Controlling Factors of Weak Acid and Base Concentrations in Urban Dewwater—Comparison of Dew Chemistry with Rain and Fog Chemistry—

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Dewwater was collected from January 1993 to December 2000 in Yokohama, Japan, and analyzed for weak acid anions with other major chemical components. The volume-weighted average and medium pH of the dewwater were 4.88 and 6.08, respectively, at our sampling site. Weak acids (carbonate, nitrite, sulfite, formate, and acetate ions) were the major species in the dewwater and were several times higher than those in the rain- and fogwater. The concentrations of these species and ammonium ion can be estimated by the resistance model. The estimated values of N(III) correlate relatively well with the measured values, which shows the origin of N(III) in dewwater is nitrous acid in the ambient air. On the other hand, ammonium ion in the dewwater originated from not only gaseous ammonia but also aerosol ammonium ions. Hydrogensulfite ions in the dewwater which originated from sulfur dioxide are an important species as the precursor of the sulfate and they were stabilized by forming hydroxyalkanesulfonate (HASA). Formic acid and acetic acid in the dewwater originated mainly from gas, while the oxalic acid is from aerosol.

The formation of dewwater on a surface such as plant leaves enhances the absorption of water-soluble gases and the retention of dry deposition on it.[1] It has been reported that the pH and ion concentrations, in particular, calcium ion and weak acid anions such as carbonate, formate, acetate, nitrite, and sulfite, in dewwater are higher than those in rain- or fogwater.[2–5]

Nitrite plays an important role in the photochemical formation of the hydroxyl radical in dewwater,[6,7] but the sources of nitrite in the dewwater are not well understood. Hydrogensulfite ion is an important species as the precursor of sulfate ion and can be stabilized by forming hydroxymethanesulfonate (HMSA), an adduct of hydrogensulfite ion and formaldehyde.[8] HMSA could be the major component of S(IV) in fog- and cloud water.[9,10] The formation of HMSA results in lowering the pH[11] and enhancing the dissolution of sulfur dioxide into dewwater.[8] Okochi et al.[4] reported that hydroxyalkanesulfonate (HASA) in addition to HMSA may be present in dewwater, but there are few reports on the concentration of HASA in dewwater. Formic and acetic acids are ubiquitous components in the atmosphere. Formic and acetic acids may contribute between 41 and 65% to the free acidity of precipitation in some remote areas.[12] Kawamura et al.[13] calculated the pH of urban rainwater in the presence of carboxylic acids and reported that carboxylic acids, especially formic, acetic, and oxalic acids, can contribute to lowering the pH in the range from 0.1 to 1.9 pH units. Only a few studies, however, have so far been reported to clarify the behavior of weak acids in dewwater.

The purpose of this study is to clarify the following three points about weak acids and the weak base ammonia in dewwater: (1) the sources of N(III) and ammonia, (2) the estimation of the hydroxyalkanesulfonate (HASA) concentration, and (3) the controlling factors of the carboxylic acid concentrations. For the purpose, the concentrations of the dewwater were estimated from the corresponding species in the ambient air by the resistance model for mass transfer.[4] The correlation between the measured values and the estimated values is discussed in this paper.

Experimental

Dew- and rainwater were collected from January 1993 to December 2000 on the roofs of the five-story buildings on the campus of Kanagawa University in Yokohama, Japan. Details of the sampling point and methods were described in previous papers.[4,5] Aerosol smaller than 7.07 µm in particle diameter was collected by a low-volume air sampler (Nippon Kagaku Kogyo, model 9023). Acid and ammonia gases were collected by an impregnated filter method using cellulose filter papers.[14,15] Fogwater was also collected at the midslope (680 m a.s.l.) of Mt. Oyama (1252 m a.s.l.), which is about 50 km west-southwest of Tokyo and abuts the southwest side of the Kanto Plain. The samples were collected using an automatic fogwater sampler. Although the sampling site of the fogwater was different from that of dewwater, the components are compared to those of dewwater as a typical wet deposition.

The water samples were weighed and filtered with a 0.45-µm pore-size membrane filter (Advantec A045A025A). The electric conductivity, pH, and water soluble components (Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_2^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, $HCOO^-$, CH_3COO^-, and $C_2O_4^{2-}$) were measured using an electric-conductivity meter (Kyoto Electronics CM-117), a pH meter (Toa Electronics HM-60S), and an ion chromatograph (for cations except proton, Dionex DX-100 with a column of Dionex IonPac CS12; for anions except carboxylates, Dionex DX-100 with a column of Dionex IonPac AS12 or Dionex 2000i/sp with a column of Dionex IonPac AS4A; for carboxylates, Dionex Bio-LC with a column of Dionex IonPac AS4A-SC or Dionex IonPac AS11). The dissolved organic and inorganic carbons were measured with a TOC analyzer (Shimadzu TOC-5000). Aldehydes (formaldehyde, acetaldehyde, hydroxyacetaldehyde, glyoxal, and methylglyoxal) in the dewwater were measured by the DNPH-HPLC method.[16] The aerosol samples were weighed and the water-soluble components were extracted from the filters into 10 ml ultra pure water in a Teflon beaker by irradiating with ultrasonic waves. The acid and ammonia gases collected on the filters were also extracted in the same manner as the aerosols. These solutions were analyzed in a similar manner to that used for the dewwater.

The data of wind speed, temperature, and relative humidity used in the calculation of the resistance model were provided from Yokohama Local Meteorological Observatory, which was located about 8 km southeast from our sampling site.

