Fogwater Chemistry at a Mountainside in Japan

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Fogwater had been observed for 4.5 years from July 1988 to December 1992 at the midslope of Mt. Oyama at the southwest of the Kanto plains. Rainwater, aerosol, and gases had been also collected and analyzed at the fog sampling station to investigate the characteristics and acidification mechanism of fogwater. The pH of fogwater ranged from 2.61 to 7.00 and the fog with very low pH values and high ion and aldehyde concentrations were frequently observed in spring and summer. The fogwater at the site was acidified primarily by nitric acid gas absorbed in fogwater and the acid fraction of most of the fogwater ranged from 0.3 to 0.01. The acidity of fogwater is controlled by the amount of the acidic pollutants in the atmosphere, the concentrations of the neutralizing components for the acidic fogwater, primarily NH_3 gas concentration, the liquid water content in air, and the distance between the sampling station and the lowest altitude of the fog in upslope fog.

Fogwater and cloudwater are much polluted in most areas of North America¹⁾ and Europe.²⁾ Waldman et al.³⁾ observed the polluted fogwater in the urban area in Los Angels which had very low pH values (the minimum pH value was 1.7) and high ion concentrations and reported that the largest cause of acid fog was nitric acid in air than sulfur compounds (the equivalent ratio of nitrate to sulfate was 2.5 to 1). In Japan, Okita⁴⁾ and Ohta et al.⁵⁾ observed fog events at Mt. Norikura in the mountainous area of central Japan and at Mt. Tsukuba in the northeast of the Kanto plain (the minimum pH values were 3.0 and 2.8, respectively). Mimura and Shinozaki⁶⁾ had also reported low pH values of fogwater (pH 3.05 to pH 4.58) with respect to three fog events in 1978 at Mt. Oyama, where we are presently observing fog.

The fogwater with a very low pH value and high ion concentrations were observed at the beginning and the end of fog events because of the change of liquid water content in air. However, the components of the fog at the mountainside forest are also affected by some other factors and the components of an upslope fog changed remarkably with the meteorological conditions and the air pollution at the leeward base.⁷⁾ We have been observing fogwater at a mountainside and studying the factors controlling pH values and the constituents of fogwater. We analyzed aerosol and gas as well as fog water at our fog sampling station and will report the fogwater chemistry, the effect of the gaseous and aerosol components on the fogwater characteristics, and the mechanism of the fog acidification.

Experimental

Site Description. We have collected fogwater, rainwater, aerosol, and gas samples at Oyama Afuri Shrine located at the mountainside (700 m a.s.l.) of Mt. Oyama (1252 m a.s.l.; about 15 km north of Sagami Bay), eastern rim of Tanzawa-Oyama Quasi-National Park since July 1988. Mt. Oyama abuts on the southwest of the Kanto plains and is about 50 km west-south-west of Tokyo as shown in Fig. 1 and the south of the mountain is covered by a natural fir (*Abies firma*) forest. The nearest large pollutant sources are the Keihin industrial district along the seacoast of Tokyo Bay and the Tokyo urban areas. When a sea breeze blows, the air mass at Isehara city, the foot of Mt. Oyama and about 7 km southeast of sampling station, rises up to Mt. Oyama. When the humid air mass is transported from the direction of Isehara and cooled on the rise along the slope, an upslope fog is formed at Mt. Oyama.

We also collected rainwater, aerosol, and gases at an urban area in Yokohama. The sampling point is located on the roof of a four-floor building in Kanagawa University in Yokohama and is 30 km southwest of Tokyo as shown in Fig. 1.

