Effect of Acid Deposition on Urban Dew Chemistry in Yokohama, Japan

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Dews or frosts formed on artificial collectors were collected during the early morning in Yokohama in 1993 and 1994 and analyzed for weak acids as well as major inorganic ions. In 1993 (n=21) the dew pH ranged from 3.23 to 7.12 and averaged 4.60; in 1994 (n=56) it ranged from 4.11 to 7.74 and averaged 5.41. Based on the average, NH_4^+ and Ca^{2+} were major cations (423 and 178 μequiv L^{-1} for NH_4^+ and Ca^{2+} in 1993, respectively, and 454 and 274 μequiv L^{-1} in 1994, respectively) and SO_4^{2-} was the dominant anion (344 μequiv L^{-1} in 1993 and 271 μequiv L^{-1} in 1994) in dew water. The dew chemistry was characterized by relatively high concentrations of weak acid anions, particularly hydrogensulfite ion (HSO_3^-). Dew water sometimes had very high acidity (the minimum pH was 3.23 during the period of this research), which might have been due to the aqueous oxidation of S(IV). From a resistance model calculation, the S(IV) concentration in dew water was suggested to be influenced by the dissolution of HCHO from the atmosphere and the subsequent formation of HMSA.

Dew is formed on surfaces cooled by nocturnal radiation on a clear night and in the early morning under a light wind. Under such conditions, the concentrations of various pollutants are high in the atmosphere because atmospheric diffusion is depressed. Dew water dissolving water-soluble pollutants from the atmosphere may have harmful influences on the contacted materials. It has been reported that dew formed on plant leaves enhances the dry deposition velocity of acid gases, such as HNO_3 and SO_2, and may have an important role in acid deposition to vegetation.[1,2] On the other hand, the deterioration of automobile coatings by acid rain is pointed out,[3] it may also be enhanced by dew in the evaporation process. Only a few studies, however, have so far been made to clarify dew chemistry and its environmental effects.

The early studies of dew chemistry emphasized only some inorganic ion species.[4,5] Brimblecombe and Todd[5] found that the pH of individual dew droplets lay crudely between 5 and 7, and that roughly equal concentrations of potassium and sodium were present in dew water. In the last decade, the mean pH of 'bulk' dew water formed on the surfaces of chemically inert collectors has been reported to be 4.0 (sample number, n=15) by Pierson et al.,[6] 6.82 (n=20) by Foster et al.,[7] and 6.37 (n=93) by Wanger et al.[8] In general, the pH values and concentrations of various ions in dew water are much higher than those in rainwater.[7,8] Pierson et al.[6] have suggested that dew water was acidified mainly by SO_2,[7] although some fraction of SO_2 dissolved in dew remained unchanged as S(IV). On the other hand, Chameides[9] studied the generation of acid dew from dry deposition of HNO_3 as well as SO_2, using a model involving dynamical resistance, surface resistance, and reactions in dew droplets. Recently, it was clarified that some fraction of S(IV) in dew water was present as hydroxyalkanesulfonate (HASA),[10] which was the adduct of S(IV) with aldehydes. However, it remains a question as to what factors determine the S(IV) concentration in dew water, and how the aqueous oxidation of S(IV) to sulfuric acid proceeds.

The purpose of this study was to clarify dew chemistry, because there is little knowledge about it. Thus, dews or frosts formed on artificial collectors were collected in the early morning and analyzed for formate, acetate, and dissolved organic carbon (DOC) in addition to major inorganic ions in 1993 and 1994. In this paper, the following is reported: (1) mean chemical composition of bulk dew water and temporal variation of the dew composition; (2) the origins of major ions in dew water; (3) the factors controlling the S(IV) concentration in dew water.

Experimental

Sampling Method. Dew or frost samples were collected in 1993 and 1994, except for July and August, on the roof of a four-storied building located on the campus of Kanagawa University in Yokohama City, which is a typical urban area in Japan. The sampling point was located less than 3 km from the Tokyo Bay area, with the surroundings being residential areas. The dew collector consisted of a 0.1-mm-thick Teflon sheet (90 cm×45 cm in 1993 and 90 cm×90 cm in 1994) mounted on a 10-cm-thick slab of a styrofoam with double-stick tape. When the collector was placed (at about 19:30), it was rinsed thoroughly with ultrapure water and swept with tissue paper (Kimwipers®). In the early morning of the following day (usually, at about 7:30), dew or frost was scraped off with a chemically clean Teflon® scraper and transferred to a clean Teflon® bottle.

Temporal dew samplings were performed twice on April 21—22 and October 14—15, 1994, by putting three collectors at the same time and collecting the dew water formed on the collectors every two or three hours. During that period, gaseous species (SO_2, HNO_3, HCl, NH_3) were also collected with a five-stage filter pack system, which comprised a 47 mm polycarbonate aerosol holder connected to four multiholder adapters (Nuclepore Co.), at a flow rate of 20 L min^{-1}. The first filter was a quartz fiber filter (Advantec Co., QR-100) to remove atmospheric aerosols. The second and third filters were for collecting acid gases. They were 47 mm cellulose filters (Whatmann No. 41) impregnated with 1% (w/v) Na_2CO_3/glycerol in a water solution and dried in a desiccator containing silica gel over a period of twenty-four hours. The fourth and fifth filters were for collecting ammonia gas. They were 47 mm cellulose filters impregnated with 5% (w/v) H_3PO_4/glycerol in a water solution and dried in the same way.

The data concerning the concentrations of the other gases (O_x, NO, and NO_2) and SP (suspended particle), wind speed, wind direction, atmospheric temperature, and relative humidity were provided from the Atmospheric Protection Bureau of Yokohama City Office. They were measured at the building of Kanagawa Ward Government Office, which was located southeasterly about 1 km from our sampling site.

In order to measure the accumulation and evaporation rate of dew water, the dew amounts were weighed from the evening to the next morning by putting the dew collector on a balance (Sartorius Co., LC-34000P). The weight was recorded every one minute using a personal computer (Epson PC-486 Note AS) connected to the balance. Strictly speaking, although dew might have been formed on a stainless-steel saucer of the balance besides the dew collector surface, we ignored the dewfall amount on the saucer because most of the saucer was covered with the dew collector, and it was difficult to measure the amount exactly.

Analytical Method. Dew or frost samples were weighed and filtrated with 0.45-μm pore-size membrane filters (Advantec Co.). The electric conductivity, pH, and concentrations of anions (Cl^-, $HCOO^-$, CH_3COO^-, NO_2^-, NO_3^-, SO_3^{2-}, SO_4^{2-}) were measured immediately after sample collection so as to prevent chemical changes in the constituents, using an electric-conductivity meter (Kyoto Electronics Ltd., CM-117), pH meter (Toa Electronics Ltd., HM-60S), and ion chromatography (Dionex Co., 2000i/sp; separation column, IonPac AG4 and AS4). The residual samples were stored at 4 °C in a refrigerator after filtrating, and were measured within three weeks. Ca^{2+} and Mg^{2+} were analyzed by ICP-AES (Seiko Instruments Inc., SPS1500) or ion chromatography (Dionex Co., DX-100; separation column, IonPac CG12 and CS12). Other cations (NH_4^+, Na^+, K^+) were analyzed with ion chromatography (Dionex Co., QIC; separation column, IonPac CG3 and CS3 or Dionex Co., DX-100; separation column, IonPac CG12 and CS12). The dissolved organic and inorganic carbon concentrations (they are shortened to be DOC and DIC, respectively) were measured with a TOC analyzer (Shimadzu Co., TOC-5000).

