Fogwater Chemistry in an Urban Atmosphere

J. WILLIAM MUNGER, DANIEL J. JACOB, JED M. WALDMAN, AND MICHAEL R. HOFFMANN

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

Analyses of fogwater collected by inertial impaction in the Los Angeles basin and the San Joaquin Valley indicated unusually high concentrations of major and minor ions. The dominant ions measured were NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, and H$^+$. Nitrate exceeded sulfate on an equivalent basis by a factor of 2.5 in the central and coastal regions of the Los Angeles basin but was approximately equal in the eastern Los Angeles basin and the San Joaquin Valley. Maximum observed values for NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$ were 10.0, 12.0, and 5.0 meq l$^{-1}$, while the lowest pH observed was 2.2. Iron and lead concentrations of over 0.1 mM and 0.01 mM, respectively, were observed. High concentrations of chemical components in fog appeared to correlate well with the occurrence of smog events. Concentrations in fogwater were also affected by the physical processes of condensation and evaporation. Light, dissipating fogs routinely showed the highest concentrations.

**INTRODUCTION**

Laboratory [Schwartz, 1983; Martin, 1983; Hoffmann and Jacob, 1983] and field [Cass and Shair, 1980; Cox, 1974; McMurry et al., 1981; Smith and Jeffery, 1975; Wilson and McMurry, 1981] studies have indicated that droplet-phase chemistry is important in SO$_2$ oxidation. Droplet-phase oxidation of SO$_2$ occurs, in part, via the following reactions:

\[ \text{SO}_2(g) \rightarrow \text{SO}_2(aq) \]  
(1)

\[ \text{SO}_2(aq) \rightarrow \text{H}^+ + \text{HSO}_3^- \]  
(2)

\[ 2\text{HSO}_3^- + \text{O}_2 \rightarrow \text{H}^+ + \text{SO}_4^{2-} \]  
(3)

\[ \text{HSO}_3^- \rightarrow \text{H}^+ + \text{SO}_4^{2-} \]  
(4)

In Los Angeles, Cass [1975] observed a correlation between the occurrence of high sulfate aerosol levels during the afternoon and the presence of coastal fog and low clouds in the morning. The mean SO$_2$ to SO$_4^{2-}$ conversion rate during July in Los Angeles is 6% hr$^{-1}$ [Cass, 1981], whereas gas-phase reactions can account for, at most, conversion rates of 4.5% hr$^{-1}$ [Sander and Seinfeld, 1976]. Morgan and Lifeson [1980] reported that light misting rainfalls emanating from low stratus clouds in Los Angeles resulted in pH values as low as 2.9 with correspondingly high SO$_4^{2-}$ and NO$_3^-$ concentrations. Waldman et al. [1982] have previously reported pH values near 2.2 in urban fog. Furthermore, Hegg and Hobbs [1981] have reported S(IV) to S(VI) conversion rates of 4.0 to 300% hr$^{-1}$ in wave clouds over western Washington.

In addition to its importance as a chemical reaction site, fog may exert a significant influence on scavenging and deposition, on human health, and on vegetation. Fog forms in the ground layer where gases and aerosols are most concentrated. Because fog droplets are approximately 100 times smaller than rain drops, they should be more concentrated than rain, and mass transfer should not limit the kinetics of fog droplet reactions [Schwartz, 1983; Baboolal et al., 1981].

In light of these results and the expectation that fog droplets (or the fine aerosol remaining after fog has evaporated) are sites for rapid conversion of SO$_2$ to SO$_4^{2-}$ we began a study to characterize the chemical composition of fogwater. Because of the physical similarity to clouds, fog is expected to exhibit the same chemical processes occurring in clouds and, to some degree, aquated submicron aerosols. Information about the chemistry of fogwater may be applicable to the broader questions about ambient acid formation and acidic precipitation. The role of fog in the nocturnal chemistry of SO$_2$ has been examined by Jacob and Hoffmann [1983].

**METHODS**

Fogwater was collected with a rotating arm collector (RAC), which was modified from an original design reported by Mack and Pilie [1975]. A 67.5-cm-long, Teflon-coated steel tube with 10 x 0.95 cm slots milled into opposite sides at each end of the tube is rotated at 1700 rpm with a 1.5-HP induction motor. This rotation imparts a relative velocity of ~50 m/s to the slots. Droplets impact in the slots and are driven by centrifugal force into 30-ml polyethylene bottles attached at the ends of the arms. During operation, the pivot of the arm is 1.4 m above ground level. Based upon changes in particle-size distributions measured with a laser optical particle counter during operation in a cloud chamber, the RAC was determined to have a lower-size cut of ~8 μm [Jacob et al., 1982]. The bulk of liquid water in fogs is contributed by droplets larger than 8 μm, but droplets smaller than 8 μm may be more concentrated than those that are actually collected. Consequently, the concentration of species in fogwater may be slightly underestimated. With this design, up to 2 ml min$^{-1}$ of fogwater has been collected during dense fog and 0.1 to 1.0 ml min$^{-1}$ during lighter fog. Collection efficiency under these conditions is estimated to be greater than 80%, based on laboratory calibration. We are currently working on a fog sampler with a lower-size cut in order to characterize the chemistry of the smaller fog droplets.

