

# Acid Fog

by Michael Hoffmann

VIRTUALLY ALL the world's air pollution episodes or disasters are known to have been associated with heavy fog conditions. During the five days in December of 1952, for instance, when thick fog virtually deprived London of light at noon, the death rate rose dramatically from the normal daily average of 250 to approximately 1,000 per day. As the fog dissipated and was removed, its effects began to diminish. By the time the death rate finally returned to normal three months later, the fog had claimed 12,000 excess deaths.

Pollution episodes of the same order of magnitude on a per capita basis have occurred in the Meuse Valley of Belgium near Liege and, in the U.S., in Donora, Pennsylvania. These episodes have usually only been considered extreme and rare examples of the damage possible from acidic fog and associated air pollutants. Our research at Caltech has indicated that on occasion the concentrations of acid in fog in certain areas of southern California do not differ greatly from those calculated for the London fog of 1952.

Over the years, the public has become more aware of the concept and reality of acidic deposition, primarily through the phenomenon of acid rain. Acid fog is now also fairly well known, and some may even be informed that acid snow has been observed. Yet while the publicity given to acid deposition phenomena may be relatively recent, the phenomena themselves most definitely are not. In a landmark textbook, *Air and Rain*, which was published in 1872, Robert Angus Smith not only presented at length his own research on acid rain in Brit-



*Thick fog blankets London in December 1952, turning noon into night. During the five-day siege of fog the death rate quadrupled.*

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ain and Europe but discussed previous studies on the acidity of fog dating from as long ago as 1811. So although we at Caltech have contributed significantly to understanding the processes that lead to the acidification of fogs and clouds and subsequent production of acid rain, we have in fact rediscovered phenomena that were familiar to scientists at the beginning of the 19th century.

Our rediscovery has proceeded by studying the acid concentrations of fog, or low-lying clouds, in southern California. Clouds, we now know, are very active environments for the conversion of sulfur dioxide to sulfuric acid. For many years, though, the primary pathway for oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  was thought to be in the gas phase. At first, an active form of oxygen and, later, ozone were believed to be involved in the gas-phase reactions; eventually, we settled on the hydroxyl radical — a very reactive species generated in photochemical environments when sunlight is present. But as it turns out, none of the known rates of gas-phase reactions can predict the observed atmospheric conversion rates of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  or other products, such as ammonium sulfate or ammonium bisulfate. Based on our current research, it is apparent that reactions occurring in clouds and aquated haze aerosol can account for much of the rapid conversion seen in urban and even rural atmospheres.

The acidification phenomenon begins primarily when the combustion of fossil fuels produces  $\text{SO}_2$  and  $\text{NO}_x$ . Normally unreactive, nitrogen and oxygen combine through high-temperature combustion to form  $\text{NO}$ , which is subsequently oxidized to  $\text{NO}_2$ . These gases are discharged into the atmosphere and dispersed by turbulent mixing and advection. Though the gas-phase reactions are not extremely fast under ambient conditions, the  $\text{SO}_2$  and  $\text{NO}_x$  in the atmosphere can be oxidized to produce  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  gases. Nitric acid remains in the gas phase. But once the concentration of the gaseous sulfuric acid reaches a sufficiently high level, homogeneous nucleation occurs and particles or droplets of pure sulfuric acid form. Some of these sub-micron droplets of  $\text{H}_2\text{SO}_4$  will be neutralized by ammonia gas derived primarily from agricultural activities. If the acidic particles are large enough, they can settle to the earth by sedimentation; otherwise, this dry form of deposition is accomplished through turbulent transport to the surface.

The fastest production of sulfuric acid occurs in clouds. Absorbed by clouds, the fairly soluble  $\text{SO}_2$  is dissolved into the liquid phase and, as a result of chemical reactions taking place within this assemblage of liquid water droplets, it is transformed into  $\text{H}_2\text{SO}_4$  (that is,  $\text{H}^+$ ,  $\text{HSO}_4^-$ , and  $\text{SO}_4^{2-}$  in the aqueous phase). As similar pathways are open for the

conversion of the nitrogen oxides to nitric acid, clouds will accumulate predominantly these two acids. And when precipitation occurs, of course, the acids are brought back down to earth.

Besides acid rain's wet and dry forms of deposition, we have recently discovered a mode of precipitation that has not previously been taken into account. We call this phenomenon "occult" precipitation. As the clouds and fogs move through the environment, the acidic droplets are deposited on trees — which are very good fogwater collectors — and, through them, drip down to the earth. In coastal regions, it turns out, vegetation can receive up to 50 percent of its total moisture during the year from the occult precipitation of impacted cloudwater and fogwater.

