Tellus (1987), *39B*, 383–397

Hygroscopic properties of atmospheric aerosol in Riverside, California

By M. J. ROOD*, D. S. COVERT and T. V. LARSON, *Environmental Engineering and Science Program, Department of Civil Engineering, FX-10, University of Washington, Seattle, WA 98195, USA*

(Manuscript received 11 August; in final form 16 December 1986)

ABSTRACT

The hygroscopic properties of atmospheric aerosol were investigated by performing in-situ optical measurements under controlled temperature and relative humidity conditions. Complementary measurements included ambient relative humidity and aerosol filter sampling. Measurements were performed in Riverside, California during the months of August and September, 1983. Experimental results indicate that ambient aerosol particles, with diameters less than 2 μm, exhibited deliquescence between 73 and 78% relative humidity during 52% of the measurements. During a one-week intensive sampling period, ambient aerosol particles existed as droplets during 86% of the tests and were dry during the balance of those measurements. When ambient aerosol droplets were detected, they were supersaturated with respect to solute concentration during 71% of tests and were otherwise subsaturated with respect to solute concentration.

1. Introduction

The widespread presence of atmospheric aerosol particles, consisting of H_2O soluble compounds and liquid H_2O at relative humidities (RH) less than 100%, has many important consequences. The simple fact that wet particles are larger than their dry counterparts has a direct bearing on aerosol radiative transfer properties including visibility reduction (Toon and Pollack, 1976; White and Roberts, 1977; Tang et al., 1981, and Sloane, 1984). An increase in available surface area and reactivity of the aerosol to certain gases can potentially increase with increasing amounts of liquid H_2O. Such gases include SO_2, NH_3, N_2O_5 and HNO_2, and H_2O_2 (Freiberg, 1974; Cadle and Robbins, 1961; Brock and Durham, 1984, and Hoffman and Jacob, 1984). An increase in interfacial surface area and reactivity has potentially important consequences for gas phase chemistry not yet completely understood. Aqueous solution droplets also provide a medium for interactions not favored in the gas phase, for example the oxidation of SO_2 by H_2O_2 (Penkett et al., 1979). In addition, the solution's composition determines the partitioning between the gas and liquid phases of labile, H_2O soluble species. For the case of acidic and basic gases, the amount of liquid H_2O associated with the aerosol particles can also determine atmospheric vapor pressure products (Tang, 1980a and Stelson and Seinfeld, 1982a, b) and thus the kinetics of condensation and evaporation (Larson and Taylor, 1983).

In this paper, the topic of hygroscopic properties of atmospheric aerosol is addressed. The discussion is limited to particles with diameters less than 2 μm that, in general, exhibit hygroscopic properties (Winkler and Junge, 1972; Charlson et al., 1974; Hänel, 1976, and Covert et al., 1979). Fig. 1 (A, B, and C) illustrates several possibilities for different states of hydration that are possible for a hygroscopic

* Currently at the Environmental Engineering and Science Program, Department of Civil Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

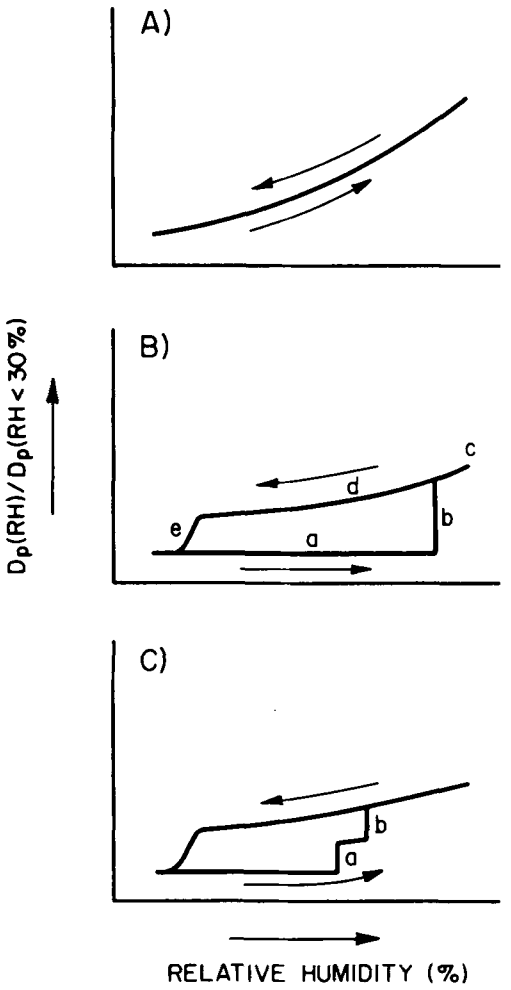

Fig. 1. Diagram exhibiting aerosol particle size response as a function of relative humidity for hygroscopic compounds that do not exhibit deliquescent properties (A), pure hygroscopic compounds that exhibit deliquescent properties (B) and a mixture of hygroscopic compounds that have deliquescent properties (C).

aerosol. A particle composed of a hygroscopic compound with no deliquescent properties responds to changes in RH by monotonically increasing or decreasing in size resulting from condensation or evaporation of H_2O, respectively (Fig. 1A). This particle is in stable equilibrium with its surrounding as a solution droplet over typical ambient conditions. Some pure compounds, that exhibit deliquescence, have the capability to display a phase change in response to increasing RH conditions (Fig. 1B). A particle consisting of such a pure deliquescent compound exists in a dry crystalline state at a sufficiently low RH value (Fig. 1B-a). At some increased RH value (the deliquescence humidity), H_2O rapidly condenses onto the particle to form a droplet that is saturated with respect to solute concentration (Fig. 1B-b). At an RH value above the solute's deliquescence humidity, the particle's solute concentration is subsaturated (Fig. 1B-c). This phase change creates the potential for a difference in the hygroscopic response of a particle when exposed to increasing compared to decreasing RH conditions, known as hysteresis (Orr et al., 1958; Junge, 1963 and Tang, 1980b). Under decreasing RH conditions, the solute does not recrystallize at the deliquescence humidity but remains as a droplet (Fig. 1B-d). The particle's solute concentration becomes supersaturated resulting in a metastable state. Such a metastable equilibrium state exists at a local minimum Gibbs free energy and persists until RH decreases below a critical value at which crystallization occurs (Fig. 1B-e). At that point, efflorescence occurs such that the particle's liquid H_2O evaporates and its solute crystallizes resulting in a dry crystalline particle. Mixed deliquescent salts can exhibit one or more phase changes as illustrated in Fig. 1C-a, b (Tang, 1980b and Spann and Richardson, 1985). The first abrupt increase in particle size is a result of a phase change from a solid crystal to a heterogeneous droplet containing a solid core (Fig. 1C-a). The second abrupt increase in particle size occurs as the particle becomes a homogeneous droplet resulting from dissolution of the droplet's solid core (Fig. 1C-b). Thus, a particle's solute can exist in a subsaturated, saturated or supersaturated aqueous state or as a dry crystal with its hygroscopic properties depending on its chemical composition and RH history.

It is difficult, if not impossible, to study the hygroscopic properties of atmospheric aerosol particles by placing them on a foreign substrate such as a filter. Such type of technique can cause changes in particle size, provide sites for capillary condensation and introduce a surface with its own physical and chemical properties (Pueschel et al., 1971). Also, impaction and filtration has the potential to internally mix particles that exist as external mixtures under in-situ conditions.

Therefore, we have examined the hygroscopic properties of ambient aerosol particles using in-situ optical methods. Our field measurements were made as part of a cooperative experiment at the University of California, Riverside with the Statewide Air Pollution Research Center, in August and September of 1983.

