京都大学防災研究所年報　第46号 B 平成15年
Annuals of Disas. Prev. Res. Inst., Kyoto Univ., No. 46B, 2003

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

Hiromasa UEDA, Hikaru SATSUMABAYASHI*, and Mizuo KAJINO

* Nagano Research Institute for Health and Pollution

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 SO_2 emission amounted to the maximum 6×10^4 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 SO_2, NO, NO_2 and O_3, and PM10. Water-soluble inorganic species, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, Cl^- in the aerosol and precipitation were analyzed.

Annual mean concentration of SO_2 was increased 3.8 times and those of SO_4^{2-} were 1.5 and 1.6 times in aerosol and precipitation. Because of the excess amount of SO_4^{2-} formation, driving out NO_3^- and 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 SO_4^{2-} and HSO_4^- . These facts was explained successfully by a multi-component gas-aerosol equilibrium.

Keywords: acidification, aerosol and precipitaion, 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 SO_2 emission amounted to the maximum 6×10^4 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 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, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, 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 monitoring 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 SO_2, NO, NO_2 and O_3, and PM10.

Water-soluble inorganic species, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, 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 NO_3^-, Cl^- and 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 (Millpore HAWP02500), water-soluble inorganic species, Na^+, K^+, Mg^{2+}, Ca^{2+},

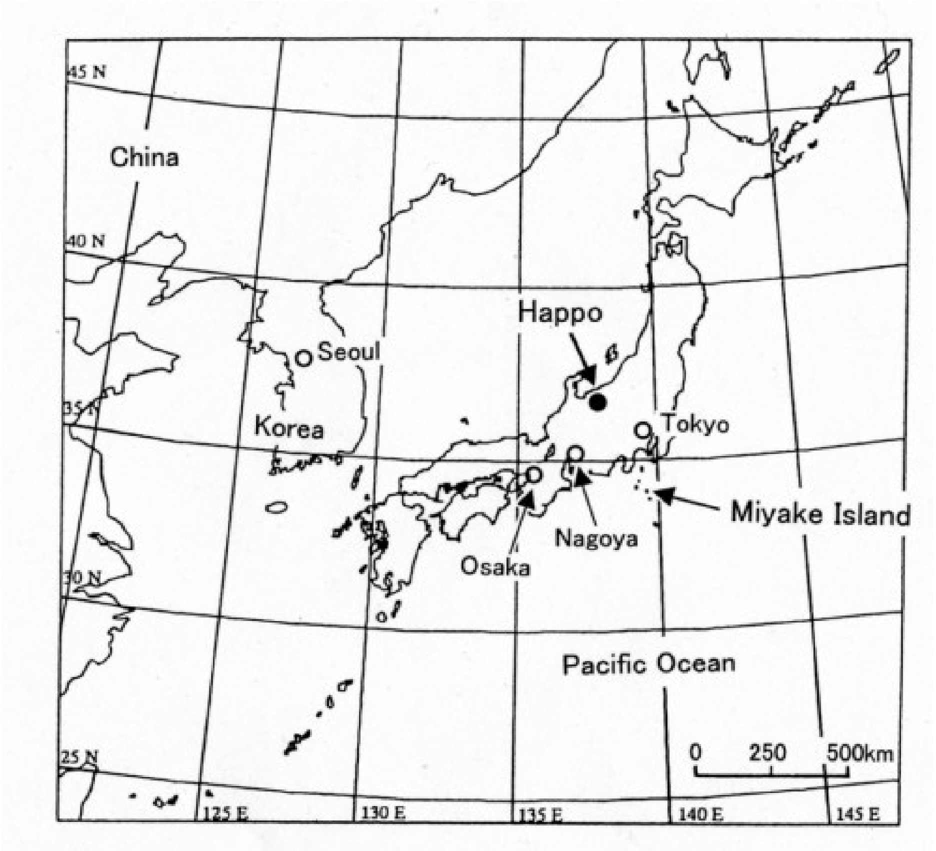


Fig. 1 : Map showing site, Happo and other locations mentioned in the text.

NH_4^+, SO_4^{2-}, NO_3^-, 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 (Millpore AAWP04700), the water-soluble components were determined in the same way as that for aerosol.

At the same time gaseous pollutants, such as SO_2 , NO, NO_2 and O_3, and PM10 were monitored every one hour. SO_2 was analyzed by ultraviolet fluorescence method (Thermo Electron, Model 43C-TL), NO, NO_2 by chemical luminescence method (Thermo Electron, Model 42C-TL), O_3 by ultraviolet absorption method (Thermo Electron, Model 49C) and PM10 by β-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 equlibrium. Thnat 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 =

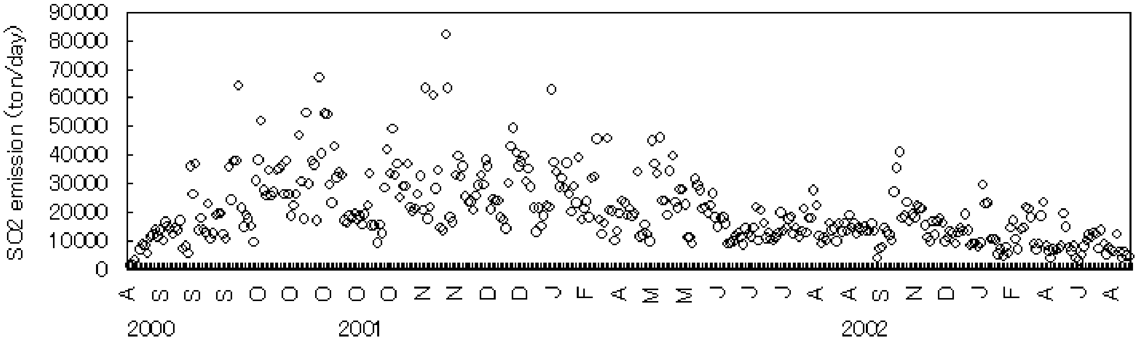


Fig. 2 : Time variation of SO_2 emission at Miyakejima volcano.