**SITE DESCRIPTIONS**

Figure 1 indicates the sites at which fogwater was collected. The Pasadena site, which is located on the roof of a four-story building on the Caltech campus, is in a predominantly residential neighborhood 25 km north of downtown Los Angeles. There are no major pollutant sources in the immediate vicinity. The Lennox site was selected because of its close proximity to both industrial and mobile pollutant sources and its high frequency of marine fog in late autumn; it is situated on the roof of a one-story building at a busy intersection within 100 m of a
Fig. 1. Map of fog sampling sites in Southern California. Los Angeles area sites are indicated on the inset.

major freeway and 6 km from the ocean. Major point sources near the Lennox site include an oil refinery, power plant, Los Angeles International Airport, and several other industrial facilities.

The Oildale site, near Bakersfield, is in an area with higher sulfur emissions from secondary oil recovery operations and is subject to extensive fog ('Tule fog'), which persists throughout the San Joaquin Valley during the early winter. The sampler was placed on the roof of an air-quality monitoring station (about 4 m aboveground). Upland is 60 km NE of downtown Los Angeles. A steel plant and several other heavy industries are located within 30 km of this site, which is also on the roof of an air-quality monitoring station in a residential area.

FOG PATTERNS

In Los Angeles, fog generally occurs during two distinct periods: November through January and April through June. At the two inland sites, Pasadena and Upland, fog occurs sporadically in the night and early morning throughout the fog seasons. Fogs along the coast tend to form repeatedly for several nights, lifting for only part of the day. In the San Joaquin Valley, fog forms for extended periods during the early winter months and often persists throughout the day.

ANALYTICAL METHODS

The sample-handling and analytical protocol is illustrated in Figure 2. Analysis of the sample began as soon as collection ended; measurement of pH and separation of preserved aliquots was completed within 30 min. In the field, samples were stored over ice, then refrigerated when brought back to the laboratory; pH was determined in the field with a Radiometer PHM 80 meter. Sulfite was preserved by addition of CH₂O at pH 4 to form hydroxymethanesulfonic acid (HMSA) [Dasgupta et al., 1980; Fortune and Delling, 1982]; 3,5-diacetyl-1,4-dihydrolutidine (DDL) formed by reaction of formaldehyde and acetyl acetone in the presence of NH₄⁺ [Nash, 1953] is stable for at least 7 days [Rietz, 1980]. Sulfite is known to interfere with this reaction [Nash, 1953], but no correction was made. Addition of HNO₃ to achieve a concentration of 0.16 M was used to stabilize an aliquot for trace-metal analyses. Beginning with the Oildale samples, aliquots were filtered through 0.4-μm Nuclepore membranes in the field. Because of extremely high cation and anion concentrations in fogwater, samples usually had to be diluted before analysis. With sample dilution, complete analyses of volumes as small as 5 ml was practicable.

Major cations were determined on a Varian AA5 atomic absorption spectrophotometer by using an air-acetylene flame. Lanthanum was added to the entire aliquot used for AAS in order to release calcium and magnesium. Ammonium was determined by the phenol-hypochlorite method [Solérzano, 1967]. Anions were determined by ion chromatography (IC), using a 3-mM NaHCO₃/2.4-mM Na₂CO₃ eluent. Aliquots of sample were spiked to give the same HCO₃⁻/CO₃²⁻ concentration as the eluent in order to eliminate the water dip that interferes with F⁻ and Cl⁻ peaks. Galloway et al. [1982] suggest that low molecular weight carboxylic acids are present in rainwater. Considering the high aldehyde concentrations observed in fogwater, it is likely that the corresponding acids are present as well. If present, these acids would be a positive interference with fluoride. The absorbance of DDL formed
FOG SAMPLE-HANDLING PROTOCOL

Fig. 2. A schematic flow diagram indicating fog sample-handling protocol and analytical procedures.

from CH\textsubscript{3}O was measured at 412 nm on a Beckman Acta III spectrophotometer.

The preserved solution for S(IV) was injected into the IC and eluted with 1 mM KHP [Dasgupta et al., 1980]. Because the F\textsuperscript{−} and Cl\textsuperscript{−} peaks coeluted with the hydroxyminethanesulfonate (HMSA) using this eluent, the S(IV) in the samples could not be directly quantified. Instead, S(IV) was taken as the difference between the SO\textsubscript{4}\textsuperscript{2−} concentration in the preserved aliquot and the SO\textsubscript{4}\textsuperscript{2−} concentration in the unpreserved aliquot, measured by the usual IC methods. The first value would be SO\textsubscript{4}\textsuperscript{2−} only, the second would be the sum of SO\textsubscript{4}\textsuperscript{2−} and SO\textsubscript{3}\textsuperscript{2−}. After December 7, S(IV) was measured by a colorimetric method, using 5,5′-Dithiobis-(2-nitrobenzoic acid) DTNB [Humphrey et al., 1970]. Trace metals were determined by flameless atomic absorption (Varian AA6 equipped with a CRA 90 or Perkin-Elmer 360 with a HGA 2100). Gas-phase concentrations of SO\textsubscript{2}, NO\textsubscript{3}, O\textsubscript{3} were made continuously at the Lennox, Upland, and Oildale sites by conventional instrumental methods.