Results and Discussion

Chemical Composition of Dew Water. Twenty-one dew or frost samples were collected in 1993; the dewfall ranged from 25.0 to 139 g m^{-2} and averaged 64.0 g m^{-2}. In 1994, fifty-six samples were collected and the dewfall ranged from 0.62 to 244 g m^{-2} and averaged 70.6 g m^{-2}. Table 1 shows the volume-weighted mean concentrations and ranges of the major ions in dew water in 1993 and 1994 together with the data from three papers.[7,8,11] The mean pH was lower in 1993 than in 1994, although the mean concentrations of NH_4^+, Na^+, K^+, Cl^-, and NO_3^- were nearly equal in both years. The concentrations of other ions were higher in 1994 than in 1993, and, particularly, there were large differences in the SO_3^{2-} and HSO_3^- concentrations. One of the reasons is due to a delayed measurement of those ions in 1993 because S(IV) is easily oxidized to S(VI) in water. The concentrations of SO_3^{2-} and HSO_3^- were calculated from the total S(IV) concentration (measured as SO_3^{2-} by ion chromatography) and pH according to the dissociation equilibrium of sulfurous acid (H_2SO_3). In the calculation, it was assumed that S(IV) in dew water was present only as free S(IV), namely as $SO_2{\cdot}H_2O$, HSO_3^-, and SO_3^{2-}, although a part of S(IV) was present as hydroxymethanesulfonate (HMSA) in dew water.[10]

Based on the average, NH_4^+ and Ca^{2+} were the major cations and SO_4^{2-} was the dominant anion in dew water

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

	This study				Mulawa et al.	Foster et al.		Wanger et al.
	1993 $n=21$		1994 $n=52^{a)}$		Warren, Michigan $n=9$—40	Indianapolis, Indiana $n=20$		Fayetteville, Arkansas $n=93$
pH	4.60	(3.23—7.12)	5.41	(4.11—7.74)	3.62—8.20	6.82	(6.2—6.8)	6.37
NH_4^+	423	(32.9—1290)	454	(64.1—3470)	65 ± 26	6.9	(3.7—105)	94
Na^+	129	(13.1—891)	128	(21.2—709)	20 ± 6	3.9	(1.4—8.9)	7.8
K^+	28.9	(6.03—162)	22.8	(4.58—147)	4.1 ± 3	1.3	(2.8—26)	9
Mg^{2+}	30.6	(6.74—211)	66.3	(5.58—794)	31 ± 11	32.6	(12.2—70)	11
Ca^{2+}	178	(33.3—1414)	274	(28.9—2064)	690 ± 935	150	(50—266)	115
Cl^-	184	(28.3—1230)	165	(32.4—1013)	106 ± 252	6.1	(3.3—16)	11
NO_3^-	85.5	(13.7—584)	92.4	(10.1—1003)	166 ± 282	25.5	(2.2—78)	38
SO_4^{2-}	344	(41.6—1272)	271	(20.5—1864)	242 ± 312	31.6	(3.8—106)	66
HCO_3^-	61.8	(2.41—456)	40.7	(0—435)	NA	146	(43—374)	NA
NO_2^-	66.0	(0—206)	75.7	(0—257)	NA	4.0	(0.9—9.6)	NA
SO_3^{2-}	2.75	(0—37.2)	36.1	(0—1237)	NA	0.6	(0—3.4)	NA
HSO_3^-	20.1	(0—199)	179	(0—1507)	NA	NA		NA
$HCOO^-$	32.7	(2.51—96.8)	52.2	(0—251)	NA	2.6	(0—12.4)	17.1
CH_3COO^-	31.7	(6.75—162)	41.3	(0—263)	NA	1.1	(0—16.8)	12.3
DOC	12.3	(2.81—51.9)	13.6	(3.09—62.3)	NA	NA		NA

All units are μequiv/L except pH and DOC (mg L^{-1}). a) Except for pH where $n=56$. NA represents not analyzed value.

each year. Dew chemistry was characterized by relatively high concentrations of weak acid anions, such as bicarbonate (HCO_3^-), nitrite (NO_2^-), sulfite (SO_3^{2-}), and hydrogensulfite ion (HSO_3^-), while they were usually only slightly present in rain water. Furthermore, the organic anions, formate ion ($HCOO^-$) and acetate ion (CH_3COO^-) were present at the sixth or seventh high concentrations among the anions. These weak acids can not be ignored in dew water. Figure 1 shows the relationship between the sum of cations and the sum of anions, which are all of the anions shown in Table 1 or major anions in rain water, namely: Cl^-, NO_3^-, and SO_4^{2-}. It is obvious that the sum of cations is higher than the sum of Cl^-, NO_3^-, and SO_4^{2-}, and is nearly equal to the sum of all the anions listed in Table 1.

The dew composition, as given in some other papers, are also given in Table 1. Among those, only the data reported by Mulawa et al.[12] represent the composition of dew water collected in an urban area. Compared to those papers, the concentrations of NH_4^+, Na^+, K^+, Cl^-, NO_2^-, $HCOO^-$, and CH_3COO^- were high in the dew water collected at our sampling site. The high concentrations of Na^+ and Cl^- were reflected by the short distance from the coast (about 3km) to our sampling site. The mean SO_4^{2-} concentration in our dew samples was higher than the value reported by Mulawa et al.,[12] while the mean NO_3^- concentration was lower. Although the differences may be reflected by the concentrations of the corresponding pollutants, namely SO_2, SO_4^{2-}, NO, NO_2, PAN, HNO_3, N_2O_5, NO_3^-, and so on, in the air, our information concerning the concentration of those pollutants is limited.

Fig. 2 shows the frequency distribution of the pH of dew water in 1993 and 1994, together with that of rain water, which was collected every 1 mm at the same site (886 samples) by an auto rain sampler in 1994. The dew pH distributed more widely than the rain pH and the mean pH of dew water was higher than that of rain water (4.64). The minimum pH of dew water was lower than that of rain water, and the environmental effect of acid dew may have been important.

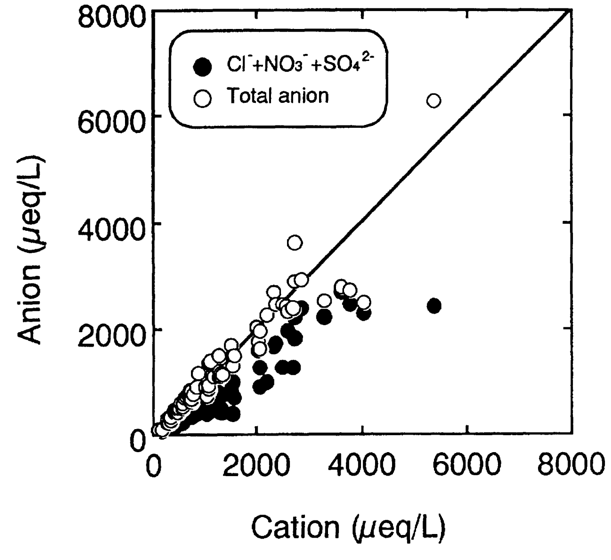

Fig. 1. Relationship between the sum of cations and the sum of anions or the sum of chloride, nitrate, and sulfate ions. The straight line represents one-to-one line between the sum of cations and anions.