2. Methods

A schematic of the instruments and sample flow is presented in Fig. 2. Atmospheric aerosol was sampled at a flow rate of 300 l/min through a 7 m tall inlet stack and then an opaque 0.5 m^3 mixing chamber that operated at ambient temperature and RH conditions. The sample flow was then divided and directed to one of three integrating nephelometers (Ahlquist and Charlson, 1967) where the aerosol's light scattering coefficient (b_{sp}) was measured under select thermodynamic states. RH was computed from cooled mirror dew point and dry bulb temperature measurements.

One portion of the aerosol sample was directed to a nephelometer (MRI Inc., Model 1550) that operated outdoors at ambient temperature and RH conditions. This flow was periodically heated to a maximum temperature of 30°C above ambient conditions for 0.1 s and then rapidly cooled to ambient temperature immediately upstream of the nephelometer. Heat was applied to the continuous flow sample for 5-min periods twice an hour. This mode of operation periodically subjected the sample to an RH less than 15% yet measured b_{sp} of this "thermally dried" aerosol at ambient temperature and RH conditions. H_2O associated with the particles in stable equilibrium (Figs. 1A and 1B-c) will recondense onto the particles upon cooling to ambient conditions, but H_2O associated with the particles in metastable equilibrium do not return to the particles as a result of hysteresis (Fig. 1B-d). Evaporation of metastable liquid H_2O results in a decrease in particle size causing a decrease in b_{sp}. The aerosol particles are considered to exist in metastable equilibria if the ratio R_{th} (b_{sp} measured at ambient RH without upstream heating to b_{sp} measured at ambient RH with upstream heating) is significantly greater than unity (i.e., greater than 1.02).

The remaining portion of the sample flow was diluted with dry, filtered air to reduce the samples' RH to a value <35%. The aerosol then passed through a cyclone with a 50% collection efficiency at 2.0 μm particle diameter. Part of this sample was drawn through an integrating nephelometer (optically similar to a MRI Inc.,

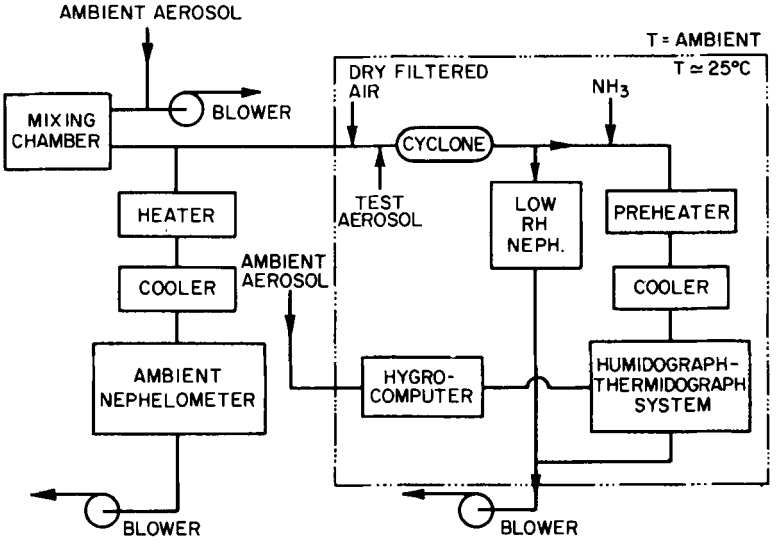

Fig. 2. Block diagram of ambient aerosol sampling system.

Model 1560). Data from this nephelometer were used as a normalizing factor for the ambient b_{sp} measurements to give a "dilution dried" light scattering ratio R_{dl} (b_{sp} measured at ambient RH to b_{sp} measured at an RH value $<35\%$).

The second portion of the diluted sample passed through a preheater-cooler assembly that optionally heated the continuous flow sample to a predetermined constant temperature to vaporize relatively volatile liquid and solid components from the aerosol particles (Rood et al., 1987). As aerosol excited the heater section, it was rapidly cooled to 25°C and then drawn through the "humidograph-thermidograph" system. Such instrumentation has been described in detail (Covert et al., 1972; Larson et al., 1982; Weiss et al., 1982; Waggoner et al., 1983, and Rood, 1985) but will be described briefly for clarity.

The "humidograph" measures b_{sp} as a function of controlled RH conditions in a continuous flow system as presented in Fig. 3A. Aerosol initially passes through a wetted-wall humidifier and then briefly heated to 60°C within 0.1 s to decrease the sample's RH to a value less than 20%. Subsequent cooling increases the aerosol's RH to its final value measured at the nephelometer inlet. Careful control of the humidograph's cooling process insures that none of the aerosol is exposed to a lower temperature (or higher RH) subsequent to leaving the heater. Therefore, the highest RH experienced by the aerosol is at the inlet of the nephelometer. RH is scanned by applying heat to the humidifier's wetted wall. During an RH scan, b_{sp} and RH values are measured and stored in a microcomputer. The resulting "humidogram" consists of a plot of b_{sp} that is normalized to its initial low RH value versus the controlled RH value at which b_{sp} was measured.

The "thermidograph" measures b_{sp} at a constant RH and temperature while the aerosol flow is exposed to a gradually increasing temperature upstream of the nephelometer (Fig. 3B). Aerosol sampled by the thermidograph initially passes through a humidifier that increases the aerosol's RH to a value greater than 80%. As aerosol exits the humidifier, it is heated for 0.1 s in a stainless steel heater tube. After heating, the aerosol is cooled to 25°C. The aerosol's b_{sp} value is then measured at an RH value between 65 and 68% by an integrating nephelometer (optically similar to an MRI Inc., Model 1560). As heater tempera-

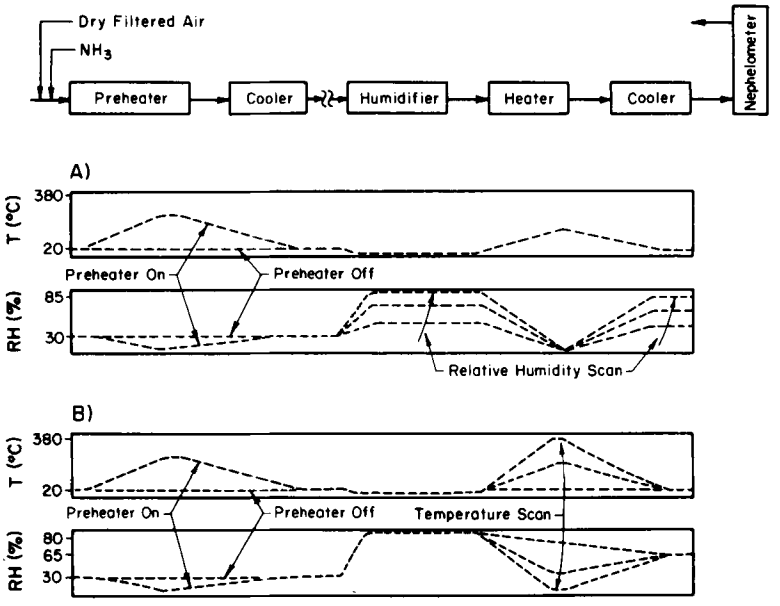

Fig. 3. Block diagram of integrated humidograph-thermidograph system and the temperature and relative humidity exposure patterns as aerosol flows through the humidograph (A) and thermidograph (B).

ture is scanned from 25 to 380°C, b_{sp} and heater temperature data are measured and stored in a microcomputer. Such a temperature scan is performed in 3.5 min. The resulting "thermidogram" consists of a plot of b_{sp}, normalized to its maximum value, versus the heater temperature at which b_{sp} was measured.

