

# Fogwater Chemistry at a Mountainside Forest and the Estimation of the Air Pollutant Deposition via Fog Droplets Based on the Atmospheric Quality at the Mountain Base

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Fogwater chemistry has been observed at Mt. Oyama abutting on the Kanto Plain in Japan. Many air pollutants are deposited via fog droplets, and the nitrogen deposition rate via fogwater is at the same level as that via rainwater. The fogwater concentrations depend on the air pollutant concentrations, liquid water content, and the fog base altitude estimated from the meteorological data for the mountain base. The air pollution dominating the concentrations of fogwater components can be estimated from the sulfur dioxide concentration at the base of the mountain. The concentrations of fogwater components were dominated by the absorbing rates of air pollutants into the fog droplets and were not inversely proportional to the LWC. The concentration of fogwater can be estimated approximately from the SO<sub>2</sub> concentration at the mountain base, the fog base altitude, and the LWC measured for the fogwater.

## Introduction

Acid fog has been attracting interest as a form of acid deposition. Frequent occurrences of very acidic fog were reported in Los Angeles, where the lowest pH value reached 1.7 (1). Acid fog causes strong environmental effects; 4000 people died in London during a week in 1952 when the SO<sub>2</sub> concentration was high and an acid fog of pH 1.5–1.8 (2) was formed. Acid rain also injured tens of thousands of people in Japan in foggy drizzle events during 1973 and 1975 by irritating eyes, throat, and skin. Acid fog events occur not only in urban areas but also on mountainsides near the urban area. Fog droplets readily absorb air pollutants and effectively scavenge them from the atmosphere by their deposition on mountainside forests (3). On the mountainside, the multiple chemical stress of the co-occurrence of ozone and acid fog was present (4), and the deposition fluxes of air pollutants via fog droplets on the forest were large (5, 6). Therefore, the effect of acid fog on forest dieback has been discussed (7). The authors have analyzed fogwater at Mt. Oyama situated at the east end of the Tanzawa Mountains, which lie at the southwest part of the Kanto Plain. There is a virgin fir forest at Mt. Oyama, and most of the firs have been dying during the past decades (8). The acid fog may be one of the causes

of the dying because fir seedlings were reported to be damaged by the application of an acid solution of a pH lower than 3 (9). Acid fog events have occurred at Mt. Oyama (10–12), where the measured lowest pH value of fog was 1.95 in 1994 (13). At the sampling station, aldehydes were also determined to be at high concentration (14). Mt. Oyama is not a highly polluted area in Japan. The mean concentrations of air pollutants at Isehara City Hall, at the base of Mt. Oyama, were lower than their mean values in Japan (12).

Air pollutants affect the chemical composition of the fog droplets, and many investigations of the chemistry of urban fogwater have been reported on the basis of equilibrium and kinetic theories (15–18). Mountainside fogwater chemistry has been also reported. Choularton et al. investigated the cloud chemistry at Great Dun Fell and reported the converting pathway of nitrogen oxide to nitrate (19), the aqueous-phase oxidation of sulfur dioxide (20), and the conversion of ammonia to ammonium ion (21). In Japan, Okita et al. (22, 23) analyzed cloudwater at Mt. Norikura in the center district and at Mt. Tsukuba in the Kanto District. They reported minimum pH values of 3.0 and 2.8, respectively. Murano et al. (24) observed fog events with high acidities at Mt. Akagi in the Kanto district whose major acidic component was nitric acid. Recently, Minami and Ishizaka (25) reported acid fog events at Mt. Norikura caused by sulfuric acid and nitric acid, where the pH values were reported to be 3.30–4.25.

In the fogwater chemistry on the mountainside, the transfer process of air pollutant in gaseous phase to fogwater and the scavenging of air pollutant via the polluted fogwater deposition on the forest canopies are important (26). However, there have been few reports discussing the scavenging effect of fog on air pollutants on the basis of the observed data of the chemistry of the fogwater covering on a mountainside forest and the meteorology at the fog event. In our sampling site, there is a valley from a meteorological station to the sampling site, where upslope fog rises up as a natural wind tunnel to study of the dynamic change of the components of the fogwater at a mountainside. In this paper, therefore, we will summarize the chemical composition of fogwater and show that the air pollutants concentration of an upslope fog over a mountainside forest can be estimated from the air pollutant concentration and the fog characteristics, that is, the LWC and the fog base altitude.

## Experimental Section

At Afuri shrine located at midslope of Mt. Oyama, since July 1988, we have collected fog samples using a string-type collector with a refrigerator to store the fog samples and a time recorder (11, 12). Fogwater collected on the strings flowed down to Teflon bottles in the refrigerator. Every 50–60 mL of fogwater samples was stored in each bottle from the beginning of a fog event, although the volume of the last sample of the fog event was smaller. The altitude of the sampling station is 680 m above sea level, and the fog data obtained there in 1995 are analyzed in this paper. Mt. Oyama, whose top elevation is 1252 m above sea level, is about 50 km west-southwest of Tokyo and abuts on the southwest of the Kanto Plain as shown in Figure 1. Fog events occur at Mt. Oyama when the valley wind blows and the relative humidity is high at the base of the mountain. Rain samples were also collected at the fog sampling station to compare the concentrations of the rainwater components with those of the fogwater components. The rain collector was composed of a funnel, a polypropylene bottle, and a filter holder with a 1.2- $\mu$ m pore size membrane filter mounted between the funnel and the bottle as reported earlier (27).