0.99 for gaseous NH_3, R = 0.93 for HNO_3 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 μ_i of species i be defined as

$$\mu_i = \mu_i^0 + R\,T \ln a_i \;, \tag{1}$$

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

$$\Sigma\, \nu_{ij}\; \mu_i = 0 \;, \tag{2}$$

where ν_{ij} is the stoichiometric coefficient of the i-th species in the j-th reaction, μ_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

$$K_j = \Pi\; a_i^{\nu_{ij}} = \exp\left[-\frac{\Sigma\, \nu_{ij}\; \mu_i^0}{R\,T}\right], \tag{3}$$

where the standard chemical potential μ_i^0 can be calculated from the thermodynamic relation based on the standard molar Gibbs free energy of formation ΔG^0, molar enthalpy of formation ΔH^0 and molar heat capacity at constant pressure Cp (Denbigh, 1981);

$$\begin{aligned}\frac{\mu_i^0}{R\,T} \;&=\; \frac{\Delta G_i^0}{R\,T_0} + \frac{\Delta H_i^0 (T_0/T^{-1})}{R\,T_0} \\ &\quad + Cp_i \frac{(1 + \ln(T_0/T) - T_0/T)}{R}\;.\end{aligned} \tag{4}$$

and data on ΔG^0, ΔH^0 and Cp 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

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

where γ_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 γ_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^3-air is calculated by

$$\mathrm{W} = \frac{\Sigma\; C_i}{\Sigma\; m_{io}(a_{\mathrm{W}})}, \tag{6}$$

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

	Gas (ppb)		Aerosol (μ g/m^3)					Precipitaion(mg/L)		
	SO_2	O_3	PM10	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	pH	SO_4^{2-}	NH_4^+
Annual mean										
Before eruption [a)]	0.4	52	8[e)]	2.5	0.32	0.05	0.85	4.98	1.00	0.19
After eruption [b)]	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 [c)]	0.2	38	14	2.2	0.20	0.02	0.75	4.99	0.29	0.01
After eruption [d)]	3.3	46	17	6.5	0.24	0.03	1.56	4.54	1.40	0.15

[a)] From July 1999 to June 2000, [b)] from August 2000 to July 2001, [c)] 1999, and [d)] 2000.
[e)] Suspended particles less than 10μm in diameter.

where C_i is the aqueous phase concentration of electrolyte i in mole per 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 $a_W = RH/100$.

For the activity coefficient γ_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_2 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_2 emission was the maximun level of about 6×10^4 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_2 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_3 level did not change but SO_2 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 particuraly interesting. SO_4^{2-} in aerosol increased by 52% and NH_4^+ by 32%. In contrast, NO_3^- and Cl^- decreased. As for the precipitation composition, SO_4^{2-} and NH_4^+ 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_2 in gas phase and SO_4^{2-} and NH_4^+ in aerosol increased 17 times, 3.0 times and 2.1 times, respectively. In the presipitatin SO_4^{2-} and NH_4^+ increased 4.8 times.and 1.5 times, respectively.

4.2 Convertion rate SO_2 gas to SO_4^{2-} aerosol

During the volcanic effluents is transported, SO_2 gas is transformed into SO_4^{2-} aerosol in the atmospheric reactions. These reactions occur homogeneously and heterogeneously. The conversion ratio of sulfur com- pounds are defined as;

$$Fs = \frac{[S]_{SO_4^{2-}}}{([S]_{SO_4^{2-}} + [S]_{SO_2})}, \qquad (7)$$

where $[S]_{SO_4^{2-}}$ and $[S]_{SO_2}$ are concentrations of sulfur in the forms of SO_2 and SO_4^{2-}. Figure 3 illustrates the time variation of Fs. When air

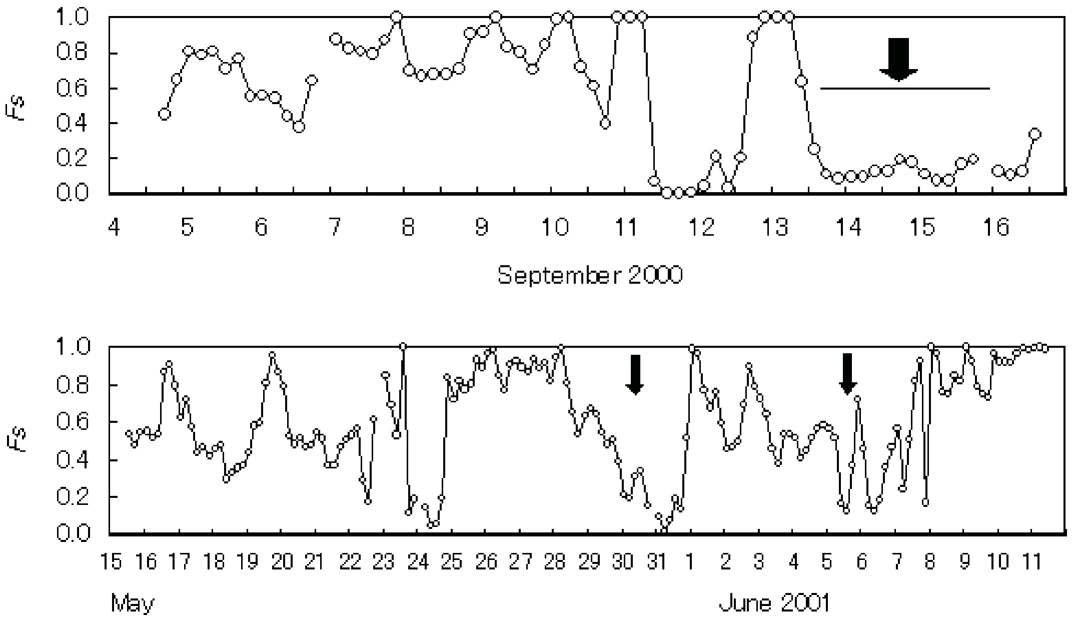


Fig. 3 : *Fs* (SO_4^{2-} conversion ratio) at Happo in September 2000 and May and June 2001. Arrows are air mass transported from Miyake island.

masses passed over the volcano and the volcanic effluents were directly supplied to it, Fs 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 refered to as the young and aged sulfur, respectively.

