Air Pollution Processing by Radiation Fogs

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Abstract Several fog episodes occurred in California's San Joaquin Valley during winter 2000/2001. Measurements revealed the fogs to generally be less than 50 m deep, but to contain high liquid water contents (frequently exceeding 200 mg/m^3) and large droplets. The composition of the fog water was dominated by ammonium (median concentration= 608 μN), nitrate (304 μN), and organic carbon (6.9 ppmC), with significant contributions also from nitrite (18 μN) and sulfate (56 μN). Principal organic species included formate (median concentration= 32 μN), acetate (31 μN), and formaldehyde (21 μM). High concentrations of ammonia resulted in high fog pH values, ranging between 5.8 and 8.0 at the core measurement site. At this high pH aqueous phase oxidation of dissolved sulfur dioxide and reaction of S (IV) with formaldehyde to form hydroxymethanesulfonate are both important processes. The fogs are also effective at scavenging and removal of airborne particulate matter. Deposition velocities for key solutes in the fog are typically of the order of 1–2 cm/s, much higher than deposition velocities of precursor accumulation mode aerosol particles. Variations were observed in deposition velocities for individual constituents in the order $NO_2^->$fogwater$>NH_4^+>$TOC $\sim SO_4^{2-}>NO_3^-$. Nitrite, observed to be enriched in large fog drops, had a deposition velocity higher than the average fogwater deposition velocity, due to the increase in drop settling velocity with size. Species enriched in small fog drops (NH_4^+, TOC, SO_4^{2-}, and NO_3^-) all had deposition velocities smaller than observed for fogwater. Typical boundary layer removal rates for major fog solute species were estimated to be approximately 0.5–1 μg m^{-3} h^{-1}, indicating the important role regional fogs can play in reducing airborne pollutant concentrations.

Keywords fog · aerosol · air pollution · deposition

1 Introduction

Fogs are comprised of tiny water droplets, typically ranging in size from several micrometers to several tens of micrometers (Pruppacher & Klett, 1997). These drops form by water vapor condensation onto aerosol particles known as cloud condensation nuclei (CCN). Water soluble constituents in the CCN determine the initial composition of the fog. Fog drop composition is further influenced by dissolution of soluble gases and aqueous phase chemical reactions. While much has been learned about fog

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interactions with key inorganic aerosol species (e.g., ammonium sulfate and nitrate), it is only in recent years that investigators have begun examining interactions between fogs and carbonaceous aerosols and volatile organic compounds.

During winter persistent high pressure over the Great Basin of the western United States often creates a strong subsidence inversion over California's Central Valley, with a base typically a few hundred meters off the valley floor and below the surrounding mountain ridges (Holets & Swanson, 1981). With the help of the mountains, this strong inversion forms a lid over the air basin, trapping cool, moist air within the valley. Subsiding air results in clear skies, providing excellent conditions for strong radiative cooling at night and, if sufficient moisture is present, formation of dense, widespread radiation fogs.

Interactions of fogs and clouds with air pollution have been studied at several locations around the world (e.g., Acker et al., 2002; Borys, Lowenthal, & Mitchell, 2000; Bower et al., 2000; Choularton et al., 1997; Facchini et al., 1992; Fisak et al., 2002; Fuzzi et al., 1988; Husain et al., 2000; Igawa, Matsumara, & Okochi, 2002; Jacob, Munger, Waldman, & Hoffmann, 1986; Laj et al., 1997; Lin & Saxena, 1991; Noone et al., 1992; Wobrock et al., 1994). Fogs have two important, competing effects on aerosol populations: (1) new aerosol mass formation through gas scavenging and chemical reaction in the droplets leading to non-volatile species (e.g. conversion of SO_2 to sulfate) that remain in the particle phase after droplet evaporation and (2) aerosol particle scavenging followed by deposition through droplet settling and/or impaction. The relative importance of these two processes depends on the environment in which the fog forms: meteorological conditions, number and composition of aerosol particles, gas phase chemical composition, and other factors. The net effect of a fog on atmospheric aerosol concentrations may change during a fog event; oxidation could be more important at the beginning of the fog event when reactant concentrations are higher, while deposition rates may increase over time with the growth of fog droplets (Lillis, Cruz, Collett, Richards, & Pandis, 1999).

Previous studies of sulfur oxidation in San Joaquin Valley (SJV) fogs have shown that dissolved sulfur dioxide can react rapidly, either being oxidized to sulfate or reacting with carbonyl compounds to form hydroxyalkylsulfonic acids (Munger, Tiller, & Hoffmann,

1986; Rao & Collett, 1995). Variations in SJV fog drop composition with size are known to influence the rates of chemical reactions as well (Hoag, Collett, & Pandis, 1999; Reilly et al., 2001).

Deposition due to fog drop sedimentation or impaction has been known to be an important removal process for atmospheric pollutants for a long time (Waldman & Hoffmann, 1987). Some studies have tried to assess the deposition fluxes by fog in the SJV by modeling (Lillis et al., 1999) or by measurements (Collett, Sherman, Moore, Hannigan, & Lee, 2001). Relatively few measurements exist, however, regarding atmospheric removal of fog solutes by drop deposition or how drop-size dependent fog composition affects removal rates for individual chemical species.

