

# Effects of Miyakejima Volcanic Effluents on Airborne Particles and Precipitation in Central Japan

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## Synopsis

Miyakejima volcano began to erupt from 8 July 2000 which is located in the Northwest Pacific Ocean and 200 km south from Tokyo Metropolitan area. Its  $\text{SO}_2$  emission amounted to the maximum  $6 \times 10^4$  ton/day which was about the same level as the anthropogenic emission of China (54,800 ton/day) and twenty times larger than Japanese one (3,120 ton/day), and is decreasing to  $10^4$  ton/day. Aerosol and precipitation, together with gaseous pollutants have been observed from two years before the eruption to present on a prominent mountain ridge, Happo ridge (1850m ASL and 330 km north from the volcano), presuming them to be representative of the mid-troposphere air quality over central Japan. Short time sampling of aerosols was made for three hours every day, while four-hours sampling was done consecutively in the intensive observation periods. One-day collection was made for precipitation and every one-hour monitoring was done for  $\text{SO}_2$ , NO,  $\text{NO}_2$  and  $\text{O}_3$ , and PM10. Water-soluble inorganic species,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  in the aerosol and precipitation were analyzed.

Annual mean concentration of  $\text{SO}_2$  was increased 3.8 times and those of  $\text{SO}_4^{2-}$  were 1.5 and 1.6 times in aerosol and precipitation. Because of the excess amount of  $\text{SO}_4^{2-}$  formation, driving out  $\text{NO}_3^-$  and  $\text{Cl}^-$ , it took their place in the aerosol, and sometimes existed as sulfuric acid mist after exhausting ammonium gas. It makes the aerosol at pH values less than 1 and partitioned into  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$ . These facts were explained successfully by a multi-component gas-aerosol equilibrium.

**Keywords:** acidification, aerosol and precipitation, volcanic effects, gas-aerosol equilibrium, mid troposphere

## 1. Introduction

Miyakejima volcano began to erupt from 8 July 2000. It is 800 m high ASL and located in the Northwest Pacific Ocean and 200 km south from Tokyo Metropolitan area. Its  $\text{SO}_2$  emission amounted to the maximum  $6 \times 10^4$  ton/day which was about the same level as the anthropogenic emission of China (54,800 ton/day) and twenty

times larger than Japanese one (3,120 ton/day), and is decreasing to  $10^4$  ton/day (Kanno, 2002). Such a large emission has not been experienced in the Northeast Asia and every inhabitant has been evacuated from Miyakejima Island. Since it is not so far from Tokyo Metropolitan area, it has been causing severe air pollution in central Japan, episodically  $\text{SO}_2$  concentration being more than 300 ppb in Tokyo and its surroundings. Thus, the

volcanic emission is considered to cause severe influences also on the regional scale, and result in the acceleration of environmental acidification.

The purpose of this paper is to elucidate the effects of volcanic effluents on the atmospheric aerosols and precipitation. Aerosol and precipitation, together with gaseous pollutants have been observed from two years before the eruption to present on a prominent mountain ridge, Happo ridge (1850m ASL and 330 km north from the volcano), presuming them to be representative of the mid-troposphere air quality over central Japan. Since Happo ridge is a prominent ridge in the Central Mountainous region of which area is 150km×200km and is about 1000m high, the atmosphere at this level is stably stratified and the air quality may be generally regarded as the representative of that in the mid troposphere. Thus, a special attention was focused on the aerosol and precipitation in this mid troposphere.

Since volatile inorganic components in the aerosols are also important in the environmental acidification and eutrophication, short time sampling of aerosols was made for three hours every day, while four-hours sampling was done consecutively in the intensive observation periods. One-day collection was made for precipitation and every one-hour monitoring was done for gaseous pollutants and PM10. Water-soluble inorganic species,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  in the aerosol and precipitation were analyzed.

## 2. Observation

### 2.1 Observation site and sampling period

The observation was made at Happo Ridge National Acid Rain Monitoring Station which is sited at 1850m ASL, 36.69° N, 137.80° W, in the Central Mountainous area in central Japan. It is located 300 km north from the volcano and more than 200 km from large industrial and urban areas, Tokyo metropolitan area and Nagoya area, as illustrated in Figure 1. Aerosol and rain/snow, together with gaseous pollutants and PM10 were monitored/sampled on the roof of the monitoring station at 3m high from the ground. The moni-

toring station is surrounded by nude place, grassland and shrub zone of *pinus pumila* and there is no emission in less than 2 km range. In addition, the nearest village is 5 km east and 700m ASL.

Aerosol and precipitation, together with gaseous pollutants have been observed from two years before the eruption to present, i.e., May 1998. Short time sampling of aerosols was made from 12:00 to 15:00 LST every day, while four-hours sampling was done consecutively four times/day starting from 0:00 in the intensive observation periods. One-day collection was made from 9:00 LST for precipitation and every one-hour monitoring was done for  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{O}_3$ , and PM10.

Water-soluble inorganic species,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  in the aerosol and precipitation were analyzed. Volcanic pollutants are transported mainly in the free troposphere for long distances and sometimes diffused downward into the planetary boundary layer.

### 2.2 Sampling method and chemical analysis

Aerosol was collected on the polyflon tape filter (Sumitomo, Type WP-500-50, 100mm wide and 10m long) at a flow rate of 150 l/min by means of an automatic tape air sampler (Kimoto, Model-195A). Four-hours sampling was performed consecutively during the intensive observation periods, from 4 to 16 September 2000 and from 15 May to 11 June 2001, while three-hrs. sampling from 12:00 to 15:00 LST every day was made in the other period. Such a short term sampling is essential to investigate volatile components like  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{NH}_4^+$  in aerosols. The precipitation collection was made consecutively for every 24 hrs, starting from 9:00 to the next 9:00 LST by an automatic wet-only precipitation collector (Ogasawara, US-420). The aerosol and precipitation samples were stored in the freezer and refrigerator, respectively.

Aerosol sampling filter was dipped in 30 ml pure water and water-soluble aerosol species were extracted by a vibrator for 1 hr. After filtering it by membrane filter (Millipore HAWP02500), water-soluble inorganic species,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,

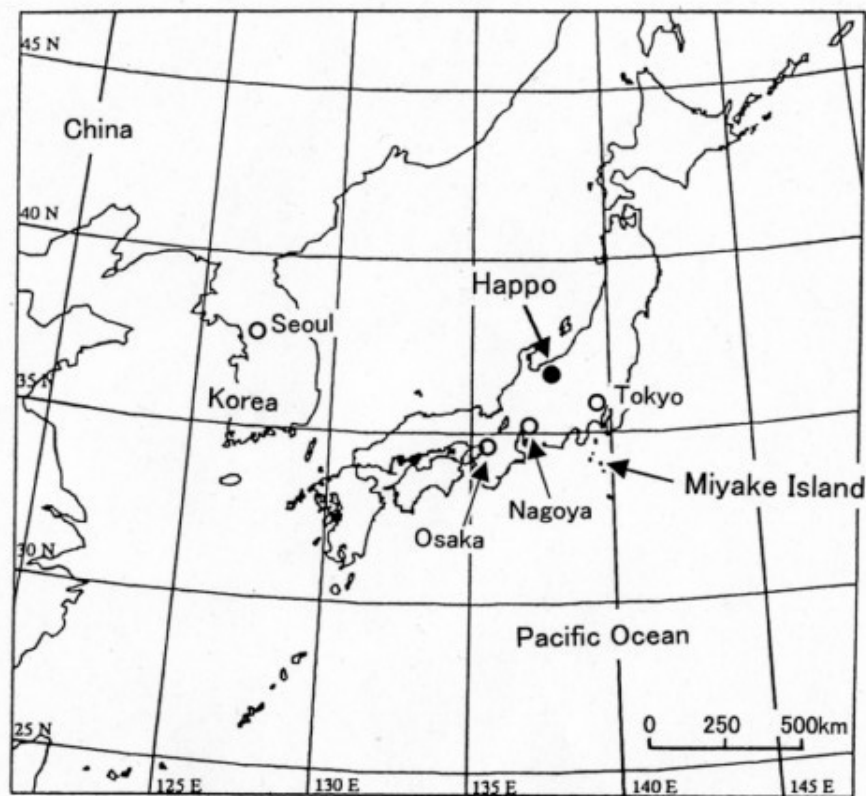


Fig. 1 : Map showing site, Happo and other locations mentioned in the text.