Results and Discussion

Frequency of Dew Occurrence and Dewwater Composition. Four hundred and thirty-six dewwater samples were collected during 8 years from January 1993 to December 2000. The dewfall amount ranged from 0.62 to 416 g m^{-2} and averaged 83.1 g m^{-2}. The annual frequency of the dew occurrence was about 20% and was the highest during the winter season. Although the relative humidity during the summer season is the highest of all the seasons, the frequency of dew occurrence was the lowest because this season includes the rainy season in Japan. Table 1 shows the volume-weighted mean concentrations and the ranges of the major ions and dissolved organic carbon (DOC) in the dewwater in Yokohama from January 1993 to December 2000, together with the data from four other studies.[3,6,17,18] The pH of the dewwater collected at our sampling site ranged from 3.04 to 7.88, and changed with the season (volume-weighted average, spring 4.40, summer 4.23, autumn 5.56, winter 5.99), and the annual volume-weighted average and medium pH were 4.88 and 6.08, respectively. The acidity of the dewwater increased with the increase in the ratio of nitrate to total anions in most of the dewwater samples in Yokohama. Mulawa et al.[19] noted that dewwater has a high concentration of calcium ion and a high pH value due to the deposition of calcium carbonate in the dewwater. At our sampling site, there was a relatively poor correlation between the concentration of calcium and carbonate (correlation coefficient, 0.38), although the fraction of calcium ion in the dewwater was higher than that in the rainwater. As compared with the rainwater, the dewwater composition was affected by the soil components such as calcium because the dewwater was formed near the ground. Ammonium ion was the major cation at all sampling sites except Indianapolis, while the dominant anion was different among these sites in Table 1.

The weak acid anions such as carbonate, formate, acetate, nitrite, and sulfite occupied about forty percent of the total anions in Yokohama. In Sakai and Glendora, the weak acids were also the dominant anions. The concentrations of these weak acids can be neglected in rainwater but they cannot be neglected in dewwater. The ratio of these weak acid concentrations to that of the total anions increased with the increase in the pH value and ranged from 0.02 to 0.79 in Yokohama.

N(Ⅲ) Chemistry of Dewwater. Nitrite ion concentration in dewwater is high, as shown in Table 1, but its source is not well understood. At our sampling site, the concentrations of N(Ⅲ) in the rainwater ranged from 0 to 8.4 µmol dm^{-3} and the volume-weighted average concentration (1.3 mol dm^{-3}) was about 1/60 of that in dewwater. One of the reasons for the high concentration in dewwater is that dewwater is formed at nighttime when the nitrous acid concentration in the atmosphere is

Table 1. Volume-Weighted Mean Concentrations and Ranges of Major Ions and Dissolved Organic Carbon (DOC) in Dewwater

	Present work Yokohama, Japan	Takenaka et al.[18] Sakai, Japan	Arakaki et al.[6] Higashi-Hiroshima, Japan	Foster et al.[3] Indianapolis, Indiana	Pierson and Brachaczek[17] Glendora, California
n[a)]	184–436	4–10	9	20	18–20
pH	4.88 (3.04–7.88)	6.48 (5.53–7.29)	6.2 (5.1–6.6)	6.82 (6.2–6.8)	4.70 (4.14–6.24)
NH_4^+	404 (33–6759)	202	85.7 (41.2–127)	34.2 (3.7–105)	185 (88–429)
Na^+	120 (12–2906)	86.0	6.8 (1.2–26.3)	3.9 (1.4–8.9)	40 (12–91)
K^+	19 (2.6–297)	10.0	1.4 (0.6–3.5)	8.5 (2.8–26)	8 (2–19)
Mg^{2+}	36 (2.2–794)	15.1	3.0 (1.0–10.2)	32.6 (12.2–70)	22 (6–66)
Ca^{2+}	213 (11–8904)	60.3	17.4 (3.6–49.0)	150 (50–266)	126 (34–280)
Cl^-	163 (23–3294)	98.4	14.8 (2.4–65.3)	6.1 (3.3–16)	37 (8–416)
NO_3^-	117 (10–3931)	18.1	27.3 (6.7–68.6)	25.5 (2.2–78)	84 (35–527)
SO_4^{2-}	217 (31–5161)	47.5	32.2 (8.4–93.8)	31.6 (3.8–106)	82 (18–230)
HCO_3^-	46 (0.06–651)	N.A.[f)]	N.A.[f)]	146 (43–374)	N.A.[f)]
NO_2^-	84 (0–945)	58.0	9.1 (2.3–17.4)	4.0 (0.9–9.6)	15 (5–60)
S(IV)	125 (0–3729)	14.0	N.A.[f)]	0.6 (0–3.4)	28 (3–49)
For[b)]	39 (0–880)	13.6	N.A.[f)]	3.6 (0–12.4)	118 (44–930)
Ace[c)]	29 (0–464)	24.6	N.A.[f)]	1.1 (0–16.8)	52 (25–313)
Oxa[d)]	1.7 (0–16)	N.A.[f)]	N.A.[f)]	N.A.[f)]	2.1 (0.7–41)
DOC[e)]	15 (1.5–214)	N.A.[f)]	N.A.[f)]	N.A.[f)]	N.A.[f)]

All units are in µeqiv dm^{-3} except pH and DOC (mg dm^{-3}).

a) sample number, b) formate, c) acetate, d) oxalate, e) dissolved organic carbon, f) not analyzed.