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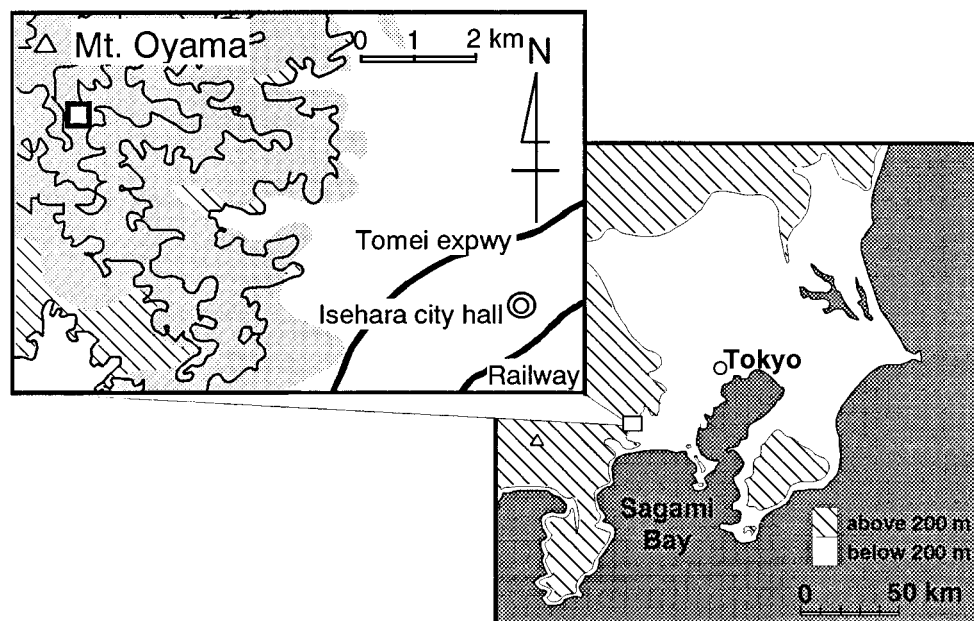


FIGURE 1. Map around fog sampling station. The screen and the square show the wooded region and the fog sampling point, respectively.

TABLE 1. Concentrations of Fog and Rain Components at Mt. Oyama in 1995

sample	frequency of fog event (%)	precipitation amount (mm)		pH	concentration (mequiv L <sup>-1</sup> )								
					H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
fog	3.33	41 <sup>a</sup>	min	2.59	1	48	0	0	0	0	18	34	29
			max	6.05	2568	6130	5881	536	698	1587	5805	4264	3081
			av	3.66	216	696	110	25	33	72	240	487	273
rain		1437	min	4.09	0.1	0	3	0	1	4	11	2	10
			max	7.05	80	118	71	11	14	367	62	96	86
			av	4.83	15	14	30	3	6	22	31	18	30
			av concn ratio (fog/rain)				14	50	4	8	5	3	8

<sup>a</sup> Estimated value on the assumption of the fog deposition velocity of 0.14 mm h<sup>-1</sup>.

The rain and fogwater samples were collected every week to be analyzed in our laboratory.

Aerosol and gases were also collected at the sampling station. A low-volume air sampler (Nippon Kagaku Kogyo, Ltd, model 9023) was used for the collection of aerosol smaller than 7.07  $\mu$ m in particle diameter at a pumping rate of 15 L min<sup>-1</sup>. The acidic and basic gases (SO<sub>2</sub>, HNO<sub>3</sub>, HCl, and NH<sub>3</sub>) were collected by the filter method (28, 29) at a pumping rate of 2 L min<sup>-1</sup>. After the sample collection, the filters were irradiated with an ultrasonic wave in pure water to dissolve water-soluble components in the aerosol and the gaseous components trapped on the filters. Ultrasonic irradiation has been reported to accelerate the degradation of chemical contaminants in the water to inorganic ions as the final products (30). It could have changed the chemical composition of the filter samples, but the determined values have not been corrected in this paper.

The pH, conductivity, and concentrations of the major ions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and NH<sub>4</sub><sup>+</sup>) in the fog, rain, and aerosol samples were measured. For the analysis of gaseous components, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup> were determined. The pH and the conductivity were measured with a Toa Electronics HM-60S pH meter and a Kyoto Electronics CM-117 conductivity meter, respectively. The anions were determined by a Dionex 2000i/SP ion chromatograph with a column of Dionex IonPac AS4A. The cations, other than proton, were determined by a Dionex DX-100 ion chromatograph with a column of Dionex IonPac CS12.

