FOG, CLOUD, AND DEW CHEMISTRY

Final Report

for

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1800 15th. St.
Sacramento, California 95814

Eric Fujita, Project Manager

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Prof. Michael R. Hoffmann

Principal Investigator

Environmental Engineering Science
W. M. Keck Laboratories
California Institute of Technology
Pasadena, California 91125

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EXECUTIVE SUMMARY

Background

In our previous studies, we had established that fog- and cloudwater in Southern California was consistently acidic (pH 1.7 to 4.0). As a continuation of that work, we have expanded both the intensity of our sampling effort and the detail of our chemical characterization.

The principal objectives of this research project were:

1. to develop refined instrumentation for the collection of cloud- and fogwater and to automate the fogwater collection process,

2. to carry out multiple site sampling and analysis of aerosol, gases, clouds, and fogs in the Los Angeles (LA) coastal zone, in the Riverside area, at elevated sites in the Los Angeles basin, in the Santa Barbara Channel area, and in the southern San Joaquin Valley,

3. to characterize dew chemistry,

4. and to correlate cloud— and fogwater data with standard air quality measurements.

Our first principal objective was to construct an automated fogwater collector, which would allow fogwater monitoring to be done more conveniently. This objective has been achieved; the development effort resulted in the granting of a United States Patent (No. ---1---
4,697,462) for the design of a fog- and cloudwater collector with an associated automatic collection and field storage system. The results of this work are presented in Chapters 1, 2, and 3 of the final report.

With the aid of automated collectors, we were able to determine the spatial and temporal variation of fog/cloud chemistry within large areas of fog occurrence. The second array of principal objectives were all achieved; detailed reports of these efforts are given in Chapters 4, 5, 6, 7, 12, 13, 14, 15, 16, 17, and 18 of the final report.

After an preliminary investigation of dew chemistry in a variety of locations in the LA Basin, further investigations were halted because the relative importance of dew as a depositional pathway for atmospheric acidity was established to be negligible. Other investigators have confirmed our assessment of the importance of dew chemistry/deposition relative to dry deposition, wet deposition, and fog-derived deposition. This work has been reported in the Ph.D. thesis of J. M. Waldman (Ph.D., Caltech, 1986). With the encouragement and approval of the CARB project officers, we shifted our focus from dew to a preliminary investigation of the cloudwater chemistry in the Sierra Nevada Mountains. Results of this work are reported in Chapter 10.

Research objective number 4 was explored for fogs in the San Joaquin Valley, in the Los Angeles basin, and in the Santa Barbara Channel area. Using the techniques of multiple linear regression, a significant correlation was observed between the average nighttime cloud- and fogwater loadings of H+ and NO3− and the maximum levels of O3, NOx, and NO recorded during the preceding days. Regression equations that were obtained were found to be reliable for predicting fogwater loadings of H+ and NO3−.

Regions of high fog/cloud frequency that have been studied in detail include the Los Angeles coastal area, where previous work suggests that the highest acidities occur. the Riverside–San Bernardino area, which is subject to fog during the height of the smog season. the Santa Barbara Channel area, and the Southern San Joaquin Valley, in which the occurrence of highly acidic fogs is held in check by substantial ammonia emissions.
limited ventilation documented by previous tracer studies of the Santa Barbara Channel and presence of fog and high humidity there suggest that rapid S(IV) (i.e. total SO\textsubscript{2} aqueous) oxidation in the Channel results in highly acidic fog. As predicted pH values in the vicinity of the Santa Barbara Channel have been found to range from 2.1 to 3.5. Preliminary investigations of mountain-top cloud chemistry were performed in Sequoia National Park. In conjunction with fog and cloud sampling, we have performed more detailed measurements of deposition during fog.

In addition to determining the inorganic speciation of fog and cloudwater, we have determined the role of carboxylic and sulfonic acids in fog acidification. Our previous work has shown the covariance of very high levels of S(IV) and formaldehyde, suggesting the presence of aldehyde–S(IV) adducts (i.e. sulfonic acids). We have determined quantitatively the higher aldehydes and a series of dicarbonyls such as glyoxal, methyl glyoxal and biacetyl; furthermore we have identified a variety of sulfonic acid salts formed by reaction of S(IV) with aldehydes in the droplet phase.

Overview

Clouds, fogs, and haze aerosols are subjected to the same chemical processes because of their physical similarities. For example, cloud- and fogwater droplets are found in the size range of 2 to 50 \textmu m, while deliquescent haze aerosol will be in the range of 0.01 to 1 \textmu m. On the other hand, raindrops are approximately 100 times larger than cloud and fog water droplets (0.1 to 3 mm). However, a more important determinant of aqueous-phase chemistry within the droplets is the liquid water content (LWC); values of LWC range from 0.1 to 1.0 g m\textsuperscript{3} in clouds, from 0.01 to 0.5 g m\textsuperscript{3} in fogs, and from 10 to 100 \mu g m\textsuperscript{3} in haze aerosols. The presence of condensation nuclei, which are composed of both soluble and insoluble materials, is essential for the formation of atmospheric water droplets. Accretion or evaporation of water to or from the condensation nuclei or droplet is forced by the difference between the ambient and
local humidities, and is affected by the droplet surface tension and the chemical potential of
the solutes in the liquid phase. During droplet growth, the temperature within the droplet
differs from the ambient temperature due to the release of latent heat, which in turn depends
upon the instantaneous growth rate.

Fog and cloud droplets are highly effective at scavenging certain gases and particles
present in the atmosphere. The overall fraction of material incorporated into fog droplets
depends upon nucleation scavenging and gas transfer. The initial chemical speciation may be
altered by in situ chemical transformations and subsequent droplet-phase scavenging. The
total concentration of species \( i \) in a parcel of air is given by

\[
[C_i]_T = [C_i]_L + P_{C_i}(RT)^{-1} + [C_i]_a
\]

where \([C_i]_T\) is the total concentration of \( C_i \) (mol m\(^{-3}\)) in the atmosphere, \([C_i]_L\) is the
concentration of \( C_i \) in the droplet phase in units of mol m\(^{-3}\) \(([C_i]_L = L[C_i])\), \([C_i]_g\) is the
concentration (mol m\(^{-3}\)) of \( C_i \) in the gas phase \(([C_i]_g = P_{C_i}(RT)^{-1})\), and \([C_i]_a\) is the
concentration of \( C_i \) in the non-activated aerosol. \( R \) is the universal gas constant (atm m\(^3\)
\( \text{mol}^{-1} \text{K}^{-1} \)) and \( T \) is temperature in degrees K.

Fog- and cloudwater often have extremely low pH values (e.g. 1.7 < pH < 4) and
extremely high concentrations of sulfate (1 to 20 mM), nitrate (1 to 20 mM), ammonium ion
(0.1 to 20 mM) and trace metals (1 to 1000 \( \mu \text{M}\)). Waldman et al. (1) and Munger et al. (2)
have summarized concentrations reported for fogs and clouds sampled in California and
elsewhere around the world. Of special interest are the high values observed for \( \text{SO}_4^{2-}, \text{NO}_3^-\),
\( \text{S(IV)}, \text{CH}_2\text{O}, \text{Fe}, \text{Mn}, \text{Pb} \) and \( \text{Cu} \) in fogwater. These values and their time-dependent
changes indicate that fogs and clouds provide a very reactive environment for the
accumulation of \( \text{HNO}_3 \) and \( \text{H}_2\text{SO}_4 \). Concomitant incorporation of \( \text{NH}_3 \) gas and calcareous dust
into the droplet phase neutralizes some of the acidity. In the pH domain typically encountered
in fogs and clouds (pH 2–7), absorption of \( \text{SO}_2(g), \text{HNO}_3(g), \text{H}_2\text{O}_2(g) \), and \( \text{NH}_3(g) \) is
thermodynamically favorable because of their relatively high Henry's Law coefficients.

Of the metals commonly found in atmospheric water droplets, Fe, Mn and Cu are expected to be potential catalysts for the in situ oxidation of S(IV) with molecular oxygen. Iron and Mn have been found in concentrations as high as 400 µM and 15 µM in fog (1-7). Model calculations indicate that metal-catalyzed autoxidations along with oxidation by H₂O₂, O₃, and OH may contribute significantly to the overall sulfate formation rate in atmospheric droplets, particularly in the range of Fe and Mn concentrations observed in urban fog (8-10).

In addition to transition metal ions a wide variety of other chemical constituents have been found in clouds. For example, carbonyl compounds, such as aldehydes and ketones, have been found to influence liquid-phase sulfur dioxide chemistry through their reactions with SO₂ to form stable α-hydroxyalkanesulfonates. Field measurements have detected formaldehyde at concentrations of greater than 100 µM in fog- and cloudwater samples collected in Southern California (11-13). The concentrations of glyoxal and methylglyoxal occasionally approach or exceed that of CH₂O. In addition to each one of the aldehydes present the corresponding carboxylic acid has been observed, although formic and acetic acid dominate the low molecular weight carboxylic acids. They are found in concentrations as high as 100 µM.

The presence of CH₂O and H₂O₂ (2 - 50 µM) in conjunction with S(IV) at levels higher than those predicted by gas/liquid solubility equilibria suggests that α-hydroxymethanesulfonate (HMS, HOCH₂SO₃) production stabilizes a fraction of S(IV) with respect to oxidation. Equilibrium calculations using available thermodynamic and kinetic data for the reaction of SO₂ and CH₂O demonstrate that elevated concentrations of S(IV) in fog water cannot be achieved without consideration of sulfonic acid production, HORHSO₅ (11). Munger et al. (13) have identified and quantified HMSA using ion-pairing chromatography. Other S(IV) adducts which have been observed in cloudwater droplets include those formed with glyoxal, methylglyoxal, acetaldehyde, and hydroxyacetaldehyde.

Jacob et al. (14-17) have systematically characterized the interaction of H₂SO₄, HNO₃, NH₃ and in fog, aerosol, and the gas phase. The observed spatial patterns of concentrations
were shown to closely reflect the distribution of SO$_2$, NO$_x$, and NH$_3$ emissions within well-defined regions. Furthermore, they (16) have compared field data for the H$_2$SO$_4$–HNO$_3$–NH$_3$ system with thermodynamic calculations of the aerosol composition. Close agreement has been found between field measurements and theoretical predictions. Their field studies have shown that typical wintertime conversion rates for S(IV) in fogs were about 5% hr$^{-1}$ and about 1% hr$^{-1}$ in haze aerosol.

Gas-phase reactions of SO$_2$ with ozone (O$_3$), hydroxyl radical (OH·), and hydroperoxyl radical (HO$_2$·) are too slow to account for observed rates of sulfate production in humid urban atmospheres (18–19) and in wave clouds (20). Consequently, the catalytic autoxidation of SO$_2$ in deliquescent haze aerosol and hydrometeors appears to be a viable non-photolytic pathway for the rapid formation of sulfuric acid in humid atmospheres (21–26). In addition, hydrogen peroxide and ozone have been established as important aqueous-phase oxidants of dissolved SO$_2$ (26). Oxidation by H$_2$O$_2$ seems to be most favorable under low pH conditions (pH < 4) because of a rapid rate of reaction and a negative pH-dependence that favors the facile conversion of HSO$_3$ to sulfate. In comparison, metal-catalyzed autoxidation and oxidation of S(IV) with O$_3$ tend to proceed more slowly with decreasing pH (27).

Limiting factors in the autoxidation pathways are the total concentration of the active metal catalyst and its equilibrium speciation as a function of pH. Los Angeles fog water contains high concentrations of iron, manganese, copper, nickel and lead (3,4,6,7). Of these metals, Fe, Mn and Cu are expected to be the most effective catalysts for the reaction of S(IV) with molecular oxygen (25–27). Model calculations indicate that metal-catalyzed autoxidations may contribute significantly to the overall sulfate formation rate in atmospheric droplets, particularly in the range of Fe and Mn concentrations observed in urban fog. However, the composition of the precursor haze aerosol or cloud condensation nuclei will determine to a large extent the observed chemical speciation of the droplet phase.

Chameides (28) has predicted based on model calculations that aqueous-phase free radical pathways can contribute substantially to the generation of acidity via the in situ
oxidation of S(IV) and HCHO to S(VI) and formic acid, respectively. The principal oxidants of S(IV) as identified by Chameides were H₂O₂, O₃, ·OH, and HO₂⁻. Parameters found to affect the S(IV) to S(VI) conversion rate were the accommodation coefficient for the reactive species of interest, the liquid water content, and the ambient levels of SO₂ and HNO₃. Seigneur and Saxena (29) have predicted that gas-phase hydrocarbon chemistry will dominate ·OH chemistry (i.e., aqueous-phase ·OH chemistry due to radical scavenging appears to be inconsequential). While Mozurkewich (30) argues that nitrate radical, NO₃, is unlikely to play an important role in the nighttime chemistry of a cloud because of its low Henry's Law constant (~ 0.03 M atm⁻²). Jacob (31) has shown that radical pathways are very important for the chemistry of remote clouds in terms of formate production and in terms of the buildup of peroxymonosulfuric acid, a S(VI)–peroxide intermediate of high oxidation potential (32).

Aqueous-phase pathways for the production of nitric acid are relatively minor contributors to nitrate accumulation in the droplet phase because of the low Henry's Law constants for NO₂ and NO and because of second–order reaction kinetics with respect to [NO₂] (33–34). The pathways for S(IV) transformation involve reactions with H₂O₂, O₃, O₂ (Fe³⁺ and Mn²⁺ catalyzed), ·OH, HONO, CH₃OOH, CH₃CO₂H, PAN, HO₂⁻, HCHO, and soot.

Summary of Major Observations

1. A new collector that has a lower minimum size cutoff and a higher sampling rate was designed, built, and utilized in several field sampling programs. An additional advantage of this collector, the Caltech Active Strand Collector (CASC), is the absence of external moving parts, making it safer for unattended operation, and the capability of being connected to an automatic sampling system. (vide infra, Daube, Jr., et al., United States Patent Number 4,697,462, 1987; Chapters 1 & 2)
2. A side-by-side comparison of the previous collector, the Rotating Arm Collector (RAC) and the CASC was performed. In thin fog conditions the ratio of collection rates (CASC/RAC) exceeded the theoretical value. Because the CASC has a lower lower size cut than the RAC, it samples a greater fraction of the droplet spectrum. In thin fogs a significant fraction of the droplets may be in a size range that is only collected by the the CASC. If droplet evaporation on the strands were occurring the opposite trend would be observed. (Chapter 3)

3. Comparison of the chemical composition of the CASC and RAC samples indicated a possible size-dependent variation in droplet composition. RAC samples, which contain a greater proportion of large droplets, were enriched in Na⁺, Mg²⁺, Ca²⁺, and Cl⁻. These ions are associated with soil dust and sea salt, both of which are found in large aerosol. Concentrations of NO₃⁻, SO₄²⁻, and NH₄⁺, which make up the smaller aerosol, showed no difference between the two samplers. These data suggest that large condensation nuclei lead to large droplets, thus the RAC samples, which contain a greater proportion of large drops, have higher concentrations of ions associated with the large aerosol. (Chapter 3)

4. Droplet deposition during fog has been shown to play an important role in the enhancement of acidic deposition. During stagnation episodes, pollutant removal from the Southern San Joaquin Valley requires at least 5 days, while the enhancement of deposition by fog formation leads to pollutant lifetimes on the order of 6–12 hours. Thus, in an environment characterized by flat, open landscape and low wind speed, droplet sedimentation can be the dominant removal mechanism of pollutants during prolonged stagnation episodes with fog. (Chapters 4, 5, 6 & 7)
5. Deposition rates for major species were 5 to 20 times greater during fogs than during non-foggy periods. Sulfate deposition rates ($V_d$) during fog ranged from 0.5 to 2 cm s$^{-1}$ with a median value of 1.0 cm s$^{-1}$. Similar enhancements were observed for nitrate deposition. Ten hours of fog-induced deposition was found to be comparable to the deposition resulting from 10 cm of rainfall. (Chapter 7)

6. A systematic characterization of the atmospheric $\text{H}_2\text{SO}_4$-$\text{HNO}_3$-$\text{NH}_3$ system was conducted in the fogwater, the aerosol, and the gas phase at a network of site in the San Joaquin Valley. The concept of atmospheric alkalinity has been developed to interpret observed concentrations in terms of the buffering capacity of the atmosphere with respect to inputs of strong acids. The major components of fogwater alkalinity were found to be the conjugate bases of weak organic acids such as acetic acid, formic acid, lactic acid, and propionic acid. Secondary production of strong acids, $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$, under stagnant conditions resulted in a complete titration of available alkalinity at the sites farthest from $\text{NH}_3$ sources. Steady-state $\text{SO}_2$ conversion rates of 0.4 to 1.1 % hr$^{-1}$ were observed. Fog did not appear to enhance the conversion of $\text{NO}_x$. (vide infra, Jacob et al., *J. Geophys. Res.* 91, 1073–1088, 1986; Chapter 4).

7. Concentrations of $\text{HNO}_3$ and $\text{NH}_3$ were determined in the field under both foggy and non-foggy conditions, simultaneously with aerosol and fogwater composition. Observed concentrations were found to compare favorably with thermodynamic model predictions. In this model, the equilibrium composition was calculated by minimizing the Gibbs free energy of a system composed of the following species: in the gas phase $\text{H}_2\text{SO}_4$, $\text{HNO}_3$ and $\text{NH}_3$; in the aqueous phase $\text{H}^+$, $\text{HSO}_4^-$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$, and $\text{NH}_4^+$; and the solid phases $\text{NH}_4\text{HSO}_4$, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, $(\text{NH}_4)_2\text{SO}_4$, $\text{NH}_4\text{NO}_3$, $(\text{NH}_4)_2\text{SO}_4\cdot 3\text{NH}_4\text{NO}_3$, and $(\text{NH}_4)_2\text{SO}_4\cdot 2\text{NH}_4\text{NO}_3$. (vide infra, Jacob et al., *J. Geophys. Res.* 91, 1089–1096, 1986; Chapter 5).
8. The fate of SO$_2$ emitted in the San Joaquin Valley under stagnant foggy conditions was determined by the release of an inert tracer and the concurrent monitoring of SO$_2$ and SO$_4^{2-}$ concentrations. At night, SO$_2$ was found to be trapped in a dense fog layer below a strong and persistent inversion base. Lack of ventilation led to the accumulation of SO$_2$ and sulfate in the atmosphere. The rate of oxidation of SO$_2$ to sulfate was determined to be $\sim 3$ % hr$^{-1}$. Production of acidity from the oxidation of SO$_2$ fully titrated the NH$_3$(g) present before the fog and led to a progressive drop of the fogwater pH. The tracer data indicated that about 40% of the air transported upslope in the afternoon was returned to the valley in the night-time drainage flow. (vide infra, Jacob et al., *Atmos. Environ.* 21, 1305–1314, 1987; Chapter 6)

9. Formaldehyde, formate, and acetate have been determined in fog and cloudwater at a number of locations in Southern California. Up to 190 µM formate and acetate was seen in samples from the San Joaquin Valley. HCHO concentrations as high as 500 µM have been observed. Fog from Riverside had maximum concentrations of 1500 and 500 µM formate and acetate while HCHO was as high as 380 µM. Average formate and acetate concentrations near Santa Barbara and San Pedro were in the range of 10 to 60 µM with HCHO ranging between 10 and 20 µM. High aqueous-phase concentrations of organic acids are observed either near sources where ambient levels are high or at sites where the cloudwater pH is high. (Chapters 11, 12 & 13)

10. Hydroxymethanesulfonate (HMS) has been determined to be an important chemical species in fog and cloud water. Concentrations of HMS as high as 300 µM have been observed. HMS was determined in fog water by a novel ion-pairing chromatographic method. HMS represents an important source of acidity for water droplets and a significant atmospheric reservoir for S(IV). (vide infra, Munger et al., *Science* 231.
11. Aldehydes in cloudwater samples have been analyzed by two independent methods. In the one case, dinitrophenylhydrazone derivatives were prepared and analyzed by HPLC on a C$_{18}$ column. In the second case, the aldehydes were derivatized with 3-methyl-2-benzothiazoline hydrazone and separated on a reversed-phase C$_{18}$ column. Using these methods we have detected substantial concentrations of formaldehyde, acetaldehyde, glyoxal, hydroxyacetaldehyde, and methylglyoxal. In addition, the biacetyl was observed at measurable concentrations. At San Pedro [HCHO] ranged from 14 to 62 µM, [CH$_3$CHO] ranged from 2 to 5 µM, [CHOCHO] ranged from 1 to 31 µM, and [CH$_3$COCHO] ranged from 5 to 27 µM. While at Riverside, [HCHO] ranged from 6 to 197 µM, [CHOCHO] ranged from 1 to 139 µM, and [CH$_3$COCHO] ranged from 1 to 108 µM. (Chapters 12, 13, 14)

12. Kinetic and thermodynamic data obtained for the addition of S(IV) species with several aldehydes, including benzaldehyde, glyoxal, methylglyoxal, acetaldehyde, hydroxyacetaldehyde, and glyoxylic acid, was used to predict their effectiveness as reservoirs for S(IV) in atmospheric water droplets. Equilibrium calculations in an open atmosphere indicate that hydroxyacetaldehyde, glyoxal, glyoxylic acid, and to a smaller extent, methylglyoxal, lead to potentially significant enrichment of S(IV) in the liquid phase, although HMS is an even better reservoir for S(IV). Scavenging of SO$_2$ from the gas-phase due to hydroxyalkylsulfonate formation becomes important at high liquid water contents, pH ≥ 5, and when an excess partial pressure of the aldehyde is present. The overall dissolution of RCHO and SO$_2$ into a droplet and the subsequent formation of the hydroxyalkylsulfonate, also results in a net increase in acidity, which in a weakly buffered solution, can be more than a unit drop in pH.
13. Acidic cloudwater was consistently observed in intercepted stratus collected along the Santa Barbara Channel coast. Ventura and Pt. Mugu, which are immediately adjacent to the coast, were the most acidic. Casitas Pass, which is further inland was somewhat less acidic. (Chapter 15)

14. Nitrate is equivalent to or slightly greater than sulfate in the Santa Barbara Channel intercepted stratus. The NO$_3^-$:SO$_4^{2-}$ ratio was found to be $\leq 2$. In contrast the ratio of NO$_x$ to SO$_2$ in local emissions and in the LA basin is $\geq 2$. (Chapter 15)

15. Fogwater collected at Riverside was highly concentrated. Ammonium concentrations ranged from 8 to 26 mN; NO$_3^-$ ranged from 6 to 29 mN; and SO$_4^{2-}$ ranged from 1.4 to 6.2 mN. (Chapter 14)

16. pH values in Riverside fogwater dropped to 2.3, despite the presence of excess NH$_3$ in the gas phase during the day. HNO$_3$ is the dominant acid. At night, reduced vertical mixing and drainage flows would isolate the sampling site from the NH$_3$ emission area. Continued production of HNO$_3$ via NO$_3^-$ and N$_2$O$_5$-pathways could then acidify the fog. Fog on the floor of the basin may still be in contact with the NH$_3$ emissions and would not be acidic. This mechanism implies that there could be a region of acidic fogwater on the slopes surrounding the Riverside/San Bernardino basin. (Chapter 14)

17. The preexisting aerosol is not completely scavenged by the fog forming at Riverside. Scavenging efficiencies computed from fogwater loading and concurrent or prior aerosol samples are typically $< 50\%$. These radiation fogs never achieve high enough supersaturations to activate all of the aerosol. (Chapter 14)
18. Cloudwater samples collected in Sequoia National Park varied widely in chemical composition, both within the course of one event and from one event to another. The pH of the samples ranged from 4.4 to 5.7. The most acidic sample was not the sample with the highest ionic loading, indicating the importance of the varying composition of the sample in determining its acidity. (Chapter 10)

19. Organic acids were seen to be important contributors to the overall composition of many of the samples collected in Sequoia National Park. In some instances the concentrations of formate and acetate were comparable to those of nitrate and sulfate. (Chapter 10)

20. The advance of cold fronts into the Park seems to lead to higher aerosol and gas-phase concentrations than would be seen under normal mountain-valley circulation patterns, particularly during the night and morning hours. The arrival of these increased concentrations prior to and during cloud impaction on the mountain slopes leads to higher cloudwater concentrations than would otherwise be expected. (Chapter 10)

21. A size-fractionating inlet on the Caltech Active Strand Collector was used to collect intercepted stratus on San Pedro Hill. Ions associated with soil dust and sea salt (Ca$^{2+}$, Mg$^{2+}$, and Na$^+$) were enriched in the large droplet fraction. The secondary aerosol ions (NH$_4^+$, SO$_4^{2-}$, and to some extent H$^+$) were enriched in the small droplet fraction. Ions that are associated with gas-phase species (HCl and HNO$_3$) showed mixed behavior. The concentrations of several components that exist partly in the gas phase (e.g. Cl$^-$, HCOOH, and CH$_3$COOH) appear to be independent of droplet size.
Multiple linear regression analysis has shown that $[H^+]$ in the droplet phase in the Santa Barbara Channel area, as an example, can be predicted by

$$[H^+]_{aq} = 29.2(O_3) + 33.8(NO_x) - 35.8(NO) - 157.1$$

where $[H^+]_{aq}$ is the average nightly cloudwater loading of $H^+$ expressed in neq m$^{-3}$ and $(O_3), (NO_x),$ and $(NO)$ are the maximum hourly gas-phase concentrations of $O_3, NO_x,$ and $NO,$ respectively, in parts per hundred million (pphm). The correlation coefficient for this relationship is 0.84. Similar equations are available for other components and for different locations.

Conclusions

1. Riverside California, which often has high pH fogwater and is near emission sources, had the highest concentrations of carbonyl compounds and organic acids reported to date in the literature. Low pH fogs (~2) can arise in the Riverside area due to downslope flow of polluted air that is depleted in ammonia.

2. The formation of hydroxymethanesulfonate (HMSA) contributes to high concentrations of CH$_2$O observed in fogwater.

3. Oxidation of aromatic hydrocarbons and ozonolysis of isoprene appear to be the two important sources of the dicarbonyl compounds found in fogs.

4. The pre-existing aerosol, which is the principal determinant of fogwater composition, is not completely scavenged by the radiation fogs due to the relatively low water supersaturation levels. High degrees of supersaturation are necessary to activate all of
the aerosol. Coastal stratus clouds are highly efficient scavengers of pre-existing aerosol.

5. Cloudwater is routinely acidic (pH \(\approx 3\)) in the Santa Barbara Channel area.

6. HCl is volatilized from sea-salt aerosol by exchange with HNO\(_3\); when clouds appear the HCl is rescavenged.

7. Sources for acidity in the Santa Barbara Channel appear to be the oxidation of local emissions of NO\(_x\) and SO\(_2\), or transport of polluted air from Los Angeles.

8. Some of the variability in cloudwater chemical composition can be explained by changes in cloud liquid water content. Changes in concentration can also occur during periods of relatively constant liquid water content. Removal by drizzle results in decreases in concentration. Wind shifts, enhanced turbulence, or entrainment from aloft may account for increases in concentration.

9. Differences in the composition of size-fractionated cloudwater samples indicate that large droplets are formed from sea salt and soil dust, which are large aerosol, and small droplets are formed on small secondary aerosol composed of primarily ammonium sulfate and ammonium nitrate.

10. Model calculations show that a reduction in sources of NH\(_3\) in the LA Basin will result in the production of uniformly acidic fogs with pH \(\approx 2\). This scenario could become a reality with the commercial and residential development of land in the Chino area. A similar situation exists in the Southern San Joaquin Valley.
Recommendations for Future Research

Two areas for future research are the size-dependence of droplet chemical composition, and turbulent mixing processes in cloud and fog layers. A size-fractionating inlet has been developed for use with the Caltech Active Strand Collector. Samples collected from one coastal stratus cloud event indicate that large droplets are derived from large sea-salt and soil-dust aerosol and small droplets are formed from secondary ammonium sulfate and nitrate aerosol. Future work should refine the size-fractionating inlet in order to provide a sharper size cut and verify the performance of the inlet. A comprehensive experiment to determine the size dependence of droplet composition would include size-fractionated aerosol sampling, measurement of aerosol and droplet size distributions, cloud liquid water content. An adequate means for determining liquid water content in ground-based sampling is not presently available. Gravimetric methods for LWC determination do not allow sufficient time resolution to follow fluctuations in LWC from due to the turbulence in the cloud. Other locations, with different aerosol characteristics need to be investigated.

Results presented here and results of other studies indicate that entrainment from aloft is an important factor controlling cloud and fog chemical composition. Formation of HNO₃ via the NO₂ + NO₃ → N₂O₅ reaction is likely in the inversion layer above the cloud or fog. The mountains surrounding the Riverside basin and the coastal mountains in Los Angeles and the Santa Barbara Channel are ideal sites to study this phenomenon. A comprehensive experiment to identify the role of above-cloud reaction and entrainment mixing would include a vertical array of aerosol, gas, and cloudwater samplers and meteorological instruments.

