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Drop size-dependent chemical composition of clouds and fogs. Part II: Relevance to interpreting the aerosol/trace gas/fog system

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Abstract

Size-resolved fog drop chemical composition measurements were obtained during a radiation fog campaign near Davis, California in December 1998/January 1999 (reported in Reilly et al., Atmos. Environ. 35(33) (2001) 5717; Moore et al., Atmos. Environ. this issue). Here we explore how knowledge of this size-dependent drop composition—particularly from the newly developed Colorado State University 5-Stage cloud water collector—helps to explain additional observations in the fog environment. Size-resolved aerosol measurements before and after fog events indicate relative depletion of large ($>2\,\mu$m in diameter) particles during fog accompanied by a relative increase in smaller aerosol particle concentrations. Fog equivalent air concentrations suggest that entrainment of additional particles and in-fog sedimentation contributed to observed changes in the aerosol size distribution. Calculated deposition velocities indicate that sedimentation was an important atmospheric removal mechanism for some species. For example, nitrite typically has a larger net deposition velocity than water and its mass is found preferentially in the largest drops most likely to sediment rapidly. Gas–liquid equilibria in fog for NO_3^-/HNO_3, NH_4^+/NH_3, and $NO_2^-/HONO$ were examined. While these systems appear to be close to equilibrium or relative equilibrium during many time periods, divergences are observed, particularly for low liquid water content ($<0.1\,g\,m^{-3}$) fogs and in different drop sizes. Knowledge of the drop size-dependent composition provided additional data useful to the interpretation of these deviations. The results suggest that data from multi-stage cloud water collectors are useful to understanding fog processes as many depend upon drop size.

Keywords: Fog chemistry; Radiation fog; Sacramento Valley; Deposition velocity; Occult deposition; Phase equilibrium; Nitrous acid

1. Introduction

Clouds and fogs affect the fate of some atmospheric species via both chemical and physical processes. A classic example is the uptake and oxidation of $SO_{2(g)}$ to $SO_{4(aq)}^{2=}$ in drops, and subsequent rapid removal via deposition. Drop surfaces have also been suggested as important reaction sites. For example, the presence of a wet surface layer on atmospheric aerosol particles has been associated with the production of $HONO_{(g)}$ (Notholt et al., 1992). Several different cloud water collectors have been developed and samples obtained during field and long-term sampling campaigns designed to study the chemical composition of clouds and the resulting environmental effects at many locations (Bower et al., 2000; Anderson et al., 1999; Collett et al.,

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1999; Fuzzi et al., 1998; Choularton et al., 1997; Wobrock et al., 1994; Heintzenberg, 1992; among others).

During December 1998 and January 1999, a radiation fog sampling campaign was conducted near Davis, California. Drop size-dependent fog water composition was measured in seven fog events (12/18/98 event: 3:22–12:00 PST; 1/4/99 event: 20:08–1/5/99 10:00; 1/9/99 event: 3:00–10:36; 1/10/99 event: 2:45–10:00; 1/10/99 #2 event: 22:50–1/11/99 9:42; 1/11/99 event: 23:00–1/12/99 9:42; 1/13/99 event: 5:50–9:17). "Bulk" fog water samples were collected using the Caltech Active Cloud water Collector #2 (CASCC2) which has a 50% efficiency collection diameter (D_{p50}) of 3.5 μm (Demoz et al., 1996). Two fog drop fractions were collected using the two-stage size-fractionating Caltech Active Strand Cloud water Collector (sf-CASCC) (D_{p50}s ≈ 17 and 4 μm) (Moore, 2002; Demoz et al., 1996). A unique feature of this campaign was one of the first field deployments of the Colorado State University 5-Stage cloud water collector (CSU 5-Stage) which separates collected drops into five fractions (experimental D_{p50}s: 25.5, 29, 17.5, 11.5 and 4.5 μm from largest (Stage 1) to smallest (Stage 5)) (Moore et al., 2002; Straub and Collett, 2002). While there is more overlap between drop fractions in the CSU 5-Stage than intended, the very-largest drops are collected uniformly on Stage 1 and are effectively separated from the smallest drops. The CSU 5-Stage collected seven sample sets during three of the events (1/4/99 S(ample)#1: 20:08–22:00; 1/4/99 S#2: 23:00–1/5/99 1:00; 1/4/99 S#3: 2:00–4:00; 1/9/99 S#1 4:00–6:00; 1/9/99 S#2 7:00–9:00; 1/10/99 S#1: 4:00–6:00; 1/10/99 S#2: 6:52–9:00). Fog chemical composition for this campaign has been previously reported (Reilly et al., 2001), and a companion paper (Moore et al., this issue) focuses on the observations of size-dependent drop composition made with the CSU 5-Stage collector. Briefly, the measured inorganic chemical composition in all drop size fractions from these fogs was dominated by nitrogen species—particularly NH_4^+ and NO_3^-, although NO_2^- was a significant component in some drop fractions (Moore et al., this issue). Drop composition varies strongly with size in these fogs (see Moore et al., this issue; Figs. 5–10). In general, the CSU 5-Stage data suggest there is up to a factor of ≈ 30 difference in concentration between drop sizes for important species (e.g. NO_3^-) (see Moore et al., this issue, Tables 4–5), significantly broader (2–3X) than observed in the two stage collector.

In this paper, we take advantage of the more detailed knowledge of drop size-dependent chemical composition—particularly from the CSU 5-Stage—in combination with additional measurements to analyze the fog environment during the sampling campaign. We start with additional gas and size-resolved aerosol particle measurements. Then we present the observed deposition rates and explore the state of phase equilibrium for selected species. These analyses show the clear benefit of obtaining size-resolved fog drop concentrations. Multi-stage cloud water collectors can provide important information relevant to understanding and interpreting fog processing of aerosol particles and trace gases.

2. Experimental methods

The site in Davis, the cloud water collectors, the collector sampling protocols, fog water sample analytical methods and accompanying fog microphysical and ambient meteorological measurements have been previously described (Moore et al., this issue; Reilly et al., 2001). Here we focus on the additional measurements reported in this paper.