To get an idea of the acidity of rainfall, we have to know its pH — which is defined as the negative logarithm of hydrogen ion activity (that is, concentration). A pH of 7 — a concentration of  $10^{-7}$  molar — is considered neutral, so that any pH lower than 7 should ordinarily indicate notable acidity. But this value does not take into account the equilibrium between carbon dioxide as a gas naturally present in the atmosphere and carbon dioxide in the aqueous phase. When dissolved in water, aquated carbon dioxide dissociates to give a proton and bicarbonate with a resultant pH of 5.6 for the above atmospheric concentration. Rainfall has always, of course, been acidic; but the pH values of acid rain are much less than the anticipated "clean" background level of 5.6.

Public attention has focused on the northeastern part of the United States as the area where the most severe acid precipitation is taking place. Rainfall in the New England states typically has a pH of 4, while 4.2 would be a low value for Florida, for instance. And though measurements of the pH of rainfall in southern California have gone as low as 2.9, the acidity of the region's rain is, on the average, one-third less than in the northeast. A typical value for Pasadena in 1979- 1980 was 4.8; in Riverside in the eastern part of the Los Angeles basin, where there are bases — such as soil dust, and ammonia from cattle feedlots and other agricultural activities — that can neutralize some of the acidity in the droplet phase, the pH was about 5.2; and at Big Bear in the San Bernardino Mountains, the value was determined to be 5.65 in 1979.

The severity of acid deposition in south-

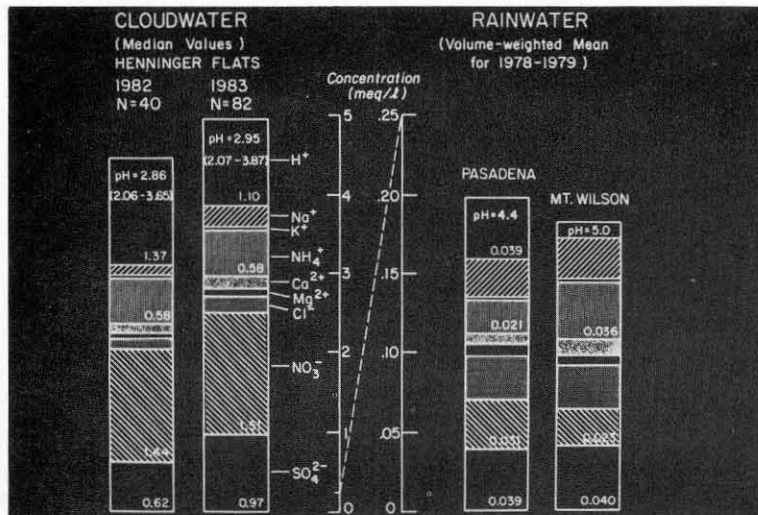
ern California cannot be assessed, however, only on the basis of the average pH of rainfall. Our research on the acidity of fog in this area indicates that the field of acid deposition must be widened to include phenomena whose acidity may be 100 times that of acid rain.

An important finding in southern California was that air quality — the visibility and sulfate loading of the atmosphere — is directly related to relative humidity or, under certain circumstances, to the presence of fog along the coast. When the fog burns off in the morning, visibility in the afternoon is quite low and particulate sulfate concentrations in the atmosphere are quite high. On days of high relative humidity, generally when it's greater than 50 percent, a haze aerosol occurs. An aerosol is usually called smog, but it's actually a precursor of fog since it contains aquated particles that cause light scattering and visibility reduction.

As our data strongly indicated a correlation between fog and sulfate pollution in the

*Views of the San Gabriel Mountains from the roof of Keck Laboratory compare a typical clear winter day (top) with the familiar summer smog (bottom). The smog is actually a haze aerosol that occurs on days of high relative humidity.*





The chemical composition of cloudwater at Henninger Flats in the San Gabriel Mountains is compared above with that of rainwater in Pasadena and on Mount Wilson.

southern California atmosphere, we suspected that the aquated droplets of both fog and haze aerosol would comprise a very active environment for the conversion of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>. The situation in fogs and clouds is very similar. For a cloud droplet or a fogwater droplet to form, there has to be a condensation nucleus. The condensation nucleus can be soil dust, sea salt aerosol along the coast, fly ash from power plants, or secondary or haze aerosol. Under the appropriate conditions of relative humidity and temperature, water will then condense on the particles' surface and either a cloud or a fog, when the cloud is at the ground, will be formed.

The chemical composition of the fog will, to some extent, be a direct function of the chemical composition of the condensation

nucleus from which it was formed. Part of that nucleus will be soluble, and those soluble chemical components will go into the aqueous phase. In the atmosphere certain gases will partition into the aqueous phase and undergo various chemical reactions. Among the many organic and inorganic reactions taking place in this droplet phase and contributing to the acidification of fogs and clouds, the ones that particularly interest us produce sulfuric, nitric, and sulfonic acids.

