J. KOSAE Vol. 22, No. E 2 (2006) pp. 69~77
Journal of Korean Society for Atmospheric Environment

# High Atmospheric Loading for $SO_2$ and Sulfate Observed in the Kanto Area, Japan During the Miyakejima Volcanic Eruption

**Chang-Jin Ma*, Renqiu Cao[1)], Susumu Tohno[1)] and Mikio Kasahara[2)]**
*Department of Environmental Science, Fukuoka Women's University, Fukuoka, Japan*
[1)]*Graduate School of Energy Science, Kyoto University, Kyoto, Japan*
[2)]*Institute of Science and Technology Research, Chubu University, Aichi, Japan*

(Received 1 September 2006, accepted 13 December 2006)

## Abstract

Combined gas and aerosol measurements at a downwind area of the volcanic plume would be essential for helping to access the impact of the volcanic eruption on the local ecosystem and residents. An intensive and the fine time resolution measurement of $SO_2$, sulfate and PM2.5 was made to estimate their distribution in the Kanto area of Japan during the Miyakejima volcanic eruption period. In Tokyo, the 1 hr average $SO_2$ concentration observed before the eruption was 23.9 ppbv, while that of after eruption was 140.4 ppbv. In the Saitama Prefecture, the average concentration of $SO_2$ marked in the present study was two times higher than the average before the volcanic eruption. The PM2.5 mass concentrations in Sitama ranged from 3.8 to 136 $\mu g\ m^{-3}$. Sulfate accounts for 4.4~39.6% of PM2.5 in Sitama. The good correlationship between the concentrations of $SO_2$ and sulfate was obtained. The results of the VAFTAD and HYSPLIT models indicate that $SO_2$, sulfate, and PM2.5 measured in the present study would be expected to be significantly affected by the Miyakejima volcanic plume.

**Key words** : Miyakejima, Volcano, $SO_2$, Sulfate

## 1. INTRODUCTION

Miyakejima (Fig. 1) is an island in the Izu group, southeast of Honshu, Japan. Miyakejima has a population of 3,800 people over an area of 55.5 $km^2$. Miyakejima (34°04′N, 139°31′E) is also one of the most active volcanoes in Japan. It has erupted several times in recent history.

On July 14, 2000, Mount Oyama (813 m) began another series of eruptions, and by September, the island was completely evacuated. After a four-year period of volcanic emissions, residents were allowed to return permanently on February 1, 2005.

The high atmospheric loading for $SO_2$ was frequently observed in the volcanic period because of the large amount of $SO_2$ emission from the Miyakejima (Iino and Terada, 2003). The effects of $SO_2$ on people and the environment become worse, in particular under the wintertime metrological condition. During wintertime, a temperature inversion occurs frequently when cold air close to the ground is trapped by a layer of warmer air. As the

* Corresponding author. Tel : +81-92-661-2411(ext. 373),
Fax : +81-92-661-2415, E-mail : ma@fwu.ac.jp

inversion continues, air becomes stagnant and air pollutants are trapped close to the ground.

The purpose of the present study is to characterize $SO_2$, sulfate, and PM2.5 measured in the Kanto area, Japan during the Miyakejima volcanic eruption.

## 2. MATERIAL AND METHODS

An intensive measurement of $SO_2$, sulfate, and PM2.5 was conducted at the Oukubo in Saitama, which is 200 km away from Miyakejima, from 21 November to 26 November 2001. Location of measurement site indicated by a filled circle is given in Fig. 1.