During the fog events of 1/9/99, 1/10/99 and 1/10/99 #2 as well as periods before and after each, NH_3 and HNO_3 were continuously measured using pairs of coated glass ETH annular denuders (Oberholzer et al., 1992). The fog-free sampling periods are 1/8/99 16:00–1/9/99 2:30, 1/9/99 11:00–1/10/99 2:21, 1/10/99 10:33–22:28, and 1/11/99 10:00–19:12. There was typically a delay of 30 min during the transition between fog and fog-free sampling. This "contamination" is mitigated by the long overall sampling periods (8 to 14 + hours). The time resolution is relatively poor, but the intention was to match measurements with the fog event and pre- and post-event size-resolved aerosol sampling. The denuders were coated with 0.05 M NaF (HNO_3) or 0.2 M H_3PO_4 (NH_3) in the field by swirling 5 ml of the solution inside the annulus twice followed by drying with N_2. Critical orifices controlled the denuder flow rates (≈ 16.7 l min^{-1}). Each denuder was extracted with 3 ml of deionized water typically within a few hours of the sampling period. The denuders were operated with Teflon impactors at the inlet to minimize contamination by aspirated drops (Oberholzer et al., 1992). The inlet height was approximately vertically co-located with the CSU 5-Stage collector (1–1.5 m above the ground).

Size-resolved aerosol measurements were obtained before and after the same three fog events using a Micro Orifice Uniform Deposit Impactor (MOUDI) (Marple et al., 1991). The MOUDI inlet was also vertically co-located with the CSU 5-Stage. Teflon substrates were immediately removed from the MOUDI between events and frozen prior to laboratory extraction using 4.8 ml of deionized water with 0.2 ml of ethanol used to wet the substrate. Centrifuge tubes containing the substrates and extract solution were rotated for at least one hour to ensure the extraction of all soluble material. Upon returning from the field, subsequent laboratory tests revealed that the flow rate through the MOUDI was somewhat lower than optimal (23 l m^{-1}) theoretically resulting in slightly higher stage D_{p50}s (see Moore, 2002, for details). There was no evidence of condensation within the MOUDI during sampling. High ambient humidities during the campaign should have limited particle bounce and loss of nitrate (Zhang and McMurry, 1992). A residual black insoluble material was observed on the substrates following aqueous extraction.

For most of the Davis fog events, deposition flux measurements were obtained by placing one pair of Teflon squares ($0.298\,m^2$) directly on the turf adjacent to the cloud water collectors. Deposition plate measurements were synchronized with the fog water sampling and used 2 h sampling periods (matching the CSU 5-Stage). At the end of each sampling period, the water on each square was collected by pipette, immediately weighed and aliquoted for subsequent laboratory analysis. Further details regarding the deposition flux measurements can be found in Collett et al. (2001).

Denuder and MOUDI extracts and the deposition samples were all analyzed using the Dionex DX-500 ion chromatography (IC) systems described in Moore et al. (this issue). In addition to the analytical uncertainty for various species previously reported, additional sources of observational uncertainty (e.g. flow rate, extraction and denuder efficiency, among others) are incorporated in the overall value. For NH_3, the relative standard deviation is thus approximately 7% (14% for HNO_3). The ratio of the 95% confidence level minimum detection limit (MDL) to the observed concentrations was $< 2\%$ for NH_3 and from 17 to 42% for HNO_3. Despite attempting to minimize the analytical detection limits by increasing the IC injection volumes, only ammonium, nitrate, and sulfate were present in reportable quantities in the aerosol samples. Reported MOUDI uncertainties combine those for the analytical method and the estimated flow rate (5%). The relative standard deviations based upon the deposition plate pairs are 5%, 5%, 4%, 5%, and 9% for nitrite, water, ammonium, nitrate and sulfate, respectively. These values are similar to the species' reported analytical uncertainties.

A Particulate Volume Monitor (PVM-100, Gerber Scientific, Inc., Reston, VA) used in the study may not have accurately reported the ambient fog liquid water content (LWC) due to the large drop sizes present at certain times during the fog events. This problem has been previously identified (Wendisch et al., 2000; Wendisch, 1998). The effective drop diameter (Wendisch, 1998), D_{eff}, was calculated from the PVM-100's particle surface area and LWC channels. While this calculation is subject to the same measurement errors, during the time periods ($\approx 80\%$) where D_{eff} exceeded $20\,\mu m$, LWC values derived from the total water mass collected in the Caltech fog collectors were substituted for the PVM-100 data. The revised LWC data set is more consistent with additional observations in the fogs (see Moore, 2002).

3. Observed gas and size-resolved aerosol particle concentrations

Ammonia concentrations from 3.3 to 12.7 ppbv were observed (Fig. 1). The measured HNO_3 concentrations are near zero in and out-of-fog (0.025–0.064 ppbv) (not shown) and should be treated with caution given the relative uncertainty and proximity to the MDL.

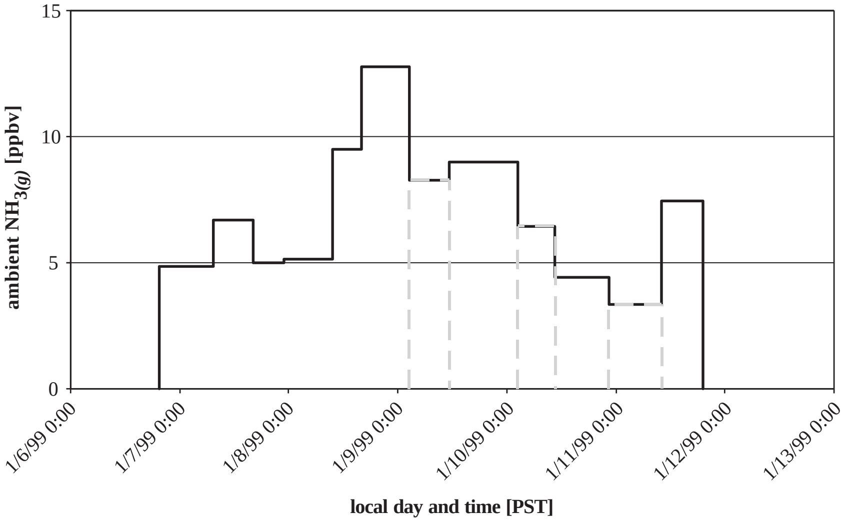

Fig. 1. Ambient ammonia concentrations. The gray dashed lines indicate the 1/9/99, 1/10/99 and 1/10/99 ♯2 fog events. As described in the text, the propagated uncertainty is ≈ 7% (not shown).