Publications

The points summarized above are discussed in detail in the relevant chapters of the main body of the report. The primary data collected as a part of this research has been
documented in the Appendices of the Ph.D. theses of J. M. Waldman (1986), D. J. Jacob (1985), and J. W. Munger (1989). Copies of these theses can be obtained for a nominal charge from University Microfilms in Ann Arbor, Michigan. In addition the following publications have resulted directly from research activity related to this contract:


Table 1. Fogwater Concentrations in Riverside

<table>
<thead>
<tr>
<th></th>
<th>Vol ml</th>
<th>pH</th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>µN</th>
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<tr>
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<td>8</td>
<td>8</td>
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<td>8</td>
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<td>362</td>
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<td>371</td>
<td>20100</td>
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<td>11096</td>
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<td>43</td>
<td>158</td>
<td>819</td>
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<td></td>
</tr>
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</table>

|                |        | µM  |     |      |      |      |     |      | g m⁻³ |
|----------------|--------|-----|-----|------|------|------|------|------|
| 28 February 1986 |      |     |     |      |      |      |     |      |
| N              | 4      | 4   | 4   | 4    | 4    | 4    | 4    | 4    |    |
| Minimum        | 16     | 4.24| 35  | 8340 | 106  | 23   | 130  | 6050 |    |
| Maximum        | 92     | 5.22| 64  | 18100| 209  | 55   | 384  | 13300|    |
| Avg vol wt     | 4.59   | 48  | 9588| 122  | 27   | 178  | 7050 |    |

|                |        |     |     |      |      |      |     |      | g m⁻³ |
|----------------|--------|-----|-----|------|------|------|------|
| 23 January 1986 |      |     |     |      |      |      |     |      |
| N              | 8      | 8   | 8   | 8    | 8    | 4    | 8   | 4    | 8  |
| Min            | 1430   | 13  | 165 | 0    | 106  | 56   | 49  | 0.90 |    |
| Max            | 3960   | 64  | 279 | 0    | 346  | 237  | 103 | 1.01 | 0.074 |
| Avg vol wt     | 1929   | 40  | 194 | 0    | —    | —    | 73  | 0.96 |    |

|                |        |     |     |      |      |      |     |      | g m⁻³ |
|----------------|--------|-----|-----|------|------|------|------|
| 28 February 1986 |      |     |     |      |      |      |     |      |
| N              | 4      | 4   | 4   | 4    | 4    | 4    | NA  | 4    |    |
| Min            | 1810   | 5   | 175 | 6    | 357  | 134  | NA  | 0.94 |    |
| Max            | 3660   | 15  | 370 | 25   | 576  | 267  | NA  | 0.97 |    |
| Avg vol wt     | 2096   | 11  | 221 | 14   | 444  | 163  | 0.95| 0.109|    |
Table 2. Cloudwater Composition Along the Santa Barbara Channel

**Laguna Peak Cloudwater 5 August – 14 August 1986**

| Vol ml | pH | Na⁺ | NH₄⁺ | Ca²⁺ | Mg²⁺ | Cl⁻ | NO₃⁻ | SO₄²⁻ | SO₄²⁻xs²⁻ | µN | S(IV)CH₂O | H₂O₂ | HFo | HAc | H⁺ | −/+ | LWC gm⁻³ |
|--------|----|-----|------|------|------|-----|------|-------|-----------|----|-----------|------|------|-----|-----|-----|-----|------|
| N      | 20 | 20  | 20   | 20   | 20   | 20  | 20   | 20    | 20        | 20 | 20        | 20   | 20   | 20   | 20  | 20  | 20  |
| Min    | 2.69 | 9   | 143  | 4    | 3    | 46  | 344  | 276   | 275       |    | 0.75      | 0.02 |      |      |     |     |     |
| Max    | 3.46 | 318 | 686  | 73   | 88   | 350 | 1410 | 1340   | 1335      |    | 1.57      | 0.39 |      |      |     |     |     |
| Avg    | 3.07 | 68  | 337  | 16   | 20   | 122 | 702  | 590    | 582       |    | 1.05      | 0.21 |      |      |     |     |     |
| Avgvol wt | 3.16 | 47  | 276  | 11   | 15   | 122 | 702  | 590    | 582       |    | 1.05      | 0.21 |      |      |     |     |     |

**Laguna Road Cloudwater 5 August – 14 August 1986**

| Vol ml | pH | Na⁺ | NH₄⁺ | Ca²⁺ | Mg²⁺ | Cl⁻ | NO₃⁻ | SO₄²⁻ | SO₄²⁻xs²⁻ | µN | S(IV)CH₂O | H₂O₂ | HFo | HAc | H⁺ | −/+ | LWC gm⁻³ |
|--------|----|-----|------|------|------|-----|------|-------|-----------|----|-----------|------|------|-----|-----|-----|-----|------|
| N      | 20 | 20  | 20   | 20   | 20   | 20  | 20   | 20    | 20        | 20 | 20        | 20   | 20   | 20   | 20  | 20  | 20  |
| Min    | 2.58 | 119 | 445  | 21   | 28   | 102 | 612  | 425   | 407       |    | 0.81      |      |     |     |     |     |     |
| Max    | 3.49 | 1070| 1780 | 162  | 247  | 758 | 2140 | 2630   | 2500      |    | 1.31      |      |     |     |     |     |     |
| Avg    | 3.06 | 367 | 857  | 65   | 90   | 325 | 1030 | 1000   | 956       |    | 1.03      |      |     |     |     |     |     |
| Avgvol wt | 3.12 | 319 | 807  | 59   | 79   | 299 | 926  | 860    | 822       |    | 1.02      |      |     |     |     |     |     |

- 20 -
### Ventura Hill Cloudwater 30 July – 14 August 1986

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<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>SO₄²⁻ xs *</th>
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<td>32</td>
<td>32</td>
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<td>74</td>
<td>405</td>
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<td>104</td>
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<th>HFO</th>
<th>HAC</th>
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<th>LWC μM g⁻¹ m⁻³</th>
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### Casitas Pass Cloudwater 31 July – 14 August 1986

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<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
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<td>149</td>
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<th>H₂O₂</th>
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<th>HAC</th>
<th>H⁺</th>
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<td>7</td>
<td>4</td>
<td>19</td>
<td>7</td>
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SO₄²⁻ xs * = Excess Sulfate = Total Sulfate – Marine Sulfate
Table 3. Fogwater Concentrations at Elevated Sites in the Los Angeles Basin

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<th>V(mL)</th>
<th>pH</th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>CH₂O</th>
<th>LWC</th>
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<tr>
<td></td>
<td></td>
<td>µM</td>
<td>µM</td>
<td>µM</td>
<td>µM</td>
<td>µM</td>
<td>µM</td>
<td>µM</td>
<td>µM</td>
<td>g m⁻³</td>
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**San Pedro Hill 1987**

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<th>pH</th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>CH₂O</th>
<th>LWC</th>
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<td>44</td>
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<td>28</td>
<td>39</td>
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<td>736</td>
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**Henninger Flats 1987**

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<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>CH₂O</th>
<th>LWC</th>
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* RCOOH = [RCOOH] + [RCO₂]
Table 4. Fogwater Concentrations in the San Joaquin Valley

**Bakersfield 1984**

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<tr>
<th>pH Range</th>
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<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>HFo</th>
<th>LWC</th>
</tr>
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<tbody>
<tr>
<td>N</td>
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<td>16</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Avg</td>
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<td>33</td>
<td>122</td>
<td>819</td>
<td>2070</td>
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**McKittrick 1984**

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<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>HFo</th>
<th>LWC</th>
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**Buttonwillow 1984**

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<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>HFo</th>
<th>LWC</th>
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**Visalia 1984**

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<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>HFo</th>
<th>LWC</th>
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<tbody>
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<td>13</td>
<td>13</td>
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<tr>
<td>Avg</td>
<td>5.5–7.2</td>
<td>6</td>
<td>1080</td>
<td>17</td>
<td>2</td>
<td>115</td>
<td>341</td>
<td>265</td>
<td>53</td>
</tr>
</tbody>
</table>
CHEMISTRY OF A FOGWATER DROPLET

Figure 1. The chemistry of a fogwater droplet is indicated schematically. Important chemical processes involve a multiphasic system that includes solid, liquid, and gas phases.
Figure 2. A schematic diagram of the automatic fogwater collection system. Details are provide in Chapter 1.
Figure 3. A frequency distribution of formaldehyde concentrations observed in Santa Barbara Channel cloudwater at four different locations. Results of the cloudwater study conducted in the Santa Barbara Channel are discussed in detail in Chapter 15.
Figure 4. A frequency distribution for pH values in Santa Barbara Channel cloudwater at three locations. Details are provided in Chapter 15.
Figure 5. A concentration vs. time profile for hydrogen peroxide concentration as a function of time in Santa Barbara Channel cloudwater collected at La Jolla Peak. Detailed results of the cloudwater study conducted in the Santa Barbara Channel are provided in Chapter 15.
Figure 6. Streamlines calculated for the prevailing winds recorded during the morning of 24 July 1985 during a period of heavy stratus cloud impaction along the coast. The streamlines indicate that a portion of the Los Angeles air mass transported out to sea at night can be transported north into the Santa Barbara Channel. The chemical composition of the cloudwater at elevated sites along the coast is characteristic of LA cloudwater.
Figure 7. Average nightly cloudwater loadings (solid line) of H⁺ predicted using maximum hourly O₃, NO, and NOₓ concentrations observed the preceding day, and the actual observations at Ventura for 6 nights during the summer of 1986.
Figure 8. Average nightly cloudwater loadings (solid line) of NO$_3^-$ predicted using maximum hourly O$_3$, NO, and NO$_x$ concentrations observed the preceding day and the actual observations at Ventura for 6 nights during the summer of 1986.
References


A cloud water collector is disclosed comprised of a sampler duct having a plurality of spaced Teflon strands, in the form of screens, mounted across the conduit at an acute angle facing the open inlet of the conduit. Droplets in a cloud sample are drawn into the conduit by a fan located at the back end of the conduit, impact upon the Teflon strands and are drawn down to the lower ends of the strands, where they drop and the accumulated droplets are diverted to a sample bottle for collection. The cloud water collector can be automated to collect a plurality of successive cloud water samples by an automated sampler containing a reservoir into which cloud water obtained in the cloud water collector is discharged. A motor-driven turntable is provided which holds a plurality of sample bottles. When the reservoir is filled to a predetermined volume, apparatus, such as a liquid level sensor, actuates a valve to open and discharge the liquid sample from the reservoir into one of the bottles at a filling station on the turntable. The valve then closes and the turntable rotates to index the next bottle beneath the reservoir at the filling station, and the operation is repeated to fill the latter bottle. When all of the bottles on the turntable have been filled, the indexing mechanism is deactivated and liquid accumulating in the reservoir is diverted to an overflow bottle.
ACTIVE CLOUDWATER COLLECTOR

Inventors: Bruce C. Daube, Jr.; Richard C. Flagan; Michael R. Hoffmann, all of Pasadena, Calif.

Assignee: California Institute of Technology, Pasadena, Calif.

Filed: May 27, 1986

ABSTRACT

A cloud water collector is disclosed comprised of a sampler duct having a plurality of spaced Teflon strands, in the form of screens, mounted across the conduit at an acute angle facing the open inlet of the conduit. Droplets in a cloud sample are drawn into the conduit by a fan located at the back end of the conduit, impact upon the Teflon strands and are drawn down to the lower ends of the strands, where they drop and the accumulated droplets are diverted to a sample bottle for collection. The cloud water collector can be automated to collect a plurality of successive cloud water samples by an automated sampler containing a reservoir into which cloud water obtained in the cloud water collector is discharged. A motor-driven turntable is provided which holds a plurality of sample bottles. When the reservoir is filled to a predetermined volume, apparatus, such as a liquid level sensor, actuates a valve to open and discharge the liquid sample from the reservoir into one of the bottles at a filling station on the turntable. The valve then closes and the turntable rotates to index the next bottle beneath the reservoir at the filling station, and the operation is repeated to fill the latter bottle. When all of the bottles on the turntable have been filled, the indexing mechanism is deactivated and liquid accumulating in the reservoir is diverted to an overflow bottle.

25 Claims, 17 Drawing Figures
ACTIVE CLOUDWATER COLLECTOR

BACKGROUND OF THE INVENTION

This invention relates to the collection of fog water or cloud water and, more particularly, to the collection of cloud water by a device wherein cloud droplets impact upon Teflon strands and are funneled into a sample bottle.

Under supersaturated conditions in the atmosphere, fog droplets form by activation of condensation nuclei and rapidly grow to diameters of 1 to about 100 microns. Recent reports of extremely high acidities in fogs, and clouds intercepting mountain slopes, have raised concern regarding related environmental consequences. Air quality control agencies in areas exposed to acidic fog have expressed the need to establish networks of sites monitoring the chemical composition of fog on a routine basis.

Various types of fog water collectors have been designed, including use of a filter medium to capture the water on impaction and dripping from large obstacles, such as sails.

U.S. Pat. No. 3,889,532 discloses apparatus for collecting fog water consisting of a slotted rotatable tube. The tube is rotated, and fog droplets are collected by impaction on the tube. Centrifugal force causes the water to flow outward toward the ends of the tube where it is collected in small vials. However, the device of this patent presents safety problems and is not suitable for automation.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improved cloud water collector which efficiently collects fog droplets in the 1 to 100 micron diameter range.

Another object of the invention is the provision of a cloud water collector of the above type capable of preserving the size and chemical composition of fog droplets through all stages of collection.

A still further object is to provide a cloud water collector which rapidly collects relatively large amounts of liquid cloud water for wet chemical analysis.

Yet, another object is to provide a cloud water collector which is inexpensive to construct, is reliable and requires minimal maintenance.

Another object is the provision of an efficient cloud water collector which can be automated and including means for automating such collector.

A still further object is to provide an automated sampler, which is particularly useful in combination with the above-noted cloud water collector, or which can be used for collection of rain water samples.

According to the invention, there is provided a cloud water collector comprised of a sampler duct, e.g., in the form of a square box, open at both ends, and having a fan at the back of the duct. The fan draws the cloud through the sampler from the front of the duct, and the droplets in the cloud are impacted on Teflon (polytetrafluoroethylene or a copolymer of tetrafluoroethylene and hexafluoropropylene) strands or filaments which are strung in the form of a screen on a frame. The screen formed of the Teflon strands is inclined at an acute angle, preferably about 35° from vertical, facing the front of the duct.

The droplets in the cloud impacting upon the Teflon strands of the screen are drawn down by both the air drag and by gravity to the bottom of the screen where the water droplets accumulate and are diverted to a sample bottle, and the collected bottle of water is then analyzed chemically.

In preferred practice, the Teflon strand diameter, the spacing of the strands forming the screen, and the angle of the screen have values which provide efficient and rapid collection of fog droplets in the 1 to 100 micron size range while avoiding collection of the sub-micron aerosol particles. Also, in preferred practice, a honeycomb element is provided between the fan and the screen of Teflon strands, to straighten the flow of the sample cloud through the duct and provide uniform flow of the cloud sample across the duct and through the Teflon screen, to improve the performance of the collector.

The cloud water collector of the invention is easily constructed, inexpensive, and operates in a reliable manner.

The cloud water collector of the invention can be modified for automating the device so as to automatically collect successive cloud water samples. The automating means comprises a motor-driven turntable which holds a plurality of sample bottles. The cloud water sample provided by the cloud water collector is discharged into a reservoir having a liquid level sensor. When the reservoir is filled to the predetermined level, the sensor actuates a valve to open same and discharge the sample from the reservoir into one of the bottles on the turntable. The valve closes and the turntable then rotates to index the next bottle beneath the reservoir and the operation is repeated to fill the latter bottle with additional sample cloud water provided by the cloud water collector.

Alternatively, a timer can be employed instead of a liquid level sensor, which actuates a valve to discharge the cloud water sample from the reservoir into the bottle below the reservoir, when a pre-set time interval has elapsed. If desired, a combination of liquid level sensing and timer means can be employed, as described in greater detail below.

The automation device, per se, can also be employed for automatically collecting rain water samples instead of cloud water samples. When so employed, rain water is collected in a funnel and then directed to the reservoir from which it is automatically discharged into the sample bottles in the manner noted above.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more clearly understood by reference to the preferred embodiments set forth hereinafter, taken in conjunction with the accompanying drawings, wherein:

FIG. 1 is a side elevational view of a preferred cloud water collector according to the invention;

FIG. 1a is an enlarged elevational view of the front portion of the device of FIG. 1, showing the inclined screens formed of Teflon strands for collecting cloud water droplets;

FIG. 2 is a front view of the device of FIG. 1, taken on line 2--2 of FIG. 1, with the Teflon screens removed;

FIG. 3 is a rear view of the device of FIG. 1, taken on line 3--3 of FIG. 1, with the fan removed;

FIG. 4 is an elevational view of one of the screens of Teflon strands shown in FIG. 1a;

FIG. 4a is a side view of the Teflon screen of FIG. 4;
FIG. 5 is a plan view taken on line 5—5 of FIG. 1, showing the trough for cloud water sample collections; FIG. 6 is a section taken on line 6—6 of FIG. 5; FIG. 7 is a detail illustrating the means connected to the trough of FIG. 6 for discharging cloud water collected in the trough of FIG. 6, into a sample bottle; FIG. 8 is an adapter inlet which can be connected to the front of the cloud water collector of FIG. 1, which prevents the larger rain droplets from entering the device; FIG. 9 is a top view of the adapter inlet of FIG. 8; FIG. 10 is a front elevation of the automated sampler employed in conjunction with the cloud water collector of FIGS. 1—9; FIG. 11 is a detailed front elevation view of the carousel assembly for supporting the sample bottles, of FIG. 10; FIG. 12 is another detail of the sampler device of FIG. 1, showing the collector reservoir and overflow device employed in conjunction therewith; FIG. 13 is a plan view of the carousel or turntable of FIG. 11; FIG. 14 is a block diagram of the associated elements for operating the automated sampler of FIG. 10; and FIG. 15 illustrates use of the automated sampler of FIG. 10 for collecting rain water samples.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIGS. 1, 2 and 3 of the drawings, numeral 20 indicates a cloud water collector according to the invention, comprising an outer housing 21 having a front section 22 and a rear section 24, the front being open at 26 and the back of the collector being open at 28. The housing of collector 20 is in the form of a box having an essentially square cross-section, the rear section 24 of the collector being flared outwardly as indicated at 29 to accommodate a fan or blower 30 in a rear portion 32. The front and rear sections are provided with flanges 25 which are connected by bolts 27.

The outer housing 21 of the cloud water collector is preferably comprised of a clear poly (methyl methacrylate) resin (Plexiglas). Other clear inert plastics can be employed, such as polypropylene or polyethylene. However, the latter two materials tend to degrade in sunlight over a period of time.

Viewing also FIG. 1a, a series of three screens 34, each formed of two parallel rows of Teflon strands or filaments, and described in greater detail below, are mounted and inclined at an acute angle in the front section 22 of the collector, adjacent the open front end 26 thereof. A honeycomb element 36 is mounted across substantially the central portion of the collector between the front and rear sections 22 and 24 thereof. The fan 30 is mounted on a bracket 38 which is suitably bolted at 40 to a support member 42 mounted on the back 28 of the collector.

Now referring to FIGS. 1a, 4 and 4a, the screens 34 are each formed of a rectangular frame 43 comprised of two stainless steel upper and lower rods 44, preferably Teflon coated, suitably fastened at their ends to opposite side bars 46. Stiffener webs 45 are positioned across frame 43 adjacent the rods 44 at the top and bottom of the frame and are suitably welded at 49 to the opposite side bars 46. The rods 44 are threaded at 47 to received a Teflon strand 48 which is wound around the rods 44 in a vertical direction along the entire width of the screen extending from one side bar 46 to the opposite side bar. It has been found that in order to obtain efficient collection of fog droplets of a size ranging from 1 to 100 microns in diameter, and particularly of droplets in the range of about 5 to about 30 microns, the main portion of fog droplets which impact and collect on the Teflon strands, a preferred diameter of the Teflon strands ranges from about 0.015" to about 0.025", an optimum strand diameter being 0.020".

The spacing between adjacent strands of the filament 48, and hence the spacing between the threads 47 receiving the strands, is preferably between 0.06" and 0.08", optimally about 0.070".

It is preferred to minimize the size or diameter of the Teflon filament while still maintaining it sufficiently large so that it is strong and durable and does not break over a long period of use. The space between adjacent strands mounted on the rods 44 of the frame 43 should be sufficiently large to permit free flow of the cloud water sample through the screen while permitting efficient impaction of fog droplets from the flow of the cloud sample, on the Teflon filaments. Referring to FIG. 1a, it will be noted that each of the screens 34 is comprised of two parallel rows 50 of the Teflon strands 48 mounted on the opposite rods 44.

Referring now to FIGS. 1 and 1a, the Teflon screens 34 are mounted at an acute angle, most particularly at an angle of 35° to the direction of the incoming flow of the cloud sample introduced through inlet 26. For this purpose, grooves 52 are provided in the opposite side walls 54 of the front section 22 of the collector, such grooves being inclined at a 35° angle to accommodate the side bars 46 of each of the Teflon screens 34 mounted in parallel inclined relation at such angle in the front section of the collector. It will be seen that in the present embodiment, three collector screens 34 are employed, mounted parallel to each other, and in closely spaced relation within the front section of the collector. The frames 43 of the screens are suitably fastened at 56 and 58 in brackets 60 and 62 mounted respectively in the top 64 and bottom 66 of the front section of the collector.

In the embodiment illustrated in FIGS. 1 and 1a employing three Teflon screens 34, since there are two rows of Teflon strands 50 for each screen, there is a total of six rows of Teflon strands in the three screen arrangements shown. In such an arrangement, with Teflon strands of the optimum diameter of 0.020" and a spacing of 0.070", the first row of strands on the first screen 34 facing the inlet 26 samples about 28% of the incoming cloud sample flow, and when all six rows of strands formed by the three screens are included, such six rows sample about 86% of the total air. While it is preferred not to employ more than three Teflon screens 34, only one or two of such screens can be employed if it is desired to slow the collection rate down.

Although the optimum angle of inclination of the screens is 35°, as noted above, the angle of the Teflon screens can range from about 30° to about 40°. Inclining the screens at such angles, particularly the optimum angle of 35°, prevents resuspension in the air flow of fog droplets impacted onto the Teflon filaments. Further, once the droplets are collected on the strands, it is desirable that they be removed from the environment of the sample flow as quickly as possible to prevent evaporation. The above noted angle of inclination aids in obtaining rapid flow of the droplets down the filaments for collection as quickly as possible. A baffle 67 is provided and suitably connected to the top of the housing.
21 and formed of a front downwardly sloping portion 69 which directs the incoming cloud sample downwardly away from the upper structure of the frames 43 including the upper rods 44, and a rear upwardly sloping portion 71, which deflects the air stream passing through screens 34 upwardly across the conduit formed by housing 21.

Referring to FIGS. 5, 6 and 7, a trough 68 is provided across the bottom 66 of the front section 22 of the collector, such trough being inclined downwardly from the opposite side walls 54 of the front portion 22, to the center thereof, as indicated at 70, and terminating in a central discharge outlet 72. A funnel 74 is positioned in the discharge outlet, to which is connected one end of a tube 76, the opposite end of the tube being connected to 15 a sample bottle 78.

It will accordingly be seen that water droplets flowing down the Teflon filaments 48 of the six rows 50 of such strands provided by the three screens 34, will collect in the trough 68 and pass via the funnel 74 and 20 tube 76 into the collection bottle 78.

In operation, the fan 30, which can conveniently operate on 12-14 volt D.C. current, draws a sample cloud through the open front end 26 of the collector and into contact with the Teflon filaments 48 of the 25 screens, causing fog droplets to impact on and flow down the Teflon strands 48 of the screens 34. The velocity of flow can be of the order of about 9 meters per second. Droplets below a certain size pass between the Teflon filaments and are not collected thereon, while larger droplets above a certain size collect on the filaments. Droplets in the range of 1 to 100 microns diameter are efficiently collected and, particularly, droplets in the size window of 5 to 30 microns in diameter. While droplets of a size of about 3.8 microns can be collected at 50% efficiency, droplets of the order of 10 microns size and above can be collected at practically 100% efficiency.

The honeycomb element 36 in FIGS. 1 and 3 functions as a flow straightener, that is, it produces uniform flow of the cloud sample across the collector and removes swirls and reduces turbulence created by the fan. Although the honeycomb element can be omitted, the presence of the honeycomb element positioned between the Teflon screens 34 and the fan 30 substantially improves the performance of the device. This arrangement also aids in reducing contamination of the cloud sample and facilitates introduction of a clean, non-contaminated cloud sample into the collector for impingement with the Teflon strands 48.

When the cloud water collector described above is to be employed for sampling during rain, a rain adapter shown in FIGS. 8 and 9 is attached to the front open end 26 of the collector.

The rain adapter indicated at 80 is in the form of a clear plastic member, such as poly (methyl methacrylate) (Lucite), having a downwardly sloping, closed top 82 connected to opposite sides 84 of triangular shape, the lower edges of which terminate in a horizontally positioned, open bottom 86. The inner end of the rain adapter 80 terminates in a square conduit 88 having a flange 90 mounted around its inner end.

The rain adapter 80 can be mounted on the front 26 of the cloud water collector by attaching the flange 90 of the adapter to the flange 92 on the front of the cloud water collector, by suitable fasteners, such as bolts. During the rain, while the air flow sample is drawn in through the open lower end 86 of the adapter, as indicated by the arrow 94, and into the front section of the cloud water collector for impingement on the Teflon screens 34, in the normal manner of operation as noted above, the larger rain droplets impinge on the top 92 of the rain adapter and flow down the top, but such droplets have too much inertia and are unable to be drawn upwardly through the open bottom 86 and into the adapter and the collector, with the air or cloud sample to be collected.

Typical operating parameters for the cloud water collector of the invention described above and shown in the drawings are set forth in the following table:

<table>
<thead>
<tr>
<th>TABLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLOUD WATER COLLECTOR OPERATING PARAMETERS</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Strand dia., ( \mu \text{m} ) (in.)</td>
</tr>
<tr>
<td>Strand length, in (ft.)</td>
</tr>
<tr>
<td>Sampling flow, m( ^3 )/min. (cfm)</td>
</tr>
<tr>
<td># of rows of strand</td>
</tr>
<tr>
<td>Strand spacing, mm (in.)</td>
</tr>
<tr>
<td>% of air sampled, 1st row</td>
</tr>
<tr>
<td>% of air sampled, total</td>
</tr>
<tr>
<td>Total sampled flow, m( ^3 )/min.</td>
</tr>
<tr>
<td>50% size cut (theor.), ( \mu \text{m} )</td>
</tr>
<tr>
<td>Stokes number (10 fl-Di droplets), mVmin.</td>
</tr>
<tr>
<td>Inlet velocity, m/s</td>
</tr>
<tr>
<td>Velocity @ strands, m/s (MPH)</td>
</tr>
<tr>
<td>Coll. rate in 0.5 g/m( ^3 ) fog, 10 ( \mu \text{m} ) droplets, ml/min.</td>
</tr>
<tr>
<td>Operating voltage, v.</td>
</tr>
</tbody>
</table>

The cloud water collector of the invention described above and illustrated in FIGS. 1 to 9 of the drawings can be operated manually so that when a sample bottle of cloud water liquid is filled, it is removed from the apparatus and another bottle is manually connected to the device for collecting another sample, and so on. However, it is often preferred to automate the device so that each sample bottle, when filled with cloud water liquid, is automatically removed from the device and a new bottle arranged in its place to collect the next sample. This permits the cloud water collector to be set up in the field and left to automatically collect the fog water samples, thus providing manpower savings.

Accordingly, there is described below and shown in FIGS. 10 to 14 of the drawings a preferred embodiment of a device which can be employed in conjunction with the cloud water collector described above for automating the collector and obtaining multiple samples of cloud water for chemical analysis.

Referring to FIGS. 10–13 of the drawings, numeral 100 is an automated sampler device, according to the invention, which can be employed in conjunction with the cloud water collector 20 of FIG. 1, for obtaining samples of cloud water collected in collector 20. Preferably, the automated sampler 100 is incorporated in a refrigerator 102 which aids in maintaining the chemical composition of the cloud water samples without change, for example, as a result of evaporation. However, it will be understood that the use of a refrigerator for the automated sampler hereof is not necessary.

When employing the automated sampler 100, the sample collection tube 76 of the cloud water collector, as seen in FIG. 7, is connected directly to a reservoir 104, which is arranged to discharge a predetermined volume of collected cloud water via a valve A sequentially into a plurality of large sample bottles 106, and via a valve B sequentially into a plurality of small sample bottles 108 supported on a turntable or carousel 110.
which is rotated by a shaft 112 connected to a central support block 114 attached to the center of the carousel by the fastener 116. The shaft 112 and central support block 114 are interconnected by a pair of oppositely disposed pins 113 on the shaft 112, which are received in oppositely disposed slots 115 in the lower portion of the support block 114. The shaft 112 and support block 114 are driven by a motor 118 through a worm gear 122 mounted in a centrally positioned frame 122. The shaft 112 and central support block 114 are received in a central aperture 126 of a support member 124 to maintain the carousel in a substantially central position during operation. The frame 122 is connected to the support member 124 by suitable fasteners (not shown), and hence, the support member supports the frame 122, motor 118 and carousel 110. The support member 124 is mounted at opposite ends on outer support blocks 129 attached to opposite side walls 131 of the refrigerator.