Filter sampling was performed concurrently with the above measurements by drawing ambient aerosol through a one stage impactor, nitric acid denuder tube and then a 25 mm diameter nylon filter at a flow rate of 10 l per minute (modified version from Appel et al., 1984). The diffusion tube's ability to collect gaseous HNO_3 was tested in the laboratory after the field experiment and was determined to have a 98% collection efficiency at an inlet HNO_3 concentration of 10 ppbv. The 50% cut point for the impactor was 2.0 μm particle diameter. Filter samples were taken from 06.00 to 10.00, 10.00 to 15.00, 15.00 to 21.00 and 21.00 to 06.00 hours daily for the duration of the experiment. Sample volumes were measured with a dry gas meter that was located downstream of an air-tight diaphragm vacuum pump. Filter blanks and particulate laden filters were weighed during the experiment with an electro-balance (Cahn Model 21) that was located in a controlled temperature and RH room (21°C, 50% RH). Filters were subsequently analyzed for chloride, nitrate, sulfate, sodium and potassium ions with ion chromatography (Dionex Model 10 and Model 2000ISP).

3. Results

Mean values and standard deviations of parameters that were measured during the one week intensive sampling period are summarized in Table 1. Averaging times were based on filter sample time periods. Average b_{sp} values are those reported for both ambient and low RH (RH < 35%) conditions and are based on 10 minute averages.

A time series of ambient RH, measured deliquescence humidity and the ratios R_{th} and R_{dl} data are presented for the time period between 11 and 19 September 1983 in Fig. 4A. R_{dl} values ranged from 1.06 to 2.15 with a mean value of 1.61. R_{th} ranged from 1.00 to 1.21 with a mean value 1.08. Ambient RH, deliquescence humidity, R_{dl}, and R_{th} data are also presented for a one-day time period in Fig. 4B. The values of R_{th} and R_{dl} undergo a rapid decrease at 1600 PST and then a subsequent increase at approximately 2000 PST at approximately 30 and 47% RH, respectively. They also remain approximately constant as ambient RH increases from 30 to 47%.

Table 1. *Summary of Riverside, CA ambient relative humidity, ambient aerosol particulate mass concentration and b_{sp} data*

Time period	21.00–06.00	06.00–10.00	10.00–15.00	15.00–21.00
Relative humidity (RH (%))	63.3	63.1	37.0	40.1
	(19.9)+	(13.1)	(8.1)	(10.1)
b_{sp} ($\times 10^{-4}$ m^{-1}) (RH < 35%)	1.34	1.69	1.90	1.56
	(0.64)	(0.67)	(0.80)	(0.67)
b_{sp} ($\times 10^{-4}$ m^{-1}) (ambient RH)	2.36	3.05	2.88	2.14
	(1.14)	(1.24)	(1.43)	(0.96)
R_{dl}*	1.76	1.81	1.47	1.36
	(0.42)	(0.28)	(0.23)	(0.16)
Sub-μm aerosol particulate mass concentration (μg/m^3)	53	87	87	70
	(19)	(27)	(36)	(21)
Total number of observations				
relative humidity			164	
b_{sp}			979	
filters			20	

( )+ = standard deviation.

* R_{dl} = ratio of b_{sp} measured at ambient RH to b_{sp} measured at a controlled RH less than 35% RH.

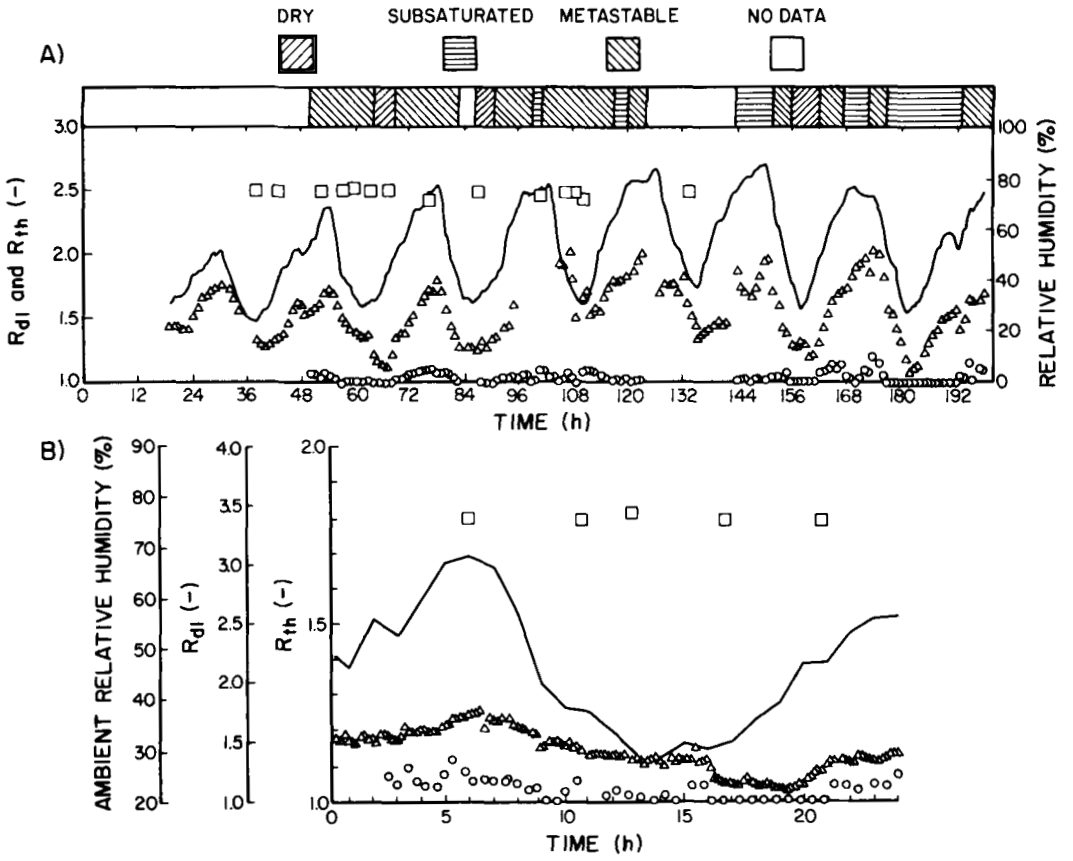

Fig. 4. Ambient relative humidity (line), deliquescence humidity (square), R_{th} (circle) and R_{dl} (triangle) data presented as a time series between 11 and 19 September 1983 (A) and for 13 September 1983 (B).

Fig. 5A presents a scatter plot of R_{dl} versus RH data for the intensive one week sampling period. R_{th} values are identified on the basis of whether simultaneous R_{dl} values were greater than 1.02. R_{th} values greater than 1.02 were considered to be an indication of metastable droplets. We also plotted the value of R, which is defined as the ratio R_{dl}/R_{th}, versus RH in Fig. 5B. This was done to correct for the effect of metastable liquid H_2O and therefore allow for a consistent basis to compare humidograph and R_{dl} data.

Humidograph measurements were performed three times daily during the intensive sampling period. Fig. 6 presents select humidograms of Riverside aerosol. Examples of humidograms exhibiting hygroscopic behavior are presented in panels 6A and 6B while deliquescent behavior is presented in panel 6C. The deliquescent point occurs at 77% RH in this case. A time series of the ambient aerosols' measured deliquescent humidity is shown in Fig. 4A. The deliquescence humidity values are typically higher than ambient RH conditions during days 1 through 5 except during high ambient RH conditions in the early morning hours. After the morning of day 6 there was no measurable deliquescence humidity during the humidograph measurements.

