EXECUTIVE SUMMARY OF FINAL REPORT

"Characterization of Reactants, Reaction Mechanisms and Reaction Products Leading to Extreme Acid Rain and Acid Aerosol Conditions in Southern California"

ARB Contract No. AO-141-32

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In August of 1981, a joint research project involving the California Institute of Technology and Meteorology Research, Inc., was initiated. A detailed proposal entitled "Characterization of Reactants, Reaction Mechanisms and Reaction Products Leading to Extreme Acid Rain and Acid Aerosol Conditions in Southern California" had been submitted five months earlier.

The principal research objectives of that joint program were as follows:

1. To determine the composition of cloud droplets and of the ambient submicron aerosol during conditions of extreme acidity in the Los Angeles basin. Specific emphasis will be placed on identifying and quantifying the major oxidants and reductants in cloud water and precipitation samples and determining the relative contributions of the various constituents to acidity.

2. To determine the relationship of the pH, strong acid and oxidant concentrations of cloud or precipitation water samples to the composition of the background air and submicron aerosol.

3. To check for consistency with one or more of the hypothesized sulfur or nitrogen oxidation mechanisms and to develop mechanisms to explain the oxidation rates, pH levels, and sulfate and nitrate levels found during this and previous studies.

4. To demonstrate the occurrence of non-photochemical oxidation processes.

These objectives were formulated in light of analyses of Cass (1975, 1978, 1979, 1981), Cass and Shair (1980) and Morgan and Liljestrand (1980). Cass (1978) has shown that the worst sulfate pollution episodes occur during periods of high relative humidity and when the day begins with low clouds or fog in coastal areas, while Cass and Shair (1980) have reported nighttime conversion rates (5.8% hr⁻¹) for SO₂ in the Los Angeles sea breeze/land
breeze circulation system to be statistically indistinguishable from
typical daytime conversion rates (5.7% hr\(^{-1}\)) for the month of July in
the Los Angeles basin. Morgan and Liljestrand (1980), in their study
of rainfall in the Los Angeles basin, have reported that light, misting
precipitation events occasionally resulted in very low pH values (e.g.
\( \text{pH} = 2.9 \)) and correspondingly high \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) concentrations.

Fog water composition is being studied at Caltech to further under­
stand important water-phase chemical reactions in the atmosphere, their
specific mechanisms, plus the conditions that may catalyze or inhibit
them.

In its similarity to clouds with respect to physical characteristics,
fog is expected to highlight the chemical processes occurring in the
clouds aloft. Being located in the polluted ground layer, the composition
of fog water has been found by us to caricature that of cloud water. In
addition, since fog can be conveniently and inexpensively sampled, intensive
research on fog water may afford significant insights about ambient acid
formation and acidic precipitation.

As a link between atmospheric processes and aqueous chemistry, the
composition of fog reflects the impact that regional air pollution may be
having on precipitation acidity as well as the occurrence and physical
character of visibility degradation. This includes haze aerosol formation
plus the frequency and severity of fog episodes. Collection and chemical
analysis of fog water in the Los Angeles area done recently by Caltech
has highlighted the significance of physical processes in controlling
fog water composition.

The development of two fog water collection methods has been under
way since the fall of 1981 at Caltech. Both methods are based on inertial
impaction theory; that is, fog droplets cannot make turns as rapidly as
the fluid in which they are suspended. To quantitatively sample fog, it
is important that only the fog droplets are removed from the air, while
the non-aqueous, predominantly smaller, aerosols are not. This is to
insure that the actual \textit{in situ} composition of the aqueous droplets is
measured. The inertial impactors are designed to establish fairly sharp
cut-offs for the size of particles efficiently collected. The fog collector employed in the field sampling has been calibrated. The Caltech Rotating Arm Collector (RAC) prototype has a cut-off of 15-16 microns. For typical fog droplet size distribution, this cut-off allows more than 80% mass collection.

The study of fog in Southern California is of particular interest in more than one respect. Since rain occurs infrequently in Southern California, an important fraction of the total wet removal of sulfate and nitrate may be due to fog; also the condensation/evaporation cycle of fog droplets will affect significantly the aerosol composition (Figure 1). Furthermore, fog has a moderately long residence time in a highly polluted ground layer.