high. In the atmosphere, the nitrous acid (HONO) concentration generally shows a maximum in the nighttime and a minimum in the daytime due to photochemical degradation during the day.[20–23] The nitrous acid concentration during the dewwater sampling period was measured; it ranged from 0.1 to 9.0 ppb with a mean of 2.5 ppb at the sampling site. Dewwater may play an important role as a sink of nitrous acid at night. For the open system, the aqueous phase N(III) ($HNO_2 + NO_2^-$) concentration (mol dm^{-3}) can be estimated by the following Eqs.

$$[\mathrm{N(III)}] = H^*_{\mathrm{HONO}}\, p_{\mathrm{HONO}} \tag{1}$$

$$H^*_{\mathrm{HONO}} = H_{\mathrm{HONO}}\,(1 + K_a / [\mathrm{H}^+]) \tag{2}$$

where p_{HONO} is the mean partial pressure of the nitrous acid (atm) during the dewwater sampling period, H_{HONO} is Henry's law constant of nitrous acid (49 mol dm^{-3} atm^{-1}),[24] and K_a is the acid dissociation constant of nitrous acid ($10^{-3.15}$ mol dm^{-3}).[25] However, the concentration is estimated to be a very large, unfeasible value, when the pH of dewwater becomes high. The concentration should be estimated by the resistance model for mass transfer while one considers the transfer resistance in the air.[26]

The total N(III) concentration (mol dm^{-3}) in dewwater is defined as follows:

$$[\mathrm{N(III)}] = F_{\mathrm{HONO}}\, t / (w \times 10^{-3}) \tag{3}$$

$$F_{\mathrm{HONO}} = C_{\mathrm{HONO}}(z)\, v_d \tag{4}$$

where F_{HONO} is the downward flux of nitrous acid to the dewwater (mol cm^{-2} s^{-1}), t is the dewwater collection period(s), w is the dewfall amount (g cm^{-2}), $C_{\mathrm{HONO}}(z)$ is the concentration of nitrous acid (mol cm^{-3}) at the height (z) where the nitrous acid concentration in the air was measured, 1 m, and v_d is the dry deposition velocity of nitrous acid to dewwater droplet (cm s^{-1}). The v_d can be expressed as the reciprocal of the sum of the transfer resistance:

$$v_d = 1 / (r_a + r_b + r_c) \tag{5}$$

where r_a is the aerodynamic resistance (s cm^{-1}), r_b is the sublayer resistance (s cm^{-1}), and r_c is the surface resistance (s cm^{-1}). r_a is related to the rate of turbulent mixing of the species as follows:

$$r_a = \{\ln (z / z_0) - C_1\}/(k\, u^*) \tag{6}$$

$$u^* = k\, u / \{\ln (z_r / z_0) - C_2\} \tag{7}$$

where z_r is the reference height, C_1 and C_2 are diabatic correction terms ($-5\ z\ L$ and $-5\ z_r\ L$, respectively, where L is the Monin Obukov length in cm), k is von Karmen's constant (0.4), u is the wind speed (cm s^{-1}), and u^* is the friction velocity (cm s^{-1}). r_b is controlled by the rate of molecular and turbulent transport across the atmospheric sublayer in contact with the surface:[27]

$$r_b = 5\, u^{*-1} \times [(v / D - 1) + \ln \{1 + 0.83 \times (v / D - 1)\}] \tag{8}$$

where D is the molecular diffusion coefficient of nitrous acid (0.15 cm^2 s^{-1}),[28] and v is the kinematic viscosity (cm^2 s^{-1}). r_c is related to the concentration of species at the effective surface of deposition, and is represented as follows:

$$r_c = n_M f / \{A\, H^*_{\mathrm{HONO}} \times 10^{-3} \times (w / \tau + dw / dt)\} \tag{9}$$

$$f = 1 / 3 / (\coth(q)/q - 1 / q^2) \tag{10}$$

$$q = r \times (\tau D_a)^{-1/2} \tag{11}$$

where n_M is the surface number density (cm^{-3}), A is Avogadro's number, dw/dt is the accumulation rate of dewwater (g cm^{-2} s^{-1}), r is the radius of a dew droplet (cm), τ is the chemical lifetime of nitrous acid in dewwater(s), D_a is the aqueous phase molecular diffusion coefficient (cm^2 s^{-1}). The values, z_0, z_r, k, L, v, n_M, f, and τ, were assumed to be the same as in the previous paper.[4]

The concentration profile in the air can be calculated by the transfer resistance obtained by these Eqs.[29] Figures 1a and 1a′

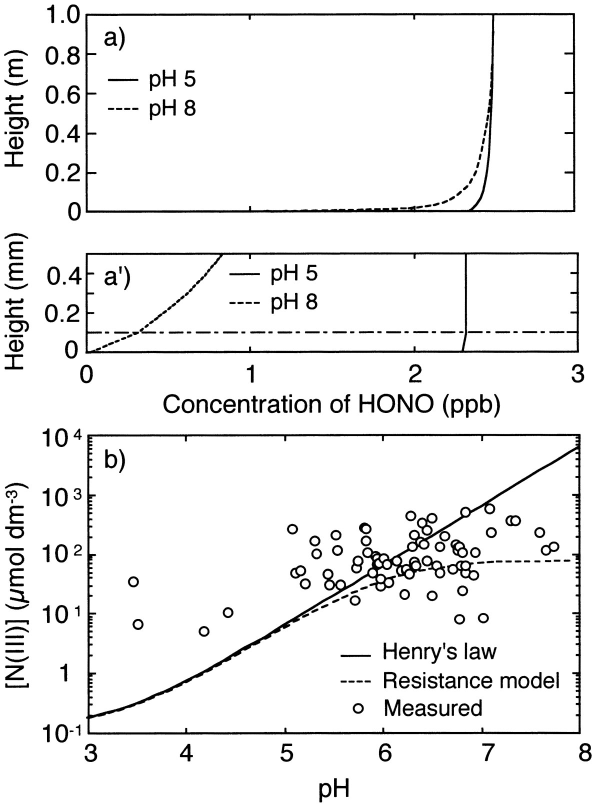

Fig. 1. Concentration profile of nitrous acid in the air on the surface of dewwater (a and a′) and the relationship between the measured and estimated N(III) concentrations and pH (b). The values estimated by resistance model were calculated by using the average values obtained at the sampling site (concentration of nitrous acid 2.5 ppb, temperature 15.4 °C, relative humidity 82.8%, wind speed 2.30 m s^{-1}, dewfall amount 83.1 g m^{-2}, and accumulation rate 17.3 g m^{-2} h^{-1}).