The air pollution and the meteorological phenomena have been measured at the city hall of Isehara situated at the base

of Mt. Oyama by the Air Preservation Section of Kanagawa Prefecture. Wind direction, wind speed, temperature, relative humidity, and NO, NO<sub>2</sub>, SO<sub>2</sub>, and oxidant concentrations have been measured at the city hall, and we used some of these data in this paper.

## Results and Discussion

**Air Pollutant Deposition via Fog Droplets.** The concentration ranges and the volume-weighted average values of the major components of fog and rain at Mt. Oyama in 1995 are shown in Table 1, as well as the fog event frequency. The fogwater collector stopped the fog collection not only when it was out of order but also when the fog event frequently occurred within 1 week and 36 samples were already stored in the refrigerator of the collector. The fog event frequency in Table 1 was then defined as the measured total fog event period divided by the total operating hours of the collector in 1995. There were 175 fog samples collected in 1995, and the ratios of the total concentration of cations to that of anions were in the range of 0.90–1.55. When the ion concentration was low, the ratios tended to be greater than 1. The ratios of 158 samples were between 0.9 and 1.3. It has been reported that fogwater contains considerable amounts of organic acids of formate, acetate, oxalate, etc. (31, 32) and hydroxymethanesulfonate (HMSA) (33). The cation-rich data must be caused by these organic anions present in fogwater that were not determined in this study.

The lowest pH of fog in 1995 was 2.59 at the sampling station, and the average pH of the fog was lower than that of rain by 1.17. The average concentrations of fog compo-

TABLE 2. Correlation Factors between Concentrations of Fog Components<sup>a</sup>

concn	[NH <sub>4</sub> <sup>+</sup> ]	[Na <sup>+</sup> ]	[K <sup>+</sup> ]	[Mg <sup>2+</sup> ]	[Ca <sup>2+</sup> ]	[Cl <sup>-</sup> ]	[NO <sub>3</sub> <sup>-</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]	total
[H <sup>+</sup> ]	0.705	-0.011	0.183	0.236	0.310	0.571	0.810	0.732	0.796
[NH <sub>4</sub> <sup>+</sup> ]		0.090	0.536	0.446	0.599	0.778	0.892	0.872	0.954
[Na <sup>+</sup> ]			0.323	0.813	0.419	0.494	0.105	0.254	0.297
[K <sup>+</sup> ]				0.569	0.606	0.425	0.485	0.549	0.548
[Mg <sup>2+</sup> ]					0.738	0.705	0.405	0.541	0.603
[Ca <sup>2+</sup> ]						0.650	0.561	0.605	0.673
[Cl <sup>-</sup> ]							0.610	0.720	0.848
[NO <sub>3</sub> <sup>-</sup> ]								0.786	0.919
[SO <sub>4</sub> <sup>2-</sup> ]									0.912

<sup>a</sup> Correlation factors larger than 0.75 are italic.

nents were 3–50 times higher than those of rain components. The annual deposition flux can be calculated as the product of the mean ion concentration and the annual precipitation amount. The amount via fog droplets is the product of 365 d yr<sup>-1</sup>, 24 h d<sup>-1</sup>, the frequency of fog events, and the fog deposition velocity (mm h<sup>-1</sup>). The fog deposition velocity depends on the LWC and the wind speed, but the representative value, 0.14 mm h<sup>-1</sup> (34), was used in the calculation of the estimated precipitation amount via fog droplets in Table 1. The precipitation amount of rainwater was 35 times higher than that of fogwater. Vong et al. reported that fogwater deposition equals or exceeds the average precipitation at the elevated sites where fog events frequently occur (35). The concentration ratios of most of the components in fogwater to those of rainwater in Table 1 were smaller than 35. However, the ratio of the ammonium ion was larger than this value, that of nitrate was close to this value, and the deposition flux of nitrogen via fog was at the same level as that via rain at the point. The nitrogen saturation of the soil becomes an important problem in the dieback forest (36); the nitrogen saturation was recently reported in the Rocky Mountains where the wet deposition flux was about 4 kg of N ha<sup>-1</sup> yr<sup>-1</sup> (37). The deposition of nitrogen at the sampling station via rainwater was calculated from the data in Table 1 to be 6.4 kg of N ha<sup>-1</sup> yr<sup>-1</sup>, and the nitrate ion was abundant in the soil of Mt. Oyama (38). The deposition flux via fog is more significant at a mountainside forest at a high altitude where fog events occur more frequently (6), and the contribution of fogwater to the nitrogen saturation must be large in a mountainside forest near an urban region, such as in Mt. Oyama.