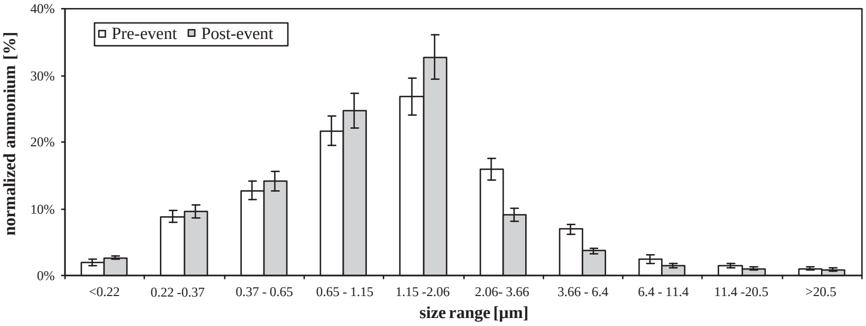

Fig. 2. Normalized (by mass) MOUDI ammonium concentrations pre- and post-1/10/99 fog event. Error bars shown are as described in the text.

This is an ammonia-rich environment. The presence of ammonia gas during the in-fog periods is consistent with the low LWC, the high fog pH ($\approx$5.5–7.5, CSU 5-Stage), and the partitioning of ammonia between phases. The very low HNO_3 observations are also consistent with its very high solubility. It is usually not observed in the gas-phase in fogs (e.g. Colvile et al., 1994; Waldman and Hoffmann, 1987; among others), and the damp environment and rapid deposition velocity may have limited gas-phase concentrations between events. (Deposition velocity and partitioning are discussed below.)

MOUDI results for ammonium, nitrate and sulfate are similar so only the relative pre- and post-1/10/99 fog event ammonium concentrations are shown (Fig. 2). Total observed MOUDI inorganic ion mass increased $\approx 2.3\,\mu g\,m^{-3}$ during the 1/9/99 event to $17\,\mu g\,m^{-3}$ followed by a $3\,\mu g\,m^{-3}$ decrease after the 1/10/99 event (individual species mirrored the collective changes). This mass change may partly be accounted for by changes in mixing height and entrainment of air from above the boundary layer (not measured, evidence for entrainment of additional mass discussed below).

While many of the changes are within the measurement uncertainty, there is a uniform relative decrease of mass in particles $>2\,\mu m$ in diameter for the species measured (and relative increase for smaller particles) for both events. This is consistent with large particle depletion during fogs, although fine particles remain as has been observed before (Hoag et al., 1999; Ishizaka and Qian, 1994). Activated large aerosol particles form the largest fog drops and are more rapidly removed by sedimentation (Pruppacher and Klett, 1997). As suggested by Schell et al. (1997), this relative depletion of coarse mode aerosol is consistent with the size-dependent drop chemical concentration profiles observed as drop concentrations do not increase with size (Moore et al., this issue, Figs. 5–10). High observed fog deposition fluxes (Section 4) are also consistent with this pre- and post-fog aerosol particle size distribution. In a Po Valley, Italy study where advection and entrainment were on-going features of the fogs, the mass of aerosol particles $<0.3\,\mu m$ in diameter increased between pre- and in-cloud measurements, but large aerosol particles were nucleated into drops and lost (Noone et al., 1992).

Interpreting the MOUDI data is confounded by the fact that emissions, advection, and losses are constantly occurring and are not easy to control for given that the time resolution must be poor in order to gather sufficient mass to measure. However, during and between the 1/9/99 and 1/10/99 fog events the surrounding air mass seems to have remained reasonably constant, winds were typically light ($<3\,m\,s^{-1}$) and other nearby locations experienced similar foggy conditions. Data from the second event on 1/10/99 are not presented due to frontal passage during post-fog aerosol sampling. Selected species' equivalent air concentrations, the product of the LWC and the aqueous-phase concentrations, in the fog may suggest if advection and/or entrainment of particles, additional solute mass, or incorporation of cleaner air masses occurred. For example, in a closed system total fog solute equivalent air concentrations should remain constant throughout, although if calculations are derived from observations from multi-stage collectors the relative contributions from each fraction may shift. Increasing equivalent air concentrations indicate incorporation of new solute mass to the system and decreasing concentrations, removal. Fog water concentrations are often expressed as equivalent air concentrations as changes in LWC can mask changes in underlying solute concentrations. For fogs where sedimentation leads to species removal, the equivalent air concentrations are typically lower at the end of the event (Fuzzi et al., 1988). Equivalent air concentrations for all species were calculated for the CASCC2 and both fractions of the sf-CASCC for the Davis fog events. Results for NO_3^- are shown in Fig. 3 (NH_4^+ and $SO_4^=$ follow similar patterns and only NO_3^- is shown in the interests of space). Only the 12/18/98 and 1/11/99 fog events show the classic temporal evolution—increasing concentrations during fog development as