While much is now known about the inorganic composition of SJV fogwater, little is known about the scavenging and removal of carbonaceous aerosol by these fogs. Although the net effect of SJV fog episodes is expected to be to reduce atmospheric loadings of carbonaceous aerosol, the magnitude of this removal was unknown prior to the fog study component of the California Regional Particulate Air Quality Study (CRPAQS) reported here.

In order to improve our understanding of the role fogs play in influencing aerosol concentrations in California's Central Valley, Colorado State University made measurements of the chemical and physical properties of fogs at several SJV locations during winter 2000/2001. These observations form the basis for efforts to better characterize SJV fog composition and interactions between the fogs and air pollutants, especially fine particles. Our approach to the study and key findings are summarized here.

2 Experimental Approach

Colorado State University conducted measurements of fog properties at several SJV sites as part of the CRPAQS (California Air Resources Board, 2002) intensive winter field campaign. Measurements began in mid-December 2000 and extended through early February 2001. Fog samples were collected during CRPAQS at one core site (Angiola, California) and three satellite sites. The Angiola core site is located in the center of the SJV (35°35′N, 119°32′W, 60 m above sea level), surrounded by a large agricultural

area. The site was enclosed by a wire mesh fence, where fog collectors and other instruments were set up. Additional automated fog sampling systems were deployed at three satellite sites elsewhere in the SJV: Helm, Bakersfield, and McKittrick. The Helm and McKittick sites were rural, with Helm located north of Angiola and McKittrick in the southern SJV. The Bakersfield satellite site was at an urban location in the city of Bakersfield in the southern SJV. While fog samples were collected at Helm and Bakersfield, no fog was observed at McKittrick.

A Gerber Scientific Particulate Volume Monitor (model PVM-100; Gerber, 1991) was used to provide continuous measurements of liquid water content (LWC) at Angiola. LWC measurements provide a record of fog presence and fog density. When the LWC reaches a threshold value (usually set at 75 mg/m^3 for a period of 15 min), the data acquisition system paged a site operator to come to the site and begin fog collection. PVM calibrations (both of LWC and particle surface area (PSA)) were regularly performed using a manufacturer supplied calibration disk.

A Caltech Active Strand Cloud Collector (CASCC) (Demoz, Collett, & Daube, 1996) was used to collect bulk fog samples at Angiola. The CASCC employs a fan to draw air across six rows of 508 μm Teflon strands. Fog drops are collected based on their inertia. Collected droplets run down the strands, through a Teflon sample trough and Teflon sample tube, and are collected in a polyethylene collection bottle. The lower size cut of this collector is approximately 3.5 μm diameter. A Caltech Heated Rod Cloud Collector (CHRCC) (Demoz et al., 1996) was also used in a few fog events when air temperatures fell below freezing. This sampler features collection of supercooled drops onto stainless steel cylinders. Periodically, the collector is shut off and the collection surfaces internally heated to melt the accumulated rime. A bulk stainless steel CASCC (ss-CASCC) (Herckes, Lee et al., 2002) was used to collect fog for analysis of total organic carbon (TOC) and individual organic species. The design of the ss-CASCC is similar to the CASCC, except the ss-CASCC uses stainless steel walls, stainless steel collection strands, a stainless steel trough and sampling tube, and glass sample bottles. The CASCC, CHRCC and ss-CASCC collectors were used to collect sequential fog samples at time intervals between 1 and 2 h throughout each fog event. A size-fractionating CASCC (sf-CASCC) (Demoz et al., 1996) was used to collect and analyze drop size-resolved fog samples. The sf-CASCC is similar to the CASCC but has an extra inlet stage (four rows of eight 12.7 mm diameter Teflon rods) to capture large fog drops. The sf-CASCC was operated during CRPAQS with a 7.5 m/s average sampling velocity, yielding 50% size cuts for the two stages of approximately 21 and 4 μm. A CSU 5-stage fog collector was also operated in selected fog episodes to provide greater resolution of fog composition changes across the drop size spectrum. The design, operation, and performance of this instrument are described in detail elsewhere (Moore, Sherman, Reilly, & Collett, 2002; Straub & Collett, 2002).

Fog deposition measurements were carried out using two deposition plates deployed together. These 0.30 m^2 deposition plates are made of Teflon and have previously been deployed in Davis, California radiation fog (Collett et al., 2001). The plates are square and have a trough milled near their perimeter. The trough serves to accurately define a collection area and to prevent contamination from material that may come in contact with the edges of the plate. Samples were typically collected at 2 h intervals to match other cloud composition measurement periods and to provide sufficient sample for composition analysis, including measurement of TOC.

During each fog event collected fog samples were immediately brought to a field lab for processing. Samples were weighed to determine collected volume then aliquotted for immediate pH measurement and stabilization of other species for later measurement in our laboratory in Colorado. Fog sample pH was measured on site with a pH meter and a Microelectrodes, Inc. Model MI-710 pH combination electrode, calibrated with pH 4 and 7 buffers.

