

AEROSOL PARTICLE PROCESSING AND REMOVAL BY FOGS: OBSERVATIONS IN CHEMICALLY HETEROGENEOUS CENTRAL CALIFORNIA RADIATION FOGS

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(Received 7 July 2000; accepted 31 January 2001)

Abstract. Fog composition and deposition fluxes of fog water and fog solutes were measured in six radiation fog events in San Joaquin Valley, California during winter 1998/1999. Measurements made at 2 hr intervals with 0.30 m² and 0.06 m² Teflon deposition plates yielded excellent reproducibility (relative standard deviations of 3.8–6.0%) for water, nitrate, sulfate and ammonium. Water fluxes measured at 5 min intervals with a recording balance agreed well with the deposition plate measurements before 8:00 AM. After 8:00 AM evaporation proved problematic. The average deposition velocity from the study for fog nitrate (3.8 cm s⁻¹) was less than those for fog sulfate (5.1 cm s⁻¹) and ammonium (6.7 cm s⁻¹). All three species generally exhibited smaller deposition velocities than fog water. The species dependent trend in deposition velocities was consistent with preferential enrichment of these species in small fog drops (nitrate > sulfate > ammonium).

Keywords: ammonium, California, deposition, fog chemistry, fog collection, nitrate, sulfate

1. Introduction

Fogs play an important role in the atmospheric cycling of many chemical species. While significant attention is often directed toward particle production in fogs and clouds, fogs are also capable of contributing substantially to particle removal. Fogs can be effective scavengers of both particles and soluble gases, which are subsequently removed from the atmosphere by drop deposition to the ground. In low wind speed environments with simple topography, sedimentation dominates fog drop removal (Dollard and Unsworth, 1983).

Numerical simulations by Lillis *et al.* (1999) suggest that fogs forming in the San Joaquin Valley (SJV) of California contribute substantially to removal of atmospheric nitrogen species. Fog removal of sulfate appears to roughly offset new sulfate production in this environment. The long lifetimes of SJV fogs make them important contributors to particle removal.

Measurements of SJV fog composition reveal that individual species concentrations vary with drop size (Collett *et al.*, 1994, 1999; Bator and Collett, 1997; Rao and Collett, 1995, 1998). Similar observations have been made at other locations (e.g., Munger *et al.*, 1989; Ogren *et al.*, 1989, 1992; Schell *et al.*, 1997; Laj *et*



al., 1998; Xu *et al.*, 1999). Because drop sedimentation rates increase with drop size, deposition velocities of individual species should depend on their distributions across the fog drop size spectrum.

In order to improve our understanding of pollutant removal by SJV fogs, a more complete set of fog composition and deposition measurements was obtained in winter 1998/1999. The goals of this study were to (1) evaluate the suitability of several fog deposition measurement methods, (2) characterize individual species deposition velocities, and (3) examine the relation between the deposition velocity of an individual chemical species and its distribution across the fog drop size spectrum.

2. Experimental Approach

Fog samples and fog deposition samples were collected in an open field near Davis, California during December 1998 and January 1999. Fog samples were collected with a Caltech Active Strand Cloudwater Collector Version 2 (CASCC2) and with a size-fractionating CASCC (Demos *et al.*, 1996). Fog drops are collected in the CASCC2 by inertial impaction ($D_{50} = 3.5 \mu\text{m}$) on a bank of Teflon strands. The size-fractionating CASCC features two impaction stages, in order to collect small ($4 < D < 17 \mu\text{m}$) and large ($D > 17 \mu\text{m}$) fog drops separately. Both collectors were mounted approximately 3 m above the ground.

Fog deposition was sampled using four square Teflon deposition plates placed on the ground. Collected fog water is scraped from the interior of the plate. Two different plate sizes (0.06 and 0.30 m^2) were tested. Fog water deposition was also measured at 10 sec intervals using a recording balance system. A balance with a 0.03 m^2 metal pan and 10 mg resolution was placed on a submerged cement block level with the surrounding ground. The 10 sec raw data were processed to quantify fog water flux at 5 min intervals.