A series of large sample bottles 106 is mounted circumferentially adjacent the outer periphery of the carousel in a circular rack 128 supported on the carousel by support pins 130. The large bottles 106, e.g., of 60 ml capacity each.

There are also provided in the rack 128 three concentric circles of smaller holes 134 for receiving the small bottles 108, there being 20 of the small bottles 134 in each of the three concentric circles of holes, for receiving 20 of the small bottles 108, e.g., having a capacity of 8 ml each in the present embodiment.

It will accordingly be seen that at the sample bottle-filling station X, as shown in FIGS. 10 and 11, there will be one large sample bottle 106 and three oppositely disposed small bottles 108.

Referring to FIG. 12, an overflow line 136 is connected to the discharge conduit 138 from the bottom of reservoir 104, such overflow conduit discharging into an overflow bottle 140. A vent 142 is provided at the top of the reservoir 104. A liquid level sensor 144, in the form of a photoelectric cell, is provided to monitor a predetermined volume of cloud water received in the reservoir 104.

Now referring to FIGS. 10 and 11, an auxiliary line 146 is connected to the discharge conduit 138, a valve B being disposed in the discharge line 146, for actuation to fill three of the small bottles 108, simultaneously with actuation of valve A for filling one of the large bottles 106 at the filling station X. An air cylinder powered device 148 is arranged to actuate a sliding assembly 149 carrying three hypodermic needles 150 communicating with line 146. Each of the needles 150 has a fluid inlet 151 communicating with the line 146 and a vent tube 153. Each of such needles pierces a septum 152 which tops each of the small bottles 108 when the support assembly 149 is urged downwardly. The air powered assembly is actuated by the opening of valve A, while at the same time, the timer 154 actuates the valve B, to fill the large bottle 106 and the small bottles 108 simultaneously. During this filling operation of about 20 seconds, the timer 157 is in the “on” interval. The timer 157 then switches to the “off” interval again, closing valve A, while timer 154 closes valve B, to permit reservoir 104 to again be filled with sample liquid.

In a third mode of operation employing both the level sensor 144 and the timer 157, for actuating valve B, if either the time has elapsed as set by timer 157, for filling the reservoir 104 to a predetermined volume, or the collected volume of liquid as indicated by the level sensor 144 has been achieved, whichever occurs first, valve A will be opened by either the level sensor or the timer 157, to permit discharge of liquid into the large bottle 106, while at the same time simultaneously the timer 154 opens valve B to permit discharge of liquid sample into the small bottles 108, after which valves A and B are closed, as noted above, to permit repeated filling of the reservoir 104. This third mode of operation is preferred.

The automated sampler 100, when set up to collect cloud water samples in conjunction with the cloud water collector 20, operates as follows:

A fog detector indicated at 155, which is basically a miniature version of the cloud water collector 20, is actuated, and when fog is present, such fog detector collects a sample amount of the fog water and deposits it onto a resistance grid, indicated at X. A circuit (not shown) senses the charge on the resistance grid 156, due to the presence of the fog water, and trips a relay 158 which supplies power from power source 160 to the various components in the device, as noted below, including fan 30 of the cloud water collector 20.

Fog water collected in the cloud water collector 20 is discharged via tube 76 into the reservoir 104. According to one mode of operation, when the liquid sample collected in the reservoir 104 reaches a predetermined volume, as indicated by the level sensor 144, the sensor actuates the valve A to open same to discharge the liquid sample into the bottle 106 at the fill station X. Simultaneously, with the opening of valve A, a timer indicated at 154 opens valve B to discharge liquid from reservoir 104 via hypodermic needles 150 into each of the three small sample bottles 108 at station X. In one example of operation, valve B remains open for about 5 seconds to discharge a total of 15 ml of sample liquid (5 ml per bottle) in the three small 8 ml bottles 108. During this same period of time, sample liquid flows from reservoir 104 into the large 60 ml sample bottle 106. The timer 154 then closes valve B. However, valve A remains open to discharge the remainder of the liquid in reservoir into the large bottle 108. If the pre-set volume of liquid collected in reservoir 104 is 60 ml, then 45 ml of liquid is collected in a total period of 20 seconds in the large 60 ml sample bottle 106. When the reservoir 104 is emptied, valve A closes to permit the reservoir 104 to again fill with cloud water. When valve A closes, the air powered cylinder is actuated to withdraw the hypodermic needles 150 from the small bottles to the position shown in FIG. 11.

According to a second mode of operation, a timer 157 is employed in conjunction with valve A, instead of level sensor 144. In this mode of operation, the timer 157 times the interval for filling the reservoir 104, say, one hour. This is the “off” interval of the timer 157. At the end of such time, the timer actuates the valve A, while at the same time, the timer 154 actuates the valve B to fill the large bottle 106 and the small bottles 108 simultaneously. During this filling operation of about 20 seconds, the timer 157 is in the “on” interval. The timer 157 then switches to the “off” interval again, closing valve A, while timer 154 closes valve B, to permit reservoir 104 to again be filled with sample liquid.

In this mode of operation employing both the level sensor 144 and the timer 157, for actuating valve A, if either the time has elapsed as set by timer 157, for filling the reservoir 104 to a predetermined volume, or the collected volume of liquid as indicated by the level sensor 144 has been achieved, whichever occurs first, valve A will be opened by either the level sensor or the timer 157, to permit discharge of liquid into the large bottle 106, while at the same time simultaneously the timer 154 opens valve B to permit discharge of liquid sample into the small bottles 108, after which valves A and B are closed, as noted above, to permit repeated filling of the reservoir 104. This third mode of operation is preferred.
After the accumulated liquid has been discharged from the reservoir 104 into the sample bottles at filling station X, and valves A and B have been closed, a counter, indicated at 162, which is responsive to the closing of valve A, actuates an indexing mechanism 164, which in turn actuates the motor 118 and worm gear 120 to rotate the carousel a predetermined amount so as to move the filled bottles from the filling station X and to advance the next row comprised of one large bottle 106 and three small bottles 108 into position at the filling station X. The above-described operation for filling the large bottle 106 and the small bottles 108 at fill station X is repeated until all of the 20 large bottles and 60 small bottles on the carousel are filled. At the end of this time, the counter 162 shuts off power to the indexing mechanism 164 and causes diversion of liquid filling the reservoir 104, through the overflow tube 136 and into the overflow bottle 140.

An event logger (printer) 166 records the time when sampling begins and when the carousel indexes to a new position.

It will be understood that, if desired, the automated sampler can be used for filling only the large sample bottles 106 and omitting the small sample bottles 108. Under the circumstances, components for filling the small bottles, including valve B and its associated timer 154, the auxiliary discharge line 146, air cylinder 148, and the hypodermic needle devices 150 can be omitted.

Further, if desired, the above-described mechanism for actuating the automated sampler, including the small fog detector 155, and its associated resistance grid 156 and relay 158 can be omitted, and the power source at 160 can be turned on manually or by any other means at any time.

In addition, the automated sampler 100 can be employed separately, that is, without combining it with the cloud water collector 20, e.g., for collecting rain water. In the latter case, viewing FIG. 15, a rain water collecting funnel 168 can be connected to the tube 76 for discharge of a sample of rain water into the liquid reservoir 104. The automated sampler then functions in the manner described above for collecting multiple samples of the rain water so collected. When not in use for collecting rain water, a cover indicated by dotted lines 170 can be placed over the funnel 168.

From the foregoing, it is seen that the invention provides an improved device for collecting cloud water or fog water for chemical analysis which operates efficiently and rapidly to collect substantial amounts of liquid water for chemical analysis, and which is reliable, simple to construct and inexpensive. In addition, the cloud water collector can be automated by use in combination with an automated sampler device to collect multiple samples of fog water in the field, with a minimum of attention and labor expense. Further, the automation device can be employed separately for collecting rain water.

Since various additional changes and modifications of the invention will occur to and can be made readily by those skilled in the art without departing from the invention concept, the invention is not to be taken as limited except by the scope of the appended claims.

What is claimed is:

1. A cloudwater collector comprising a conduit open at opposite ends, including an air inlet at a front end thereof to permit entry of a cloudwater containing air sample into said conduit, and an air outlet at the opposite back end thereof, a plurality of spaced Teflon strands in said conduit adjacent the front end thereof, said strands being mounted across said conduit at an acute angle facing said inlet, the diameter of said strands being such that water droplets from a cloudwater sample, of a size range of 1-100 microns are collected on the strands upon impact therewith, said acute angle being such that the impacted droplets flow down said strands and drain into the bottom of said conduit, a fan at the back end of said conduit adjacent said air outlet for drawing a sample of air containing cloudwater through said inlet into said conduit, means for reducing turbulence and producing essentially uniform flow of said air sample across said conduit, and means for collecting a sample of the water droplets from the bottom of said conduit.

2. The cloudwater collector of claim 1, said Teflon strands being wound in vertical spaced relation on a frame and forming a screen containing two parallel rows of said strands on said frame.

3. The cloudwater collector of claim 2 including a plurality of said screens mounted in spaced parallel relation at said acute angle across said conduit.

4. The cloudwater collector of claim 2, said Teflon strands and said screen being mounted at an angle of 30°-40° across said conduit facing said inlet.

5. The cloudwater collector of claim 2, said Teflon strands having a diameter such that water droplets from a cloudwater sample, of a size ranging from 5-30 microns, are efficiently collected on the Teflon strands.

6. The cloudwater collector of claim 2, said Teflon strands having a diameter ranging from 0.015" to 0.025".

7. The cloudwater collector of claim 1, said means for reducing turbulence and producing essentially uniform flow of said air sample across said conduit comprising a honeycomb element mounted across said conduit between said Teflon strands and said fan.

8. The cloudwater collector of claim 1, said means for collecting said water droplet sample comprising a drain in the bottom of said conduit, a funnel connected to said drain, a sample bottle, and tube means communicating said funnel with said sample bottle.

9. The cloudwater collector of claim 1 including a frame for said Teflon strands, said frame having upper and lower threaded rods, said Teflon strands wound on said threaded rods in vertical spaced relation, and forming a screen containing two parallel rows of said strands on said frame, and including a plurality of said screens mounted in spaced parallel relation, said Teflon strands and said screens being mounted at an angle of 35° across said conduit facing said inlet.

10. The cloudwater collector of claim 9, said Teflon strands having a diameter of about 0.020" and a spacing between strands of about 0.070".

11. The cloudwater collector of claim 10, said means for reducing turbulence comprising a honeycomb element mounted across said conduit between said Teflon strands and said fan, and said means for collecting said water droplet sample comprising a drain in the bottom of said conduit, a funnel connected to said drain, a sample bottle, and a tube means communicating said funnel with said sample bottle.

12. The cloudwater collector of claim 1 including means for automating the collection of successive cloud water samples, said automating means comprising
a reservoir in fluid communication with said sample collecting means, said turntable means adapted to support a plurality of containers thereon, means associated with said reservoir for automatically discharging a predetermined volume of cloudwater from said reservoir into a preselected container on said turntable means, and means to actuate said turntable means to index a successive container to be filled into operative relation with said reservoir when said preselected container has received said predetermined volume of cloudwater.

13. The cloudwater collector of claim 12, said automatic discharge means comprising valve means operable to open when said predetermined volume of cloudwater has been collected to discharge same into said container, said turntable indexing means being actuated when said valve means is closed.

14. The cloudwater collector of claim 12, said automatic discharge means comprising a liquid level sensor for said reservoir and valve means associated with said liquid level sensor, said liquid level sensor actuating said valve means when said reservoir is filled with cloudwater to a predetermined level to discharge the cloudwater from said reservoir into said preselected container.

15. The cloudwater collector of claim 12, said automatic discharge means comprising timer means for timing the flow of cloudwater into said reservoir over a preselected time interval and valve means associated with said timer means, said timer means actuating said first valve means closing same after a predetermined time interval and valve means associated with said reservoir for automatically discharging a predetermined volume of cloudwater in said reservoir, and means associated with said liquid level sensor to monitor collection of said predetermined volume of cloudwater in said reservoir to open and fill a first bottle at said fill station.

16. The cloudwater collector of claim 12, said automatic discharge means comprising a liquid level sensor for said reservoir and valve means associated with said liquid level sensor, said liquid level sensor actuating said valve means when said reservoir is filled with cloudwater to a predetermined level to discharge the cloudwater from said reservoir into said preselected container, and also including timer means for timing the flow of cloudwater into said reservoir over a preselected time interval and valve means associated with said timer means, said timer means actuating said valve means after said preselected time interval, to discharge the cloudwater from said reservoir into said preselected container.

17. The cloudwater collector of claim 12 including means for deactivating said turntable indexing means when all of the containers on said turntable have been filled, and means for thereafter diverting incoming cloudwater from said reservoir to an overflow container.

18. The cloudwater collector of claim 12 including means for actuating said automatic means when cloudwater is present, for discharge of sample liquid from the sample collecting means of said cloudwater collector, to said reservoir.

19. The cloudwater collector of claim 12, said means for automatically discharging a predetermined volume of cloudwater from said reservoir including, a first valve means, a second valve means, means for actuating said first valve means when said predetermined volume of cloudwater has been collected in said reservoir to open and fill a first container at a fill station on said turntable, timer means for actuating said second valve means when said first valve means has been actuated, to open and fill a second smaller container at said fill station on said turntable, said timer means closing said second valve means after a pre-set time interval, and said means for actuating said first valve means closing same after a longer pre-set time interval, and means for sensing the closing of said first valve means, to actuate said indexing means to index successive first and second containers for advancement to said fill station.

20. The cloudwater collector of claim 19, said means to actuate said first valve means including a liquid level sensor means to monitor collection of said predetermined volume of cloudwater in said reservoir, and means associated with said liquid level sensor means to actuate said first valve means.

21. The cloudwater collector of claim 19 including a timer means to monitor collection of said predetermined volume of cloudwater in said reservoir, and means associated with said last-mentioned timer means to actuate said first valve means.

22. The cloudwater collector of claim 19 including a rack on said turntable adapted to support a plurality of said first containers in a circle adjacent the outer periphery of said turnable and a plurality of said second smaller containers in a concentric circle adjacent said first containers.

23. The cloudwater collector of claim 1, including means for automating the collection of successive cloudwater samples, said automating means comprising a reservoir in fluid communication with said sample collecting means, a carousel, means supporting said carousel for limited rotation, a rack on said carousel adapted to support a plurality of said first sample bottles in a circle adjacent the outer periphery of said carousel and a plurality of said second sample bottles in concentric circles adjacent said circle of first containers, a fill station on said carousel wherein one of said first bottles and a plurality of said second bottles in said concentric circles are in a row, a discharge line from said reservoir, a first valve in said discharge line adapted to discharge liquid from said reservoir into one of said first bottles at said fill station, a second valve in said discharge line adapted to discharge liquid from said reservoir into the second bottles in said row at said fill station, a liquid level sensor to monitor collection of a predetermined volume of cloudwater in said reservoir, means associated with said liquid level sensor to actuate said first valve means when said predetermined volume of cloudwater has been collected in said reservoir to open and fill a first bottle at said fill station, timer means for actuating said second valve when said first valve has been actuated, to open and fill the second bottles in said row at said fill station, said timer means closing said second valve after a pre-set time interval, and said means for actuating
said first valve closing same after a longer pre-set time interval,

driving means to actuate the carousel to index a successive row of a first bottle and a plurality of second bottles at said fill station,

means for sensing the closing of said first valve to actuate said driving means to index a successive row of bottles at said fill station, said last-mentioned means including a counter for deactivating said driving and indexing means when all of the bottles on said carousel have been filled at said fill station,

an overflow tubing connected to the discharge line from said reservoir, and

an overflow bottle connected to said overflow tube, for receiving liquid from said reservoir after deactivation of said driving and indexing means by said counter.

24. The cloudwater collector of claim 23, and also including timer means for timing the flow of cloudwater into said reservoir over a preselected time interval to actuate said first valve after said pre-set time interval, to discharge cloudwater from said reservoir into said first bottle at said fill station, said liquid level sensor or said last-mentioned timer means actuating said first valve to discharge the cloudwater from said reservoir after said predetermined volume is achieved or said preselected time interval has elapsed, whichever occurs first.

25. The cloudwater collector of claim 23, said second smaller bottles having a septum cover thereon, and means for piercing said septum bottles at the fill station for introduction of sample liquid to said bottles when said second valve has been opened.

* * * * *
Instrument to collect fogwater for chemical analysis

Daniel J. Jacob, a) Jed M. Waldman, Mehrdad Haghi, b) Michael R. Hoffmann, and Richard C. Flagan c)

Environmental Engineering Science, W. M. Keck Engineering Laboratories, California Institute of Technology, Pasadena, California 91125

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An instrument is presented which collects large samples of ambient fogwater by impaction of droplets on a screen. The collection efficiency of the instrument is determined as a function of droplet size, and it is shown that fog droplets in the range 3–100-µm diameter are efficiently collected. No significant evaporation or condensation occurs at any stage of the collection process. Field testing indicates that samples collected are representative of the ambient fogwater. The instrument may easily be automated, and is suitable for use in routine air quality monitoring programs.
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I. DESIGN

The instrument (shown in Fig. 1) collects fogwater by inertial impaction of fog droplets on a screen. The screen is made of two layers of 330-µm-diameter Teflon monofilament strung vertically on a frame between two Teflon-coated threaded rods [Fig. 1(c)]. It is placed at an incline (θ = 35°) that the deposition to vegetation canopies is considerably enhanced. Recent reports of extremely high acidities in fogs, and clouds intercepting mountain slopes, have raised concern regarding related environmental consequences. Air quality control agencies in areas exposed to acidic fog have expressed the need to establish networks of sites monitoring the chemical composition of fog on a routine basis. A fogwater sampler to be used in such programs must meet four basic requirements: (1) efficiency collect fog droplets in the 1–100-µm size window while avoiding collection of the submicron nonactivated aerosol, (2) preserve the size and chemical composition of fog droplets through all stages of collection, (3) rapidly collect large amounts of liquid water for wet chemical analysis, (4) be automated, inexpensive to construct, and require minimal maintenance. A recent paper from our group has elaborated on design criteria for fogwater collectors, and reported that none of the currently available instruments is satisfactory in all respects. A rotating arm collector developed in our laboratory has been shown to provide samples representative of the ambient fogwater, but it is not suitable for automation and presents safety problems. We describe herein a collector that we have recently developed explicitly to provide a simple, reliable, and inexpensive instrument for routine monitoring.

Further, inclining the screen at 35° prevents resuspension of impacted droplets into the air flow, which would occur if the screen was placed vertically. Accumulation of water on the screen proceeds by formation of large droplets spaced at intervals along the Teflon strings; these droplets rapidly grow large enough (about 1–2-mm diameter) to flow down. A Teflon funnel drains the fogwater collected at the bottom of the screen into a storage bottle directly below. The instrument is set on a platform surmounted by a wind vane so that the inlet is oriented into the wind at all times. Automation of instrument start up may be provided by a number of methods.

The flow of air through the duct is 22 m³ min⁻¹, but only a fraction of that air is actually sampled because of the spacing between strings. Based on the dry diameter of the strings, each of the two layers samples 42% of the air flowing through the duct, and the sampling efficiency of the instrument is about [1 – (0.58)²] = 66%. In practice, accumulation of water on the strings will slightly increase the impaction surface area and, therefore, the amount of air sampled. About 90 ml of sample is collected per hour in a fog of typical liquid water content 0.1 g m⁻³. This is sufficient for most analytical purposes.

The principle of operation is that inertia prevents droplets approaching the strings from following the curved flow streamlines around the strings. The deviations of droplet trajectories increase with droplet inertia, and droplets above a certain size deviate sufficiently to collect on the strings. The efficiency of this process is characterized by the Stokes number St:

$$St = \frac{\rho D^2 U \cos \theta}{18 \mu R},$$

(1)

where ρ is the density of the droplet, D is the droplet diameter, μ is the viscosity of air, and R is the radius of the string. The Reynolds number of the flow through the duct is sufficiently high (10⁷), and the Mach number is sufficiently low (0.03), that the collection efficiency can be satisfactorily described as simply a function of St and the droplet Reynolds number Re_D. Experimental data is available for the collection efficiency of particles on cylinders as a function of these two dimensionless groups. For 1–100-µm-diameter droplets, St ranges from 0.14–1400 and Re_D from 0.5–50.
The collection efficiency of our instrument was determined as a function of droplet size from the data of Refs. 8–10, for various ambient wind velocities and an inlet oriented into the wind (Fig. 2). The impaction Stokes number was calculated by taking $R$ equal to the radius of the dry strings. Droplets in the range 3–100-$\mu$m diameter are efficiently collected. Droplets in the size window 10–30-$\mu$m diameter, which typically account for over 95% of the total liquid water content in fog, are collected with over 90% efficiency under all sampling conditions. Fog droplets below 3-$\mu$m are poorly collected, but represent only a very small fraction of the total suspended liquid water. Collection of submicron aerosol by convective diffusion to the strings is very inefficient: the calculated collection efficiency is 4% for a 0.001-$\mu$m-diameter particle, and decreases with increasing particle size. Thus, contamination of fogwater samples due to collection of submicron aerosol is effectively avoided. Anisokinetic sampling biases for very large droplet sizes depend considerably on the ambient wind speed. Wind speeds in radiation fogs are in general less than 2 m $s^{-1}$, but we have frequently found higher velocities (up to 10 m $s^{-1}$) in coastal advection fogs. Positive collection biases require ambient wind velocities $>10$ m $s^{-1}$, which could be found in clouds intercepting mountain slopes but are unlikely in other situations.

Perturbation of the ambient relative humidity during the sampling process may change the size of the fog droplets by condensation or evaporation and, therefore, affect chemical concentrations in the sample. Aerodynamic cooling as the droplets are accelerated at the inlet leads to condensation, and aerodynamic heating as the droplets are deceler-

![Diagram](image_url)
Comparison of four samples collected on 12 June 1984 at Henninger Flats (Ref. 12).

TABLE I. Comparison of fogwater concentrations of samples collected simultaneously with the screen collector (SC) and the rotating arm collector (RAC) side by side.

<table>
<thead>
<tr>
<th></th>
<th>H⁺</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>NH₄⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC/RAC</td>
<td>1.08 ± 0.11</td>
<td>0.71 ± 0.04</td>
<td>0.70 ± 0.10</td>
<td>0.71 ± 0.04</td>
<td>1.14 ± 0.14</td>
<td>0.93 ± 0.10</td>
<td>0.85 ± 0.06</td>
<td>0.99 ± 0.07</td>
</tr>
<tr>
<td>Fe</td>
<td>1.11 ± 0.34</td>
<td>1.12 ± 0.18</td>
<td>0.85 ± 0.28</td>
<td>1.05 ± 0.27</td>
<td>0.99 ± 0.12</td>
<td>1.04 ± 0.08</td>
<td>2.34 ± 0.24</td>
<td></td>
</tr>
</tbody>
</table>

*Comparison of four samples collected on 12 June 1984 at Henninger Flats (Ref. 12).

Evaporation on the strings must also be investigated. Aerodynamic heating near the strings leads to a localized subsaturation. Assuming that the compression is adiabatic, the maximum temperature gradient at the surface of the string is

\[ \Delta T = \frac{(U_s \cos \theta)^2}{2C_p}, \]  

where \( C_p \) is the heat capacity of air. We find \( \Delta T = 0.03 \) K, which corresponds to a decrease in relative humidity of about 0.2%. More important as sources of thermodynamic modification are the fluctuations of the ambient relative humidity in fog: rapid oscillations of up to 1% relative humidity in amplitude have been reported in a radiation fog.\(^13\) Mass transfer calculations for a flow of air at 99% relative past a bank of cylinders\(^14\) indicate an overall rate of evaporation from the screens of \( 10^{-3} \) g min⁻¹. This is small compared to the collection rates achieved.

II. FIELD TESTING

The collector was first tested during a stratus cloud sampling program conducted on the mountain slopes above the Los Angeles basin.\(^12\) Collection rates were in the range 0.5–1.5 ml min⁻¹. Four samples were collected simultaneously with the rotating arm collector, and the chemical compositions of the samples were compared (Table I). Concentrations were not significantly different between the two instruments, and usually within the errors previously documented between two rotating arm collectors set side by side.\(^5\)

The similarity of compositions between samples collected by the screen collector and the rotating arm collector is striking, considering that the two instruments have very different collection efficiency vs droplet size characteristics (Fig. 2). A likely explanation is that most of the fogwater mass is present in a narrow droplet size window around 20–100 \( \mu m \) diameter,\(^12\) and that small fog droplets are not sufficiently different in composition from the bulk fogwater to significantly affect the overall concentration. Small droplets have generally condensed on small nuclei and, therefore, are not systematically more concentrated than the larger droplets.

The dependence of fog droplet composition on droplet size is an interesting question which has not been studied to date. Our collector could be conveniently used for such a study; different portions of the droplet size distribution could be sampled by using screens of different string diameters.

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Elton F. Daly and Joseph J. Fontana constructed the collector and offered valuable practical suggestions. We thank an anonymous reviewer for valuable comments. This work was funded by the California Air Resources Board.

\(^{12}\) Present address: Center for Earth and Planetary Physics, Harvard University, Cambridge, Massachusetts.
\(^{13}\) Present address: Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.
\(^{14}\) To whom correspondence should be addressed.


CHAPTER 3

A Comparison of Two Cloudwater/Fogwater Collectors:
The Rotating Arm Collector
and the
Caltech Active Strand Collector

by

Jeff Collett, Jr., Bruce Daube, Jr., J. William Munger, and Michael R. Hoffmann*

Environmental Engineering Science
W. M. Keck Laboratories
California Institute of Technology
Pasadena, California 91125

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* To Whom Correspondence Should be Addressed
Abstract

A side-by-side comparison of the Rotating Arm Collector (RAC) and the Caltech Active Strand Collector (CASC) was conducted at an elevated coastal site near the eastern end of the Santa Barbara Channel. The CASC was observed to collect cloudwater at rates of up to 8.5 ml min⁻¹. The ratio of cloudwater collection rates was found to be close to the theoretical prediction of 4.2:1 (CASC:RAC) over a wide range of liquid water contents (LWC). At low LWC, however, this ratio climbed rapidly, possibly reflecting a predominance of small droplets under these conditions, coupled with a greater collection efficiency of small droplets by the CASC. The RAC collected cloudwater samples with significantly higher concentrations of Na⁺, Ca²⁺, Mg²⁺, and Cl⁻ than were collected by the CASC. These higher concentrations may be due to differences in the chemical composition of large vs. small droplets. No significant differences were observed in concentrations of NO₃⁻, SO₄²⁻, or NH₄⁺ in samples collected by the two instruments.
Introduction

The development of the Caltech Active Strand Collector (Daube et al., 1987) led to a need to compare the performance of this collector with the Rotating Arm Collector (Jacob et al., 1984) used in previous studies of fog and cloudwater chemistry in California. Of particular interest were the rate of sample collection by each instrument and the comparability of the chemical composition of the samples collected by the two instruments. In order to make these comparisons we needed a location at which we could sample several fog events with widely varying liquid water contents and chemical compositions. Side-by-side comparison of the collectors under these conditions would provide a good test of the relative performance of the two instruments.

Site Description and Measurement Techniques

Sampling Site

The site selected for the collector comparison was the roof of a one story building located at 475 m, just below the summit of La Jolla Peak. La Jolla Peak is situated 3 km NNE of Pt. Mugu at the eastern end of the Santa Barbara Channel. The collectors were placed approximately 15 m apart with the exhaust from each directed away from the other collector.

This site was selected because of its elevation, its proximity to the ocean, and its location away from major anthropogenic sources. The combination of elevation and proximity to the ocean were expected to result in frequent impaction of coastal stratus moving inland with the nighttime sea breeze during the summer period we planned to sample. The location away from any immediately neighboring anthropogenic sources was expected to provide a variety of cloudwater compositions, these varying with the
mesoscale transport conditions associated with each event. Previous work had suggested that the site might be subjected to pollutant laden air masses originating in the Los Angeles Basin (Shair et al., 1982) or from oil platforms located in the coastal waters to the west (California Air Resources Board, 1982). These types of air masses, if associated with periods of coastal stratus, could result in the presence of highly polluted cloudwater at the site. Alternatively, it was expected that periods of air movement from the southwest (not associated with offshore flow from the South Coast Air Basin) during periods of coastal stratus would result in the presence of much cleaner cloudwater at the site.

- Measurement Techniques

Cloudwater samples were collected simultaneously with the Rotating Arm Collector (RAC) and the Caltech Active Strand Collector (CASC) depicted in Figures 1 and 2, respectively. The RAC (Jacob et al., 1984) utilizes a 1.5 HP motor to drive a 63 cm solid stainless steel rod at 1700 rpm. Each end of the rod has a slot milled into its leading edge to collect the impacting fogwater droplets. High density polyethylene (HDPE) bottles mounted on each end of the rod catch the fogwater sample as it is accelerated outward from each slot. Collection rates of up to 2 ml/min have been obtained in the field with this instrument. A scale model calibration of the RAC indicated a 50% lower size cut, based on droplet diameter, of 20 µm for the RAC.