Sample aliquots were prepared for major ion analysis by pipetting 500 μl of sample into a polypropylene autosampler vial. Inorganic anion (NO_3^-, NO_2^-, SO_4^{2-}, and Cl^-) concentrations were determined using a Dionex DX-500 ion chromatograph equipped with an AG4A-SC guard column, AS4A-SC separation column, a Dionex Anion Self-Regenerating Suppressor (ASRS), and a conductivity detector. Separation was achieved using a 1.8 mM Na_2CO_3/l.7 mM $NaHCO_3$ eluent at a flow rate of 2.0 ml/min. Inorganic cation (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) concentrations were determined using a

second DX-500 ion chromatograph equipped with Dionex CG-12 and CS-12 guard and separation columns, a Dionex Cation Self Regenerating Suppressor (CSRS), and a conductivity detector. Separation was achieved using a 20 mM methanesulfonic acid eluent at a flow rate of 1.0 ml/min. Both IC systems were calibrated daily using a series of lab-prepared ion standards. Calibration accuracy was monitored by injection of independent, NIST traceable standards.

Formaldehyde was preserved by adding a HCHO preservation solution containing bisulfite (20 mM NaOH, 10 mM CDTA, 3 mM $NaHSO_3$) to form hydroxymethanesulfonate (HMS). Samples were then analyzed by fluorescence spectrophotometry (Dong & Dasgupta, 1987). This method measured the free formaldehyde and any HMS in the solution before preservation. Aliquots were prepared for trace metal analysis by acidification to near pH 1 with trace metal grade nitric acid. Samples were analyzed for Fe and Mn using a Varian Model 640Z Graphite Furnace Atomic Absorption Spectrometer (GFAAS) with Zeeman background correction.

Aliquots for later analysis of organic acids were prepared by addition of a small volume of chloroform,

which acts as a biocide. C1–C3 carboxylic acids and oxalic acid were analyzed using a Dionex DX500 ion chromatograph (IC) with conductivity detection. The organic acid column in this analysis was a Dionex AS-11 separation column with an AG-11 guard column. Separation was achieved using a 0.5 mM NaOH eluent at a flow rate of 2.0 ml/min. The IC was calibrated daily using a series of lab-prepared standards.

Sample aliquots for total organic carbon (TOC) analysis were prepared by pipetting 5–20 ml of sample, depending on available sample volume, into a pre-baked glass vial and sealing with a Teflon-lined cap. TOC was measured using a Shimadzu TOC-5000A analyzer. Additional sample was filtered through baked quartz filters (Pall Gelman Pallflex Tissuquartz) to make a distinction between the dissolved phase (dissolved organic carbon, DOC) and the insoluble phase of the fog water.

Several procedures were used to ensure the integrity of each fog measurement, including calibrating instruments, cleaning collectors before each event, taking blanks, and analyzing replicate samples. Fog collector blanks were collected by spraying deionized water onto the collection strands and allowing it to flow through the normal sample collection flow path
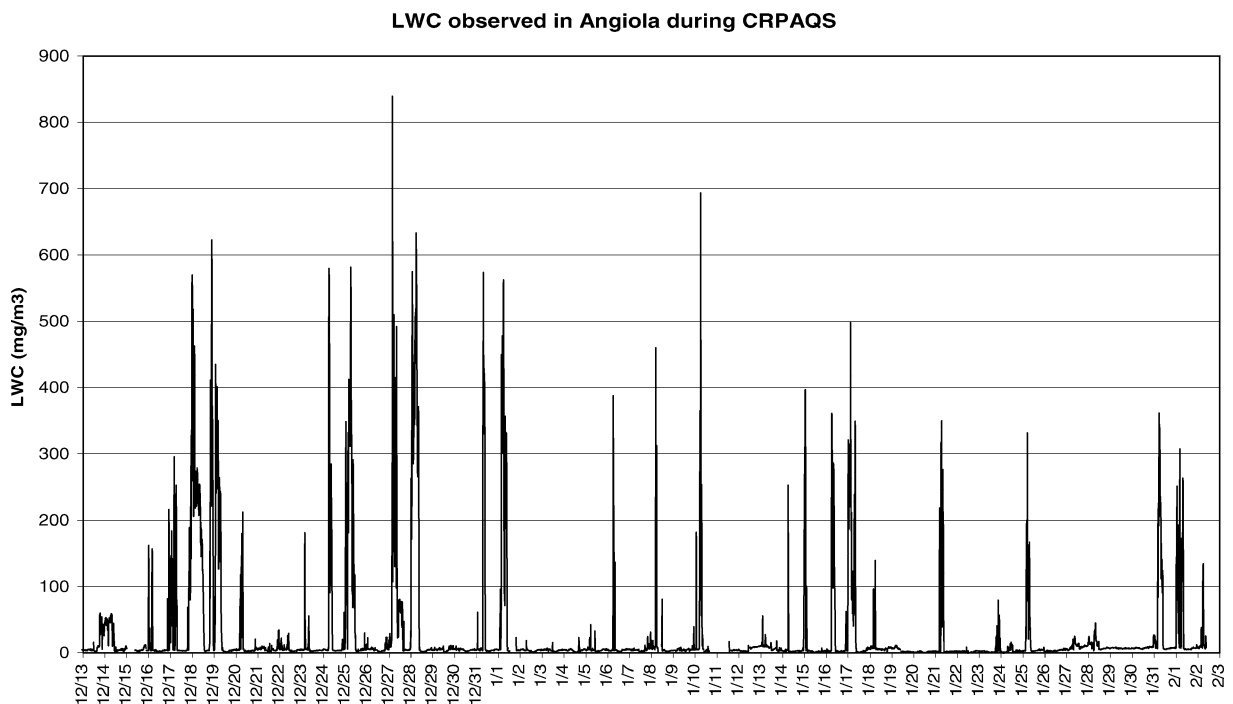