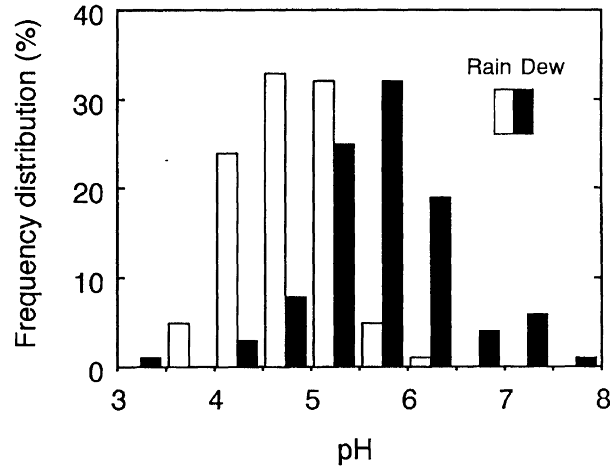

Fig. 2. The frequency distribution of pH of dew water and rain water. Rain water was collected every 1 mm by an auto rain sampler in 1994.

Origins of Major Ions in Dew Water. Table 2 gives the correlation coefficients among the deposition fluxes of the major inorganic ions including N(III) and S(IV), total HCOOH ([$HCOO^-$] + [HCOOH]), total CH_3COOH ([CH_3COO^-] + [CH_3COOH]), dissolved inorganic carbon (DIC), and dissolved organic carbon (DOC) in dew water observed in 1994. The deposition fluxes were calculated by multiplying each concentration by the accumulated dew volumes and dividing by the collector area. We can see that there are strong correlations ($r = 0.82$) among the Na^+, Cl^-, and Mg^{2+} fluxes in dew water. The slopes of the regression lines between the Cl^- fluxes and the Na^+ fluxes, and between the Mg^{2+} fluxes and the Na^+ fluxes are 0.929 and 0.233, respectively. They are nearly equal to each sea salt ratio (1.17 and 0.288, respectively), indicated that the Cl^-, Na^+, and Mg^{2+} ions in dew water were derived mainly from the deposition of sea salt.

The NH_4^+ fluxes correlated closely to the N(III) and S(IV) fluxes ($r = 0.820$ and 0.724, respectively). It is likely that the increase in the dew pH caused by the absorption of NH_3, as well as $CaCO_3$, enhanced the dissolution of weak acids and S(IV) and N(III) in dew water, which may be derived from atmospheric SO_2 and HNO_2, respectively. It is difficult to consider the dissolution of NO_2 as being the origin of N(III) in dew water, because Henry's law constant of HNO_2 (49 $M\,atm^{-1}$)[12] is about 5000-times higher than that of NO_2 (1×10^{-2} $M\,atm^{-1}$),[12] although the HNO_2 concentration is lower than the NO_2 concentration in urban air (their ranges are 1—8 ppb and 50—250 ppb, respectively) ($M = mol\,dm^{-3}$).[12] Moreover, since it is indicated that HNO_2 is formed throughout the night due to the nighttime increase of the HNO_2/NO_x ratio,[13] it seems reasonable to suppose that N(III) in dew water is derived from the dissolution of HNO_2.

	H^+	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	N(III)	S(IV)	HCOOH	CH_3COOH	DIC
NH_4^+	-0.069													
Na^+	0.639	0.160												
K^+	0.276	0.431	0.706											
Mg^{2+}	0.486	0.345	0.857	0.711										
Ca^{2+}	0.093	0.533	0.075	0.188	0.459									
Cl^-	0.591	0.354	0.822	0.606	0.850	0.320								
NO_3^-	0.613	0.248	0.605	0.488	0.667	0.357	0.638							
SO_4^{2-}	0.253	0.682	0.405	0.544	0.689	0.689	0.616	0.399						
N(III)	-0.178	0.820	0.045	0.381	0.258	0.378	0.103	0.134	0.432					
S(IV)	-0.233	0.724	-0.205	0.145	0.019	0.507	-0.041	-0.073	0.569	0.573				
HCOOH	0.154	0.509	0.359	0.528	0.584	0.389	0.517	0.296	0.675	0.443	0.320			
CH_3COOH	0.080	0.655	0.419	0.700	0.523	0.423	0.516	0.321	0.624	0.568	0.422	0.624		
DIC	0.011	0.606	-0.050	0.179	0.142	0.221	0.131	0.163	0.475	0.645	0.468	0.353	0.381	
DOC	0.032	0.846	0.302	0.549	0.534	0.609	0.544	0.443	0.746	0.642	0.657	0.658	0.776	0.484

Table 2. Correlation Coefficients Among Deposition Fluxes of Various Components in Dew Water Collected in 1994

Although Pierson et al.[6] and Mulawa et al.[11] observed strong correlations between the SO_4^{2-} and NO_3^- concentrations in dew water, there was only a weak correlation between them ($r = 0.399$) in the dew water at our sampling site. Chang et al.[14] reported that the major source of dew nitrate was HNO_3 vapor, and in a few cases N_2O_5. There were relatively high correlations between the NO_3^- fluxes and the Na^+, Mg^{2+}, and Cl^- fluxes ($r = 0.605$, 0.667, and 0.638, respectively), indicating that HNO_3 reacted with sea salts in the air and deposited together with sea salts into dew water. On the other hand, the SO_4^{2-} fluxes were closely correlated to the NH_4^+, Mg^{2+}, and Ca^{2+} fluxes ($r = 0.682$, 0.689, and 0.689, respectively). Butler[15] reported that $CaSO_4$, which might be formed in the atmosphere or on surfaces by the interaction of $CaCO_3$ or other alkaline particles with SO_2 or H_2SO_4, was a major form of the dry deposition of sulfate salt. Therefore, at our sampling site, SO_4^{2-} may have also deposited as $CaSO_4$ into dew water from the air, though it is likely that the aqueous oxidation of S(IV), which was originated from dissolution of atmospheric SO_2, to S(VI) in dew water may have proceed when Ca deposited as the chemical forms of $CaCO_3$, dolomite ($CaCO_3 \cdot MgCO_3$), and CaO.[15] The relatively high correlation coefficients between NH_4^+ and SO_4^{2-} indicates that SO_4^{2-} deposited into dew water as NH_4HSO_4 or $(NH_4)_2SO_4$ or that the absorption of NH_3 into dew water was accelerated as the dew pH decrease due to the aqueous oxidation of S(IV). However, it was not clarified as to which among the ammonium salt, calcium salt, or aqueous oxidation of S(IV) contributed mainly to the SO_4^{2-} in dew water.

The Factors Controlling Dew pH—Equilibrium Model Calculation—. The mean pH of dew water was higher than that of rain water; there are three reasons for this. Firstly, very small deposition fluxes of water-soluble acid gas, such as HNO_3 and HCl, exist during the night time. As mentioned in the preceding section, Cl^- in the dew water was derived from sea salt at our sampling site, and HCl could be ignored as the origin of Cl^- in dew water. Secondly, the aqueous oxidation of S(IV) to S(VI) proceeds only slightly. S(IV) ($HSO_3^- + SO_3^{2-}$) was the second abundant anion in dew water in 1994 (Table 1). Thirdly, the acidity of dew water is neutralized by NH_3 gas and Ca salts, such as $CaCO_3$. NH_4^+ and Ca^{2+} were dominant cations in dew water at our sampling site. In this section, we try to determine the factors controlling the dew pH using an equilibrium model. For simplicity, it assumed that the dew pH is controlled by the dry deposition of $CaCO_3$ and the absorption of CO_2, SO_2, HNO_3, and NH_3 according to Henry's Law, and that the aqueous oxidation of S(IV) to S(VI) does not proceeded.