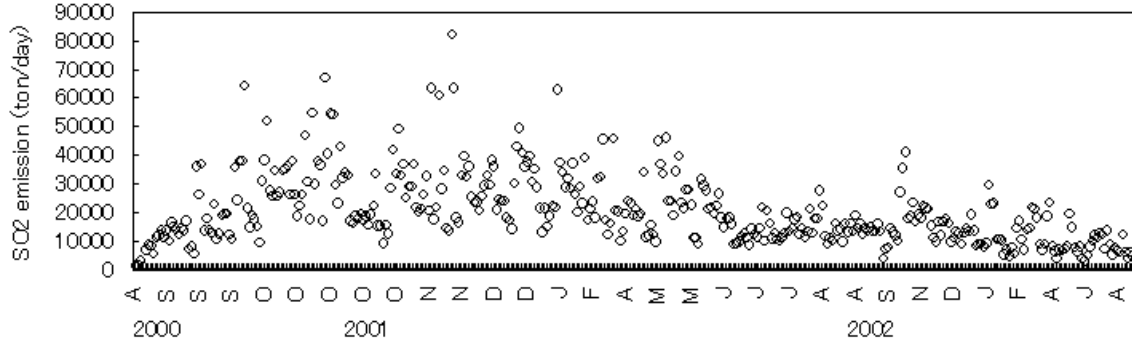
$\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and oxalic acid in the extract were determined by ion-chromatography (Dionex, DX-120 and 4000i). Conversion of the weight concentrations at 810 hPa were done to that at 1013 hPa. Precipitation samples were also filtrated by membrane filter (Millipore AAWP04700), the water-soluble components were determined in the same way as that for aerosol.

At the same time gaseous pollutants, such as  $\text{SO}_2$ , NO,  $\text{NO}_2$  and  $\text{O}_3$ , and PM10 were monitored every one hour.  $\text{SO}_2$  was analyzed by ultraviolet fluorescence method (Thermo Electron, Model 43C-TL), NO,  $\text{NO}_2$  by chemical luminescence method (Thermo Electron, Model 42C-TL),  $\text{O}_3$  by ultraviolet absorption method (Thermo Electron, Model 49C) and PM10 by  $\beta$ -ray absorption method (Thermo Electron, Model FH 62-C14).

### 3. Multicomponent gas aerosol equilibrium model

Atmospheric aerosols are generally multicomponent particulates and are composed of water-soluble inorganic compounds, organic carbons, elemental carbon, trace metals and water. Of these components, volatile inorganic components such as nitrate, chloride and ammonium are particularly important together with sulfate in the environmental acidification and eutrophication.

Since their partitioning between gas and aerosol phases will be changed significantly when the volcanic effluents are added, a multicomponent gas aerosol equilibrium model (Kim et al., 1993a, 1993b; Kim and Seinfeld, 1995) was used to see the volcanic effluents effects on the equilibrium. That model could be used successfully in the previous paper (Ueda et al., 1998) to explain behaviors of these volatile species in the urban aerosols at remote sites in Central Japan, and shown to predict the gas-aerosol equilibrium with high accuracy, i.e., the correlation coefficients were  $R =$



**Fig. 2** : Time variation of SO<sub>2</sub> emission at Miyakejima volcano.

0.99 for gaseous NH<sub>3</sub>,  $R = 0.93$  for HNO<sub>3</sub> and  $R = 0.97$  for HCl.

Brief description of the multicomponent gas aerosol equilibrium model will be presented below. Volatile components in aerosols exist in solid phase at low relative humidities RH and in liquid phase at higher RH, the critical RH being the deliquescent point. They attain to multicomponent gas aerosol equilibrium, when the aerosols are exposed to air for long time. The thermodynamics model takes into account all of the important inorganic components, i.e., sulfate, nitrate, chloride, ammonium, sodium, potassium, magnesium, calcium and water.

At relative humidities RH less than the deliquescent point, let chemical potential  $\mu_i$  of species  $i$  be defined as

$$\mu_i = \mu_i^0 + R T \ln a_i, \quad (1)$$

then, the chemical equilibrium can be written as (Denbigh, 1981)

$$\sum \nu_{ij} \mu_i = 0, \quad (2)$$

where  $\nu_{ij}$  is the stoichiometric coefficient of the  $i$ -th species in the  $j$ -th reaction,  $\mu_i^0$  the standard chemical potential of the  $i$ -th species at temperature  $T$  and pressure  $p$ , and  $a_i$  the activity.

The equilibrium constant  $K_j$  for  $j$ -th reaction is given as

$$K_j = \Pi a_i^{\nu_{ij}} = \exp \left[ -\frac{\sum \nu_{ij} \mu_i^0}{R T} \right], \quad (3)$$

where the standard chemical potential  $\mu_i^0$  can be calculated from the thermodynamic relation based

on the standard molar Gibbs free energy of formation  $\Delta G^0$ , molar enthalpy of formation  $\Delta H^0$  and molar heat capacity at constant pressure  $C_p$  (Denbigh, 1981);

$$\frac{\mu_i^0}{R T} = \frac{\Delta G_i^0}{R T_0} + \frac{\Delta H_i^0 (T_0/T^{-1})}{R T_0} + C_{p_i} \frac{(1 + \ln(T_0/T) - T_0/T)}{R}. \quad (4)$$

and data on  $\Delta G^0$ ,  $\Delta H^0$  and  $C_p$  were listed in NBS Thermodynamic Tables (Wagman et al., 1982).

At relative humidities higher than the deliquescent point, atmospheric aerosols are regarded as concentrated aqueous solutions. The equilibrium constant  $K_j$  for  $j$ -th reaction can be written as

$$K_j = \Pi a_i^{\nu_{ij}} = \Pi (\gamma_i m_i)^{\nu_{ij}}, \quad (5)$$

where  $\gamma_i$  is the activity coefficient and  $m_i$  is the molality.

Essential part of the model is how to determine the activity  $a_i$  and so how to determine the molality  $m_i$  and activity coefficient  $\gamma_i$ . The molality  $m_i$  is based on water as the solvent and the water content be estimated by the ZSR relationship (Zdanovskii, 1948; Stokes and Robinson, 1966). Assuming water activity  $a_W$  in the aerosols under equilibrium with air be equal to the relative humidity RH of air, the mass concentration of water in the aerosols  $W$  kg-water/m<sup>3</sup>-air is calculated by

$$W = \frac{\sum C_i}{\sum m_{io}(a_W)}, \quad (6)$$

**Table 1** : Annual mean and two months mean air quality just before and after the eruption of Miyakejima volcano.

|                                         | Gas (ppb)       |                | Aerosol ( $\mu\text{g}/\text{m}^3$ ) |                               |                              |                 |                              | Precipitation (mg/L) |                               |                              |
|-----------------------------------------|-----------------|----------------|--------------------------------------|-------------------------------|------------------------------|-----------------|------------------------------|----------------------|-------------------------------|------------------------------|
|                                         | SO <sub>2</sub> | O <sub>3</sub> | PM10                                 | SO <sub>4</sub> <sup>2-</sup> | NO <sub>3</sub> <sup>-</sup> | Cl <sup>-</sup> | NH <sub>4</sub> <sup>+</sup> | pH                   | SO <sub>4</sub> <sup>2-</sup> | NH <sub>4</sub> <sup>+</sup> |
| Annual mean                             |                 |                |                                      |                               |                              |                 |                              |                      |                               |                              |
| Before eruption <sup>a)</sup>           | 0.4             | 52             | 8 <sup>e)</sup>                      | 2.5                           | 0.32                         | 0.05            | 0.85                         | 4.98                 | 1.00                          | 0.19                         |
| After eruption <sup>b)</sup>            | 1.5             | 53             | 15                                   | 3.8                           | 0.33                         | 0.03            | 1.12                         | 4.92                 | 1.63                          | 0.24                         |
| 2 months mean; from August to September |                 |                |                                      |                               |                              |                 |                              |                      |                               |                              |
| Before eruption <sup>c)</sup>           | 0.2             | 38             | 14                                   | 2.2                           | 0.20                         | 0.02            | 0.75                         | 4.99                 | 0.29                          | 0.01                         |
| After eruption <sup>d)</sup>            | 3.3             | 46             | 17                                   | 6.5                           | 0.24                         | 0.03            | 1.56                         | 4.54                 | 1.40                          | 0.15                         |

<sup>a)</sup> From July 1999 to June 2000, <sup>b)</sup> from August 2000 to July 2001, <sup>c)</sup> 1999, and <sup>d)</sup> 2000.