The acidification process starts with sulfuric acid, nitric acid, NO<sub>x</sub>, SO<sub>2</sub> in the gas phase, aldehydes, ammonia, and water. First, gas-to-particle conversions occur to form solid or liquid particles, which then deliquesce. Next, light-scattering haze aerosol droplets form with particle diameters near 0.5 microns (10<sup>-6</sup> meters). These droplets may be quite acidic, containing nitrate, sulfate, sulfonates, ammonium ion, and free acidity. Given proper conditions, what is called activation then occurs and fogwater or cloudwater droplets are produced. The measurements we've made at different stages in this process show that, on a volume basis, the haze droplets are much more acidic than the fogwater or cloudwater droplets, which in turn tend to be more acidic than the much larger rainwater droplets.

We have called this interdependence between smog and fog the smog-fog-smog cycle. As the temperature drops rapidly in the evening after a warm day when a large amount of water has evaporated, the relative

Fog also comes in on little cat feet near Riverside near the foot of the San Bernardino Mountains.



humidity increases, water condenses on the haze aerosol droplets, and acidic chemical components are introduced into the aqueous phase. During the course of the fog the gaseous components are dissolved and diluted, more acidity is produced in the droplet phase, and, as once again the temperature goes back up and the relative humidity goes back down, the droplets begin to evaporate. The acidity of the droplets affected by evaporation at this stage in the cycle is very high. Eventually, a haze aerosol reappears, providing the seed for the production of smog on the subsequent day. Until a new primary meteorological condition comes in to break it up, the cycle of smog and fog will continue.

To obtain the cloudwater and fogwater for our measurements, we developed a device called a rotating arm collector (RAC). The collector looks like a propeller or helicopter blade with sampling bottles firmly attached to the periphery blades. Rotating at a velocity of roughly 1,800 rpm, the collector's blades sweep out a cylinder of air and capture fogwater droplets by inertial impaction. While the smaller particles or unactivated condensation nuclei in the fog follow the fluid mechanical streamlines around the rotating blade, the larger fogwater droplets, due to their inertia, strike the leading edge of the blade and are forced inside. Once inside, they hit a tube or cylinder and are pushed outward by centrifugal force into the sampling bottles. In side-by-side comparisons with cloudwater collectors designed at other universities, the Caltech collector has proven to be a superior collection device under a wide range of operating conditions.

Our collector has a droplet size cut of roughly 10 to 20 microns. Fogwater droplets have a mass median diameter of 20 microns, and none are found smaller than 2 microns in diameter. In most fogs, however, the droplets are less than 50 microns. So although the collector accumulates only a certain fraction of the smaller fogwater droplets in the range of interest of 2 to 100 microns, it collects those greater than 15 microns with close to 100 percent efficiency.

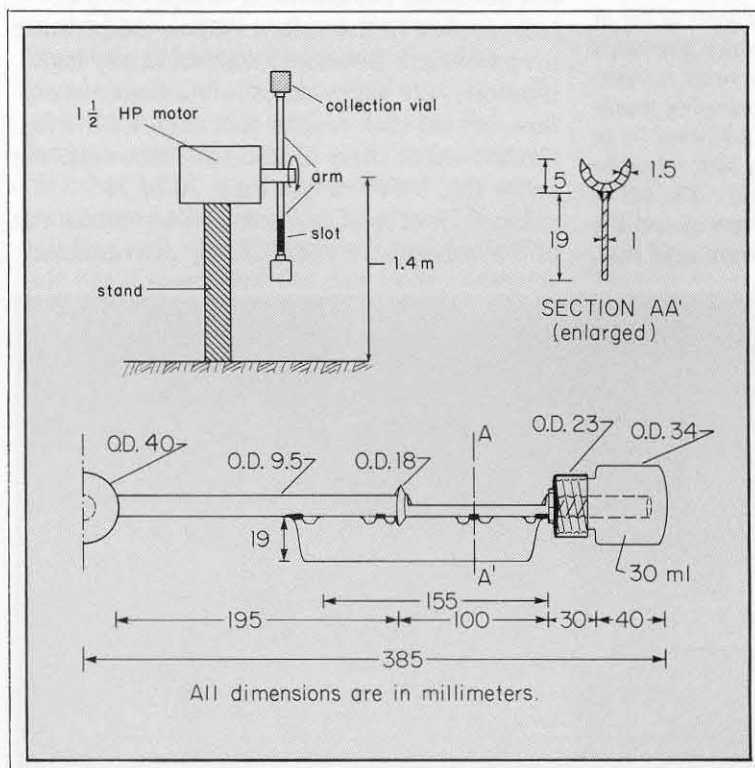
In the field, we use a laser optical particle counter to determine the droplet size distribution and the number of fog droplets present. To measure the amount of water in the atmosphere, or what is called the liquid water content, we use a laser transmissometer, which measures the attenuation of a 9.2- micron laser beam over a 10-meter path length. A

cyclone separator enables us to filter out of the fog the unactivated condensation nuclei so that we can determine their chemical composition. We also determine the composition of the haze aerosol before and after the fog, measure all the gases in the gas phase, and then do all the chemical analyses to understand what occurs within a fog or cloud environment over the course of time.