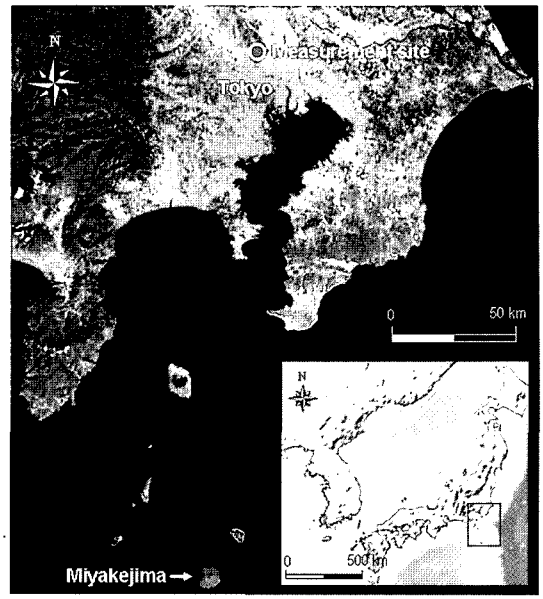



**Fig. 1. Map showing the Miyakejima and the Saitama measurement site.**

For the real-time measurements of ambient $SO_2$ and the particulate sulfate contained in fine particulate matter (PM2.5), the Series 8400S Ambient Particulate Sulfate Monitor (R & P) was operated. This monitoring instrument provided 15-minute average of the ambient particulate sulfate concentration for us. PM2.5 was also collected on an impactor surface that is heated to a high volatilization temperature every 15-minute. A 5 L/min inlet flow passes a PM2.5 cyclone and an activated carbon denuder. A 1 L/min part of the flow passes a Nafion humidifier and an impactor, where the wetted particles impact onto a platinum strip. After accumulation of particles over a time period of 5 to 10 minutes, the particles on the strip are flash evaporated by fast resistive heating of the strip. The resulting $SO_2$ is detected by fluorescence detection in the Pulse Analyzer. Typically five- or ten-minute averages of the PM2.5 sulfate concentration are determined from the measured $SO_2$ concentration.

The tapered element oscillating microbalance (TEOM®, Series 1400a) monitor measured the mass concentration of PM2.5 in real time. In recent years, the TEOM® is one of instruments widely adopted for the continuous measurement of ambient particulate matters. The TEOM® operates under the following principles. Ambient air is drawn in through a heated inlet. It is then drawn through a filtered cartridge on the end of a hollow, tapered tube. The tube is clamped at one end and oscillates freely like a tuning fork. As particulate matter gathers on the filter cartridge, the natural frequency of oscillation of the tube decreases. The mass accumulation of particulate matter is then determined from the corresponding change in frequency. Mass concentration data are reported in micrograms per cubic meter at standard averaging time of 15 minute.

During the field measurement period, the range of wind speed was $1 \sim 3\ m\ s^{-1}$ and it was generally blowing from the southeast. The temperature and relative humidity were around $4.0 \sim 19.5°C$ and $32 \sim 53\%$, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1 Distribution of $SO_2$ in Tokyo

Fig. 2 shows the general monitoring sites of atmospheric environmental measurement marked higher $SO_2$ concentration than 100 ppbv in Tokyo on November 23, 2001. These monitoring sites are 180 km faraway from Miyakejima and distributed with-

in a 15 km radius.

Data are 1 h average $SO_2$ concentrations provided by the National institute for environmental studies, Japan. Monitoring of $SO_2$ was performed by $SO_2$ analyzer (DKK, GFS-32). Typical measuring range of $SO_2$ analyzer is 0~50 ppm with ±2% accuracy of full scale.

High abundance of $SO_2$ (higher than 100 ppbv) was observed at 8 sites among total 49 general monitoring sites. Especially, 5 sites (Sinagawaku, Outaku, Chiyodaku, Chuouku, and Minatoku) located at the southeast part of Tokyo show relatively higher $SO_2$ concentration.

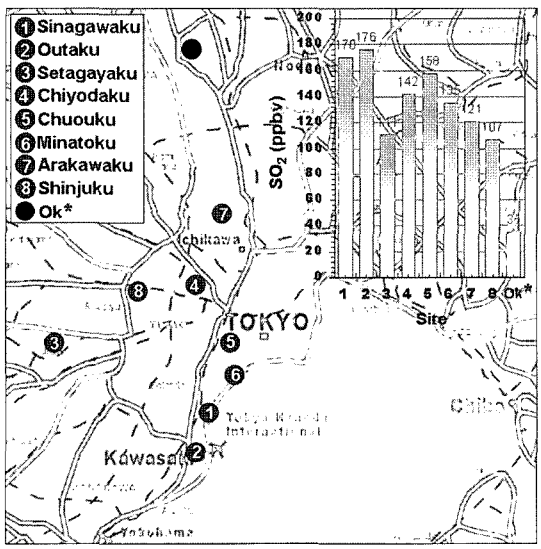



**Fig. 2. General monitoring sites marked higher $SO_2$ concentration than 100 ppbv in Tokyo on Nov. 23, 2001. Data are 1 h average $SO_2$ concentrations provided by the National Institute for Environmental Studies, Japan. *Okubo in Saitama**