In equilibrium, the charge balance among the corresponding ions in dew water is established as follows:

$$\begin{aligned}&[H^+]+[NH_4^+]+2[Ca^{2+}]\\&\quad=[OH^-]+[HCO_3^-]+2[CO_3^{2-}]\\&\qquad+[HSO_3^-]+2[SO_3^{2-}]+[NO_3^-]\end{aligned}\tag{1}$$

with

$$[NH_4^+]=\frac{K_{ha}\cdot K_{a1}}{K_w}p_{NH_3}\cdot[H^+] \qquad [OH^-]=\frac{K_w}{[H^+]}$$

$$[HCO_3^-]=\frac{K_{hc}\cdot K_{c1}}{[H^+]}p_{CO_2} \qquad [HSO_3^-]=\frac{K_{hs}\cdot K_{s1}}{[H^+]}p_{SO_2}$$

$$[CO_3^{2-}]=\frac{K_{hc}\cdot K_{c1}\cdot K_{c2}}{[H^+]^2}p_{CO_2} \qquad [SO_3{}^2-]=\frac{K_{hs}\cdot K_{s1}\cdot K_{s2}}{[H^+]^2}p_{SO_2}$$

$$[NO_3^-]=\frac{K_{hn}\cdot K_{n1}}{[H^+]}p_{HNO_3}$$

In the equations, K_{ha}, K_{hc}, K_{hs}, and K_{hn} represent Henry's Law constants of NH_3, CO_2, SO_2, and HNO_3, respectively, which are $K_{ha}=62\ M\,atm^{-1}$, $K_{hc}=3.4\times10^{-2}\ M\,atm^{-1}$, $K_{hs}=1.24\ M\,atm^{-1}$, and $K_{hn}=2.1\times10^5\ M\,atm^{-1}$ at 25 °C.[12] The constants K_{a1}, K_{c1}, K_{c2}, K_{s1}, K_{s2}, and K_{n1} represent the first or second dissociation constants of $NH_3 \cdot H_2O$, $CO_2 \cdot H_2O$,

$SO_2 \cdot H_2O$, and HNO_3, respectively, which are $K_{a1}=10^{-4.65}$ M, $K_{c1}=10^{-6.35}$ M, $K_{c2}=10^{-10.33}$ M, $K_{s1}=10^{-1.86}$ M, $K_{s2}=10^{-7.19}$ M, and $K_{n1}=15.4$ M.[16] K_w is the ion product of water, namely $K_w=1.0\times10^{-14}$ M.[2] Fig. 3 shows the relationship between the Ca^{2+} concentration and the pH in dew water in 1993 and 1994. In this figure, three curved lines and one straight line were calculated from the equilibrium model under some different conditions of SO_2, NH_3, and HNO_3. Compared with the solid curved line and the dashed-dotted curved line, we can see that the dew pH has a difference of about 0.6 unit in the range of high Ca^{2+} concentration when there is a ten-fold difference in the SO_2 concentration in the air. However, in the range of a very low Ca^{2+} concentration, there is small difference in the pH. On the other hand, compared with the solid curved line and the dashed curved line, we can see that NH_3 has an effect of neutralizing the dew acidity only in the range of very low Ca^{2+} concentration. As shown by the dotted straight line in the figure, HNO_3 has a great effect on acidifying dew water over a wide range of Ca^{2+} concentrations.

The upper limits of the measured dew pH were nearly equal to the dashed curved line, indicating that the dew pH was controlled mainly by CO_2, NH_3, and $CaCO_3$ when the acid gas concentrations of SO_2 and HNO_3 were very low. Although the measured values fit relatively well to those calculated, there were several samples whose pH deviated significantly from the equilibrium values. It is indicated that HNO_3 is absorbed into dew water or that the aqueous oxidation of S(IV) is proceeded in dew water equilibrated with atmospheric SO_2. Among these deviated samples, the chemical composition of dew water collected in March 11, 1994, which had the highest acidity (pH 3.23) is shown in Fig. 4. The proportion of $SO_4{}^{2-}$ was 47% in the total ion concentration, and the proportion of $NO_3{}^-$ was only 4%. Furthermore, S(IV) was not detected in the dew water. Therefore, it is obvious that the dew water was acidified by H_2SO_4 formed by the aqueous oxidation of S(IV). Other dew water, which had a high acidity, also showed a tendency to have a low S(IV) concentration and high S(VI) concentration.

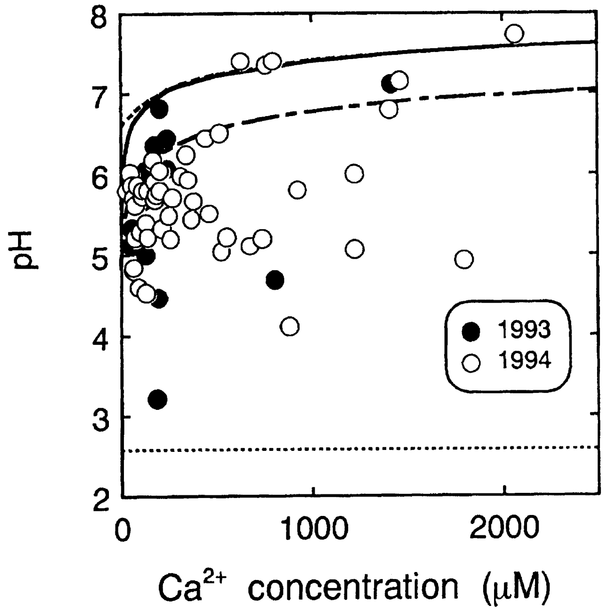

Fig. 3. Relationship between Ca^{2+} concentration and pH in dew water in 1993 and 1994. The solid curved line, dashed-dotted curved line, dashed curved line, and dotted straight line represent the relationship under the atmosphere containing SO_2 (1 ppb), SO_2 (10 ppb), SO_2 (1 ppb)+NH_3 (5 ppb), and SO_2 (1 ppb)+NH_3 (5 ppb)+HNO_3 (1 ppb) in the presence of CO_2 (350 ppm), respectively.

Temporal Variation in the Dew Composition. The variation in the dew amounts is shown in Fig. 5 as a function of time on June 16—17, 1994, together with the air temperature and relative humidity. When the temperature dropped and the relative humidity rose, dew water was accumulated at a nearly steady rate. After about 90 min from sunrise (4:25), the dew began to evaporate rapidly as the temperature rose and the relative humidity quickly dropped. The accumulation and evaporation rate were obtained by dividing the slope of the regression line between the time and weight by the collector surface area. The accumulation process was defined as the range of time from when the weight began to increase at a steady state (for example, at about 23:00 on June 16 in Fig. 5) to when the weight began to be constant (for example, at about 6:00 on June 17 in Fig. 5), while the evaporation process was defined as the range of time from when the weight began to decrease (for example, at about 6:15 on June 17 in Fig. 5) to when the collection of dew water was finished (for example, at about 7:30 on June 17 in Fig. 5). The accumulation rates ranged from 9.3 to 16 $g\,m^{-2}\,h^{-1}$ and averaged 11 $g\,m^{-2}\,h^{-1}$ (n=6), while the evaporation rates ranged from 13 to 31 $g\,m^{-2}\,h^{-1}$ and averaged 22 $g\,m^{-2}\,h^{-1}$ (n=6) in 1994. Based on their averages in 1994, the evaporation rate was two-times larger than the accumulation rate, although there were not enough measured values.