An ambient aerosol's response to heating and NH_3 injection upstream of the humidograph are illustrated in Fig. 6D through 6F. These humidograms were obtained within a period of 60 minutes. The ambient aerosol exhibited hygroscopic behavior without deliquescence as presented in Fig. 6D. Increasing the preheater

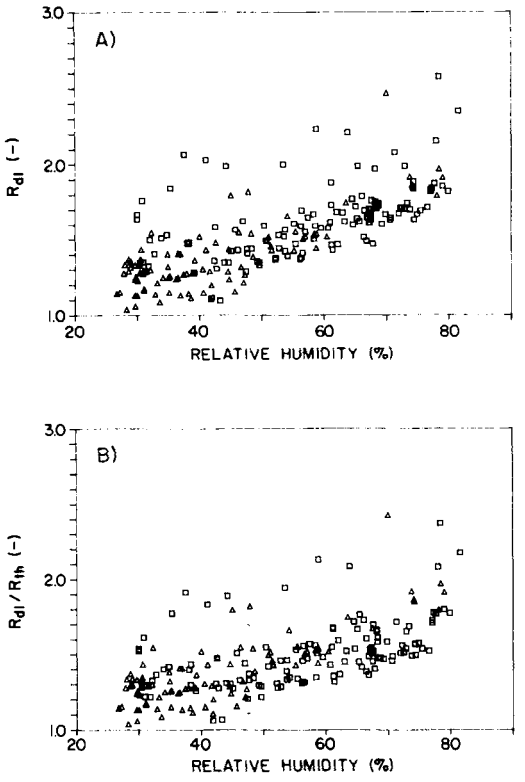

Fig. 5. Scatter plots of R_{dl} versus ambient relative humidity (A) and R, defined as the radio R_{dl}/R_{th}, versus ambient relative humidity (B) for data obtained between 11 and 19 September 1983. Data points are plotted as triangles or squares to indicate when R_{th} was ≤ 1.02 or > 1.02, respectively.

temperature from 25°C to 100°C did not appreciably change the observed hygroscopic response (Fig. 6E). Increasing the preheater temperature to 190°C accompanied by upstream injection of gaseous NH_3 caused the aerosol to deliquesce at an RH of 78% (Fig. 6F).

A summary of the aerosol's deliquescent behavior, including the effects of heating and NH_3 injection upstream of the humidograph, is presented in Fig. 7. It is important to note that the humidograph began scanning RH at a value of approximately 50% and therefore could not detect deliquescence humidities below that value. Deliquescence was observed during 52% of the ambient humidograph tests that were conducted during the entire duration of the experiment. Upon deliquescence, normalized b_{sp} increased by a mean value of 17% (range: 7 to 33%) at a mean RH value of 75% (range: 72 to 78%). Increasing the maximum upstream heater temperature to 100°C, increased the likelihood that the aerosol would deliquesce to 64%, but did not increase the mean deliquescence humidity or the relative increase in b_{sp} during deliquescence. Additional heating to 190°C accompanied by upstream injection of gaseous NH_3 resulted in more frequent and pronounced deliquescent behavior, as well as an increase in the mean deliquescence humidity. In this case the aerosol exhibited deliquescence during 95% of the humidograph measurements, mean normalized b_{sp} increased to 27% (range: 12 to 45%) upon deliquescence and the mean deliquescence humidity was 77% RH (range: 74 to 79%).

Select types of ambient thermidograms that were observed in Riverside are presented in Fig. 8. The abrupt decrease in normalized b_{sp} within the first 30°C of temperature scan that is apparent in Figs. 8A and 8B is due to the evaporation of metastable liquid H_2O (Larson et al., 1982 and Rood et al., 1987). In contrast to Figs. 8A and 8B, the thermidogram presented in Fig. 8C does not display such a decrease in b_{sp}. Such behavior indicates the absence of metastable liquid H_2O. Another point of interest is the aerosol's thermal decomposition characteristics at heater temperatures greater than 60°C. Discussion of such characteristics are beyond the scope of this paper. Effects of thermal and NH_3 treatment of the ambient aerosol upstream of the thermidograph are also presented in Figs. 8D through 8F. Injection of gaseous NH_3 upstream of the thermidograph did not produce an appreciable change in thermidogram curve shape when compared to the ambient thermidogram (cf. Figs. 8D versus 8E). This was typically observed in Riverside. However, heating the aerosol to 190°C with the injection of gaseous NH_3 upstream of the thermidograph (Fig. 8F) produced consistent thermidogram curve shapes that were unlike the ambient thermidograms. The resultant curve structure typically exhibited an abrupt decrease in normalized b_{sp} within the first 30°C of heater temperature scan due to efflorescence and another decrease in b_{sp} between 250 and 350°C. Thermidograph results are summarized in Table 2.

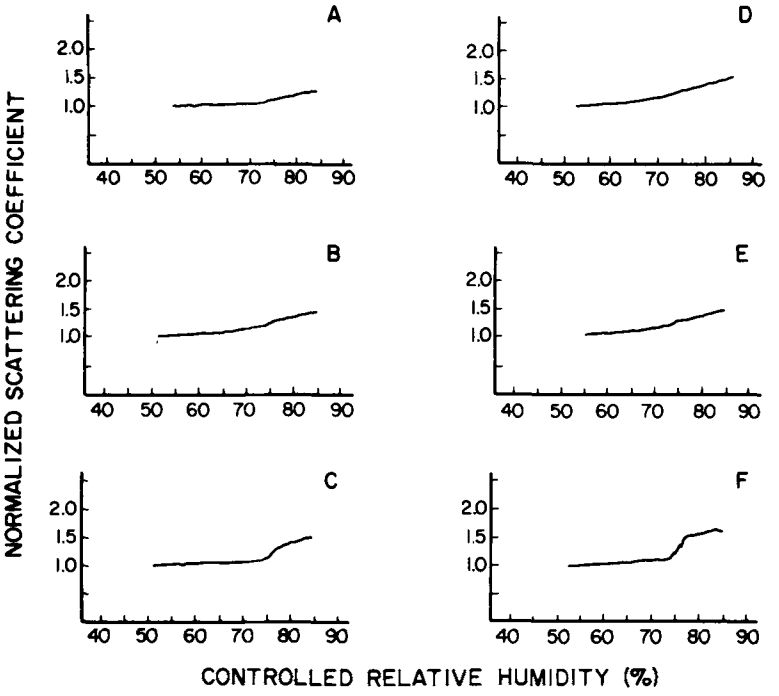

Fig. 6. Humidograms of ambient aerosol that are hygroscopic without (A and B) and with (C) deliquescent properties. Complimentary humidograms of ambient aerosol (D), ambient aerosol preheated to 100°C (E) and ambient aerosol preheated to 190°C with upstream NH_3 vapor injection (F) are also presented.

Table 2. *Summary of thermidograph results reported as percent b_{sp} remaining after heating the sample flow to the specified heater temperature*

Test type	% b_{sp} remaining at the specified heater temperature			
Average heater temperature	65°C	170°C	228°C	345°C
Ambient aerosol	95.7	68.1	50.3	19.9
	(4.4)+	(7.8)	(9.1)	(5.4)
Ambient aerosol with NH_3 addition	95.9	69.0	52.2	21.1
	(4.3)	(8.0)	(9.0)	(5.4)
Ambient aerosol with 190°C preheat and NH_3 addition	85.6	84.3	85.3	39.4
	(3.4)	(3.4)	(2.8)	(3.8)

( )+ = standard deviation.