To estimate the variation of $SO_2$ concentration by volcanic emission, Table 1 summarizes $SO_2$ concentration measured at 8 general monitoring sites in Tokyo before and after volcanic eruption. The data of $SO_2$ concentrations were also provided by the National institute for environmental studies, Japan. Since the volcanic eruption of the Miyakejima began on July 14, 2000, the data of 1 day and 1 h average $SO_2$ concentrations measured in November, 1999 were compared to those measured in November, 2001. In the case of data averaged on a day, the $SO_2$ average concentration of 8 sites measured after eruption was roughly 3 times higher than those before the eruption. In particular, $SO_2$ concentration of the site number 4 (Chiyodaku) increased 5 times after volcanic eruption.

In the present study, a t-test was conducted to determine whether the means of two populations, which were designed by the maximum level of 1 day average $SO_2$ concentration before and after eruption, are statistically different from each other. The null hypothesis for the t-test is that the means are homogeneous. As a result of t-test, the 95% confidence interval ranges (from −0.205 to −0.095) does not include zero, so the null hypothesis can be rejected. This indicates that the two means are significantly different from each other.

On the other hand, the maximum $SO_2$ concen-

**Table 1. $SO_2$ concentration measured at 8 General monitoring sites in Tokyo before and after volcanic eruption. The data of $SO_2$ concentrations were provided by the National Institute for Environmental Studies, Japan.**

| Site No.[a] | Maximum of 1 day average (ppbv) | | | Maximum of 1 h average (ppbv) | | |
|---|---|---|---|---|---|---|
| | Before eruption[a] | After eruption[c] | c/b | Before eruption[b] | After eruption[c] | c/b |
| 1 | 11 | 33 | 3.0 | 28 | 170 | 6.1 |
| 2 | 11 | 28 | 2.5 | 21 | 176 | 8.4 |
| 3 | 10 | 19 | 1.9 | 21 | 111 | 5.3 |
| 4 | 6 | 30 | 5.0 | 16 | 144 | 9.0 |
| 5 | 13 | 34 | 2.6 | 34 | 158 | 4.6 |
| 6 | 15 | 32 | 2.1 | 33 | 136 | 4.1 |
| 7 | 7 | 26 | 3.7 | 17 | 121 | 7.1 |
| 8 | 11 | 23 | 2.1 | 21 | 107 | 5.1 |

[a]: Site numbers in Fig. 2; [b]: Nov. 1999; [c]: Nov. 2001

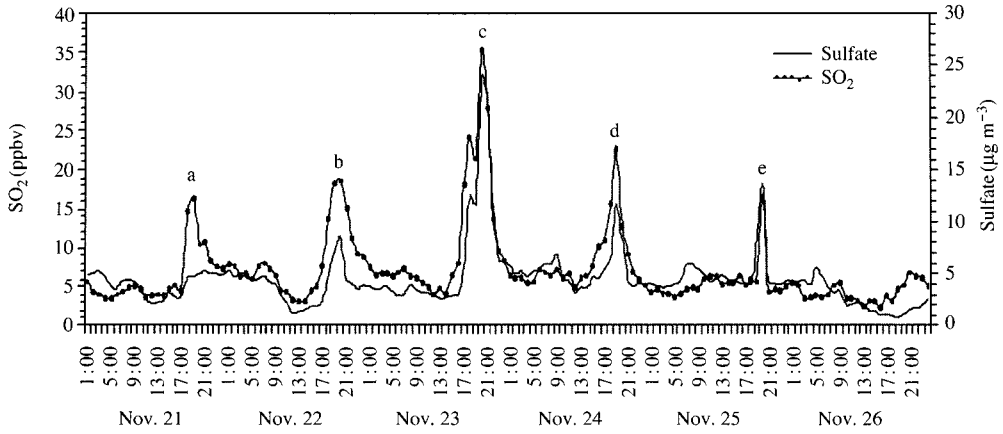



**Fig. 3. Time series variations of $SO_2$ and sulfate concentration from Nov. 21 to Nov. 26, 2001. The measurements were performed at Saitama.**