The correlation factors between the concentrations of fog components were calculated and are shown in Table 2. The factor between the total ion concentration and the concentration of each component other than metal ions was high. This means that the chemical composition, other than metal ions, was almost the same in every fog event. The correlation factors between anions and both hydrogen and ammonium ions were in the order, NO<sub>3</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup>. This means that the contribution to the acidity of fog at the sampling station was in the order of nitric acid > sulfuric acid > hydrogen chloride. The order was the same as the concentration order. Sulfate ion concentration is reported to be greater than nitrate ion concentration for most of the fog data previously reported (6). At our sampling station, the concentration of nitric acid gas was about the same order as that of SO<sub>2</sub>, and the concentration of nitrate ion was the highest among the anions in urban fogwater (16). The correlation factors of these cations with chloride ion were low. The major source of chloride ion is the hydrogen chloride emitted from incinerators and sea salt. The correlation factor between sodium ion and chloride ion was also low, although chloride ion concentration was high when sodium ion concentration was high. The contribution of hydrogen chloride and sea salt to the chloride ion concentration in fogwater was different in

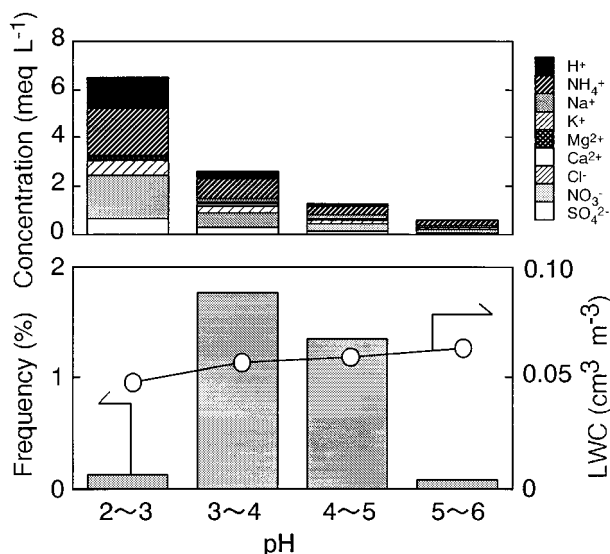


FIGURE 2. Relationship between the frequency, liquid water content, and the ion concentration and pH of fogwater.

each fog event, while the acid fog event with the lowest pH (pH 1.95) at Mt. Oyama resulted from an air mass highly polluted with HCl (13).

Figure 2 shows the relationship between the volume-weighted average ion concentration, the fog event frequency, and the LWC and pH of fogwater. The periodic frequency of a very acidic fog event, where the pH was 2.59–3.00, was about 0.13%, while the frequency was 0.086% for fogwater pH between 5.00 and 5.32. The frequency was the highest when the pH was 3–4. The LWC did not change with the pH of the fogwater, and the average LWC of acidic fogwater was about the same as that of neutral fogwater. In the calculation of the average LWC for pH 5–6, the maximum and minimum LWC values were omitted because there were only five data points in the range. With a decrease in pH, the concentrations of protons and ammonium ions increased. The concentrations of other metal ions did not change with pH, except at pH 5–6, where all the ion concentrations were low and the percentage of ammonium ion was greater than that in other pH droplets. The percentage of each anion scarcely changed with the solution pH, although the percentage of nitrate ion was much greater at pH 2–3 than those in solutions of pH larger than 3. Nitric acid was the major component that acidified the fog droplets at Mt. Oyama. This is also shown by the high correlation factor between proton concentration and nitrate ion concentration in Table 2.

**Effect of Air Pollution on Major Ion Concentrations.** In the case of upslope fog, the concentrations of fogwater components were affected by air pollution at the base of the mountain. The correlation factors between the ion con-

TABLE 3. Correlation Factors between Concentrations of Fog Components and SPM and SO<sub>2</sub> Concentrations

concn	[H <sup>+</sup> ]	[NH <sub>4</sub> <sup>+</sup> ]	[Na <sup>+</sup> ]	[K <sup>+</sup> ]	[Mg <sup>2+</sup> ]	[Ca <sup>2+</sup> ]	[Cl <sup>-</sup> ]	[NO <sub>3</sub> <sup>-</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]	total
SPM	0.314	0.404	-0.112	0.138	0.097	0.232	0.332	0.361	0.223	0.359
SPM <sub>60</sub> <sup>a</sup>	0.381	0.510	-0.122	0.049	0.176	0.294	0.481	0.464	0.266	0.466
SO <sub>2</sub>	0.549	0.472	-0.144	0.135	0.044	0.251	0.321	0.519	0.421	0.477
SO <sub>2,60</sub> <sup>a</sup>	0.673	0.570	-0.059	0.133	0.205	0.405	0.498	0.686	0.526	0.630

<sup>a</sup> SPM<sub>60</sub> and SO<sub>2,60</sub> means the correlation factors limited for the samples collected in less than 60 min. The correlation factors between SPM and SO<sub>2</sub> and between SPM<sub>60</sub> and SO<sub>2,60</sub> were 0.562 and 0.478, respectively.