show the concentration profile on the dewwater collector from 1.0 m and 0.5 mm for the case of pH 5 and pH 8 for dewwater, which is calculated by using the average ambient air concentration, 2.5 ppb, and other average values measured at the sampling site. When the pH is 8, there is a large concentration gradient in the air on the surface of the dewwater, while the small concentration gradient was formed when the pH is 5. The relationship between the estimated N(III) concentration and pH in the dewwater is shown in Fig. 1b, where the values were calculated in the same manner as those in Figs. 1a and 1a′. In Fig. 1b, the values calculated from Henry's law and the measured values are also shown. In low pH region, the values estimated by the transfer resistance model are equal to the values estimated from Henry's law, because the dissolution process is the limiting process in the transport. In high pH region, however, the values estimated from the transfer resistance model are much lower than the values estimated by Henry's law, because the transfer process in the air is the limiting process in the transport. The measured values tend to increase with the increase of pH as estimated, and N(III) is supersaturated in some dewwater samples.

Figure 2 shows the relationship between the concentrations estimated by the resistance model and the measured concentration for N(III) in the dewwater. The estimated values were calculated by using the ambient air concentration at the sampling site, the dewwater characteristics (pH, dewwater amount, etc.), and the meteorological data measured during the dewwater sampling. These values were correlated relatively well (correlation coefficient, 0.44), although the estimated values deviates to some extent and the average measured value was 2.2 times larger than the average estimated value. There may be some reasons for the difference of the measured values from the estimated values. The contribution of the dissolution of NO and NO_2 into the dewwater is negligible because Henry's law constants for NO (1.9×10^{-3} mol dm^{-3} atm^{-1})[24] and NO_2 (1.0×10^{-2} mol dm^{-3} atm^{-1})[24] are about 25,000 and 5,000 times lower than that for nitrous acid (49 mol dm^{-3} atm^{-1}). Lammel and Perner[30] analyzed nitrite in aerosol particles and suggested that the aerosol particles would be a source of nitrous acid, but nitrite ion can not be detected in the aerosol collected at the sampling site. Pandis and Seinfeld[31] suggested that the actual hydrogen ion concentration affecting Henry's law equilibrium of weak acids in the fog and cloud droplets was different from the hydrogen ion concentration of the mixture. They noted that the apparent supersaturation with weak acids in the bulk samples occurs when the samples were mixed with the droplets of the different sizes and different pH values and when the pH of some droplets exceeds the pK_a. The dew droplets have a large size distribution, and hence the pH of the dew droplets would be different from each other. The apparent supersaturation of N(III) may occur in dewwater, which is one of the reasons of the difference between the measured and the estimated values.

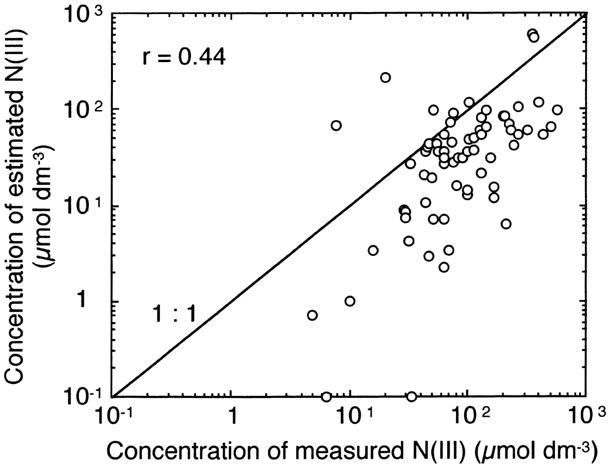

Fig. 2. Relationship between the estimated N(III) concentration by resistance model and the measured concentration in the dewwater. The values estimated by resistance model were calculated by using concentrations of nitrous acid in the ambient air at the sampling site and pH in the dewwater.

Ammonium Ion/Ammonia Chemistry of Dewwater. The open circle in Fig. 3 shows the relationship between the concentrations estimated by the resistance model using the molecular diffusion coefficient of ammonia (0.25 cm^2 s^{-1}),[28] Henry's law constant (62 mol dm^{-3} atm^{-1}),[24] and the measured concentration for ammonium ion and ammonia in the dewwater. These values were not correlated well (correlation coefficient, −0.06), and the average measured value was 2.2 times larger than the average estimated value. Ammonium ion is enriched in fine aerosol particles (particle diameter $<$ 2 μm),[32] which may contribute to the dewwater components. The ammonium ion concentration during the dewwater sampling period was measured; it ranged from 18 to 692 nmol m^{-3} with a mean of 239 nmol m^{-3} at the sampling site. The deposition velocity of ammonium ion obtained from multiple regression analysis was already reported in the previous work as 0.152 cm s^{-1}.[5] The closed circle in Fig. 3 shows the estimated values