tration averaged on an hourly shows severe atmospheric loading for every site. The average 1 h $SO_2$ concentration observed before the eruption was 23.9 ppbv, while that of eruption period was 140.4 ppbv. From this result, it can be considered that though large eruption has not occurred since the largest eruption at Aug. 18, 2000, small explosions continuously occurred. As a result, a significant amount of gases, especially $SO_2$, was loaded in Kanto area.

### 3.2 Time series variations of $SO_2$, sulfate, and PM2.5 in Saitama

Fig. 3 displays the time-resolved concentrations of $SO_2$ and sulfate at an intensive measurement site of Oukubo, Saitama from November 21 to November 26, 2001. Both $SO_2$ and sulfate concentrations indicate a strong time serial fluctuation during full measurement period. The concentration of $SO_2$ was varied from 2.4 to 35.3 ppbv with an average of 7.2 ppbv. Sulfate was in the range of 0.9 to 23.8 μg $m^{-3}$ with an average of 4.5 μg $m^{-3}$. The average concentration of $SO_2$ (7.2 ppbv) ranked in the present study was two times higher than that (3.6 ppbv) monitored at 45 sites in the Saitama Prefecture before volcanic eruption (November 1999) (The environmental data base of the National institute for environmental studies (http://www.nies.go.jp/igreen/td_disp.html)).

Five-case of episodes (from a to e in Fig. 3) showing higher $SO_2$ concentration than 15 ppbv were happened. As shown in Fig. 3, though the peak "a" is not like others, most of the peaks for $SO_2$ were regularly found between 17:00 and 21:00 throughout sampling duration. As stated by Ma *et al.* (2004), there was no regularly high loading of $SO_2$ in another urban area of Kansai, Japan in the same season. Therefore, we cannot conclude that the periodical high abundance of $SO_2$ in the present study is the typical urbanic time series variation of $SO_2$. Moreover, the remarkable peaks of sulfate between 17:00 and 21:00 in the present study can be comparable to the time-resolved sulfate concentration measured at another coastal site in same season. According to the research performed by Danalatos and Glavas (1999) at the Mediterranean coastal site of Greece, there was no outstanding peak of sulfur concentration between 17:00 and 21:00. Consequently, the periodical high atmospheric loading of sulfate found in the present study may not the typical phenomenon of coastal region. As mentioned above, though a similar fluctuation of $SO_2$ concentration in another urban site of Japan, as one of possibilities of this periodically (between 17:00 and 21:00) high sulfur concentration, a meteorological phenomenon can be considered. Pollutants tends to be trapped in the nocturnal boundary layer, which forms when the solar heating ends and the radiative cooling and