centration of each fog component and the concentrations of suspended particulate matter (SPM), sulfur dioxide, and oxidants that were measured at the base of the sampling station, Isehara City Hall, were examined. The ion concentration depends on SPM and SO<sub>2</sub> concentrations as shown in Table 3, while there was no relationship between the ion concentrations and oxidant concentration. In a fog event with a low LWC, it took a long time to obtain a fog sample, and the atmospheric quality changed during the long sampling period. The correlation factor was then calculated for the limited samples collected during 60 min. The correlation factors increased to larger values as shown in Table 3. The mechanism of gas formation and the reaction process of SO<sub>2</sub> is much different from, for example, that of nitrogen oxide as the precursor of nitrate ion (39), but there were some correlations between the fog components concentrations and the SO<sub>2</sub> concentration. SO<sub>2</sub> can be a good predictor of fogwater ion concentrations at this site. The reason SO<sub>2</sub> can be the predictor is that the major source of pollutant gases at the sampling site is the Kanto Plain, where there is a big manufacturing district and heavy traffic. Isehara, at the base of Mt. Oyama, lies in the way of the land and sea breeze between the Kanto Plain and the Sagami Bay (40), which is due to the topography shown in Figure 1, and the pollutant gases come on the breeze. Therefore, the SO<sub>2</sub> concentration is large whenever the concentrations of air pollutant gases that are readily scavenged by fog droplets are large in the air mass transported to the mountain base. However, SO<sub>2</sub> cannot be a good predictor of fogwater ion concentration in general. If there were some air pollutant sources at the base of the mountain, SO<sub>2</sub> concentration was not to be the indicator of air pollution. Other than the reason stated above, the data for SO<sub>2</sub> may contain other gaseous concentrations. The Japanese standard method of the determination of SO<sub>2</sub> is the oxidation of the dissolved SO<sub>2</sub> in the absorbing solution by hydrogen peroxide followed by a conductivity determination. The SO<sub>2</sub> data then contain the concentration of not only SO<sub>2</sub> but also some other gases, such as hydrogen chloride and nitric acid, although the concentrations of these gases are lower than that of SO<sub>2</sub> (41). Figure 3 shows the relationship between the volume-weighted average ion concentration in the fogwater and the SO<sub>2</sub> concentration at the base of the sampling station averaged during the collection period of the corresponding fogwater sample. The concentration of fogwater increased with the increase in SO<sub>2</sub> concentration, as expected from Table 3.

#### Effect of Fog Base Altitude on Major Ion Concentrations.

Gaseous air pollutants are readily absorbed into the fog droplets (15), and the polluted fog droplets collide with the leaves of the trees by wind and deposit on the forest (7). The scavenging effect of fog is very effective at the mountainside because of the turbulent eddies on the canopies (5). The fogwater absorbs pollutants, and the scavenging effect is the most effective at the fog base (42). The polluted fog droplets deposit on the forest around the fog base, and the pollutant concentration in the fog droplets is diluted by the freshly formed fog droplets during the transport of air mass from the fog base to the fog sampling station. The concentrations of the fogwater components are then dependent on the fog

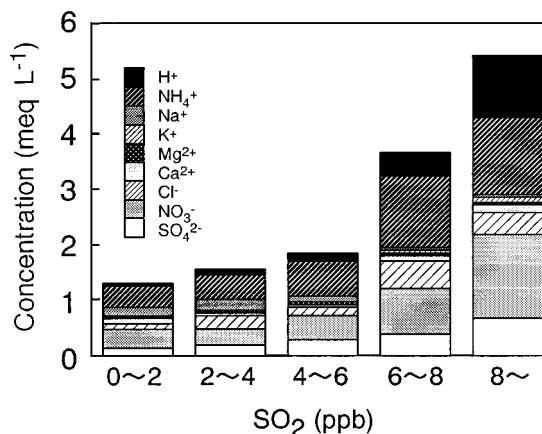


FIGURE 3. Relationship between major ion concentration in fogwater and sulfur dioxide concentration.

base altitude (FBA). The value of FBA,  $h$ , can be estimated by Henning's equation (43) as follows:

$$h = 125 \times (T_0 - D_0) + h_0 \quad (1)$$

In eq 1,  $T_0$  and  $D_0$  are the temperature (°C) and the dew point (°C), respectively, at the meteorological station at the base of the mountain and  $h_0$  is its altitude. The meteorological data used in this study were obtained at Isehara City Hall, whose altitude was about 25 m. The dew point was calculated by the following empirical equations (44):

$$E_{\text{sat}} = 6.11 \times 10^{(7.5 \times T / (T + 237.3))} \quad (2)$$

$$E = E_{\text{sat}} \times \text{RH} / 100 \quad (3)$$

In eqs 2 and 3,  $E_{\text{sat}}$  is the saturating vapor pressure (hPa) corresponding to the ambient temperature,  $T$  (°C);  $E$  is the vapor pressure (hPa); and RH is the relative humidity (%). In the calculation of  $D_0$ ,  $E_{\text{sat}}$  corresponding to  $T_0$  at the base of the mountain was obtained at first from eq 2, and the  $E_{\text{sat}}$  value and the relative humidity at the base were substituted in eq 3. The  $E$  value obtained from eq 3 was then substituted for  $E_{\text{sat}}$  in eq 2 to obtain the corresponding  $T$  value, which was  $D_0$  to be substituted in eq 1.