The CASC (Daube et al., 1987) employs a fan to draw air across six angled banks of 510 µm teflon strands at a velocity of 9 m s⁻¹. Cloudwater droplets in the air parcel are collected on the strands by inertial impaction. The collected droplets run down the strands, aided by gravity and aerodynamic drag, through a teflon sample trough into a HDPE collection bottle. This instrument has a theoretical lower size cut of 3.5 µm, based on droplet diameter, and has collected cloudwater at rates of up to 8.5
ml min$^{-1}$ in the field.

The major ions, Cl$^-$, SO$_4^{2-}$, and NO$_3^-$, were measured in our laboratory using a Dionex 2020i ion chromatograph with a Dionex AS-4 column and a bicarbonate-carbonate eluent. Na$^+$, Ca$^{2+}$, and Mg$^{2+}$ concentrations were determined using a Varian Techtron AA6 atomic absorption spectrophotometer. NH$_4^+$ was measured by the phenol-hypochlorite method (Solorzano, 1967) using an Alpkem flow injection analyzer.

Sample Comparison Results

- Collection Rate

The rates of cloudwater collection by the two instruments were compared for 22 periods during which samples were collected simultaneously. The theoretical ratio of collection rates between the two instruments is 4.2:1 (CASC:RAC). This figure is based on the expected air sampling rates of each instrument. In Figure 3 the actual collection rate data from this study are depicted along with this theoretical line. The data are plotted as the ratio of CASC to RAC collection rates vs. CASC collection rate. Most of the data points are scattered closely about the theoretical line. Several points at low CASC collection rate, however, fall well above this line, indicating that under these conditions the performance of the CASC relative to the RAC is much better than expected.

Since the collection rate of the CASC is proportional to the liquid water content (LWC) of the cloud, these particular samples indicate that under low LWC conditions the collection efficiency of the RAC declines to a greater extent than that of the CASC. This may be due to the differing lower sizecuts of the two instruments. Typically low LWC clouds have a greater proportion of liquid water residing in smaller droplets (Best, 1951a). Since the RAC collects only those droplets above 20 $\mu$m
efficiently, it may be sampling less than half of the droplet spectrum under these conditions. The 3.5 µm lower size cut of the CASC, however, allows it to sample the bulk of the available liquid water.

- Chemical Composition

Of the 22 samples collected simultaneously by the CASC and the RAC, 11 were chosen for a comparison of major ion composition. These 11 samples were collected on three different nights in July and August of 1985. The other 11 samples were relatively small in volume. Since small volume samples are more likely to show signs of contamination than large ones, these samples were not used for this portion of the collector comparison. Trends exhibited by those samples used in the comparison, however, were generally observed in the low volume samples as well.

Seven ions were used for comparison of the samples: \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), \( \text{Cl}^- \), \( \text{NH}_4^+ \), \( \text{Mg}^{2+} \), \( \text{Ca}^{2+} \), and \( \text{Na}^+ \). Along with \( \text{H}^+ \), these ions form the bulk of the ionic composition for all 11 samples. Figures 4 through 10 depict the sample comparison for each ion. Data is plotted as concentration in the CASC sample vs. concentration in the RAC sample. The eleven samples exhibited a wide range of concentrations for each of these ions. Also plotted on each graph is a 1:1 line. If the collected sample pairs were identical in composition, the data points should deviate from this line only due to random errors in analysis.

In the case of \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), and \( \text{NH}_4^+ \) the data points seem fairly well matched with the 1:1 line. Deviation is more evident amongst the \( \text{Cl}^- \), \( \text{Na}^+ \), \( \text{Mg}^{2+} \), and \( \text{Ca}^{2+} \) compositions. In all four cases it appears that the RAC collects these ions preferentially, particularly when the ions are present at higher concentrations.

A statistical analysis was performed to determine whether the deviations suggested above were significant. A linear relationship of the form given by equation 1
\[ Y_i = \alpha + \beta X_i + \mu \quad (1) \]

may be hypothesized where \( Y_i \) and \( X_i \) are the matrices of CASC and RAC concentrations of ion "i", respectively, and "\( \mu \)" represents the error in the equation. Typically the values of \( \alpha \) and \( \beta \), the intercept and the slope, are estimated using the method of ordinary least squares (OLS). When there are errors in the measurement of both the dependent and independent variables, however, OLS provides a biased estimate of the slope (Johnston, 1984; Maddala, 1977).

Two estimation methods are commonly used to remedy this problem of bias. One requires a fairly accurate knowledge of the magnitudes of the errors. In order to utilize this approach, simultaneous data is needed on side–by side CASC and side–by–side RAC sampling. Since this was not available, the second estimation method was utilized. This method, known as the Instrumental Variable (IV) method (Johnston, 1984), provides a consistent estimate of both the slope and intercept. The method requires a matrix of variables correlated with the \( X \) variables but uncorrelated with the errors in the \( X \) variables.

The particular method utilized for this comparison has been described in detail by Bartlett (1949), and is a modification of earlier work by Wald (1940). The mean of the coordinates \((x,y)\) is used to define one point of the fitted line. To determine the slope, the \( n \) data points are divided into three groups which are non–overlapping in either the \( x \) or the \( y \) direction. The groups should be chosen so that the two extreme groups are as near \( n/3 \) as possible. The slope of the fitted line is then defined by the slope of the join of the mean coordinates, \((x_1,y_1)\) and \((x_3,y_3)\), for the two extreme groups.

While Bartlett's method provides a consistent estimate for the slope and intercept of the relationship (1) it is not as efficient as OLS. A decrease in efficiency results in an increase in the size of the confidence limits placed on these estimates.
When faced with a situation where there are errors in the independent variables, however, it becomes necessary to sacrifice some efficiency to gain an unbiased estimator. Table 1 lists the results of applying this method to the Na⁺, Cl⁻, Ca²⁺, and Mg²⁺ data. The slope and the corresponding 95% confidence limits are given for the CASC vs. RAC comparison for each ion. A slope greater than one indicates preferential collection of that ion by the RAC while a slope less than one indicates that the CASC collects the ion preferentially. A slope of one indicates no preferential collection. The results in Table 1 indicate that at the 95% confidence level the RAC collects Na⁺, Cl⁻, and Ca²⁺ preferentially. Preferential collection of Mg²⁺ by the RAC is indicated at the 90% confidence level. Data for NH₄⁺, NO₃⁻, and SO₄²⁻ indicated no preferential collection of these ions by either collector.

Typically larger condensation nuclei lead to the formation of larger cloud droplets in the lower portions of a cloud not subjected to significant horizontal entrainment of dry air (Best, 1951b, Mason and Chien, 1962, Hudson, 1984). Since sea salt and soil dust are found to reside in the larger end of the aerosol size spectrum (Seinfeld, 1986), the elements found predominantly in these types of particles (e.g. Cl⁻, Na⁺, Mg²⁺, and Ca²⁺) will reside there as well. Therefore, as cloud droplets form on the available aerosol nuclei and grow by condensation, it should be expected that these elements would be found predominantly in the upper end of the droplet size spectrum. In the more mature portions of a cloud this trend may be obscured somewhat as droplet coalescence becomes increasingly important (Mason, 1971).

The fact that the RAC preferentially collected Na⁺, Cl⁻, Mg²⁺, and Ca²⁺ is consistent with its lower collection efficiency for small droplets. Since these droplets should come predominantly from condensation on smaller aerosol nuclei, they are likely to contain much lower concentrations of Na⁺, Cl⁻, Mg²⁺, and Ca²⁺. The smaller droplets, collected efficiently by the CASC, act to dilute the concentrations of these four ions in the CASC samples.
In an intercomparison of fogwater collectors conducted at Henninger Flats in (Hering et al., 1987), some of the devices collected samples with higher concentrations of soil dust cations, notably Ca\(^{2+}\) and Mg\(^{2+}\), and Na\(^{+}\). Data from a comparison of a Desert Research Institute linear–jet impactor and a RAC exhibited trends very comparable to those seen in the current study for Na\(^{+}\), Ca\(^{2+}\), and Mg\(^{2+}\): preferential collection by the RAC (Hering et al., 1987). A lower size cut of between 2 and 5 \(\mu m\) has been reported for the DRI jet impactor (Katz, 1980), comparable to the lower size cut for the CASC. Some speculation was made about whether the preferential collection by the RAC was due to differences in the lower size cuts of the collectors or due to some other factor. The final conclusion was that this difference was due to intense research activity at the site which probably led to soil dust particles being kicked up. These dense particles would be sampled more efficiently by the RAC than by the DRI jet impactor due to differences in the sampler inlets (Waldman, 1985). No explanation was offered for the preferential collection of Na\(^{+}\), which is primarily derived from sea spray.

In the CASC vs. RAC comparison both samplers were located on a rooftop away from possible sources of soil dust contamination. During sampling periods the rooftop was heavily wetted by deposition from the dense fog, providing further protection from soil dust contamination. There was also very little activity at the site. The combination of these factors in the current study suggests that perhaps the differences seen are due to differences between the collectors in the collection efficiency of small droplets.

During the CASC vs. RAC comparison no significant collection preferences for any ion were exhibited by the CASC. This happened despite the fact that aerosol NO\(_3^-\), SO\(_4^{2-}\), and NH\(_4^+\), resulting primarily from gas–to–particle conversion processes, are found predominantly in the fine particle fraction (Seinfeld, 1986). Since smaller cloud droplets should tend to have smaller condensation nuclei, it might be expected that
these ions would reside mostly in the smaller droplets and therefore be collected preferentially by the CASC. The situation is not so simple, however, since cloudwater concentrations of all three of these ions may be altered by absorption of precursor gas phase species followed by chemical reaction. \( \text{NH}_3(g) \) can be absorbed by the droplets and protonated to form \( \text{NH}_4^+ \); \( \text{HNO}_3(g) \) can be absorbed, followed by deprotonation to yield \( \text{NO}_3^- \); \( \text{SO}_2(g) \) can be absorbed and oxidized to \( \text{SO}_4^{2-} \). The first two processes are extremely rapid. The oxidation of \( \text{S(IV)} \) to \( \text{S(VI)} \) in cloudwater is also rapid in the presence \( \text{H}_2\text{O}_2 \) or a metal catalyst (Hoffmann and Jacob, 1984). All three of these processes occur throughout the droplet size spectrum making them likely candidates for masking the signature of aerosol \( \text{NO}_3^- \), \( \text{NH}_4^+ \), and \( \text{SO}_4^{2-} \).

Summary

A comparison of cloudwater collection characteristics of the Caltech Active Strand Collector (CASC) and the Rotating Arm Collector (RAC) was conducted at an elevated coastal site near the eastern end of the Santa Barbara Channel during the summer of 1985. Of particular interest were the rates of collection and the chemical comparability of the samples obtained using each instrument.

Collection rates as high as 8.5 ml min\(^{-1}\) were obtained using the CASC in this study. Collection rates for the RAC have been seen to go as high as 2 ml min\(^{-1}\) in past studies. During this intercomparison the ratio of CASC to RAC collection rates was found to be close to the theoretical prediction of 4.2:1 over a wide range of LWC. At low LWC, however, this ratio climbed rapidly. This may be attributable to the differing lower size cuts of the two instruments: since the CASC collects small droplets more efficiently than the RAC, its performance relative to the RAC should increase in thinner fogs and clouds where the mass median droplet diameter decreases.

Concentrations of \( \text{Na}^+ \), \( \text{Cl}^- \), \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), \( \text{NH}_4^+ \), \( \text{Ca}^{2+} \), and \( \text{Mg}^{2+} \) in simultaneous
samples collected by the two instruments were compared. Preferential collection of Na\(^+\), Cl\(^-\), and Ca\(^{2+}\) by the RAC was observed to occur with a confidence level greater than 95%. Preferential collection of Mg\(^{2+}\) by the RAC was observed to occur with a confidence level greater than 90%. This preferential collection may also be attributable to the differing lower size cuts of the two samplers since these ions, derived primarily from soil dust and sea spray, may be expected to reside primarily in larger cloud droplets which make up a larger fraction of each RAC sample. No significant preferential collection by either collector was observed for NO\(_3^-\), SO\(_4^{2-}\), or NH\(_4^+\).
References

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Table 1. Slopes Different from One for CASC vs. RAC Sample Ionic Composition Comparison

<table>
<thead>
<tr>
<th>Ion</th>
<th>Slope</th>
<th>95% Confidence Limits</th>
</tr>
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<tbody>
<tr>
<td>Na⁺</td>
<td>0.34</td>
<td>(0.18, 0.50)</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.42</td>
<td>(0.22, 0.61)</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.37</td>
<td>(0.08, 0.66)</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.58</td>
<td>(0.14, 1.03)</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. Caltech Rotating Arm Collector.
Figure 2. Caltech Active Strand Collector. Air flow is from right to left through the collector as viewed in the figure.
Figure 3. Comparison of CASC and RAC cloudwater collection rates.
Figure 4. Comparison of NO₃⁻ concentrations in CASC and RAC samples. A line of perfect correlation is included for reference.
Figure 5. Comparison of SO₂⁻ concentrations in CASC and RAC samples. A line of perfect correlation is included for reference.
Figure 6. Comparison of Cl⁻ concentrations in CASC and RAC samples. A line of perfect correlation is included for reference.
Figure 7. Comparison of NH₄⁺ concentrations in CASC and RAC samples. A line of perfect correlation is included for reference.
Figure 8. Comparison of Mg²⁺ concentrations in CASC and RAC samples. A line of perfect correlation is included for reference.
Figure 9. Comparison of Ca²⁺ concentrations in CASC and RAC samples. A line of perfect correlation is included for reference.
Figure 10. Comparison of Na⁺ concentrations in CASC and RAC samples. A line of perfect correlation is included for reference.
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Figure 7. Comparison of $\text{NH}_4^+$ concentrations in CASC and RAC samples. A line of perfect correlation is included for reference.
Figure 8. Comparison of Mg$^{2+}$ concentrations in CASC and RAC samples. A line of perfect correlation is included for reference.
Figure 9. Comparison of Ca\textsuperscript{2+} concentrations in CASC and RAC samples. A line of perfect correlation is included for reference.
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CHAPTER 4

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The $\text{H}_2\text{SO}_4$-$\text{HNO}_3$-$\text{NH}_3$ System at High Humidities and in Fogs

1. Spatial and Temporal Patterns in the San Joaquin Valley of California

Daniel J. Jacob,1 J. William Munger, Jed M. Waldman, and Michael R. Hoffmann

Environmental Engineering Science, W. M. Keck Engineering Laboratories, California Institute of Technology, Pasadena

A systematic characterization of the atmospheric $\text{H}_2\text{SO}_4$-$\text{HNO}_3$-$\text{NH}_3$ system was conducted in the fog and aerosol and the gas phase at a network of sites in the San Joaquin Valley of California. Spatial patterns of concentrations were established that reflect the distribution of $\text{SO}_2$, $\text{NO}_x$, and $\text{NH}_3$ emissions within the valley. The concept of atmospheric alkalinity was introduced to interpret these concentrations in terms of the buffering capacity of the atmosphere with respect to inputs of strong acids. Regional trends of predominantly acidic and alkaline fog water were identified. Fog water was found to be alkaline in most of the valley, but small changes in emission budgets could lead to widespread acidic fog. An extended stagnation episode was studied in detail: progressive accumulation of $\text{H}_2\text{SO}_4$-$\text{HNO}_3$-$\text{NH}_3$ species was documented over the course of the episode and interpreted in terms of production and removal mechanisms. Secondary production of strong acids $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ under stagnant conditions resulted in a complete titration of available alkalinity at the sites farthest from $\text{NH}_3$ sources. A steady $\text{SO}_2$ conversion rate of 0.4-1.1% h$^{-1}$ was estimated in the stagnant mixed layer under overcast conditions and was attributed to nonphotochemical heterogeneous processes. Removal of $\text{SO}_2$ was enhanced in fog compared to nonfoggy conditions. Conversion of $\text{NO}_x$ to $\text{HNO}_3$ slowed down during the stagnation episode because of reduced photochemical activity; fog did not appear to enhance conversion of $\text{NO}_x$. Decreases in total $\text{HNO}_3$ concentrations were observed upon acidification of the atmosphere and were attributed to displacement of $\text{NO}_3^-$ by $\text{H}_2\text{SO}_4$ in the aerosol, followed by rapid deposition of $\text{HNO}_3(g)$. The occurrence of fog was associated with general decreases of aerosol concentrations due to enhanced removal by deposition.
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INTRODUCTION

Extremely high acidities have been reported in fogs and low stratus clouds collected in southern California [Munger et al., 1983; Brewer et al., 1983; Waldman et al., 1985; Jacob et al., 1984a, 1985]. The acidity of these fogs was due to $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$, while $\text{NH}_3$ was found to be the main alkaline species titrating the acidity [Jacob et al., 1984a]. Therefore one can attempt to model the “acid fog” phenomenon by consideration of acid-base neutralization processes in the $\text{H}_2\text{SO}_4$-$\text{HNO}_3$-$\text{NH}_3$ atmospheric system.

Ammonia is released directly to the atmosphere from a variety of sources [Cass et al., 1982], but $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ are mostly produced by atmospheric oxidation of reduced sulfur and nitrogen compounds. Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ proceeds in the gas phase [Calvert and Stockwell, 1984], in concentrated aerosol [Kaplan et al., 1981; Crump et al., 1983], and in dilute aqueous solutions [Martin, 1984]. Oxidation of $\text{NO}_x$ to $\text{HNO}_3$ proceeds in the gas phase by the reaction $\text{NO}_2 + \text{OH}$ and may also proceed heterogeneously following scavenging by aerosol of $\text{NO}_3$ and $\text{N}_2\text{O}_5$ produced from the reaction $\text{NO}_2 + \text{O}_3$ [Heikes and Thompson, 1983]. Nitrite is slowly oxidized to $\text{NO}_3^-$ in dilute solutions [Damschen and Martin, 1983]. Using data available for (IV) and (NIII) oxidation reactions, Jacob and Hoffmann [1983] predicted that aqueous phase oxidation of $\text{S(IV)}$ in fog droplets could be an important source of $\text{H}_2\text{SO}_4$ under polluted conditions; on the other hand, they found that aqueous phase oxidation of $\text{N(III)}$ provided only a very small source of $\text{HNO}_3$.

Sulfuric acid is present as an aerosol under usual atmospheric conditions, but $\text{HNO}_3$ and $\text{NH}_3$ have substantial vapor pressures over ammonium nitrate aerosol [Stelson and Seinfeld, 1982]. The atmospheric residence times of $\text{HNO}_3$ and $\text{NH}_3$ are strongly dependent on their partitioning between the gas phase and the aerosol. The gaseous species are quickly removed by deposition (1–5 cm s$^{-1}$ for $\text{HNO}_3(g)$ over grass [Huebert, 1983]). On the other hand, secondary particles formed from $\text{H}_2\text{SO}_4$-$\text{HNO}_3$-$\text{NH}_3$-$\text{H}_2\text{O}$ mixtures are typically in the size range 0.1–1 μm and have low deposition velocities of the order of 0.01–0.1 cm s$^{-1}$ [Sehmel, 1980; Slinn, 1982]. The occurrence of fog enhances the removal of aerosol species because growth of particles to fog droplet size considerably increases their deposition rates. Fog droplet deposition velocities of 2–7 cm s$^{-1}$ over short grass [Dollah and Unsworth, 1983] and 2–4 cm s$^{-1}$ over a dirt surface [Waldman, 1986] have been reported.

A general mechanism to account for fog water acidity in polluted atmospheres may therefore include six fundamental processes: (1) emissions of $\text{SO}_2$, $\text{NO}_x$, and $\text{NH}_3$, (2) pollutant transport, (3) secondary production of $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$, (4) detailed chemical speciation within the $\text{H}_2\text{SO}_4$-$\text{HNO}_3$-$\text{NH}_3$-$\text{H}_2\text{O}$ system, (5) scavenging by fog droplets, and (6) in-fog aqueous phase oxidation of reduced N and S species.

The San Joaquin Valley of California is an excellent "field laboratory" for the interpretation of fog water composition in terms of the above processes. It is the site of major oil recovery operations, which release large amounts of $\text{SO}_2$ and $\text{NO}_x$. In addition, agricultural and livestock-feeding activities provide important sources of $\text{NH}_3$. Severe stagnation episodes, associated with persistent fog and low-lying stratus clouds, occur frequently during the winter months. These stagnation episodes are caused by persistent temperature inversions based a few hundred meters above the valley floor and below the surrounding mountain ridges [Holts and Swanson, 1981]. Tracer studies have documented the lack of ventilation in the valley during these prolonged episodes [Reible, 1982].

In a preliminary study at a single site from December 1982 to January 1983, Jacob et al. [1984a] documented the main
features of aerosol and fog water chemical composition during stagnation episodes in the San Joaquin Valley. The main features observed were as follows: (1) important accumulation of secondary aerosol proceeds under nonfoggy but stagnant conditions, (2) significant pollutant deposition occurred over the course of fog events, (3) SO$_2$ conversion in fogs did not exceed a few percent per hour, and (4) the fog water pH was determined by the availability of NH$_3$ to neutralize the H$_2$SO$_4$ and HNO$_3$ present.

A more comprehensive study was conducted during January 1984, of which this report presents the main results. Aerosol, fog water, and gas phase concentrations were monitored at a network of sites. Spatial and temporal variations of atmospheric concentrations are established that reflect both the geographical distribution of emission sources and the meteorological conditions. The concept of atmospheric alkalinity is introduced to predict the potential for high-acidity fog events. Pollutant accumulation and removal over the course of a stagnation episode are characterized under both foggy and nonfoggy conditions. The rate of oxidation of SO$_2$ to H$_2$SO$_4$ is estimated. The effect of stagnation on HNO$_3$ production is discussed. The partitioning of the H$_2$SO$_4\cdot$HNO$_3\cdot$NH$_3$ system between the gas phase, the aerosol, and the fog water is interpreted in a companion paper in terms of a thermodynamic model [Jacob et al., this issue]. The complete fog water, aerosol, and gas phase data set is given by Jacob [1985].

**Experimental**

The volumetric concentrations of aerosol, HNO$_3$(g), and NH$_3$(g) were monitored at eight sites over the period December 31, 1983, to January 14, 1984 (Figure 1). Samples were collected twice daily (0000–0400 and 1200–1600 PST) at the six valley sites and once daily (1000–1600 PST) at the two mountain sites (Tehachapi and Lake Isabella). The sampling stations were located on platforms 15 m above the ground (Wasco and Tehachapi), on the roof of a building or trailer (Bakersfield, Lost Hills, Buttonwillow, McKittrick, and Visalia), or on the ground, 1.5 m above a grassy area (Lake Isabella). Two open-faced 47-mm Gelman Zellon Teflon filters (1-μm pore size) were operated side by side (10 L min$^{-1}$) to provide duplicate determinations of the inorganic content of the aerosol. A flat cover 15 cm above the filters prevented collection of large particles by sedimentation. The Stokes number at the filter inlet is 0.05 for a 50-μm-diameter particle, so that even large aerosol droplets should be efficiently sampled [Davies and Subbaiah, 1982]. Under foggy conditions the determinations of total aerosol NO$_2^-$ and NH$_4^+$ may be subject to errors because of evaporative losses (see the appendix), and those numbers subject to error were excluded from the data interpretation. A 47-mm Gelman Nylasorb nylon filter collected gaseous nitric acid immediately downstream of one of the Teflon filters, and an oxalic-acid-impregnated glass fiber filter collected gaseous ammonia immediately downstream of the other Teflon filter.

The filters were sealed in petri dishes and kept at 4°C following collection. The Teflon filters were extracted in 10 mL of distilled deionized water (Corning Megapure) for 90 min, using a reciprocating shaker; complete extraction was indicated by insignificant concentrations in repeated extractions. The extracts were analyzed for major ions using standard methods previously described by Munger et al. [1983]. The nylon filters were extracted for 90 min, using a reciprocating shaker in a solution 3 mM HCO$_3^-$ and 2.4 mM CO$_3^{2-}$ (a conventional ion chromatography eluant). Oxalic-acid-impregnated filters were extracted and analyzed following the protocol of Russell [1983]. Ion chromatography revealed low levels of Si(IV) in the Teflon filter extracts, but these concentrations were small compared to SO$_4^{2-}$, and their contributions were ignored. Although most of the aerosol sulfur is expected to be present as SO$_4^{2-}$, some of the measured SO$_4^{2-}$ may have resulted from the oxidation of reduced sulfur species on the filter or in the extract.

Fogs were sampled by event at four sites (Figure 1). Fog water samples were collected with a rotating arm collector [Jacob et al., 1984b] for intervals ranging from 30 min to 3 hours. The rotating arm collector has a theoretical sampling rate of 5 m$^3$ min$^{-1}$ and has been shown to collect fog water samples without evaporation or condensation. Laboratory calibration has indicated a lower size cut (50% collection efficiency) of 20-μm diameter. Because the instrument collects fog droplets by direct impaction and does not require drawing air through an inlet, large fog droplets are efficiently collected. Liquid water content in the fog was determined from the sampling rate of the instrument, assuming that 60% of the total liquid water sampled was actually collected [Waldman, 1986].

Fog water samples were preserved and analyzed for major ions and trace metals following the protocol described by Munger et al. [1983], with the exception described below. In fog water samples, significant Si(IV) concentrations are found during conventional anion analysis by ion chromatography. A possible explanation is the formation of stable but reversible Si(IV)-RCHO adducts, such as CH$_3$OH$\cdot$SiO$_2$ [Munger et al., 1984]. The standard ion chromatographic method (Dionex AS-3 column, [3 mM HCO$_3^-$ + 2.4 mM CO$_3^{2-}$] eluent, 3 mL min$^{-1}$ flow rate) proposed by Dionex Corporation [1981] and used by Munger et al. [1983] does not clearly separate Si(IV) and NO$_3^-$. Better separation is achieved with a weaker eluent or with the Dionex AS-4 column, but quantification of Si(IV) remains unsatisfactory. To solve this problem, aliquots for anion determination were spiked to 0.09 M H$_2$O$_2$ several minutes prior to injection and simultaneously made alkaline.
by the usual addition of HCO₃⁻ and CO₃²⁻ to match the eluent; this procedure was found to result in the quantitative oxidation of HSO₄⁻ and CH₃OHSO₄⁻ standards to SO₄²⁻ and the total suppression of the S(IV) peak in fog water samples. Sulfur(IV) concentrations were separately determined by a pararosaniline colorimetric method on aliquots preserved with buffered (pH 4) CH₂O immediately upon sample collection [Dasgupta et al., 1980]. Fog water SO₄²⁻ concentrations were calculated by subtracting the S(IV) concentrations thus obtained from the SO₄²⁻ concentrations determined by ion chromatography. Concentrations of carboxylate ions were determined by ion exclusion chromatography [Keene et al., 1983].

To date there are no standardized sampling procedures for the collection of fog water and aerosol samples for chemical analysis. Therefore it is important to assess the errors associated with our methods. A detailed discussion of sampling biases, artifacts, and standard errors on our data is presented in the appendix.

Hourly average concentrations of SO₂ were measured at Bakersfield by the Getty Oil Company and at McKittrick, Kernridge, and Lost Hills by West Side Operators (WSO). Concentrations of nitrogen oxides, CO, and O₃ were monitored at Kernridge by WSO. Surface winds were measured by WSO (Lost Hills, Kernridge, McKittrick, and Maricopa), Getty Oil Company (Bakersfield), National Weather Service (NWS) (Bakersfield and Fresno), Lemoore Naval Air Force Base, and Kern County Fire Department (Tehachapi). Upper level winds were measured at Edwards Air Force Base, located in the Mojave Desert on the SE side of the Tehachapi Mountains. Mixing heights were measured hourly by WSO at Kernridge with an acoustic sounder. Additional weather data were available from the National Weather Service station at Bakersfield.

To account for the equilibria between gas and aerosol phases, we define S(VI), N(V), and N(−III) to represent the element at the given oxidation state, both in the gas and aerosol phases. Thus N(V) includes HNO₃(g) and NO₃⁻, and N(−III) includes NH₃(g) and NH₄⁺. We further define [A] as the concentration of constituent A in fog water (moles per liter of water), and (A) as the concentration of A in air (moles per cubic meter of air). Concentrations of HNO₃(g) will generally be given in equivalents, for consistency with the units of NO₃⁻ and NH₄⁺ concentrations. "Equivalent" in that sense refers to the proton donor/acceptor capacity of the gas when scavenged by the aerosol. Both HNO₃(g) and NH₃(g) contribute one equivalent per mole; 1 ppb = 43 neq m⁻³ at 5°C.

WEATHER PATTERN AND POLLUTANT TRANSPORT

Figure 2 shows the profile versus time of mixing heights and stratus cloud bases over the valley floor during the sampling program. Two types of mixing height diurnal patterns were observed.