Fig. 6 shows the temporal variation in the chemical composition of dew water formed on April 21—22 and October 15, 1994. The time of sunrise was 5:00 and 5:47 on April

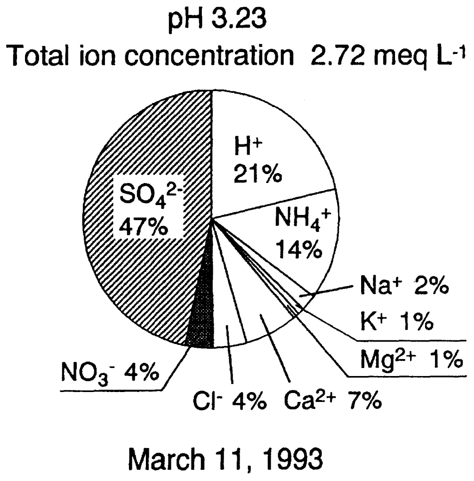

Fig. 4. Chemical composition of dew water with the highest acidity collected in March 11, 1994.

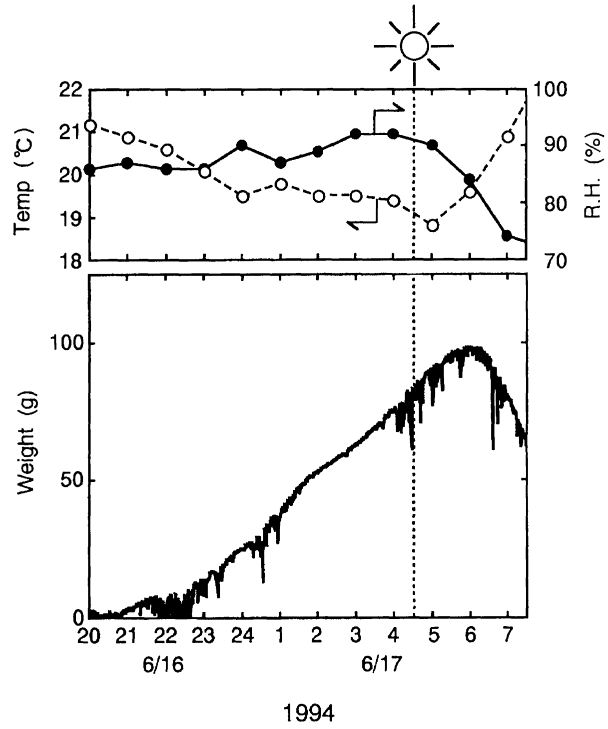

Fig. 5. The variation of dew amounts together with air temperature and relative humidity as a function of time on June 16—17, 1994.

22 and October 15, respectively. The dew collected on April 21—22 was accumulated until the end of the sampling time. The pH and S(IV) concentration increased, while the total ion concentration decreased. The dew collected on October 15 was accumulated from 0:00 to 6:00, but evaporated later. The total ion concentrations in the dew water decreased during the accumulation process, and increased during the evaporation process, indicating that dewfall was one of important factors controlling the concentration of the major ions in dew water. On the other hand, the pH slightly decreased and the S(IV) concentration increased in both the accumulation and evaporation process of dew. Although the concentrations of almost all of the major ions in the dew water collected on October 15 were nearly equal to those in the dew water collected on April 21—22, the pH and S(IV) concentrations in the dew water on October 15 were considerably higher. The SO_2 concentration in the atmosphere was 1.56 ppb and 1.97 ppb at the beginning of dew formation on April 21 and October 15, respectively, and approximately equal on both days. The S(IV) concentrations at the beginning of dew water on April 21 and October 15 were 4.94 and 117 μM, respectively, while they were estimated to be 1.17 and 98.0 μM according to the atmospheric concentration and the apparent Henry's Law constants of SO_2. As the dew water was accumulated, the differences between the measured and calculated S(IV) concentrations increased (at the end of the accumulation process, the measured values were 12.3 and 123 μM on April 22 and October 15, respectively, while the calculated values were 2.48 and 42.0 μM on April 22 and October 15, respectively). Therefore, it is obvious that the S(IV) concentration in dew water is not controlled by only the SO_2 concentration in the air. Furthermore, the S(IV) concentration increased during the sampling time in both dew events, regardless of the dewfall variation. This indicates that dewfall is not an important factor for controlling the S(IV) concentration in dew water.

Fig. 7 shows the temporal variation in the deposition fluxes of NH_4^+ and Ca^{2+} as the dominant cations and Cl^-, NO_3^-, S(IV), and S(VI) (SO_4^{2-}) as the dominant anions. The deposition fluxes were calculated from the data shown in Fig. 6 by subtracting the preceding deposition amount of each ion from the deposition amount until a given collection time. For example, the deposition fluxes from 0:00 to 3:00 on April 22

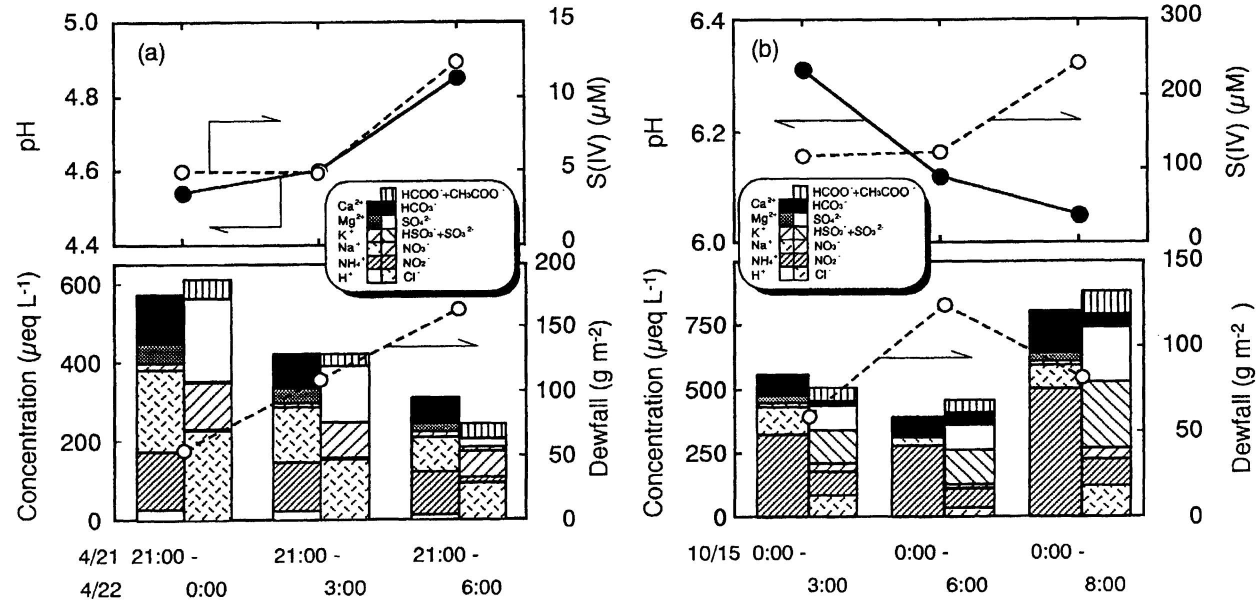

Fig. 6. The temporal variation of chemical composition of dew water on April 21—22 and October 15, 1994.