RESULTS

Table 1 describes the conditions before and during the fog sampling. Samples from Pasadena were collected both after

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>Sampled Interval, hr</th>
<th>Conditions During Fog</th>
<th>Prior Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pasadena</td>
<td>November 15, 1981</td>
<td>2040-0115</td>
<td>Light wind SSW–N; sampled beginning to end of fog.</td>
<td>Fair, good air quality.</td>
</tr>
<tr>
<td>Pasadena</td>
<td>November 23, 1981</td>
<td>2320-0130</td>
<td>Light S–SE wind; 14°–12°C; fog thickened to near drizzle; sampled beginning to end of fog.</td>
<td>Hazy and smoggy.</td>
</tr>
<tr>
<td>Lennox</td>
<td>December 7, 1981</td>
<td>2305-0840</td>
<td>Light westerly wind; traffic volume and ambient pollutants began to increase at 0530; missed first hour of fog, sampled until fog lifted.</td>
<td>Previous night foggy, smoggy during day, NO\textsubscript{x} alert called (NO\textsubscript{x} = 0.8 ppm).</td>
</tr>
<tr>
<td>Lennox</td>
<td>December 18, 1981</td>
<td>2315-0043</td>
<td>Light westerly wind; sampled from beginning of fog; fog persisted until morning.</td>
<td>Previous night foggy; high NO\textsubscript{x} levels during day.</td>
</tr>
<tr>
<td>Pasadena</td>
<td>December 20, 1981</td>
<td>745-845</td>
<td>Light northerly wind; 10°C; fog began before 0700; sampled until fog lifted.</td>
<td>Previous day was fair.</td>
</tr>
<tr>
<td>Oildale</td>
<td>January 14, 1982</td>
<td>0200-0750</td>
<td>Light southerly wind; 3°–4°C, thin fog.</td>
<td>Overcast all of preceding day; dense fog on previous night.</td>
</tr>
<tr>
<td>Pasadena</td>
<td>January 17, 1982</td>
<td>2130–2200</td>
<td>Sample collected as fog dissipated.</td>
<td>Smog and haze during the afternoon.</td>
</tr>
<tr>
<td>Upland</td>
<td>May 14, 1982</td>
<td>0630–0910</td>
<td>Light and variable wind, 12°C, thin fog.</td>
<td>Low clouds and ground haze throughout night.</td>
</tr>
</tbody>
</table>
clean air days and smoggy days. The fogs in Lennox followed smoggy days. Olddale samples were collected during a period of extensive and persistent fog in the San Joaquin Valley. Samples at Upland were collected after dawn, when the haze that had been present during the night thickened enough to be collected.

The high and low concentrations of major ions, sulfate, and formaldehyde in fogwater during eight fog events are presented in Table 2. Concentrations of most ions in the second set of Pasadena samples, which followed a smoggy day, were higher than in the first Pasadena fog event. At Lennox the concentrations of major ions in fog were even higher than the Pasadena samples. Some of the fog samples from Lennox contained significant amounts of suspended solids. The greatest amount was in the final sample taken from the December 7 fog event during morning rush hour as the fog was dissipating.

The present sampling method does not differentiate between particles within droplets and particles greater than 8 μm that are independent of water droplets. Because the minimum size for activating condensation nuclei in ambient fog is much smaller than the collector cutoff size, most particles collected in fog, with the exception of hydrophobic material, can be assumed to be associated with droplets.

A single fogwater sample collected in Pasadena on January 17 had exceptionally high concentrations. The sulfate and nitrate concentrations were the maximum values observed in any fog. Fogwater collected in Olddale also had very high nitrate and sulfate concentrations as well as the highest NH₄⁺, CH₂O, and S(IV) concentrations. The Upland fog samples were also characterized by high levels of acidity and acidic anions.

Concentrations of trace metals in the fog samples were also elevated, as shown in Table 3. During some of the fog events, metal concentrations varied over an order of magnitude. The usual pattern was for high concentrations at the beginning and end of the event. Lead and iron concentrations exceeded 1.0 mg L⁻¹ (0.01 mM) on occasion.

The anion-to-cation ratios were close to unity for most of the samples, but there were discrepancies in some samples. In light of the large dilutions necessary to bring high concentrations down into suitable analytical ranges, the ion balances were reasonable. There were apparent excesses of cations in some of the samples that had large quantities of particles present. Calculation of the ion balance by using the concentrations of cations in filtered aliquots yielded better results. The aliquot for anions was routinely filtered prior to injection into the IC. This does not explain the apparent anion deficiency (or cation excess) in the fogwater samples collected from Olddale. The inclusion of SO₄²⁻ in the anion sum does not completely make up the deficit either; however, sulfate in aliquots from these samples was not measured immediately. Even though preservation techniques were used, sulfate may be underestimated. Considering the high concentrations of aldehydes, it is probable that the corresponding carboxylic acids were present in the fogwater; this would account for some of the apparent anion deficiency. Other factors that may contribute to poor ionic balances are losses of ions to particle surfaces via sorption and formation of adducts and complexes of indeterminant charge.