Methods. We analyzed fogwater, rainwater, gas, and aerosol. We collected fogwater with an automatic fogwater sampler composed of a fog sensor, teflon strings, a fan, a refrigerator with teflon bottles on a turn table to store fog samples, and a time recorder. The details were reported elsewhere⁸⁾ and every 50 to 60 mL of fogwater samples are stored in each bottle in the refrigerator. The rainwater was collected by a bulk sampler equipped with a membrane filter (Millipore; pore size, 1.2 μm; diameter, 47 mm). The refrigerated fogwater and the rainwater were brought back to the laboratory of Kanagawa University every week. Fogwater and rainwater samples were divided into two parts; one was used for the measurement of pH and conductivity and the other was filtered through a membrane filter (Millipore; pore size, 0.45 μm) and stored in a refrigerator until the chemical analysis. Aerosol was collected by a low-volume air sampler equipped with a silica fiber paper (Toyo Filter QR 100) and gases were collected by filter method using cellulose filter papers coated with 1% sodium carbonate–1% glycerol for acid gases or coated with 5% phosphoric acid–5% glycerol for ammonia gas.⁹,¹⁰⁾ Then, their water-soluble components were extracted into pure water by irradiating ultrasonic waves and filtered to prepare sample solutions. The nitrogen oxide, sulfur dioxide, and oxidant concentrations and the meteorological data were measured continuously at the sampling station in Mt. Oyama and Isehara city office by Environment Department, Kanagawa Prefecture Government and we used the reported data.

Chemical Analysis. A number of chemical parameters

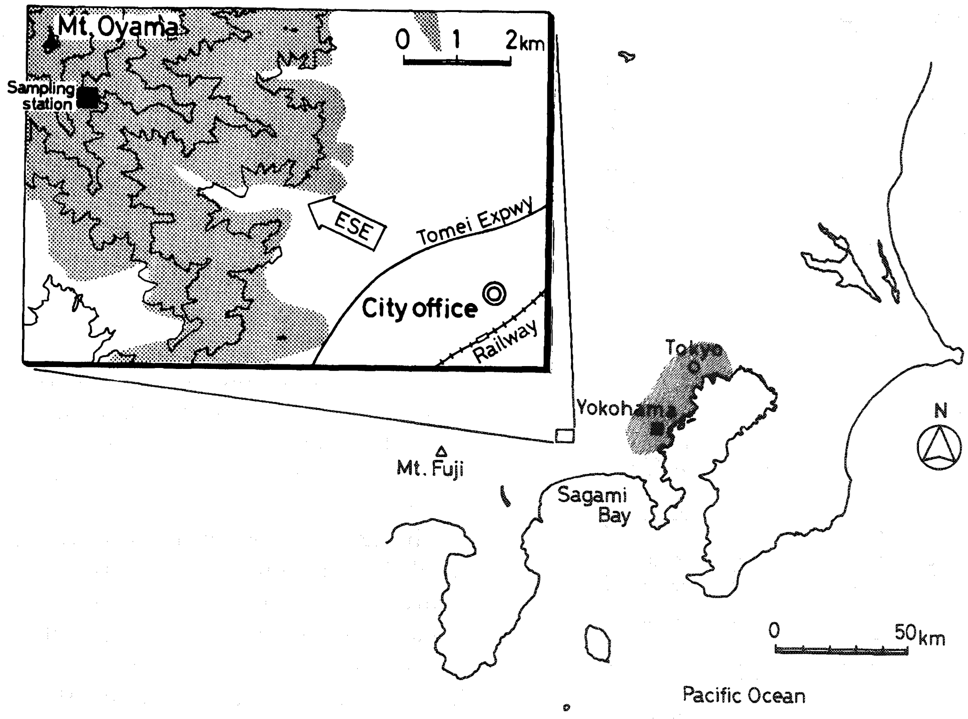

Fig. 1. The location of fog sampling station (square); Dotted area and shaded area are forest and Keihin manufacturing district, respectively, and double circle is the city office of Isehara.

including pH, conductivity, and the concentrations of major ions (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) were measured for fogwater and rainwater and aerosol samples. Aldehydes, formic acid, and some trace metal ions were also determined for fogwater.

The solution of acid gas sampler were analyzed for chloride, nitrate, and sulfate ions to determine hydrogen chloride, nitric acid, and sulfur dioxide and the solution of ammonia gas sampler was analyzed for ammonium ion. The values of pH and conductivity were measured with a pH meter (Toa Electronics HM-60S) and a conductivity meter (Kyoto Electronics CM-117), respectively. The inorganic anions and formic acid were determined with an ion chromatograph (Dionex 2000i/SP or Dionex DX-100). Alkali metal ions and ammonium ions were determined by an ion chromatograph (Dionex QIC), magnesium ion was determined by an atomic absorption spectrophotometer (Shimadzu AA-630-02), and calcium and trace metal ions were determined with an inductively coupled plasma atomic emission spectrophotometer (Seiko Instruments SPS 1500). Aldehydes were measured by DNPH method[11] with HPLC (Shimadzu LC-6A).