The conversion rate of young SO_2 gas to SO_4^{2-} aerosols was estimated. Assuming excess sulfur is not supplied on the way to Happo ridge and the convertion proceeds in a first order reaction, the convertion rate Kt is given for the initial Fs value be zero is given as follows;

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

where$\Delta\ t$ is the traveling time from the volcano to Happo and determined from the backward trajectory. The convertion rate Kt is presented in Figure 4 for the period of 13-15 September 2000. Here the traveling time was 12-18 hours. The convertion 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 convertion 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 convertion rate, i.e., about 1%/hr (An et al., 2001).

The daytime convertion rate is about a half, compared with the value 3.7%/hr under the active photochamical oxidants episodes when polluted air masses over Tokyo metropolitan area were transported into this central mountaneous area on clear summer days (Sasaki et al., 1988). Thus, the present convertion rate should be understod 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 O_3 and water-soluble components, SO_4^{2-} and Ca^{2+}

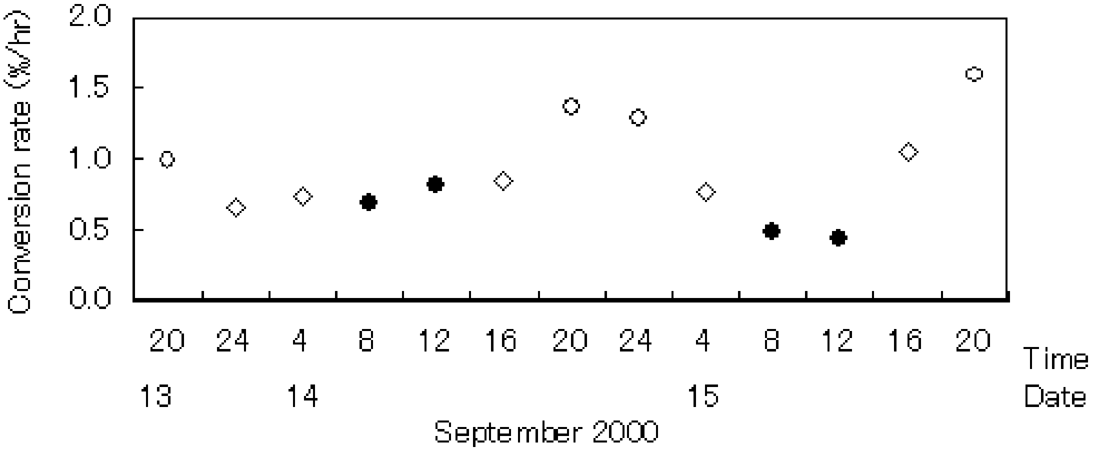


Fig. 4 : SO_2 conversion rates during transport from Miyakejima to Happo. Open circle are air mass transported in daytime and fulled circles are at night.

in aerosol and hourly precipitation rate. Four-hours averages of hourly PM10, and SO_2 concentrations were also presented. At first, it is noted that the non sea-salt contribution in sulfate, nss-SO_4^{2-} amounted to more than 98% of total SO_4^{2-} in both observation periods. Non sea-salt contribution of 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 SO_4^{2-} and 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 SO_4^{2-} concentration in aerosols ranged in 4-9 $\mu g/m^3$. It was much higher than the monthly average 2.6 $\mu g/m^3$ in September 1999, i.e., in the same period one year before the eruption, and annual average of 2.5 $\mu g/m^3$ in the year of 1999. In contrast, SO_2 concentration was less than 5 $\mu g/m^3$, under a comparatively high concentration condition of O_3, 40-50 ppb. It indicates that SO_2 was almost oxidized into SO_4^{2-} in the atmospheric photochemical reactions. However, in the period from 13 to 15 September, Happo ridge was attacked by severe SO_2 pollution. SO_2 concentration reached to extremely high values around $200\mu g/m^3$. At the same time the SO_4^{2-} concentration attained to 30-40$\mu g/m^3$ which had not been experienced at Happo and other monitering stations (Satsumabayashi et al., 1999) before the volcanic eruption. In this period SO_4^{2-} concentration showed the similar diurnal pattern to O_3, increasing in daytime and decreasing at night. The similar patern was also seen in PM10. It indicates that photochemical reactions were active to produce a large amount of SO_4^{2-} and so PM10. In contrast, on 11 September high concentration of 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 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, SO_4^{2-} concentration exceeded $10\mu g/m^3$ and on 26 May it attained $25\mu g/m^3$. Different from the SO_4^{2-} episodes in 6-8 September, Ca^{2+} concentration as

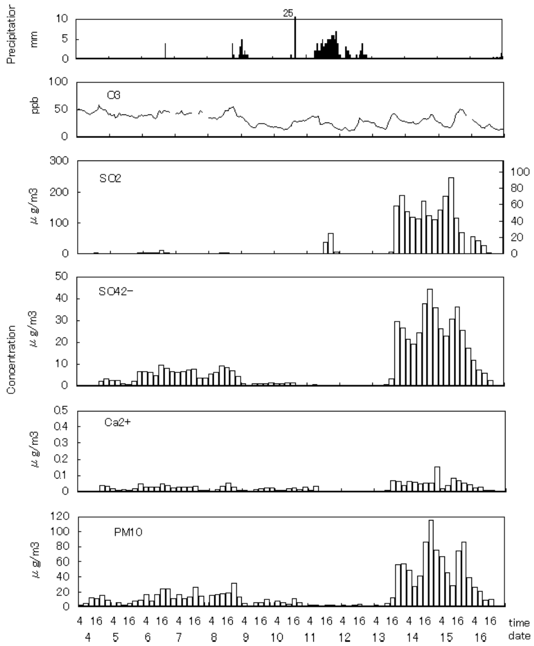


Fig. 5(a) : Time variations of hourly precipitation and concentrations of O_3, SO_2, SO_4^{2-}, Ca^{2+} and PM10 at Happo in September 2000.