<sup>e)</sup> Suspended particles less than  $10\mu\text{m}$  in diameter.

where  $C_i$  is the aqueous phase concentration of electrolyte  $i$  in mole per  $\text{m}^3$ -air and  $m_{io}(a_W)$  is the molality (mole/kg) of a single-component aqueous solution of electrolyte  $i$  that has a water activity  $a_W = \text{RH}/100$ .

For the activity coefficient  $\gamma_i$  in highly-concentrated aqueous solution with many other strong electrolytes, several methods have been developed by Bromley (1973), Meissner and Kusik (1973) and Pitzer (1979) of which Pitzer method is adopted in the present model.

## 4. Results and discussion

### 4.1 Change of annual mean air quality caused by volcanic eruption

SO<sub>2</sub> emission from Miyakejima volcano was estimated from the airplane measurement done once or twice a week together with the volcanic activity data and presented in Figure 2 (Konno, 2002). For about 6 months after the start of eruption on 8 July 2000, Miyakejima volcano was very active and the SO<sub>2</sub> emission was the maximum level of about  $6 \times 10^4$  ton/day. It was about the same level as the anthropogenic emission of China (54,800 ton/day) and twenty times larger than Japanese one (3,120 ton/day) (Kannari et al., 2001). After that the volcanic activity has weakened and become steady and the SO<sub>2</sub> emission is about  $10^4$  ton/day from May 2002.

Annual mean air qualities before and after the volcanic eruption are compared and presented in

Table 1. As for the gaseous pollutants after the eruption, O<sub>3</sub> level did not change but SO<sub>2</sub> concentration increased four times. However, it is still very low level compared with the urban air in Tokyo metropolitan area (3-7 ppb, 1999) (Ministry of Environment, 2000). Change of aerosol composition is particularly interesting. SO<sub>4</sub><sup>2-</sup> in aerosol increased by 52% and NH<sub>4</sub><sup>+</sup> by 32%. In contrast, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> decreased. As for the precipitation composition, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> increased by 63% and 26% but pH value did not change significantly.

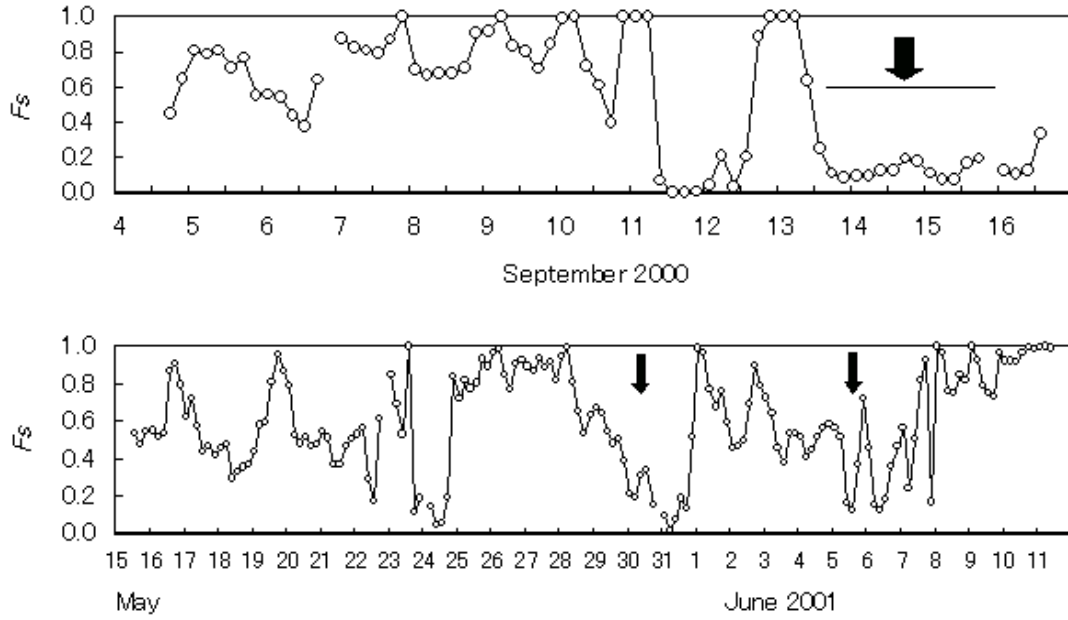
These changes are more clearly seen in two-months mean air qualities from August to September in 1999 and 2000 (Table 1). SO<sub>2</sub> in gas phase and SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> in aerosol increased 17 times, 3.0 times and 2.1 times, respectively. In the precipitation SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> increased 4.8 times and 1.5 times, respectively.

### 4.2 Conversion rate SO<sub>2</sub> gas to SO<sub>4</sub><sup>2-</sup> aerosol

During the volcanic effluents is transported, SO<sub>2</sub> gas is transformed into SO<sub>4</sub><sup>2-</sup> aerosol in the atmospheric reactions. These reactions occur homogeneously and heterogeneously. The conversion ratio of sulfur compounds are defined as;

$$F_s = \frac{[S]_{\text{SO}_4^{2-}}}{([S]_{\text{SO}_4^{2-}} + [S]_{\text{SO}_2})}, \quad (7)$$

where  $[S]_{\text{SO}_4^{2-}}$  and  $[S]_{\text{SO}_2}$  are concentrations of sulfur in the forms of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>. Figure 3 illustrates the time variation of  $F_s$ . When air



**Fig. 3 :**  $F_s$  ( $\text{SO}_4^{2-}$  conversion ratio) at Happo in September 2000 and May and June 2001. Arrows are air mass transported from Miyake island.

masses passed over the volcano and the volcanic effluents were directly supplied to it,  $F_s$  values at Happo ridge was always less than 0.2, otherwise it was larger than 0.6 and sometimes exceeded 0.9. The former and the latter sulfur are referred to as the young and aged sulfur, respectively.

The conversion rate of young  $\text{SO}_2$  gas to  $\text{SO}_4^{2-}$  aerosols was estimated. Assuming excess sulfur is not supplied on the way to Happo ridge and the conversion proceeds in a first order reaction, the conversion rate  $Kt$  is given for the initial  $F_s$  value be zero is given as follows;

$$Kt = -\frac{\Delta \ln(1 - F_s)}{\Delta t}, \quad (8)$$

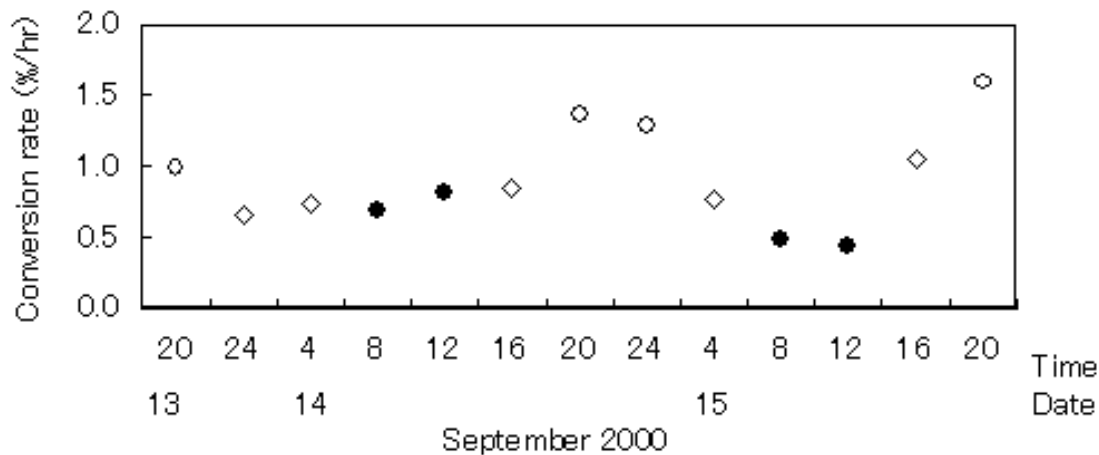
where  $\Delta t$  is the traveling time from the volcano to Happo and determined from the backward trajectory. The conversion rate  $Kt$  is presented in Figure 4 for the period of 13-15 September 2000. Here the traveling time was 12-18 hours. The conversion rate was 0.90%/hr on average. Because of the higher reactivity in the daytime, it showed a maximum 1.59%/hr in daytime and minimum 0.44%/hr at night. On 29-30 August 2000, 30 May 2001 and 5 June 2001 the average conversion rate was 1.21%/hr, 1.20%/hr and 1.02%/hr, respectively. The regional air quality model RAQM

simulation for these episodes also supported the present conversion rate, i.e., about 1%/hr (An et al., 2001).