Results and Discussion

Fogwater Composition. We have observed fogwater at Mt. Oyama and the total number of collected fog samples were 1169 during 4.5 years from July 1988 to December 1992. The ranges of all the fog samples and the data of typical fog events for pH and major ion and aldehyde concentrations are shown in Table 1. The pH range, the mean pH value calculated from the volume-weighted average hydrogen ion concentration, and the median pH value were 2.61—7.00, 3.90, and 4.27, respectively. Table 1 also shows the concentration ranges of the rain samples collected at the fog sampling station and at an urban site in Yokohama. The major ion concentrations of rain at the sampling station are lower than those at Yokohama in general and the concentrations of the chemical species in fogwater are much higher than those of rainwater. In fogwater, volume-weighted average concentrations of major anions, chloride, nitrate, and sulfate, were approximately equal to each other, although they were not always comparable to each other for the respective fogwater samples.

Hydrophilic aldehydes were highly concentrated and the glyoxal concentration was very high especially when the fogwater was acidic. Formic acid in fogwater was also measured and the maximum concentration observed was 133 μM. However, formic acid concentration was lower than 10 μM in usual and other carboxylic acids were rarely detected, whereas some carboxylic acids were found in fogwater at Mt. Akagi located at 100 km north-north-west of Tokyo.[12]

Figure 2 shows monthly fog event period and fogwater pH range observed in 1992. When all of the 36 bottles in the refrigerator become full or the sampler gets out of order, the sampler stops and the fog cannot be collected. Then, the ratio of the fog sampler operating time to the total time of each month is also shown in Fig. 2. The fog events are observed in spring and summer more frequently than other seasons. The sampling

Table 1. Concentrations of Fogwater and Rainwater Observed at Mt. Oyama and Yokohama (1991—1992)

		Concentration (μequiv dm^{-3})															
Location	Date	pH	H^+	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	FA[a]	AA[b]	PA[c]	HA[d]	GL[e]	MG[f]
Fogwater	3/23—10/27/91	3.02—6.59	0—948	0—3777	4—2890	0—203	1—694	3—1619	8—831	7—3036	11—1397	0—21	0—4	0—2	0—18	0—39	0—14
at Mt. Oyama	5/25/91	3.26	598	2136	230	63	81	246	358	1286	1397	21	2	1	7	39	9
	1/29—12/8/92	2.62—6.78	0—2380	0—5549	0—5503	0—924	0—2082	0—1843	0—2331	0—5692	15—4448	0—40	0—7	0—1	0—26	0—97	0—30
	6/19/92	2.62	2380	4816	305	6	125	528	2331	2778	2953	7	4	1	10	97	16
Rainwater																	
at Mt. Oyama	1/1—12/26/91	3.77—6.55	0—168	0—310	0—212	0—194	0—99	0—176	5—289	0—329	4—291						
	1/7/92—1/1/93	4.14—5.56	4—72	0—224	0—399	0-77	2—136	0—501	0—425	1—483	6—354						
at Yokohama	1/1—12/26/91	3.49—5.56	2—321	0—419	0—420	0—65	0—204	0—496	22—694	8—438	19—445						
	1/7/92—1/1/93	3.51—5.54	3—308	2—494	0—263	0—39	2—224	0—576	8—509	11—459	18—614						

a) Formaldehyde ($HCHO$); b) Acetaldehyde (CH_3CHO); c) Propionaldehyde (C_2H_5CHO); d) Hydroxyacetaldehyde ($CH_2(OH)CHO$); e) Glyoxal ($HCOCHO$); f) Methylglyoxal (CH_3COCHO). Aldehyde concentrations were measured by DNPH method.[11)]

station at Mt. Oyama is covered with fog for about 20% of a day on the average in June and August and the median and mean pH values of fogwater were low in the seasons. The monthly mean air quality and meteorological data at the sampling station and Isehara, the foot of Mt. Oyama, were obtained in 1992 by Environment Department, Kanagawa Prefecture Government and are shown in Table 2. Acid fog is observed frequently in the foggy season because the concentration of oxidant, which is the index of the concentration of the secondary pollutants such as nitrate,[13)] is also high in the season as shown in Table 2. In autumn and winter, the fog events are rarely observed because the northerly wind is dominant and the relative humidity is comparatively low in the Kanto plains. In these seasons, the oxidant concentration was low on the average and the pH values of fogwater are high.