In the first pattern (December 31 to January 1, January 10–12, and January 14), ground-based inversions formed by radiation at night and broke up the following afternoon, leading to mixing heights in excess of 1000 m above ground level (AGL). This pattern was usually associated with clear skies or high cloudiness, but fogs in ground-based inversions were occasional occurrences (for example, at Bakersfield on December 31). Figure 3a gives the average wind vectors on the days when this pattern was observed. A net slow NW flow was observed on the valley floor, and upper level winds were NW; this is the usual flow in the area and reflects the circulation around the Pacific High off the California coast. Terrain influences in the southern end of the valley led to convergence of the flow in the SE corner of the valley. Surface winds in the valley frequently shifted in direction, and erratic low winds were typically observed under nighttime stable conditions.

Concentrations of trace gases at Kernridge were lowest on the days when this first pattern was observed (Figure 2) and so were aerosol concentrations [Jacob, 1985]. Because net horizontal transport was very slow (Figure 3a), it is unlikely that surface winds ventilated the valley by transport over the mountain ridges in the SE corner of the valley. Aerosol concentrations at Tehachapi and Lake Isabella remained much lower than in the valley, which is evidence against such transport. Instead, pollutant removal was due to rapid vertical mixing as the inversion broke up in the afternoon; this vertical mixing diluted the polluted air parcels and allowed their rapid transport by strong upper level NW winds to the surrounding air basins.

A different mixing height pattern was observed on January 2–7; during that period a strong temperature inversion based a few hundred meters above the ground persisted over the valley. This inversion was due to mesoscale subsidence associated with a stationary high-pressure system (Great Basin High) centered over southern Idaho and northern Nevada. Upper level winds at Edwards Air Force Base switched from NW to east during that period (circulation around the Great Basin High), and afternoon winds at Tehachapi were SE. The valley was capped throughout the January 2–7 period by a stratus cloud filling the upper part of the mixed layer (Figure 2); this cloud frequently intercepted the McKittrick site 250 m above the valley floor. On the night of January 4–5 the stratus base lowered sufficiently to cause fog at elevated sites on the valley floor (Kernridge and Bakersfield NWS station), although most of the valley floor remained overcast. On the nights of January 5–6 and 6–7 the stratus base lowered sufficiently to fill the entire mixed layer, as shown in Figure 2, and dense fog was observed throughout the valley. The cloud layer then deepened considerably on January 7–8; mixing heights rose to above 1000 m AGL, and drizzle fell on the valley floor. On January 9 the inversion base dropped again, but upper level winds had switched back to NW. After January 10 the first mixing height pattern (surface inversions at night breaking up in the afternoon) was again observed.

The capping of the valley by a persistent inversion based at a lower altitude than the surrounding mountain ridges obviously restricted ventilation. Concentrations of trace gases at Kernridge (Figure 2) increased over the stagnant January 2–7 period and dropped on January 8, when the mixing height rose above the mountain ridges. Concentrations then increased again on January 9–10 and dropped on January 10.

Winds in the valley during the January 2–7 period are shown in Figure 3b. Net horizontal transport was extremely slow. Cross-valley winds were dominant south of Lost Hills; farther north, however, a net flow north out the valley was observed. Reible [1982] had previously observed similar flow patterns during stagnation episodes in the valley and found pollutant transport in the southern end of the valley to be extremely complex because of the upslope flow/downslope flow systems associated with the mountain/valley breezes. He concluded from a series of tracer releases that the southern San Joaquin Valley behaved as a stirred tank with a mixing time of 1–2 days, slowly ventilated by the outflow at its northern end. We will try to interpret our data in terms of this simple model, and for that purpose we define the "southern San Joaquin Valley" (SSJV) as that portion of the valley south of the Kern County line (see Figure 1).

Figure 3b indicates a zone of inflow along the western edge of the SSJV and two possible outflows to the north and to the
Fig. 2. Concentrations of SO₂, NOₓ, and CO at Kernridge: the bold lines were obtained by smoothing the data with a digital filter. Also given are mixing heights (stratus cloud tops) measured at Kernridge and stratus cloud bases measured at the Bakersfield National Weather Service station. The reference altitude is that at Lost Hills, the lowest site on the valley floor. Kernridge hourly mixing height data were missing for January 8–9 (dotted line in the mixing height profile), and mixing heights for that period were interpolated from scattered measurements at Kernridge and cloud top data from pilot reports. Discontinuities in the mixing height profile at the altitude of Kernridge indicate a surface inversion at Kernridge. Discontinuities in the mixing height profile at 1000 m AGL indicate a mixing height in excess of 1000 m AGL.
east. However, very little transport of boundary layer air is expected over the mountain ridges on the eastern edge of the valley. The inversion did not break down or lift near the slopes: the stratus cloud intercepted the Bakersfield-Tehachapi highway as a well-defined fog layer, and the community of Tehachapi always remained sunny and clear. Further, winds in the SSJV were entirely decoupled from the circulation aloft, as indicated by the upper level winds to the east at Edwards AFB and the SE winds at Tehachapi. Aerosol concentrations remained very low at Tehachapi and Lake Isabella throughout the episode.

Therefore slow transport north out of the valley was the main outflow for SSJV air. Resultant winds at Lemoore, Fresno, and Lost Hills were consistent (Figure 3b). Projections of these winds on the valley axis (150°) yielded average speeds of 0.24, 0.26, and 0.22 m s⁻¹ at each site, respectively. Since the SSJV is about 100 km long, this flow led to an average residence time of 5 days for an air parcel within the SSJV. The accumulation pattern for CO at Kernridge (Figure 2) suggests approach of a steady state by January 5, which is consistent with a residence time of 5 days.

**AVERAGE S(VI), N(V), AND N(−III) CONCENTRATIONS AT EACH SITE**

The SSJV is the site of important SO₂, NOₓ, and NH₃ emissions (Table 1). The geographical distribution of the main emission sources is shown in Figure 1. Most of the NH₃ is emitted from confined-feeding operations concentrated on the east side of the valley, especially around Bakersfield and Visalia. Another important source of NH₃ is cropland, which occupies most of the land in the valley floor not used for oil recovery operations, and the associated fertilizer use. Emissions of SO₂ and NOₓ are concentrated in the east side and west side oil fields of the SSJV; the oil field emissions originate mostly from small boilers, which release their exhausts 10–20 m above the ground and therefore affect the immediate surroundings. Mobile sources (two major highways, off-road farm equipment, and city traffic) also contribute to NOₓ emissions.

Spatial patterns of aerosol and fog water concentrations (Tables 2 and 3a–3c) directly reflected the distribution of emission sources. The gaseous content of aerosol in the valley was dominated by SO₄²⁻, NO₃⁻, and NH₄⁺, which typically contributed over 90% of the total measured ionic loading. Concentrations of N(−III) were highest at Bakersfield and Visalia, near the large cattle feedlots, and lowest on the west side (Lost Hills and McKittrick). Mountain sites (Lake Isabella and Tehachapi), which have no important local NH₃ sources, had very low N(−III) concentrations.

Concentrations of S(VI) were highest at Bakersfield, which is within the east side oil fields; they were also high at McKittrick, which is within the west side oil fields, and at Buttonwillow, directly downwind of the west side oil fields. Concentrations of S(VI) at Wasco, Lost Hills, and Visalia were lower, reflecting their respective distances from oil recovery operations. Concentrations of S(VI) at the two mountain sites were very low and indicated no observable impact from the valley air.

Because most of the NOₓ was emitted from the same sources as SO₂, one would expect the spatial distribution of N(V) concentrations to be similar to that of S(VI). Indeed, N(V) concentrations were highest at Bakersfield; however, N(V) concentrations at McKittrick were low. The lack of NH₃ at McKittrick frequently led to acidic conditions, in which N(V) would be mostly present as HNO₃(g) and therefore quickly removed by deposition. This point will be addressed in more detail below. Concentrations of N(V) were higher at Visalia than would be expected from the spatial distribution of S(VI); Visalia is an important population center, and emissions from mobile sources were probably the dominant source of N(V) precursors at that site.

Fog water concentrations of trace metals were consistent with the above analysis (Table 3b). Concentrations of Ni and V, which are almost exclusively associated with residual oil burning [Cooper and Watson, 1980], were high at Bakersfield,
TABLE 1. \( \text{SO}_2 \), \( \text{NO}_x \), and \( \text{NH}_3 \) Emission Inventories for the Southern San Joaquin Valley

<table>
<thead>
<tr>
<th>Source</th>
<th>Emissions, t d(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_2 )(^{a})</td>
<td></td>
</tr>
<tr>
<td>Oil production</td>
<td>116</td>
</tr>
<tr>
<td>east side</td>
<td>69</td>
</tr>
<tr>
<td>west side</td>
<td>1</td>
</tr>
<tr>
<td>Agriculture</td>
<td>6</td>
</tr>
<tr>
<td>Mobile sources</td>
<td>1</td>
</tr>
<tr>
<td>Total emissions</td>
<td>1972</td>
</tr>
<tr>
<td>( \text{NO}_x )(^{b})</td>
<td></td>
</tr>
<tr>
<td>Stationary sources(^{c})</td>
<td>138</td>
</tr>
<tr>
<td>Mobile sources</td>
<td>52</td>
</tr>
<tr>
<td>Total emissions</td>
<td>190</td>
</tr>
<tr>
<td>( \text{NH}_3 )(^{d})</td>
<td></td>
</tr>
<tr>
<td>Livestock</td>
<td>46</td>
</tr>
<tr>
<td>Soil</td>
<td>18</td>
</tr>
<tr>
<td>Fertilizer use</td>
<td>10</td>
</tr>
<tr>
<td>Domestic</td>
<td>3</td>
</tr>
<tr>
<td>Fuel combustion</td>
<td>2</td>
</tr>
<tr>
<td>Total emissions</td>
<td>79</td>
</tr>
</tbody>
</table>

See Figure 1 for definition of southern San Joaquin Valley. Area is 7930 km\(^2\).

\(^{a}\)Aeromonitor, Incorporated [1984]. December 1982 data.

\(^{b}\)California Air Resources Board [1982], 1979 data.

\(^{c}\)Mostly oil and gas production.

\(^{d}\)Jacob [1985]. January 1984 data.

McKittrick, and Buttonwillow and low at Visalia. Concentrations of Pb, which is emitted by automobile exhaust, were high in the population centers (Bakersfield and Visalia) and low at rural sites (McKittrick and Buttonwillow).

Overall, the large differences in S(VI), N(V), and N(−III) concentrations that were observed from one site to another over distances of only a few tens of kilometers show that the composition of the \( \text{H}_2\text{SO}_4\)-\( \text{HNO}_2\)-\( \text{NH}_3 \) system at each site was strongly determined by the nature of emission sources in the immediate vicinity. A chemical balance on primary aerosol (based on the work by Cooper and Watson [1980]) indicated that all but a negligible fraction of the total S(VI) in the valley was of secondary origin. However, in spite of the time required for oxidation of \( \text{SO}_2 \) to \( \text{H}_2\text{SO}_4 \), the areas of \( \text{SO}_2 \) emissions matched the areas of high S(VI) concentrations. This supports our observation that horizontal pollutant transport on the valley floor was very slow. Under such conditions, fog water acidity should be directly determined by the relative abundances of local acidic (\( \text{SO}_2 \), \( \text{NO}_2 \)) and alkaline (\( \text{NH}_3 \)) emissions. Indeed, Table 3 indicates that fog water acidity differed greatly from site to site, depending on the availability of \( \text{NH}_3 \) to neutralize S(VI) and N(V); low pH values were found at McKittrick and very high pH values were found at Visalia. The pH of fog samples collected simultaneously at four sites during the widespread January 7 fog event clearly showed this spatial pattern (Figure 4). Acidic fog was consistently observed at McKittrick but never at the other sites.

Acidic fog had frequently been observed at the Bakersfield site during the previous winter [Jacob et al., 1984a]. In view of the close balance of acids and bases at that site, small fluctuations in emissions can result in a lack of available base to titrate acid inputs. To predict the vulnerability of an atmosphere to an “acid fog” problem, one must have a quantitative measure of the acid-neutralizing capacity of that atmosphere. To this end we now introduce the concept of atmospheric alkalinity, defined by analogy to the concept of alkalinity used in the aquatic chemistry literature [Stumm and Morgan, 1970].

**Atmospheric Alkalinity**

We define fog water alkalinity \([\text{ALK}]\) as the deficiency of aqueous phase \( \text{H}^+ \) with respect to the reference system of “neutralized” fog water species (\( \text{CAT}^{+*} \), \( \text{Cl}^{-} \), \( \text{NO}_3^{-} \), \( \text{SO}_4^{2-} \), \( \text{S}^{4-} \), \( \text{CO}_2 \), \( \text{HA} \)). \( \text{CAT}^{+*} \) refers to cations other than \( \text{H}^+ \), and \( \text{HA} \) refers to undisassociated weak acids other than \( \text{CO}_2 \). In the pH range 3–8 the following expression for \([\text{ALK}]\) can be used to a good approximation:

\[
[\text{ALK}] = \sum [\text{A}^{-}] + [\text{S}^{4-}] + [\text{HCO}_3^{-}] + [\text{NH}_3(aq)] + [\text{OH}^-] - [\text{H}^+] \tag{1}
\]

The main \( \text{S}^{4-} \) species in the pH range 2–7 are expected to be \( \text{HSO}_4^{-} \) and stable monovalent \( \text{S}^{4-} \) adducts [Jacob and Hoffmann, 1983; Munger et al., 1984; Boyce and Hoffmann, 1984]. Therefore the monovalent form of \( \text{S}^{4-} \) is most appropriate for use as reference. If \( \text{CO}_2 \) was the only weak acid present, fog water at the reference point ([\( \text{ALK} \]) = 0) would correspond to pure water in equilibrium with atmospheric \( \text{CO}_2 \) and the corresponding reference \( \text{pH} \) would be about 5.6; because additional weak acids are present, the reference \( \text{pH} \) is lower. At the concentrations of carboxylic acids found in the San Joaquin Valley (Table 2) the reference \( \text{pH} \) is of the order of 4.5. This is still above the threshold at which environmental damage from “acid fog” may be anticipated [Scherbatskoy and Klein, 1983; Granett and Musselman, 1984; Hoffmann, 1984].

Fog water with \([\text{ALK}] < 0\) is said to contain inorganic acidity, and its \( \text{pH} \) is lower than that of the reference system. Such fog water has zero buffer capacity with respect to further inputs of strong acids, which may then lead to extremely acidic conditions. We will use the presence of inorganic acidity as an operational definition of the term “acid fog.” Alkaline fog water (defined by \([\text{ALK}] > 0\)) has a \( \text{pH} \) higher than that of the reference system and will neutralize acid inputs until exhaustion of the alkalinity. However, \([\text{ALK}] \) is not a true measure of the acid-neutralizing capacity of the fog water because it ignores exchanges with the gas phase. In particular, alkaline fog water may support a substantial \( \text{NH}_3 \) vapor pressure [Jacob et al., this issue], which provides an additional source of acid-neutralizing capacity to the fog water. Further, fog water alkalinity depends on the fraction of the aerosol scavenged in the fog. To use alkalinity as a measure of the acid-neutralizing capacity of the atmosphere with respect to acid fog, we need to introduce a more general concept, atmospheric alkalinity.

The atmospheric alkalinity (\( \text{ALK} \)) (equivalents per cubic meter of air) is the sum of total aerosol alkalinity and gas phase alkalinity in an atmosphere. That atmosphere may or may not contain fog. The reference system is the same as that used for defining fog water alkalinity; gas phase \( \text{CO}_2 \) and other weak acids are reference species. The aerosol alkalinity (\( \text{ALK}_a \)) is given by (1), where fog water concentrations (moles per liter of water) are replaced by total aerosol concentrations (moles per cubic meter of air). The gas phase alkalinity is given by the proton donor and acceptor capacities of water-soluble atmospheric gases with respect to the reference system. Atmospheric alkalinity is a conserved quantity upon fog formation and can therefore be used to predict the potential for acid fog from aerosol and gas phase measurements taken under nonfoggy conditions. Atmospheric alkalinity also gives the amount of strong acids that may be emitted to the atmo-
sphere before an acid fog problem is to be feared and is thus a useful tool for regulatory purposes.

For the subset of samples analyzed for carboxylic acids we calculated the fog water alkalinity [ALK] as follows:

\[
[\text{ALK}] = [\text{HCOO}^-] + [\text{CH}_3\text{COO}^-] + [\text{CH}_3\text{CH}_2\text{COO}^-] + [\text{CH}_3\text{CH(OH)COO}^-] + [\text{HCO}_3^-] + [\text{NH}_4(aq)] + [\text{OH}^-] - [\text{H}^+]
\]

where \([\text{H}^+]\) was directly measured, and the concentrations of alkalinity-contributing species were determined from the fog water concentrations and the equilibrium constants for the acid-base equilibria at 5°C. Smith and Martell [1976] and Martell and Smith [1977] give \(K_a\) values of \(1.7 \times 10^{-4}\) M, \(1.7 \times 10^{-5}\) M, \(1.3 \times 10^{-5}\) M, and \(1.3 \times 10^{-6}\) M for HCOOH, CH₃COOH, CH₃CH₂COOH, and CH₃CH(OH)COOH, respectively. \(K_a = 1.5 \times 10^{-5}\) M for NH₃, and \(K_a = 2.0 \times 10^{-12}\) M² for H₂O dissociation. Concentrations of
TABLE 2. Aerosol, HNO$_3$(g), and NH$_3$(g) Data, December 31, 1983 to January 14, 1984

<table>
<thead>
<tr>
<th>Site</th>
<th>Number of Samples</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>NH$_4^+$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Cl$^-$</th>
<th>NO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>HNO$_3$(g)</th>
<th>NH$_3$(g)</th>
<th>N(V)</th>
<th>N(−III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakersfield Range</td>
<td>30</td>
<td>&lt;4-56</td>
<td>&lt;4-19</td>
<td>144-1149</td>
<td>6-75</td>
<td>&lt;4-12</td>
<td>&lt;20-67</td>
<td>85-467</td>
<td>78-855</td>
<td>&lt;4-46</td>
<td>19-483</td>
<td>93-471</td>
<td>209-1204</td>
</tr>
<tr>
<td>Mean</td>
<td>15</td>
<td>4</td>
<td>6</td>
<td>16</td>
<td>7</td>
<td>8</td>
<td>27</td>
<td>276</td>
<td>336</td>
<td>16</td>
<td>146</td>
<td>292</td>
<td>706</td>
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<tr>
<td>Wasco Range</td>
<td>29</td>
<td>&lt;4-86</td>
<td>&lt;4-20</td>
<td>74-584</td>
<td>4-43</td>
<td>&lt;4-10</td>
<td>&lt;20-93</td>
<td>23-419</td>
<td>19-312</td>
<td>&lt;4-54</td>
<td>&lt;17-273</td>
<td>54-431</td>
<td>95-648</td>
</tr>
<tr>
<td>Mean</td>
<td>12</td>
<td>4</td>
<td>6</td>
<td>16</td>
<td>7</td>
<td>4</td>
<td>22</td>
<td>195</td>
<td>137</td>
<td>19</td>
<td>70</td>
<td>214</td>
<td>378</td>
</tr>
<tr>
<td>Lost Hills Range</td>
<td>25</td>
<td>&lt;4-48</td>
<td>&lt;4-7</td>
<td>55-553</td>
<td>4-57</td>
<td>&lt;4-11</td>
<td>&lt;20-43</td>
<td>4-310</td>
<td>16-214</td>
<td>&lt;4-174</td>
<td>&lt;17-88</td>
<td>40-414</td>
<td>55-617</td>
</tr>
<tr>
<td>Mean</td>
<td>11</td>
<td>&lt;4</td>
<td>4</td>
<td>17</td>
<td>&lt;4</td>
<td>&lt;4</td>
<td>&lt;20</td>
<td>132</td>
<td>108</td>
<td>40</td>
<td>31</td>
<td>172</td>
<td>254</td>
</tr>
<tr>
<td>Mckittrick Range</td>
<td>29</td>
<td>5-70</td>
<td>&lt;4-13</td>
<td>28-424</td>
<td>6-43</td>
<td>&lt;4-10</td>
<td>&lt;20-71</td>
<td>10-246</td>
<td>36-802</td>
<td>&lt;4-164</td>
<td>&lt;17-205</td>
<td>21-347</td>
<td>37-457</td>
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<tr>
<td>Mean</td>
<td>17</td>
<td>&lt;4</td>
<td>4</td>
<td>20</td>
<td>4</td>
<td>21</td>
<td>89</td>
<td>195</td>
<td>34</td>
<td>34</td>
<td>123</td>
<td>258</td>
<td></td>
</tr>
<tr>
<td>Buttonwillow</td>
<td>18</td>
<td>4-51</td>
<td>&lt;4-10</td>
<td>36-663</td>
<td>6-68</td>
<td>&lt;4-11</td>
<td>&lt;20-41</td>
<td>34-400</td>
<td>31-579</td>
<td>&lt;4-37</td>
<td>18-645</td>
<td>77-406</td>
<td>135-1001</td>
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<tr>
<td>Mean</td>
<td>19</td>
<td>&lt;4</td>
<td>4</td>
<td>30</td>
<td>31</td>
<td>5</td>
<td>23</td>
<td>184</td>
<td>188</td>
<td>12</td>
<td>131</td>
<td>196</td>
<td>437</td>
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<tr>
<td>Visalia Range</td>
<td>14</td>
<td>&lt;4-16</td>
<td>&lt;4-7</td>
<td>108-359</td>
<td>6-37</td>
<td>2-5</td>
<td>&lt;20-41</td>
<td>73-318</td>
<td>35-129</td>
<td>&lt;4-15</td>
<td>184-662</td>
<td>73-322</td>
<td>484-869</td>
</tr>
<tr>
<td>Mean</td>
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<td>&lt;4</td>
<td>4</td>
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<td>20</td>
<td>&lt;20</td>
<td>175</td>
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<td>7</td>
<td>450</td>
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<td>689</td>
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<td>&lt;4-4</td>
<td>&lt;8-32</td>
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<td>&lt;4-23</td>
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<td>&lt;8-44</td>
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<tr>
<td>Mean</td>
<td>10</td>
<td>&lt;4</td>
<td>4</td>
<td>8</td>
<td>11</td>
<td>&lt;4</td>
<td>&lt;20</td>
<td>9</td>
<td>9</td>
<td>16</td>
<td>19</td>
<td>25</td>
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</tr>
<tr>
<td>Tehachapi Range</td>
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<td>&lt;4-140</td>
<td>&lt;8-73</td>
<td>10-126</td>
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<td>&lt;4-18</td>
<td>&lt;17-74</td>
<td>&lt;8-68</td>
<td>&lt;8-84</td>
</tr>
<tr>
<td>Mean</td>
<td>17</td>
<td>12</td>
<td>11</td>
<td>46</td>
<td>8</td>
<td>11</td>
<td>17</td>
<td>34</td>
<td>18</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values are in nanoequivalents per cubic meter. See Jacob [1985] for the complete data set.
*From January 5 to January 14.
*From December 31 to January 7.

HCO$_3^-$ were calculated by assuming equilibrium with $P_{CO_2} = 340$ ppm, $X_{KH} = 7.07 \times 10^{-6}$, and $T = 5^\circ C$. We assumed $SIV = 0$ in our calculations; free SIV is mostly divalent at $pH > 7$, but there is strong evidence that SIV in fog water actually combined with aldehydes to form stable adducts [Munger et al., 1984]. These SIV-aldehyde adducts remain monovalent over a higher range of $pH$, up to $pH 11.7$ for the SIV-formaldehyde adduct [Sørensen and Andersen, 1970]. Even if SIV was actually divalent at $pH > 7$, SIV concentrations in fog water at such high $pH$ values were low (Table 3, Visalia), and the contribution of SIV$^2-$ to the fog water alkalinity would be very small.

Estimating (ALK), from the available aerosol data was less straightforward. We assumed that the ions on the right-hand side of (1), possibly plus additional weak acid anions, constituted the aerosol ionic content unaccounted for in our chemical analysis. By a charge balance on the aerosol we obtained:

$$\text{ALK}_a = (\text{Na}^+) + (\text{K}^+) + (\text{NH}_4^+) + 2(\text{Ca}^{2+}) + 2(\text{Mg}^{2+}) - (\text{Cl}^-) - (\text{NO}_3^-) - 2(\text{SO}_4^{2-})$$  (3)

Since we have argued that the inorganic acidity in fog is mostly controlled by species in the H$_2$SO$_4$—HNO$_3$—NH$_3$ system, we will assume that the only gas phase contributors to (ALK) are HNO$_3$(g) and NH$_3$(g). A calculation of the ultimate alkalinity of an air parcel should include SO$_2$(g); however, the contribution of SO$_2$(g) to (ALK) may be limited by the slow rate of SO$_2$ scavenging by fog [Jacob and Hoffmann, 1983]. For now we ignored the SO$_2$(g) contribution and calculated the atmospheric alkalinity from the expression:

$$\text{ALK} = \text{ALK}_a + (\text{NH}_3(g)) - (\text{HNO}_3(g))$$  (4)

Average alkalinities at each site are given in Table 4a. Because of the possibility of HNO$_3$ or NH$_3$ volatilization from aerosol filter samples collected in fog (see appendix), (ALK) and (ALK)$_a$ were calculated only for nonfoggy conditions. (ALK) and (ALK)$_a$ were usually small numbers determined by the difference of two large numbers, so the standard errors were fairly large. The calculation of the fog water alkalinity [ALK] involved subtracting a small number from a large number; the resulting standard errors were small and were not indicated explicitly.

TABLE 3a. Liquid Water-Weighted Average For Water Concentrations of Major Ions, December 31, 1983, to January 14, 1984

<table>
<thead>
<tr>
<th>Site</th>
<th>Number of Samples</th>
<th>pH Range</th>
<th>H$^+$</th>
<th>Na$^+$</th>
<th>NH$_4^+$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Cl$^-$</th>
<th>NO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>S(IV)</th>
<th>E$'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakersfield</td>
<td>16</td>
<td>5.10-6.92</td>
<td>2.0</td>
<td>42</td>
<td>3270</td>
<td>169</td>
<td>33</td>
<td>122</td>
<td>819</td>
<td>2070</td>
<td>384</td>
<td>0.057</td>
</tr>
<tr>
<td>Mckittrick</td>
<td>58</td>
<td>2.68-5.23</td>
<td>93</td>
<td>11</td>
<td>480</td>
<td>39</td>
<td>5</td>
<td>15</td>
<td>250</td>
<td>345</td>
<td>43</td>
<td>0.11</td>
</tr>
<tr>
<td>Buttonwillow</td>
<td>7</td>
<td>5.01-6.79</td>
<td>5.6</td>
<td>13</td>
<td>1067</td>
<td>82</td>
<td>10</td>
<td>47</td>
<td>522</td>
<td>760</td>
<td>74</td>
<td>0.050</td>
</tr>
<tr>
<td>Visalia</td>
<td>13</td>
<td>5.51-7.23</td>
<td>0.1</td>
<td>6</td>
<td>1080</td>
<td>17</td>
<td>2</td>
<td>115</td>
<td>341</td>
<td>265</td>
<td>12</td>
<td>0.049</td>
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</tbody>
</table>

Unless otherwise indicated, concentrations are in microequivalents per liter of water. See Jacob [1985] for the complete data set.
*Average liquid water content, based on the total amount of water collected and the total sampling time.
TABLE 3b. Liquid Water-Weighted Average Fog Water Concentrations of Trace Metals, December 31, 1983, to January 14, 1984

<table>
<thead>
<tr>
<th>Site</th>
<th>Number of Samples</th>
<th>Fe</th>
<th>Mn</th>
<th>Pb</th>
<th>Cu</th>
<th>Ni</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakersfield</td>
<td>5</td>
<td>438</td>
<td>31</td>
<td>134</td>
<td>19</td>
<td>29</td>
<td>41</td>
</tr>
<tr>
<td>McKittrick</td>
<td>42</td>
<td>76</td>
<td>6</td>
<td>27</td>
<td>12</td>
<td>48</td>
<td>91</td>
</tr>
<tr>
<td>Buttonwillow</td>
<td>6</td>
<td>142</td>
<td>17</td>
<td>44</td>
<td>82</td>
<td>44</td>
<td>32</td>
</tr>
<tr>
<td>Visalia</td>
<td>6</td>
<td>144</td>
<td>7</td>
<td>61</td>
<td>7</td>
<td>11</td>
<td>8</td>
</tr>
</tbody>
</table>

Concentrations are in micrograms per liter of water. See Jacob [1985] for the complete data set.

The western edge of the SSJV currently suffers from a general acid fog problem, as shown by the average negative values of (ALK). In the remainder of the valley, (ALK) > 0, and fog water is not usually acidic. However, the average values of (ALK) at Bakersfield and Wasco presently amount to less than 20% of (SVI) (N(V)) equivalent concentrations. If NH3 emissions in the SSJV decrease by 20% compared to their current level, for example, because of a decline of the cattle industry or fluctuations in the soil moisture and temperature, a general acid fog situation in the east side of the SSJV will result. The same result will be achieved by a 20% increase in (SVI) (N(V)) equivalent concentrations due to a rise in SO2 and NOx emissions. Fog water alkalinity at Visalia will not be affected by these changes in SSJV emissions, considering the large (ALK)/(SVI) (N(V)) ratio at that site; therefore there is little risk that an acid fog problem in the SSJV could spread to the northern part of the San Joaquin Valley.