Figure 4 shows the effect of FBA on the total ion concentration of fogwater and LWC. The concentrations of fog components at the sampling station decreased with the lowering of the fog base. When the fog base was not lowered, the concentrations of fogwater components were kept at high levels. The dependence of the concentrations of fogwater components on FBA must be affected by the vegetation and the canopy structure (6). The liquid water content decreased with the increase in FBA, and the fog at the sampling station was thin in most of the cases when FBA was close to the sampling station. The fog with an FBA of under 100 m was also very thin, and all four samples were collected over a long period (80–426 min). The fog events with an exceptionally low FBA may occur as foggy rain events.

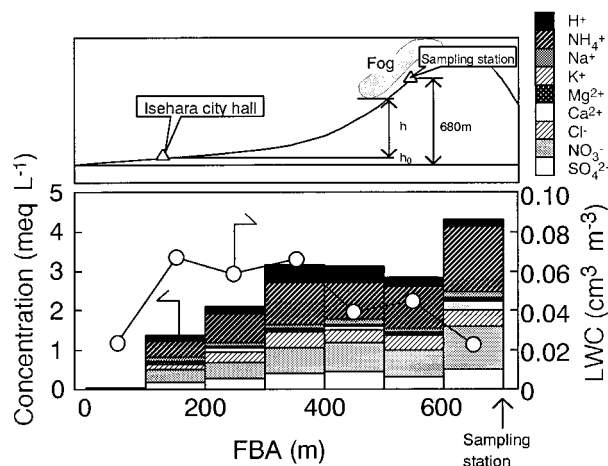


FIGURE 4. Total ion concentration and LWC vs fog base altitude (FBA).

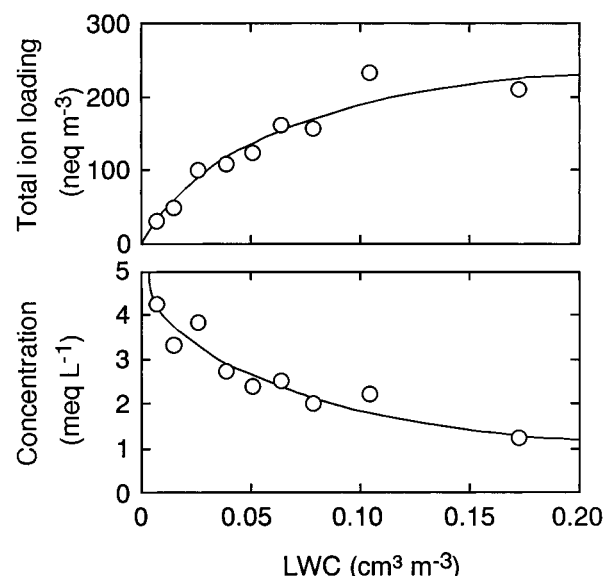


FIGURE 5. Relationship between major ion concentration and ion loading and liquid water content (LWC). The solid lines are the values estimated from eqs 8 and 9.

**Effect of LWC on Major Ion Concentrations.** It is usually estimated that the ion concentration of the fogwater is inversely proportional to the LWC (45), and the ion loading, which is calculated as the product of the ion concentration in the fogwater and LWC, is not affected by LWC. Figure 5 shows the relationship between the average ion concentration and ion loading and LWC. In the calculation of the values, every 20 data points according to LWC were averaged. The concentration decreased with the LWC, but total ion loading increased with the LWC. This cannot be explained by equilibrium theories but by kinetic theories.

The rate of absorption of a gas into an aqueous phase is given by the following equation (46):

$$F = k_g(C_{\text{gas}} - C_{\text{gas,eq}}) \quad (4)$$

where  $C_{\text{gas}}$  is the concentration in the gas phase,  $C_{\text{gas,eq}}$  is the value in equilibrium with the instantaneous molarity in the liquid, and  $k_g$  is the gas-phase mass transfer coefficient. When the chemical species in the aqueous phase are not equilibrated with those in the gas phase and  $C_{\text{gas,eq}}$  can be ignored as compared with  $C_{\text{gas}}$ , the concentration in the aqueous

TABLE 4. Total Atmospheric Concentration ( $\{C\}$ ), Delay Constant ( $a$ ), and Correlation Factor ( $r$ ) for the Major Components of Fogwater<sup>a</sup>

	$\{C\}$ (nequiv $\text{m}^{-3}$ )	$a \times 10^7$	$r$
$\text{H}^+$	53.50	1.742	0.723
$\text{NH}_4^+$	124.6	1.010	0.927
$\text{Na}^+$	7.31	0.0788	0.936
$\text{K}^+$	2.67	0.393	0.897
$\text{Mg}^{2+}$	2.79	0.171	0.945
$\text{Ca}^{2+}$	5.73	0.141	0.918
$\text{Cl}^-$	28.5	0.462	0.891
$\text{NO}_3^-$	78.8	0.835	0.891
$\text{SO}_4^{2-}$	34.0	0.515	0.941
total ion	309.4	0.6655	0.959