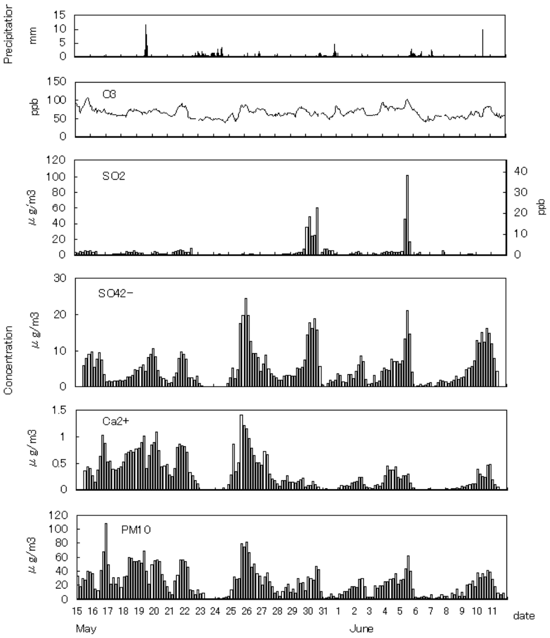


Fig. 5(b) : Time variations of hourly precipitation and concentrations of O_3, SO_2, SO_4^{2-}, Ca^{2+} and PM10 at Happo from May to June 2001.

well as PM10 increased significantly and in phase. Maximum concentrations of Ca^{2+} and PM10 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 PM10. Maximum values of SO_2 and SO_4^{2-} were $100\mu g/m^3$ and $20\mu g/m^3$, respectively.

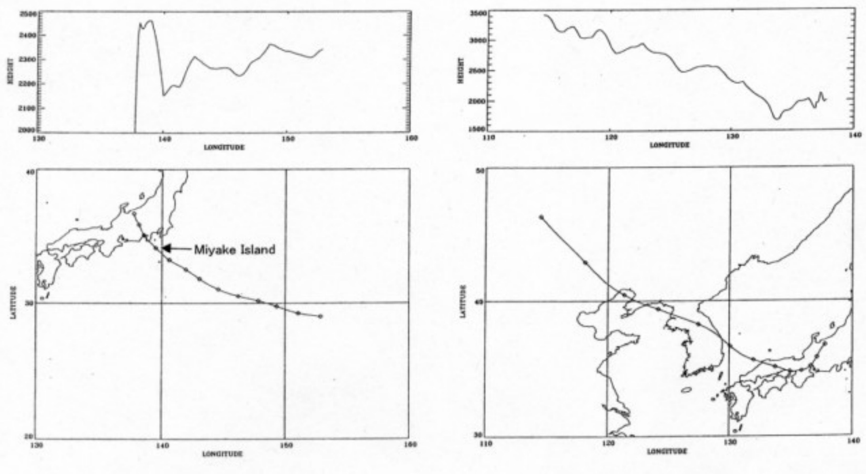
In order to estimate the major origins of the high concentration pollutants, backward trajectory analysis was made. Assuming pollutants to be transported to Happo ridge of 2000 m ASL along the iso-potential temperature plane, the backward trajectories for 3 days were calculated for the objective analysis 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 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 montly 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).

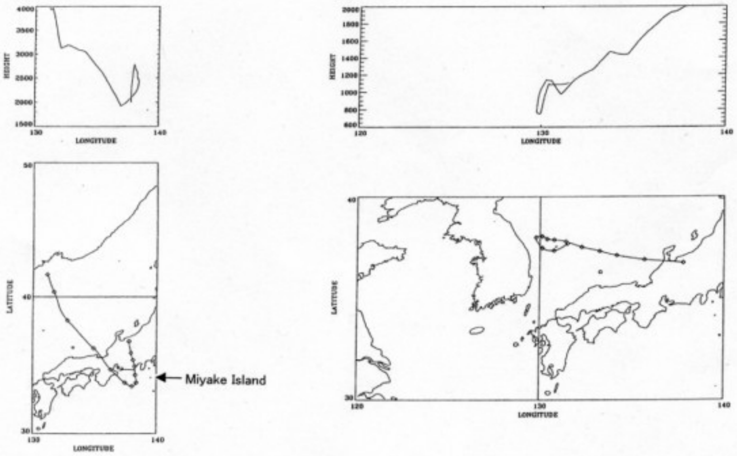
Air mass on 11 June was also considered to be transported along the similar route but not passed over the yellow sand areas. It was more aged than the former and almost all SO_2 had been transformed to SO_4^{2-}. The similar backtrajectory was observed in the 6 to 9 September event (not shown).

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



(a) 2000 9/15 1200LST – 9/12 1200LST (b) 2001 5/19 0000LST – 5/16 0000LST



(c) 2001 5/30 1200LST – 5/27 1200LST (d) 2001 6/11 0000LST – 6/8 0000LST

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 (◇) 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 SO_4^{2-}, NO_3^-, Cl^- as anion and NH_4^+, K^+, Ca^{2+}, Mg^{2+}, 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 SO_4^{2-} was dominant, NO_3^- was 1/4 to 1/15 portion and Cl^- was contained slightly. As for cation the dominant component was NH_4^+, but 1/3 or 1/7 portion was other alkaline ions such as K^+, Ca^{2+}, Mg^{2+}, Na^+.