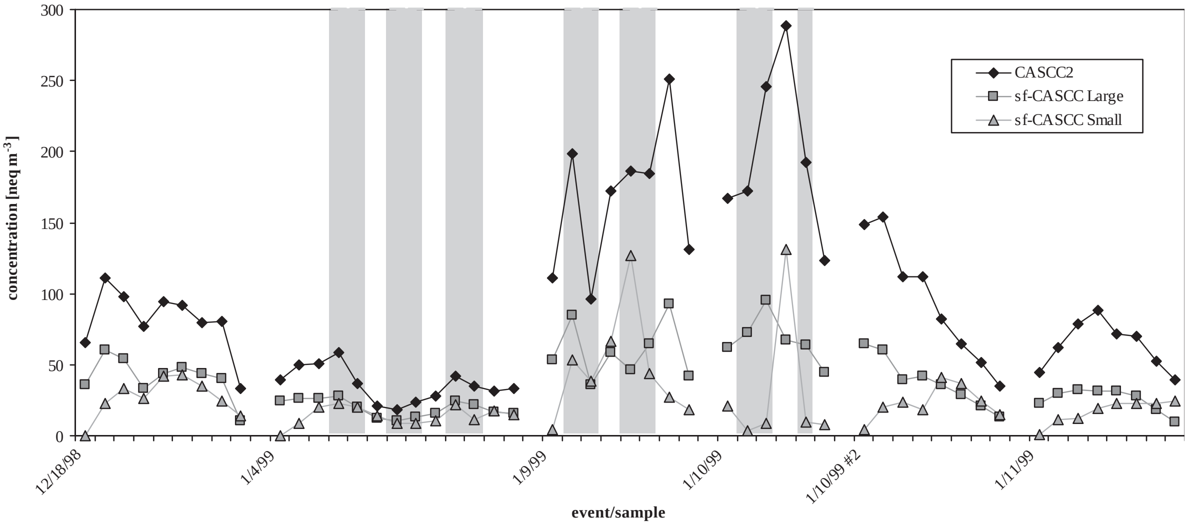

Fig. 3. Equivalent air concentrations for nitrate by collector, all Davis fog events. Units are nano-equivalents m^{-3} air. The gray-shaded areas correspond to CSU 5-Stage sample sets.

solute mass is incorporated, peaking during maturation and then decreasing during dissipation. The relative increase in the sf-CASCC small drop fraction contribution as the drops evaporate at the end of the cycle and large drop fraction domination at the start of these events are consistent with this interpretation. Although the 1/4/99 and 1/10/99 ♯2 event concentrations do not show all these same classic elements, the equivalent air concentrations of nitrate across the two sf-CASCC fractions are smoothly varying similar to observations during the first and last events. In sharp contrast, during both the 1/9/99 and 1/10/99 fog events there are abrupt increases in the small sf-CASCC drop fraction equivalent air concentrations (e.g. a factor between observations of ≈ 1.6 to >10 for nitrate) not explainable by concurrent decreases in the large fraction solute mass. This suggests advection/entrainment of new mass into the smallest drops in the fog system are partly responsible for the observations. While consistent differences were observed between the CASCC2 bulk and the weighted-average "bulk" concentrations from the multi-stage collectors for low LWC ($<0.1\,\mathrm{g\,m^{-3}}$) sampling periods (Moore et al., 2002), the CASCC2 concentration patterns largely mirror the sum of the two sf-CASCC fractions.

4. Fog drop deposition

Gravitational settling of fog drops is an important feature in the lifecycle of fogs (Roach et al., 1976). Field and modeling studies indicate that settling and the wet removal of solutes dissolved in the drops is a very important atmospheric loss mechanism for these species (Lillis et al., 1999; Bott, 1991; Pandis and Seinfeld, 1989; Waldman and Hoffmann, 1987). Pollutant deposition rates for particular species can be elevated relative to their clear sky/dry values (Waldman and Hoffmann, 1987).

In lieu of measuring species flux, investigators have typically measured the water flux and then multiplied that by the bulk cloud composition (e.g. Fuzzi et al., 1991; Pierson et al., 1987; among others). However, if both the composition of the drops and their removal rate by sedimentation vary with size, this method may yield a misleading result. That approach can be evaluated by calculating the deposition velocity ($v_{\mathrm{d},i}$) for species i:

$$v_{\mathrm{d},i} = F_i / C_i, \tag{1}$$

where F_i is the measured material flux collected on the deposition plates, and C_i is the concentration measured at a reference height. C_i is typically derived from the observed bulk cloud chemistry.

The assumptions implicit in this approach for calculating the deposition velocity include: no evaporation/condensation, the deposition plates represent a "realistic" surface, the measured composition is not affected by drop mixing prior to collection, and no ground sources exist for the species of interest. CASCC2 data are used for consistency with earlier measurements. While Eq. (1) is for total flux, the assumption that all deposition is via sedimentation is not uniformly true. However, several studies indicate that sedimentation dominates turbulent deposition for Davis-type conditions with low wind speeds, large drops, and low surface roughness (Thalmann et al., 2002; Fitzjarrald and Lala, 1986; Dollard and Unsworth, 1983). As a result, the flat surrogate surface Teflon plates used for

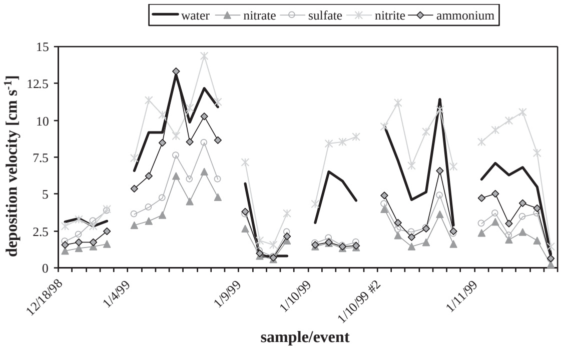

Fig. 4. Calculated deposition velocity for select species and water, all Davis fog events. Error bars (not shown) are described in the text.

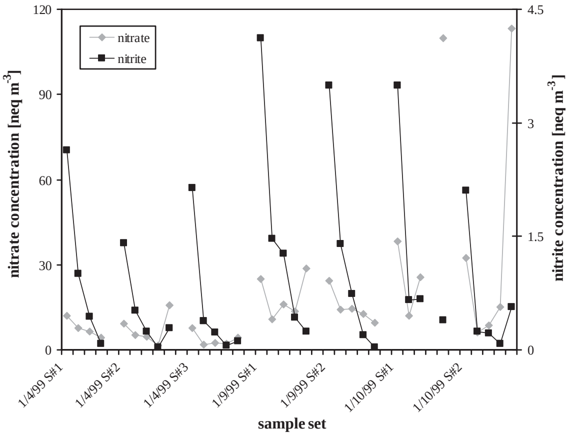

Fig. 5. Equivalent nitrate and nitrite air concentrations in the CSU 5-Stage, all Davis data. Sampling period times are in the text. Error bars (not shown) include analytical and LWC uncertainties and are generally < 15%. The plot is from left-to-right: Stage 1 (largest) to Stage 5 (smallest) for each sample set. No 1/4/99 S♯1 Stage 4 and 1/10/99 S♯1 Stage 5 data are available.

the measurements are expected to yield reasonable estimates of deposition fluxes for water and solutes.