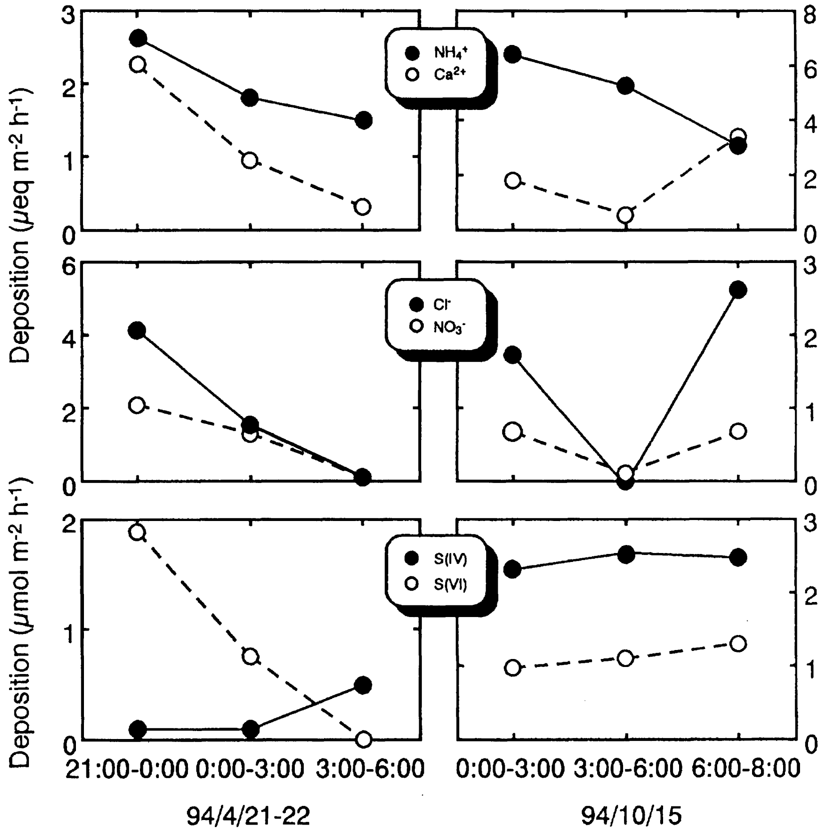

Fig. 7. The temporal variation of deposition fluxes of some dominant ions in dew water on April 21—22 and October 15.

in Fig. 7 were estimated by subtracting the deposition amount from 21:00 on April 21 to 0:00 on April 22 from the deposition amount from 21:00 on April 21 to 3:00 on April 22, and dividing that by the duration, three hours. Though the deposition fluxes of Cl^-, NO_3^-, and S(VI) from 0:00 to 3:00 on both days were calculated to be minus, they are regarded as being zero in Fig. 7, because it was impossible for those ions to evaporate from the dew water into the air. This may have been caused by experimental errors, including the weight measurement of the dew amount, the measurement of those ion concentrations, and the dewfall variation among the dew collectors.

As the time elapsed, the NH_4^+ deposition fluxes decreased on both days, and the final deposition fluxes became 57 and 48% of the first deposition fluxes on April 21—22 and October 15, respectively. This indicates that NH_3 gas was absorbed from the air into dew water during the first stage of dew formation. Ca^{2+}, Cl^-, and NO_3^- showed similar deposition behaviors into each dew-water sample, while those deposition behaviors were different between both dew-water samples. On the other hand, the behaviors of S(IV) and S(VI) were different from other ions, suggesting that both S(IV) and S(VI) were influenced by various aqueous reactions, such as the oxidation of S(IV) to S(VI) and the formation of HMSA[10] in dew water. It is very important to clarify the factors controlling the S(IV) concentration, as we have seen, because dew water is acidified by the aqueous oxidation of S(IV) to S(VI). In the next section we quantitatively discuss the factors controlling the S(IV) concentration in dew water using a resistance model.

Factors Controlling the S(IV) Concentration in Dew Water. In general, the atmospheric boundary layer is stable when dew is formed. Under such atmospheric conditions, there are positive vertical concentration gradients of the depositing species with respect to the height above the ground. Therefore, under no progress of the aqueous oxidation of S(IV) to S(VI), the S(IV) concentration (M) in dew water is defined as

$$[\mathrm{S(IV)}] = \frac{F_{\mathrm{SO_2}} \cdot t}{w \times 10^{-3}}, \tag{2}$$

$$F_{\mathrm{SO_2}} = C_{\mathrm{SO_2}}(z_r) \cdot v_d. \tag{3}$$

In these equations, $F_{\mathrm{SO_2}}$ is the downward flux of SO_2 to the dew water in mol cm^{-2} s^{-1}, t is the sampling duration in s, w is the dewfall amount in g cm^{-2}, $C_{\mathrm{SO_2}}(z_r)$ is the concentration of SO_2 at the reference height (z_r) in mol cm^{-3}, and v_d is the dry deposition velocity in cm s^{-1}. The reference height is regarded as the sampling height of gases, and equals 1 m. The v_d can be expressed as the reciprocal of the sum of the transfer resistance. For instance, we can write Eq. 4, where r_a is the aerodynamic resistance in s cm^{-1}, r_b is the sublayer resistance in s cm^{-1}, and r_c is the surface resistance in s cm^{-1}; $C(z_0)$ and $C(0)$ are the concentration of SO_2 at a roughness length of z_0 and the interface between the air and the dew surface, respectively.

$$\begin{aligned} r &= \frac{1}{v_d} \\ &= \frac{1}{F_{SO_2}}\{(C_{SO_2}(z_r) - C_{SO_2}(z_0)) + (C_{SO_2}(z_0) - C_{SO_2}(0)) \\ &\qquad + C_{SO_2}(0)\} \\ &= r_a + r_b + r_c. \end{aligned} \tag{4}$$

The aerodynamic resistance (r_a) is related to the rate of turbulent mixing of the species from the reference height (z_r) to the surface, and can be represented by 17.

$$r_a = \frac{1}{ku^*}[\ln(\frac{z_r}{z_0}) - C_1)] \tag{5}$$

$$u^* = ku[\ln(\frac{z_r}{z_0}) - C_2]^{-1}. \tag{6}$$

Here k is von Karmen's constant (equals 0.4), u is the wind speed in cm s^{-1}, u^* is the friction velocity in cm s^{-1}, and C_1 and C_2 are diabatic correction terms. Under a stable condition, both C_1 and C_2 equal to $-5\ z_r/L$, where L is the Monin Obukov length in cm.

The sublayer resistance (r_b) is controlled by the rate of molecular and turbulent transport across the atmospheric sublayer in contact with the surface. Under a sufficiently smooth surface and light wind, r_b can be represented by 18.

$$r_b = \frac{5}{u^*}\left[(\frac{v}{D} - 1) + \ln(1 + 0.83(\frac{v}{D} - 1))\right]. \tag{7}$$

In Eq. 7, D is the molecular diffusivity, which equals to 0.13 in cm^2 s^{-1} for SO_2, and v is the kinematic viscosity in cm^2 s^{-1}.