Figure 1 Timeline of fog LWC during the CRPAQS study winter intensive in 2000/2001.

into a sample bottle. Minimum detection limits based on collector blanks were well below the measured concentrations for major species reported here. Measurement precision values, expressed as relative standard deviations (RSD) and based on replicate fog sample analyses were in the range of 2–8% for TOC, DOC, major inorganic ions (NO_2^-, NO_3^-, SO_4^{2-}, and NH_4^+), organic acids, S(IV), and HCHO. RSD for TOC and major ion concentrations in fog deposition samples were in the range of 6–11%.

3 Results and Discussion

Several fog episodes were successfully sampled in December, January, and early February. In sum, more than 200 fog samples were collected from the various fog collectors. Figure 1 depicts a timeline of fog liquid water content (LWC) during the study period. The sampled fog events are as follows: Dec 17/18, started at 22:15 and finished at 12:00; Dec 18/19, the fog started at 23:00, then lifted, but came back again at 1:20 until 7:30 in the morning; Jan 6th, supercooled fog present from 6:00 to 8:00; Jan 10th, samples collected from 6:15 to 7:55; Jan 15th, samples collected from 23:30 to 3:00; Jan 17th, a supercooled fog event lasting from 00:00 to 7:00; Jan 21st, samples collected from 6:00 to 9:00; Jan 25th, a patchy fog event, occurring intermittently from 3:30 until 8:00; Jan 31st, fog from 4:00 until 9:30; Feb 1st, a patchy fog event from 1:00 to 5:20.

Characteristics of the fogs observed during CRPAQS were somewhat different than we have observed in other SJV radiation fog studies (Collett et al., 1999; Moore, Sherman, Reilly, Hannigan et al., 2004a, Moore, Sherman, Reilly, & Collett, 2004b). The fog layer was often very shallow, rarely reaching even to the top of a 100 m measurement tower at the core site. In addition, LWC values were high. In our experience, SJV radiation fogs are often rather "thin," with LWC frequently less than 100 mg/m^3. By contrast, the fogs observed in this study frequently had LWC in excess of several hundred mg/m^3. Drop sizes in the fogs were also very large, with effective diameters measured by the PVM often in the 20–35 μm range, contributing to rapid settling velocities. At times the drops became so large that the fog began to form what appeared to be drizzle, unusual for such a shallow cloud layer. It is believed that the

shallowness of the fog layer probably contributed to direct radiative cooling of fog drops, resulting in strong condensational growth that increased individual drop sizes and overall fog LWC. This phenomenon has been discussed previously by Roach (1976). As we'll see below, the large fog drop sizes generated in these fogs produce high fog solute deposition velocities.

Table I depicts species concentration ranges (and medians) in bulk fog water sampled at the Angiola core site. Figure 2 depicts a typical composition of Angiola fog water measured during the study. The chemical composition of the fogs was dominated by nitrogen species, with important contributions also from organic compounds and sulfate. Ammonium and nitrate were the most abundant individual compounds; nitrite and sulfate were also found to be present at significant concentrations as were several organic compounds, including formate, acetate, and formaldehyde. Abundant gas phase ammonia absorbed by fog drops helps keep the fog pH relatively high, with pH values typically well above 6. A comparison of measured anion and cation concentrations revealed a charge balance typically

Table I Summary of bulk fog sample composition

Species	Number of samples	Concentration range	Median
pH (pH units)	36	5.85–8.04	6.73
Cl^- (μN)	36	10.5–39.8	16.3
NO_3 (μN)	36	78.1–1872.1	303.5
NO_2 (μN)	36	4.7–131.9	17.7
SO_4^{2-} (μN)	36	12.9–329.5	56.5
Formate (μN)	22	14.9–120.7	31.6
Acetate (μN)	22	5.0–197.2	31.4
Propionate (μN)	22	ND–10.4	1.7
Pyruvate (μN)	22	ND–0.7	0.7
Oxalate (μN)	22	3.2–24.9	7.2
Na^+ (μN)	36	0.13–22.5	5.8
K^+ (μN)	36	1.9–18.6	4.3
NH_4^+ (μN)	36	193.2–2203.7	608.3
Mg^{2+} (μN)	36	4.2–24.8	5.3
Ca^{2+} (μN)	36	5.6–101.5	10.7
HCHO (μM)	36	2.6–49.3	21
Fe (μg l^{-1})	24	16.9–341.9	77.5
Mn (μg l^{-1})	24	0.9–16.5	4.1
TOC (ppmC)	22	2.3–41.9	6.9

ND Not detected – the response was below the detection limit for this species.