Six series of fog samples were collected during the late fall of 1981 and early winter of 1982 - three at Caltech, two at Lennox (Los Angeles International Airport) and one at Bakersfield. The procedure for chemical analysis of the samples is described in Figure 2. Typical results are shown in Figure 3. Table I gives a comparison of the data obtained in this study with that of previous investigators.

The chemical loading of these fog samples is, in general, considerably higher than in previously reported studies, reflecting the inordinately high aerosol, SO$_2$ and NO$_x$ concentration levels in the Los Angeles atmosphere. It is also much higher than values reported by Liljestrand (1980) for rain in the Los Angeles basin.

In Figure 4 sulfate concentration versus nitrate concentration is plotted; the nitrate/sulfate ratio is constantly about 2.5. This differs markedly from investigations of rain in the Northeastern United States, where this ratio is always found to be smaller than 1. This underlines the particular importance of NO$_x$ loading and oxidation in the boundary layer of the L.A. atmosphere, and corroborates the general increase in NO$_x$ emissions throughout the United States as observed by Galloway and Likens (1981).
Unusually high concentrations of trace metals and formaldehyde were also observed. The concentrations of cations were relatively high, but much closer to values previously reported for fog.

- Rain Water Chemistry

The presence of sulfuric and nitric acids in precipitation has been documented by rain water monitoring programs worldwide (Likens et al., 1979; Petrenchuk and Selezneva, 1970; Granat, 1972). Rain water acquires acidity by a combination of physical and chemical atmospheric processes (Hales, 1972; Scott, 1978) including gas and particle scavenging plus homogeneous and heterogeneous chemical conversion mechanisms. Condensed phase processes such as those occurring in cloud water have been indicated as having major significance (Hegg and Hobbs, 1981). Precipitation in and around urban centers is noted to be many times more acidic than unpolluted rain. The study of the suspended water droplets in clouds and fog has been pursued to identify the conditions leading to raindrop acidity (Falconer and Falconer, 1980).

Rain water sampling originally initiated by Liljestrand (1980) was continued during the 1981-1982 wet season. Rain water collectors based on the original Liljestrand design were placed on Mt. Wilson, on Mt. Lee and on the roof of Keck Labs at Caltech. Both large volume and sequential small fraction collector arrays were used at each site. Results for the important parameters are summarized in Tables II and III. These results are in general agreement with those reported previously by Liljestrand and Morgan (1980, 1981). Interesting differences were observed between the Mt. Wilson site (elev. 5710') and the Pasadena site (elev. 600'). When the pH was relatively low (pH 4.2) at Pasadena, a higher pH (pH 5.3) was observed at Mt. Wilson. The converse was also observed on a number of occasions (i.e. a high pH was observed at Caltech while a relatively low pH was observed at Mt. Wilson). The switch in trends appears to depend on the trajectory of the storm. These differences should provide an ideal study situation to determine the relative contribution of in-cloud conversion processes and below cloud scavenging to the net production of acidity in rainfall.
- Cloud Water Chemistry

Cloud water samples were collected during November, 1981 (23 and 24) and May, 1982 (21 and 22) by Meteorology Research, Inc., using a Mohnen cloud water impaction device mounted on their Queen Air Sampler. Samples were collected at seven sites along the coast between Malibu and Orange County. Results of this aspect of the study have been reported by Richards et al. (1983). In general, the values observed for pH and major component concentrations are higher than those observed in rainwater but lower than those observed in fog water. Nonetheless, the relatively high concentrations observed in cloud water indicate that clouds may be an active site for NO\textsubscript{x} and SO\textsubscript{2} transformation. The lower concentrations observed in the clouds on the night of 23 November 1981 than observed in the ground level fog at Pasadena are consistent with normal atmospheric gradients. Of particular interest are the relatively high observed concentrations of formaldehyde and sulfite in the aqueous phase. The concentration of S(IV) appears to be in excess of those levels that would result from a straight-forward equilibrium partitioning according to Henry's Law.

