Change of aerosol and precipitation in the mid troposphere over central Japan caused by Miyake volcano effluents

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Abstract

Miyake volcano began to erupt on 8 July 2000. Its SO₂ emission amounted to a maximum 6×10⁴ ton per day, which is equivalent to the total anthropogenic emission in northeast Asia and is 20 times larger than that of Japan. It has then decreased gradually but remains at a level of 10⁴ ton per day even now. Here airborne volatile-component partitioning among gas, aerosols and raindrops caused by the volcanic effluents and evidence of its change were investigated by continuous observation of aerosols, together with gas and precipitation measurements, on a prominent mountain ridge and from analysis based on a multicomponent thermodynamic equilibrium model. The volcanic SO₂ is converted to sulphate aerosols in the atmospheric reactions, and both cause environmental acidification. On the other hand, the abundant sulphate changes the thermodynamic equilibrium of volatile NO₃⁻, Cl⁻, NH₄⁺ components between gas and aerosol, which in turn changes the dry and wet deposition processes of volatile components on the ground and causes additional environmental effects. Keywords: aerosol, acidification, sulfate, nitrate, chloride, volcano, volatile component, gas-aerosol partitioning, thermodynamic equilibrium.

1 Introduction

Miyake volcano began to erupt from 8 July 2000. Its maximum SO₂ emission 6x10⁴ ton/day (Kanno [4]) was at the same level as the total anthropogenic emission in the Northeast Asia (Klimont et al. [7]). It is equivalent to the anthropogenic emission in China (54,800 ton/day)² and twenty times larger than Japanese (3,120 ton/day)³ (Kannari et al. [3]). Such a large emission has not been
experienced in the Northeast Asia and every inhabitant in Miyake island has been evacuated.

Miyake volcano is located in a small island (55 km²) in the northwest Pacific Ocean and 200 km south from Tokyo. Since it is not so far from Tokyo Metropolitan area, it has been causing severe air pollution in central Japan, episodically SO₂ being more than 300 ppb, about ten times larger than the environmental standard, in Tokyo and its surroundings. Thus, its influence on regional scale, such as environmental acidification, is of a great concern.

In the present work airborne volatile-components partitioning among gas, aerosols and raindrops caused by the volcanic effluents and evidence of its change were investigated from a continuous observation of aerosols, together with gas and precipitation measurements, on a prominent mountain ridge and from its analysis based on a multicomponent thermodynamic equilibrium model.

2 Observation

Aerosol and rain/snow, together with gaseous pollutants have been observed from two years before the eruption on a prominent mountain ridge, Happo ridge (1850m ASL and 300 km north from the volcano) in the central mountainous region. They are assumed as the representative of mid-troposphere air quality over central Japan. In this work a special attention was paid on volatile components such as NH₄⁺, NO₃⁻, Cl⁻ in aerosols. Thus, short time sampling of aerosols was made for three hours every day on polyflon tape filter by an automated high-volume sampler, while four-hours sampling was done consecutively in the intensive observations. Such a short time sampling is essential to minimize evaporation of volatile inorganic aerosols on the filter. For precipitation one-day collection was made, and for gaseous SO₂, NO, NO₂, O₃, and for PM10 every one-hour monitoring was done. Water-soluble inorganic species, Na⁺, K⁺, Mg²⁺, Ca²⁺, NH₄⁺, SO₄²⁻, NO₃⁻, Cl⁻ in aerosol and precipitation were analysed using ion-chromatography. Details of the sampling and analytical methods have been described elsewhere (Sasaki et al. [10]).

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. [5, 6]) was used to see the volcanic effluents effects on the equilibrium. That model could be used successfully in the previous paper (Ueda et al. [12]) 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 between
prediction and observation were \( r = 0.99 \) for gaseous \( \text{NH}_3 \), \( r = 0.93 \) for gaseous \( \text{HNO}_3 \) and \( r = 0.97 \) for gaseous \( \text{HCl} \).