The daytime conversion rate is about a half, compared with the value 3.7%/hr under the active photochemical oxidants episodes when polluted air masses over Tokyo metropolitan area were transported into this central mountainous area on clear summer days (Sasaki et al., 1988). Thus, the present conversion rate should be understood as the value for the sulfur be transported in the less polluted and colder mid troposphere, while the latter figure was obtained under active photochemical oxidants episodes at the ozone levels of 100-130ppb and at high temperatures of 300-310K.

#### 4.3 Time variations of aerosol components and gaseous pollutants after the volcanic eruption

Intensive observations were made from 4 to 16 September 2000 and from 15 May to 11 June 2001, both of which were done after the volcanic eruption. Figure 5 illustrates time series of  $\text{O}_3$  and water-soluble components,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$



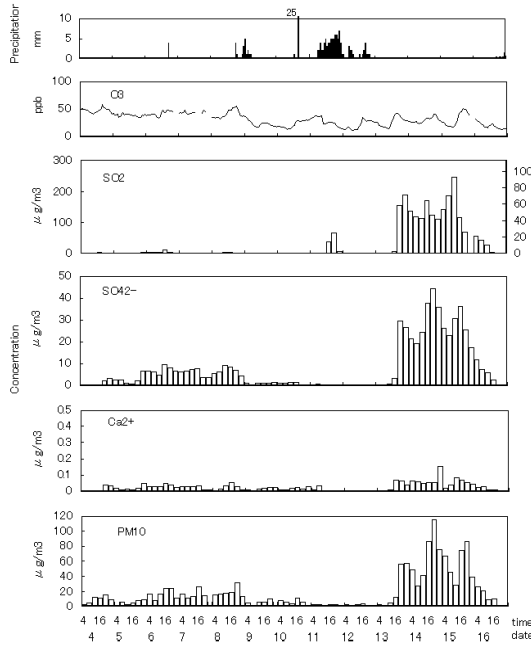
**Fig. 4** :  $\text{SO}_2$  conversion rates during transport from Miyakejima to Happo. Open circle are air mass transported in daytime and filled circles are at night.

in aerosol and hourly precipitation rate. Four-hours averages of hourly PM10, and  $\text{SO}_2$  concentrations were also presented. At first, it is noted that the non sea-salt contribution in sulfate, nss- $\text{SO}_4^{2-}$  amounted to more than 98% of total  $\text{SO}_4^{2-}$  in both observation periods. Non sea-salt contribution of  $\text{Ca}^{2+}$  was 86% and 98% in the September observation and in the May-June observation, respectively. These facts suggest that aerosols at Happo ridge were not influenced so much by sea salt. Thus, only the total concentrations of  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  were presented in Figure 5.

In the time series of the September observation presented in Figure 5(a), we can distinguish several patterns of air quality. From 6 to 8 September  $\text{SO}_4^{2-}$  concentration in aerosols ranged in  $4\text{--}9 \mu\text{g}/\text{m}^3$ . It was much higher than the monthly average  $2.6 \mu\text{g}/\text{m}^3$  in September 1999, i.e., in the same period one year before the eruption, and annual average of  $2.5 \mu\text{g}/\text{m}^3$  in the year of 1999. In contrast,  $\text{SO}_2$  concentration was less than  $5 \mu\text{g}/\text{m}^3$ , under a comparatively high concentration condition of  $\text{O}_3$ , 40–50 ppb. It indicates that  $\text{SO}_2$  was almost oxidized into  $\text{SO}_4^{2-}$  in the atmospheric photochemical reactions. However, in the period from 13 to 15 September, Happo ridge was attacked by severe  $\text{SO}_2$  pollution.  $\text{SO}_2$  concentration reached to extremely high values around  $200 \mu\text{g}/\text{m}^3$ . At the same time the  $\text{SO}_4^{2-}$  concentration attained to  $30\text{--}40 \mu\text{g}/\text{m}^3$  which had not been

experienced at Happo and other monitoring stations (Satsumabayashi et al., 1999) before the volcanic eruption. In this period  $\text{SO}_4^{2-}$  concentration showed the similar diurnal pattern to  $\text{O}_3$ , increasing in daytime and decreasing at night. The similar pattern was also seen in PM10. It indicates that photochemical reactions were active to produce a large amount of  $\text{SO}_4^{2-}$  and so PM10. In contrast, on 11 September high concentration of  $\text{SO}_2$  was recorded but the concentrations of other pollutants were at low levels. It is due to washout and rainout under severe rain.

The May-June observation period was just before the Japanese rainy season, in which moving cyclones and anticyclones passed along the Japan islands from SW to NE at an interval of few days. Sometimes Asian dust, called the yellow-sand, attacked Japan, which is originated from Takla Makan, Gobi, Ordos deserts or Loess plateau in China and transported in westerly winds (Wang et al., 2000). In this season atmospheric photochemical reactions are most active and the monthly mean concentrations of  $\text{O}_3$  were 75, 67 and 58 ppb in April, May and June, respectively, while it is 41 ppb in September 2000. As seen in Figure 5(b), several patterns of air quality can also be distinguished. In the period from 15 to 23 May,  $\text{SO}_4^{2-}$  concentration exceeded  $10 \mu\text{g}/\text{m}^3$  and on 26 May it attained  $25 \mu\text{g}/\text{m}^3$ . Different from the  $\text{SO}_4^{2-}$  episodes in 6–8 September,  $\text{Ca}^{2+}$  concentration as

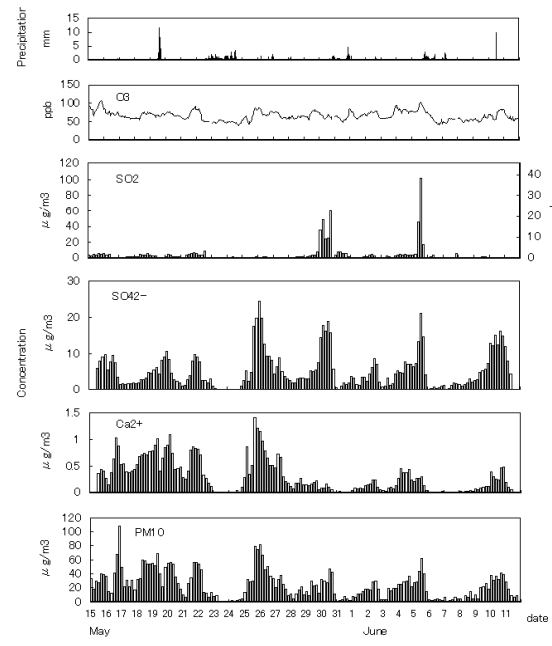


**Fig. 5(a)** : Time variations of hourly precipitation and concentrations of  $O_3$ ,  $SO_2$ ,  $SO_4^{2-}$ ,  $Ca^{2+}$  and  $PM_{10}$  at Happo in September 2000.

well as  $PM_{10}$  increased significantly and in phase. Maximum concentrations of  $Ca^{2+}$  and  $PM_{10}$  were  $1.4\mu g/m^3$  and  $108\mu g/m^3$ , much higher than the annual averages of  $0.16$  and  $8.0\mu g/m^3$  in 1999, respectively, while  $SO_2$  concentration was less than  $6\mu g/m^3$ . Similar pattern was also seen in 9 to 11 June. In contrary, from 30 May to 5 June  $SO_2$  concentration increased together with  $SO_4^{2-}$  and  $PM_{10}$ . Maximum values of  $SO_2$  and  $SO_4^{2-}$  were  $100\mu g/m^3$  and  $20\mu g/m^3$ , respectively.

In order to estimate the major origins of the high concentration pollutants, backward trajectory analysis was made. Assuming pollutants to be transported to Happo ridge of 2000 m ASL along the iso-potential temperature plane, the backward trajectories for 3 days were calculated for the objective analysis wind field, GANAL, of 10 km by 10 km, provided by Japan Meteorological Agency (Hayashida et al., 1991). They are presented in Figure 6.