**DISCUSSION**

Figure 3 presents the ionic composition of individual fog samples as a function of time. Concentrations of all ions decrease sharply during the first few hours of the fogs in Lennox; however, the ionic proportions do not change appreciably. In most cases, concentrations in the fogwater rose as the fog...
disappeared. The short duration fogs, which were usually very light fogs that resulted in low collection rates, also had high concentrations. Physical processes of droplet growth by accretion of water vapor, followed by evaporation, appear to account for this pattern.

Dilution by droplet growth could take place without any appreciable change in liquid water content (LWC) if the sedimentation rate was high enough to balance the condensation rate. Work by Roach et al. [1976] suggests that a significant portion of the liquid water formed during a fog event is lost, presumably to ground surfaces. During the periods over which concentrations were decreasing, collection rates, which are a function of LWC, remained constant. Advection of more dilute fog could account for this pattern.

In Figures 4 and 5 the concentration of selected ions, normalized to their initial concentration, are depicted. If physical factors are responsible, the patterns will be nearly identical for ions that are controlled by the same factors or have common sources. The nearly hundredfold increase in Ca$^{2+}$ and Mg$^{2+}$, and the concomitant drop in H$^+$ concentration in the final two samples collected in the December 7 fog at Lennox, coincided with morning rush hour traffic, which would generate a large amount of road dust. Concentrations of other ions were increased during that period, as a result of evaporation, but not to the extent that Ca$^{2+}$ and Mg$^{2+}$ increases (25 times their initial concentrations); [Na$^+$] and [Cl$^-$] increased by a factor of 5, and [SO$_4^{2-}$], [NO$_3^-$], and [NH$_4^+$] returned to their initial concentrations. Acidity was nearly neutralized at the end of this fog event. In association with the increased [Ca$^{2+}$] and [Mg$^{2+}$], an increase in suspended particles, [Pb] and [Fe], was observed at the same time as a rise in CO levels at Lennox, coinciding with the morning traffic. Transfer of gaseous NH$_3$ into the droplets could account for the increase in [NH$_4^+$] and simultaneous drop in [H$^+$] during the December 7 Lennox fog event, while the other ions were maintained at constant concentrations. However, if the NH$_3$ had been present when the fog initially formed, it would have been immediately scavenged because of its high solubility at low pH. Unless there was a local source for NH$_3$, advective transport must be invoked to account for the apparent increase in [NH$_4^+$].

In Pasadena, [H$^+$] and [NO$_3^-$] simultaneously increased while the other ions were decreasing. This may be evidence for the nocturnal formation of HNO$_3$ via the following reactions [Graham and Johnston, 1978]:

\[
\begin{align*}
\text{NO} + \text{O}_2 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \\
\text{NO}_2 + \text{NO}_3 & \rightarrow \text{N}_2\text{O}_5 \\
\text{N}_2\text{O}_5 + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3
\end{align*}
\]

### TABLE 3. Ranges of Selected Trace-Metal Concentrations in Fog Samples

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>Fe (μg l$^{-1}$)</th>
<th>Mn (μg l$^{-1}$)</th>
<th>Pb (μg l$^{-1}$)</th>
<th>Cu (μg l$^{-1}$)</th>
<th>Ni (μg l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pasadena</td>
<td>Nov. 15, 1981</td>
<td>90–2,100</td>
<td>18–160</td>
<td>250–270</td>
<td>1–15</td>
<td>2–21</td>
</tr>
<tr>
<td>Pasadena</td>
<td>Nov. 15, 1981</td>
<td>920–1,770</td>
<td>34–56</td>
<td>1,310–2,540</td>
<td>88–140</td>
<td>8–14</td>
</tr>
<tr>
<td>Lennox</td>
<td>Dec. 18, 1981</td>
<td>1,020–2,080</td>
<td>25–81</td>
<td>1,700–2,250</td>
<td>84–1,400</td>
<td>32–54</td>
</tr>
<tr>
<td>Pasadena</td>
<td>Dec. 20, 1981</td>
<td>340</td>
<td>42</td>
<td>156</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upland</td>
<td>May 14, 1982</td>
<td>430–570</td>
<td>1,690–2,400</td>
<td>156–185</td>
<td>155–213</td>
<td></td>
</tr>
</tbody>
</table>

Alternatively, the increase in HNO$_3$ could result from scavenging or diffusion of fine aerosol to the droplets or by advection of fog with higher NO$_3^-$ concentrations.

In nearly all the cases the dominant ions in the fog samples were NO$_3^-$, SO$_4^{2-}$, H$^+$, and NH$_4^+$, which are the major components of secondary aerosol in Los Angeles [Cass, 1979]. These ions account for over 90% of the solutes in the initial stages of the Lennox samples. The highest concentrations were observed when the fog was preceded by smoggy days. Because secondary aerosols are effective condensation nuclei [Barrett et al., 1979], they will exert a considerable influence on the composition and concentration in fogwater. When the concentration of secondary aerosol is high, the subsequent fogwater will also have high concentrations. The fraction of NO$_3^-$ and SO$_4^{2-}$ neutralized by NH$_3$ (measured in terms of NH$_4^+$) will largely determine the free acidity of the fog that first deliquesces. In this connection it is noteworthy that the initial fogwater samples collected at Lennox are the most acidic, and subsequent samples during the event are progressively more neutral, while at Pasadena and Upland the converse is true.