Fig. 4 shows the calculated deposition velocities based upon measurements of species flux, the revised LWC data, and bulk cloud water composition for all of the Davis samples. Nitrite, water, ammonium, nitrate and sulfate are shown. Collett et al. (2001) previously reported deposition velocities for these fog events for water, ammonium, nitrate and sulfate, but not nitrite, using LWC values from the PVM-100 only. As several authors have suggested that $HONO_{(g)}$ has a ground source in some conditions (Stutz et al., 2002; Harrison et al., 1996), if not these specifically, this should be considered the net nitrite deposition velocity.

The deposition velocity for nitrite (mean 7.5 cm s^{-1}, range 1.5–14.3 cm s^{-1}) generally exceeds that for water (mean 6.0 cm s^{-1}, range 0.8–13.1 cm s^{-1}). In contrast, ammonium (mean 4.1 cm s^{-1}, range 0.6–13.4 cm s^{-1}) has a somewhat lower deposition velocity than water, followed by sulfate (mean 3.3, range 0.6–8.5 cm s^{-1}) and nitrate (mean 2.4 cm s^{-1}, range 0.2–6.5 cm s^{-1}). Similar results for nitrate, ammonium and sulfate have been found previously in other Central Valley locations and are a function of the species' solubility and their interaction with the fog (Collett et al., 2001, 1998; Waldman and Hoffmann, 1987). HONO's dry deposition velocity is estimated to be on the order of 2 cm s^{-1} (Harrison et al., 1996), the same as HNO_3 (1–5 + cm s^{-1}) (Wesely and Hicks, 2000), and values < 1 cm s^{-1} have been observed in some conditions (Harrison et al., 1996). The occult deposition velocity calculated here suggests that fog water can provide an important net removal mechanism for NO_2^- from the atmosphere to the ground. These results illustrate that the assumption that fog water and solutes have the same deposition velocity may be in error by as much as a factor of five in some instances.

The trend of deposition velocities (nitrite > water > ammonium > sulfate > nitrate) is consistent with their drop size-dependent composition observed in the fog (Moore et al., this issue). Nitrite concentrations tended to be elevated in large fog drops. In contrast, nitrate, sulfate and ammonium concentrations were relatively elevated in small fog drops, with nitrate exhibiting the largest relative difference. Examining equivalent air concentrations data for the CSU 5-Stage can provide further insight to these observations. The nitrate and nitrite equivalent air concentrations based upon all of the CSU 5-Stage samples sets are shown in Fig. 5. Nitrate is again used as a surrogate for ammonium and sulfate as the three important species have generally similar behavior. While Stage 1 and 5 nitrate concentrations can be roughly equal, most of the nitrate mass is in the smaller drops. Thus, nitrate's deposition velocity is lower than water's due to the differences in distribution. In the 1/10 data the highest small drop (Stage 5) concentrations observed correspond to the largest relative differences between the water and nitrate deposition velocities. In contrast, nitrite equivalent air concentrations are consistently elevated in the largest (Stage 1) drops. Time periods when proportionately more mass is found in the smaller drops (the 1/4/99 event in particular) correspond to the periods where nitrite's deposition velocity is closer to or less than water's. This suggests that the gradient in nitrite concentrations observed in the CSU 5-Stage on 1/4/99 (Moore et al., this issue) may not be a sampling artifact, but may instead reflect real variations. The CSU 5-Stage data are useful to help explain the observed deposition velocities. The relative advantage of the CSU 5-Stage in separating collected drops by size compared to the sf-CASCC is evident in these events when solute masses are concentrated at the extremes of the drop distribution.

5. Gas/liquid equilibria in fog

Measurements of fog water concentrations from the three collectors and gas-phase measurements (where available) are used to explore whether or not gas/liquid equilibrium exists for several important species. Phase equilibria are investigated for the NH_4^+/NH_3, NO_3^-/HNO_3 and NO_2^-/HONO systems. In the discussion that follows, the use of the terms "super-saturation" and "sub-saturation" are with respect to the gas-phase concentrations of the species indicated, and do not refer to the lack of equilibrium with respect to water vapor for drops in fog.

Species that partition between the gas- and aqueous-phase may not be at phase equilibrium for many reasons. Disequilibrium may be caused by rapid variations in LWC, whether measurements are at the center or edge of the cloud (related to LWC variations), species' solubility, liquid-phase reactions, and associated mass transport limitations (Leriche et al., 2000; Voisin et al., 2000; Audiffren et al., 1998; Ricci et al., 1998; Winiwarter et al., 1994; Heintzenberg, 1992; Pandis and Seinfeld, 1992; Winiwarter et al., 1992). Organic films in polluted fogs may also limit the ability of species to achieve equilibrium across the gas/liquid/organic interface (Facchini et al., 1992b). Species that are less soluble are less likely to become "trapped" in rapidly growing or evaporating drops and thus are more likely to be at equilibrium (Bower et al., 1991). A modeling study has also suggested that vertical in-cloud gas-phase concentration gradients may cause apparent deviations from equilibrium in the composition of the settling drops (Bott and Carmichael, 1993). Finally, the act of sampling drops while mixing them together may also introduce a supersaturation in H^+ which will affect partitioning of many of the weak acids and bases of interest (Winiwarter et al., 1992; Pandis and Seinfeld, 1991; Perdue and Beck, 1988). Drops of the same size may not be composed of the same species due to the external mixture of cloud condensation nuclei that they form on. Therefore, these mixing effects may occur even if drop separation by size between cloud water collector stages is improved as in the CSU 5-Stage.

Several field studies have investigated gas-/aqueous-phase equilibria for species such as low molecular weight organic acids, ammonia, nitric acid, formaldehyde, H_2O_2, and S(IV) (Ricci et al., 1998; Laj et al., 1997; Munger et al., 1995, 1989; Facchini et al., 1992a b). While it is not always known why deviations from phase equilibrium occur, pH-, LWC- and drop size-dependent compositions have all been suggested as possible reasons in addition to time-integrated sampling, the occurrence of in-cloud reactions—particularly between S(IV) and H_2O_2—and the presence of species absorbed to colloidal particles in the drop. Species may exhibit equilibrium in some conditions and not in others (e.g. Munger et al., 1995, 1989).