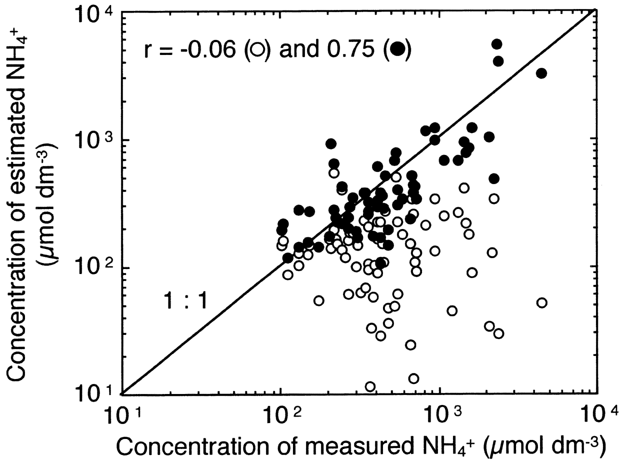

Fig. 3. Relationship between the estimated NH_4^+ concentration and the measured concentration in the dewwater. The open circle is estimated from the deposition of only gaseous ammonia by using resistance model and the concentrations of ammonia in the ambient air at the sampling site and pH in the dewwater, while the closed circle is estimated from the deposition of not only gaseous ammonia but also aerosol ammonium ion.

Table 2. Volume-Weighted Mean Concentrations and Ranges of Hydroxyalkanesulfonate and Aldehyde in Dewwater in Yokohama from January 1993 to November 2000

HASA[a]			Aldehyde		
$HCH(OH)SO_3^-$	109	(0–1991)	$HCHO$	18	(0–520)
$CH_3CH(OH)SO_3^-$	2.1	(0–168)	CH_3CHO	2.0	(0–94)
$HOCH_2CH(OH)SO_3^-$	2.2	(0–129)	$HOCH_2CHO$	3.2	(0–71)
$CH(OH)_2CH(OH)SO_3^-$	3.8	(0–168)	$CHOCHO$	5.3	(0–87)
$CH_3COCH(OH)SO_3^-$	4.5	(0–415)	CH_3COCHO	4.9	(0–137)
$HCH(O^-)SO_3^-$	0.75	(0–39)			
$CH_3COCH(O^-)SO_3^-$	0.30	(0–4.9)			

All units are in µmol dm^{-3} except $HCH(O^-)SO_3^-$ and $CH_3COCH(O^-)SO_3^-$ (nmol dm^{-3}). a) HASA concentrations are calculated from each aldehyde, total S(IV) concentration, and formation constant of HASA ($10^{9.82}$ for $HCH(OH)SO_3^-$, $10^{5.84}$ for $CH_3CH(OH)SO_3^-$, $10^{6.30}$ for $HOCH_2CH(OH)SO_3^-$, $10^{7.96}$ for $CH(OH)_2CH(OH)SO_3^-$, $10^{8.91}$ for $CH_3COCH(OH)SO_3^-$, $10^{5.34}$ for $HCH(O^-)SO_3^-$, $10^{4.73}$ for $CH_3COCH(O^-)SO_3^-$).[33]

obtained not only from the resistance model of gas components but also the aerosol contribution calculated by the deposition velocity and the measured ammonium ion concentration in aerosol. The values were correlated well (correlation factor, 0.75), and the measured values were close to the estimated values (the average measured value was 1.2 time larger than the average estimated value). Therefore, the origin of ammonium ion in dewwater is not only ammonia gas but also ammonium ion in aerosol. The precise transport equation should be investigated further for the case that both gas and aerosol contribute to the component in dewwater.

S(IV) Chemistry of Dewwater. The high concentration of S(IV) is one of the significant characteristics of dewwater.[4] Hydrogensulfite ion in dewwater is an important species as the precursor of sulfate, but is stabilized by forming hydroxymethanesulfonate (HMSA),[8] while fog- and rainwater contains only a very small amount. The total S(IV) concentration in dewwater is defined as follows:

$$[S(IV)]_{total} = [H_2SO_3]_{free} + [HSO_3^-]_{free} + [SO_3^{2-}]_{free} + [HASA] \quad (12)$$

It can be assumed that HASA is formed only from five species of aldehyde (formaldehyde, acetaldehyde, hydroxyacetaldehyde, glyoxal, and methylglyoxal) because these aldehydes were the major components in the dewwater.

$$[HASA] = [HCH(OH)SO_3^-] + [CH_3CH(OH)SO_3^-] + [HOCH_2CH(OH)SO_3^-] + [CH(OH)_2CH(OH)SO_3^-] + [CH_3COCH(OH)SO_3^-] + [HCH(O^-)SO_3^-] + [CH_3COCH(O^-)SO_3^-] \quad (13)$$