Air masses on 15 September and on 30 May passed over Miyakejima area and transported directly to Happo ridge. Volcanic emission erupted up to 1000-3000m levels (Chino, 2001) and a part of  $SO_2$  was converted to  $SO_4^{2-}$  in the photochemical reactions. Such direct transport of the volcanic



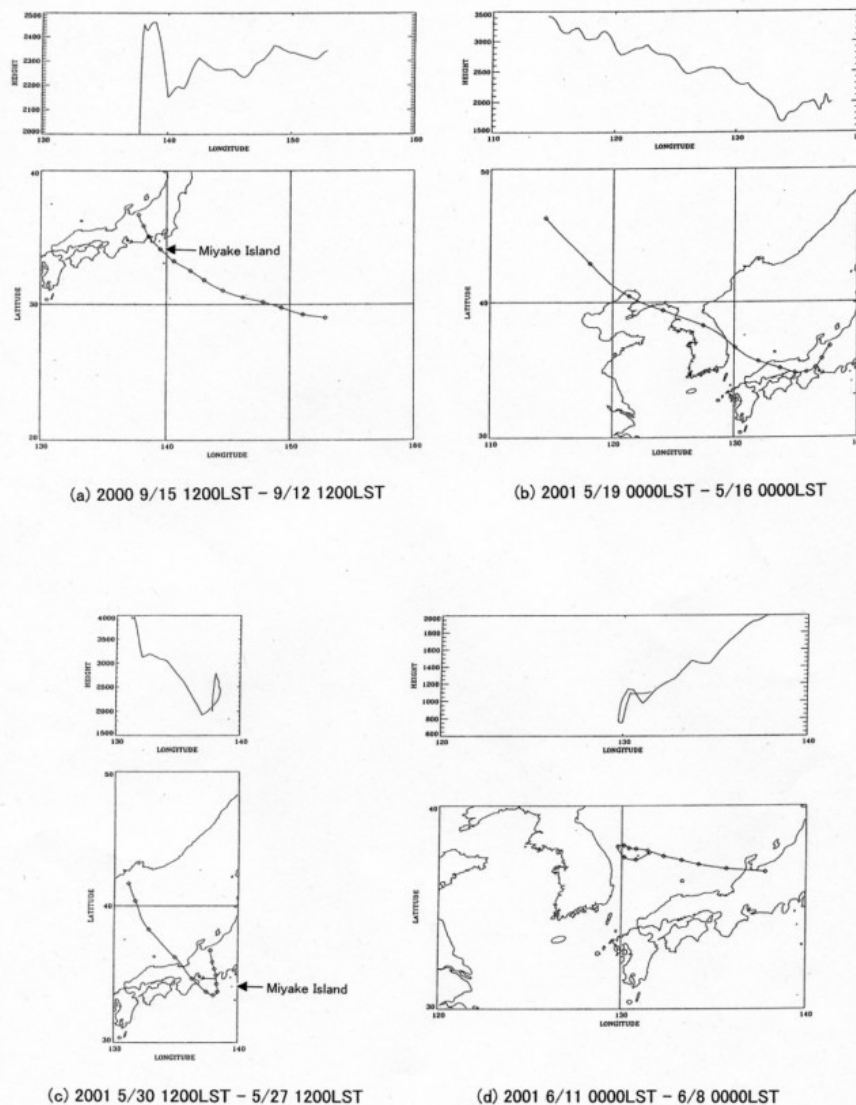
**Fig. 5(b)** : Time variations of hourly precipitation and concentrations of  $O_3$ ,  $SO_2$ ,  $SO_4^{2-}$ ,  $Ca^{2+}$  and  $PM_{10}$  at Happo from May to June 2001.

emission was also occurred on 5 June 2001 and on 28-29 August 2000. As shown in Figure 7, in these air masses with direct supply of volcanic effluents  $NO_3^-$  and  $Cl^-$  concentrations in aerosols were significantly low compared with the monthly averages before the eruption. Air mass on 19 May had passed over Loess plateau in the Northeast China and then took large amount of  $SO_2$  from mega cities such as Beijing, Seoul, and Osaka. This is a typical yellow sand event. It is designated by Japan Meteorological Agency and also predicted successfully by an yellow sand deflation and transport model (Wang et al., 1999).

Air mass on 11 June was also considered to be transported along the similar route but not passed over the yellow sand areas. It was more aged than the former and almost all  $SO_2$  had been transformed to  $SO_4^{2-}$ . The similar backtrajectory was observed in the 6 to 9 September event (not shown).

#### 4.4 Volcanic effects on water-soluble composition and ion balance in aerosols

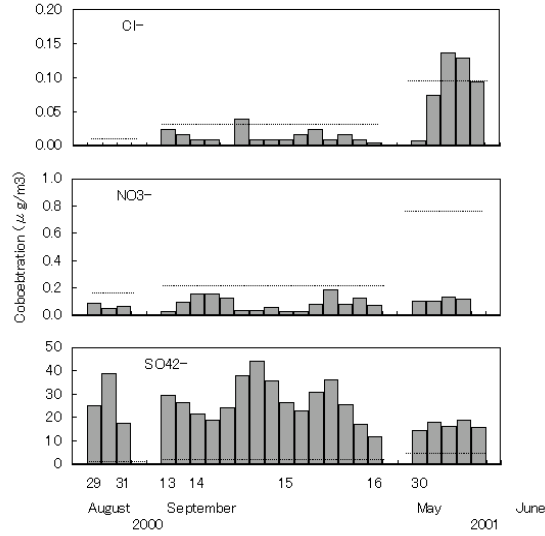
Typical water-soluble compositions and ion balances of aerosols before and after the volcanic



**Fig. 6** : Isentropic backward trajectories calculated from Happo at the 2000m level for 15 September 2000 and 19 May, 30 May and 11 July 2001. Open rhombuses ( $\diamond$ ) are inserted at 6-hour intervals.

eruption are compared in Figure 8. At first it is noted that the total ion concentrations after the eruption were much larger than before eruption, but more significant differences were seen in the aerosol composition and the ion balance. When  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  as anion and  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  as cation were took into account, the ion balance before eruption was good, i.e., within more than 90 % as typically seen in Figures 9 (a), (b). Of the anion components  $\text{SO}_4^{2-}$  was dominant,  $\text{NO}_3^-$  was 1/4 to 1/15 portion and  $\text{Cl}^-$  was contained slightly. As for cation the dominant component was  $\text{NH}_4^+$ , but 1/3 or 1/7 portion was other alkaline ions such as  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ .

After eruption aerosol compositions changed drastically. At first, it is noted that cation was dominated by  $\text{SO}_4^{2-}$  and exceed two times more than total cation. It suggests such aerosols might be strongly acidic. When the volcanic  $\text{SO}_2$  supplied to the mid troposphere is converted into  $\text{SO}_4^{2-}$  during long distance transport, the  $\text{SO}_4^{2-}$  at first reacts with gaseous ammonium to form  $(\text{NH}_4)_2\text{SO}_4$  aerosols. Since sufficient amount of gaseous ammonia and crustal alkaline ions are hardly supplied to the mid troposphere, they are sometimes exhausted. Then, the excess  $\text{SO}_4^{2-}$  is at the alkaline deficit state or exist as sulfuric acid mist, and then the aerosols exhibit strong acid-

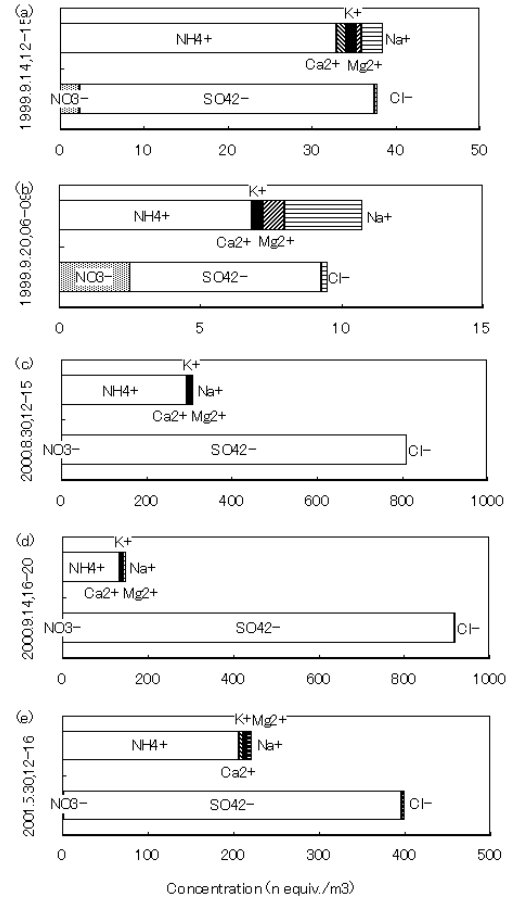


**Fig. 7 :** Concentrations of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  of air mass effected volcanic gas in Miyake islands at Happo. Dased lines are monthly average concentrations before the volcanic eruption.

ity. It is true for young aerosols which have just affected by the volcanic gas (Figure 8(d)). However, when the aerosols are aged after traveling for long distances and for long time, alkaline components increase gradually. It can be seen typically in Figures 8(c) and (e).