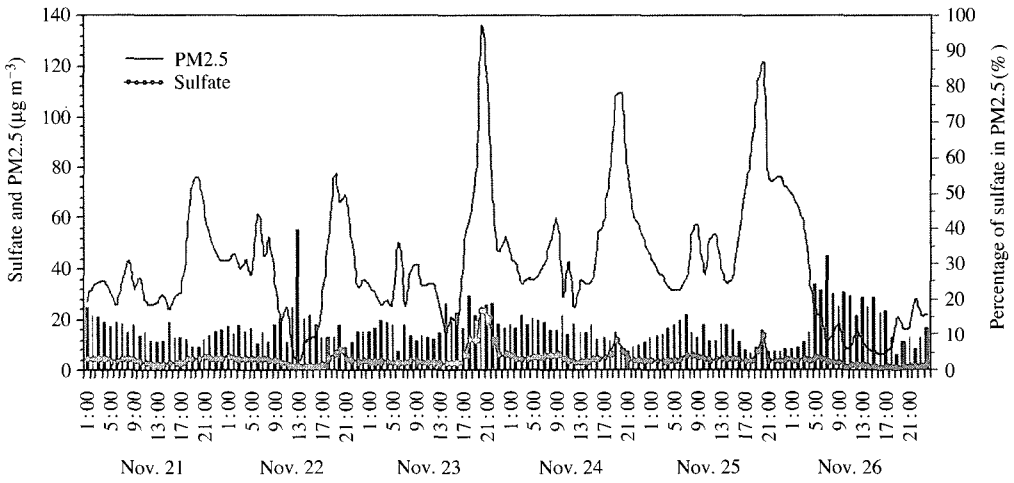



**Fig. 4. Time series variations of PM2.5 and sulfate concentration measured at Saitama from Nov. 21 to Nov. 26, 2001. Bars mean the percentage of sulfate to PM2.5.**

surface friction stabilize the lowest part of the atmospheric boundary layer. Therefore $SO_2$ from the local and volcanic sources accumulated and was oxidized to sulfate.

In the case of sulfate, the calculated residence time is generally estimated to be between 2.7 and 7.2 days (Seinfeld and Pandis, 1998). Thus particulate sulfate would be expected to be influenced by long-range transport from other far way regions (Luria *et al.*, 1996). Also, the oceanic emissions of dimethyl sulfide (DMS: $CH_3SCH_3$) are known to be a major primary source of natural sulfur in the remote marine atmosphere (Bates *et al.*, 1987). Thus when air masses were originated from Pacific Ocean, sulfate aerosol as the oxidation product of DMS probably contributed to the mass concentration of sulfate.

Fig. 4 presents the temporal variation of PM2.5 and sulfate concentrations measured at Saitama from November 21 to November 26, 2001. The percentage of sulfate in PM2.5 also indicated as bars in Fig. 4. The range of PM2.5 concentration is between 3.8 and 136 μg $m^{-3}$ with an average of 41.9 μ $m^{-3}$. Average PM2.5 concentrations in the day time (07:00 ~ 17:00) and in the night time (18:00 ~ 06:00) were varied from 10.9 to 45.7 μg $m^{-3}$ and from 43.9 to 68.1 μg $m^{-3}$, respectively. Night time average PM2.5 concentration (57.2 μg $m^{-3}$) was higher than day time average PM2.5 concentration (30.2 μg $m^{-3}$).

The time series fluctuation of PM2.5 was roughly accorded with that of sulfate. Moreover, the predominant peaks are still occurred between 17:00 and 21:00 in everyday throughout the whole duration of monitoring. Therefore, an overall increase in PM2.5 during an intensive measurement might be associated with sulfate formed by the Miyakejima volcanic activities.

Chuersuwan *et al.* (2000) evaluated the time-resolved PM2.5 data in urban area of New Jersey that is the most densely populated in the United States. They reported that a pronounced peak of PM2.5 between 06:00 ~ 09:30 was noticeable in winter. Hence, the periodical high abundance of PM2.5 exhibited in the present study may not the typical pattern of urban area in wintertime.

Fig. 5 shows the plotting of $SO_2$ versus sulfate (a) and of sulfate versus PM2.5 (b). There is a good correlationship between $SO_2$ and sulfate with 0.7 $R^2$ level. Elsewhere, as mentioned earlier, with the exception of the case of "a" in Fig. 3, most of the peaks for $SO_2$ were in accord with those of sulfate for the whole duration of monitoring. Hence, it can be reasonably suggested that $SO_2$ was the precursor of sulfate. In other words, the sulfate concentration