In the following discussion, $[CH(OH)SO_3^-CH(OH)SO_3^-]$, $[CH_3CH(O^-)SO_3^-]$, $[HOCH_2CH(O^-)SO_3^-]$, and $[CH(OH)_2CH(O^-)SO_3^-]$ were neglected because the formation constants of these HASAs are unknown and the contribution of the adducts with sulfite may be very small because of the low corresponding aldehydes concentration in the ambient air. The formation constant of HASA (K_{f1}, K_{f2}) and the hydration constant of aldehyde (K_h)[33] are defined as follows:

$$K_{f1} = [RCH(OH)SO_3^-]/[RCHO]_{free}[HSO_3^-]_{free} \quad (14)$$

$$K_{f2} = [RCH(O^-)SO_3^-]/[RCHO]_{free}[SO_3^{2-}]_{free} \quad (15)$$

$$K_h = [RHC(OH)_2]/[RCHO]_{free} \quad (16)$$

$$[RCHO] = [RCHO]_{free} + [RHC(OH)_2] \quad (17)$$

The concentrations of free hydrogensulfite, free sulfite, and HASA were estimated by the total S(IV) and each aldehyde concentration, the formation constants of HASA, and the hydration constants of each aldehyde. The volume-weighted average concentrations of hydrogensulfite and sulfite ion are 4.0 (0–69) µmol dm^{-3} and 0.65 (0–34) µmol dm^{-3}, respectively. Table 2 shows the volume-weighted average concentrations and ranges of HASA and aldehyde in dewwater in Yokohama from January 1993 to December 2000. The hydroxymethanesulfonate (HMSA) concentration was about 85% of the total S(IV) concentration and the ratio of the HMSA concentration to the total formaldehyde ($HCHO + H_2C(OH)_2 + HCH(OH)SO_3^- + HCH(O^-)SO_3^-$) concentration was high (86%). In the United States, it was reported that the ratios of total formaldehyde to HMSA concentration ranged from 4 to 90 and that the free formaldehyde ranged from 75 to 99% of the total formaldehyde concentration in cloud- and fogwater.[9] The HASA concentrations were the lowest in summer throughout a year because of the low atmospheric sulfur dioxide concentration (spring 2.08 ppb, summer 0.74 ppb, autumn 1.41 ppb, winter 2.13 ppb) in our sampling site.

The S(IV), HMSA, and hydroxyethanesulfonate (HESA) concentrations of dewwater were also estimated by the resistance model with atmospheric sulfur dioxide, formaldehyde and acetaldehyde gas concentrations, and atmospheric conditions.[4] Figure 4 shows the temporal variation of the S(IV), HMSA, and HESA concentrations of measured and estimated by resistance model in the dewwater on November 24–25, 2000. The estimated values of total S(IV) corresponded well with the measured values, ranging from 70 to 97%. In this case, the supersaturation caused by the pH distribution of dew droplets does not occur because the pH of the dew samples was 6–8 and was much larger than in the pH-sensitive region. The estimated values of total S(IV) were slightly lower than the measured values because the other HASA, expect for HMSA and HESA, would be present in the dewwater. The estimated

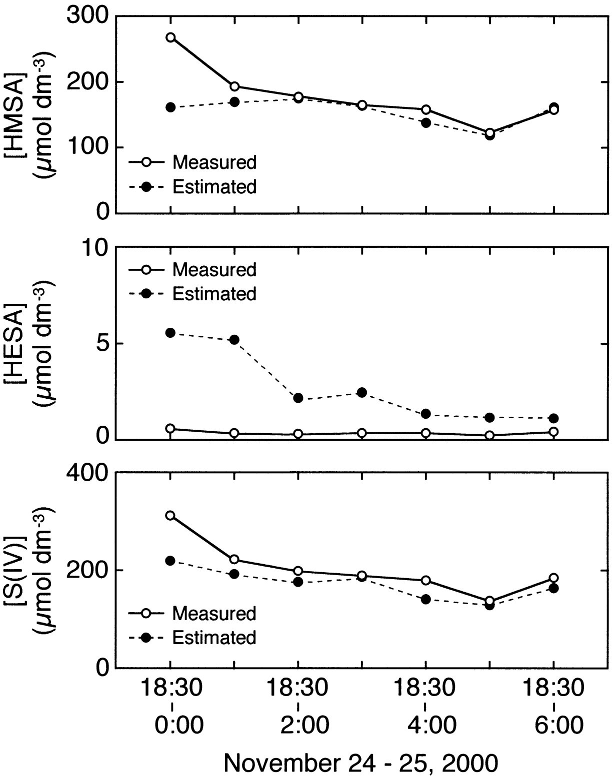

Fig. 4. Comparison with the total S(IV), HMSA, and HESA concentrations of measured and estimated by resistance model in the dewwater in Yokohama on November 24–25, 2000.

values of HMSA also corresponded well with the measured values. On the other hand, the estimated values of HESA were higher than the measured values. Martin et al.[34] reported that the rate of decomposition of HESA at pH 2 is 300 times faster than that of HMSA. The HESA would not be very effective at protecting S(IV) from oxidation in the dewwater.