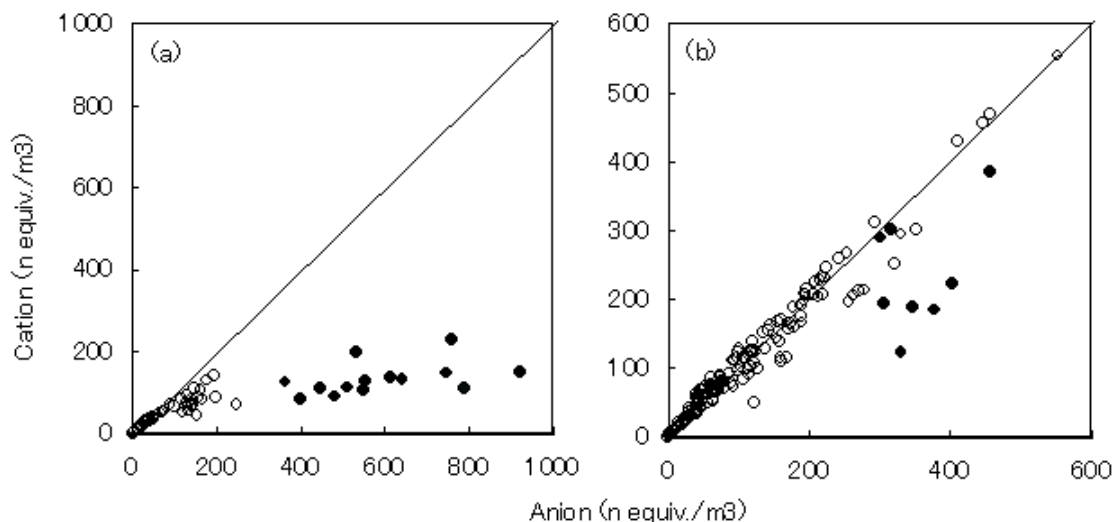
It is well known that in urban aerosols good ion balance is usually established, when  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  are adopted for it. In Tokyo metropolitan area and surroundings, Sasaki et al. (1988) obtained 99% balance with the correlation coefficient  $r=0.996$ . They also noticed that the deviation toward the anion side sometimes occurred when highly polluted air mass was prevailing.

Ion balance in the aerosols after eruption was calculated and illustrated for intensive observation periods in Figure 9. In this diagram filled circles represent air mass transported directly from



**Fig. 8 :** Compositions of aerosol components at Happo when air mass has passed through near Miyakejima: (a) and (b) before eruption in Miyakejima, and (c)-(e) after eruption.

Miyakejima volcano. In the September observation when the volcano was most active, aerosols affected directly by the volcanic gas always showed significant imbalance. Excess of anion attained to  $770 \text{ n equiv./m}^3$ . It was much larger than the maximum values  $90 \text{ n equiv./m}^3$  observed in the same area by Sasaki et al. (1988). In addition, it was usual that equivalent concentration of  $\text{SO}_4^{2-}$  almost balanced with that of  $\text{NH}_4^+$  in the case of urban aerosols in Tokyo metropolitan ares (Sasaki et al., 1988). Relation between equivalent concentrations of  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  were presented in Figure 10. As senn in the diagram, it is true for the low concentration range, but when the aerosols were affected directly by the volcanic gas and contained high concentration  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  concentration was much less than the equivalent concentration of  $\text{SO}_4^{2-}$ . This imbalance suggests co-existence of  $\text{HSO}_4^-$  and  $\text{H}^+$ , together with  $\text{SO}_4^{2-}$ .



**Fig. 9** : Relationship between anion and cation at Happo in (a) 4 to 16 September 2000 and (b) 15 May to 11 June 2001. Anion is total of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , and cation is total of  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . Filled circles are air mass transported from Miyakejima in 1600 LST on 13 September to 2400 LST on 15 September 2000, 0000 LST to 2000 LST on 30 May 2001 and 0800 LST to 2000 LST on 5 June 2001.

That will be discussed later on the basis of multi-component gas-aerosol equilibrium.

In the May-June observation, the excess anion was approximately 200 n equiv./m<sup>3</sup> (Figure 10), when the volcanic effluents had affected directly to the Happo air mass. However, when the pollution level was high but transported from Asian continent with alkaline yellow sand, ion balance was fairly good and sometimes shift slightly to the cation side. This is supposed due to the undetermined carbonates, since calcium is the dominant component of yellow sand and exists mainly as  $\text{CaCO}_3$  (Nishikawa et al., 2000).

#### 4.5 Aerosol acidification and change of gas-aerosol equilibrium of volatile inorganic components by volcanic eruption

At first the fraction of  $[\text{NH}_4\text{HSO}_4] + [\text{H}_2\text{SO}_4]$  was roughly estimated by assuming the total  $\text{SO}_4^{2-}$  and  $\text{H}^+$  concentrations were written as follows;

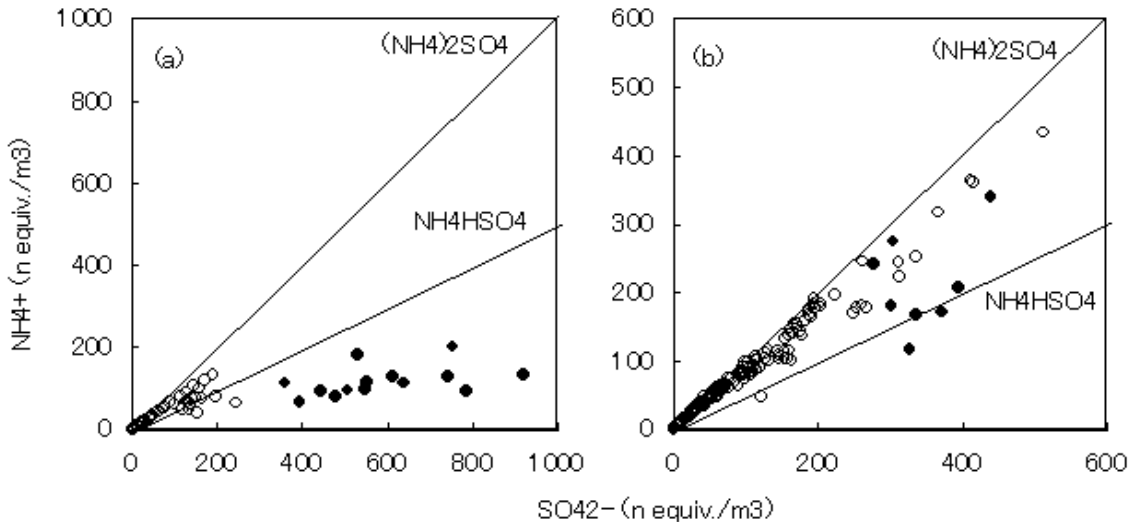
$$\begin{aligned}\Sigma [\text{SO}_4^{2-}] &= [(\text{NH}_4)_2\text{SO}_4] + [\text{NH}_4\text{HSO}_4] + [\text{H}_2\text{SO}_4] \\ \Sigma [\text{H}^+] &= [\text{NH}_4\text{HSO}_4] + [\text{H}_2\text{SO}_4]\end{aligned}$$

where [ ] denotes concentration in n-equiv./m<sup>3</sup>. In the volcanic aerosols in September 2000 the

fraction of  $[\text{NH}_4\text{HSO}_4] + [\text{H}_2\text{SO}_4]$  in  $\Sigma[\text{SO}_4^{2-}]$  was 69-85%, while in May and June 2001 it was 13-64%. Thus, such aerosols affected by the volcanic eruption were strongly acidic.

In order to see details of the aerosol acidification by the volcanic effluents, the multicomponent gas aerosol equilibrium model described in section 3 was used. Using the observed concentrations of sulfate, nitrate and chlorate in aerosol and gas phases and other crustal aerosol compositions, acidity and  $\text{HSO}_4^-$  concentration were calculated for their temperature and relative humidity. The calculation was made for typical set of aerosols with and without direct effects of volcano, and the predicted result was presented in Table 2. When the volcanic effluents affected directly, gaseous ammonium was exhausted by sulfate and thus gas-aerosol partitioning was almost on the aerosol side. The pH value of aerosols was less than 1.0 and sometimes negative. Partitioning between  $[\text{SO}_4^{2-}]$  and  $[\text{HSO}_4^-]$  is interesting. As the pH decreased,  $\text{HSO}_4^-$  fraction, i.e.,  $[\text{HSO}_4^-]/([\text{SO}_4^{2-}] + [\text{HSO}_4^-])$ , increased. In the strongly acidic aerosols at pH=0.05, the  $\text{HSO}_4^-$  fraction 76%. In contrast, in the air mass which did not pass over the volcano the aerosol pH value was 2.15, and almost all sulfate existed as  $\text{SO}_4^{2-}$ .