Fog liquid water content (LWC) was measured at ~ 3 m height using a Gerber Scientific Particulate Volume Monitor (PVM-100). Fog samples were generally collected at 1 hr intervals and deposition samples at 2 hr intervals. Collected samples were weighed and aliquotted for later analysis by ion chromatography. Fog collectors and deposition plates were cleaned and blanks taken prior to each event.

3. Results and Discussion

Six fog episodes were sampled during the study. Typical of SJV fogs, the pH was high (usually between 6 and 7) and the inorganic composition was dominated by nitrate and ammonium, with lesser concentrations of sulfate and small concentrations of chloride, sodium, potassium, calcium and magnesium. Hourly average fog liquid water contents varied between 0.03 and 0.26 g m^{-3} .

TABLE I
Flux measurements and their precision

Species	Flux (neq m ⁻² min ⁻¹)			Number of replicates		Relative standard deviation (%)	
	Minimum	Maximum	Mean	Small plates	Large plates	Small plates	Large plates
Nitrate	12.7	213.0	71.4	21	26	5.2	4.0
Sulfate	3.3	26.5	9.5	21	26	4.8	4.4
Ammonium	42.0	290.3	140.1	21	26	5.3	6.0
Water	0.02 ^a	0.54 ^a	0.28 ^a	26	30	4.1	3.8

^a Fluxes of water are given in g m⁻² min⁻¹.

Fog deposition samples were collected during approximately thirty periods. In a few cases where water volume was insufficient, a plate was contaminated, or replicate plate water volumes showed substantial disagreement, samples were excluded from further consideration. The remaining deposition samples were examined in replicate pairs (two large plate samples or two small plate samples) to determine measurement reproducibility.

3.1. FOG WATER AND SOLUTE FLUX MEASUREMENTS FROM THE DEPOSITION PLATES

Table I lists the number of replicate pairs (for small and large plates), the minimum, maximum and mean measured fluxes for each ion, and the relative standard deviation for replicate measurement of each species' flux using the small and large deposition plates. Fog water flux rates averaged 0.28 g m⁻² min⁻¹ (range 0.02 to 0.54 g m⁻² min⁻¹) during the six fog episodes. Flux rates for nitrate and ammonium were highest among the chemical species, averaging 71 and 140 nano-equivalents (neq) m⁻² min⁻¹, respectively. Sulfate flux rates averaged only 9.5 neq m⁻² min⁻¹. Both the small and large deposition plates provided precise measurements, with relative standard deviations of 4–6% for flux measurements of water, nitrate, sulfate and ammonium.

Waldman and Hoffmann (1987) report fog composition and flux values for several fog events sampled in the southern SJV, approximately 400 km southeast of Davis, in winter 1984/1985. LWC values during these events were similar to, but somewhat higher than, those reported here. Ammonium and nitrate concentrations were similar to those observed in the current study; sulfate concentrations were typically much higher. Deposition fluxes of nitrate and ammonium spanned similar ranges in the two studies. Deposition fluxes of sulfate, however, were typically several times higher in the earlier fog episodes, consistent with the intervening de-