The partitioning of the atmospheric alkalinity between the gas phase and the aerosol is of interest. Scavenging of NH3(g) to form ammonium salts of weak acids could be a source of important alkalinity in the aerosol or fog water. Indeed, significant alkalinitities were found in fog water; however, aerosol collected under nonfoggy conditions was never significantly alkaline. Although the error bars on the determinations of (ALK) were large, the absence of positive (ALK) values in the presence of large excesses of NH3(g), as at Visalia, strongly suggests that the alkaline ammonium salts are volatile under nonfoggy conditions. This hypothesis is supported by concurrent sampling of aerosol and fog water at Visalia, where NH3 was in excess of NO3− and SO4 2− in the fog water but not in the dried aerosol. Artifact aerosol neutralization should not occur during filter storage (see appendix).

Under nonfoggy acidic conditions the aerosol contained significant inorganic acidity when SVI was present in excess of N(−III). This occurred in six of the samples, all at McKittrick. In the remainder of the samples collected under acidic conditions the aerosol was neutralized, and the inorganic acidity was entirely present in the gas phase as HNO3(g). This observation is in agreement with aerosol equilibrium models [Bassett and Seinfeld, 1983]; NH3(g) is scavenged by acid sulfate aerosol until this aerosol is neutralized as (NH3)2SO4. Excess NH3 may then combine with HNO3 to add NH4NO3 to the aerosol phase, but HNO3 in excess of NH3 remains in the gas phase.

The contributions of different species to fog water alkalinity are shown in Table 4b. The main contributors to [ALK] at Bakersfield and Buttonwillow were formate and acetate. Formic and acetic acids are efficiently scavenged in fog water at pH > 5; they are highly soluble, as indicated by their large Henry's law constants (Hformic,298K = 3.7 × 10^3 M atm^−1, Hacetic,298K = 8.8 × 10^4 M atm^−1 [Weast, 1984]), and they are mostly dissociated, as indicated by their acidity constants (see above). At Visalia the fog water pH was much higher than at Bakersfield or Buttonwillow, and the contribution from HCO3^− to [ALK] was correspondingly larger. Carboxylate anions did not provide higher contributions at Visalia than at Bakersfield or Buttonwillow; since carboxylic acids are already efficiently scavenged at pH 5–6, raising the pH higher leads to little additional scavenging.

**TABLE 4b. Average Alkalinitities at Each Site**

<table>
<thead>
<tr>
<th>Site</th>
<th>Number of Samples</th>
<th>ALK_1, ALK_2, ALK_3, ALK_4, ALK_5, ALK_6</th>
<th>L*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakersfield</td>
<td>28</td>
<td>111 ± 31, 20 ± 30, 19 ± 13, 14 ± 8, 11 ± 7, 8 ± 3</td>
<td>210</td>
</tr>
<tr>
<td>Wasco</td>
<td>27</td>
<td>46 ± 19, 12 ± 8, 11 ± 7, 10 ± 6, 8 ± 4, 6 ± 3</td>
<td>-98</td>
</tr>
<tr>
<td>Lost Hills</td>
<td>23</td>
<td>-11 ± 6, 8 ± 4, 7 ± 3, 5 ± 2, 3 ± 1, 1 ± 0</td>
<td>183</td>
</tr>
<tr>
<td>McKittrick</td>
<td>17</td>
<td>131 ± 28, 130 ± 27, 129 ± 26, 128 ± 25, 127 ± 24, 126 ± 23</td>
<td>220</td>
</tr>
</tbody>
</table>

**TABLE 3c. Liquid Water-Weighted Average Fog Water Concentrations of Carboxylic Acids, December 31, 1983, to January 14, 1984**

<table>
<thead>
<tr>
<th>Site</th>
<th>Number of Samples</th>
<th>Formate</th>
<th>Acetate</th>
<th>Lactate</th>
<th>Propionate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakersfield</td>
<td>2</td>
<td>45</td>
<td>155</td>
<td>15</td>
<td>9</td>
</tr>
<tr>
<td>McKittrick</td>
<td>26</td>
<td>22</td>
<td>3</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Buttonwillow</td>
<td>2</td>
<td>144</td>
<td>59</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Visalia</td>
<td>6</td>
<td>53</td>
<td>65</td>
<td>7</td>
<td>0</td>
</tr>
</tbody>
</table>

Concentrations are in micromol per liter of water. See Jacob [1985] for the complete data set.

**ACCUMULATION AND REMOVAL OF H2SO4•HNO3•NH3 SPECIES OVER THE COURSE OF A SEVERE STAGNATION EPISEODE**

The goal of this section is to interpret the accumulation of SVI, N(V), and N(−III) species over the course of the January 2–7 severe stagnation episode, in terms of atmospheric production and removal mechanisms. As shown in Figure 5, the stagnation episode was generally associated with high concentrations of SVI, N(V), and N(−III). The inversion base was roughly stable at h = 400 m AGL throughout the episode, and the residence time for air parcels in the SSJV was t_r = 5 days. Therefore deposition was a more important removal pathway than ventilation for species with deposition velocities > 0.1 cm s^−1. The highest concentrations on the SSJV floor (Bakersfield, Wasco, and Lost Hills) were observed on January 5, after 4 days of stagnation under nonfoggy, overcast conditions; low aerosol deposition rates in the absence of fog allowed high levels of pollutant accumulation. Dense, widespread valley fogs on the mornings of January 6 and 7 (Figure 2) were associated with general decreases in aerosol con-
TABLE 4b. Contributions of Different Species to Fog Water Alkalinity

<table>
<thead>
<tr>
<th>Site</th>
<th>Number of Samples</th>
<th>Free Acidity*</th>
<th>Formate, μeq L⁻¹</th>
<th>Acetate, μeq L⁻¹</th>
<th>Lactate, μeq L⁻¹</th>
<th>Propionate, μeq L⁻¹</th>
<th>HCO₃⁻, μeq L⁻¹</th>
<th>NH₄⁺(aq), μeq L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakersfield</td>
<td>2</td>
<td>-1</td>
<td>45</td>
<td>134</td>
<td>15</td>
<td>9</td>
<td>6</td>
<td>&lt;1</td>
</tr>
<tr>
<td>McKittrick</td>
<td>38</td>
<td>-123</td>
<td>22</td>
<td>1</td>
<td>2</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Buttonwillow</td>
<td>2</td>
<td>-8</td>
<td>142</td>
<td>44</td>
<td>3</td>
<td>&lt;1</td>
<td>1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Visalia</td>
<td>6</td>
<td>&lt;1</td>
<td>53</td>
<td>65</td>
<td>7</td>
<td>&lt;1</td>
<td>92</td>
<td>2</td>
</tr>
</tbody>
</table>

Contributions calculated from fog water pH.
*Free acidity = [H⁺] - [OH⁻].

Concentrations, probably due to rapid deposition of fog droplets. Jacob et al. [1984a] have previously suggested that enhanced aerosol deposition in fogs efficiently limits pollutant accumulation during stagnation episodes, and our data support this hypothesis. Further decreases in atmospheric concentrations were observed on January 7–8, due to the rise of the inversion base (Figure 2) and deposition from drizzle.

As S(VI) and N(V) were produced over the course of the stagnation episode, significant inorganic acids were observed at Wasco, Lost Hills, and McKittrick. At Bakersfield, sufficient N(−III) was available to totally neutralize acid inputs. Because of the remarkably stable mixing height and the lack of ventilation we can attempt to apply stirred-tank considerations to calculate the rates of H₂SO₄ and HNO₃ production in the SSJV. The residence time τ of a species in a stirred tank is given by the expression:

$$\frac{1}{\tau} = \frac{v}{h} + \frac{1}{\tau_a} + k$$ (5)

where v is the deposition velocity and k is a first-order chemical loss rate. Of special interest is the period January 2–5, ranging from the onset of stagnation to the first widespread valley fog. The SSJV floor (Bakersfield, Wasco, and Lost Hills) remained overcast throughout that period, and roughly constant values of v and k may be expected. We can thus follow the evolution over 4 days of a very well-controlled stagnant atmospheric system.

Production of H₂SO₄

Concentrations of S(VI) increased progressively on the SSJV floor during the nonfoggy January 2–5 period. Concentrations remained very low at Visalia, which is out of the SSJV and far from SO₂ sources. Sulfur dioxide, the main precursor of S(VI) in the SSJV, has a deposition velocity of the order of 1 cm s⁻¹ over grass [Sehmel, 1980]. A steady state for SO₂ in the SSJV should therefore be approached on a time scale of the order of 1 day after the onset of stagnation, and this appeared to be the case at Kernridge (Figure 2). Measured concentrations of SO₂ at Bakersfield, Kernridge, and Lost Hills during January 3–5 averaged 25, 12, and 3 ppb, respectively; a strong spatial gradient in SO₂ concentrations was maintained because mixing was slow. Modeling of SO₂ transport under stagnant conditions [Aerosenvironment, Incorporated, 1984] indicates that the SO₂ concentration field in the SSJV should be bounded on the lower end at Wasco and Lost Hills and on the upper end at Bakersfield. Therefore we expect steady state SO₂ concentrations in the SSJV mixed layer to range between 3 and 25 ppb. A stirred-tank calculation based on the volume of the SSJV mixed layer and the emission data of Table 1, assuming chemical loss to be slower than deposition (VSO₂ = 1 cm s⁻¹), gives an average steady state SO₂ concentration of the order of 9 ppb in the SSJV. This is consistent with our observations.

The accumulation pattern of S(VI) on the SSJV floor was consistent with a pseudo first-order conversion rate of SO₂ to S(VI). Concentrations of S(VI) increased relatively steadily during the January 3–5 period, when SO₂ concentrations were approaching steady state. This steady conversion of SO₂ maintained important differences in S(VI) concentrations from site to site within the SSJV. A time lag for S(VI) production was clearly seen at Bakersfield on January 2, attributable to the time required for SO₂ to accumulate after the onset of stagnation. The profiles of S(VI) concentrations in the SSJV did not suggest an approach of steady state by January 5; the residence time of S(VI) aerosol in the SSJV under nonfoggy conditions was thus longer than 3 days, indicating a deposition velocity V∞(S(VI)) < 0.05 cm s⁻¹ (equation 5). This is in agreement with predicted deposition velocities for particles in the 0.05- to 1-μm size range at low wind velocities [Sehmel, 1980]. Over the period January 3–5, S(VI) was produced in the SSJV much faster than it was removed, and we can to a first approximation equate the observed rate of S(VI) accumulation to the rate of SO₂ conversion. The average rates of S(VI) accumulation during January 3–5 were 9 neq m⁻³ h⁻¹ at Bakersfield, 3 neq m⁻³ h⁻¹ at Wasco, and 3 neq m⁻³ h⁻¹ at Lost Hills; from the assumed steady state SO₂ concentration field in the SSJV (range 3–25 ppb, average 9 ppb), we estimate an average SO₂ conversion rate in the range 0.4–1.1% h⁻¹.

Because of the lack of photochemical activity during the stagnation episode (see Figure 6 and discussion below), conversion of SO₂ to H₂SO₄ must have proceeded predominantly in the aerosol and the cloud droplets. A likely pathway is metal-catalyzed autoxidation in the aqueous phase [Hoffmann and Jacob, 1984], which does not require photochemically generated oxidants. Considering that a stratus cloud filled a large fraction of the mixed layer during the period of January 3–5, an important question is to determine if the principal site for S(IV) oxidation was the cloud or the haze aerosol below. Concentrations of SO₂ progressively decreased at Kernridge during the foggy January 5–7 period, while concentrations of CO and NOₓ (which was emitted from the same sources as SO₂) kept on increasing. This is strong evidence that removal of SO₂ from the atmosphere was enhanced in the presence of fog. From Figure 2 the rate of SO₂ scavenging by fog appears to be on the order of 5% h⁻¹. This enhanced scavenging of SO₂ in fog does not necessarily imply enhanced production of S(VI); S(IV) may be stabilized in the aqueous phase by formation of adducts [Munger et al., 1983, 1984] or removed by deposition before being oxidized. We tried to evaluate S(VI) production directly in fog droplets by comparing S(VI) concentrations in successive fog water samples collected at one site, using Ni and V as conservative tracers for sulfur. However, we did not obtain statistically significant rates of SO₂ conversion in fog water (2 ± 6% h⁻¹ at Bakersfield, 0 ± 3% h⁻¹ at McKittrick [see Jacob, 1985]). This failure to find statistically significant rates is probably due to the complex nature of fog droplet growth and transport.
Fig. 5. Aerosol and gas phase concentrations and atmospheric alkalinites at the six valley sites over the period January 1–8. An open circle on top of the data bar indicates that the gas phase species was not measured. A plus sign on top of the data bar indicates that volatilization from the filter in fog could have affected the aerosol measurement (see the appendix).
Production of HNO₃

In addition to H₂SO₄, HNO₃ was produced. However, N(V) did not accumulate as steadily as S(VI). Concentrations of N(V) in the SSJV increased rapidly at the onset of stagnation (January 2–3) but did not increase after January 3. Nitrogen oxides accumulated steadily throughout the stagnation episode (Figure 2), showing no indication of loss from chemical conversion. Concentrations of N(V) did not show the large differences from site to site that were observed for S(VI), even though SO₂ and NO, mostly originated from the same combustion sources.

A logical explanation for these observations is that the rate of HNO₃ production was slow during the stagnation episode because of the widespread and persistent low overcast. Figure 6 shows the NO and O₃ concentration profiles at Kernridge. Ozone levels prior to the onset of stagnation were relatively high, indicating substantial photochemical activity; HNO₃ production by the reaction NO₂ + OH should proceed rapidly under those conditions. Also, O₃ was always present in excess of NO, so that HNO₃ could be produced at night by heterogeneous pathways initiated by the reaction NO₂ + O₃. 

[Heikes and Thompson, 1983]. After the onset of stagnation, however, the overcast restricted photochemical activity, and very low O₃ concentrations were observed: OH concentrations were probably very low. Further, since NO progressively accumulated to levels sufficient to titrate O₃ fully, the reaction NO₂ + O₃ did not proceed. Therefore little secondary production of HNO₃ would be expected in the SSJV after January 3. Fog did not perceptibly enhance the conversion of NO₂ to HNO₃; concentrations of NO₂ at Kernridge kept on increasing during the January 5–7 foggy period, similarly to CO, which is not water-soluble. This is consistent with the poor solubilities of NO and NO₂ in water at atmospheric concentrations [Schwartz and White, 1981].

The NO₃⁻ aerosol present after January 3 was therefore mostly aged aerosol, slowly mixing within the SSJV. As mixing proceeded, the differences in NO₃⁻ concentrations from site to site become progressively weaker. Concentrations of N(V) at Bakersfield and Wasco were similar on January 4–5, even though S(VI) concentrations were much higher at Bakersfield. At Lost Hills and McKittrick, acidification of the atmosphere coincided with a brief increase in HNO₃(g) concentrations, immediately followed by an important drop in total N(V) concentrations. This indicates displacement of NO₃⁻ by H₂SO₄ in the aerosol, followed by rapid deposition of HNO₃(g). The atmospheric lifetime for HNO₃(g) is thus short (<0.5 days), which implies a large deposition velocity (>1 cm s⁻¹).

Accumulation of NH₃

Almost all of the NH₃ emitted in the SSJV during the stagnation episode was used to neutralize acid inputs. The fate of the resulting (SO₄²⁻, NO₃⁻, NH₄⁺) aerosol has been discussed above. At Visalia, however, acid inputs were small, and a large fraction of total N(−III) remained in the gas phase as NH₃(g). No accumulation of NH₃(g) was apparent at that site over the course of the episode, and this suggests an atmospheric residence time of <0.5 days for NH₃(g) (deposition velocity of >1 cm s⁻¹). Frequent fog and drizzle after January 5 at Visalia resulted in an important depletion of NH₄⁺ aerosol, but NH₃(g) concentrations were unaffected. Ammonia is poorly scavenged at the high pH values typical of Visalia fog water [Jacob et al., this issue].

Stirred-Tank Simulation

The above discussions have shown that the profiles of concentrations versus time during a stagnation episode can be successfully interpreted, based on stirred-tank considerations of pollutant accumulation and removal; however, the differences in concentrations from site to site clearly indicate that a stirred-tank model for the SSJV as a whole is not an adequate modeling tool. The major reason is that internal mixing is slow. Nevertheless, the success of the stirred-tank model in interpreting the data at individual sites suggests that one could model the SSJV by subdividing it into a number of cells where the stirred-tank approximation could be properly invoked. Such an exercise is beyond the scope of this paper; however, for the sake of illustrating and summarizing our discussion of field data we will present the results of a stirred-tank calculation applied to the entire SSJV. The accumulation of constituent A in such a model is described by

\[ \frac{d(A)}{dt} = E_A + k'(B) - k(A) \]

\[ -\frac{1}{h} \left[ (A_p v_{Ap}) + (A_A v_{AA}) + (A_p v_{Ap}) - (A) v_{p} \right] = \frac{1}{\tau} \]  

where \( A_p, A_A, \) and \( A_p \) are the gas phase, aerosol phase, and fog water phase species, respectively, \( E_A \) is the emission rate averaged over the volume of the mixed layer (moles per cubic meter per day), and \( k' \) is the pseudo first-order rate for conversion of precursor \( B \) to \( A \). We simultaneously solved the coupled stirred-tank equations for \( S_O, NO_x, S(VI), N(V), \) and \( N(−III) \). The model conditions are given in Table 5 and are for the most part deduced from our discussion of the field data. The emission data are those of Table 1, averaged over the volume of the SSJV mixed layer. We assumed that the aerosol was a neutralized mixture under nonfoggy conditions if \( N(−III) \) was in excess of \( S(VI) \), and that the formation of \( NH_3NO_3 \) aerosol was sufficiently favored to prevent \( HNO_3 \) and \( NH_3 \) from coexisting in the gas phase under any condition (valid if the atmosphere is sufficiently humid). The simulation was run for 4 days from the beginning of the episode, with a foggy period extending from \( t = 2 \) days to \( t = 3 \) days. On the basis of results presented by Jacob [1985], Jacob et al. [this issue], and Waldman [1986] we made the simplifying assumptions that (1) 30% of the aerosol is present in the fog water at any given time, (2) \( HNO_3(g) \) is 100% scavenged under all foggy conditions, and (3) \( NH_3(g) \) is 100% scavenged.
in fog under acid conditions but not scavenged at all under alkaline conditions.

Figure 7 shows the predicted concentration profiles. Aerosol accumulates rapidly under nonfoggy conditions and is partially removed by fog. The main features of the observed concentration profiles are reproduced, in particular, the accumulation patterns for $\text{SO}_3^{2-}$ and $\text{NO}_3^-$. The emission rates of Table 1 lead to concentrations of species that are in the range of those observed. Some excess alkalinity as $\text{NH}_4^+(g)$ remains present throughout the episode.

**CONCLUSION**

A systematic characterization of the $\text{H}_2\text{SO}_4$-$\text{HNO}_3$-$\text{NH}_3$ system in the fog water, the aerosol, and the gas phase was conducted at a network of sites in the San Joaquin Valley of California. Spatial patterns of atmospheric concentrations reflected the geographic distribution of oil recovery operations ($\text{SO}_2$, $\text{NO}_x$) and livestock feeding and agricultural activities ($\text{NH}_3$). The acidity of the fog water was found to be determined by the relative abundances of local acidic ($\text{SO}_2$, $\text{NO}_x$, $\text{NH}_3$) and alkaline ($\text{NH}_4^+$) emissions. A region of prevailing acidic conditions was identified on the western edge of the valley, where $\text{NH}_3$ emissions were low. Elsewhere, sufficient $\text{NH}_3$ was available to fully titrate the acidity. In the southern end of the valley, where major oil recovery operations release large amounts of $\text{SO}_2$ and $\text{NO}_x$, a precarious atmospheric balance was found between high concentrations of acids and bases.

The concept of atmospheric alkalinity was introduced as a quantitative measure of the acid-neutralizing capacity of the atmosphere with respect to fog. On the basis of this concept we predicted the regional potentials for high-acidity fog events in the San Joaquin Valley. We concluded that small changes in the activities of the agricultural industry or the oil industry could lead to widespread "acid fog" in the southern end of the valley.

Pollutant concentrations in the valley were strongly affected

**TABLE 5. Parameters for Stirred-Tank Model Simulation**

<table>
<thead>
<tr>
<th>Species</th>
<th>Deposition velocities, cm s$^{-1}$</th>
<th>Conversion rates, % h$^{-1}$</th>
<th>Emission rates, µmol m$^{-3}$ d$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SO}_2$</td>
<td>1</td>
<td>桟</td>
<td>0.95</td>
</tr>
<tr>
<td>$\text{NO}_x$</td>
<td>0.1</td>
<td>桟</td>
<td>1.3</td>
</tr>
<tr>
<td>Nonactivated aerosol</td>
<td>0.05</td>
<td>桟</td>
<td>1.4</td>
</tr>
<tr>
<td>fog droplets</td>
<td>4</td>
<td>桟</td>
<td>桟</td>
</tr>
<tr>
<td>$\text{HNO}_3(g)$</td>
<td>3</td>
<td>桟</td>
<td>桟</td>
</tr>
<tr>
<td>$\text{NH}_4(g)$</td>
<td>3</td>
<td>桟</td>
<td>桟</td>
</tr>
</tbody>
</table>

Residence time of air parcels: 5 days. Mixing height: 400 m AGL; Initial conditions: ($\text{H}_2\text{SO}_4$) = ($\text{HNO}_3$) = ($\text{NH}_3$) = 0 at $t = 0$; Fog from $t = 2$ to $t = 3$, $t$ is stated in days throughout.

Fig. 7. Stirred-tank simulation of pollutant accumulation in the SSJV over the course of a stagnation episode. The simulation conditions are given in Table 5.

by the height of the mixed layer and by the occurrence of drizzle or fog. Mixing heights above 1000 m AGL efficiently ventilated the valley. A severe stagnation episode was documented when a temperature inversion based a few hundred meters above the valley floor persisted for 6 days. Progressive accumulation of $\text{H}_2\text{SO}_4$-$\text{HNO}_3$-$\text{NH}_3$ species in the mixed layer was observed and interpreted in terms of atmospheric production and removal mechanisms. The accumulation patterns were consistent with very low deposition velocities for secondary ($\text{SO}_2^{2-}$, $\text{NO}_3^-$, $\text{NH}_4^+$) aerosol under nonfoggy conditions (< 0.05 cm s$^{-1}$), and high deposition velocities for $\text{HNO}_3(g)$ and $\text{NH}_3(g)$ (> 1 cm s$^{-1}$). Decreases in aerosol concentrations were observed following fogs and were attributed to the rapid deposition of fog droplets. Therefore the occurrence of fog was found to effectively limit pollutant accumulation during stagnation episodes.

Secondary production of strong acids under stagnant conditions entirely titrated available alkalinity at the sites farthest from $\text{NH}_3$ emissions. A steady conversion rate of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ was estimated at 0.4–1.1% h$^{-1}$ under overcast stagnation conditions. Conversion of $\text{NO}_x$ to $\text{HNO}_3$ was rapid at the beginning of the episode but dropped as the widespread and persistent low overcast reduced photochemical activity. Removal of $\text{SO}_2$ was found to be enhanced in fog, compared to nonfoggy conditions, but $\text{NO}_x$ was not scavenged in fog. Acidification of the atmosphere was associated with a brief increase in $\text{HNO}_3(g)$ followed by a drop in total N(V) concentrations; this was explained by the displacement of aerosol $\text{NO}_3^-$ by $\text{H}_2\text{SO}_4$, followed by rapid deposition of $\text{HNO}_3(g)$.

**APPENDIX: ERROR ANALYSIS**

**Fog Water Concentrations**

A recent intercomparison study of fog water collectors [Hering and Blumenthal, 1985; Waldman, 1986] has demonstrated that the California Institute of Technology rotating arm collector provides reproducible and representative samples under both light and heavy fog conditions. The uncertainty on the concentrations of major ions (determined from samples collected with two rotating arm collectors set side by side) was found to be about 15%. Errors due to chemical analysis in the laboratory were about 5% for all analyzed ions. No significant differences in ionic concentrations were found between samples collected concurrently with the rotating arm collector, a jet impactor [Katz, 1980], and a screen collector [Brewer et al., 1983], set side by side.

Ionic balances are an indicator of whether all ionic components in the sample have been accounted for in analysis. Ionic
balances in the fog water samples were 0.98 ± 0.18 at Bakersfield
(n = 15), 1.02 ± 0.09 at McKittrick (n = 53), 1.11 ± 0.18
at Buttonwillow (n = 7), and 0.60 ± 0.17 at Visalia (n = 12).
The ionic balances were calculated from the following molar
ratio:

\[
\text{Ionic balance} = \frac{[\text{Cl}^-] + [\text{NO}_3^-] + 2[\text{SO}_4^{2-}] + [\text{S IV}]}{[\text{H}^+] + [\text{Na}^+] + [\text{NH}_4^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}]} \tag{A1}
\]

where S(IV) was assumed to be monovalent [Jacob and Hoff-
mann, 1983]. We have argued previously (equation (2)) that
this is a good assumption even at high pH. The most reliable
ionic balances were found at McKittrick, while at Visalia
there was a considerable and consistent anion deficiency.
Fog water at Visalia had a consistently high pH and as a conse-
quently could contain important alkalinity; therefore addi-
tional weak acid anions must be considered in an ionic bal-
ance. In fog water with low pH, such as at McKittrick, weak
acids are mostly present in undissociated form and thus (A1)
represents a good balance of cations to anions.

The principal ionic contributors to alkalinity in the pH
range 3–8 are expected to be HCO_3^- and carboxylic ions.
Fog water concentrations of four carboxylic ions were deter-
mined on a subset of the fog water data set (Table 3). For that
subset we calculated the concentrations of the anionic forms
of the weak acids from equilibrium at the fog water pH and
with the acidity constants given in the text. Before inclusion
of weak acids the ionic balances were 1.03 ± 0.09 at McKittrick
(n = 25) and 0.49 ± 0.15 at Visalia (n = 6); after inclusion of
weak acids the ionic balances were 1.06 ± 0.11 at McKittrick
and 0.75 ± 0.15 at Visalia. The McKittrick samples had little
alkalinity, and the ionic balance remained close to unity.
At Visalia on the other hand, ionic balances were greatly im-
proved. There was still an anion deficiency at Visalia, likely
due to undetermined weak acids.

**Aerosol, HNO_3(g), and NH_4(g) Concentrations**

The filter methods used in this study may lead to two major
types of error: (1) N(V) and N(−III) artifacts, and (2) random
errors from the sampling process. We will address each in
order. An additional source of error could be the neutraliza-
tion of acidic and alkaline aerosol by absorption of NH_4(g)
and HNO_3(g), respectively, during filter storage; however,
blank oxalic-acid-impregnated filters and nylon filters were
found to remain blank even after extended storage. Therefore
aerosol neutralization during storage did not seem to occur.

Stelson and Seinfeld [1982] have shown that an increase in
temperature at constant dew point during sampling may vol-
talitize ammonium nitrate collected on Teflon filters and result
in artifact HNO_3(g) and NH_4(g). Further, absorption of gase-
ous nitric acid on the Teflon filter may result in artifact aeros-
ol nitrate [Spicer and Schumacher, 1979; Appel et al., 1980].
In an intercomparison study of gaseous nitric acid measure-
ment methods, Spicer et al. [1982] found good agreement be-
tween the dual-filter method (used here) and other methods.
Further, they found that the dual-filter method was accurate
in measuring total N(V).

The study of Spicer et al. [1982] was conducted under hot,
dry conditions. Potential biases are different under the cool,
humid conditions found in the San Joaquin Valley. Nighttime
samples (0000–0400 PST) were probably unaffected by volatil-
ization because temperatures during the sampling period
either remained constant or decreased. During the day, tem-
perature changes were usually small because of the overcast
conditions; temperatures recorded hourly at Bakersfield be-
tween 1200 and 1600 PST increased on only five of the 15
sampling days and never increased by more than 1°C, except
on January 14 (when a 3°C increase was observed). Still, an
increase of 1°C in temperature at constant dew point may
increase the dissociation constant \( K = P_{NH_3} \times P_{NO_2} \) by
a factor of 2 under high-humidity conditions [Stelson and Sein-
feld, 1982]. The formation of aerosol ammonium nitrate is
strongly favored thermodynamically, and aerosol concen-
trations could not be significantly affected by volatilization;
on the other hand, high relative errors may occur in the
determination of the gas present at the lowest concentration.
Since that concentration was often near or below the detection
limit, the error was of little consequence.

Teflon filters run in dense fog accumulated drops of liquid
water at the surface. In those particular cases the filters were
dried in the open before being sealed. Nitric acid scavenged
in acidic fog volatilizes during drying, leading to an underesti-
mate of total aerosol NO_3^- . No significant NO_3^- loss should
occur in nonacidic fog because in that case NO_3^- remains
in the aerosol phase as the fog dissipates. Similarly, NH_4^+
should not volatilize in acidic fog. Volatilization of NH_4^+
from filters collected in alkaline fog depends on the stability
of the ammonium salts of weak acids, which appear to be vol-
atile; some volatilization of NH_4^+ was found to occur in a
sample collected during fog at Visalia [Jacob, 1985].