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 \( \text{RH} \) and in liquid phase at higher \( \text{RH} \), the critical \( \text{RH} \) 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 humidity \( \text{RH} \) less than the deliquescent point, let chemical potential \( \mu_i \) of species \( i \) be defined as

\[
\mu_i = \mu_i^0 + RT \ln a
\]

then, the chemical equilibrium can be written as

\[
\Sigma v_{ij} \mu_i = 0 ,
\]

Where \( v_{ij} \) 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

\[
K_j = \Pi a_i^{vij} = \exp[-\Sigma v_{ij} \mu_i^0 / RT],
\]

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 \( C_p \);

\[
\frac{\mu_i^0}{RT} = \frac{\Delta G^0_i + \Delta H^0_i (T_0/T-1)}{RT_0} + \frac{C_p_i (l + \ln(T_0/T) -T_0/T)}{R},
\]

and data on \( \Delta G^0 \), \( \Delta H^0 \) and \( C_p \) were listed in NBS Thermodynamic Tables (Wagman et al., [13]).

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

\[
K_j = \Pi a_i^{vij} = \Pi ( \gamma_i m_i^{0} )^{vij},
\]

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. Assuming water activity \( a_w \) in the aerosols under equilibrium with air be equal to the relative humidity \( \text{RH} \) of air, the mass concentration of water in the aerosols \( W \) kg-water m\(^{-3}\)-air is calculated by

\[
W = \Sigma C_i / \Sigma m_i^0(a_w),
\]

where \( C_i \) is the aqueous phase concentration of electrolyte \( i \) in mole m\(^{-3}\)-air and \( m_i^0(a_w) \) is the molality (mole kg\(^{-1}\)) 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, Pitzer method [9] is adopted in the present model.
4 Results and discussion

4.1 Change of air quality caused by volcanic eruption

Annual mean air quality after eruption showed significant changes. As for the gaseous pollutants, SO$_2$ increased four times, although it was still at very low level compared with that in Tokyo metropolitan area [8] (3-7 ppb in 1999), but O$_3$ level did not change. As for the precipitation, SO$_4^{2-}$ and NH$_4^+$ increased by 63% and 26% but pH value did not change significantly.

Change of aerosol composition is particularly interesting. SO$_4^{2-}$ and NH$_4^+$ in aerosol increased by 52% and 32%, while NO$_3^-$ and Cl$^-$ decreased. These changes were more clearly seen in two-months mean air qualities from August to September in 1999 and 2000, i.e., before and after eruption. The pH in the precipitation decreased from 5.11 to 4.50.

Figure 1 illustrates time series of aerosol-phase SO$_4^{2-}$, NO$_3^-$, Cl$^-$, NH$_4^+$ and gaseous SO$_2$ concentrations, in that significantly different patterns can be distinguished. Cases i, ii and vi were for air masses under direct influence of the volcanic plume and cases iii, iv and v were for the Asian continental outflows, which are discriminated by the trajectory analysis of air masses backward from the observation site. In the continental outflows aerosol-phase NO$_3^-$ and SO$_4^{2-}$ were at high levels but gaseous SO$_2$ were low, indicating that anthropogenic SO$_2$ and NOx emitted in the continent were converted to sulphate and nitrate during long-range transport. In addition, it is noted SO$_4^{2-}$ almost balanced to NH$_4^+$ in the aerosols. In contrary, in the air masses under direct volcanic influence, both SO$_2$ and SO$_4^{2-}$ concentrations increased several times. In particular, in the period from 13 to 15 September 2000, SO$_2$ concentration reached extremely high values around 200 $\mu$g m$^{-3}$ and the SO$_4^{2-}$ concentration attained to 30-40 $\mu$g m$^{-3}$ which had not been experienced before eruption. The SO$_4^{2-}$ concentration showed the diurnal pattern similar to O$_3$, increasing in daytime and decreasing at night. The similar pattern was also seen in PM10. It indicates that photochemical reactions actively produce a large amount of SO$_4^{2-}$ and so PM10. In this period aerosol-phase NH$_4^+$ increased but NO$_3^-$ and Cl$^-$ decreased significantly, except for Cl$^-$ in case vi when sea-salt contribution was extraordinarily high.