CRPAQS typical fog mass composition
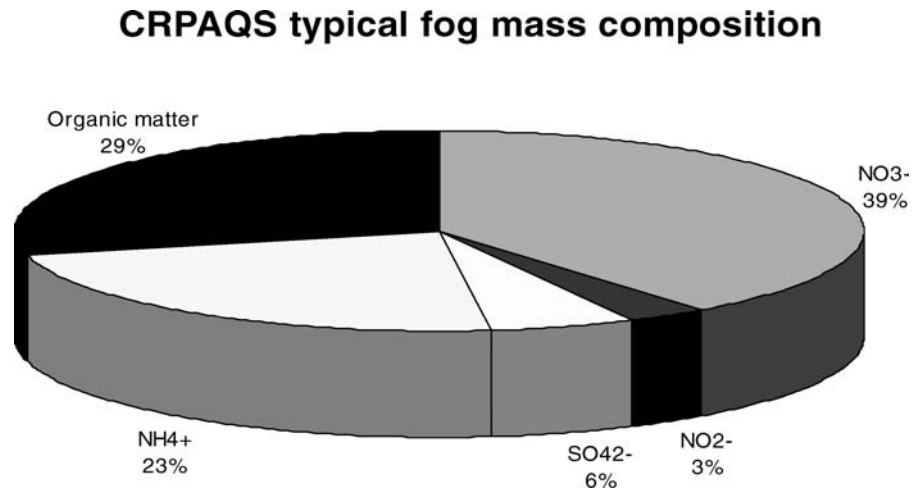
within 10%, suggesting that most of the major charged species were included in our target analytes and measured accurately.

Comparison of fog composition at Angiola with compositions measured at Bakersfield and Helm (not shown here) reveals that Angiola and Helm, both rural sites, have generally similar fog compositions. Urban Bakersfield fog contained greater concentrations of sulfate and nitrite. Comparison of Bakersfield fog composition measurements in this and other recent SJV fog studies with measurements made in the 1980s reveals a statistically significant decrease in fog concentrations of sulfate and an increase in fog pH. These changes are consistent with intervening declines in SO_2 emissions in the southern SJV, which should translate into less production of sulfate and greater availability of ammonia to raise fog pH.

Results of the study indicate the important role that SJV fogs play in processing of organic carbon. SJV fogs contain a rich mix of organic compounds, with major constituents including formaldehyde, formate, and acetate. Approximately 25% of the fog organic carbon, on average, is present as undissolved, suspended material in the droplets (see Herckes, Lee et al., 2002 for details). Many organic compounds typically associated with atmospheric aerosol particles (e.g., markers for particles produced from vehicle exhaust, residential wood burning and other sources) have been previously observed in radiation fogs in Davis, California (Herckes, Hannigan, Trenary, Lee, & Collett, 2002) and were observed here in CRPAQS fogs as well, indicating active fog processing of particulate organic matter.

Measurements made with the size-fractionating fog collectors provide insight into the drop size-dependence of various chemical species in CRPAQS fogs. In contrast to previous SJV fog studies (Moore et al., 2004a, b) in a more urban area (Davis, California), the pH values of large and small CRPAQS fog droplets were often similar, although higher pH values were observed in large drops during some periods. Figure 3 illustrates the relative lack of fog pH drop size-dependence observed with the CSU 5-stage collector during three events in which it was operated. For inorganic species, significant concentration differences were seen between large and small drop fractions. Chloride, ammonium, sulfate, nitrate, potassium, magnesium and calcium were all enriched in smaller drops; total Fe and Mn showed no preference of enrichment; nitrite was enriched in larger drops. Figure 4 illustrates the size-dependent composition observed for sulfate and nitrite, examples of species observed to be enriched in small and large drops, respectively. The enrichment of nitrite in large drops in some cases is consistent with a slightly higher pH in these larger drops and resulting enhancements to the solubility of gas phase nitrous acid. The size dependence of many of the species observed here is consistent with patterns observed previously in SJV fogs (Collett et al., 1999; Moore et al., 2004a, b). TOC was observed to be strongly enriched in small drops. Formate and acetate showed slight enrichment in small drops during many sample periods. Oxalate was more strongly enriched in small fog drops. Formaldehyde was slightly enriched in small fog drops during most sampling periods as illustrated in Figure 5.
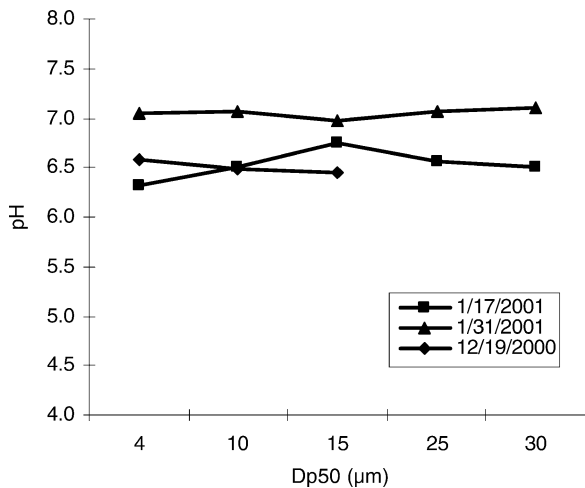
Figure 3 Drop size-dependence of fog pH measured in three separate fog episodes. Data come from the CSU 5-stage collector. The pH measured in each drop size fraction is plotted vs. the drop size collected with 50% efficiency (Straub & Collett, 2002) for each stage. Insufficient sample was collected to measure pH in all collection stages on 12/19.