"Random errors" are of three types: (1) uncertainty in the
flow rate through the filter, (2) uncertainty in the efficiency of
recovery by extraction, and (3) analytical error. Because the first
two sources of error affect the sample as a whole, we
expect a correlation to exist between the errors on the differ-
ent species. To test for these errors, concentrations of SO_4^{2-},
NO_3^-, and NH_4^+ were determined in duplicate for \( n = 45 \)
pairs of filter samples "1" and "2," collected side by side.
Concentrations of Cl^- were also determined, but the errors
on those concentrations were generally lower than the Cl^- filter
blank. The relative differences in the determinations of X for
the 45 pairs of duplicate samples were statistically analyzed as
follows:

\[
D_X = \frac{2(X_2 - X_1)}{X_1 + X_2} \tag{A2}
\]

\[
\sigma = \left[ \frac{\sum (D_X)^2}{n} \right]^{1/2} \tag{A3}
\]

Standard deviations \( \sigma \) on the determination of SO_4^{2-}, NO_3^-, and NH_4^+ were 18.6, 18.8, and 19.1%, respectively. These results are comparable to those reported by Russell and Cass
[1984] for similar measurements. Student "t" tests for paired
data at the 5% level of significance did not show significant
differences between sampling positions 1 and 2 for SO_4^{2-},
NO_3-, or NH_4^+ at any site, therefore no significant effects
from the differences in backup filters were apparent.

We found \( D_{SO_4^{2-}}, D_{NO_3^-}, \) and \( D_{NH_4^+} \) to be strongly corre-
lated \( (r^2 = 0.71 \) between \( D_{SO_4^{2-}} \) and \( D_{NH_4^+} ; r^2 = 0.69 \) between
\( D_{NO_3^-} \) and \( D_{NH_4^+} \)). These correlations must be taken into ac-
count in the error analyses of quantities calculated by differ-
ences of concentrations, such as (ALK) or gas phase concen-
trations predicted by thermodynamic models [Jacob et al., this
issue]. We resolved \( \sigma \) into its component \( \sigma_{\text{p}} \), associated with
pump operation and filter extraction, and its component
\( \sigma_{\text{A,X}} \), associated with chemical analysis. The error char-
characterized by $\sigma_r$ may be assumed to be the same for $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$, while the errors due to analysis should be uncorrelated. Because $\sigma_s$ is small, we can write as an approximation:

$$\sigma^2 = \sigma_r^2 + \sigma_{AX}^2$$  \hspace{1cm} (A4)

By statistical analysis of the differences between $NH_4^+$, $NO_3^-$, and $SO_4^{2-}$ concentrations we obtained $\sigma_r = 18.1\%$, $\sigma_{AX,SO_4^{2-}} = 4\%$, $\sigma_{AX,NO_3^-} = 5.1\%$, and $\sigma_{AX,NH_4^+} = 6.3\%$. These analytical errors are consistent with our laboratory precision.

No duplicate analyses were made for $Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$. Replicate analyses of standards indicate $\sigma_{AX}^2$ of about 5% for these four ions. Duplicates for $NH_4^+$ and $HNO_3$ determinations were not collected, but the $\sigma_{AX}^2$ values should be the same as for $NH_4^+$ and $NO_3^-$, respectively. In addition to the analytical error, concentrations of all constituents were assumed to be subject to the same error $\sigma_r$. This assumption implies that the variability of the flow rate through the filter is the major contributor to $\sigma_r$, which seems justified, since filter extraction efficiencies are better than 95% [Russell and Cass, 1984].

The analytical detection limits for a 4-hour sample correspond to 4 neq m$^{-3}$ for $NO_3^-$, $SO_4^{2-}$, $HNO_3$, and cations other than $NH_4^+$, and 8 neq m$^{-3}$ for $NH_4^+$. Filter blanks for all constituents except $Cl^-$ and $NH_4^+$ were below these detection limits. Because of substantial filter blanks, effective detection limits for $NH_4^+$ and $Cl^-$ for a 4-hour sample were 17 neq m$^{-3}$ and 20 neq m$^{-3}$, respectively.

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D. J. Jacob, Center for Earth and Planetary Physics, Harvard University, Cambridge, MA 02138.


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The $\text{H}_2\text{SO}_4$-$\text{HNO}_3$-$\text{NH}_3$ System at High Humidities and in Fogs

2. Comparison of Field Data With Thermodynamic Calculations

Daniel J. Jacob, Jed M. Waldman, J. William Munger, and Michael R. Hoffmann

Environmental Engineering Science, W. M. Keck Engineering Laboratories, California Institute of Technology, Pasadena

Concentrations of $\text{HNO}_3(g)$ and $\text{NH}_3(g)$ determined in the field were compared to predictions from aerosol equilibrium models. The products of $\text{HNO}_3(g)$ and $\text{NH}_3(g)$ concentrations measured under cool and humid nonfoggy conditions agreed in magnitude with predictions from a comprehensive thermodynamic model for the atmospheric $\text{H}_2\text{SO}_4$-$\text{HNO}_3$-$\text{NH}_3$-$\text{H}_2\text{O}$ system. Observed concentrations of $\text{NH}_3(g)$ in fogs were generally consistent with those predicted at equilibrium with fog water, but important discrepancies were noted in some cases. These discrepancies may be due to fluctuations in fog water composition over the course of sample collection or to the sampling of nonfoggy pockets of air present within the fog. Detectable concentrations of $\text{HNO}_3(g)$ (up to 23 neq m$^{-3}$) were often found in fogs with pH < 5 and were attributed to the sampling of nonfoggy air or to the slow rate of $\text{HNO}_3(g)$ diffusion to fog droplets. Concentrations of $\text{HNO}_3(g)$ in fogs with pH > 5 were below the detection limit of 4-8 neq m$^{-3}$. 
The $H_2SO_4\cdot HN_3O_3\cdot NH_3$ System at High Humidities and in Fogs
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INTRODUCTION

The chemical speciation of the $H_2SO_4\cdot HN_3O_3\cdot NH_3\cdot H_2O$ system between atmospheric phases has been the subject of much recent interest. Sulfuric acid nucleates with water vapor under usual atmospheric conditions [Kiang et al., 1973], but $HN_3O_3$ remains in the gas phase at relative humidities up to about 98% [Nair et al., 1983]. Ammonia is scavenged by acidic sulfate aerosols until eventual neutralization is achieved; however, it has a substantial vapor pressure over ammonium nitrate aerosol. A key question to our understanding of aerosol nitrate formation is the determination of $NH_3$ and $HNO_3$ vapor pressures over aerosol formed from $H_2SO_4\cdot HN_3O_3\cdot NH_3\cdot H_2O$ mixtures.

A number of thermodynamic models have attempted to answer that question. Tang [1980] and Stelson and Seinfeld [1982a] studied the effect of relative humidity and $pH$ on the vapor pressures of $HNO_3$ and $NH_3$ over their aqueous solutions. Stelson and Seinfeld [1982b] determined the dependence on temperature and relative humidity of the ammonium nitrate aerosol dissociation constant $K = P_{HNO_3} \times P_{NH_3}$, and later reported [Stelson and Seinfeld, 1982c] that addition of $H_2SO_4$ to the mixture does not lower $K$ greatly unless the $H_2SO_4/HN_3O_3$ ratio is very large. Saxena et al. [1983] and Bassett and Seinfeld [1983, 1984] proposed comprehensive multiphase thermodynamic models for the $H_2SO_4\cdot HN_3O_3\cdot NH_3\cdot H_2O$ system.

All of the above models are basically consistent one with the other and represent various degrees of sophistication in the treatment of the $H_2SO_4\cdot HN_3O_3\cdot NH_3$ system. The Bassett and Seinfeld models offer at present the greatest level of chemical detail. In these models the equilibrium composition is calculated by minimizing the Gibbs free energy of a system composed of the gas phase species $H_2SO_4(g)$, $HNO_3(g)$, and $NH_3(g)$; the aqueous phase species $H^+$, $HSO_4^{-}$, $SO_4^{2-}$, $NO_3^{-}$, and $NH_4^{+}$; and the solid phases $NH_4HSO_4(s)$, $(NH_4)H(SO_4)_2(s)$, $(NH_4)_2SO_4(s)$, $NH_4NO_3(s)$, $(NH_4)_2SO_4\cdot 3NH_3NO_3(s)$, and $(NH_4)_2SO_4\cdot 2NH_4NO_3(s)$. The Bassett and Seinfeld [1984] model considers in addition the increase in vapor pressure due to the Kelvin effect and thus predicts the size distribution of $NO_3^{-}$ aerosol from the size distribution of $SO_4^{2-}$ aerosol. The Bassett and Seinfeld [1983] model ignores the Kelvin effect, but this is reported to cause only a negligible underestimate of $K$. In the special case of the $HNO_3\cdot NH_3\cdot H_2O$ system the Bassett and Seinfeld [1983] model reduces to the Stelson and Seinfeld [1982b] model, which uses the same thermodynamic data and ionic strength correction procedures.

The hygroscopic aerosol is an aqueous solution at high humidities, and Table 1 gives the reactions determining the speciation of $HNO_3$ and $NH_3$ under those conditions. $K$ decreases rapidly with increasing humidity above the deliquescence point [Stelson and Seinfeld, 1982b]. Above 100% relative humidity, fog droplets form by activation of condensation nuclei, resulting in a considerable increase of the atmospheric liquid water content and a corresponding enhancement of $HNO_3$ and $NH_3$ heterogeneous condensation. Fog droplets are not at stable equilibrium with the surrounding water vapor, and thermodynamic models predicting $K$ as a function of relative humidity cannot be applied; however, $HNO_3(g)$ and $NH_3(g)$ concentrations at equilibrium with the fog water can be directly calculated from measured fog water concentrations. Fog droplets are sufficiently dilute solutions that the Debye-Hückel expression for activity coefficients [Stumm and Morgan, 1981] is appropriate.

In fogs the equilibrium partitioning of $HNO_3$ and $NH_3$ between the gas phase and the fog water can be determined from the liquid water content, the fog water $pH$, and (R1)–(R3). Liquid water contents in fog range from 0.01–1 g m$^{-3}$, and fog water $pH$ values have been found to range from about 2 to 8 [Munger et al., 1983; Jacob et al., this issue]. Over 99% of total $HNO_3$ at equilibrium with fog water is scavenged as $NO_3^{-}$ in this range of conditions (reaction (R1)). No measurable $HNO_3(g)$ should therefore be found at equilibrium in fog, even acidic fog. On the other hand, the equilibrium speciation of $NH_3$ is strongly dependent on droplet $pH$, liquid water content, and temperature. The fraction $F$ of total $NH_3$ scavenged by fog is given by:

$$F = \frac{LRTK_{1} \left[ 1 + (K_{2}[H^+]) \right]}{1 + LRTK_{2} \left[ 1 + (K_{3}[H^+]) \right]}$$

(1)

where the equilibrium constants $K_2$ and $K_3$ are the $K_{298}$ values of Table 1 corrected for temperature with the Van’t
TABLE 1. Dissociation and Vapor Pressure Equilibria of HNO₃ and NH₃

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction</th>
<th>$K_{298}$ kcal mol⁻¹</th>
<th>$\Delta H_{298}$ kcal mol⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1)</td>
<td>HNO₃(g) = NO₃⁻ + H⁺</td>
<td>3.2 × 10⁶ M² atm⁻¹</td>
<td>-17.3</td>
<td>Schwartz and White [1981]</td>
</tr>
<tr>
<td>(R2)</td>
<td>NH₃(g) = NH₄(aq)</td>
<td>7.4 × 10¹ M atm⁻¹</td>
<td>-6.8</td>
<td>Hales and Drewes [1979]</td>
</tr>
<tr>
<td>(R3)</td>
<td>NH₄(aq) + H⁺ = NH₄⁺</td>
<td>1.7 × 10⁶ M⁻¹</td>
<td>-12.5</td>
<td>Smith and Martell [1976]</td>
</tr>
</tbody>
</table>

The reader is referred to Jacob et al. [this issue] for a description of sampling sites, analytical methods, and a detailed analysis of measurement errors and biases associated with our sampling techniques.

We will generally present HNO₃(g) and NH₃(g) concentrations in units of equivalents per cubic meter, for consistency with the units of NO₃⁻ and NH₄⁺ aerosol concentrations. "Equivalent" in that sense refers to the proton donor or acceptor capacity of the gas when scavenged by the aerosol. Both HNO₃(g) and NH₃(g) contribute one equivalent per mole; 1 ppb = 43 neq m⁻³ at 5°C.

NONFOGGY CONDITIONS

The main site of the San Joaquin Valley sampling program was located in Bakersfield, California. The Bakersfield data are given in Table 2. For comparison with the Bassett and Seinfeld [1983] model the aerosol compositions were reduced to model mixtures of SO₄²⁻, NO₃⁻, NH₄⁺, and H⁺. This was done by assuming concentrations of H⁺ and OH⁻ to satisfy electroneutrality with the measured concentrations of SO₄²⁻, NO₃⁻, and NH₄⁺. The presence of other ions in the real aerosol will perturb the thermodynamics, but this perturbation should be small because the ions SO₄²⁻, NO₃⁻, and NH₄⁺ contributed over 90% of the total aerosol ionic content [Jacob et al., this issue]. Aerosol concentrations of HCO₃⁻ and COO⁻ were not determined, but the balances of NH₄⁺ to (NO₃⁻ + SO₄²⁻) in Table 2 show no evidence of excess NH₄⁺ attributable to HCO₃⁻ or COO⁻ ammonium salts. Alkaline ammonium salts appear to be volatile under nonfoggy conditions [Jacob et al., this issue]. Therefore the (SO₄²⁻, NO₃⁻, NH₄⁺, H⁺) mixture is an adequate model for the ionic content of the Bakersfield aerosol.

We applied the Bassett and Seinfeld [1983] model to describe two different partitioning modes for SO₄²⁻ and NO₃⁻: (1) SO₄²⁻ and NO₃⁻ present exclusively in different aerosol phases ("external mixture"), and (2) SO₄²⁻ and NO₃⁻ al-

Fig. 1. Fraction of NH₃ scavenged by fog water at equilibrium. All fog droplets are assumed to be at the same pH. Liquid water contents of 0.05 g m⁻² (solid line) and 0.5 g m⁻² (dashed line) are considered.

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>NH$_4^+$</th>
<th>NO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>NH$_3$(g)</th>
<th>HNO$_3$(g)</th>
<th>Temperature, °C</th>
<th>Relative Humidity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dec. 31</td>
<td>0000-0345</td>
<td>573</td>
<td>351</td>
<td>351</td>
<td>19</td>
<td>17</td>
<td>7.8 ± 0.9</td>
<td>96</td>
</tr>
<tr>
<td>1200-1610</td>
<td>669</td>
<td>467</td>
<td>379</td>
<td>158</td>
<td>4</td>
<td>10.8 ± 0.6</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>Jan. 1</td>
<td>0215-0815</td>
<td>242</td>
<td>170</td>
<td>89</td>
<td>212</td>
<td>&lt;4</td>
<td>10.4 ± 0.6</td>
<td>96</td>
</tr>
<tr>
<td>1200-1610</td>
<td>275</td>
<td>161</td>
<td>161</td>
<td>68</td>
<td>35</td>
<td>13.3 ± 0.7</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>Jan. 2</td>
<td>0000-0415</td>
<td>273</td>
<td>168</td>
<td>109</td>
<td>67</td>
<td>14</td>
<td>7.2 ± 1.1</td>
<td>89</td>
</tr>
<tr>
<td>1200-1620</td>
<td>344</td>
<td>201</td>
<td>124</td>
<td>107</td>
<td>25</td>
<td>11.8 ± 0.7</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Jan. 3</td>
<td>0000-0415</td>
<td>545</td>
<td>370</td>
<td>226</td>
<td>483</td>
<td>&lt;4</td>
<td>9.1 ± 0.8</td>
<td>87</td>
</tr>
<tr>
<td>1200-1615</td>
<td>769</td>
<td>445</td>
<td>445</td>
<td>113</td>
<td>11</td>
<td>9.2 ± 0.6</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Jan. 4</td>
<td>1200-1700</td>
<td>1057</td>
<td>427</td>
<td>660</td>
<td>55</td>
<td>24</td>
<td>9.9 ± 1.3</td>
<td>80</td>
</tr>
<tr>
<td>Jan. 5</td>
<td>0100-0510</td>
<td>1141</td>
<td>442</td>
<td>731</td>
<td>63</td>
<td>6</td>
<td>6.9 ± 0.8</td>
<td>95</td>
</tr>
<tr>
<td>1200-1615</td>
<td>923</td>
<td>362</td>
<td>596</td>
<td>60</td>
<td>19</td>
<td>8.8 ± 0.6</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>Jan. 6</td>
<td>0000-0415</td>
<td>1149</td>
<td>388</td>
<td>855</td>
<td>47</td>
<td>7</td>
<td>7.4 ± 0.6</td>
<td>95</td>
</tr>
<tr>
<td>Jan. 7</td>
<td>0000-0405</td>
<td>272</td>
<td>142</td>
<td>118</td>
<td>52</td>
<td>6</td>
<td>6.8 ± 0.6</td>
<td>95</td>
</tr>
<tr>
<td>Jan. 9</td>
<td>1420-1825</td>
<td>260</td>
<td>85</td>
<td>219</td>
<td>139</td>
<td>8</td>
<td>7.3 ± 0.6</td>
<td>86</td>
</tr>
<tr>
<td>Jan. 10</td>
<td>0000-0415</td>
<td>621</td>
<td>117</td>
<td>570</td>
<td>60</td>
<td>46</td>
<td>6.2 ± 0.6</td>
<td>89</td>
</tr>
<tr>
<td>1200-1615</td>
<td>533</td>
<td>152</td>
<td>417</td>
<td>48</td>
<td>14</td>
<td>6.9 ± 0.8</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>Jan. 11</td>
<td>1200-1615</td>
<td>144</td>
<td>105</td>
<td>78</td>
<td>65</td>
<td>46</td>
<td>9.0 ± 0.7</td>
<td>71</td>
</tr>
<tr>
<td>Jan. 12</td>
<td>0000-0415</td>
<td>345</td>
<td>204</td>
<td>149</td>
<td>157</td>
<td>&lt;4</td>
<td>3.0 ± 0.9</td>
<td>91</td>
</tr>
<tr>
<td>1200-1615</td>
<td>331</td>
<td>244</td>
<td>169</td>
<td>334</td>
<td>26</td>
<td>11.2 ± 1.0</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>Jan. 13</td>
<td>0000-0400</td>
<td>486</td>
<td>283</td>
<td>407</td>
<td>208</td>
<td>&lt;4</td>
<td>4.6 ± 0.7</td>
<td>96</td>
</tr>
<tr>
<td>0700-1115</td>
<td>729</td>
<td>349</td>
<td>475</td>
<td>122</td>
<td>6</td>
<td>5.9 ± 0.8</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>1200-1615</td>
<td>855</td>
<td>437</td>
<td>507</td>
<td>240</td>
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Complete aerosol analyses are reported by Jacob [1985a]. Values are in nanomole equivalents per cubic meter unless otherwise indicated; time is local time (PST); and relative humidity is calculated from temperature and dew point.

The Basset and Seinfeld [1983] model was run with the computer code provided by Basset [1984]. This code required as input the total (gas plus aerosol) concentrations of H$_2$SO$_4$, HNO$_3$, and NH$_3$, the temperature, and the relative humidity. To calculate the errors on the predictions from the errors on the measurements, 100 sets of input variables were generated for each data point from a random scheme based on the observed values and standard errors for each of the variables; standard errors on the experimental determinations of concentrations were taken from Jacob et al. [this issue]. The expected values and standard errors for the output variables were determined from the outputs for the 100 sets of input variables. Results are shown in Figures 2a and 2b. The aerosol was predicted to be entirely aqueous except in a few cases (indicated on Figures 2a and 2b). The standard errors on the predicted values of K were mostly due to errors on the determinations of temperature and relative humidity; they were not affected by errors on H$_2$SO$_4$, HNO$_3$, and NH$_3$ concentrations in the external mixture assumption and were affected only very weakly in the internal mixture assumption. On the other hand, errors on the concentrations of the individual gases were strongly affected by errors on the determinations of concentrations, especially when a close balance existed between total NH$_3$ and total acids (HNO$_3$ + H$_2$SO$_4$). In those cases error bars were very large.

The products of partial pressures observed in the field agreed in magnitude with the values of K predicted by the model. However, the model predictions were consistently too low. Predictions with the external mixture assumption were closer to observations than with the internal mixture assumption. The model appeared to give better predictions for individual gases than for K, but this is deceiving. First, the errors on the predicted gas concentrations were large. Second, K was often so small that one of the gases was almost entirely depleted, and the remaining gas was then simply present at its concentration in excess of the neutralized aerosol.
**Stelson and Seinfeld [1982b]** also found that the products of vapor pressures over aqueous aerosol were systematically underpredicted by their model, by factors similar to the ones we observed. **Harrison and Pio [1983]** did not find such a systematic trend, although their determinations may have been subject to large errors because of the considerable fluctuations in temperatures and relative humidities over the course of the sampling periods. Because of the many complicated processes occurring in the atmosphere it is difficult to assess the significance of the model underpredictions. Consideration of droplet curvature would increase the predicted K, but Bassett and Seinfeld [1984] found this increase to be negligible. Laboratory data of vapor pressures over concentrated ammonium nitrate solutions should provide a check on the accuracy of the thermodynamic calculations, but they are unavailable at this time.

The dual-filter method is known to be subject to positive interferences, that is, concentrations of HNO$_3$(g) and NH$_3$(g) may be overestimated [Appel et al., 1980]. Volatilization of NH$_4$NO$_3$ from the Teflon prefilt er leads to artifact HNO$_3$(g) and NH$_3$(g), but in our case this problem is minimized because temperatures and relative humidities remained stable over the course of the sampling periods (Table 2). Another source of positive interference is the displacement of NO$_3^-$ or NH$_4^+$ by nonvolatile material collected on the filter, for example, acid sulfates or alkaline carbonates. However, if such displacement reactions occurred on the filter, this would mean that the atmosphere itself was not at equilibrium; in that case, HNO$_3$(g) and NH$_3$(g) atmospheric concentrations could have differed substantially from their equilibrium values.

Indeed, a possible explanation for the discrepancies observed is that the atmosphere was not at chemical equilibrium. The NH$_3$ observed at Bakersfield originated mostly from local ground level sources [Jacob et al., this issue]; HNO$_3$ and NH$_3$ may not have had time to mix sufficiently for equilibrium to be achieved. The incorporation of HNO$_3$(g) and NH$_3$(g)
into the aerosol at high humidities proceeds mostly by heterogeneous condensation, which can be a slow process. Based on the calculations of Fuchs and Sutugin [1971] over a range of representative conditions, one finds that the diffusion-controlled equilibration time of a gas with low vapor pressure may range from minutes to hours (depending, among other things, on the "sticking coefficient" of the gas molecule on the aerosol).

**Foggy Conditions**

Nine concurrent samples of fog water, HNO$_3$(g), and NH$_3$(g) were collected during the winter 1983–1984 San Joaquin Valley sampling program at Bakersfield and several other sites, and 19 more samples were collected in a similar program conducted the following winter. All samples were collected during intervals with dense fog throughout. The data are given in Table 3. Concentrations of NH$_3$(g) at equilibrium with the fog water were calculated from (R2) and (R3):

$$\text{(NH}_3\text{(g))} = \frac{1}{RTK_2K_3} [\text{NH}_4^+]/[\text{H}^+] \quad (2)$$

where $[\text{NH}_4^+]$ and $[\text{H}^+]$ are the fog water concentrations (equivalents per liter of water), and (NH$_3$(g)) is the NH$_3$(g) concentration (equivalents per liter of air). The standard errors on predicted (NH$_3$(g)) were determined from standard errors of $\pm 1^\circ\text{C}$ on temperature and 15% on the determinations of $[\text{NH}_4^+]$ and $[\text{H}^+]$ [Jacob et al., this issue]. Several fog water samples were generally collected over the course of one NH$_3$(g)-sampling period; equilibrium NH$_3$(g) concentrations were calculated from the fog water concentrations in each individual sample and then time averaged. Results are shown in Table 3 and Figure 3.

The NH$_3$(g) concentrations calculated from (2) were consistent with observed NH$_3$(g) concentrations in 22 of the 28 comparisons; they agreed to within a factor of 2 for NH$_3$(g) concentrations above the detection limit (nine cases) and correctly predicted NH$_3$(g) concentrations below the detection limit (13 cases). In the remaining six comparisons, however, the agreement was poor. Nonattainment of equilibrium is an unlikely explanation for the observed discrepancies; equilibration of NH$_3$(g) with fog water $p^* \cdot H > 5$ is achieved rapidly because of the relatively low solubility of NH$_3$ [Chameides, 1984]. Also, see discussion by Jacobs [1985b] and Chameides [1985]). However, a major source of error in our calculations is that the fog droplets collected in a fog water sample were not of uniform composition. Fog droplets supporting a
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Measurement errors for NH₃(g) and HNO₃(g) were about 20%. Detection limits depended on filter run time [Jacob et al., this issue]. N/A = not analyzed.


Average over time of NH₃(g) concentrations predicted from fog water concentrations and equation (2).

Detection limit.

Measurable partial pressure of NH₃ contain alkalinity, and [H⁺] will not be conserved upon the mixing of alkalinity-containing droplets of different compositions in the sample. Further, (NH₃(g)) is proportional to 1/[H⁺], a quantity which is not properly averaged by measurement of pH in the collected sample. The resulting errors will depend on the extent of nonuniformity in the fog water composition and are difficult to estimate, but they could clearly account for most of the discrepancies. The large variations in pH often observed between two consecutive fog water samples (Table 3) are indicative of the variability in fog water composition.

The largest discrepancies were observed for four sampling periods at Buttonwillow when the fog water pH was in the range 5–6. In those four cases, equilibrium with fog water considerably underpredicted the observed NH₃(g) concentrations. Fog water at pH 5–6 scavenges most of the atmospheric NH₃ (Figure 1) but returns it to the gas phase upon evaporation [Jacob et al., this issue]. An explanation for the large discrepancies that were sometimes observed in this pH range is the existence within the fog of pockets of air undersaturated with respect to water vapor [Gerber, 1981]. These air pockets would support much larger concentrations of NH₃(g) than the bulk foggy atmosphere and would correspondingly affect the measured NH₃(g) concentration. Further, sampling of undersaturated air may evaporate fog droplets previously collected on the aerosol prefilter and cause artifact NH₃(g).

Concentrations of HNO₃(g) in fogs were at or below the detection limit in fogs with pH > 5, but detectable HNO₃(g) concentrations (5–23 neq m⁻³) were found in fogs with lower pH. The presence of HNO₃(g) in acidic fog cannot be explained on the basis of equilibrium with fog water. However, the presence of HNO₃(g) can be explained by the substantial vapor pressure of HNO₃(g) over the acid precursor aerosol; undersaturated air pockets within the fog would support HNO₃(g) at equilibrium. An additional explanation is that detectable HNO₃(g) concentrations may subsist for some time in the fog because of the slow rate of HNO₃(g) diffusion to the droplets. Chameides [1984] reports that scavenging of HNO₃(g) by diffusion to the fog droplets proceeds on a time scale of a few minutes, but this time may be longer if organic films form at the surface of the droplets [Gill et al., 1983].

CONCLUSION

Concentrations of HNO₃(g) and NH₃(g) were determined in the field under both foggy and nonfoggy conditions, simultaneously with aerosol and fog water composition. Observed concentrations were compared to predictions from thermodynamic models.

Measurements under nonfoggy, cool, and humid conditions (temperatures 3–13°C, relative humidities 60–100%) were compared to predictions from the Bassett and Seinfeld [1983] model for the H₂SO₄–HNO₃–NH₃–H₂O system. The observed products of HNO₃ and NH₃ vapor pressures were of the same magnitude as those predicted by the model; however, the model predictions were consistently too low. The agreement between observations and model was slightly improved by assuming that SO₄²⁻ and NO₃⁻ were present in different phases (external mixture).

Concentrations of NH₃(g) were below the detection limit of 17–30 neq m⁻³ in fogs with pH < 5, and this is consistent with thermodynamic predictions. Substantial NH₃(g) concentrations were observed in fogs with higher pH; the observed concentrations were usually within a factor of 2 of those predicted at equilibrium with the fog water, but some

![Fig. 3. NH₃(g) concentrations at equilibrium with fog water versus observed NH₃(g) concentrations. Both were below the detection limit for 13 of the points (shaded area). Line represents 1:1 agreement between predictions and observations.](image-url)
important discrepancies were noted. These discrepancies may be due to fluctuations in fog water composition over the course of sample collection or to the presence of pockets of undersaturated air within the fog.

Concentrations of HNO$_3$(g) were at or below the detection limit of 4-8 neq m$^{-3}$ in fogs with pH > 5, but detectable concentrations (5-23 neq m$^{-3}$) were often found in fogs with lower pH. Because HNO$_3$(g) should not be present at equilibrium with fog water, we attribute our observations to the presence of undersaturated air within the fog or to the slow rate of HNO$_3$(g) diffusion to the fog droplets.