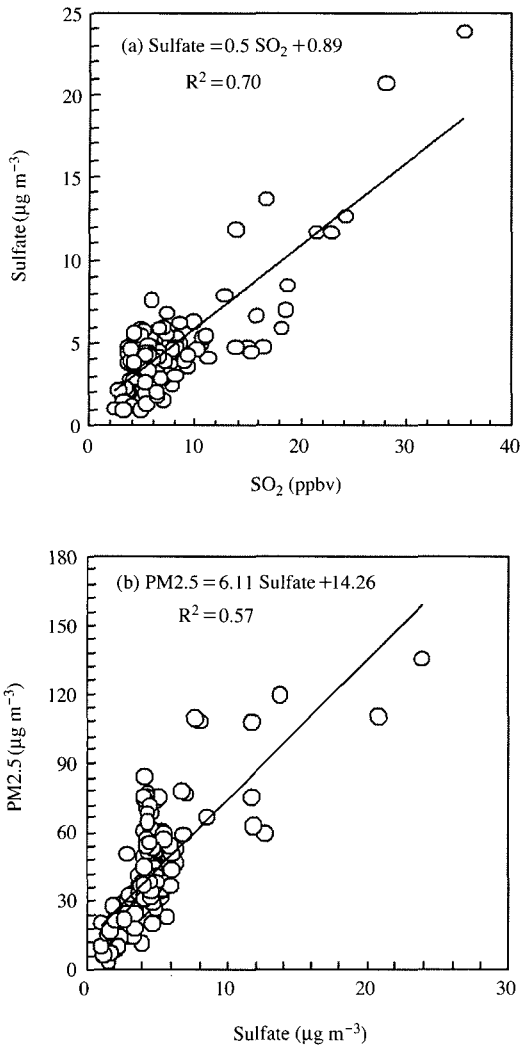
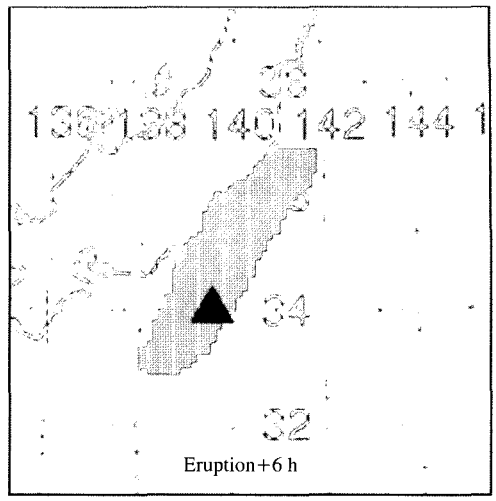
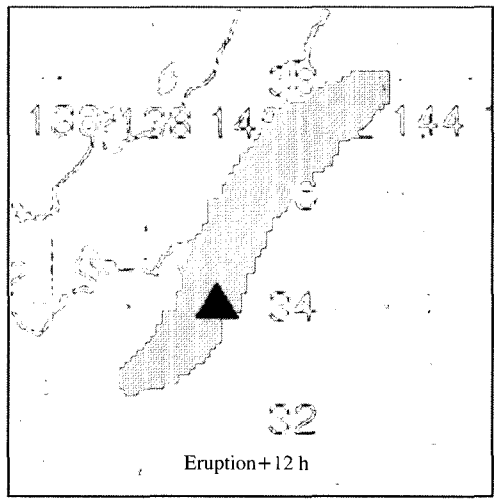



**Fig. 5. Plotting of $SO_2$ vs. sulfate (a) and of sulfate vs. PM2.5 (b).**




FL: SURFACE-200




FL: SURFACE-200

**Fig. 6. The forecast volcanic visual ash cloud simulated by the NOAA ARL 3-dimensional VAFTAL model. FL range means the upper and lower flight level.**

may be partly explained by the existence of high abundance of $SO_2$ at the measurement site in the present study.

Sulfate derives mainly from the emission of $SO_2$ followed by oxidation in the atmosphere to form sulfate aerosol. The characteristic times of the processes of formation and removal of sulfate and $SO_2$ are one to several days, so the geographical distribution of sulfate is confined principally to source regions and to regions within a few days transport distance from these sources (Carmen *et al.*, 2001).

Since the $SO_2$ lifetime is about half a day or less (Gillani *et al.*, 1981), through the conversion of $SO_2$ gas to sulfate predominantly by oxidation in moisture volcanic fog, sulfate particles might be transported from the volcanic vent to the Kanto area.

On the other hand, the fact that the $SO_2$ half life

values up to 69 hours (Lusis *et al.*, 1978) and down to 1.9 hours (Mezaros *et al.*, 1977) have been reported. Thus, the episodically high $SO_2$ concentration showing higher than 100 ppbv at 8 monitoring sites located in southern part of Tokyo can be also affected by the result of volcanic originated $SO_2$ dispersion.