After eruption aerosol compositions changed drastically. At first, it is noted that cation was dominated by SO_4^{2-} and exceed two times more than total cation. It suggests such aerosols might be strongly acidic. When the volcanic SO_2 supplied to the mid troposphere is converted into SO_4^{2-} during long distance transport, the SO_4^{2-} at first reacts with gaseous anmonium to form $(NH_4)_2SO_4$ aerosols. Since sufficient amount of gaseous ammonia and crustal alkaline ions are hardly supplied to the mid troposphere, they are sometimes exhausted. Then, the exess SO_4^{2-} is at the alkaline deficit state or exist as sulfuric acid mist, and then the aerosols exhibit strong acid-

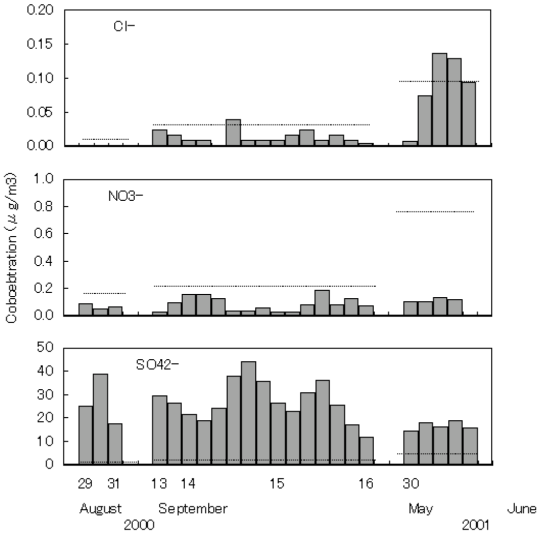


Fig. 7 : Concentrations of Cl^-, NO_3^- and SO_4^{2-} of air mass effected volucanic gas in Miyake islands at Happo. Dased lines are monthly average concentrations before the volcanic eruption.

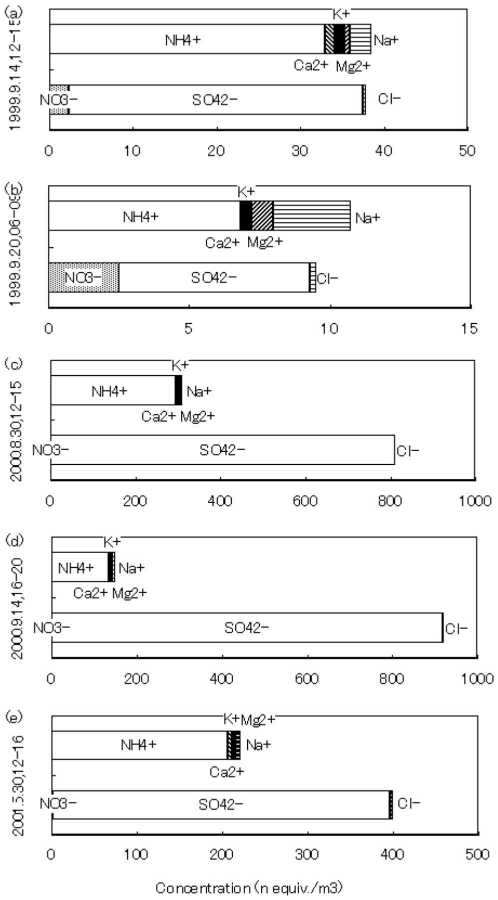


Fig. 8 : Compositions of aerosol components at Happo when air mass has passed through near Miyakejima: (a) and (b) before eruption in Miyakejima, and (c)-(e) after eruption.

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 SO_4^{2-}, NO_3^-, Cl^- , NH_4^+, K^+, Ca^{2+}, Mg^{2+}, 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 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 n equiv./m^3. It was much larger than the maximum values 90 n equiv./m^3 observed in the same area by Sasaki et al. (1988). In addition, it was usual that equilvalent concentration of SO_4^{2-} almost balanced with that of NH_4^+ in the case of urban aerosols in Tokyo metropolitan ares (Sasaki et al., 1988). Relation between equivalent concentrations of SO_4^{2-} and 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 SO_4^{2-}, NH_4^+ concentration was much less than the equivalent concentration of SO_4^{2-}. This imbalance suggests coexistence of HSO_4^- and H^+, together with SO_4^{2-}.

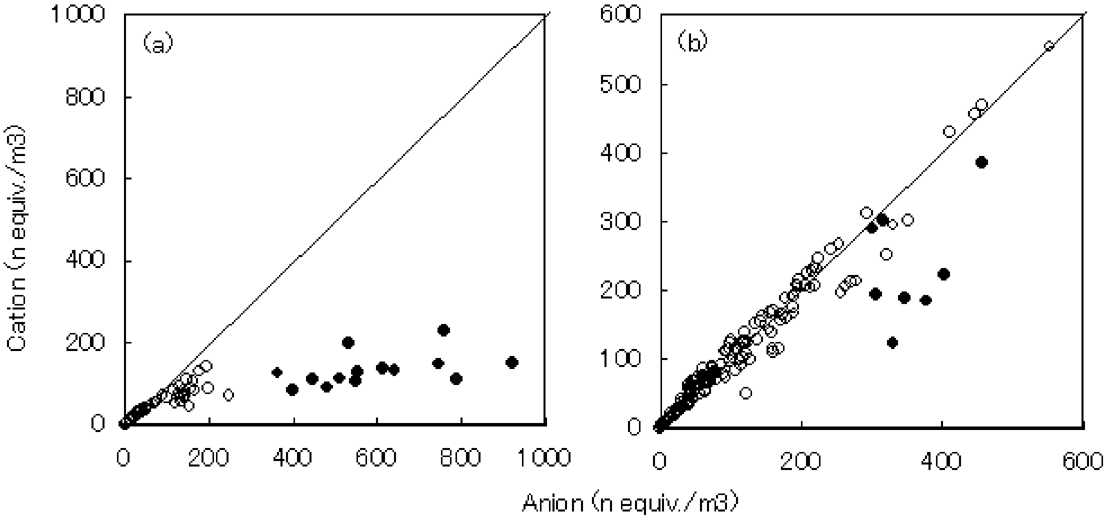


Fig. 9 : Relationship between anion and cation at Happo in (a) 4 to 16 September 2000 and (b) 15 May to 11 June 2001. Anion is total of Cl^-, NO_3^- and SO_4^{2-}, and cation is total of Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}. Fulled circles are air mass transported from Miyakejima in 1600 LST on 13 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 multicomponent gas-aerosol equillibrium.