4.2 Time variation of aerosol components and gaseous pollutants after volcanic eruption

Typical water-soluble compositions and ion balances of aerosols before and after eruption are presented in Figure 2. Here, they are compared for air masses that have passed through almost identical route near Miyake volcano. Before eruption the ion balance was good, when SO$_4^{2-}$, NO$_3^-$, Cl$^-$ were adopted as anion and NH$_4^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Na$^+$ as cation. Even for the continental outflows after eruption it was also in case (not shown). Good ion balance could be seen in urban aerosols also. In the central Japan 99% balance was obtained with the correlation coefficient $r=0.996$ (Sasaki et al. [10]). Furthermore, even when SO$_4^{2-}$ was at high level, it took gaseous NH$_3$ into aerosol to form (NH$_4$)$_2$SO$_4$ aerosols.
That is, the equivalent concentration of $\text{SO}_4^{2-}$ almost balanced to that of $\text{NH}_4^+$. Even after the volcanic eruption it is true in the cases of continental outflows. It is clearly seen in Fig.1, and thus the increase of $\text{SO}_4^{2-}$ after eruption has resulted in the increase of aerosol-phase $\text{NH}_4^+$.

Figure 1: Time series of aerosol-phase $\text{Cl}^-$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{SO}_4^{2-}$, $\text{NH}_4^+$ and gaseous $\text{SO}_2$ concentrations at Happo.
Figure 2: Aerosol composition at Happo in air masses that had passed over Mivake island. a. In 1200-1500LST 14 Sept. 1999 before eruption: b, c and d, in 1200-1500LST 30 Aug. 2000, in 1600-2000LST 14 Sept. 2000 and in 1200-1600LST 30 May 2001, respectively, after eruption.

After eruption aerosol composition has changed drastically. At first, it is noted that cation exceeded by two times more than total cation. It suggests such aerosols might be strongly acidic. When a large amount of $SO_4^{2-}$ is produced from the volcanic $SO_2$ in the mid troposphere, at first it takes gaseous $NH_3$ into aerosol to form $(NH_4)_2SO_4$ aerosols. However, if much larger amount of $SO_4^{2-}$ were produced, gaseous $NH_3$ and alkaline crustal ions in the mid troposphere would be exhausted. Then, the excess $SO_4^{2-}$ is at the alkaline deficit state or exists as sulphuric acid mist, and then the aerosols exhibit strong acidity. It is true for young aerosols that have been transported directly after passing nearby the volcano (Fig. 2c). For aged aerosols alkaline components are added but insufficiently (Fig. 2b and d). This imbalance suggests co-existence of $HSO_4^-$ and $H^+$, together with $SO_4^{2-}$.

In order to see detailed change of aerosol composition caused by the volcanic effluents, a multicomponent gas aerosol equilibrium model was used. This model could be used successfully in the previous paper to explain behaviours of volatile species in the urban aerosols at remote sites in this central Japan. It predicted the gas-aerosol equilibrium with high accuracy, i.e., the correlation coefficients were $r = 0.99$ for gaseous $NH_3$, $r = 0.93$ for $HNO_3$ and $r = 0.97$ for $HCl$. 
Using the observed concentrations of total nitrate and total chloride, respectively, both in aerosol and gas phases, together with sulphate concentration and other crustal aerosol compositions, gas-aerosol partitioning of volatile components $\text{NO}_3^-$, Cl$^-$ and $\text{NH}_4^+$ were calculated for their temperature and relative humidity conditions. The undetermined aerosol acidity and the free acid concentration, i.e., H$^+$ and $\text{HSO}_4^-$, were also obtained at the same time. The calculation was made for typical set of aerosols before and after eruption, and the predicted result was presented in Table 1.

In the air masses under direct volcanic influence the averaged pH value of aerosols was 0.00. 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 to 78%. In contrast, before eruption the aerosol pH value was 2.08, and almost all sulphate existed as $\text{SO}_4^{2-}$.

Table 1: Gas-aerosol partitioning before and after eruption.

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<th>Species</th>
<th>Conc. µg m$^{-3}$***</th>
<th>Gas-phase fraction</th>
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<th>Observed</th>
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<td>0.39</td>
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<table>
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<th>Species</th>
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<th>Gas-phase fraction</th>
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<td>0.98</td>
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* Concentrations of ammonia, nitrate and chloride are total of gas and particulate.  
** Average from 1200LST 13 Sept. to 0300LST 14 Sept. 1999.  

