamburello, "Spectroscopic Capture of 1 Hz Volcanic SO_2 Fluxes and Integration with Volcano Geophysical Data," *Geophysical Research Letters*, Vol. 36, No. 21, 2009, Article ID: L21309 doi:10.1029/2009GL040494

[19] J. Stix, G. Williams-Jones and C. Hickson, "Applying the COSPEC at Active Volcanoes," In: G. Williams-Jones, J. Stix and C. Hickson, Eds., *The COSPEC Cookbook*: *Making SO_2 Measurements at Active Volcanoes*, *IAVCEI*, *methods in volcanology*, Vol. 1, 2008, pp. 121-167.

[20] B. Galle, C. Oppenheimer, A. Geyer, A. McGonigle, M. Edmonds and L. A. Horrocks, "A Miniaturized Ultraviolet Spectrometer for Remote Sensing of SO_2 Fluxes: A New Tool for Volcano Surveillance," *Journal of Volcanology and Geothermal Reseach*, Vol. 119, No. 1-4, 2003, pp. 241-254. doi:10.1016/S0377-0273(02)00356-6

[21] L. A. Rodríguez, I. M. Watson, M. Edmonds, G. Ryan, V. Hards, C. M. M. Oppenheimer and G. J. S. Bluth, "SO_2 Loss Rates in the Plume Emitted by Soufriere Hills Volcano, Montserrat," *Journal of Volcanology and Geothermal Research*, Vol. 173, No. 1-2, 2008, pp. 135-147. doi:10.1016/j.jvolgeores.2008.01.003

[22] T. Mori and M. Burton, "The SO_2 Camera: A Simple, Fast and Cheap Method for Ground-based Imaging of SO_2 in Volcanic Plumes," *Geophysical Research Letters*, Vol. 33, No. 24, 2006, Article ID: L24804. doi:10.1029/2006GL027916

[23] G. J. S. Bluth, J. M. Shannon, I. M. Watson, A. J. Prata and V. J. Realmuto, "Development of an Ultra-Violet Digital Camera for Volcanic SO_2 Imaging," *Journal of Volcanology and Geothermal Research*, Vol. 161, No. 1-2, 2007, pp. 47-56. doi:10.1016/j.jvolgeores.2006.11.004

[24] M. P. Dalton, I. M. Watson, P. A. Nadeau, C. Werner, W. Morrow and J. M. Shannon, "Assessment of the UV Camera Sulfur Dioxide Retrieval for Point Source Plumes," *Journal of Volcanology and Geothermal Research*, Vol. 188, No. 4, 2009, pp. 358-366. doi:10.1016/j.jvolgeores.2009.09.013

[25] M. Edmonds, R. A. Herd, B. Galle and C. M. Oppenheimer, "Automated, High Time-Resolution Measurements of SO_2 Flux at Soufrière Hills Volcano, Montserrat," *Bulletin of Volcanology*, Vol. 65, No. 8, 2003, pp. 578-586. doi:10.1007/s00445-003-0286-x

[26] U. Platt, "Differential Optical Absorption Spectroscopy (DOAS)," In: M. W. Sigrist, Ed., *Air monitoring by spectroscopic techniques*, *Chemical Analysis Series*, Vol. 127. Wiley, New York, 1994, pp. 27-84.

[27] T. Miyazaki, "Features of Historical Eruptions at Miyakejima Volcano," *Volcanological Society of Japan*, Vol. 2, No. 29, 1984, pp. 1-15.

[28] N. Iino and C. Kanagaki, "Teaching Materials Using Volcanic Ejecta and Its Environmental Impact," *Kuma-*

moto University Repository System, Vol. 58, No. 1, 2009, pp. 45-53.

[29] Miyake Village Office. http://www.miyake-so2.jp/index.php

[30] J. P. Pommereau and F. Goutail, "O_3 and NO_2 Ground Based Measurement by Visible Spectrometry during Artic Winter and Spring 1988," *Geophysical Research Letters*, Vol. 15, No. 8, 1988, pp. 891-894.

[31] J. M. Plane and C. Nien, "Differential Optical Absorption Spectrometer for Measuring Atmospheric Trace Gases," *Review of Scientific Instruments*, Vol. 63, No. 3, 1992, pp. 1867-1876. doi:10.1063/1.1143296

[32] H. Edner, P. Ragnarson, S. Spannare and S. Svanberg, "Differential Optical Absorption Spectroscopy (DOAS) System for Urban Atmospheric Pollution Monitoring," *Applied Optics*, Vol. 32, No. 3, 1993, pp. 327-333. doi:10.1364/AO.32.000327

[33] A. C. Vandaele, P. C. Simon, J. M. Guilmot, M. Carleer and R. Colin, "SO_2 Absorption Cross Section Measurement in the UV using a Fourier Transform Spectrometer," *Journal of Geophysical Research*, Vol. 99, No. D12, 1994, pp. 25599-25605. doi:10.1029/94JD02187