- Significant Results

Instrumental methods were designed, tested and implemented for the representative collection of fog water in Southern and Central California. Fog water collected during the months of November, December and January was found to contain inordinately high concentrations of major cations and anions. Concentrations of NH\textsubscript{4}\textsuperscript{+}, SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}\textsuperscript{-} and H\textsuperscript{+} were found, on occasion, to be more than two orders of magnitude higher in fog water than in rain water collected during overlapping periods. Likewise, the fog water appeared to be more concentrated in primary constituents than overlying cloud water. These results indicate that fog water represents an active environment for the transformation of pre-existing aerosol and atmospheric gases. Furthermore, these results suggest that fog and low lying clouds may play an important role in the diurnal production of sulfate and nitrate in the Los Angeles basin during certain propitious times of the year.
This unusual complementary data base of fog, cloud and rain water will be invaluable in the construction and testing of models for the scavenging of aerosols and gases and for subsequent conversion in the aqueous phase.

A reprint of our paper, which appeared in Science, has been included as part of this summary. The article by Waldman et al. (1982) should be consulted for a more complete discussion of first-year results. Overall, this research project has resulted in nine scientific publications which have been included as appendices in the Final Report by Hoffmann et al. (1983).
FOG: LINK BETWEEN ATMOSPHERIC AND WATER CHEMISTRY

Aerosol Formation from Gas Phase Nucleation

Growth by Water Condensation on Existing Nuclei

Dilution

Dissolution of Gaseous Components e.g. NO\(_x\), SO\(_2\), NH\(_3\)

Chemical Conversions

Figure 1
FOG SAMPLE-HANLDING PROTOCOL

ACID-WASHED BOTTLE

+ HNO₃ (TO 1%)

ALIQUOT FOR TRACE-METAL DETERMINATIONS (FLAMELESS AAS)

Na⁺,K⁺,Ca²⁺,Mg²⁺

REFRIGERATED

Mg²⁺ ACID-WASHED - REFRIGERATED: BOTTLE - DETERMINATION (AAS)

NH₄⁺ DETERMINATION (INDOPHENOL BLUE)

0.4 µM FILTER

FILTERABLE SOLIDS

SAVE FOR EM, X-RAY, OR OTHER ANALYSES

0.4 µM FILTER

H₂O-LEACHED BOTTLE

+ CH₂O/KHP PRESERVATIVE

F⁻,Cl⁻,NO₃⁻,SO₄²⁻ (ION CHROMATOGRAPHY)

REFRIGERATED

S(IV)²⁻ DETERMINATIONS (DITHIOBIS-NITROBENZOIC ACID)

+ COLOR REAGENT

CH₂O DETERMINATION (DIACETYL DIHYDRO-LUTIDIN)

pH

Figure 2
Figure 3
SULFATE vs. NITRATE IN LOS ANGELES FOG

Figure 4
Table I. Comparison of Fog, Cloud, and Rain water Data.