There are different calculation techniques to assess if aqueous-phase species are in equilibrium with the gas-phase. One approach used here is to calculate the theoretical (equilibrium) and actual species distribution factors which are used to derive the respective mole fractions in the aqueous-phase. The ratio of actual to theoretical aqueous-phase mole fractions is >1 if there is aqueous-phase super-saturation, and <1 if sub-saturation occurs. Following Seinfeld and Pandis (1998, p. 343)

$$f_{\mathrm{act}} = \frac{c_{\mathrm{aq}}}{c_{\mathrm{g}}}, \tag{2}$$

$$f_{\mathrm{equil}} = H_{\mathrm{eff}} RT(\mathrm{LWC}), \tag{3}$$

and

$$X_j = \frac{f_j}{1+f_j}, \tag{4}$$

where the index j is for either "act" (measured) or "equil" (theoretical), f is the distribution factor, H_{eff} is the effective pH-dependent Henry's Law constant, R is the universal gas constant, T is temperature, LWC is liquid water content and X is the aqueous-phase mole fraction. The ammonium/ammonia system partitions more strongly to the aqueous-phase as pH decreases and LWC increases. Different behavior is observed for NO_2^-/HONO as partitioning shifts towards the aqueous phase as both pH and LWC increase. In Davis fogs, both systems are expected to be partitioned between the gas and aqueous phases due to the high pH and relatively low LWC. For both HONO and NH_3 the effective Henry's constants are $>10^5\,\mathrm{M\,atm^{-1}}$ indicating high solubility in these conditions. The NO_3^-/HNO_3 system is expected to partition virtually entirely into the drops ($H_{\mathrm{eff}} > 10^{12}\,\mathrm{M\,atm^{-1}}$).

Fig. 6 shows the partitioning for the ammonium/ammonia system. The ammonium concentrations used are the weighted event average. Although within the measurement uncertainty, the results suggest that there might be a tendency for a slight sub-saturation in the aqueous-phase for the CASCC2 and large sf-CASCC drop fraction accompanied by a slight super-saturation in the small drop fraction (using the derived "bulk" concentrations from the sf-CASCC in lieu of the CASCC2 data does not change this interpretation). Rapid variations on the scale of minutes in cloud LWC can result in correspondingly rapid changes in drop volume, assuming as a simple case that no new drops are formed or lost. As mentioned above (Winiwarter et al., 1992), this can result in a lack of equilibrium between phases for the (non-water) species of interest as these species may re-partition at a slower rate than the water volume fluctuates. The magnitude and persistence of

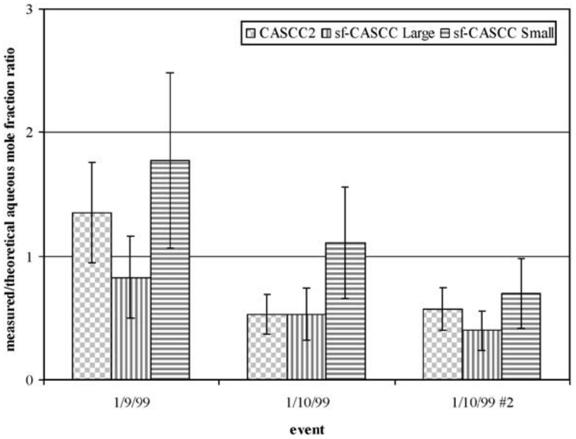

Fig. 6. Measured vs. theoretical (equilibrium) aqueous-phase ammonium mole fraction by collector and event. Gas-phase concentrations assumed to be the event mean. Error bars shown represent propagated uncertainty in analytical results, temperature, Henry's Law coefficient, and LWC and denuder data. Calculations suggest the error is on the order of ± 30% (CASCC2) and ± 40% (sf-CASCC).

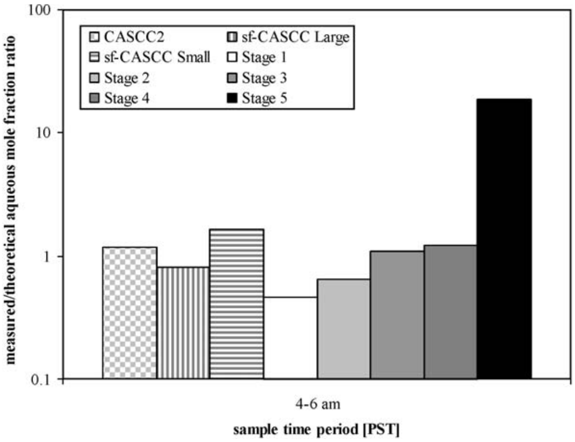

Fig. 7. Measured vs. theoretical (equilibrium) aqueous-phase ammonium mole fraction by collector/collector stage for 1/9/99, 4–6 a.m. Gas-phase concentration assumed to be the event mean. CSU 5-Stage data presented from the largest drop fraction (Stage 1) to the smallest (Stage 5) (left-to-right). The error is difficult to quantify and is not shown. Please note the use of the log scale.

these species' disequilibrium depend upon both the changes in water volume and the properties of the partitioning species. Some recent modeling work using conditions similar to the Davis fogs for the simple case described above, and featuring possible rapid in-cloud LWC variations, suggests that LWC variations could be responsible for some of the drop size dependence observed. Slight, temporary deviations from equilibrium between phases for the species tracked occurred (Kim, 2001). Owing to the problems with the PVM-100's response to large drops, only limited high time resolution LWC data are available, but calculations using the data available suggest that the LWC effect may not be large consistent with the model (Pandis and Seinfeld, 1992; Winiwarter et al., 1992). These model results, however, consider the instantaneous concentrations (not the sample average) and suggest that the NO_3^-/HNO_3 system should also be out-of-equilibrium which the data do not indicate. The large aqueous-phase nitrate and near-detection limit HNO_3 concentrations suggest the NO_3^-/HNO_3 system is in equilibrium within the measurement uncertainty (not shown). Pandis and Seinfeld (1991) suggest that up to a factor of 3 super-saturation may occur due to drop mixing. The calculation procedure outlined in Pandis and Seinfeld (1991) was used for both some sf-CASCC sample pairs and CSU 5-Stage sample sets. The results (not shown) suggested little effect, although the authors point out that the calculations can be misleading if drop separation between stages is poor.