Carboxylate Chemistry of Dewwater. Dewwater contains much carboxylic acid and the average concentrations of formate and acetate were several times higher in dewwater than in rainwater in Yokohama, while the concentrations of oxalate was about the same level (formate 3.80 µmol dm^{-3}, acetate 5.01 µmol dm^{-3}, oxalate 2.50 µmol dm^{-3} in rainwater). In the Los Angeles basin, the concentrations of formate and acetate were higher in dewwater than those in rainwater, while the concentration of oxalate was lower in dewwater than in rainwater (formate 118 µmol dm^{-3}, acetate 52 µmol dm^{-3}, oxalate 2.1 µmol dm^{-3} in dewwater; formate 7 µmol dm^{-3}, acetate 24 µmol dm^{-3}, oxalate 16 µmol dm^{-3} in rainwater).[17] There are some possibilities for the oxalate concentration in dewwater to be the same order as that in rainwater. First, the oxalate precipitates by forming calcium oxalate due to the relatively high concentration of calcium ion in the dewwater. However, the product of the oxalate and calcium concentrations did not reach the solubility product of calcium oxalate (2.1×10^{-9}, 25 °C). Second, the oxalate in dewwater is decomposed by a photochemical reaction in the early morning, and the reaction is depressed during rain. Pierson and Brachaczek[17] reported that at least 65% of the oxalate disappeared 2 hours after sunrise. Third, the scavenging process of oxalate in dewwater is different from that in rainwater. Both formate and acetate were mostly present in the gaseous form, but much oxalate was present in the aerosol form in the atmosphere.[35–37] Formate and acetate in dewwater mainly originated from the gas-phase formic acid and acetic acid in the atmosphere, respectively. There was a relatively high correlation between the formate and acetate concentrations in dewwater (correlation coefficient, 0.67), suggesting the same scavenging process for these monocarboxylates, but poor correlations between the oxalate concentration and monocarboxylates concentration (correlation coefficient, 0.22 for formate and 0.23 for acetate, respectively) in the dewwater. Formic acid and acetic acid concentration in the ambient air in Yokohama were 2.80 ppb and 2.63 ppb, and their concentration were estimated by the resistance model to be 93.1 µmol dm^{-3} and 74.4 µmol dm^{-3}, respectively, using the molecular diffusion coefficient (formic acid 0.15 cm^2 s^{-1}, acetic acid 0.13 cm^2 s^{-1})[28] and Henry's law constant (formic acid 3.6×10^3 mol dm^{-3} atm^{-1}, acetic acid 8.8×10^3 mol dm^{-3} atm^{-1}).[24] These values were higher than the measured values, but they can be regarded to be reasonable, because the concentrations of formic acid and acetic acid in the ambient air become low at night. Oxalate in the aerosol is present as a fine aerosol,[37] and the concentration in aerosol is less than 1/50 of ammonium ion in Yokohama (Oxalate 2.9 nmol m^{-3}, ammonium 153 nmol m^{-3} in Yokohama in 1997). The concentration of oxalate ion is reasonable when the same deposition velocity as that of the fine aerosol containing ammonium ion was assumed. The fine aerosol is present in the relatively high altitude atmosphere and becomes easily to be incorporated into rainwater as rainout.

Figures 5a and 5b show the relationship between the total formic and acetic acid concentrations and pH in dew- and rainwater in Yokohama and the fogwater at the midslope of Mt. Oyama, respectively. The total formic acid and acetic acid concentrations in the dewwater were high and increased with the increase of the pH value, while those in rain- and fogwater were low and increased with the decrease of pH. In rain- and fogwater, the total formic and acetic acid concentrations were high at the lower pH probably because the formic and acetic acid concentrations increased with the increase in the acid pollutant concentration in the ambient air. Figures 5a′ and 5b′ show the undissociated formic and acetic acid concentrations, which were calculated by the dissociation constants and the total concentration, respectively. These were on the same order among these precipitations, and the pH dependence was equal to each other. Therefore, the concentrations of the formic and acetic acids in the dewwater is larger than those in the rain- and fogwater because of the pH of the dewwater is higher than that of the rain- and fogwater.

Conclusions

In conclusion, the weak acid anions (carbonate, nitrite, sulfite, formate, and acetate) were major species in dewwater, while they were minor or trace species in rain- and fogwater. The N(III) concentration estimated by the resistance model from the gaseous nitrous acid concentration agreed well with the measured values and the origin of N(III) in dewwater was nitrous acid in the ambient air. On the other hand, ammonium

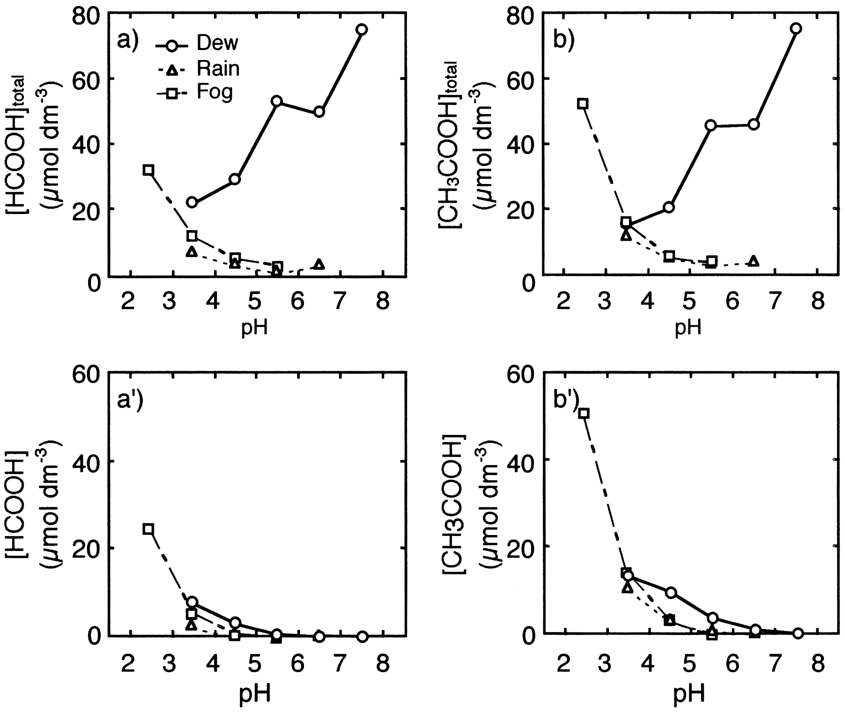

Fig. 5. Relationship between the concentrations of total formic and acetic acids (a and b) and the concentrations of undissociated form of formic and acetic acids (a′ and b′) and pH in the dew- and rainwater in Yokohama and fogwater at the midslope of Mt. Oyama in 1996.

ion in the dewwater originated from gaseous ammonia and aerosol ammonium ion. S(IV) is stabilized in dewwater by the formation of it's adducts. The hydroxymethanesulfonate (HMSA) concentration was about 85% of the total S(IV) concentration and the HASA concentrations were the lowest during summer in all seasons. The total formic and acetic acid concentrations in dewwater increased with the increase of pH value, and were much higher than those in rain- and fogwater.