<table>
<thead>
<tr>
<th>Location</th>
<th># Samples</th>
<th>Date</th>
<th>pH</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>Fe</th>
<th>CH₂O</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pasadena</td>
<td>4</td>
<td>11/15/81</td>
<td>5.25-4.74 5.6-55</td>
<td>12-496</td>
<td>4-39</td>
<td>370</td>
<td>19-360</td>
<td>7-153</td>
<td>120</td>
<td>56-280</td>
<td>130-930</td>
<td>62-380</td>
<td>0.694-2.1</td>
<td>-</td>
<td>This study</td>
</tr>
<tr>
<td>Pasadena</td>
<td>4</td>
<td>11/23/81</td>
<td>4.85-2.92 14-1200</td>
<td>320-500</td>
<td>33-53</td>
<td>1290-2380</td>
<td>140-530</td>
<td>99-360</td>
<td>180-410</td>
<td>480-730</td>
<td>1220-3520</td>
<td>481-944</td>
<td>0.92-1.77</td>
<td>3.1-3.5</td>
<td>-</td>
</tr>
<tr>
<td>Lennox</td>
<td>8</td>
<td>12/17/81</td>
<td>5.78-2.55 2-2820</td>
<td>28-480</td>
<td>6-160</td>
<td>1120-4060</td>
<td>44-4350</td>
<td>17-1380</td>
<td>115-395</td>
<td>111-1110</td>
<td>820-4560</td>
<td>540-2090</td>
<td>0.34-24</td>
<td>4.6-12.8</td>
<td>-</td>
</tr>
<tr>
<td>Lennox</td>
<td>3</td>
<td>12/17/81</td>
<td>2.81-2.52 1550-3020</td>
<td>80-166</td>
<td>19-40</td>
<td>950-1570</td>
<td>15-190</td>
<td>43-99</td>
<td>180-500</td>
<td>90-197</td>
<td>2070-3690</td>
<td>610-1970</td>
<td>1.02-2.08</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Bakersfield</td>
<td>3</td>
<td>1/14/82</td>
<td>3.07-2.90 850-1260</td>
<td>151-1220</td>
<td>39-224</td>
<td>5370-10520</td>
<td>165-1326</td>
<td>20-151</td>
<td>126-242</td>
<td>203-592</td>
<td>3140-5140</td>
<td>2250-5000</td>
<td>-</td>
<td>6.1-14.4</td>
<td>-</td>
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<tr>
<td>Pasadena</td>
<td>*</td>
<td>1/17/62</td>
<td>2.25</td>
<td>5625</td>
<td>2180</td>
<td>500</td>
<td>7870</td>
<td>2050</td>
<td>1190</td>
<td>637</td>
<td>676</td>
<td>12000</td>
<td>5060</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Los Angeles Rain (vol wt: means at 9 sites)</td>
<td>1978-79</td>
<td>5.4-4.4</td>
<td>4-39</td>
<td>4-37</td>
<td>0.24-4.9</td>
<td>1-36</td>
<td>3.9-17</td>
<td>1.7-11</td>
<td>-</td>
<td>5-52</td>
<td>11-44</td>
<td>7-56</td>
<td>.004-.17</td>
<td>-</td>
<td>Lijjestrand &amp; Morgan</td>
</tr>
<tr>
<td>Whiteface Mtn.</td>
<td>7-8/00</td>
<td>4.2-3.2</td>
<td>63-530</td>
<td>1-55</td>
<td>1-6</td>
<td>4-310</td>
<td>-</td>
<td>11-54</td>
<td>1-15</td>
<td>7-190</td>
<td>40-600</td>
<td>-</td>
<td>-</td>
<td>Falconer</td>
<td></td>
</tr>
<tr>
<td>Fog &amp; Clouds USSR</td>
<td>1961-64</td>
<td>5.3-4.7</td>
<td>5-20</td>
<td>30-104</td>
<td>15-44</td>
<td>33-100</td>
<td>20-50</td>
<td>17-83</td>
<td>-</td>
<td>59-177</td>
<td>2-13</td>
<td>13-185</td>
<td>-</td>
<td>-</td>
<td>Petrenchuk &amp; Drozdova</td>
</tr>
</tbody>
</table>

* [Na⁺], [K⁺], [Ca²⁺], [Mg²⁺], and [NH₄⁺] for filtered aliquots
<table>
<thead>
<tr>
<th>Site</th>
<th>No. of Events</th>
<th>pH</th>
<th>$H^+$</th>
<th>$NH_4^+$</th>
<th>$NO_3^-$</th>
<th>$SO_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pasadena *</td>
<td>15</td>
<td>5.2-3.7</td>
<td>6.3-199.5</td>
<td>1.5-67.1</td>
<td>1.7-88.6</td>
<td>3.5-107</td>
</tr>
<tr>
<td>Pasadena **</td>
<td>12</td>
<td>5.13-3.67</td>
<td>7.4-213.8</td>
<td>1.6-127</td>
<td>10.7-471.</td>
<td>7.5-125.</td>
</tr>
<tr>
<td>(first flush)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mt. Wilson *</td>
<td>8</td>
<td>5.29-4.42</td>
<td>5.1-38.1</td>
<td>0.8-9.0</td>
<td>5.9-21.3</td>
<td>2.2-32.8</td>
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<tr>
<td>Mt. Wilson snow</td>
<td>4</td>
<td>5.14-4.7</td>
<td>7.2-20</td>
<td>$\leq$1.0-25.1</td>
<td>2.1-7.1</td>
<td>4.4-16.3</td>
</tr>
<tr>
<td>Mt. Lee *</td>
<td>7</td>
<td>4.91-4.32</td>
<td>12.4-47.5</td>
<td>7.6-33.0</td>
<td>5.1-10.2</td>
<td>9.2-40.2</td>
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</tbody>
</table>