In the May-June observation, the excess anion was approximately 200 n equiv./m^3 (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 $CaCO_3$ (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 [NH$_4$HSO4] + [H_2SO_4] was roughly estimated by assuming the total SO_4^{2-} and H^+ concentrations were written as follows;

$$\Sigma\ [SO_4^{2-}]=[(NH_4)_2SO_4] + [NH_4HSO_4] + [H_2SO_4]$$
$$\Sigma\ [H^+]=[NH_4HSO_4] + [H_2SO_4]$$

where [ ] denotes concentration in n-equiv./m^3. In the volcanic aerosols in September 2000 the fraction of [NH$_4$HSO4] + [H_2SO_4] in $\Sigma[SO_4^{2-}]$ 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 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 anmonium was exhausted by sulfate and thus gas-aerosol partiotioning was almost on the aerosol side. The pH value of aerosols was less than 1.0 and sometimes negative. Partitioning between $[SO_4^{2-}]$ and $[HSO_4^-]$ is interesting. As the pH decreased, HSO_4^- fraction, i.e., $[HSO_4^-]/([SO_4^{2-}]+[HSO_4^-])$, increased. In the strongly acidic aerosols at pH=0.05, the 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 SO_4^{2-}.

In addition, gas-aerosol partitionings of nitrate

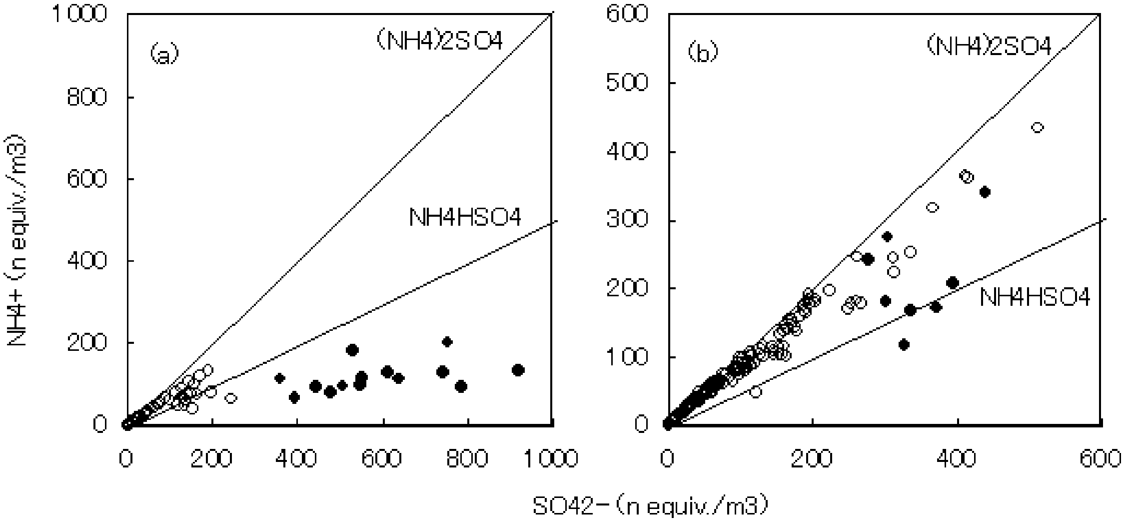


Fig. 10 : Relationship between SO_4^{2-} and NH_4^+ at Happo in (a) 4 to 16 September 2000 and (b) 15 May to 11 June 2001. Fulled circles are air mass transported from Miyakejima in 1600 LST on 13 September to 2400 LST on 15 September 2000, 0000 LST to 2000 LST on 30 May 2001 and 0800 LST to 2000 LST on 5 June 2001.

and chloride were changed drastically by volcanic eruption. The excess amount of SO_4^{2-} formation at first reacts with ammonium gas to produce $(NH_4)_2SO_4$ aerosol. After exhausting ammonium gas, then SO_4^{2-} drives out NO_3^- and 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% chlodide 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% nirate and 75% chloride in the air masses from the continent. The expelled NO_3^- and Cl^- into gas phase, i.e., gaseous HNO_3 and HCl, have more than ten times larger dry deposition velocitie of about 4 cm/s (Hauglustaine et al., 1994), compared with 0.4 cm/s for SO_2 and 0.1 and 0.016 cm/s for NO_2 and NO (Chang et al., 1989a,b).

Morerover, these gaseous HNO_3 and HCl are dissolved into water droplet more easily than other gaseous pollutants. It can be seen by the disssolution constant of species A, the so-called Henry's law constant HA defined as

$$[A(\mathrm{aq})] = H_A\ P_A \qquad (9)$$

where P_A is the partial pressure of A in gas phase (atm) and [A(aq)] is the aquasphase concentration of A (mol l^{-1}) in equilibrium with P_A. The dissolusion constants H_A are 2.1×10^5 and 727 mol l^{-1}atm^{-1} for HNO_3 and HCl more than three orders larger than 1.23 and 0.01 mol l^{-1}atm^{-1} for SO_2 and 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 detoriorate environmental acidification, together with the deposition of 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. SO_2 and other volcanic gases are absorbed in the cloud and rain droplets. In addition, secondary aerosols like SO_4^{2-} , Cl^- and NO_3^- produced in atmospheric reactions are taken into the water droplets as the principal cloud condensation nucleus and in collision precess, together with other volcanic crustal aerosols.