Fig. 9 presents a scatter plot of b_{sp} versus aerosol particulate mass concentration data that were averaged over the same time periods. Aerosol particulate mass consists of particles with diameters less than 2 μm. b_{sp} is that value measured at a controlled RH less than 35% and filterable mass concentration is determined by gravimetric analysis of the nylon filter samples. A least squares regression analysis of filterable mass data with mean b_{sp} values indicates a b_{sp} to filterable mass concentration slope of 2.1 m^2/g and a correlation coefficient is 0.85. The

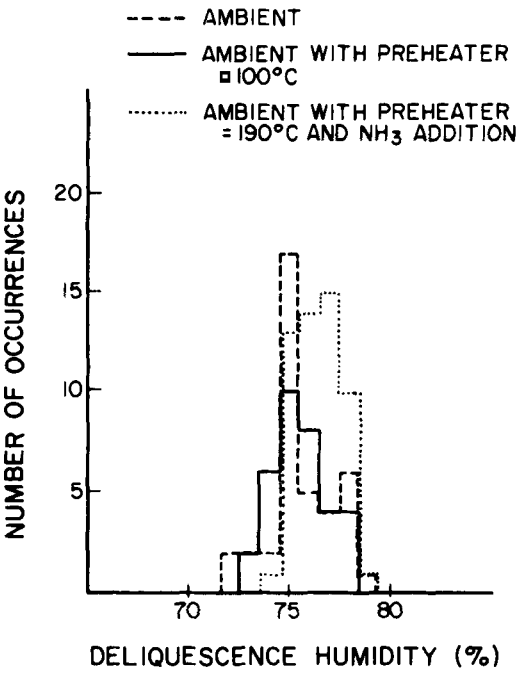

Fig. 7. Number of occurrences of a measurable deliquescence humidity versus the aerosol's deliquescence humidity for ambient aerosol, ambient aerosol preheated to 100°C and ambient aerosol preheated to 190°C with upstream NH_3 injection.

scattering to filterable mass concentration slope is less than other reported values that range from 2.7 to 3.2 m^2/g (Waggoner and Weiss, 1980). Such results could be due to the use of the denuder difference technique that captures particulate NO_3^- that has been shown to evaporate during conventional filter sampling (Appel et al., 1984) and possible artifact formation from reaction of other acidic vapors with the nylon filter. Such an observation is consistent with other experimental results that were obtained while sampling photochemically produced smogs in the California South Coast Air Basin (Brockian and Hostack, 1972).

Filterable sub-μm (less than 2 μm diameter) aerosol particulate mass concentration of chloride, nitrate, sulfate, sodium and potassium ions are summarized in Table 3. Organic and elemental carbon filterable mass concentrations, for aerosol particles less than 20 μm diameter, were measured by the Statewide Air Pollution Research Center and are also presented in Table 3 (Pitts et al., 1984). Accompanying the filter data in Table 3 are the corresponding light scattering to filterable mass concentration ratios calculated from mean b_{sp} values measured at an RH < 35% and gravimetric results from nylon filter samples.

4. Discussion of results

In contrast to the previously reported absence of deliquescent smog in the California South Coast Air Basin (Covert et al., 1979), ambient aerosols were observed to deliquesce at RH values between 73 and 78%. Such results were observed during the entire sampling period and represent 52% of the ambient humidograms. Heating the sample flow to 100°C upstream of the humidograph increased the frequency of occurrence of deliquescence from 52 to 64% but did not appreciably affect the magnitude of the deliquescence step. Although the presence of a sufficient quantity of NH_4NO_3 can suppress deliquescent behavior (Tang, 1980b), the removal of NH_4NO_3 from the particles at a heater temperature of 100°C does not explain the increased frequency of occurrence of deliquescence. Laboratory results indicate that NH_4NO_3 particles do not decompose in the humidograph-thermidograph system until heater temperatures greater than 125°C. Presumably, heating the ambient aerosol to 100°C volatilized organic compounds from the particles that suppress deliquescent behavior. Heating the ambient aerosol to 190°C along with the injection of gaseous NH_3 upstream of the humidograph caused a further increase in the probability of observing deliquescence and increased the observed deliquescence humidity to values between 74 and 78%. Experimental results indicate that at a heater temperature of 190°C, NH_4NO_3 and volatile organic compounds (i.e. chemically neutralized adipic acid) are removed from the aerosol particles while leaving $(NH_4)_2SO_4$, NH_4HSO_4 and other more refractory compounds such as Na_2SO_4 in the particles (Rood, 1985). If pure $(NH_4)_2SO_4$ was the only compound remaining in the aerosol's particles after heating the aerosol to 190°C, the deliquescence humidity would be

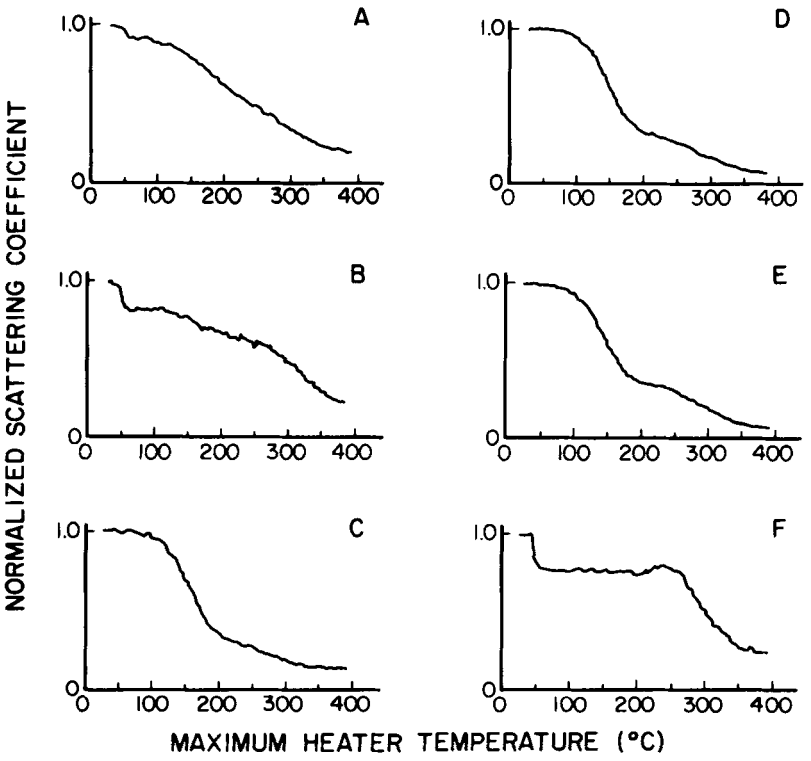

Fig. 8. Select thermidograms of ambient aerosol that display (A and B) and do not display (C) an abrupt decrease in normalized b_{sp} within the first 30°C of heater temperature scan. Also included is an ambient aerosol's thermidogram response without preheating (D), with upstream injection of NH_3 (E) and preheating to 190°C with upstream NH_3 addition (F). The thermidograms of pretreated ambient aerosol were taken at the same approximate time as the humidograms presented in Figs. 6D through 6F.