* volume-weighted means for entire events

** concentrations in initial .34 mm of rainfall
Table III. Volume-weighted mean concentrations in Los Angeles rain

<table>
<thead>
<tr>
<th>Site</th>
<th>$H^+$</th>
<th>$\text{NH}_4^+$</th>
<th>$\text{NO}_3^-$</th>
<th>$\text{SO}_4^{2-}$</th>
<th>Precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pasadena</td>
<td>$3.3 \pm 6.9$ (4.5)</td>
<td>$24 \pm 13.6$</td>
<td>$17 \pm 3.3$</td>
<td>$22 \pm 5.3$</td>
<td>$340$</td>
</tr>
<tr>
<td>Mt. Wilson</td>
<td>$19. \pm 5.4$ (4.7)</td>
<td>$5. \pm 2.2$</td>
<td>$12 \pm 2.7$</td>
<td>$13 \pm 3.1$</td>
<td>$194$</td>
</tr>
<tr>
<td>Mt. Lee</td>
<td>$18 \pm 3.8$</td>
<td>$13. \pm 1.7$</td>
<td>$28 \pm 5.9$</td>
<td>$24 \pm 5.1$</td>
<td>$144$</td>
</tr>
</tbody>
</table>

Values are in μeq λ⁻¹ ± standard error
References


**Chemical Composition of Acid Fog**

Abstract. Fog water collected at three sites in Los Angeles and Bakersfield, California, was found to have higher acidity and higher concentrations of sulfate, nitrate, and ammonium than previously observed in atmospheric water droplets. The pH of the fog water was in the range of 2.2 to 4.0. The dominant processes controlling the fog water chemistry appear to be the condensation and evaporation of water vapor on preexisting aerosol and the scavenging of gas-phase nitric acid.

In the fall of 1981, a field study was initiated to determine the chemical composition of fog water in the Los Angeles basin. Results show that the fog water is significantly more acidic and concentrated with respect to chemical composition than cloud and rain water collected in southern California. Liljestrand and Morgan (1) determined the chemical composition of rain in Los Angeles and reported that light, misting rainfalls had the highest acidity (2). Earlier fog water studies (3–5) in nonurban environments have reported concentrations of major...
ions comparable to those reported for cloud (6, 7) and rain (8) water. However, urban fogs tend to form under more polluted conditions than clouds. Our research program expands upon these earlier studies in an attempt to focus on the chemical and physical processes that occur in the atmospheric aqueous phase before a precipitation event. In the Los Angeles basin, fog and cloud water processes may represent a significant pathway for SO₂ and NOₓ oxidation and for the concomitant production of acidity. Furthermore, morning fog and low clouds along the coast have been strongly correlated with high SO₄²⁻ aerosol concentrations during the afternoon in the Los Angeles basin (9).

In this study, fog water was collected with a rotating arm collector (10). Droplets impact in slots along the ends of the arm and are driven outward by centrifugal force into sample collection bottles which serve effectively to isolate the collected liquid. In cloud chamber tests, the lower particle size cutoff for this collector was estimated to be 8 µm. Two of the collection sites were in the Los Angeles basin (Pasadena and Lennox), and the third was located in the San Joaquin Valley near Bakersfield. The Pasadena site was located in a residential neighborhood 25 km from downtown Los Angeles; the Lennox site, 2 km from the Los Angeles International Airport, was adjacent to a freeway and near two power plants and one oil refinery; and the site in the San Joaquin Valley was located in Oildale, which is surrounded by secondary oil recovery operations.

The concentration ranges of major chemical components observed during six separate fog events are listed in Table 1. These ranges represent the low and high values measured in time-sequenced samples over the duration of the particular fog events (11).

The first fog event in Pasadena followed a day with good air quality; the second fog event in Pasadena was preceded by a hazy day. Concentrations of most ions in the second fog event were much higher than in the first. The third and fourth fog events were sampled in Lennox on nights of dense coastal fog. Smog and dense haze had persisted throughout the day preceding the third fog event, accompanied by high ambient NOₓ concentrations along the coast. These samples had even higher concentrations than the Pasadena fog samples. In addition, the fog water contained a significant amount of solid material, especially the final sample taken as the fog dissipated. Most of the particles remained suspended in the samples after standing for several days, which suggests that they were too small to have been collected unless incorporated in larger droplets.