The bars exhibited in Fig. 4 suggest that sulfate accounts for major fraction of fine particle. The hourly average sulfate comprises 4.4~39.6% of PM2.5 mass concentration. The correlationship between sulfate and PM2.5 was marked $R^2$ level of 0.57 in Fig. 5.

### 3.3 Volcanic aerosol transport and dispersion

In order to estimate the volcanic ash transport and dispersion in the atmosphere, the National Oceanic Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) developed the time dependent 3-dimensional Volcanic Ash Forecast Transport And Dispersion (VAFTAD) model (http://www.arl.noaa.gov/ready/) was run. The VAFTAD calculates transport and dispersion of volcanic ash from an ash column extending from the volcano summit to the column top. This model uses spherical particles of density $2.5*10^6$g $m^{-3}$ with diameter ranging from 0.3 to 30 microns (Heffter and Stunder, 1993). Fig. 6 displays the result of the simulated forecast volcanic visual ash cloud. As the input data for model calculation, eruption time, coordinates (start point), and height of source were 18:00 23 November 2001, 34°04′43″N; 139°31′46″E and 4900 feet, respectively. The model computation of the visual ash cloud includes the magnitude of the volcanic eruption as determined by an algorithm based on the ash column top height and column depth. A detailed model description of the VAFTAD was given by Heffter and Stunder (1993). As shown in Fig. 6, the time dependent (6h after eruption (left) and 12h after eruption (right)) volcanic ash cloud dispersion is displayed. The VAFTAD simulation result (SURFACE-200) indicates that the volcanic ash flume bounds for the Kanto area after eruption. Thus the region of Saitama could be affected by the volcanic ash flume. After passing through the Kanto area, it tends toward the northeast.

In addition to VAFTAD model simulation, NOAA HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) dispersion-trajectory model "forwards" (http://www.arl. noaa.gov/ready/) was run. Fig. 7 displays the result of simulated forward aerosol dispersion. Source (start point) was 34° 04′43″N, 139°31′46″E. In Fig. 7, the area scales mean the concentration (mass (ton) $m^{-3}$) averaged between height 10~1,500 m. Since, very close to the ground, the aerosol concentration can be affected by ground surface, the integrated height level was decided from 10 m to 1,500 m. The maximum altitude (1,500 m) is the height of volcanic plume observed by the University of Tokyo. The integrated duration times are 18:00~20:00 on 23 November (UTC), 20:00~22:00 on 23 November (UTC), and 22:00 on 23~00:00 on 24.

According to the results of both VAFTAD (FL

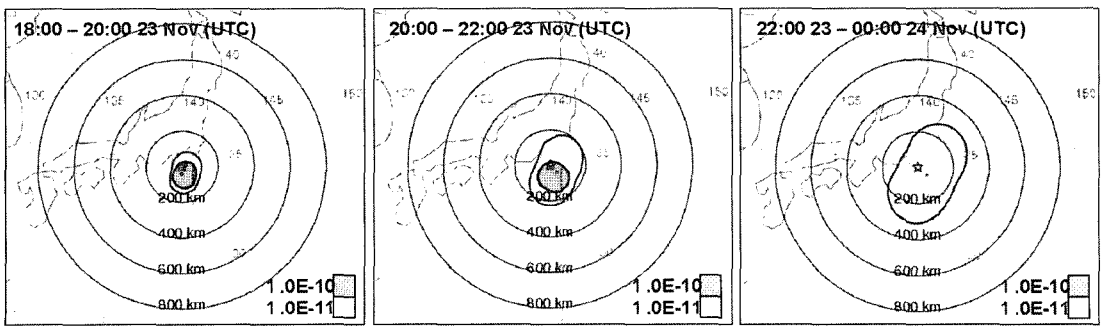



**Fig. 7. Forward aerosol dispersion simulated by the NOAA HYSPLIT dispersion-trajectory model.**

SURFACE-200) and HYSPLIT models, on November 23, the volcanic aerosols were extended to the Kanto area. Thus, $SO_2$, sulfate, and PM2.5 monitored at the measurement site (Oukubo, Saitama) of the present study would be expected to be affected by the volcanic aerosols originated from the Miyakejima.