If HNO$_3$ and NH$_3$ were present when the fog initially formed, they would be scavenged rapidly as well and influence the fogwater composition [Jacob and Hoffmann, 1983]. However, the combination of cooler temperatures and higher humidity before the onset of fog will probably force NH$_3$ and HNO$_3$ to condense into the particulate phase [Stelson and Seinfeld, 1982; Stelson, 1982], which can be scavenged via nucleation or diffusion as the fog forms.

Figure 6 is a conceptualization of the condensation/evaporation cycle for fog droplets and illustrates the link between fogwater chemistry and the chemistry of smog and haze aerosol. High atmospheric concentrations of aerosol precursors appear to result in highly concentrated fogwater. Likewise, dissipation of highly concentrated fog results in very concentrated and reactive aerosol. The high trace-metal content in fogs would catalyze SO$_2$ oxidation. This link between fog and subsequent aerosol can be seen in the correlation reported by Cass [1975] between morning fog and high humidity and high aerosol sulfate concentrations in the afternoon.

### THE ROLE OF ALDEHYDES IN FOG DROPLETS

Aldehydes are released as primary emissions from combustion sources and are generated photochemically from hydrocarbons [National Research Council, 1981]. The peroxide radical is an important byproduct of these reactions. Aldehydes are photochemically destroyed, with OH- and HO$_2$ as byproducts. Intermediates in aldehyde reaction pathways also play a role in the gas-phase reaction networks of SO$_2$ and NO$_x$.

Concentrations of formaldehyde as high as 0.5 mM were present in the Los Angeles fogwater samples. Other aldehydes,
such as acetaldehyde and benzaldehyde, are present in the Los Angeles atmosphere [National Research Council, 1981; Grosjean, 1982], and their presence in fogwater samples at comparable concentrations has been confirmed by the hydrazone derivative method [Fung and Grosjean, 1981]. Aldehydes react with \( \text{HSO}_3^- \) according to the following general stoichiometry:

\[
\text{HSO}_3^- + \text{RCHO} \rightleftharpoons \text{RCHOHSO}_3^- \quad (9)
\]

The formation constant for the formaldehyde-bisulfite addition complex, HBSA, has a maximum of about \( 10^7 \) between
Fig. 4. (a-h) Nondimensional concentrations of individual ions in fog collected on December 7-8, 1981, at the Lennox sampling site. Concentrations are normalized for each component with respect to the concentrations in the initial sample (i.e., $C_i = C_i/C_i_0$). Note the differences in scale. Sampling interval indicated by the width of each bar. NA indicates that a sample was not analyzed. Magnesium and sodium, which are not shown, were nearly identical to $Ca^{2+}$ and $Cl^-$, respectively.

$PH$ 4 and 6 and drops to $10^2$ at $pH$ 9 [Dasgupta et al., 1980]. Stewart and Donnally [1932] observed a similar pattern for the formation of the benzaldehyde-S(IV) adduct. They also observed an interaction between temperature and $pH$. At low $pH$ the temperature dependence of the equilibrium was stronger than at high $pH$. Low temperature increased the stability of the complex. The molar ratio of formaldehyde to S(IV) in the fog samples ranged from 0.9 to 17. Using Dasgupta's constants, the free S(IV) concentration in the fog ranges from 5% to 60% of the total. The equilibrium partial pressures of SO$_2$ and CH$_3$O, required to achieve the S(IV) and CH$_3$O values measured in the fogwater, were calculated from the following mass balance relationships:

$$[S(IV)] = [SO_2(aq)] + [HSO_3^-] + [SO_3^{2-}]$$
$$+ \sum_{i=1}^{n} [R_iCHOHSO_3^-] + \sum_{j=1}^{m} [M_jSO_3^-] \quad (10)$$

$$[R_iCHO]_T = [R_iCHO] + [R_iCHOHSO_3^-] \quad (11)$$

where $R_iCHO$ represents aldehydes forming sulfonic acid adducts, and $M_j$ represents first-row transition metals forming stoichiometric sulfite complexes. Using the appropriate conditional equilibrium expressions for the concentration of the sulfonic acid adducts of CH$_2$O, CH$_3$CHO, C$_7$H$_6$O, and the sulfitoiron(III) complex, and ignoring other S(IV) adducts and complexes because of their low potential concentrations, gives

$$[S(IV)] = K_{HPSO_2} \left( 1 + \frac{K_{a_1}}{[H^+]^2} + \frac{K_{a_1}K_{a_2}}{[H^+]^2} + \frac{K_{a_1}K_{a_2}\beta}{[H^+]^2} \right) Fe(III)) \quad (12)$$

$$[R_iCHO]_T = K_{HPSO_2} \left( 1 + \frac{K_{a_1}K_{a_2}P_{SO_2}}{[H^+]^2} \right) K_{Fe(III)} \quad (13)$$