A single fog event at Bakersfield was monitored during a period of extended fog throughout the entire San Joaquin Valley. The southern portion of the valley has a number of oil fields in which steam-injection oil recovery methods are used. Consequently, the sulfur emissions are high for a nonurban, agricultural area. The fog water analyses, which were characterized by low pH values (2.9) and high [SO₄²⁻] (5.0 meq/liter), [NO₃⁻] (5.1 meq/liter), and [NH₄⁺] (10.5 meq/liter), reflect the dichotomous land use in the San Joaquin Valley.

The last sample, a single fog water sample, was collected on the night of 17 January 1982 in Pasadena. The pH of this sample (2.25) was unusually low with corresponding high [NO₃⁻] (12 meq/liter), [SO₄²⁻] (5.5 meq/liter), and [NH₄⁺] (8 meq/liter); however, the duration of this fog event was relatively short (~1 hour).

The concentrations of the major components in the California fog samples were significantly higher than in previously reported samples of fog, cloud, and rain water (Table 1). The observed values of [SO₄²⁻], [NO₃⁻], [NH₄⁺], and [H⁺] were 10 to 100 times higher than the earlier values. Values of [Na⁺], [K⁺], [Ca²⁺], [Mg²⁺], and [Cl⁻] were high but more in line with values reported for fog

Table 1. Ranges in concentrations observed during six fog events in the Los Angeles area during 1981 and 1982 (11). Representative concentrations for other fog, cloud, and rain samples are presented for comparison. The ranges shown in the values for this study are from

<table>
<thead>
<tr>
<th>Location</th>
<th>N</th>
<th>Date</th>
<th>pH</th>
<th>Concentration (meq/liter)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H⁺</td>
</tr>
<tr>
<td>Pasadena</td>
<td>4</td>
<td>11/15/81</td>
<td>5.25-4.74</td>
<td>5.6-55</td>
</tr>
<tr>
<td>Lennox</td>
<td>8</td>
<td>12/7/81</td>
<td>5.78-2.55</td>
<td>2-2,820</td>
</tr>
<tr>
<td>Lennox</td>
<td>3</td>
<td>12/17/81</td>
<td>2.81-2.52</td>
<td>1,550-3,020</td>
</tr>
<tr>
<td>Bakersfield</td>
<td>3</td>
<td>11/14/82</td>
<td>3.07-2.90</td>
<td>850-1,260</td>
</tr>
<tr>
<td>Pasadena*</td>
<td>1</td>
<td>11/17/82</td>
<td>2.25</td>
<td>5,625</td>
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<td>Los Angeles rain</td>
<td>9</td>
<td>1978</td>
<td>5.4-4.4</td>
<td>4-39</td>
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<tr>
<td>Coastal California fogs</td>
<td>9</td>
<td>1979</td>
<td>5-20</td>
<td>30-104</td>
</tr>
<tr>
<td>Whiteface Mountain</td>
<td>7</td>
<td>9/23/80</td>
<td>4.2-3.2</td>
<td>63-630</td>
</tr>
<tr>
<td>Fog and clouds, U.S.S.R.</td>
<td>1</td>
<td>1961</td>
<td>5.3-4.7</td>
<td>5-20</td>
</tr>
</tbody>
</table>

* [Na⁺], [K⁺], [Ca²⁺], [Mg²⁺], and [NH₄⁺] for filtered aliquots.

Fig. 1. Ionic composition in serial samples collected during three Los Angeles fog events; PST, Pacific standard time. The width of each bar represents the sampling interval. Fog formation and dissipation (that is, the beginning and end of individual fog events) are indicated by arrows. Fog had formed at least 1 hour prior to the taking of the first sample on 7 December 1981; sampling on 17 December 1981 ended before the fog dissipated. The effect of dilution and concentration changes in ionic concentration.
and cloud water in other areas. High values of [CH$_2$O], [Fe], [Mn], and [SO$_2^-$] (30 to 260 µeq/liter) were also found. The observed concentrations of S(IV) appear to be in excess of those predicted by Henry's law considerations, although formation of sulfonic acid derivatives and iron sulfito complexes can account for this apparent discrepancy (12).

Figure 1 illustrates the changes in total ionic concentration, with respect to time for three fog events. A concave trend in the profile of concentration versus time (decreasing at the beginning and rising toward the end) was observed. Changes in the absolute concentration of individual ions that are proportional to the changes in total concentration indicate that water vapor condensation and the evaporation of fog droplets are the dominant processes. Sharp decreases in concentration during the first few hours of the fog events in Lennox were due primarily to initial droplet deliquescence on preexisting aerosol. Similarly, most of the increase in concentration that was observed as the fog dissipated was due to evaporation and the regeneration of fine aerosol. These physical effects apparently play a dominant role in determining fog chemistry in the Los Angeles basin.