Deposition fluxes for fog water and measured fog solute species were determined from the amount of collected material divided by the collection area and the collection time. Results were averaged for the two deposition plates deployed in parallel. Observations of the deposition fluxes of fog water and measured solute species were analyzed, in conjunction with measured
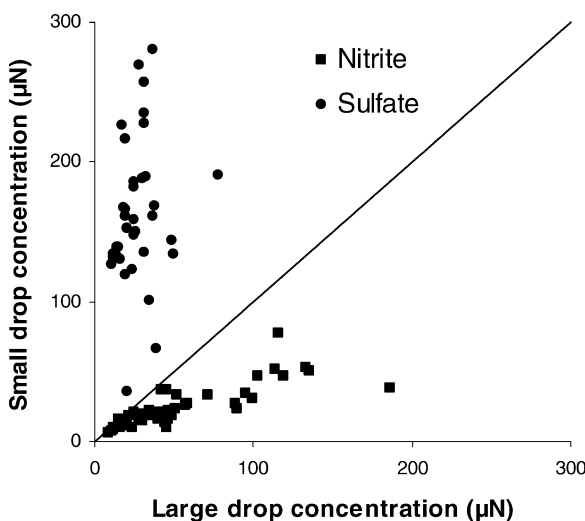
airborne fog water solute concentrations and LWC, to obtain deposition velocities. The deposition velocity for a species is determined by dividing the species deposition flux (at the deposition plate) by its airborne concentration (at the height of the fog collector). The airborne concentration of each species is the product of its aqueous phase concentration in collected fog water and the fog LWC. The airborne concentration of fog water is the LWC. Deposition of fog water in environments with low wind speeds, low surface roughness, and large drops tends to be dominated by sedimentation (e.g., Thalmann, Burkhard, Wrzesinsky, Eugster, & Klemm, 2002). Deposition velocities in this study varied significantly between solutes, a pattern previously noted in urban radiation fogs (Collett et al., 2001). Figure 6 presents the average (along with the range) deposition velocities determined for fog water and for several key fog solutes. One readily notes the relatively high deposition velocities, typically on the order of 1–2 cm/s, much higher than expected for ammonium nitrate, ammonium sulfate, or organic carbon contained in accumulation mode aerosol particles. Such high deposition velocities lead to rapid removal of air pollutants during fog episodes.

The average deposition velocity was lowest for nitrate and highest for nitrite. Overall the order of average deposition velocities was $NO_2^- > water > NH_4^+ > TOC \sim SO_4^{2-} > NO_3^-$. The observed trends in solute deposition velocities reflect the non-uniform distribution of fog solutes across the fog drop size spectrum.
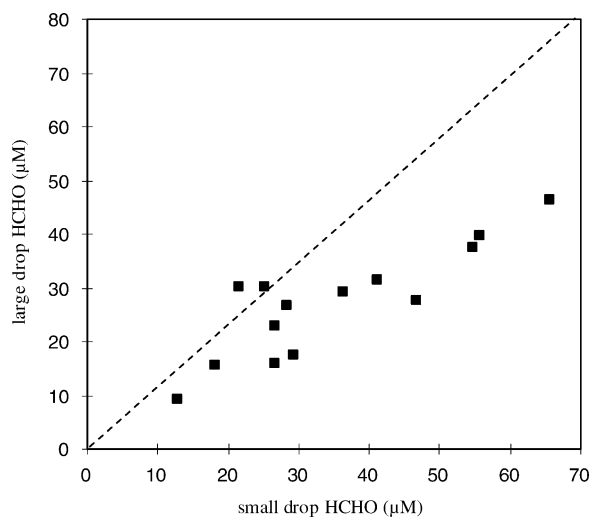

Figure 4 Drop size-dependent concentrations of sulfate and nitrite observed in Angiola fogs. Samples were collected with the sf-CASCC. Nominal size ranges for the small and large drop size fractions are 4–21 μm and >21 μm diameter, respectively.