$$[Fe(III)]_T = [Fe(III)] + [Fe(III)SO_3^-] \quad (14)$$

where $\beta$ is the formation constant for an Fe(III) - S(IV) complex; $K_H$ is Henry's Law constant for $R_iCHO$; $K_H$ is Henry's Law constant for SO$_2$; $K_{a_1}$ and $K_{a_2}$ are acid dissociation constants; $K_{Fe(III)}$ is the bisulfite adduct formation constant, $P_{RCHO}$ and $P_{SO_2}$ are partial pressures. Substitution of the aldehyde and metal mass balances into (12) gives

$$[S(IV)] = \frac{K_{HPSO_2}}{[H^+]^2} \left[ [H^+]^2 + K_{a_1}K_{a_2}P_{SO_2} \right]$$

$$+ \sum_{i=1}^{n} \frac{K_{a_1}K_{a_2}[Fe(III)]_T[H^+]^2}{[H^+]^2 + \beta K_{a_1}K_{a_2}K_{Fe(III)}P_{SO_2}} + \sum_{j=1}^{m} \frac{K_{a_1}K_{a_2}K_{Fe(III)}[M_jSO_3^-]}{[H^+] + K_{a_1}K_{a_2}K_{Fe(III)}P_{SO_2}} \quad (15)$$

The appropriate equilibrium constants are given in Table 4.
In the absence of adduct formation the equilibrium partial pressures of CH2O calculated from fogwater data range from 16 ppb to 76 ppb, which are reasonable values for the Los Angeles atmosphere [Grojean, 1982]. Adduct formation would lower the equilibrium partial pressure. The highest values of S(IV) found in some fog samples cannot be completely accounted for by aldehyde and iron-complex equilibria alone. Measured sulfitic is 4–5 times higher than the predicted equilibrium value, even with $P_{SO_2}$ as high as 30 ppb at the Los Angeles sites or 50 ppb at Oildale, which are the highest values for those sites. The lower concentrations of S(IV), however, are comparable to the values predicted from equilibrium considerations. Stable organic and inorganic sulfitic species in ambient aerosols have been demonstrated to exist [Izatt et al., 1978; Eatough et al., 1978]. Aldehydes may play an important role in the atmospheric chemistry of S(IV) as stabilizers that retard oxidation of S(IV), and possibly as sources of peroxides and free radicals through their photochemistry. More data on the aldehyde content of the atmosphere are necessary to ascertain their role in the heterogeneous chemistry of SO2.

**NITRATE TO SULFATE EQUIVALENT RATIOS**

As is indicated in Figure 7, $[NO_3^-]$ in Pasadena and Lennox was about 2.5 times $[SO_4^{2-}]$; at Oildale and Upland the ratio was closer to 1 : 1. The nitrate to sulfate ratios in fogwater differ markedly from that observed in Los Angeles area rainwater [Liljestrand and Morgan, 1981]. In rainwater the equivalent ratio was less than 1 for coastal and central Los Angeles sites and increased to unity at Riverside at the eastern edge of the basin. Fogwater exhibited the opposite trend: $[NO_3^-]$ exceeded $[SO_4^{2-}]$ at the coastal and central Los Angeles sites and decreased to near one at the most inland site (Upland). Beside the differences in their source strengths (NOx emissions exceed SO2 emissions by a factor of 2.5 in Los Angeles), there are important differences in the kinetics of their respective oxidations and scavenging processes, as is discussed by Jacob and Hoffmann [1983].

**SODIUM CHLORIDE RATIOS**

As Figure 8 illustrates, most of the fogwater samples had Na/Cl ratios near that of seawater. There were a few samples with excess Cl−, which may be due to local sources. The highest excess of Cl− was found in Lennox fog during morning rush hour, which suggests lead bromochloride salts from automobile emissions as a possible Cl− source. Those samples also had high [Pb]. Two of the samples with excess Na+ were collected at the beginning of fog events and may be affected by soil and dust. However, the other samples with excess Na+ were extremely acidic. Reaction between marine aerosol and acidic gases or aerosol may be volatilizing HCl in the fog or the preceding aerosol as suggested by Eriksson [1960] and Hitchcock [1980]. The resulting fog would be deficient in Cl−.

**COMPARISON TO OTHER DATA**

Fog and cloudwater ionic concentrations as high as in some of these samples have been observed previously (see Table 5). At many of the sites, pH values were in the range 3 to 4, but none were as low as the most extreme values for the Los Angeles area fogs. The concentration ranges for the cations Na+, K+, Ca2+, and Mg2+ in other regions overlap with the concentration ranges observed in Southern California. The extreme values reported here, which were found in light fogs and in the Lennox sample that was laden with particles, are somewhat higher. Ammonium concentrations are comparable, but the extreme values observed in this study are about 10 times the maxima for previously reported data. Sulfate concentrations are comparable to other reported values, while nitrate concentrations are considerably higher in the California fogs, which is to be expected because of the dominance of NOx emissions. Furthermore, high concentrations of HNO3, which can be easily scavenged by fogwater, have been measured in the Los Angeles atmosphere [Appel, 1981].