<sup>a</sup> The constants,  $\{C\}$  and  $a$ , are defined by eqs 8 and 9.

phase is estimated by

$$C_{\text{liq}} = k_g S C_{\text{gas}} t / V \quad (5)$$

where  $C_{\text{liq}}$  is the concentration in the fogwater,  $S$  is the total surface area of the fogwater,  $C_{\text{gas}}$  is the concentration in the gas phase,  $t$  is the average scavenging time of the gaseous species into fogwater floating in the atmosphere, and  $V$  is the total volume of the fogwater, i.e., the LWC. The total atmospheric concentration,  $\{C\}$ , is defined by

$$\begin{aligned} \{C\} &= C_{\text{gas}} + C_{\text{liq}} V \\ &= V C_{\text{liq}} / (k_g S t) + C_{\text{liq}} V \end{aligned} \quad (6)$$

The total atmospheric concentration can also be derived as a function of  $C_{\text{liq}}$  and  $V$  from equilibrium theories, and the first term in eq 6 ( $C_{\text{gas}}$ ) is negligible in the derived equation when the dimensionless Henry's law constant ( $C_{\text{liq}}/C_{\text{gas}}$ ) is very large. If the fog droplets are spheres, the area is shown as the function of the volume as in eq 7 on the assumption that the fog droplet has a homogeneous diameter:

$$S = (36\pi n)^{1/3} V^{2/3} \quad (7)$$

where  $n$  is the number of the fogwater droplets. In the derivation of these equations, it is simply assumed that the fog droplets have a homogeneous diameter and that the diameter is constant for all the fog events. In a real fog, there is a droplet size distribution, and the ion concentration depends on the droplet size (47). However, it is very difficult to discuss with the consideration of the fog droplet size distribution, and the size and its distribution change with time depending on the local meteorology were not measured in this study because of the difficult determination. Therefore, the assumption limits the estimation. The concentration in the fog droplets and the ion loading ( $L$ ) can be defined by

$$C_{\text{liq}} = \{C\} / (a + V) \quad (8)$$

$$L_{\text{liq}} = \{C\} / (aV^{-1} + 1) \quad (9)$$

$$a = 1 / \{ (36\pi / V_{\text{droplet}})^{1/3} k_g t \} \quad (10)$$

where  $a$  is the delay constant, and  $V_{\text{droplet}}$  is the average volume of the fogwater droplets. If the delay constant is very small, i.e.,  $t$  or  $k_g$  are very large, eq 8 changes to be  $C_{\text{liq}} = \{C\} / V$ .

The  $a$  and  $\{C\}$  values for major ions in fogwater obtained by regression analysis between  $1/C_{\text{liq}}$  and  $V$  are shown in Table 4 with the correlation factors. The derivation of eqs 8 and 9 was for gaseous species, but it can be also applied to the components in an aerosol. The total atmospheric concentration,  $\{C\}$ , of most of major ions was smaller than

TABLE 5. Average Concentrations (nequiv m<sup>-3</sup>) of Soluble Components in Aerosol and Acidic and Basic Inorganic Gases

soluble components in aerosol									acidic and basic inorganic gases			
H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NH <sub>3</sub>	HCl	HNO <sub>3</sub>	SO <sub>2</sub>
4.3	129	15	5.3	5.9	7.5	16	29	111	50	11	12	18

<sup>a</sup> The data were obtained at the fog sampling station at Mt. Oyama in 1995.

the average concentration in the ambient air of the sampling station shown in Table 5. This was caused by the scavenging effect of the fogwater formed below the sampling station as explained in the preceding session. The total atmospheric concentration of nitrate ion was much larger than the sum of the gas and aerosol concentrations, which means that nitrate ion in fogwater was supplied not only from aerosol and nitric acid gas but also from other species, such as HNO<sub>2</sub> and NO<sub>2</sub>. The small delay constant for metal ions may mean that these components were scavenged as the condensation nuclei of the fog droplets and  $k_g$  was very large, where equilibrium theories can be applied. The delay constant of the components supplied from gaseous species was much larger than that of metal ions. The scavenging coefficient of gaseous and particulate species by cloud droplets was reported to be between 60% and 100% (48), but some delay time is needed for absorbing these species. The value of  $k_g$  for very small particles is estimated to be the ratio of the diffusivity to the radius (26), and it is calculated to be 1 m s<sup>-1</sup>, because the diffusivity of gas molecules in air is about 10<sup>-5</sup> m<sup>2</sup> s<sup>-1</sup> and the radius of fog droplets is about 10<sup>-5</sup> m. From the delay constant for nitrate ion, the average scavenging time,  $t$ , was calculated to be about 40 s, although it depended on the mass transfer coefficient, the diameter of the fog droplets, and so on.