Change of Fogwater Components during An Acid Fog Event. Fogwater components change greatly with time in a fog event. Figure 3 shows the data of a fog event observed on 19 June, 1992 at the sampling station. This fog event has the minimum pH value of 2.62 and this value is the lowest pH in 1992. The inorganic ion concentrations, the inorganic ion loadings, the pH of the fogwater, the liquid water content (LWC), and the relative humidity (RH) were shown as a function of time in Fig. 3. The ion loading was determined as the value of the product of the concentration of fogwater and the volume of fogwater divided by the product of the air aspirated and the sampling efficiency[8)].

In Fig. 3, the fog appeared at about 10 o'clock with the decrease of the relative humidity at Isehara and disappeared after 21 o'clock with the decrease of the relative humidity at the sampling point. The fog formation depends much on the relative humidity at Isehara because the fog at the sampling station is formed in general from the humid air mass transported from Isehara by cooling on the rise along the slope. The liquid water content of the fog decreases with the decrease of the relative humidity at Isehara, although the fog is usually not formed when the relative humidity is very high and it is raining at Isehara. The concentrations of fogwater components vary as the change of liquid water content, although the loading of each ion in the fogwater was almost constant from 10 o'clock to 18 o'clock. The pH value changed definitely with the liquid water content and was the minimum when the liquid water content was the lowest.

Effect of Gaseous and Aerosol Components on Fogwater Components. The fogwater is affected appreciably by the gaseous and aerosol components in the atmosphere equilibrated with the fog-droplets. Some of the fogwater components were supplied from the aerosol of the sea salt particles transported from the Sagami bay and of ammonium nitrate and ammonium sulfate salts transported from the Keihin industrial district and the Tokyo urban areas. It is reported

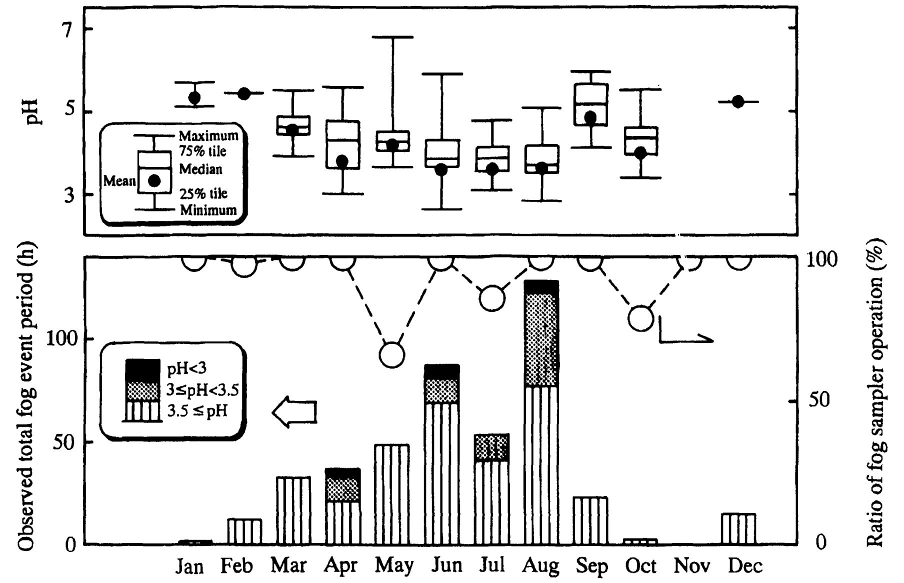

Fig. 2. Monthly fog events period and pH range at the sampling station in Mt. Oyama.