As seen in section 4.1, annual mean consentra-

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_4^{2-}		ammonium		$[SO_4^{2-}]/([SO_4^{2-}]+[HSO_4^-])$	nitrate	chloride
	μ g/m^3	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	036	0.25

tions of SO_4^{2-} and NH_4^+ in presipitation 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_4^{2-} and NH_4^+ 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_2 and aerosol SO_4^{2-} were at high concentration levels, while the compositions in Figures 11 (a) and (b) are for aged air masses passed same course befor 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_4^{2-} 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, respectively. 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_3^- and Cl^-, 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_4^{2-} 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_2 and 5 orders larger than NO_2, 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_3^- and Cl^- together with SO_4^{2-} are contained both in aerosols and precipitation (Figure 12). It is because calcium contained originally in yellow sand in the form of $CaCO_3$ could react with the excess sulfate and netralize 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

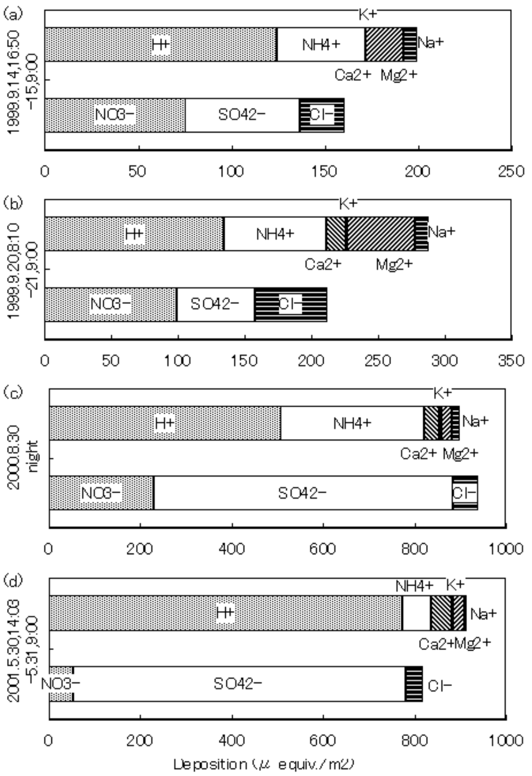


Fig. 11 : Compositions of precipitation components at Happo when air mass has passed through near Miyakejima: (a) and (b) before eruption in Miyakejima, and (c) and (d) after eruption.

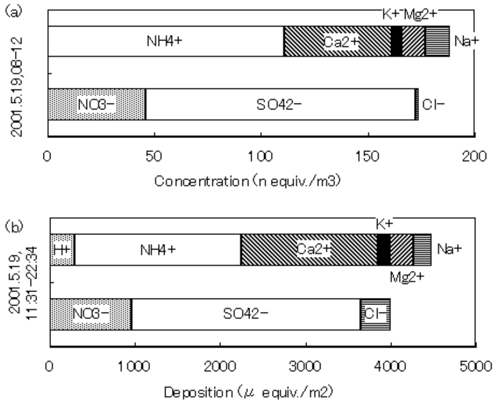


Fig. 12 : Compositions of aerosol and precipitation components at Happo when air mass containing yellow sand transported: (a) aerosol and (b) precipitation.

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 Δ pH=0.5-0.7. These values are for before eruption, and thus it might be reasonable to understand the increase of pH, Δ 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 SO_2 emission amounted to the maximum 6×10^4 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. 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 SO_2 and aerosol SO_4^{2-} increased simultaneously, and reached $200\mu g/m^3$ and 40 $\mu g/m^3$, respectively. During their transportation, SO_2 was converted to SO_4^{2-}. The convertion rate was 1.0%/hr on the average, it being about two times faster in daytime than at night. Annual mean concentration of SO_2 were increased 3.8 times and those of PM10 and aerosol SO_4^{2-} and NH_4^+ were 1.9, 1.5 and 1.3 times, respectively. For the precipitation SO_4^{2-} and NH_4^+ concentrations were 1.6 and 1.3 times and H+ concentration increases by 15% (pH=0.10). The annual wet deposition of SO_4^{2-} inreased 1.9 times.

In contrast, aerosol concentrations of NO_3^- and Cl^- decreased under the influence of volcanic effuents. That is caused by the excess amount of SO_4^{2-} formation. That is, the produced SO_4^{2-} at first exhausted ammonium gas to form $(NH_4)_2SO_4$ aerosol and then, driving out NO_3^- and Cl^-, it took their place in the aerosol. It makes the aerosol acidic, i.e., pH values less than 1 and partitioned sulfate into SO_4^{2-} and HSO_4^-. These facts was explained successfully by a multicomponent gas-aerosol equilibrium.

The expelled NO_3^- and Cl^- into gaseous phase, i.e., HNO_3 and HCl gases, have more than ten times larger dry deposition velocities, compared with those of SO_2, NO_2 and NO. It enhances nitrate and chloride to dry- deposition the ground. Morerover, these HNO_3 and HCl gases are dissolved into water droplet much more easily than other gaseous pollutants. Their dissolusion constants HA are 2.1×10^5 and 727 mol $l^{-1}atm^{-1}$ for HNO_3 and HCl more than three orders larger than 1.23 and 0.01 mol $l^{-1}atm^{-1}$ for SO_2 and 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 detoriorate environmental acidification, together with the deposition of SO_2 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.

Acknowledgments

This work was supported by the National Science Foundation for the Special Academic Field "Aerosol Science". We would like to acknowledge the Ministry of Environment for its supply of monitoring data of SO_2, O_3, PM10 and precipitation at Happo Ridge National Acid Rain Monitoring Station. Thanks also to Dr. T. Kanno for supply of SO_2 emmision data from Miyakejima volcano, Dr. M. Nishikawa for his discussion on yellow sand and to the Center for Global Environmental Research in National Institute for Environmental Studies for the backward trajectory calculation.

References

An,J., Ueda,H., Wang,Z., Matsuda,K. and Kajino,M. (2003): Simulations of monthly mean nitrate concentrations in precipitation. Atmos. Environment, Vol.37, pp.201-229.

Bromley,L.A. (1973): Thermodynamic properties of strong electrolytes in aqueous solutions. AIChE, Vol.19, pp.313-320.

Chang,Y.-S., Carmichael,G.R., Kurita,H. and Ueda,H. (1989a): The transport and formation of photochemical oxidants in central Japan, Atmos. Environment, Vol.23, pp.363-393.