The present equilibrium model predicts the observed peculiar behaviours of volatile components, i.e., the change of gas-aerosol partitioning of volatile components caused by the volcanic eruption. At first gaseous $\text{NH}_3$ was taken into aerosols by the excess amount of sulphate. Thus, its gas-aerosol partitioning was almost on the aerosol side and resulted in enrichment of $\text{NH}_4^+$ in aerosols, while the gaseous $\text{NH}_3$ fraction before eruption was 19%. After exhausting $\text{NH}_3$ gas, the excess amount of $\text{SO}_4^{2-}$ expels $\text{NO}_3^-$ and $\text{Cl}^-$ and took their place in the aerosol. The gas-aerosol equilibrium model predicts that 95% of nitrate and 98% chloride are expelled to gas phase even though the equilibrium generally tends to shift to gas phase at low temperature in the mid troposphere. Those values of gas fraction are in a great contrast with 29% and 39% for nitrate and chloride, respectively, in the air masses before eruption. The predicted peculiar behaviours of volatile components are well confirmed by the observation as seen in Table 1.
The expelled HNO₃ and HCl gases have large dry deposition velocity (Hauglustaine et al. [2]), about 4 cm/s, more than ten times larger than NO₃⁻ and Cl⁻ aerosols. Thus a large amount of their dry deposition might occur in regional scale and enhances the environmental acidification caused by the volcanic SO₂ and sulphate depositions. Furthermore, since NH₄⁺ aerosol taken by SO₄²⁻ has much lower deposition velocity than NH₃ gas, the uptake of NH₄⁺ inhibits dry deposition and so environmental neutralization.

**Figure 3:** Precipitation composition for air masses that had passed over Mivake island. a. In 1650LST 14 Sept. - 0900LST 15 Sept. 1999 before eruption; b. In 1400-2400LST 30 Aug. 2000; c. In 1400LST 30 May - 0900LST 31 May 2001, after eruption.

Precipitation compositions before and after eruption are compared in Fig. 3. Here, the compositions in Figure 3b and c are typical in the air masses under direct volcanic influence, while the compositions in Figure 3a is for air masses passed along the same course before eruption. At first, SO₄²⁻ after eruption was at much higher concentrations than that before eruption and made the precipitation more acidic. 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 chloride in the precipitation shows a great contrast to these in aerosols. Even after eruption precipitation contained a large amount of NO₃⁻ and Cl⁻, in contrast to very low concentrations of nitrate and chloride aerosols. It is because the expelled HNO₃ and HCl gases can be readily dissolved into cloud and precipitating waters. That mechanism was well-understood by their extremely large values of dissolution constants, i.e., the so-called Henry’s law constants of HNO₃ and HCl being 2.1x10⁵ and 727 mol l⁻¹ atm⁻¹ which were more than three orders larger than that for SO₂ and NO₂ (Seinfeld and Pandis [11]). Thus, the expelled HNO₃ and HCl gases were absorbed in the precipitating water massively and deposited on the ground.
5 Conclusions

Miyake volcano began to erupt from 8 July 2000. It is located in the Northwest Pacific Ocean and 200 km south from Tokyo metropolitan area. Its SO$_2$ emission amounted to a maximum 6x10$^4$ 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 has been decreasing to 10$^4$ ton/day.

Aerosols and precipitation, together with gaseous pollutants have been observed from two years before the eruption. 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, SO$_2$ was converted to SO$_4^{2-}$. Annual mean concentration of SO$_2$ was 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 1.7 and 1.3 times. NO$_3^-$ and Cl$^-$ concentrations were also increased significantly, and H$^+$ concentration increases by 15% ($\Delta$pH=0.06).

In contrast, aerosol concentrations of NO$_3^-$ and Cl$^-$ decreased under the influence of volcanic effluents. That was 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$_4$)$_2$SO$_4$ aerosol and then, driving out NO$_3^-$ and Cl$^-$, it took their place in the aerosol. It made the aerosol acidic, i.e., pH values less than 1 and partitioned sulfate into SO$_4^{2-}$ and HSO$_4^-$ . These facts were 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 be deposited to the ground through dry deposition process. Moreover, these HNO$_3$ and HCl gases are dissolved into water droplets much more and faster than other gaseous pollutants. Their dissolution constants $H_d$ are 2.1x10$^5$ 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, both dry- and wet-deposition processes of nitrate and chloride are enhanced by the excess formation of sulfate by the volcanic eruption. That is, the enhanced nitrate and chloride depositions might accelerate the environmental acidification in addition to the acidification by volcanic sulfate. Moreover, it might also affect the environmental eutrophication by NO$_3^-$ and NH$_4^+$.

References