Table 2. Monthly Mean Air Quality and Meteorological Data at the Sampling Station in Mt. Oyama and the Foot of the Mountain, Isehara in 1992

	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
Fog sampling station												
Oxidant (ppbv)	18	28	33	45	39	42	51	20	33	28	27	21
Temperature	3.6	3.3	6.0	11.1	12.0	15.9	21.6	21.7	18.0	12.2	9.1	5.3
Relative humidity (%)	61	54	79	73	78	87	84	90	80	85	75	65
Isehara												
Oxidant (ppbv)	13	17	21	43	30	25	29	16	21	19	16	15
Temperature	6.3	6.9	10.1	15.4	17.8	21.2	25.9	27.2	23.8	17.2	12.8	8.9
Relative humidity (%)	68	58	70	64	67	73	75	75	67	76	69	65

that fogwater condenses on a part of these particles and 60% of particles are scavenged by fogwater.[14] The remaining particles are scavenged by the fogwater gradually when they are transferred with fog droplets along the mountainside. Just after the water condensation on aerosol, nitric acid gas, whose Henry's law coefficient is the largest,[15] is absorbed to fogwater rapidly at the beginning of a fog event. The concentration of nitric acid gas was ca. 1 ppbv at the sampling station and the value is roughly the same as the average value in Japan.[16] This value is reasonable to interpret the measured nitrate ion and hydrogen ion concentrations in fogwater. When the liquid water content is 0.02 cm^3/m^3, which corresponds to a thin fog event, the nitric acid concentration in the fogwater becomes about 2.2 mmol/L (pH 2.65). Gaseous hydrogen chloride may also contribute to the acidification of fog droplets but its contribution must be smaller than that of nitric acid. This is because the concentration of nitric acid gas is much higher than that of hydrogen chloride gas in fog seasons. The average concentration of nitric acid gas from June to September in 1992 at the sampling station was 1.33 ppbv and the maximum value of the data observed weekly was 3.84 ppbv, while that of hydrogen chloride gas was 0.75 ppbv and its maximum value was 1.36 ppbv.

Sulfate ion in fogwater is brought about from ammonium sulfate, the major water soluble component of aerosol,[8] and from the aqueous-phase oxidation of S(IV). The principal oxidants are H_2O_2 and O_2 catalyzed by Fe(III) and Mn(II).[17] Iron and manganese ions exist in fogwater and their maximum concentrations were 4.82 and 2.32 mg L^{-1}, respectively when pH was 3.30 and sulfate ion concentration was 4.45 mequiv L^{-1}. The aqueous-phase oxidation of SO_2 probably plays an important roll in the supply of sulfuric acid to fogwater.

Absorption of Ammonia Gas into Acid Fog. Although the acidity of the fogwater is brought about primarily by acidic gases, ammonia gas also affects the pH value as a principal neutralizing species.[18] Then, we will investigate the influence of ammonia gas on the pH value.

In the atmosphere, total ammonia loading (mol m^{-3}), $\{NH_3\}_{total}$, which is the sum of the concentrations in gas and liquid phases in air, is described by Henry's law and the dissociation equilibrium of ammonium ion as follows,[19]