The dominant ions in the fog water were NH$_4^+$, H$_3$O$^+$, NO$_3^-$, and SO$_2^-$, and their highest concentrations were observed after days of dense haze. During the early phases of the Lennox fog, these ions make up ≈ 90 percent of the total ionic concentration. This result suggests that preexisting aerosol is a major determinant of the chemical composition of fog water, since these four species are the major components of the daytime aerosol haze (13).

In Los Angeles, the equivalent concentration ratio of NO$_3^-$ to SO$_2^-$ in fog water was about 2.5, which is comparable to the reported emission ratio (9). The corresponding ratio in Los Angeles precipitation was close to 1.0 (1). In the Bakersfield fog, the same ratio was ∼ 1.

The observed changes in fog water composition may have resulted either from chemical changes in the droplets or from the advection of different air masses over the sites. In Pasadena, [H$_3$O$^+$] and [NO$_3^-$] increased simultaneously as a function of time; this result suggests the transport of HNO$_3$ or N$_2$O$_5$ into the droplets (14). On 7 December 1981 in Lennox, [NH$_4^+$] doubled from the third to the fourth sampling period while there was a corresponding decrease in [H$_3$O$^+$]. Transfer of gaseous NH$_3$ into the droplets could account for this neutralization. However, the delay in the [NH$_4^+$] increase after the onset of fog suggests that the advection of fog formed on condensation nuclei with different characteristics was responsible. During the last few hours of that event, an increase in [Ca$^{2+}$], [Mg$^{2+}$], and [Fe] was observed. This increase coincides with the morning rush hour traffic on the adjacent freeway and can be attributed to the incorporation of road and soil dust into the fog. The fogs in Lennox initially exhibited a high acidity that was progressively neutralized, whereas the fogs in Pasadena became more acidic during a fog event. This result suggests differences in the composition of the aerosol preceding the fog at each site and differences in the transfer characteristics of gas or solid to liquid.

The results of this study show that the concentrations of major chemical species in fog water collected at three sites in Los Angeles and Bakersfield are significantly higher than previously reported in atmospheric water droplets. The chemistry of fog water in Los Angeles appears to be dominated by the composition of the haze-forming aerosol that precedes it. Subsequent effects of condensation and evaporation control the observed concentrations. Secondary aerosol, which has high [NH$_4^+$], [H$_3$O$^+$], [NO$_3^-$], and [SO$_2^-$], deliquesces initially to give a concentrated fog water. Further condensation of water results in dilution. After initial formation, the fog water appears to incorporate additional NH$_3$, HNO$_3$, and calcareous dust. As the fog dissipates by evaporation, higher concentrations are again observed.

In light of the inordinately high concentrations of acidic components found in Los Angeles fog, further research is needed to determine the role of aqueous atmospheric droplets in SO$_2$ and NO$_x$ conversion and acidity transport processes. High [H$_3$O$^+$], [NO$_3^-$], and [SO$_2^-$] found in fog water may have a significant effect on health and on materials and plants in urban areas such as Los Angeles and in nonurban areas such as Bakersfield.

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References and Notes
12. The Caltech rotating arm collector was modified from an original design by E. J. Mack and R. Pilie (U.S. Patent 3885532 (1975)). The impaction surfaces move at a velocity of approximately 30 m/sec. A sampling velocity that is much greater than the ambient wind speed serves to minimize the bias due to anisokinetic sampling (K. R. May, In Airborne Microbes, P. H. Gregory and J. L. Monteleit, Eds. (Society for Gener-
al Microbiology, Cambridge, England, 1967), p. 60. Thermodynamic and mass transfer calculations suggest that evaporation of the fog water is insignificant during the time of collection.

11. Immediately after collection, the pH of the sample was measured and aliquots were separated for later analyses. Major metal cations were determined by atomic absorption spectrophotometry and major anions by ion chromatography. Both NH₄⁺ and CH₂O were determined by standard colorimetric methods. Ultrapure grade HNO₃ was added to preserve the trace metals; SO₄²⁻ was stabilized by reaction with CH₂O at pH 4.


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