In addition, gas-aerosol partitionings of nitrate



**Fig. 10** : Relationship between  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  at Happon in (a) 4 to 16 September 2000 and (b) 15 May to 11 June 2001. Filled circles are air mass transported from Miyakejima in 1600 LST on 13 September to 2400 LST on 15 September 2000, 0000 LST to 2000 LST on 30 May 2001 and 0800 LST to 2000 LST on 5 June 2001.

and chloride were changed drastically by volcanic eruption. The excess amount of  $\text{SO}_4^{2-}$  formation at first reacts with ammonium gas to produce  $(\text{NH}_4)_2\text{SO}_4$  aerosol. After exhausting ammonium gas, then  $\text{SO}_4^{2-}$  drives out  $\text{NO}_3^-$  and  $\text{Cl}^-$  and took their place in the aerosol. The present multi-component gas-aerosol equilibrium model can predict these change of partitioning. The calculated result is presented in Table 2. When the volcanic effluents affected directly, more than 95% of nitrate and 98% chloride are converted to gas phase even at low temperature at the high mountain ridge. Those values of gas fraction are in a great contrast with 64% nitrate and 75% chloride in the air masses from the continent. The expelled  $\text{NO}_3^-$  and  $\text{Cl}^-$  into gas phase, i.e., gaseous  $\text{HNO}_3$  and  $\text{HCl}$ , have more than ten times larger dry deposition velocities of about 4 cm/s (Hauglustaine et al., 1994), compared with 0.4 cm/s for  $\text{SO}_2$  and 0.1 and 0.016 cm/s for  $\text{NO}_2$  and  $\text{NO}$  (Chang et al., 1989a,b).

Moreover, these gaseous  $\text{HNO}_3$  and  $\text{HCl}$  are dissolved into water droplet more easily than other gaseous pollutants. It can be seen by the dissolution constant of species A, the so-called Henry's law constant  $H_A$  defined as

$$[\text{A}(\text{aq})] = H_A P_A \quad (9)$$

where  $P_A$  is the partial pressure of A in gas phase (atm) and  $[\text{A}(\text{aq})]$  is the aqueous phase concentration of A ( $\text{mol l}^{-1}$ ) in equilibrium with  $P_A$ . The dissolution constants  $H_A$  are  $2.1 \times 10^5$  and  $727 \text{ mol l}^{-1} \text{atm}^{-1}$  for  $\text{HNO}_3$  and  $\text{HCl}$  more than three orders larger than 1.23 and  $0.01 \text{ mol l}^{-1} \text{atm}^{-1}$  for  $\text{SO}_2$  and  $\text{NO}_2$ . Thus, dry deposition and wet deposition of nitrate and chloride are enhanced by the excess formation of sulfate by the volcanic eruption. That is, the enhanced nitrate and chloride depositions deteriorate environmental acidification, together with the deposition of  $\text{SO}_2$  and sulfate.

#### 4.6 Change of precipitation composition by volcanic eruption

Changes of precipitation composition and its component concentrations caused by volcanic eruption are also of great concern for the environmental acidification.  $\text{SO}_2$  and other volcanic gases are absorbed in the cloud and rain droplets. In addition, secondary aerosols like  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  produced in atmospheric reactions are taken into the water droplets as the principal cloud condensation nucleus and in collision process, together with other volcanic crustal aerosols.

As seen in section 4.1, annual mean concentra-

**Table 2** : Components in aerosol and gas phases with and without direct effects of the volcano.

|                                |                               |       | ratio of particle/gas |         |                                                                                                      | ratio of particle/gas |          |
|--------------------------------|-------------------------------|-------|-----------------------|---------|------------------------------------------------------------------------------------------------------|-----------------------|----------|
|                                | SO <sub>4</sub> <sup>2-</sup> |       | ammonium              |         | [SO <sub>4</sub> <sup>2-</sup> ]/([SO <sub>4</sub> <sup>2-</sup> ]+[HSO <sub>4</sub> <sup>-</sup> ]) | nitrate               | chloride |
|                                | μ g/m <sup>3</sup>            | pH    | observed              | predict |                                                                                                      | predict               | predict  |
| Affected by the volcanic gas.  |                               |       |                       |         |                                                                                                      |                       |          |
| 15 Sep. 12:00-18:00            | 32.0                          | 0.06  | 0.96                  | 1.0     | 0.27                                                                                                 | 0.09                  | 0.06     |
| 15 Sep. 18:00-24:00            | 20.3                          | 0.05  | 0.94                  | 1.0     | 0.23                                                                                                 | 0.04                  | 0.02     |
| 16 Sep. 00:00-06:00            | 11.0                          | -0.15 | 0.76                  | 1.0     | 0.16                                                                                                 | 0.07                  | 0.03     |
| 16 Sep. 06:00-12:00            | 6.4                           | 0.04  | 0.75                  | 1.0     | 0.23                                                                                                 | 0.01                  | 0.07     |
| average                        | 17.4                          | 0.00  | 0.85                  | 1.0     | 0.22                                                                                                 | 0.05                  | 0.02     |
| Air masses from the continent. |                               |       |                       |         |                                                                                                      |                       |          |
| 23 Sep. 10:00-15:00            | 4.2                           | 1.5   | 0.93                  | 0.91    | 0.70                                                                                                 | 0.40                  | 0.29     |
| 24 Sep. 03:00-09:00            | 1.6                           | 2.1   | 0.39                  | 0.51    | 0.98                                                                                                 | 0.27                  | 0.17     |
| 2 Oct. 12:00-18:00             | 4.1                           | 1.4   | 0.92                  | 0.94    | 0.92                                                                                                 | 0.43                  | 0.31     |
| 2 Oct. 18:00-24:00             | 3.0                           | 1.6   | 0.77                  | 0.85    | 0.95                                                                                                 | 0.33                  | 0.21     |
| average                        | 3.2                           | 1.7   | 0.75                  | 0.80    | 0.89                                                                                                 | 0.36                  | 0.25     |

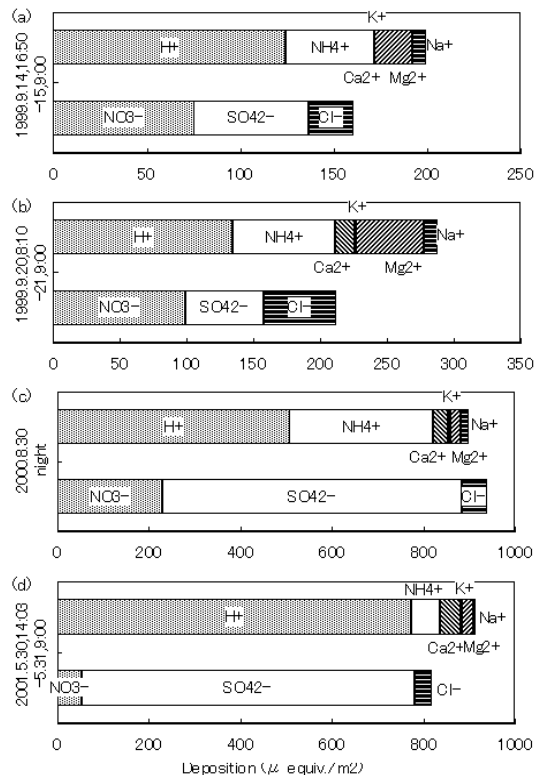
tions of SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> in precipitation increased by 63% and 26% after eruption but pH value did not change significantly (Table 1). However, for the period when the volcano was most active and the southeasterly winds were prevailing from August to September 2000, the volcanic effects were seen more clearly. When the two-months mean precipitation components from August to September in 1999 and 2000 (Table 1) are compared, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> increased 4.8 times and 15 times, respectively and the pH decreased from 4.99 to 4.54.