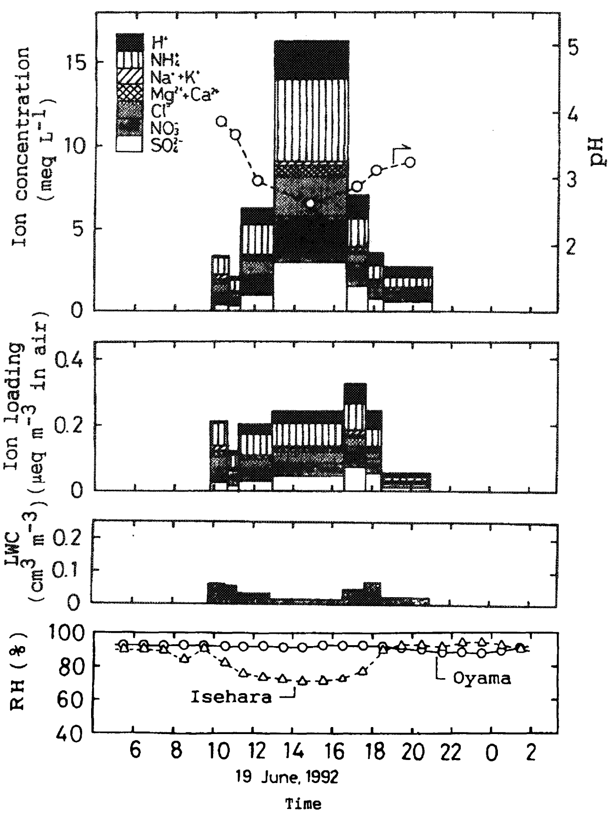

Fig. 3. Ion concentration and ion loading of fogwater, liquid water content of the atmosphere (LWC), and relative humidity (RH) as a function of time (19 June, 1992).

$$\{\mathrm{NH_3}\}_{\mathrm{total}} = \frac{p_{\mathrm{NH_3}}}{R\cdot T} + ([\mathrm{NH_3}] + [\mathrm{NH_4^+}])\cdot L \tag{1}$$

$$[\mathrm{NH_3}] = K_{\mathrm{H}}\cdot p_{\mathrm{NH_3}} \tag{2}$$

$$K_{\mathrm{a}} = \frac{[\mathrm{NH_3}][\mathrm{H^+}]}{[\mathrm{NH_4^+}]} \tag{3}$$

where $[\mathrm{NH_3}]$ and $[\mathrm{NH_4^+}]$ are $\mathrm{NH_3}$ and $\mathrm{NH_4^+}$ concentrations in liquid phase ($\mathrm{mol\,dm^{-3}}$), $[\mathrm{H^+}]$ is hydrogen ion concentration in liquid phase ($\mathrm{mol\,dm^{-3}}$), $p_{\mathrm{NH_3}}$ is partial pressure of ammonia gas (atm), R is gas constant (0.082 atm $\mathrm{dm^3\ mol^{-1}\ K^{-1}}$), T is the absolute temperatue (K), L is the liquid water content ($\mathrm{dm^3\ dm^{-3}}$), K_{H} is Henry's law coefficient (62 $\mathrm{mol\,dm^{-3}\ atm^{-1}}$ at 298 K), and K_{a} is dissociation constant of ammonium ion ($10^{-9.24}$ $\mathrm{mol\,dm^{-3}}$).

Using Eqs. 1, 2, and 3, we obtain

$$\begin{aligned}\{\mathrm{NH_3}\}_{\mathrm{total}} &= \frac{K_{\mathrm{a}}\cdot[\mathrm{NH_4^+}]}{H\cdot R\cdot T[\mathrm{H^+}]} + \left(\frac{K_{\mathrm{a}}\cdot[\mathrm{NH_4^+}]}{[\mathrm{H^+}]} + [\mathrm{NH_4^+}]\right)\cdot L \\ &= [\mathrm{NH_4^+}]\cdot\left(\frac{3.80\times10^{-13}}{[\mathrm{H^+}]} + \frac{5.75\times10^{-10}\cdot L}{[\mathrm{H^+}]} + L\right). \end{aligned} \tag{4}$$

In a closed-system, total ammonia loading corresponds to the sum of the gaseous and aqueous loadings of ammonium ion and ammonia when fog is formed and it corresponds to gaseous ammonia loading when the fog disappears. Equation 4 shows that the concentration of dissolved ammonium ion in fogwater increases with the increase of the hydrogen ion concentration for a definite total ammonia loading in air and then, ammonia gas depresses the acidity of fogwater.