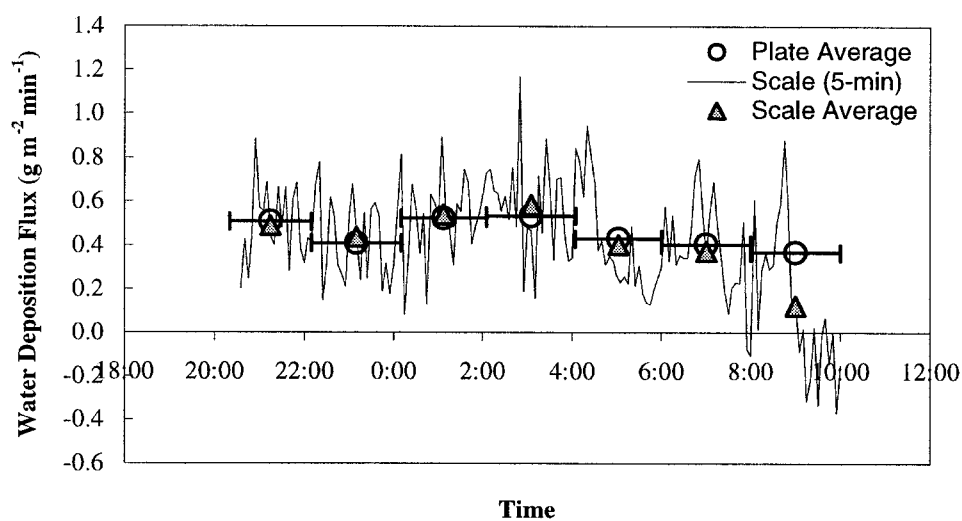


Figure 1. Fog water flux measurements made at Davis, California on January 4–5, 1999 using Teflon deposition plates and a recording balance. Horizontal bars on the plate flux measurements represent the time intervals for these measurements.

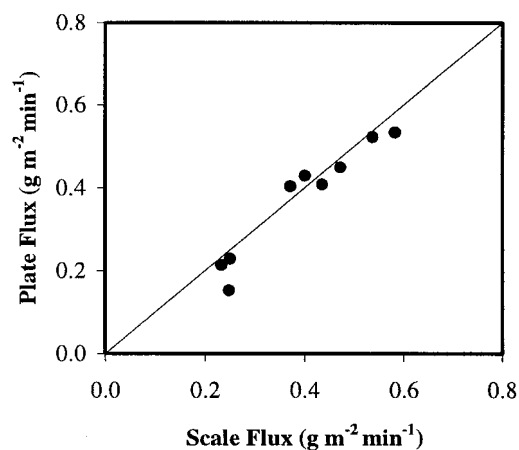


Figure 2. Comparison of fog water fluxes measured by the deposition plates vs. those measured by the recording balance for simultaneous measurement periods prior to 8:00 AM.

crease in SJV sulfate concentrations and probably also reflecting spatial variability in the large SJV.

3.2. SEMI-CONTINUOUS FOG DEPOSITION MEASUREMENTS

Fog water flux measurements made with the recording balance yielded good agreement with the deposition plate flux measurements during the night, but underestimated the flux following sunrise. Figure 1 compares the two fog water flux

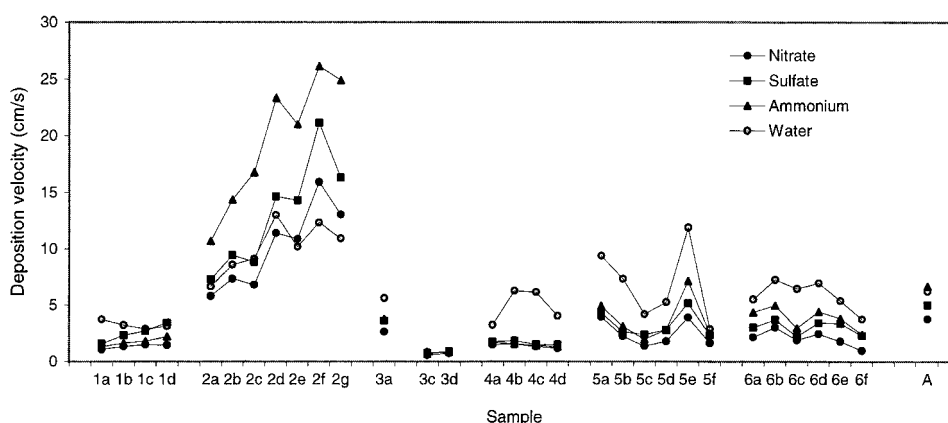


Figure 3. Fog water and fog solute deposition velocities for each deposition sampling period (typically ~ 2 hr, labeled with event number and a letter depicting the sample sequence) during the six Davis fog episodes. Study average deposition velocities (labeled 'A') for each species are presented at the right side of the diagram. Uncertainties (expressed as one relative standard deviation) in the calculated deposition velocities are estimated as 10.8% for water and 11.1, 11.7, and 12.3% for nitrate, sulfate, and ammonium. These uncertainties are based on replicate flux measurements, replicate CASCC2 sample analyses, and an estimate of 10% uncertainty in the PVM LWC.