Precipitation compositions after the volcanic eruption are compared with those before eruption, and presented in Figure 11. Here, the compositions in Figures 11(c) and (d) are typical ones when the air masses passed over Miyakejima volcano and both SO<sub>2</sub> and aerosol SO<sub>4</sub><sup>2-</sup> were at high concentration levels, while the compositions in Figures 11 (a) and (b) are for aged air masses passed same course before eruption. At first, it can be seen that the total deposition of water-soluble components was four or five times larger and acidity was stronger after eruption. SO<sub>4</sub><sup>2-</sup> concentrations are more than ten times larger than those before eruption. The pH values were 3.95 and 4.09 on 30 August 2000 and on 30 May 2001, respec-

tively. They were lower by 1.0 than the annual mean before eruption.

Nitrate and chlorate in the precipitation shows a great contrast to these in aerosols. Even after eruption precipitation contained a large amount of NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>, in contrast to very low concentrations of aerosol nitrate and chloride. It is because nitrate and chlorate expelled from aerosols into gas phase by the excess amount of SO<sub>4</sub><sup>2-</sup> can be readily dissolved into cloud and precipitating waters. That mechanism was well-understood by the multicomponent gas-aerosol equilibrium and by their extremely large values of dissolution constants, i.e., 3 orders larger than that of SO<sub>2</sub> and 5 orders larger than NO<sub>2</sub>, that will be discussed in section 4.

However, on 19 May 2001 when yellow sand storm attacked the central Japan, a large amount of NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> together with SO<sub>4</sub><sup>2-</sup> are contained both in aerosols and precipitation (Figure 12). It is because calcium contained originally in yellow sand in the form of CaCO<sub>3</sub> could react with the excess sulfate and neutralize the aerosols and precipitation. Acidity of the precipitation was increased by ΔpH=1.0, when compared with the precipitation affected by the volcanic plume. Such a neutralization of precipitation by yellow sand

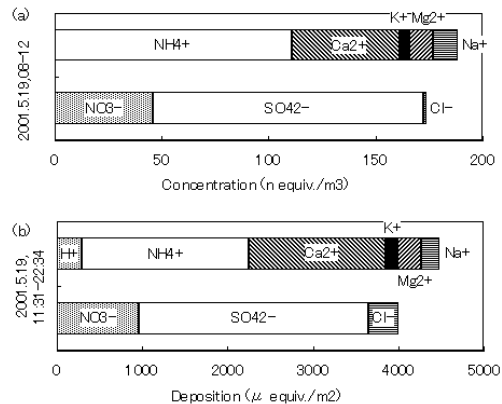


**Fig. 11** : Compositions of precipitation components at Happo when air mass has passed through near Miyakejima: (a) and (b) before eruption in Miyakejima, and (c) and (d) after eruption.

was predicted well by Ueda and Wang (2000) and Terada et al. (2002) by use of by an air quality model. They showed the yellow sand contribute to increase the monthly average pH of precipitation in April 1999 by 0.1 in the whole area of Japan but in the severe yellow sand events neutralization of acidic rain attained to  $\Delta \text{pH}=0.5\text{-}0.7$ . These values are for before eruption, and thus it might be reasonable to understand the increase of pH,  $\Delta \text{pH}=1$  observed on 19 May 2001 was due to the neutralization by yellow sand.

## 5. Conclusion

Miyakejima volcano began to erupt from 8 July 2000 which is located in the Northwest Pacific Ocean and 200 km south from Tokyo Metropolitan area. Its  $\text{SO}_2$  emission amounted to the maximum  $6 \times 10^4$  ton/day which was about the same level as the anthropogenic emission of China (54,800 ton/day) and twenty times larger than Japanese one (3,120 ton/day), and is decreasing



**Fig. 12** : Compositions of aerosol and precipitation components at Happo when air mass containing yellow sand transported: (a) aerosol and (b) precipitation.

to  $10^4$  ton/day. Aerosols and precipitation, together with gaseous pollutants have been observed from two years before the eruption to present on a prominent mountain ridge, Happo ridge (1850m ASL and 330 km north from the volcano), which can be assume to be representative of the mid-troposphere air quality over central Japan. Short time sampling of aerosols made it possible to see the detailed examination of gas-aerosol equilibrium or gas-aerosol partitioning of volatile inorganic gases.

When volcanic plume was transported directly, the concentrations of  $\text{SO}_2$  and aerosol  $\text{SO}_4^{2-}$  increased simultaneously, and reached  $200 \mu\text{g}/\text{m}^3$  and  $40 \mu\text{g}/\text{m}^3$ , respectively. During their transportation,  $\text{SO}_2$  was converted to  $\text{SO}_4^{2-}$ . The conversion rate was 1.0%/hr on the average, it being about two times faster in daytime than at night. Annual mean concentration of  $\text{SO}_2$  were increased 3.8 times and those of PM10 and aerosol  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  were 1.9, 1.5 and 1.3 times, respectively. For the precipitation  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  concentra-

tions were 1.6 and 1.3 times and H<sup>+</sup> concentration increases by 15% (pH=0.10). The annual wet deposition of SO<sub>4</sub><sup>2-</sup> increased 1.9 times.

In contrast, aerosol concentrations of NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> decreased under the influence of volcanic effluents. That is caused by the excess amount of SO<sub>4</sub><sup>2-</sup> formation. That is, the produced SO<sub>4</sub><sup>2-</sup> at first exhausted ammonium gas to form (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aerosol and then, driving out NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>, it took their place in the aerosol. It makes the aerosol acidic, i.e., pH values less than 1 and partitioned sulfate into SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup>. These facts were explained successfully by a multi-component gas-aerosol equilibrium.

The expelled NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> into gaseous phase, i.e., HNO<sub>3</sub> and HCl gases, have more than ten times larger dry deposition velocities, compared with those of SO<sub>2</sub>, NO<sub>2</sub> and NO. It enhances nitrate and chloride to dry-deposit on the ground. Moreover, these HNO<sub>3</sub> and HCl gases are dissolved into water droplet much more easily than other gaseous pollutants. Their dissolution constants *K*<sub>a</sub> are 2.1×10<sup>5</sup> and 727 mol l<sup>-1</sup>atm<sup>-1</sup> for HNO<sub>3</sub> and HCl more than three orders larger than 1.23 and 0.01 mol l<sup>-1</sup>atm<sup>-1</sup> for SO<sub>2</sub> and NO<sub>2</sub>. Thus, dry deposition and wet deposition of nitrate and chloride are enhanced by the excess formation of sulfate by the volcanic eruption. That is, the enhanced nitrate and chloride depositions deteriorate environmental acidification, together with the deposition of SO<sub>2</sub> and sulfate. Moreover, such an environmental acidification mechanism is considered to be taking place on the regional scale even now under the influence of volcanic effluents.

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## 要旨

三宅島火山は東京の南 200km の北西太平洋上に位置し、2000 年 7 月 8 日に噴火を開始した。その二酸化硫黄の放出量は最大で  $6 \times 10^4$  ton/day で、中国の人為起源の放出量と同程度 (54,800 ton/day)、日本 (3,120 ton/day) の 20 倍に匹敵した。我々は噴火開始の 2 年前から現在に至るまで、対流圏中層の大気質を代表していると考えられる、長野県八方尾根 (標高 1850m、三宅島から 330km 北) にてエアロゾル、降水、汚染気体の観測を行ってきた。エアロゾルの採取は短時間で行い、通常期は 1 日 1 回 3 時間、強化観測期間では 1 日 6 回 4 時間毎に行った。降水は 1 日毎に採取し、 $\text{SO}_2$ 、 $\text{NO}_2$ 、 $\text{O}_3$ 、PM10 などは 1 時間毎に測定した。さらに、エアロゾルと降水中の水溶性無機物質である  $\text{Na}^+$ 、 $\text{K}^+$ 、 $\text{Mg}^{2+}$ 、 $\text{Ca}^{2+}$ 、 $\text{NH}_4^+$ 、 $\text{SO}_4^{2-}$ 、 $\text{NO}_3^-$ 、 $\text{Cl}^-$  などを解析した。

$\text{SO}_2$  の月平均濃度は 3.8 倍に増加し、エアロゾルと降水中の  $\text{SO}_4^{2-}$  濃度はそれぞれ 1.5 倍、1.6 倍になった。 $\text{SO}_4^{2-}$  は過剰に存在した為、 $\text{NO}_3^-$  や  $\text{Cl}^-$  はエアロゾル相からガス相に移行し、時には硫酸ミストとして存在していた。それによりエアロゾルの pH は 1 以下になり、 $\text{SO}_4^{2-}$  や  $\text{HSO}_4^-$  となっていた。これらの事実はガス-エアロゾル平衡モデルで説明された。

キーワード：酸性化、エアロゾルと降水、火山の影響、ガス-エアロゾル平衡、対流圏中層