Figure 5 Drop size-dependent concentrations of formaldehyde observed in Angiola fogs.

Figure 6 Average deposition velocities (±range) observed for fog water and several key solute species in CRPAQS fogs. Deposition velocities are arranged from lowest to highest for comparison purposes.
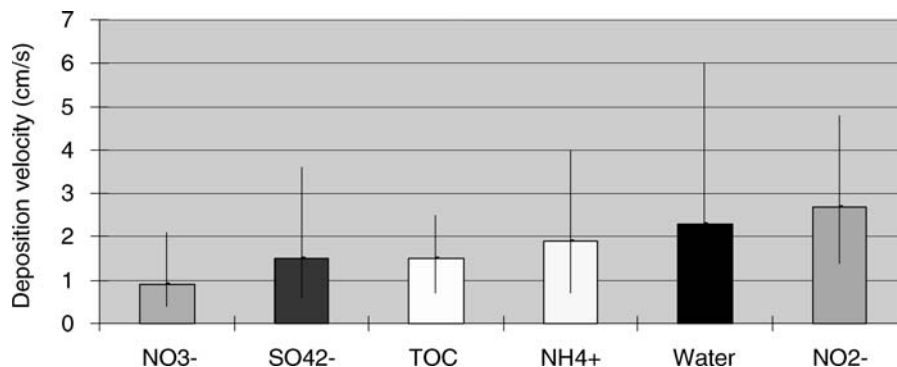
Solutes that tend to be enriched in large drops (e.g., NO_2^-) experience high deposition velocities because of the strong increase in drop sedimentation rate with drop size. Nitrite, in fact, was observed to have a deposition velocity that exceeded the average deposition velocity of fog water, due to its enrichment in faster settling, large fog drops. Species that were observed to be enriched in small fog drops (NH_4^+, TOC, SO_4^{2-}, and NO_3^-) all had deposition velocities less than the average fog water deposition velocity. One can even relate the relative deposition velocities

Figure 7 Deposition velocity vs. small/large drop concentration ratio for three CRPAQS fog samples obtained using the sf-CASCC. Points are plotted from left to right in each series for NO_2^-, NH_4^+, SO_4^{2-} and NO_3^-, respectively. The more strongly a species is enriched in small fog drops the lower its deposition velocity tends to be.

of the various species (and water) to their degree of enrichment in small fog drops. Figure 7 illustrates this for three sample fog periods, revealing that the more strongly a species is enriched in small fog drops the lower its deposition velocity. Significant differences in deposition velocities between time periods often arise, as seen in Figure 7, due to changes in fog microphysical properties.

Table II lists species mass removals for each study fog event. Longer fog events tend to produce greater mass removal amounts. Taking into account fog duration and measured fluxes, a typical fog episode removed approximately 50 μg m^{-2} h^{-1} of sulfate, 110 μg m^{-2} h^{-1} of nitrate, 100 μg m^{-2} h^{-1} of ammonium, and 70 μg m^{-2} h^{-1} as TOC.

The typical fog layer during the study was less than 50 m high. If we consider a conservative case where the measured fluxes of material are removed from a column 100 m deep, we can estimate the effects of fog episodes on boundary layer pollutant concentrations. For a typical fog episode, we estimate ambient concentration reductions of approximately 0.5 μg m^{-3} h^{-1} of sulfate, 1.1 μg m^{-3} h^{-1} of nitrate, 1.0 μg m^{-3} h^{-1} of ammonium and 0.7 μg m^{-3} h^{-1} in the form of TOC. These numbers are quite significant and indicate the effective role these fogs play as atmospheric cleansers. It is important to keep in mind, however, that some of the deposited material may be volatile (but water soluble) and subject to partial emission back into the atmosphere if the wetted ground dries following fog evaporation.

Removal of scavenged particulate species can of course be offset by aqueous phase conversion of volatile precursors to non-volatile products. The high pH droplets present in these fogs make them effective atmospheric reactors for dissolved sulfur dioxide. Both oxidation to sulfate and reaction with dissolved
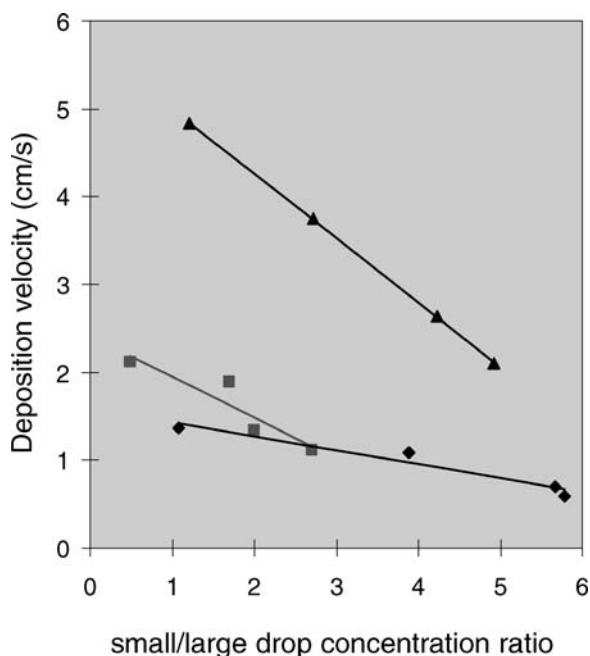
Table II Total mass removal of species by individual fog episodes