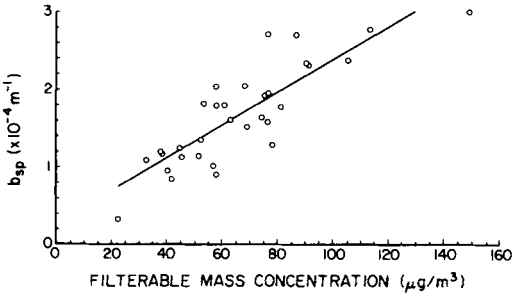

Fig. 9. Scattergram of b_{sp} versus filterable sub-μm diameter aerosol particulate mass concentration. b_{sp} values were measured at a relative humidity less than 35%.

79.5% RH (Tang, 1980b and Rood et al., 1985). Our measurements indicate a deliquescence humidity less than 79.5% RH when preheating the ambient aerosol to 190°C. Such result indicates the presence of other refractory compounds associated with $(NH_4)_2SO_4$. An internal mixture of $(NH_4)_2SO_4$ and Na_2SO_4, with a $Na^+/SO_4^=$ molar ratio of ≈ 0.2, is one possible candidate (Rood et al., 1985). Data presented in Table 3 indicates that sodium is present in sufficient quantity to produce such a mixture. Unfortunately the measurements cannot discern the extent of internal versus external mixing that exists within the aerosol particle size distribution.

It is also of interest to compare ambient deliquescence humidity field measurements with previously published thermodynamic predictions (Stelson and Seinfeld, 1982a) as presented in Fig. 10. Such comparison assumes that NH_4NO_3 and $(NH_4)_2SO_4$ are the dominant compounds controling the ambient aerosol's hygroscopic properties and that such thermodynamic predictions are

Table 3. *Composition, concentration[a], and light scattering to filterable mass concentration ratio of Riverside ambient aerosol*

Date	Time[b]	Cl^-	NO_3^-	$SO_4^=$	Na^+	K^+	Organic carbon	Elemental carbon	$\frac{b_{sp}}{[m]}$[c]
9/12	C	0.2	5.2	26.9	0.8	0.7	17.0	2.8	2.6
	D	0.2	4.9	23.2	0.6	1.0	10.9	2.8	3.4
9/13	A	0.4	7.9	13.3	0.8	0.7	29.0	12.0	3.0
	B	0.7	14.1	14.7	0.7	0.9	26.0	5.8	2.6
	C	0.5	6.1	21.1	0.5	0.3	12.0	1.9	2.5
	D	0.2	3.8	16.5	0.4	0.1	5.7	1.2	2.4
9/14	A	0.6	10.6	12.7	0.7	0.0	23.0	6.4	2.2
	B	0.7	48.2	10.3	0.6	0.1	35.0	8.1	3.5
	C	0.7	47.3	12.4	0.5	1.2	16.0	3.4	—
	D	0.5	19.4	7.0	0.5	0.1	10.0	3.2	—
9/15	A	2.1	42.4	8.9	0.7	0.0	22.0	7.4	2.6
	B	0.7	69.2	10.4	0.7	0.5	25.0	7.3	3.0
	C	0.6	37.7	8.5	0.7	0.1	23.0	5.3	2.2
	D	0.6	29.1	8.7	0.4	0.0	18.0	5.1	3.1
9/16	A	3.7	42.4	11.4	0.7	0.0	22.0	7.0	1.8
	B	1.2	51.1	39.4	0.7	0.5	36.0	8.9	2.0
	C	1.1	62.7	16.9	0.6	0.1	28.0	6.2	2.5
	D	0.5	22.1	32.1	0.3	0.1	15.0	5.0	3.1
9/17	A	0.0	33.6	13.2	0.9	0.1	26.0	4.7	2.4
	B	0.7	22.0	9.1	0.7	0.0	30.0	5.5	2.1

[a] Inorganic ion data are for aerosol particles with diameters less than 2 μm while organic and elemental carbon data are for aerosols with diameters less than 20 μm. Inorganic ion, elemental carbon and elemental carbon data are presented in units of [$\mu g/m^3$].

[b] Filter sample time is described below.

A = 06.00–10.00
B = 10.00–15.00
C = 15.00–21.00
D = 21.00–06.00

[c] Units for $b_{sp}/[m]$ are [m^2/g].

applicable to a dispersed system such as ambient aerosol. As presented in Fig. 10, all measured deliquescence humidity values are greater than their thermodynamic prediction with the most apparent discrepancies occurring at high $[NO_3^-]/([NO_3^-]+[SO_4^=])$ ratios. Care should be taken in evaluating these results because of the relatively large mass fraction of organic compounds associated with the ambient aerosol particles and the possible influence of trace material, such as sodium, on the aerosols' deliquescence and saturation humidities.

It was hypothesized by Covert et al. (1979) that the lack of observed deliquescence during earlier measurements was due to the presence of nitrate and organic compounds in the aerosol as well as the original instrument's humidification process. The present data obtained with the improved humidifier is consistent with this hypothesis since the deliquescent properties of the aerosol became more pronounced when volatile particulate components of the aerosol, such as NH_4NO_3 and volatile organic compounds, were thermally removed from the particles.

As previously discussed, hygroscopic aerosol particle solute can exist in a subsaturated, saturated or supersaturated aqueous state or in a dry crystalline form. Although a saturated solution is possible, it only occurs when the ambient RH is equal to the aerosol's deliquescence humidity. Therefore, the following discussion is limited to an aerosol's subsaturated, supersaturated, and dry states. Fig. 11 summarizes the conclusions about the hygroscopic properties of Riverside aerosol.

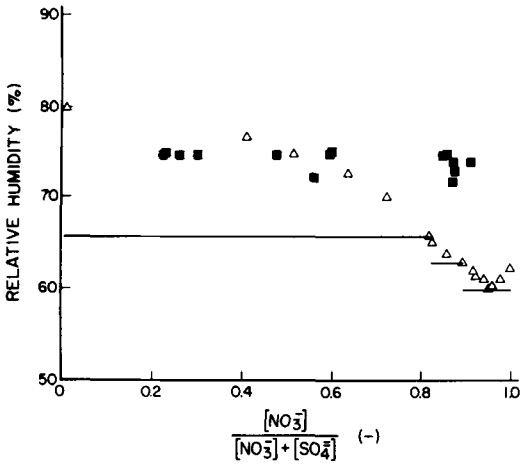

Fig. 10. Measured deliquescence humidities (squares), theoretical deliquescence humidities (lines), and theoretical saturation humidities (triangles) versus the aerosol's $[NO_3^-]/([NO_3^-] + [SO_4^=])$ molar ratio.

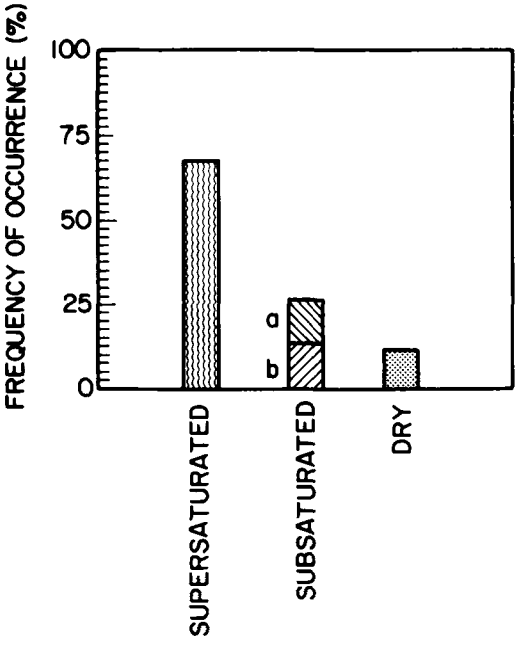

Fig. 11. Plot indicating frequency of occurrence of supersaturated, subsaturated and dry aerosols during the time period between 11 and 19 September 1983.