The CSU 5-Stage data are again useful for further interpretation. The CSU 5-Stage's drop fractions should be subject to less mixing than the other collectors. The CSU 5-Stage data suggest that the super-saturation indicated by the small sf-CASCC drop fraction results during the low LWC ($<0.1\,g\,m^{-3}$) events on 1/9 and 1/10 may be real. Fig. 7 is an extreme example, but all time periods show similar results. The super-saturation shown for the smallest drops (Stage 5) in the 4–6 a. m. sampling period is $>$ 15 and exceeds the factor of 3 that might come from mixing. For the CSU 5-Stage data, the Stage 5 fraction result suggests substantial super-saturation, decreasing to values generally near equilibrium for the larger drops. Allowing for reasonable NH_3 fluctuations around the event mean for the individual sampling periods does not alter this finding.

These results can be interpreted similarly to those in a recent Po Valley study: drops are formed on ammoniated particles and dilute much faster than ammonia can outgas (Ricci et al., 1998). The range of sub-/super-saturation values is very low compared to other studies (up to orders of magnitude have been observed (e.g. Ricci et al., 1998; Facchini et al., 1992a), but that may be collector dependent.

$HONO_{(g)}$ was not directly measured. Evidence for the presence of HONO was found in all denuders that operated at least in part during night-time conditions; no "daylight-only" denuders contained any measurable nitrite. $HONO_{(g)}$'s source is controversial, but heterogeneous and/or surface reactions are likely to be involved and some studies have suggested that water (or at least water vapor) is important (Lammel and Cape, 1996; Calvert et al., 1994; Notholt et al., 1992). Nitrite was not observed in the Davis aerosol, where our detection limit was approximately $30\,ng\,m^{-3}$. Minor amounts of aerosol nitrite have been previously reported

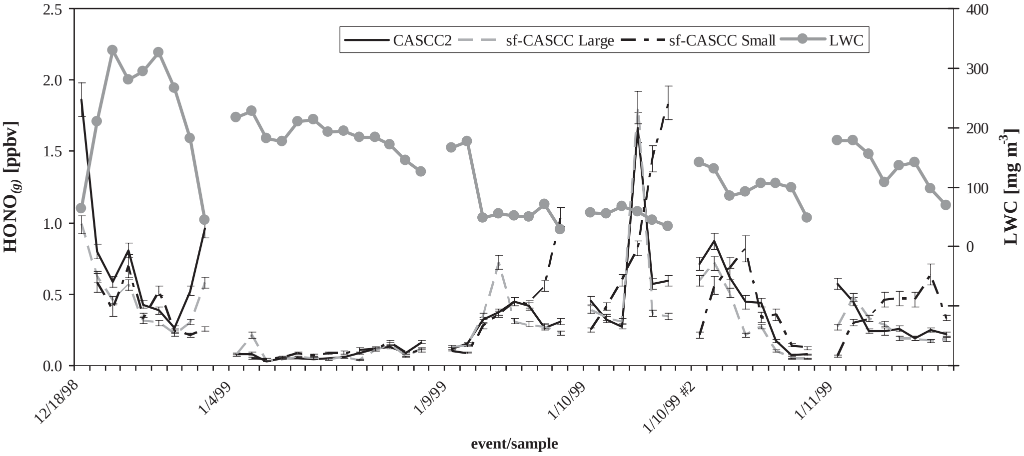

Fig. 8. Derived $HONO_{(g)}$ concentrations by collector by event/sample and observed liquid water content (axis offset for clarity). Error bars shown represent propagated uncertainty in analytical results, temperature, Henry's Law coefficient and liquid water content.

in the region (Zhang et al., 2002). In the absence of data, however, the nitrite observed in the drops is assumed to come entirely from gaseous HONO, subject to the same limitations suggested by Cape et al. (1992) in their study.

$HONO_{(g)}$ concentrations during the Davis fog events are estimated using Henry's law for the CASCC2 and sf-CASCC drop fractions. If the nitrite concentrations are at relative equilibrium, each collector/collector fraction should produce the same gas-phase concentration (Fig. 8). In general, the three collectors/collector fractions agree well and up to 2 ppbv HONO is estimated, which is consistent with previously observed in-fog values (Harrison et al., 1996; Lammel and Cape, 1996) and in-cloud nitrite concentrations persist after sunrise. Daytime foggy conditions have been associated with relatively elevated $HONO_{(g)}$ concentrations (Alicke et al., 2002; Harrison et al., 1996). Neglecting any role fog drops may play in the production of $HONO_{(g)}$, their ability to act as an $HONO_{(g)}$ reservoir prior to evaporation will perturb the timing of the surge in atmospheric OH from its photolysis, shifting it later in the day. Additionally, nitrite photolysis within the drops themselves can be an important source of OH and radicals in the aqueous-phase (Anastasio and McGregor, 2001) where oxidation of additional species, such as organics, may also occur. There are noticeable deviations from relative equilibrium; however, particularly at the beginning and end of events. As Fig. 8 shows, this is often associated with very low LWC ($<0.05\,g\,m^{-3}$). There is some association between differences in the derived $HONO_{(g)}$ concentrations and diverging pH values between the large and small sf-CASCC drop fractions, but not always, and the presence of differences appears to be independent of sunlight. Overall, gas-phase HONO concentrations derived from the sf-CASCC large and small drop fraction concentrations were approximately 88% and 129%, respectively, of the CASCC2 bulk-derived concentration, although a broad range of values was observed. In general, these results suggest relative phase equilibrium is largely achieved within the measurement uncertainty. As with the earlier results presented for ammonia/ammonium, the 1 h time resolution available for the collectors may average over some of the true atmospheric variation. We estimate the reported gas-phase HONO concentrations are probably accurate to within ± 30%. These results suggest that the role of fogs or clouds in winter-time polluted atmospheres, particularly with respect to impacts on gas- and aqueous-phase oxidation processes should be further investigated.