The acidity of fogwater is brought about by gaseous acid and acid mist and the acid components dissolved in fogwater is neutralized primarily by ammonia gas. Then, the total acidity is approximately equal to the sum of the concentrations of hydrogen ion and ammonium ion in fogwater as follows,

$$[\mathrm{Acid}]_{\mathrm{total}} = [\mathrm{H^+}] + [\mathrm{NH_4^+}], \tag{5}$$

where $[\mathrm{Acid}]_{\mathrm{total}}$ is total acidity in water ($\mathrm{mol\,dm^{-3}}$). Total acid loading, $\{\mathrm{A}\}_{\mathrm{total}}$, is defined as follows,

$$\{\mathrm{A}\}_{\mathrm{total}} = [\mathrm{Acid}]_{\mathrm{total}}\cdot L, \tag{6}$$

because gaseous acid and acid mist are transferred to fogwater just after fog is formed and the concentration of acid components remained in gas phase can be ignored. Using Eqs. 5 and 6, we obtain

$$[\mathrm{H^+}] = \frac{\{\mathrm{A}\}_{\mathrm{total}} - \{\mathrm{NH_4^+}\}}{L}, \tag{7}$$

where $\{\mathrm{NH_4^+}\}$ is $\mathrm{NH_4^+}$ loading in fogwater, which is equal to the product of $[\mathrm{NH_4^+}]$ and L. Equation 7 implies that pH value of fogwater is determined by the liguid water content and the total acid and ammonium ion loadings in air.

Figure 4 shows the measured values of pH as the function of ammonium ion loading in fogwater. The lines are the values calculated from Eq. 7 on some constant values of total acid loading and the values calculated from Eq. 4 on some constant values of total ammonia loading. The total acid and the total ammonia loadings in Fig. 4 are comparable to the measured concentration of ammonia and nitric acid gases at Mt. Oyama. The average concentration of ammonia gas in the fog season of 1992 at the sampling station was 2.9 ppbv, that is, 0.13 $\mathrm{\mu mol\ m^{-3}}$. In the calculation, the liquid water content was supposed to be a representative value, 10^{-7} $\mathrm{dm^3\ dm^{-3}}$. All of the fog samples are within the lines which were calculated supposing that both total acid loading and total ammonia loading were 0.3 $\mathrm{\mu mol\ m^{-3}}$ at the liquid water content of 10^{-7} $\mathrm{dm^3\ dm^{-3}}$. If ammonium sulfate of the major aerosol component is dissolved in fogwater, each line moves to right in parallel on Fig. 4 and pH value changes little.

The pH values also decrease with the decrease of the liquid water content and the liquid water content is one of the important factors controlling the pH value of fogwater as estimated by Eq. 7.

pH and Conductivity of Fogwater. The characteristics of fogwater are summarized well in a conductivity–pH diagram.[20] Figure 5 shows the data of all fogwater samples collected in Mt. Oyma in 1992. The

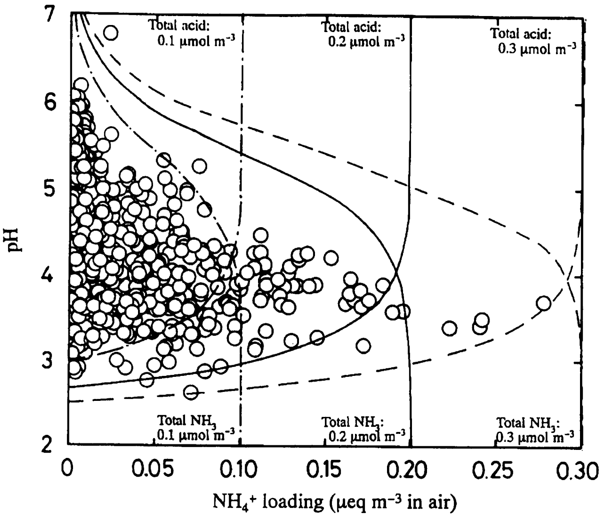

Fig. 4. Plots of pH and ammonium ion loading in fogwater (July 1988—June 1992). Lines are calculated values on the assumption of some constant values of total acid or total ammonia loadings, when the liquid water content was 10^{-7} dm^3 dm^{-3}.