Dense smog as a precursor gave rise to the most highly concentrated fogwater in Los Angeles. Other areas of the world subject to intense air pollution may also prove to have highly concentrated fogwater. Although ionic composition in the 1952 London fog was not measured, approximate calculations based on SO2 emission rates, measured SO2 concentrations, droplet residence time, and liquid water content [Wilkins, 1954a, b] gives SO42− concentrations of 11 to 46 meq l−1. For comparison, the extreme value measured during the winter of 1981–1982 in Southern California was 5 meq l−1.

**IMPLICATIONS**

Highly concentrated fogwater can have several important environmental effects. Sedimentation and impaction rates of...
Fig. 6. A schematic diagram depicting the temperature and humidity dependence for fog formation and the apparent link between atmospheric gas phase and water phase chemistry.

### TABLE 4. Equilibrium Constants Applicable to S(IV) and Aldehyde Chemistry

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$K$ or $M$ atm$^{-1}$</th>
<th>$\Delta H^\circ$ 298, kcal mol$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SO_2\text{g}(aq) \rightleftharpoons SO_2\text{aq}$</td>
<td>1.245</td>
<td>$-6.247$</td>
<td>Sillén and Martell [1971]</td>
</tr>
<tr>
<td>$SO_2\text{aq} \rightleftharpoons H^+ + HSO_3^-$</td>
<td>$1.290 \times 10^{-2}$</td>
<td>$-4.161$</td>
<td>Sillén and Martell [1971]</td>
</tr>
<tr>
<td>$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$</td>
<td>$6.014 \times 10^{-8}$</td>
<td>$-2.23$</td>
<td>Sillén and Martell [1971]</td>
</tr>
<tr>
<td>$CH_2O(g) \rightleftharpoons CH_2O(aq)$</td>
<td>$6.3 \times 10^5$</td>
<td>—</td>
<td>Ledbury and Blair [1925]</td>
</tr>
<tr>
<td>$CH_2O\text{aq} + HSO_3^- \rightleftharpoons CH_2OHSO_3^-$</td>
<td>$\leq 10^4$</td>
<td>—</td>
<td>Dasgupta et al. [1980]</td>
</tr>
<tr>
<td>$Fe^{3+} + SO_3^{2-} \rightleftharpoons FeSO_3^+$</td>
<td>$\approx 10^{10} - 10^{18}$</td>
<td>—</td>
<td>Carlyle [1971]; Hansen et al. [1976]</td>
</tr>
<tr>
<td>$C_3H_6O + HSO_3^- \rightleftharpoons C_3H_6OHSO_3^-$</td>
<td>$\leq 10^3$</td>
<td>—</td>
<td>Stewart and Donnelly [1932]</td>
</tr>
<tr>
<td>$C_2H_4O + HSO_3^- \rightleftharpoons C_2H_4OHSO_3^-$</td>
<td>$\leq 10^3$</td>
<td>—</td>
<td>by extrapolation</td>
</tr>
</tbody>
</table>
fog droplets will be greater than for dry gas and aerosol. Roach
et al. [1976] have calculated that up to 90% of the liquid water
condensed during a fog event may sediment out on the ground.
When winds accompany fog, interception of droplets by veg-
etation is also a major depositional pathway [Schlesinger and
Reiners, 1974; Lovett and Reiners, 1982]. Measurement of rain
and dry deposition fluxes alone may not adequately account for
atmospheric loadings in regions where fog is frequent. Surface
wetness from fog deposition may enhance deposition of SO2
and subsequent oxidation to SO4^{2-} (with a possible involve-
ment of trace metals) [Lindberg et al., 1979].

Fogwater deposited on leaf surfaces is highly efficient in
leaching ions from the leaves [Tukey, 1979] and may result in
some plant injury. Experiments with acid mists show plant
injury occurring at pH levels around 3 [Jacobson, 1980], which
is typical of fogwater in parts of Southern California. Damage
to building materials and metal surfaces is also possible from
deposition of acidic fog. Corrosion of statuary and building
materials has been observed in several locations throughout the
world. The role of fog in this damage is not known, although
research [Metropolitan Museum of Art, 1979] on the Horses of
San Marco (ca. 100 B.C.) in Venice, Italy, indicates that fog and
high SO2 concentrations have resulted in significant damage
during the last 50 years.

Historically, fogs have been implicated in a number of severe
pollution episodes that caused increased human mortality [En-
vironmental Protection Agency, 1971]. The most notable of
these is the infamous London Fog of 1952 [Wilkins, 1954a, b],
which caused 4000 excess deaths during the 5-day episode and
12,000 deaths over 4 months. Further research is needed to
ascertain whether the fog caused mortality or was merely a
consequence of the severe inversion conditions that caused a
build up of toxic air pollutants, which were the true agents of
mortality. Previous analysis [Larsen, 1970] suggested that
these deaths correlated well with the product of gas-phase SO2
and particle concentrations; however, sulfuric acid mists have
been implicated [Wilkins, 1954a, b].