Chang,Y.-S., Carmichael,G.R., Kurita,H. and Ueda,H. (1989b): The transport and formation of sulfates and nitrates in central Japan, Atmos. Environment, Vol.23, pp.1749-1773.

Denbigh, K. (1981): The principles of Chemical Equilibrium, 4th ed., Cambridge Univ. Press, Cambridge.

Hauglustaine,D.A., Granier,C., Brasseur,G.P., and Megie,G. (1994): The importance of atmospheric chamistry in the calculation of radiative forcing on the climate system. J. Geophys. Res., Vol.99. pp.1173-1186.

Hayashida-Amano,S., Sasano,Y. and Iikura,Y. (1991): Volcanic disturbances in the stratospheric aerosol layer over Tsukuba, Japan, observed by the National Institute for Environmental Studies Lidar from 1982 through 1986, J. Geophys. Res., Vol.96, pp.15469-15478.

Kannari,A., Baba,T., Ueda,H., Tonooka,Y. and Matsuda,K. (2001): Development of multi-pollutant emissions inventory in Japan, Proc. of 7th International Joint Seminar on the Regional Deposition Processes in the Atmosphere, pp. 136-141, Nat. Inst. for Environ. Studies, Tsukuba.

Kanno,T. (2002): Report of SO_2 emmision data from Miyakejima volcano, Japan Meteorological Agency, http://www.seisvol.kishou.go.jp/tokyo/320_miyake jima/SO_2emmission.htm.

Kayano,M. (2001): Volcanic effluents in Miyakejima Island. Proc. of Workshop on Miyakejima Island Eruption and Regional Air Pollution, pp.27-36.

Kim,Y.P., Seinfeld,J.H. and Sexena,P. (1993a): Atmospheric gas-aerosol equilibrium: I. Thermo- dynamic model. Aerosol Sci. Technol., Vol.19, pp.157-181.

Kim, Y.P., Seinfeld, J.H. and Sexena, P. (1993b): Atmospheric gas-aerosol equilibrium: II. Analysis of common approximations and activity coefficient calculation methods. Aerosol Sci. Technol., Vol.19, pp.182-198.

Kim, Y.P. and Seinfeld, J.H. (1995): Atmospheric gas-aerosol equilibrium: III. Thermodynamics of crustal elements Ca^{2+}, K^+, and Mg^{2+}. Aerosol Sci. Technol., Vol.22, pp.93-110.

Meissner, H.P. and Kusik, C.L. (1973): Aqueous solutions of two or more strong electrolytes. Ind. Eng. Chem., Process Design Develop., Vol.12, pp.205-208.

Ministary of Environment, (2000): Report of air pollution in Japan, pp.313.

Nishikawa, M., Hao,Q. and Morita,M. (2000): Preparation and evaluation of certified reference materials for Asian mineral dust, Global Environ. Res., Vol.4, pp.103-113.

Pitzer, K.S. (1979): Theory: ion interaction approach. In Activity Coefficients in Electrolyte Solutions, Edt. by Pytkowicz, R.M., Vol I, pp.209-265. CRC Press, Boca Ration, Florida.

Sasaki, K., Kurita,H., Chang,Y.-S., Carmichael,G.R., Murano,K. and Ueda,H. (1988): Behavior of sulfate, nitrate and other pollutants in the long-range transport of air pollution, Atmos. Environment, Vol.22, pp.1301-1308.

Satsumabayashi, H., Sasaki,K., Katsuno,T., Shikano,M., Ohto,M., Kurita,H., Murano,K., Hatakeyama,S., Karasudani,T. and Ueda,H. (1998): Behavior of airborne particulate secondary pollutants in the central mountainous area, Japan, J. Jpn Soc. Atmos. Environ., Vol.33, pp.284-296 (in Japanese).

Satsumabayashi, H., Sasaki,K., Katsuno,T., Shikano,M., Ohto,M., Nishizawa,K., Murano,K., Mukai,H., Hatakeyama,S., and Ueda,H. (1999): Behavior of airborne acidic and oxidative components in autumn and early spring in the central mountainous area of Japan, J. Jpn Soc. Atmos. Environ., Vol.34, pp.219-236 (in Japanese).

Terada, H., Ueda,H. and Wang,Z. (2002): Trend of acid rain and neutralization by yellow-sand in East Asia – A numerical study –, Atmos. Environment, Vol.36, pp.503-509.

Stokes,R.H. and Robinson,R.A. (1966): Interactions in aqueous nonelectrolyte solutions. I. Solute solvent equilibria. J. Phys. Chemistry, Vol.70, pp.2126-2130.

Ueda, H., Takemoto,T., Kim,Y.-P. and Sha,W. (2000): Behavior of volatile inorganic components in urban aerosols. Atmos. Environment, Vol.34, pp.353-361.

Ueda, H., Wang, Z. and Terada, H. (2000): A numerical study on acid rain and neutralization by yellow-sand in East Asia. Air Pollution, Vol.8, pp. 119-128, WIT Press.

Wagman, D.D., Evans, W.H., Parker, V.B., Schuman, , I., Harlow, S.M., Churney, K.L. and Nuttall, R.L. (1982): The NBS tables of chemical thermodynamic properties. J. Phys. Chemistry Reference Data, 11, Suppliment 2, pp.1-.200.

Wang, Z., Ueda, H. and Huang, M. (2000): A deflation module for use in modeling long-range transport of yellow-sand over East Asia. J. Geophys. Research, Vol.105, pp.26,947-26,959.

Zdanovskii,A.B. (1948): New methods for calculating solubilities of electrolytes in multicomponent systems, Zhur. Fiz. Kim. Vol.22, pp.1475-1485.

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6×10^4 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、SO_2, NO_2, 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Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, Cl^-などを解析した。

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SO_4^{2-}濃度はそれぞれ1.5倍、1.6倍になった。SO_4^{2-}は過剰に存在した為、NO_3^-や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、SO_4^{2-}やHSO_4^-となっていた。これらの事実はガスー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、ガスーエアロゾル平衡、対流圏中層