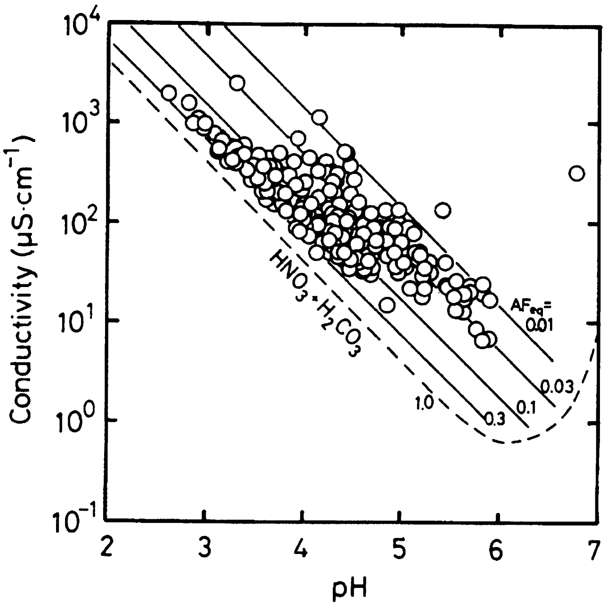

Fig. 5. The plots of pH and conductivity of fogwater (1992); The broken line shows nitric acid solution equilibrated with air containing 350 ppmv CO_2; AF_{eq} is acid fraction.

fogwater with a low pH value has a high conductivity because not only of the acid dissolved in the droplets but also of the components dissolved to neutralize the acid. An upslope fog covers mountainsides frequently and the fog bottom moves down and up along mountainside depending on the dew point of the air mass, if it keeps on blowing from the valley throughout the fog event. The fog event begins or comes to an end when the fog bottom passes over the fog sampling station. The fog droplets absorb air pollutants readily and the bottom of the fog is highly polluted, while the inner part of the fog is clean because the air pollutants are trapped at the bottom of the fog, the polluted fog-droplets are deposited on the forest of the mountainside, and fresh clean droplets are formed in the inner part.[7] In addition, the liquid water content is low in the bottom of the fog and is high in the inner part of the fog. Then, the observed values of the fogwater characteristics were shifted from the upper-left-side to the lower-right-side and were shifted back in Fig. 5 during an event of upslope fog.

In Fig. 5, the solid lines show the calculated values of conductivity[20] when acid fraction, $AF_{eq}=0.3$, 0.1, 0.03, and 0.01 and the dashed line shows the calculated values of nitric acid solution dissolving carbon dioxide in the air. The acid fraction was defined as follows,[20]

$$AF_{eq} = \frac{\text{concentration of the hydrogen ion in equivalents}}{\text{sum of concentrations of all cations in equivalents}} \qquad (8)$$

Almost all the fogwater are ranging in AF_{eq} from 0.3 to 0.01 and in pH from ca. 3 to 6. There are few data in the area where pH is higher than 4.8 and the AF_{eq} is higher than 0.03 in Fig. 5, while many data of the rainwater samples are in the area. This difference is caused by the different liquid water content between rainwater and fogwater. The liquid water content of fog is from 0.02 to 0.2 cm^3 m^{-3} and it is much smaller than that of rain, 0.1 to 1 cm^3 m^{-3}.[16] Then, the pH values of fogwater become lower than those of rainwater for a definite acid loading and the ion concentrations of fogwater become higher than those of rainwater.

The relationship between conductivity and pH for all fog samples in 1988—1991 was similar to Fig. 5. In 1990, some fogwater samples were obtained in a typhoon event (August 22, 1990). At the typhoon, the sea salt aerosol was transferred from the Pacific Ocean by strong southerly wind and the fogwater was not acidic but had a high conductivity. The pH values ranges from 5.0 to 5.6, the conductivities ranged from 39 to 503 μS cm^{-1}, and the dominant component in the fogwater samples was sodium chloride.

Conclusions

We have studied the fogwater chemistry at the mountainside of Mt. Oyama since July 1988 and have observed acid fog events frequently. Nitric acid is the dominant acid components in the very acidic fogwater. The concentrations of the fogwater components were controlled by the amount of the acidic pollutants in atmosphere, the liquid water content in air, the concentrations of the neutralizing components for the acid fogwater, primarily NH_3 gas concentration, and the distance between the sampling station and the bottom of the fog in the case of upslope fog. Fogwater occupied a characteristic area in the conductivity–pH diagram, which ranged in the acid fraction from 0.3 to 0.01 and in pH from ca. 3 to 6.

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