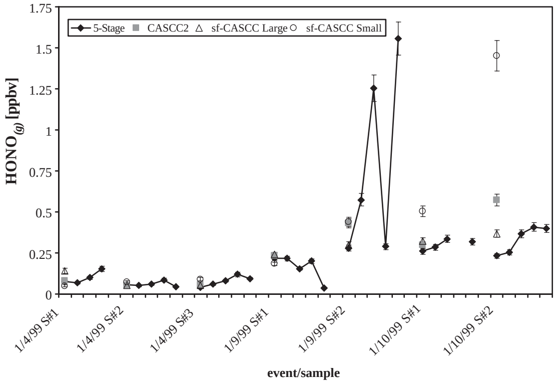

Fig. 9. Derived $HONO_{(g)}$ concentrations by collector/collector stage during all CSU 5-Stage sampling periods, plotted similarly to Fig. 5.

Concurrent CSU 5-Stage-derived HONO data for all seven sample sets are shown in Fig. 9 and again provide additional information to interpret these results. Nitrite is often higher in the CSU 5-Stage, occasionally even relatively elevated in the smallest drops, but this is balanced by changes in the pH to yield generally similar nitrous acid concentrations to the other collectors. Where the LWC exceeds 0.1 g m^{-3} (the first four sample periods shown), the CSU 5-Stage agreement with the other data is reasonably good. When the LWC is low and agreement is poor between the Caltech collectors (e.g. 2nd sample on 1/10/99), the CSU 5-Stage data can still yield consistent results across all stages.

There may be several explanations why the derived HONO concentrations from each collector/collector fraction vary and relative equilibrium between phases is not observed. Our data can suggest only relative super- or sub-saturation. The disagreement between the collectors may result from a combination of low LWC, rapidly changing microphysical conditions, and the possible influence of organic species, particulate nitrite or competing reactions. The cause or causes in each instance appear to vary. Inhomogeneities in the sampled fog water cannot entirely be ruled out, nor can sampling artifacts. However, the effect of sampling artifacts from handling ought to be magnified in the CSU 5-Stage due to the relatively reduced collected water volumes, yet the derived concentrations across the stages agree well with the exception of the first sample set on 1/9/99 (Fig. 9). Mixing between drops of different size and composition should have a more noticeable effect in the CASCC2 and sf-CASCC than the CSU 5-Stage, but, again good agreement between all collectors/collector fractions can be achieved. The relatively large drops and high pH of the Davis fogs suggest mass transport limitations may be a factor. Soluble and insoluble organic compounds were observed in these fogs (Herckes et al., 2002) which may also inhibit mass transfer in/to the drops. However, in the absence of an inhibiting organic phase on the drops, the characteristic times for interfacial mass transport, aqueous- and gas-phase diffusion are in the worst case drop (50 μm in diameter, pH = 7.5) at most a few minutes for these conditions. Competing reactions in or on the drops could account for some deviations from relative equilibrium. A first-order reaction rate constant in the worst case drops would only have to exceed 0.0002 s^{-1} for mass transfer limitations to occur, but this value rapidly increases with both decreasing pH and drop size. Further, good agreement between fractions is observed during the 12/18/98 and 1/4/99 events when relatively larger drops are present compared to the smaller drop size distributions inferred for the 1/9/99 event. Particulate nitrite, if present at near detection limit concentrations and evenly distributed across the aerosol size spectrum, might disproportionately influence the smaller drops, particularly in the low LWC conditions. Assuming no vertical concentration gradient, this should be discernible in the CSU 5-Stage and the sf-CASCC small fraction simultaneously. This is not, however, uniformly evident in the CSU 5-Stage results. If the low LWC data are associated with rapidly varying microphysical conditions as at the start and end of the fog events, small drops will grow/evaporate more rapidly than large drops. This may account for some of the variability in the observations, particularly in the first CSU 5-Stage sample set from 1/9/99. These results suggest that low LWC conditions in fog, which are often observed, may yield inter-collector performance variability.

6. Closing discussion and conclusions

Fogs are very inhomogeneous on both temporal and spatial scales. We are making integrated measurements at relatively long sampling intervals in a rapidly changing environment. The time scale of physical fluctuations in the fog is much smaller than our ability to sample fog drop chemistry (2 h in the CSU 5-Stage and deposition plates, 1 h in the Caltech collectors). Based on deposition flux data obtained in the fog using an exposed scale (Collett et al., 2001), there appears to be an approximately 20 min periodicity in the observed water flux. This periodicity has been observed at varying time scales previously in fogs (e.g. Wendisch et al., 1998; Roach et al., 1976). In future studies temporal resolution may be improved by minimizing the number of analyses performed on the collected material which would make smaller collected water volumes acceptable. Further, particular emphasis should be placed on high temporal resolution sampling during low LWC fog events needed to investigate some of the questions raised in this study. Changes in the denuder system to quantitatively observe HONO are recommended as is improved temporal resolution in both the denuder and MOUDI measurements. It may be useful to operate more than one MOUDI side-by-side to increase the likelihood of measuring species in addition to nitrate, sulfate and ammonium at concentrations above the MDL.

Nitrogen species dominate the Davis fogs. The relative change in the size-resolved aerosol distribution between fogs is consistent with the loss of larger aerosol particles by activation into drops and subsequent deposition during fog. The temporal evolution of the equivalent air concentrations suggest that only some of the fogs exhibit the classic onset, mature and dissipation stages, and indicates that entrainment may have been a factor in others as well. The derived deposition velocities illustrate how important a removal mechanism for many species occult deposition is and the importance of directly measuring species flux. Nitrite is removed relatively faster than water in fog due to its preponderance in the largest drops. Virtually all of the nitric acid gas appears to have partitioned to the drops as equilibrium predicts, but ammonium/ammonia may not be at equilibrium in this environment. Gas-phase nitrous acid appears to be present in concentrations up to 2 ppbv during the fog events. For much of the campaign, the data suggest that equilibrium partitioning between NO_2^- and $HONO_{(g)}$ may be largely achieved within the measurement uncertainty. Low LWC sampling periods, in particular, appear to be associated with deviations from equilibrium in this system. Simultaneous operation of multiple drop size-resolving collectors helps to understand and interpret the observed fog processing. The CSU 5-Stage data, although limited, help to interpret these features due to the collector's improved measurements of drop size-dependent composition. The real variation in drop size-dependent chemical composition is likely greater than can be observed in the CSU 5-Stage (see Moore, 2002), although the CSU 5-Stage yields more realistic observations than either the single- or two-stage collectors.

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