Most notable is the fact that the ambient aerosol particles existed as metastable droplets a majority of the time. We base this conclusion on the following observations.

(1) The value of R_{dl} is correlated with ambient RH.
(2) The aerosol's deliquescence humidity was generally greater than the ambient RH, as measured by the humidograph.
(3) The value of R_{th} was significantly greater than unity ($R_{th} > 1.02$) during 61% of the measurements.
(4) The only significant change in b_{sp} upon briefly heating the aerosol to 60°C was an abrupt decrease due to the evaporation of H_2O, as measured by the thermidograph.

Correlation of R_{dl} with RH was determined by applying the following empirical relationship that was developed by Hänel (1971).

$$b_{sp}(RH_0)/b_{sp}(RH) = 1/R_{dl} = [(1 - RH)/(1 - RH_0)]^{2+E}. \quad (1)$$

For RH_0 equal to 30%, the correlation coefficient and exponent, E, equalled 0.81 and 0.13, respectively. This observation is most directly explained by the change in particular volume owing to the condensation or evaporation of H_2O modulated by changes in ambient RH. This strongly suggests that the particles were aqueous droplets, even at low RH conditions. Also the observed slope of R_{dl} versus RH in Fig. 5B is consistent with observed hygroscopic growth of internally mixed $(NH_4)_2SO_4$—NH_4NO_3—H_2O aerosol in our laboratory measurements. However this result does not necessarily imply that the particles were metastable droplets. Stable subsaturated droplets could exist such that they do not exhibit deliquescence or their deliquescence humidity is lower than ambient RH conditions.

The second observation is that during the time when ambient aerosols exhibited deliquescence, their deliquescence humidity was greater than ambient RH during 61% of those measurements. This is consistent with the third observation of R_{th} being greater than 1.02 for 61% of those measurements. A value of R_{th} significantly greater than unity can only result from either the evaporation of metastable liquid H_2O or other volatile particulate material upon heating to 60°C. However, the loss of other volatile material

is not consistent with our fourth observation because the decomposition of other volatile material would be associated with a gradual decrease in b_{sp} with increasing heater temperature as opposed to the observed abrupt decrease associated with efflorescence (Fig. 8A–F).

The existence of aerosol particles in a metastable state is of particular interest. The atmospheric process that leads to their formation remains to be determined. There are two limiting cases considering aerosol composition and ambient RH that could explain the formation of metastable droplets. In one case, droplet solute composition remains fixed as the particles experience a decrease in ambient RH below the aerosol's deliquescence humidity. High RH conditions occur during the late night and early morning in the western parts of the South Coast Basin as a result of radiative cooling of the marine air in the boundary layer. During the day, RH of the air mass decreases with time and distance as it is transported inland due to mixing with warmer dryer air along the boundary of the marine front. Even if the maximum RH at the surface did not exceed the deliquescence humidity of the aerosol particles, vertical mixing within the boundary layer will result in the aerosol experiencing varying RH conditions and becoming hydrated. In the second case, RH remains fixed while the droplet's solute composition changes via chemical reaction in such a way that the aerosol's deliquescence humidity increases above the ambient RH. An intermediate case would incorporate a change in ambient RH that causes a change in aerosol particle solute composition (e.g., via evaporation) such that the resultant deliquescence humidity is greater than ambient RH conditions.

A further discussion of the cases in which aerosol particles existed as stable, subsaturated solution droplets is warranted. Subsaturated hygroscopic aerosols that did not exhibit deliquescence were considered to exist under the following conditions.

(a) Ambient humidograms exhibited hygroscopic growth without deliquescence, R_{dl} greater than 1.02, and R_{th} equal to 1.0.
(b) Ambient RH was greater than the observed deliquescence humidity, R_{dl} was greater than 1.02, and R_{th} was $=1.0$.

During the one-week intensive sampling period, stable aerosol was detected 25% of the time, 13% for condition (a) and 12% for condition (b) (Fig. 11).

Dry ambient aerosol particles were observed to exist 14% of the time during the one week intensive sampling period. Such conditions existed when R_{dl} was constant even though ambient RH was changing and R_{th} was equal to unity. Under ideal circumstances, R_{dl} should equal unity for dry particles. Although R_{dl} never exactly equalled unity, it did remain constant as ambient RH changed and R_{th} equalled unity (e.g., between 16.00 and 20.00 hours in Fig. 4B). It is assumed R_{dl} approached but did not equal unity because the two nephelometers that were used to measure R_{dl} had slightly different optics and that they were not normalized with respect to each other frequently enough to correct for zero and span drift during the experiment.

Examination of all b_{sp} measurements taken during the intensive sampling period of the experiment resulted in summary statistics of the hygroscopic properties of ambient aerosol as presented in Fig. 11. The ambient aerosol was hydrated during 86% of the tests and dry during the remaining 14% of the tests. Ambient metastable droplets existed during 61% of the tests while stable droplets existed during the remaining 25% of the tests. A temporal representation of the aerosol's state of hydration for the one week intensive sampling period is included as a bar graph at the top of Fig. 4. The aerosol was dry during the mid-afternoons of 13, 14, and 17 September. The aerosol was subsaturated during the early mornings of 15 and 17, late at night on 15 and most of the day on 18 September. The balance of these measurements indicated the presence of metastable particles in the early mornings and evenings of 13–15 and 17 September and the early mornings of 16, 18 and 19 September.

One scenario for the production of metastable aerosols involves the formation of hygroscopic aerosol droplets during high RH conditions near coastal regions of the South Coast Air Basin. Upon westward transport of the air mass, the aerosol droplets would be chemically neutralized via exposure to elevated gaseous NH_3 concentrations east of Los Angeles (Russel et al., 1983). Heating and mixing with dry air, resulting in a reduction in RH, would accompany the air mass

during transport. This would allow for the observation of metastable aerosols during intermediate increasing and decreasing RH ($30\% \leqslant RH \leqslant 80\%$) conditions in Riverside.

5. Conclusions

During September 1983, the ambient aerosol in Riverside, California typically existed as droplets. The aerosol contained metastable liquid H_2O most of the time. During an 8-day intensive sampling period, the aerosol particles were usually dry in the early afternoon at which the RH was low, were subsaturated in the early morning hours during high RH conditions and contained metastable H_2O during the late afternoon and early evening hours.

Metastable H_2O contributed 5 to 20% of the total particle light scattering coefficient. This result was deduced from a set of optical measurements that were performed under controlled temperature and relative humidity conditions. However, the presence of this metastable H_2O could not be deduced from independent measurements of ambient relative humidity and particle chemistry alone. Therefore, light extinction calculations based solely on particle chemistry, size distribution and ambient relative humidity would have produced a bias from 5 to 20%. Furthermore, chemical modeling of the aerosol that requires qualitative or quantitative knowledge of the liquid H_2O content of the particles is also subject to uncertainty. Future experiments on the frequency of occurrence, degree of mixing and/or the mechanism of formation of metastable particles should include in-situ measurements of the type described here at one or more geographical locations in an air shed. Where possible, these experiments should include simultaneous particle sampling for chemical analysis and measurement of trace compounds in the gas phase in order to examine the extent to which the presence of liquid H_2O influences atmospheric aerosol chemistry.

6. Acknowledgements

This research was performed under the auspices of the National Science Foundation under Grant number ATM-80-11395.

REFERENCES

Ahlquist, N. C. and Charlson, R. J. 1967. A new instrument for evaluating the visual quality of air. *JAPCA 17*, 467–469.