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D. J. Jacob, Center for Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138.


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CHAPTER 6

TRANSPORT AND OXIDATION OF SO₂ IN A STAGNANT FOGGY VALLEY

DANIEL J. JACOB
Center for Earth and Planetary Physics, Harvard University, Cambridge, MA 02138, U.S.A.

FREDERICK H. SHAIR
Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, U.S.A.

JED M. WALDMAN,∗ J. WILLIAM MUNGER and MICHAEL R. HOFFMANN†
Environmental Engineering Science, W. M. Keck Laboratories, California Institute of Technology,
Pasadena, CA 91125, U.S.A.

(First received 27 June 1986 and in final form 31 October 1986)

Abstract—The fate of SO₂ emitted in the San Joaquin Valley of California under stagnant foggy conditions was determined by the release of an inert tracer and the concurrent monitoring of SO₂ and SO₄²⁻ concentrations. At night, SO₂ was found to be trapped in a dense fog layer below a strong and persistent inversion based a few hundred meters above the valley floor. This lack of ventilation led to the accumulation of SO₂ and SO₄²⁻ over a major SO₂ source region in the valley. The rate of oxidation of SO₂ to SO₄²⁻ in fog was estimated at 3 ± 2 % h⁻¹. Production of acidity from the oxidation of SO₂ fully titrated the NH₃(g) present before the fog, and led to a progressive drop of the fogwater pH over the course of the night. In the afternoon, the valley was found to be efficiently ventilated by a buoyant upslope flow through the inversion. The tracer data indicated that about 40% of the air transported upslope in the afternoon was returned to the valley in the night-time drainage flow. The fates of SO₂ and SO₄²⁻ in the valley during extended high-inversion episodes appear to depend considerably on the presence of fog or stratus, and on the extent of daytime insolation.
TRANSPORT AND OXIDATION OF SO$_2$ IN A STAGNANT FOGGY VALLEY

DANIEL J. JACOB
Center for Earth and Planetary Physics, Harvard University, Cambridge, MA 02138, U.S.A.

FREDERICK H. SHAIR
Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, U.S.A.

JED M. WALDMAN,* J. WILLIAM MUNGER and MICHAEL R. HOFFMANN†
Environmental Engineering Science, W. M. Keck Laboratories, California Institute of Technology, Pasadena, CA 91125, U.S.A.

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Abstract—The fate of SO$_2$ emitted in the San Joaquin Valley of California under stagnant foggy conditions was determined by the release of an inert tracer and the concurrent monitoring of SO$_2$ and SO$_2$ concentration. At night, SO$_2$ was found to be trapped in a dense fog layer below a strong and persistent inversion based a few hundred meters above the valley floor. This lack of ventilation led to the accumulation of SO$_2$ and SO$_2$ in the valley. The rate of oxidation of SO$_2$ to SO$_2$ in fog was estimated at 3 ± 2.5 h$^{-1}$. Production of acidity from the oxidation of SO$_2$ fully titrated the NH$_3$ present before the fog, and led to a progressive drop of the fogwater pH over the course of the night. In the afternoon, the valley was found to be efficiently ventilated by a buoyant upslope flow through the inversion. The tracer data indicated that about 40% of the air transported upslope in the afternoon was returned to the valley in the night-time drainage flow. The fates of SO$_2$ and SO$_2$ in the valley during extended high-inversion episodes appear to depend considerably on the presence of fog or stratus, and on the extent of daytime insolation.

INTRODUCTION

Sulfur dioxide emitted from the combustion of fossil fuels is oxidized to H$_2$SO$_4$ in the atmosphere. The deleterious effects of SO$_2$ aerosols on visibility, deposition, and public health are well established (Appel et al., 1985; Gmur et al., 1983; Evans et al., 1984). Atmospheric oxidation of SO$_2$ can be greatly facilitated by the presence of fog, because SO$_2$ is absorbed by the fog droplets and is rapidly oxidized in the aqueous phase (Jacob and Hoffmann, 1983; Seigneur and Saxena, 1984). Fogs are usually associated with stagnant weather conditions, which can then lead to very high SO$_2$ concentrations in SO$_2$ source regions. In the Los Angeles basin, for example, it has been observed that days with high SO$_2$ concentrations are generally preceded by foggy nights (Zeldin et al., 1976; Cass, 1977).

Sulfate air pollution is a major problem in the San Joaquin Valley of California. The southern end of the valley is the site of important oil recovery by steam injection, and large amounts of SO$_2$ are emitted about 15 m above ground level by steam generators burning crude oil (Fig. 1). Stagnation high-inversion episodes are frequent in the wintertime, as mesoscale subsidence over the valley due to high pressure aloft produces a strong and persistent temperature inversion based a few hundred meters above the valley floor. Radiative cooling of the moist air trapped below the inversion leads to widespread fog and stratus within the valley. Fog typically forms shortly after sunset, and may not dissipate until the following afternoon. High-inversion episodes persisting for over a week have been documented (Holets and Swanson, 1981).

The ventilation of the valley is severely restricted during high-inversion episodes, because the base of the temperature inversion lies below the mountain ridges surrounding the valley on three sides. Reible (1982) has estimated residence times of the order of 2 days for air parcels in the southern end of the valley under these conditions. Such long residence times, combined with the persistent fog or stratus, favor the oxidation of SO$_2$ and the subsequent accumulation of SO$_2$ aerosol within the valley. In January 1984, our research group conducted an extensive aerosol field study in the San Joaquin Valley during a high-inversion episode with low stratus (Jacob et al., 1986). We observed a steady rise in SO$_2$ aerosol concentrations at all valley sites over 4 days of stagnation, and estimated a rate of SO$_2$ oxidation of 0.4–1.1 % h$^{-1}$ in the overcast mixed layer. We suggested that most of the SO$_2$ oxidation took place in the stratus cloud which occupied the upper portion of the mixed layer.

* Present address: Dept. of Environmental and Community Medicine, Rutgers Medical School, Piscataway, NJ 08854, U.S.A.
† To whom correspondence should be addressed.
A major source of uncertainty in the study of Jacob et al. (1986) was the difficulty in characterizing \( \text{SO}_2 \) transport under stagnant conditions. This transport is very complex because of the frequent wind reversals associated with mountain-valley breezes (Reible, 1982). Transport of \( \text{SO}_2 \) emitted from the Oldale oil field (Fig. 1) is of particular importance, because that source is responsible for most of the \( \text{SO}_2 \) emitted in the San Joaquin Valley (Aerovironment Inc., 1984). We present here the results of a study conducted the following year (January, 1985), which was aimed at determining the fate of the Oldale \( \text{SO}_2 \) plume. The plume was tagged with an inert tracer (\( \text{SF}_6 \)) during a high-inversion stagnation episode, and the tracer was followed in the valley and aloft. We concurrently monitored the concentration of \( \text{SO}_2 \), the composition of aerosol and fogwater, and the \( \text{SO}_2^- \) deposition fluxes. From these measurements, we will estimate the rate of \( \text{SO}_2 \) oxidation in fog.

**EXPERIMENTAL**

A continuous 23-h release of \( \text{SF}_6 \) was conducted from Oldale between 1800 LST on 4 January and 1700 LST on 5 January 1985 (LST is local standard time). The \( \text{SF}_6 \) release rate was 23.4 kg h\(^{-1}\), for a total of 538 kg \( \text{SF}_6 \) released. Grab samples of air were collected hourly at a number of fixed sites in the southern end of the valley. Networks of automobile traverses were also operated, in which grab samples were collected every mile. Two series of aircraft spirals collected samples at altitudes up to 1220 m MSL. The samples were analyzed by electron capture gas chromatography, which can detect \( \text{SF}_6 \) concentrations down to 1 ppt. The analytical procedure, and the instrument calibration procedures, have been described by Lamb (1978).

An extensive air sampling network was operated in the San Joaquin Valley during December 1984 and January 1985 (Fig 1). The complete data sets have been reported by Waldman (1986), along with detailed descriptions of sampling techniques and quality assurance tests. Aerosol samples were collected on open-faced Teflon filters, and fogwater samples were collected with a rotating arm collector (Jacob et al., 1984). The fogwater pH was determined immediately upon sample collection with a Radiometer PHM82 meter and Radiometer GK2320C combination electrode. The analysis of aerosol and fogwater samples followed the protocol of Munger et al. (1983), except for fogwater anion analysis which followed the protocol of Jacob et al. (1986). The protocol of Jacob et al. (1986) makes possible the separate determinations of \( \text{SO}_2^- \) and \( \text{S}^{\text{IV}} \) in the fog sample. Concentrations of \( \text{NH}_3 \) were determined by a dual filter method (Russell, 1983). Concentrations of \( \text{SO}_2 \) were monitored at Oldale by Texaco. Deposition fluxes of aerosol and fog droplets were measured by Waldman (1986), using polystyrene Petri dish collectors. The fog liquid water content was determined from the collection rate of the rotating arm collector, assuming a collection efficiency of 60% (Jacob et al., 1984). This method has been found to agree fairly well with other liquid water content measurement methods (Waldman, 1986).

Surface winds in the valley were determined at several sites by Texaco and West Side Operators. A tethered balloon was launched above Buttonwillow at intervals of 4–8 h, and recorded vertical profiles of temperature, relative humidity, wind speed, and wind direction from 100 to 500 m MSL. Upper air wind data were provided daily by Edwards Air Force Base, located in the Mojave desert on the other side of the Tehachapi mountains. Additional weather data were available from pilot reports and from the National Weather Service station at Oldale.
TRANSPORT OF SF₆ RELEASED FROM OILDALE

1. Weather pattern

The SF₆ release was conducted during a typical extended high-inversion episode associated with stationary high pressure over S Idaho and N Nevada (Great Basin High). Strong high pressure was observed over the valley between 1 and 5 January, and produced a persistent subsidence inversion based at 300–400 m MSL. Dense widespread fog filled the mixed layer below the inversion every night; the fog set in shortly after sunset and dissipated late in the following morning, giving way to hazy afternoon sunshine. We show in Fig. 2 some vertical profiles of temperature and relative humidity measured over Buttonwillow during 4-6 January. The inversion was very strong at night and in the morning, but weakened substantially in the afternoon because of solar heating. On the night of 5-6 January no fog was observed in the valley, and the temperature was higher than on the preceding nights; the high pressure had begun to decay. High clouds moved over the valley during that night, and rain began on the afternoon of 6 January. The inversion lifted during the afternoon of 6 January, and unstable conditions prevailed for the next few days.

The Oildale wind data for 4-6 January are summarized in Fig. 3. At night, winds were very weak and frequently shifted in direction. In the daytime, however, a well-defined upslope flow was observed, due to heating of the mountain slopes (Reible, 1982). The upslope flow set in shortly after sunrise, but remained weak until midday. Afternoon insolation of the valley floor following dissipation of the fog strengthened the upslope flow considerably, and wind velocities of 10–20 km h⁻¹ were measured at Oildale in the mid-afternoon. Surface winds in the valley were decoupled from the winds aloft; persistent and strong E winds were observed above the inversion, reflecting the circulation around the Great Basin High.

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Fig. 3. Surface winds at Oildale. The arrows indicate the mean resultant winds averaged over 6-h periods. The wind roses give the relative frequencies of the different wind directions. Times are LST.
2. Transport of SF₆

A first network of automobile traverses was operated in the southern end of the valley between 1000 and 1200 LST on 5 January, immediately after the fog had dissipated. The tracer had been released for 16–18 h by that time, and was still being continuously released. The observed concentrations of SF₆, averaged over a 10 km x 10 km grid, are shown in Fig. 4. A mass balance calculation assuming vertical mixing of SF₆ up to the base of the inversion accounted for 91% of the SF₆ released. This demonstrates the lack of ventilation of the valley during the night and morning; almost all of the SF₆ released during the night was trapped within the mixed layer. The SF₆ plume extended about 40 km N of the release site, and spread laterally over about 20 km. This extent of northward transport is consistent with the net weak S–SE winds (2–3 km h⁻¹) observed at Oildale during the night. Concentrations of SF₆ S and W of the release site were very low.

A second network of automobile traverses was operated in the valley during the mid-afternoon of 5 January, but they failed to find the SF₆ plume. The plume had apparently been transported eastward through the inversion by the upslope flow. An aircraft spiral over Oildale at 1530 LST on 5 January indicated the presence of SF₆ within the inversion layer up to at least 1200 m MSL (Fig. 5). The concentration of SF₆ did not decrease progressively with height, as would have been expected from general penetration of SF₆ through the weakened afternoon inversion. Instead, a layer of high SF₆ concentrations was observed at 1200 m MSL, which was also observed in aircraft spirals conducted over other valley sites during the same period. We conclude that SF₆ was transported

![Diagram and data table showing surface concentrations of SF₆ (ppt) at 1000-1200 LST on 5 January. The data are averaged over a 10 km x 10 km grid.]

![Graph showing vertical profile of SF₆ concentrations over Oildale at 1530 LST on 5 January.](image-url)
upward along the slopes by the buoyant afternoon upslope flow, and was spread out horizontally aloft by the strong upper-level E winds. A rough mass balance, which was based on the aircraft data and dependent on the assumption that SF₆ mixed horizontally aloft over the southern end of the valley, indicated that about 40% of the total SF₆ released was present by mid-afternoon within the inversion layer between 400 and 1200 m MSL. Clearly, the buoyant afternoon upslope flow removed a large fraction of the tracer from the mixed layer below the inversion.

The upslope flow ceased at sunset, and a net weak downslope flow developed in the evening. Winds from the N were observed during the early hours of 6 January, but gave way to weak and inconsistent winds later in the morning (Fig. 3). A network of automobile traverses was operated on 6 January between 1100 and 1400 LST (Fig. 6); high concentrations of SF₆ were found throughout the southern end of the valley. A mass balance calculation from Fig. 6, again assuming vertical mixing up to the base of the inversion, accounted for 37% of the total amount of SF₆ released. Therefore, an important fraction of the SF₆ carried upslope during the afternoon of 5 January was returned to the valley floor in the evening, and was then transported to the southern end of the valley during the night. An aircraft spiral over Oildale at 1220 LST on 6 January (Fig. 7) again showed substantial SF₆ concentrations within the inversion layer.

During the afternoon of 6 January, the upslope flow again transported SF₆ eastward out of the valley. An automobile traverse was conducted in the late afternoon over the Tehachapi pass (1200 m) in the SE end of the valley. Significant SF₆ concentrations (5–20 ppt) were found over the pass and in the Mojave desert on the other side of the mountains. No SF₆ was found to
return in the valley on 7 January, probably because of the unstable weather conditions.

TRANSPORT AND OXIDATION OF SO$_2$

Atmospheric concentrations measured at Oildale during 4–5 January are shown in Fig. 8. Concentrations of SO$_2$ were very low during the afternoon of 4 January, because of the strong upslope flow carrying SO$_2$ aloft. After the upslope flow gave way to stagnant conditions in the evening, the SO$_2$ concentration started to rise and attained a stable value of 40 ppbv at midnight. The concentration of SO$_2$ remained at about 40 ppbv until 1100 LST the following morning, and then dropped rapidly following ventilation of the valley by the upslope flow.

The high night-time SO$_2$ concentration, combined with the foggy conditions, led to a substantial increase in aerosol SO$_2^-$ concentrations at Oildale. No such increases were observed at Wasco or Buttonwillow, which were both outside the SO$_2$ plume. Fog set in at Oildale at 2000 LST on 4 January, and persisted until 0900 LST the following morning. The liquid water content of the fog was very stable, and averaged 0.20 g m$^{-3}$. Most of the aerosol SO$_2^-$ in the fog was incorporated into fog droplets (Waldman, 1986). The fogwater SO$_2^-$ concentration increased during the early hours of fog, and stabilized at midnight to an average value of 1100 μeq l$^{-1}$. The pH of the fogwater progressively dropped over the course of the night, from 6.26 to 3.75. The acidification of the fogwater resulted in the total depletion of NH$_3$(g).

The SO$_2$ sources around Oildale are spread over an area A of about 200 km$^2$ (shaded area in Fig. 1). We assume that this SO$_2$ source region can be modeled under stagnant conditions as a stirred tank of characteristic length $L = 15$ km and height $h = 130$ m (mixing height over Oildale), slowly ventilated by a steady wind of velocity $U$. The stable concentrations of SO$_2$ (40 ppbv) and fogwater SO$_2^-$ (1100 μeq l$^{-1}$) observed at Oildale between 0000 and 0700 LST then correspond to the attainment of a steady state between sources and sinks within the stirred tank. We assume that SO$_2$ oxidation in fog can be represented by a pseudo-first-order rate expression:

$$\frac{d(SO_2)}{dt} = -k(SO_2)$$  \hspace{1cm} (1)

The major sinks of SO$_2^-$ within the source region are (1) ventilation (wind velocity $U$), and (2) fogwater deposition (deposition velocity $V_d$). The steady-state fogwater SO$_2^-$ concentration in the source region is then given by:

$$\langle[SO_2^-] \rangle = \frac{2}{WRT} \frac{k}{U} \langle SO_2 \rangle + \frac{U V_d}{W} \frac{[SO_2^-]_0}{L + h}$$  \hspace{1cm} (2)

where $W$ is the liquid water content of the fog (v/v), $R$ is the universal gas constant, $T$ is temperature, $\langle SO_2 \rangle$ is the steady-state SO$_2$ partial pressure, and the subscript 0 refers to fog upwind from the source region. From Fig. 3, the average wind velocity, $U$, was between 0000 and 0600 was 4 km h$^{-1}$, so that ventilation provided a loss rate of about 27 % h$^{-1}$. Waldman (1986) measured an average fogwater deposition velocity $V_d = 1$ cm s$^{-1}$ at Oildale during the night of 4–5 January, corresponding to a deposition rate of 28 % h$^{-1}$. Therefore, the total rate of SO$_2^-$ removal from the source region (ventilation + deposition) was 55 % h$^{-1}$. The fogwater composition upwind from the source region can be estimated from fogwater samples collected at Buttonwillow simultaneously with the Oildale samples (Waldman, 1986); these samples contained SO$_2^-$ concentrations averaging 300 μeq l$^{-1}$ for a liquid water content averaging $1.4 \times 10^{-7}$ v/v. Based on $W = 2.0 \times 10^{-7}$ v/v, $\langle[SO_2^-] \rangle = 1100$ μeq l$^{-1}$, $W_d = 1.4 \times 10^{-7}$ v/v, $[SO_2^-]_0 = 300$ μeq l$^{-1}$, and $\langle SO_2 \rangle = 40$ ppbv, we calculate $k = 3$ % h$^{-1}$. An uncertainty of ±2 % h$^{-1}$ on this value is estimated from the individual uncertainties on the variables in Equation (2).

DISCUSSION

1. SO$_2$ oxidation mechanism

The oxidation of SO$_2$ to H$_2$SO$_4$ can proceed by a number of pathways. Jacob and Hoffmann (1983) and Seigneur and Saxena (1984) have modeled the chemical behavior of night-time fogs in polluted atmospheres, and discussed the relative importance of the major SO$_2$ oxidation pathways. They predict that SO$_2$ is rapidly oxidized in the initial stage of a fog by the aqueous-phase reaction of S(IV) with H$_2$O$_2$(aq), but that this reaction cannot be sustained because of the depletion of H$_2$O$_2$ by SO$_2$ present in large excess. They find that the main contributor to SO$_2$ oxidation in the mature stage of the fog is the autoxidation of S(IV) catalyzed by Fe(III) and Mn(II).

These model simulations considered very acidic fogs typical of the Los Angeles coastline (pH 2–4); in our study, however, the fogwater pH remained mostly between 4 and 6, and this can lead to important differences in the rates of SO$_2$ oxidation. Above pH 4, Fe(III) precipitates, and therefore is not a suitable catalyst for S(IV) autoxidation (Hoffmann and Jacob, 1984). The autoxidation reaction can still be catalyzed by Mn(II), which was present in the Oildale fog samples at concentrations ranging from 0.4 to 0.8 μeq l$^{-1}$ (Waldman, 1986). Assuming a Mn$^{2+}$ concentration of 0.6 μeq l$^{-1}$, an average pH of 5.1, $W = 2.0 \times 10^{-7}$ v/v, and using the rate expression proposed by Hoffmann and Calvert (1985) with the appropriate temperature correction (T = 278 K), we estimate that the SO$_2$ conversion rate by Mn(II)-catalyzed autoxidation was 0.5 % h$^{-1}$. This reaction appears to be too slow to fully account for the observed rate.
Fig. 8. Atmospheric concentrations measured at Oildale on 4-5 January. Aerosol \(\text{SO}_4^{2-}\) concentrations are in units of microequivalents m\(^{-3}\) of air, and fogwater \(\text{SO}_4^{2-}\) concentrations are in units of microequivalents per liter of fogwater.
The persistence of a high SO$_2$ concentration throughout the fog indicates a total depletion of H$_2$O$_2$ and organic peroxydes, which would otherwise rapidly oxidize SO$_2$ (Lind et al., 1987; Daum et al. (1984) have noted that SO$_2$ and H$_2$O$_2$ appear to be mutually exclusive in clouds. A more important SO$_2$ oxidation pathway is likely to be the aqueous-phase reaction of S(IV) with O$_3$ (Hoffmann, 1986), which proceeds rapidly at high pH. Under night-time stagnant conditions in the San Joaquin Valley, O$_3$ is rapidly depleted in the mixed layer by large excesses of NO (Jacob et al., 1986). However, O$_3$ concentrations aloft are likely to be higher than at ground level, and O$_3$ would diffuse to some extent from the inversion layer down into the mixed layer. A monitoring instrument at Olddale had a detection limit of 10 ppb, and did not measure detectable O$_3$ concentrations during the night of 4-5 January; however, more sensitive instruments on the west side of the valley reported O$_3$ concentrations up to 2 ppb. The rate of oxidation of S(IV) by O$_3$ in fog droplets is limited at high pH by the rate of aqueous-phase diffusion of O$_3$(aq) within the droplets (Schwartz and Freiberg, 1981; Martin, 1983; Jacob, 1986). If we assume an O$_3$ concentration of 2 ppb at Olddale, a droplet radius of 10 $\mu$m, fogwater pH and W as above, and the kinetic expression of Hoigne et al. (1985) with the mass transfer correction of Schwartz and Freiberg (1981), we find an oxidation rate for SO$_2$ by O$_3$(aq) of 2% h$^{-1}$ (with $T = 278$ K). This reaction could possibly be an important contributor to S(IV) oxidation in the San Joaquin Valley.

2. Sulfur budget

We have shown that the near-totality of SF$_6$ released between 1800 LST on 4 January and 1100 LST on 5 January (or a period of 17 h) remained trapped within the mixed layer below the inversion. The deposition velocity of SO$_2$ over grass is about 0.5 cm s$^{-1}$ under stable conditions (Sehmel, 1980); based on $h = 130$ m at Olddale, the SO$_2$ deposition rate in the valley during the night of 4-5 January was about 14% h$^{-1}$. In comparison, the SO$_2$ oxidation rate in fog was previously estimated at 3% h$^{-1}$. We find from the above loss rates that 33% of the SO$_2$ released over that 17-h period remained as SO$_2$ in the mixed layer, 55% was deposited on the valley floor, and the remaining 12% was converted to SO$_4^{2-}$. Due to the slow rate of SO$_4^{2-}$ production, the maximum SO$_2$ concentration in the valley was probably not at Olddale but more likely about 20 km downwind (to the N). Most of the SO$_4^{2-}$ produced was removed to the valley floor by rapid deposition of the fog droplets. The importance of SO$_4^{2-}$ deposition in fogs has been discussed in detail by Waldman (1986).

The rates of SO$_2$ and SO$_4^{2-}$ determined in the present study differ considerably from those determined in our study of the previous year (Jacob et al., 1986). Jacob et al. observed a steady accumulation of SO$_2$ and SO$_4^{2-}$ over 4 days of stagnation, with no apparent ventilation of the valley and little SO$_4^{2-}$ deposition. In that study, fog did not form on the valley floor; instead, the valley remained overcast as a persistent stratus cloud occupied the upper part of the mixed layer. The overcast limited daytime insolation of the slopes, thereby preventing the upflow flow from ventilating the valley. Further, the deposition of SO$_4^{2-}$ was very slow because of the lack of fog; deposition velocities of haze aerosol particles are over one order of magnitude lower than those of fog droplets (Waldman, 1986). We conclude that the rates of SO$_2$ and SO$_4^{2-}$ in the San Joaquin Valley during high-inversion episodes depend to a considerable degree on whether or not the valley is insulated, and whether fog or stratus occurs. The rate of in-fog SO$_2$ oxidation estimated in the present study is consistent with the value of 5% h$^{-1}$ estimated in the study of Jacob et al. (1986) for SO$_2$ oxidation in the stratus cloud above the valley floor.

3. Fogwater and aerosol acidity

The atmosphere of the San Joaquin Valley usually contains excess alkalinity, due to the presence of important confined cattle feeding operations which discharge large amounts of NH$_3$ (Jacob et al., 1986). On the afternoon of 4 January, the concentration of NH$_3$(g) at Olddale was 15 ppb, and the pH of the first fog sample collected that evening was high (pH 6.26). However, the pH dropped progressively over the course of the fog, as the oxidation of SO$_2$ to H$_2$SO$_4$ produced acidity which titrated NH$_3$(g). By 2300 LST, NH$_3$(g) was fully titrated, and NH$_3$(g) concentrations remained below our detection limit of 0.5 ppb until the following afternoon. High concentrations of NH$_3$(g) were again observed on the afternoon of 5 January, following dissipation of the fog and transport of the acidic aerosol out of the valley.

The decrease in fogwater pH observed after midnight was much slower than that expected from the rate of H$_2$SO$_4$ production. The pH drop from 5.5 to 3.75 over 10 h of fog, with $W = 2 \times 10^{-7}$ m/s, is equivalent to the production of 4 neq H$^+$ m$^{-2}$ h$^{-1}$ by comparison, oxidation of 40 ppb SO$_2$ at the rate of 3% h$^{-1}$ produces 100 neq H$^+$ m$^{-2}$ h$^{-1}$. It appears that most of the H$_2$SO$_4$ produced was neutralized by NH$_3$, which was continuously being released from ground sources, and therefore that the H$_2$SO$_4$ and NH$_3$ source rates were in close balance.

Jacob et al. (1986) had previously reported a similar close balance between high acidic and alkaline emissions in the Southern San Joaquin Valley. Because of the precariousness of the present acid/base balance, relatively small fluctuations in either SO$_2$ or NH$_3$ emissions could have important implications for fogwater and aerosol acidity in the San Joaquin Valley. Both SO$_2$ and NH$_3$ emissions are currently decreasing in the valley, due to the increasing use of SO$_2$ scrubbers on steam generators and the decline of the cattle industry. Therefore, it is difficult to forecast whether or not the Southern San Joaquin Valley will be affected by acid fog in the years ahead. The occurrence of acid fog episodes in the valley could have major environmental
Implications, in view of the rapidly increasing population and the important agricultural activity. In addition, our data indicate that upslope transport of the acidic aerosol produced in the valley during stagnation episodes affects the National Forests and National Parks on the west side of the Sierra Nevada. Acidic aerosols from the San Joaquin Valley could possibly be a contributing factor to the recent increase in tree necrosis observed in Sequoia National Park at elevation 1000–1500 m MSL. (California Air Resources Board, private communication, 1986). The possible role of acid fog in provoking pine needle necrosis has been previously discussed by Waldman et al. (1984).

CONCLUSIONS

An inert tracer, SF$_6$, was released from a major SO$_2$ source region in the San Joaquin Valley of California during an extended high-inversion episode. At night, the near-totality of the tracer was trapped below a strong and persistent subsidence inversion based 200–300 m above the valley floor. In the daytime, however, the upslope flow generated by the insolation of the mountain slopes was sufficiently buoyant to transport the tracer up through the inversion. About 40% of the tracer transported upslope in the afternoon was returned to the valley floor in the evening by the downslope drainage flow.

Considerable accumulation of SO$_2$ and SO$_4^{2-}$ was observed at night in the stagnant foggy boundary layer. The production of acidity from the oxidation of SO$_2$ to SO$_3^{2-}$ fully titrated the NH$_3$(g) present, and led to a progressive decrease of the fogwater pH over the course of the night. A stirred-tank approximation for the SO$_2$ source region was used to model the nighttime sources and sinks of SO$_2$ and SO$_4^{2-}$. From this model, the rate of oxidation of SO$_2$ to SO$_2^{3-}$ in fog was estimated at 3 ± 2 % h$^{-1}$. We suggest that SO$_2$ oxidation proceeded mainly in the fog droplets by reaction of S(IV) with O$_2$(aq) [catalyzed by Mn(II)] and O$_3$(aq). In the daytime, the upslope flow efficiently transported SO$_2$ and SO$_4^{2-}$ out of the valley. By comparing the results of this study to those of a study conducted the previous year, we conclude that the fates of SO$_2$ and SO$_4^{2-}$ during extended high-inversion episodes in the valley are considerably dependent on the presence of fog or stratus, and on the extent of daytime insolation.

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