The surface resistance (r_c) is related to the concentration of the species at the effective surface of deposition, and is represented by the following equations proposed by Chameides:[9]

$$r_c = \frac{n_M \cdot f}{AH^*_{SO_2} \times 10^{-3}\left[\frac{w}{\tau} + \frac{dw}{dt}\right]}, \tag{8}$$

$$f = \frac{1}{3}\left[\frac{\coth(q)}{q} - \frac{1}{q^2}\right]^{-1}, \tag{9}$$

$$q = \frac{r}{(\tau D_a)^{1/2}} = \frac{1}{(\tau D_a)^{1/2}}\left[\frac{3w}{4N\pi\rho}\right]^{1/3}. \tag{10}$$

In these equations, n_M is the surface number density in cm^{-3}, A is Avogadro's number, dw/dt is the accumulation rate in g cm^{-2} s^{-1}, $H^*_{SO_2}$ is the apparent Henry's constant in M atm^{-1}, p_0 is the atmospheric pressure in atm (equal 1 atmosphere), r is the radius of a dew drop in cm, τ is the chemical lifetime in s, D_a is the aqueous-phase molecular diffusion coefficient (2×10^{-5} cm^2 s^{-1}), N is the dewdrop concentration in cm^{-2}, and ρ is the density of water (1 g cm^{-3}). Under the condition when S(IV) is not oxidized in dew water, the chemical lifetime (τ) is infinite. Though Chameides did not consider the existence of HMSA in dew water in his model, we calculated the apparent Henry's constants under two conditions where HMSA was or wasn't formed in dew water. At first, when only SO_2 is absorbed into dew water, the apparent Henry's constant is represented as

$$H^*_{SO_2} = H_{SO_2}\left[1 + \frac{K_{s1}}{[H^+]} + \frac{K_{s1}K_{s2}}{[H^+]^2}\right]. \tag{11}$$

In Eq. 11, H_{SO_2} is physical Henry's constant of SO_2 and K_{s1} and K_{s2} are the acid-dissociation constants of sulfurous acid. On the other hand, when HMSA is formed in the presence of formaldehyde, the apparent Henry's constant is represented as follows:

$$\begin{aligned} H^{**}_{SO_2} = H_{SO_2}\Bigg[\left(1 + \frac{K_{s1}}{[H^+]} + \frac{K_{s1}K_{s2}}{[H^+]^2}\right) + \left(\frac{K_{s1}K_{HSO_3}}{[H^+]} + \frac{K_{s1}K_{s2}K_{SO_3}}{[H^+]^2}\right) \\ \times[HCHO(aq)]\Bigg] \end{aligned} \tag{12}$$

$$\begin{aligned} &[HCHO(aq)] \\ &= \frac{[HCHO]_{total}}{\left[(1 + K_{HYD}) + (\frac{K_{s1}K_{HSO_3}}{[H^+]} + \frac{K_{s1}K_{s2}K_{SO_3}}{[H^+]^2})H_{SO_2}p_{SO_2}\right]}. \end{aligned} \tag{13}$$

In Eq. 12, [HCHO(aq)] is the free formaldehyde concentration in dew water; K_{HSO_3} and K_{SO_3} are the stability constants for the reaction of hydrogensulfite and sulfite with formaldehyde ($10^{9.82}$ M^{-1} and $10^{5.34}$ M^{-1}),[19] respectively. In Eq. 13, K_{HYD} is the hydration constant (2×10^3) of formaldehyde to methylene glycol; $[HCHO]_{total}$ represents the sum of the concentrations of HCHO(aq), $H_2CH(OH)_2$, $H_2C(OH)SO_3{}^-$ and $H_2C(O^-)SO_3{}^-$, which can be estimated in a similar manner as the S(IV) concentration (Eq. 2). In the calculation of the dry deposition velocity, v_d of HCHO vapor into dew water, the apparent Henry's constant of formaldehyde (H^*_{HCHO}) is required, and is represented as

$$H^*_{HCHO} = H_{HCHO}\left[(1+K_{HYD}) + \left(\frac{K_{s1}K_{HSO_3}}{[H^+]} + \frac{K_{s1}K_{s2}K_{SO_3}}{[H^+]^2}\right)H_{SO_2}p_{SO_2}\right]. \tag{14}$$

Here, H_{HCHO} is Henry's constant of formaldehyde ($H_{HCHO} = 2.97\times10^3/(1+K_{HYD})$).

The conditions applied in the calculations are given in Table 3 for the dew event on April 21—22, 1994. In the table, (a), (b), and (c) represent the sampling time, respectively. In the calculation, the observed values were used for the temperature, relative humidity, wind speed, dewfall amount, accumulation rate, and concentration of SO_2. The surface number density and the kinematic viscosity were calculated, assuming that atmospheric pressure was 1 atm, namely 1013.25 hPa. On the other hand, the assumed values were used for the Monin Obukov length, the roughness length, the dewdrop concentration, and the concentration of formaldehyde in the ambient air. The roughness length takes the order of 10^{-4} m for a flat surface, such as water surface, flat bare land, and flat fallen snow.[20] Since the surface of the Teflon® sheet used as our dew collector was flat, it is suitable to adopt 10^{-4} m as the roughness length. Under a very stable condition (Pasquill Category F) in which dew is formed, the Monin Obukov length ranges from 8 to 35 m,[21] and the dewdrop concentration has been reported to be on the order of 50 cm^{-2} by Pierson et al.[6] We used the condition adopted by Chameides[9] for them. Although the ambient levels of HCHO were not measured in this study, there were few data available for the night-time ambient concentration. Grosjean[22] reported that the ambient concentrations

Table 3. Physical and Meteorological Conditions during Accumulation Process of Dew Water on April 21—22, 1994

Parameters		Assumed or observed values		
		Observed values		
Temperature	T/°C	(a) 15.5	(b) 15.2	(c) 14.7
Relative humidity	R.H./%	(a) 84.7	(b) 85.5	(c) 85.6
Wind speed	u/m s^{-1}	(a) 2.50	(b) 2.43	(c) 2.20
Dewfall amount	w/g cm^{-2}	(a) 6.35×10^{-3}	(b) 1.09×10^{-2}	(c) 1.63×10^{-2}
Accumulation rate	dw/dt/g cm^{-2} s^{-1}	(a) 4.96×10^{-7}	(b) 5.04×10^{-7}	(c) 5.02×10^{-7}
Concentration of SO_2	p_{SO_2}/ppb	(a) 1.56	(b) 1.27	(c) 1.61
Surface number density[20]	n_M/cm^{-3}	$\frac{6.02\times10^{23}}{28.8}\left\{1.293(\frac{273.15}{273.15+T})(\frac{p}{1013.25})(1-0.378\frac{e}{p})\right\}\times10^{-3}$		
Kinematic viscosity[20]	v/m^2 s^{-1}	$1.328\times10^{-5}(\frac{1013.25}{p})(\frac{273.15}{273.15+T})^{1.754}$		
		p: Atmospheric pressure (hPa) e: Water vapor pressure (hPa) T: Temperature (°C)		
		Assumed values		
Reference height	z_r	1	(m)	
Monin Obukov length	L	15	(m)	
Roughness length	z_0	10^{-4}	(m)	
Dewdrops concentration	N	50	(cm^{-2})	
Concentration of HCHO	p_{HCHO}	0.5 or 1	(ppb)	

a) 21:00 21—0:00 22 April, 1994; b) 21:00 21—3:00 22 April, 1994; c) 21:00 21—6:00 22 April, 1994.

of HCHO ranged from 1.5 to 7.0 ppb during the night time (20:00—6:00) on September 14—15, 1985 in Claremont, CA, and that the night-time levels were lower than the day-time levels. On the basis of the data reported by Grosjean, the ambient concentration of HCHO given in Table 3 may correspond to the low levels in urban air.