measurements during the night of January 4–5, 1999. When the fluxes are averaged to matching time intervals, they agree well from approximately 8:00 PM to 8:00 AM. After 8:00 AM, the flux obtained using the balance method is considerably lower than the deposition plate flux. After 9:00 AM the balance shows a net loss of water, indicating evaporation from the balance pan. Two factors probably contribute to the evaporation. First, the balance pan is constructed of thin metal, as opposed to the thick white Teflon used in the deposition plates, and therefore more likely to heat up when the sun rises. Second, all collected water was left on the balance during the course of the fog episode, so that the amount of water available to evaporate after sunrise was relatively large. Figure 2 compares fog water fluxes measured by the deposition plates vs. those measured by the balance for periods prior to 8:00 AM. The pooled relative standard deviation for these nine sample pairs is 7.8%, indicating good agreement between these two measurement methods during the night and early morning.

The balance flux method permits examination of temporal flux trends over short time intervals. Fog water fluxes were observed to vary widely (see e.g., Figure 1). Although there is some noise in the 10 sec data, the flux variations shown on 5 min scales appear robust. The ability to document the dynamic behavior of fog deposition will provide an opportunity to better examine in future studies the relationship between fog water flux and various physical properties (e.g., fog LWC, drop size distribution, and vertical wind velocities) and will prove valuable for testing fog model predictions.

3.3. DEPOSITION VELOCITIES

Deposition velocities for fog water and fog solutes can be obtained by dividing the measured flux of each species by its airborne concentration. The airborne concentration of each chemical species is the product of its aqueous phase concentration and the LWC. The airborne concentration of fog water is the LWC. Deposition velocities for each sampling period during the six fog episodes are shown in Figure 3.

Fog water deposition velocities range from approximately 1 cm s^{-1} late in the third fog episode to more than 10 cm s^{-1} in portions of the second and fifth fog episodes. Assuming drop deposition occurs solely by sedimentation, we can compute the size of a fog drop with a terminal settling velocity equivalent to the fog water deposition velocity. For the lower range of observed deposition velocities this may be done using Stokes' law. For higher velocities a more complicated drag relationship must be assumed. Average deposition velocities determined in the six fog episodes correspond to terminal settling velocities of drops ranging from $28 \mu\text{m}$ diameter in the third fog episode to $59 \mu\text{m}$ diameter in the second fog episode. Because settling velocities are nonlinearly dependent on drop diameter, these drop sizes should not be considered to represent the mean fog drop sizes present during the fog episodes. Although wind speeds in the Davis radiation fog episodes were quite low, mechanisms other than sedimentation probably also made some contribution to drop removal fluxes. It is also possible that the presence of large fog drops caused the PVM to underestimate fog LWC, resulting in an overestimate of deposition velocities and apparent drop size.

Fog deposition velocities of nitrate, sulfate, and ammonium vary significantly between fog episodes and, sometimes, within a given episode. Deposition velocities for nitrate range from less than 1 to over 15 cm s^{-1} , with slightly larger ranges for sulfate and ammonium. Average deposition velocities for the measured species are depicted at the right of Figure 3. The average deposition velocity for the study for nitrate (3.8 cm s^{-1}) is less than that for sulfate (5.1 cm s^{-1}), which is in turn less than that for ammonium (6.7 cm s^{-1}). These deposition velocities are much faster than dry deposition velocities expected for submicron ammonium nitrate and ammonium sulfate particles, indicating the importance of fog as a vector for accumulation mode particle removal.

Hoag *et al.* (1999) report a similar trend in deposition velocities (ammonium > sulfate > nitrate), both as determined by deposition measurements in a 1995 SJV fog episode at Fresno and in a numerical simulation of this episode. The absolute deposition velocities determined for this single Fresno fog episode were on the lower end of the range observed at Davis. The deposition velocities reported for nitrate, ammonium and sulfate by Waldman and Hoffmann (1987) (approximately $1\text{--}5 \text{ cm s}^{-1}$), were similar to those observed in most of the Davis fog episodes, but considerably lower than those observed in the second event.