CONCLUSION

Fogwater in Southern California provides a propitious envi-
ronment for the scavenging of particulate and gaseous forms of
S(IV), S(VI), N(V), and N(III); for the subsequent conversion
of S(IV) to S(VI); and for the concomitant production of aci-
dity. Unusually high concentrations of SO4^{2-}, NO3^{-}, NH4^{+},
and H^+ were observed. The highest concentrations were ob-
served during fog events preceded by smoggy days. Acidity
caused by NO3^{-} and SO4^{2-} precursors was neutralized to
some extent by scavenging of NH3 and calcareous dust.

The physical processes of condensation and evaporation,
along with scavenging and subsequent chemical conversion of
reactive gas-phase components, appear to mutually control the
temporal trends in fogwater composition. The apparent cyclical
relationship between the occurrence of smog and fog in the Los
Angeles basin is a manifestation of this phenomenon. The late
night and early morning fogs, which form more readily in a
particle-laden atmosphere, appear to accelerate and enhance
smog production, visibility reduction, and particulate sulfate
levels during the subsequent day. This relationship can be
dubbed the smog-fog-smog cycle.

Clearly, more research is needed to elucidate the mechanisms
by which fog-processed aerosols become highly reactive sites
for daytime photochemical transformations. The role of alde-
hydes and transition metals in the transport and transforma-
tion of S(IV) in atmospheric water droplets needs to be ex-
plored more intensively. Furthermore, given the millimolar
concentrations of some of the metal ions in urban fog, the effect
of metal ion catalysts on important chemical transformations
(e.g., S(IV) to S(VI)) needs to be considered more carefully in the
development of quantitative air quality models for urban
airsheds.
<table>
<thead>
<tr>
<th>Location</th>
<th>Date</th>
<th>Type*</th>
<th>pH</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>Cl⁻</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>NH₄⁺</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brooklyn, Maine</td>
<td>1930-40</td>
<td>F</td>
<td>3.5-6.3</td>
<td>95-770</td>
<td>0-140</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Houghton [1955]</td>
</tr>
<tr>
<td>SW of London</td>
<td>1960</td>
<td>C†</td>
<td>4.4-7.2</td>
<td>40</td>
<td>19</td>
<td>94</td>
<td>95</td>
<td>13</td>
<td>66</td>
<td>25</td>
<td>22</td>
<td>Oddie [1962]</td>
</tr>
<tr>
<td>Germany, Baltic Sea</td>
<td>1955-65</td>
<td>MF†</td>
<td>3.8</td>
<td>1860</td>
<td>900</td>
<td>1740</td>
<td>1500</td>
<td>240</td>
<td>750</td>
<td>2335</td>
<td></td>
<td>Mrose [1966]</td>
</tr>
<tr>
<td>Harz Mtn.</td>
<td>1955-65</td>
<td>CF‡</td>
<td>5.1</td>
<td>775</td>
<td>450</td>
<td>205</td>
<td>295</td>
<td>85</td>
<td>220</td>
<td>710</td>
<td></td>
<td>Mrose [1966]</td>
</tr>
<tr>
<td>nr. Dresden</td>
<td>1955-65</td>
<td>UF‡</td>
<td>4.2</td>
<td>3300</td>
<td>380</td>
<td>358</td>
<td>3180</td>
<td></td>
<td></td>
<td>2100</td>
<td></td>
<td>Mrose [1966]</td>
</tr>
<tr>
<td>Mt. Tsukaba, Japan</td>
<td>Nov. 1963</td>
<td>CF</td>
<td>5.6-6.5</td>
<td>360-2065</td>
<td>11-75</td>
<td>295-1270</td>
<td>180-435</td>
<td>154</td>
<td></td>
<td></td>
<td></td>
<td>Okata [1968]</td>
</tr>
<tr>
<td>Coastal California</td>
<td>Sep.–Oct. 1970</td>
<td>MF</td>
<td>77-490</td>
<td>24-235</td>
<td>96-1235</td>
<td>78-945</td>
<td>11-23</td>
<td>9-100</td>
<td>23-175</td>
<td>0-580</td>
<td></td>
<td>Mack et al. [1977]</td>
</tr>
<tr>
<td>Whiteface Mtn., N.Y.</td>
<td>Aug. 1976</td>
<td>CF‡</td>
<td>3.6-3.9</td>
<td>52-140</td>
<td>140-215</td>
<td>1.7-3.1</td>
<td>2.3-11</td>
<td>13-20</td>
<td>10-20</td>
<td>2.2-6.1</td>
<td>32-89</td>
<td></td>
</tr>
<tr>
<td>Los Angeles, Calif.</td>
<td>Jan. 80</td>
<td>C</td>
<td>4.6-6.8</td>
<td>5-400</td>
<td>0-445</td>
<td>1-760</td>
<td>2-50</td>
<td>1-70</td>
<td></td>
<td>0-230</td>
<td></td>
<td>Hegg and Hobbs [1981]</td>
</tr>
</tbody>
</table>

*Type of sample: F = fog; C = clouds aloft; CF = intercepted clouds; MF = marine fog; UF = urban fog
†Mean values of samples
‡Range of mean values; otherwise range of samples
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REFERENCES


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