Chameides[9)] reported that for water-soluble species, such as HNO_3, which had a Henry's constant higher than 10^5 M atm^{-1}, the surface resistance (r_c) was too small to affect the dry deposition velocity. To put it another way, as Henry's constant decreases, r_c increases and begins to control the velocity. The sublayer resistance (r_b) is not appreciably considered, because it is always much smaller than the aerodynamic resistance (r_a). Since Henry's constants of SO_2 and HCHO are lower than 10^5 M atm^{-1}, r_c is the controlling factor of their dry deposition velocity, even if the formation of HMSA in dew water is considered. On the other hand, the dry deposition velocity of HNO_3 is controlled by the aerodynamic resistance (r_a). Table 4 shows the dry deposition velocities of HCHO and SO_2 into dew water on April 21—22, 1994, which were estimated according to the conditions given in Table 3. Both the dry deposition velocities of HCHO and SO_2 were constant from 21:00 on April 21 to 3:00 on April 22, but increased slightly from 3:00 to 6:00 on April 22. During the sampling period, the dry deposition velocities of HCHO were nearly equal to 0.16 cm s^{-1}, which was estimated by Jayne et al.[23)] for dew water formed on grassland. The dry deposition velocities of SO_2 in the presence of 0.5 or 1.0 ppb HCHO vapor increased three to four times, or even five to seven times, as large as those of SO_2 in the absence of HCHO vapor, respectively, showing that the formation of HMSA in dew water enhanced the dry deposition velocity of SO_2.

The S(IV) concentrations were calculated according to Eqs. 2 and 3 using the dry deposition velocities given in Table 4; they are shown together with the observed S(IV) concentrations in Fig. 8. It is obvious that the measured values are higher than the values estimated under atmospheric conditions without HCHO. However, assuming that HCHO in the concentration ranges from 0.5 to 1.0 ppb is absorbed from the air into dew water, and, subsequently, HMSA is formed in dew water, we can see that the estimated values are nearly equal to the measured values. This indicates that the formation of HMSA significantly contributes to the S(IV) concentration in dew water, and that the S(IV) concentration is mainly controlled by the concentrations of SO_2 and HCHO in the air. On the other hand, the calculated values accounted for only about 20% of the measured values in the accumulation process (0:00—6:00) of dew water on October 15, even if the ambient concentration of HCHO was assumed to be 10 ppb. However, assuming that the ambient concentration of HCHO was 3 ppb, the estimated $[HCHO]_{total}$ in the dew water gave a good agreement with the measured values (the measured values were 52.7 μM from 0:00 to 3:00 and 55.8

Table 4. Dry Deposition Velocity of HCHO and SO_2 into Dew Water on April 21—22, 1994 under Various Conditions

Time/Date	V_d(HCHO)	$V_d(SO_2)$/cm s^{-1}		
	cm s^{-1}	HCHO=0 ppb	HCHO=0.5 ppb	HCHO=1.0 ppb
(a) 21:00 on 21—0:00 on 22	0.12	0.009	0.036	0.061
(b) 21:00 on 21—3:00 on 22	0.12	0.010	0.042	0.069
(c) 21:00 on 21—6:00 on 22	0.17	0.017	0.056	0.087

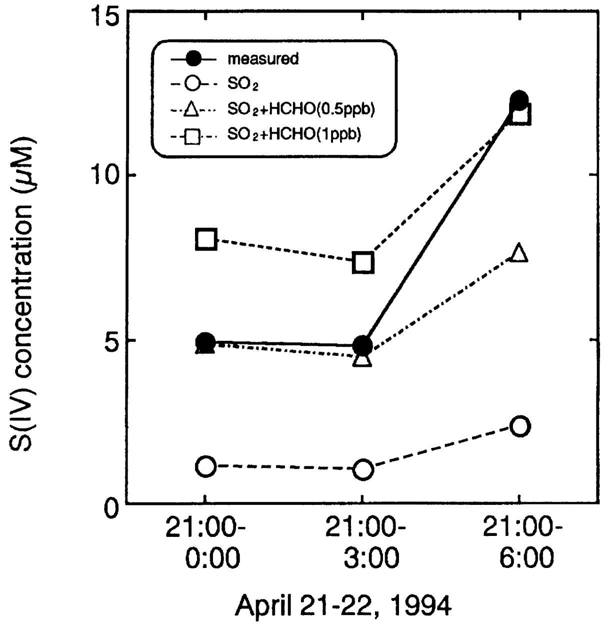

Fig. 8. Comparison with the observed and estimated S(IV) concentration in dew water on April 21—22, 1994.

μM from 0:00 to 6:00, while the estimated values were 53.5 and 65.7 μM, respectively). A possible explanation for the differences between the measured and estimated S(IV) concentrations in the dew water on October 15 may be that the other adducts of S(IV) with aldehydes, except for HCHO, were present in the dew water.

The NO_3^- concentration in the accumulation process of dew water was also estimated by the deposition model, where the infinite value was provided for the chemical lifetime (τ), because NO_3^- was unreactive. The ambient concentrations of HNO_3 were 0.27—0.36 ppb on April 21—22 and 0.22—0.41 ppb on October 15. On the other hand, the dry deposition velocities of HNO_3 were estimated to be 0.37—0.42 $cm\,s^{-1}$ on April 21—22 and 0.24—0.32 $cm\,s^{-1}$ on October 15, respectively. The NO_3^- concentration calculated using those ambient concentrations and dry deposition velocities accounted for only about 10—30% of the measured values in those dew-water samples, indicating that the dissolution of other nitrogen species, except for HNO_3, contributes significantly to the NO_3^- concentration in those dew-water samples. Chan et al.[14] reported that the deposition of N_2O_5 could be the main source of nitrate in dew water when the NO_2 concentration was high (13—16 ppb) on Allegheny Mountain in southwest Pennsylvania, U.S.A. At our sampling site, the NO and NO_2 concentrations during the sampling period of the dew water were 6—20 ppb and 34—52 ppb on April 21—22 and 98—120 ppb and 43—48 ppb on October 15, respectively. Therefore, the main origin of NO_3^- in the dew water formed at our sampling site may have been N_2O_5. However, there were relatively high correlations between the NO_3^- fluxes and the Na^+, Mg^{2+}, and Cl^- fluxes, as pointed out in Table 2. The origins of NO_3^- in dew water should be investigated further.

Conclusions

Dews or frosts formed on artificial collectors were collected during the early morning in Yokohama, Japan, in 1993 and 1994. Dew water generally had a weak acidity. Based on the average, NH_4^+ and Ca^{2+} were the major cations and SO_4^{2-} was the dominant anion in dew water. Dew chemistry was characterized by a relatively high concentration of weak acid anions, particularly hydrogensulfite ion (HSO_3^-), while they were usually only slightly contained in rain water. Dew water sometimes had a very high acidity (the minimum pH was 3.23 during the period of this research), which might be according to the oxidation of S(IV) to sulfuric acid. The S(IV) concentration in dew water was suggested to be influenced by the dissolution of HCHO from the atmosphere and a subsequent formation of HMSA. On the other hand, it was indicated that the NO_3^- concentration in urban dew water contributed to not only to HNO_3, but also to N_2O_5.

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