The physical meaning of the scavenging time is as follows. In 1992, the meteorology at the sampling point was observed by the Air Preservation Section of Kanagawa Prefecture. The wind speed measured horizontally during fog events ranged from 0 to 1 m s<sup>-1</sup> in most of the events, and the maximum was 4.6 m s<sup>-1</sup>. In the average scavenging time, 40 s, the air mass containing fog droplets moves up 20 m along the ridge line of the mountain, when the horizontal speed of the valley wind is assumed to be 0.43 m s<sup>-1</sup>. The slope at the sampling station is about 30°, and the air mass then moves up 10 m perpendicularly, while the temperature is lowered by 0.065 °C. When the ambient temperature is 10 °C, the saturating vapor pressure of water is calculated from eq 2 to be lowered by 5 × 10<sup>-5</sup> atm. The increase in the liquid water content during the transfer of the air mass in the average scavenging time was then calculated to be ca. 0.04 cm<sup>3</sup> m<sup>-3</sup> on the assumption of an ideal gas. The value 0.04 cm<sup>3</sup> m<sup>-3</sup> is in the range of the values of LWC observed at the sampling station. The formation rate of fog droplets balances their deposition rate, and the average scavenging time corresponds to the average residence time of the fog droplets at the sampling station.

The solid lines in Figure 5 were the values calculated from eqs 8 to 10 and the values for total ions in Table 4, which agreed well with the measured values. The correlation factor between the measured values and the estimated values for the total ion concentration of the fogwater was 0.943, and the averaged ratio of the measured values to the estimated values was 1.00.

**Estimation of Major Ion Concentrations.** The ion concentrations of fogwater were affected by acid gas concentration, LWC, and FBA. The fogwater composition may be estimated from these factors. Among these factors, estimation of FBA presents many problems. The value of the FBA should be about 680 m, the sampling station altitude, at the beginning of the event. There were 51 fog events

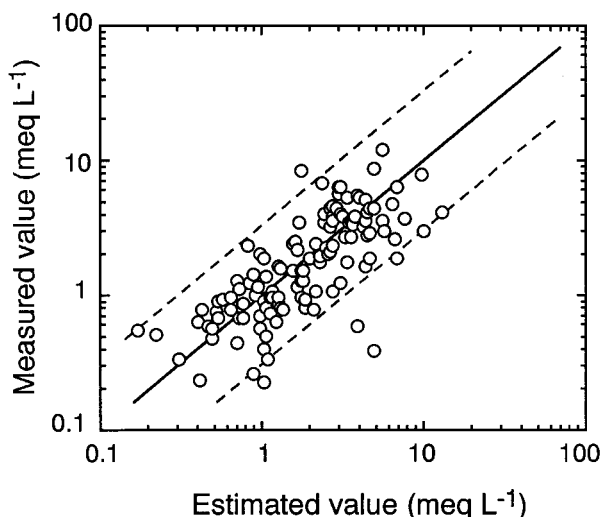


FIGURE 6. Relationship between measured values and estimated values of total ion concentration in fogwater. The total concentration in fogwater was estimated from eq 11. The solid line shows the estimated values, and the dashed lines show 300% and 30% of the estimated values.

observed at the sampling station in 1995, but FBAs at the beginning of 28 fog events were calculated to be lower than the altitude of 200 m. Some of these fog events may occur during rain events. Furthermore, there were 22 fog samples collected when the FBA was calculated to be over the altitude of the sampling station. They may be caused by local changes of wind direction, ambient temperature, and relative humidity in the mountainside, which are difficult to be estimated. Therefore, the data for some samples were excluded, and the data of 85 samples were used for further investigation; the excluded samples were those collected first in a fog event, those collected during fog events in which the FBA exceeded 680 m, and those collected during events lasting longer than 120 min. The samples collected during a long sampling period have some problems in the estimation of FBA, and the air pollutant concentration changes during the long sampling period. Figure 6 shows the relationship between the measured values of total ion concentration in fogwater and their estimated values. The estimated fogwater concentrations (mol L<sup>-1</sup>) were calculated from the regression analysis between the logarithm of the total ion concentration of fogwater (mol L<sup>-1</sup>) multiplied by (6.655 × 10<sup>-5</sup> + V) and the logarithms of the fog base altitude (m) and SO<sub>2</sub> concentration, P<sub>SO<sub>2</sub></sub> (ppb), where V is the LWC (L m<sup>-3</sup>) and the value 6.655 × 10<sup>-5</sup> L m<sup>-3</sup> is the value used in Figure 5. The estimation equation obtained by the analysis is as follows:

$$C_{\text{estimated}} (\text{eq/L}) = 5.636 \times 10^{-4} \times \text{FBA}^{0.6718} \times P_{\text{SO}_2}^{1.444} / (6.655 \times 10^{-5} + V) \quad (11)$$

The correlation factor was 0.808 between the logarithm of the estimated values and the measured values, and almost all the measured values were in the range from 30% to 300% of the estimated values as shown in Figure 6. The fogwater composition can then be estimated approximately from the

meteorological data and the air pollution in the base region of the sampling station. The major causes of the data scatter may be the incompleteness of the indicator of SO<sub>2</sub> as air pollution and the error in the estimation of FBA.

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