## 4. CONCLUSIONS

This study was intended as an investigation of the atmospheric distribution of volcanic derived $SO_2$ and sulfate in the Kanto area, Japan during the Miyakejima volcanic eruption. The $SO_2$ concentration higher than 100 ppbv was measured at the wide-spread southern part of Tokyo on November 23, 2001 when small explosions continuously were occurred. The $SO_2$ average concentration of 8 monitoring sites in Tokyo was higher roughly 3~5 times than before the eruption. The pattern of time series variation for sulfate was perfectly accorded with that of $SO_2$. The results of simulated model indicate that the volcanic flume was transported to the Kato area. The fine time-resolved data for $SO_2$ and sulfate concentrations allow us not only to identify episodes, but also to determine trends in real time.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT and VAFTAD models and/or READY website (http://www.arl. noaa.gov/ready. html) used in the present study. The model results of both HYSPLIT and VAFTAD were very helpful to data interpretation. The monitoring result for $SO_2$ concentrations provided by the National institute for environmental studies, Japan was also an effective means to estimate the regional distribution of $SO_2$ concentrations in Tokyo.

## REFERENCES

Bates, T.S., J.D. Cline, R.H. Gammon, and S.R. Kelly-Hansen (1987) Regional and seasonal variations in the flux of oceanic dimethyl sulfide to the atmosphere, Journal of Geophysical Research, 92, 2930-2938.

Carmen, M., C.M. Benkovitz, M.A. Miller, S.E. Schwartz, and O.U. Kwon (2001) Dynamical influences on the distribution and loading of $SO_2$ and sulfate over North America, the North Atlantic, and Europe in April 1987, Geochemistry, Geophysics, Geosystems 2, 2000GC000129.

Chuersuwan, N., B.J. Turpin, and C. Pietarinen (2000) Evaluation of time-resolved PM2.5 data in urban/suburban areas of New Jersey, Journal of the Air & Waste Management Association, 50, 1780-1789.

Danalatos, D. and S. Glavas (1999) Gas phase nitric acid, ammonia and related particulate matter at a Mediterranean coastal site, Patras, Greece, Atmospheric Environment, 33, 3417-3425.

Gillani, N.V., S. Kohli, and W.E. Wilson (1981) Gas-to particle conversion of sulfur in power plant plumes: I. Parametrization conversion rate for dry, moderately polluted ambient conditions, Atmospheric Environment, 15, 2293-2314.

Heffter, J.L. and B.J.B. Stunder (1993) Volcanic ash forecast transport and dispersion (VAFTAD) model, Wea. Forecasting, 8, 534-541.

Iino, N. and A. Terada (2003) Analysis of high volcanic gas concentrations at the foot of Miyakejima volcano, Japan, Journal of National Disaster Science, 25, 85-91.

Luria, M., M. Peleg, G. Sharf, D.S. Tov-Alper, N. Spitz, Y. BenAmi, Z. Gawii, B. Lifschits, A. Yitzchake, and I. Seter (1996) Atmospheric sulfur over east Mediterranean region. Journal of Geophysical Research, 101, 25917-25930.

Lusis, M.A., K.G. Anlauf, L.A. Barrie, and H.A. Wiebe (1978) Plume chemistry studies at a northern Alberta power plant, Atmospheric Environment, 12, 2429-2437.

Ma, C.-J., Y. Oki, S. Tohno, and M. Kasahara (2004) Assessment of wintertime atmospheric pollutants in an urban area of Kansai, Japan, Atmos-

pheric Environment, 38, 2939-2949.

Mezaros, E., D.J. Moore, and J.P. Jr. Lodge (1977) Sulfur dioxide-sulfate relationships in Budapest, Atmospheric Environment, 11, 345-11-11,351.

Seinfeld, J.H. and S.N. Pandis (1998) Atmospheric Chemistry and Physics, John Wiley & Sons, Inc., pp. 51-66.

The environmental data base of the National Institute for Environmental Studies, (http://www.nies.go.jp/igreen/td_disp.html).