Fog episode start date	Sample Time (h)	NO_3^- ($\mu g/m^2$)	SO_4^{2-} ($\mu g/m^2$)	NH_4^+ ($\mu g/m^2$)	TOC ($\mu gC/m^2$)
12/18/2000	9.0	2246	1223	2627	952
12/19/2000	2.3	127	50	203	72
1/15/2001	2.0	51	22	71	75
1/17/2001	7.8	393	174	526	309
1/21/2001	3.0	774	173	448	312
1/25/2001	2.5	37	26	70	66
1/31/2001	3.8	592	251	463	452
2/1/2001	1.7	96	71	101	113

formaldehyde to produce hydroxymethanesulfonic acid (HMS) are known to be important pathways for new particle mass production in SJV fogs (Jacob, Shair, Waldman, Munger, & Hoffmann, 1987; Lillis et al., 1999; Munger et al., 1986; Rao & Collett, 1995; Reilly et al., 2001). Numerical simulations using an updated version of a single drop fog chemistry model (see Reilly et al., 2001 for model description) reveal the importance of both sulfate production and formation of HMS in the studied fogs. Frequent observations of HMS in individual SJV particles during CRPAQS (Prather, personal communication) and during previous studies (Whiteaker & Prather, 2003) are consistent with the importance of this reaction pathway. Increases in fine particle organic carbon concentrations after some CRPAQS fog episodes also suggest that aqueous phase reactions of dissolved VOCs may be important in producing new, secondary organic aerosol matter as suggested elsewhere (Blando & Turpin, 2000). More work is needed to examine this hypothesis in future investigations.

The Carnegie Mellon University fog model (Fahey & Pandis, 2001; Hoag et al., 1999; Lillis et al., 1999), a drop size-resolved fog model with explicit fog microphysics, was used to simulate a CRPAQS fog episode and was able to predict the liquid water evolution, bulk aqueous-phase concentration measurements, drop size-resolved trends, and deposition fluxes for a number of species in close agreement with observed values. During the early stages of the fog, the behavior of species originating partially in the gas phase (NO_3^-, SO_4^{2-}) was heavily influenced by dissolution into the droplets and rapid aqueous phase reactions. Following these initial peaks in aqueous phase concentrations, deposition began to dominate, and the species were gradually depleted from the fog

layer. Results of this modeling effort, described in detail elsewhere (Fahey, Pandis, Collett, & Herckes, 2005), are similar to earlier model simulations of SJV fogs (Lillis et al., 1999) where the net effect of the fogs on inorganic nitrogen species was removal while production and removal of sulfate were more closely balanced.

4 Conclusions

Several San Joaquin Valley fog episodes were characterized during CRPAQS. Most of the fog episodes were relatively shallow and featured large droplets. The chemical composition of the fogs was dominated by nitrogen species, with important contributions also from organic compounds and sulfate. Ammonium and nitrate were the most abundant individual compounds; nitrite and sulfate were also found to be present at significant concentrations as were several organic compounds, including formate, acetate, and formaldehyde. Abundant gas phase ammonia absorbed by fog drops helps keep the fog pH relatively high, with pH values typically well above 6. The high pH droplets present in these fogs make them effective atmospheric reactors for dissolved sulfur dioxide. Both oxidation to sulfate and reaction with dissolved formaldehyde to produce hydroxymethanesulfonic acid (HMS) are important reaction pathways.

Results from this study indicate the important role SJV fogs play in cleansing the atmosphere via particle scavenging followed by drop deposition. Fog deposition fluxes were determined capable of reducing boundary layer atmospheric concentrations of major species (e.g., nitrate, ammonium, and organic carbon) at rates on the order of 0.5–1 $\mu g/m^3$ h. The fogs are

also effective at scavenging and removing sulfate, but this removal is offset by production of new, non-volatile sulfur compounds via aqueous phase chemistry. Preferential enrichment of major inorganic ion species in small fog drops reduces most species' deposition velocities below the deposition velocity for fog water. Nitrite, which was often enriched in large fog drops, exhibited deposition velocities higher than fog water. Accounting for drop size-dependent species concentrations is essential to accurately modeling rates of pollutant deposition in SJV fogs.

While this study has increased our understanding of the importance of fog processing of both inorganic and organic aerosol species, a significant need remains to continue studies of this type. In particular, our understanding of the production and removal of fine particle organic carbon remains in its infancy. Much more work is needed to elucidate the relative efficiencies with which fogs scavenge and deposit carbonaceous particles from different source types and to determine the extent of secondary organic aerosol formation occurring via aqueous phase reaction pathways that convert soluble VOCs to nonvolatile products that are released as aerosol particles when a fog evaporates.

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