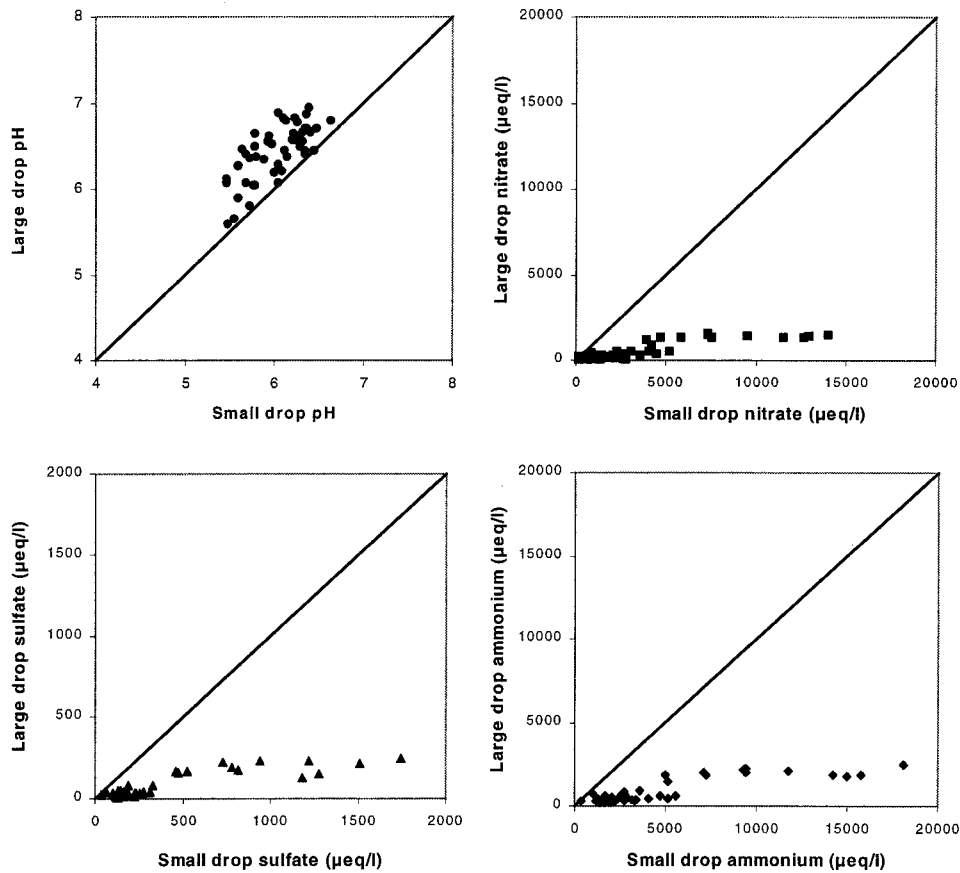


Figure 4. Comparison of the compositions of small and large Davis, California fog drops sampled using the sf-CASCC.

3.4. DROP SIZE-DEPENDENT FOG COMPOSITION AND ITS INFLUENCE ON SOLUTE DEPOSITION VELOCITIES

The drop size-dependence of individual ion concentrations is an important factor governing the relative removal rates of the ions vs. the fog water. Because drop sedimentation velocity increases strongly with drop size, species enriched in large fog drops should be removed more quickly than fog water, while species enriched in small drops should be removed more slowly. Figure 4 compares the composition of small and large Davis fog drops sampled with the sf-CASCC. The large drops contain the majority of the total fog LWC, while the small drops contain higher concentrations of nitrate, sulfate, and ammonium. Fog pH is higher in the large drops. This pattern is similar to previous observations in SJV fogs (see e.g., Collett *et al.* 1994, 1999). Figure 5 illustrates the ratios of small:large drop ion concentrations in a time series for the six fog episodes. Nitrate often exhibits stronger