Appel, B. R., Tokiwa, T., Haik, M. and Kothny, E. L. 1984. Artifact particulate sulfate and nitrate formation on filter media. *Atmos. Environ. 18*, 409–416.

Brock, J. R. and Durham, J. L. 1984. Aqueous aerosol as a reactant in the atmosphere. In: *SO_2, NO and NO_2 oxidation mechanisms: atmospheric considerations*, ed. Calvert, J. G., Ann Arbor Science, Boston, 209–249.

Brockian, A. H. and Hostack, M. A. 1972. A comparison of filterable mass and light scattering of photochemically produced aerosols. In: *Aerosols and atmospheric chemistry*, ed. Hidy, G. M. Academic Press, New York, 1183–1186.

Cadle, R. D. and Robbins, R. C. 1961. III. Physical and chemical properties, kinetics of atmospheric chemical reactions involving aerosols. *Disc. Faraday Soc. 30*, 155–166.

Charlson, R. J., Vanderpol, A. H., Covert, D. S., Waggoner, A. P. and Ahlquist, N. C. 1974. Sulfuric acid-ammonium sulfate aerosol: optical detection in the St. Louis region. *Science 184*, 156–158.

Covert, D. S., Charlson, R. J. and Ahlquist, N. C. 1972. A study of the relationship of chemical composition and humidity to light scattering by aerosols. *J. Appl. Meteorol. 11*, 968–976.

Covert, D. S., Waggoner, A. P., Weiss, R. E., Ahlquist, N. C. and Charlson, R. J. 1979. Atmospheric aerosols, humidity and visibility. In: *Character and origins of smog aerosols*, ed. Hidy, G. M. John Wiley and Sons, Inc., N.Y. 559–581.

Freiberg, J. 1974. Effects of relative humidity and temperature on iron-catalyzed oxidation of SO_2 in atmospheric aerosols. *Environ. Sci. and Tech. 8*, 731–734.

Hänel, G. 1971. New results concerning the dependence of visibility on relative humidity and their significance in a model for visibility forecast. *Contrib. Atmos. Phys. 44*, 137–167.

Hänel, G. 1976. The properties of atmospheric aerosol particles as functions of the relative humidity at thermodynamic equilibrium with the surrounding moist air. *Adv. Geophys. 3*, 73–188.

Hoffman, M. R. and Jacob, D. J. 1984. Kinetics and mechanisms of the catalytic oxidation of dissolved sulfur dioxide in aqueous solution: an application to

nighttime fog water chemistry. In: *SO_2, NO and NO_2 oxidation mechanisms: atmospheric considerations*, ed. Calvert, J. G. Ann Arbor Science, Boston, 101–172.

Junge, C. 1963. *Air chemistry and radioactivity*. New York, New York, Academic Press, p. 133.

Larson, T. V. and Taylor, G. S. 1983. On the evaporation of NH_4NO_3 aerosol. *Atmos. Environ. 17*, 2489–2495.

Larson, T. V., Ahlquist, N. C., Weiss, R. E., Covert, D. C. and Waggoner, A. P. 1982. Chemical speciation of H_2SO_4—$(NH_4)_2SO_4$ particles using temperature and humidity controlled nephelometry. *Atmos. Environ. 16*, 1587–1590.

Orr Jr., C., Hurd, K. and Corbett, W. J. 1958. Aerosol size and relative humidity. *J. Coll. Sci. 13*, 472–482.

Penkett, S. A., Jones, B. M. R., Brice, K. A. and Eggleton, A. E. J. 1979. The importance of atmospheric ozone and hydrogen peroxide in oxidizing sulfur dioxide in cloud and rainwater. *Atmos. Environ. 13*, 123–137.

Pitts, Jr., J. N., Winer, A. M. and Sweetman, J. A. 1984. Particulate and gas phase mutagens in ambient and simulated atmospheres. First Quarterly Progress Report for Contract No. A3-049-32.

Pueschel, R. F., Charlson, R. J. and Ahlquist, N. C. 1971. Reply to comments on "anomalous deliquescence of sea spray aerosol". *J. Appl. Meteorol. 10*, 163–165.

Rood, M. J. 1985. *On the metastability of atmospheric aerosols*. Ph.D. Dissertation, University of Washington, Seattle, Washington.

Rood, M. J., Covert, D. C., Larson, T. V. and Ahlquist, N. C. 1985. Measurement of laboratory and ambient aerosols with temperature and humidity-controlled nephelometry. *Atmos. Environ. 19*, 1181.

Rood, M. J., Covert, D. C. and Larson, T. V. 1987. Temperature and humidity controlled nephelometry: improvements and calibration. *Aerosol Sci. Tech.* in press.

Russell, A. G., McRae, G. J. and Cass, G. R. 1983. Mathematical modeling of the formation and transport of ammonium nitrate aerosol. *Atmos. Environ. 17*, 949–964.

Sloane, C. S. 1984. Optical properties of aerosols of mixed composition. *Atmos. Environ. 18*, 871–878.

Spann, J. F. and Richardson, C. B. 1985. Measurement of the water cycle in mixed ammonium acid sulfate particles. *Atmos. Environ. 19*, 819–825.

Stelson, A. W. and Seinfeld, J. H. 1982a. Thermodynamic prediction of the water activity, NH_4NO_3 dissociation constant, density, and refractive index for the NH_4NO_3-$(NH_4)_2SO_4$—H_2O system at 25°C. *Atmos. Environ. 16*, 2507–2514.

Stelson, A. W. and Seinfeld, J. H. 1982b. Relative humidity and temperature dependence of the ammonium nitrate dissociation constant. *Atmos. Environ. 16*, 983–992.

Tang, I. N. 1980a. On the equilibrium partial pressures of nitric acid and ammonia in the atmosphere. *Atmos. Environ. 14*, 819–828.

Tang, I. N. 1980b. Deliquescence properties and particle size change of hygroscopic aerosols. In: *Generation of aerosols and facilities for exposure experiments*, ed. Willeke, K. Ann Arbor Science, Ann Arbor, 153–167.

Tang, I. N., Wong, W. T. and Munkelwitz, H. R. 1981. The relative importance of atmopsheric sulfates and nitrates to visibility reduction. *Atmos. Environ. 15*, 2463–2471.

Toon, O. B. and Pollack, J. B. 1976. A global average model of atmospheric aerosols for radiative transfer calculations. *J. Appl. Meteorol. 15*, 225–246.

Waggoner, A. P. and Weiss, R. E. 1980. Comparison of fine particle mass concentration and light scattering extinction in ambient aerosol. *Atmos. Environ. 14*, 623–626.

Waggoner, A. P., Weiss, R. E. and Larson, T. V. 1983. In-situ rapid response measurement of H_2SO_4—$(NH_4)_2SO_4$ aerosols in urban Houston: a comparison with rural Virginia. *Atmos. Environ. 17*, 1723–1731.

Weiss, R. E., Larson, T. V. and Waggoner, A. P. 1982. In-situ rapid response measurement of H_2SO_4/$(NH_4)_2SO_4$ aerosols in rural Virginia. *Environ. Sci. Tech. 16*, 525–532.

White, W. H. and Roberts, P. T. 1977. On the nature and origins of visibility-reducing aerosols in the Los Angeles air basin. *Atmos. Environ. 11*, 803–812.

Winkler, P. and Junge, C. 1972. The growth of atmospheric aerosol particles as a function of relative humidity, Part 1: method and measurement at different locations. *J. Rech. Atmos.* (Memorial Henri Dessens), 617–638.