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References

1 M. L. Wesely, D. L. Sisterson, and J. D. Jastrow, *J. Geophys. Res.*, **95D**, 7501 (1990).

2 J. Wisniewski, *Water, Air, Soil, Pollut.*, **17**, 361 (1982).

3 J. R. Foster, R. A. Pribush, and B. H. Carter, *Atmos. Environ.*, **24A**, 2229 (1990).

4 H. Okochi, T. Kajimoto, Y. Arai, and M. Igawa, *Bull. Chem. Soc. Jpn.*, **69**, 3355 (1996).

5 M. Takeuchi, H. Okochi, and M. Igawa, *J. Jpn. Soc. Atmos. Environ.*, **35**, 158 (2000).

6 T. Arakaki, T. Miyake, M. Shibata, and H. Sakugawa, *Nippon Kagaku Kaishi*, **1998**, 619 .

7 T. Arakaki, T. Miyake, M. Shibata, and H. Sakugawa, *Nippon Kagaku Kaishi*, **1999**, 335.

8 Y. Katagiri, N. Sawaki, Y. Arai, H. Okochi, and M. Igawa, *Chem. Lett.*, **1996**, 197.

9 X. Rao and J. L. Collett, Jr., *Environ. Sci. Technol.*, **29**, 1023 (1995).

10 J. W. Munger, C. Tille, and M. R. Hoffmann, *Science*, **231**, 247 (1986).

11 T. M. Olson and M. R. Hoffmann, *Atmos. Environ.*, **23**, 985 (1989).

12 J. N. Galloway, G. E. Likens, W. C. Keene, and J. M. Miller, *J. Geophys. Res.*, **87**, 8771 (1982).

13 K. Kawamura, S. Steinberg, and I. R. Kaplan, *Atmos. Environ.*, **30**, 1035 (1996).

14 K. Takamine, S. Tanaka, and Y. Hashimoto, *Bunseki Kagaku*, **31**, 692 (1982).

15 S. Tanaka, Y. Komazaki, Y. Ikeuchi, and Y. Hashimoto, *Bunseki Kagaku*, **36**, 164 (1987).

16 S. Steinberg and I. R. Kaplan, *Intern. J. Environ. Anal. Chem.*, **18**, 253 (1984).

17 W. R. Pierson and W. W. Brachaczek, *Aerosol Sci. Technol.*, **12**, 8 (1990).

18 N. Takenaka, T. Suzue, K. Ohira, T. Morikawa, H. Bandow, and Y. Maeda, *Environ. Sci. Technol.*, **33**, 1444 (1999).

19 P. A. Mulawa, S. H. Cadle, F. Lipari, C. C. Ang, and R. T. Vandervennet, *Atmos. Environ.*, **20**, 1389 (1986).

20 J. Notholt, J. Hjorth, and F. Raes, *Atmos. Environ.*, **26A**, 211 (1992).

21 A.-M. N. Kitto and R. M. Harrison, *Atmos. Environ.*, **26A**, 235 (1992).

22 M. D. Andés-Hernåndes, J. Notholt, J. Hjorth, and O. Schrems, *Atmos. Environ.*, **30**, 175 (1996).

23 R. M. Harrison, J. D. Peak, and G. M. Collins, *J. Geophys. Res.*, **101D**, 14429 (1996).

24 J. H. Seinfeld and S. N. Pandis, "Atmospheric Chemistry and Physics," John Wiley & Sons, New York (1998), p. 341.

25 A. E. Martell and R. M. Smith, "Critical Stability Constant Volume 4: Inorganic Complexes," PLENUM PRESS, New York and London (1976), p. 47.

26 W. L. Chameides, *J. Geophys. Res.*, **92D**, 11895 (1987).

27 J. A. Garland, *Poc. R. Soc. Lond. A.*, **354**, 245 (1977).

28 J. H. Seinfeld and S. N. Pandis, "Atmospheric Chemistry and Physics," John Wiley & Sons, New York (1998), p. 975.

29 J. H. Seinfeld and S. N. Pandis, "Atmospheric Chemistry and Physics," John Wiley & Sons, New York (1998), p. 961.

30 G. Lammel and D. Perner, *J. Aerosol Sci.*, **19**, 1199 (1988).

31 S. H. Pandis and J. H. Seinfeld, *J. Geophys. Res.*, **96D**, 10791 (1991).

32 J. H. Seinfeld and S. N. Pandis, "Atmospheric Chemistry and Physics," John Wiley & Sons, New York (1998), p. 441.

33 E. A. Betterton, Y. Erel, and M. R. Hoffmann, *Environ. Sci. Technol.*, **22**, 92 (1988).

34 L. R. Martin, M. P. Easton, J. W. Foster, and M. W. Hill, *Atmos. Environ.*, **23**, 563 (1989).

35 D. Grosjean, *Environ. Sci. Technol.*, **23**, 1506 (1989).

36 R. W. Talbot, K. M. Beecher, R. C. Harris, and W. R. Cofer, Ⅲ. *J. Geophys. Res.*, **93D**, 1638 (1988).

37 H. A. Khwaja, *Atmos. Environ.*, **29**, 127 (1995).