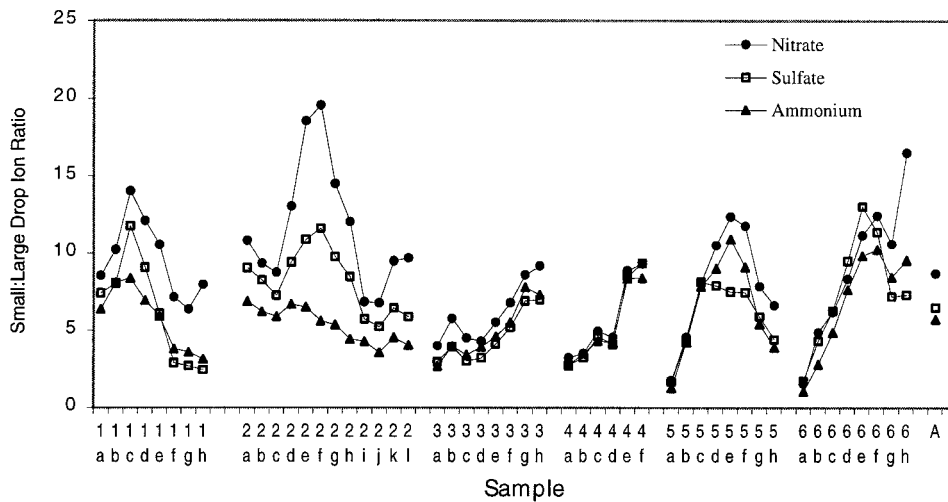


Figure 5. Time series of the ratios of small:large fog drop ion concentrations for the Davis drop size-resolved fog samples collected during six fog episodes. Samples are labeled with the event number and a letter indicating the sample sequence. Study average ratios (labeled 'A') are presented at the right of the diagram.

enrichment in small drops than does sulfate, which in turn often exhibits stronger enrichment in small drops than does ammonium.

The strong enrichment of nitrate in the small drops is consistent with the observation that nitrate generally has the smallest deposition velocity. Ammonium, which shows the lowest ratio of small:large drop concentrations, has the highest deposition velocity. Sulfate exhibits an intermediate small:large drop concentration ratio and an intermediate deposition velocity. When small:large drop concentration ratios of these three species are similar (e.g., in the fourth fog episode), they also exhibit similar deposition velocities.

Aside from the second fog episode, the nitrate, sulfate, and ammonium deposition velocities are nearly always smaller than the fog water deposition velocity, consistent with their preferential enrichment in smaller fog drops. This pattern is broken in the second fog episode, especially for ammonium. Since the sf-CASCC data only provide a crude depiction of the drop size dependent fog composition, it is possible that a pattern of increasing ion concentrations with increasing drop size in the drop spectrum above $17 \mu\text{m}$ is responsible for the enhanced ion deposition velocities. The calculated ammonium fog deposition velocity might also be enhanced by dry deposition of ammonia gas or by enhanced ammonia concentrations near the ground.

4. Conclusions

Measurements of deposited fog water using Teflon plates and a recording balance are capable of providing precise estimates of fog water and fog solute fluxes in low wind speed radiation fogs. Deposition plates of 0.3 m² collection area exposed for 2 hr provided sufficient fog water for mass determination and chemical analysis. Fog water fluxes could be monitored at 5 min intervals using a recording balance. Deposition flux rates and deposition velocities of ammonium, nitrate, and sulfate were comparable to those observed in earlier SJV fog studies, except that sulfate removal fluxes have declined over the past decade, reflecting decreases in fog sulfate concentrations. All three species generally exhibited smaller deposition velocities than fog water. The species dependent trend in deposition velocities (ammonium > sulfate > nitrate) was consistent with preferential enrichment of these species in small fog drops (nitrate > sulfate > ammonium). Application of these fog deposition measurement techniques in future studies will permit better determination of the influence of fogs on particle concentrations during winter stagnation episodes. Deposition measurements will also prove useful for evaluating model simulations of particle processing by fogs.

Acknowledgements

We are grateful to C. Anastasio for access to the sampling site, to J. Reilly for assistance in sample collection and data analysis, and to L. Trenary for assisting with data analysis. Funding for this work was provided by the San Joaquin Valleywide Air Pollution Study Agency and by the National Science Foundation (ATM-9712603 and ATM-9980540). KFM was supported by a STAR graduate fellowship (U-915364) from the USEPA. The statements and conclusions in this report are those of the Contractor and not necessarily those of the California Air Resources Board, the San Joaquin Valleywide Air Pollution Study Agency, or its Policy Committee, their employees or their members. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

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