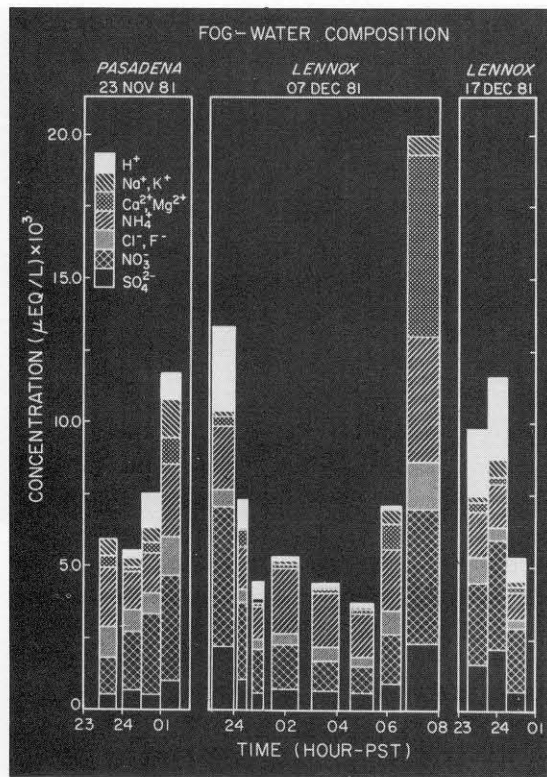
When plotted as a function of time, concentrations of major chemical components — typically sulfate, nitrate, chloride, formaldehyde, ammonium ion, calcium, magnesium, sodium, potassium, and hydrogen ion — generally follow a concave profile. At the beginning of the fog, the concentrations are high; as the fog develops, the liquid water content rises, the droplets are diluted, and the acidity drops; and, then, as evaporation takes place, the relative humidity decreases, the temperature goes up, and there is a concentration effect. As a consequence, the pH value of a fog varies as a function of time.

Most fogs follow this concave concentration-versus-time profile; not every fog, however, follows the symmetrical pattern described previously. Fogs in the Central Valley of California, for example, are seldom as acidic at the end as they are at the beginning. They usually last for longer periods of time (the longest, known as Tule fogs, can persist for up to 20 days) but undergo a gen-

*Caltech's rotating arm collector is shown in the diagram below at top left; half of the arm is enlarged below it, and at top right is a cross section through the arm of the slot in which the fogwater droplets are collected.*



A fog system developed over time presents a concave profile — high concentrations at the beginning, going down as the liquid water in fog dilutes them, and rising again as evaporation occurs. Lennox is near the Los Angeles International Airport and was one of the first sites studied.



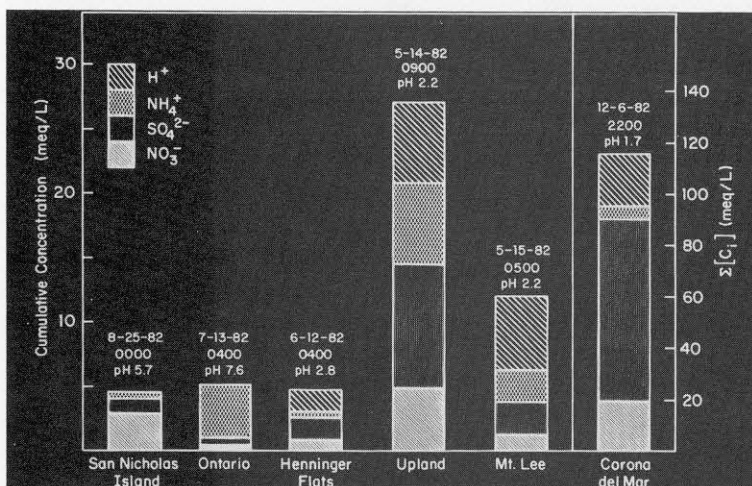
Observations of the major constituents of fog at several sites are compared with the most extreme acidity measured in southern California — in Corona del Mar (note the different scale). The pH of 1.7 is 1,000 times the acidity of typical local acid rain.

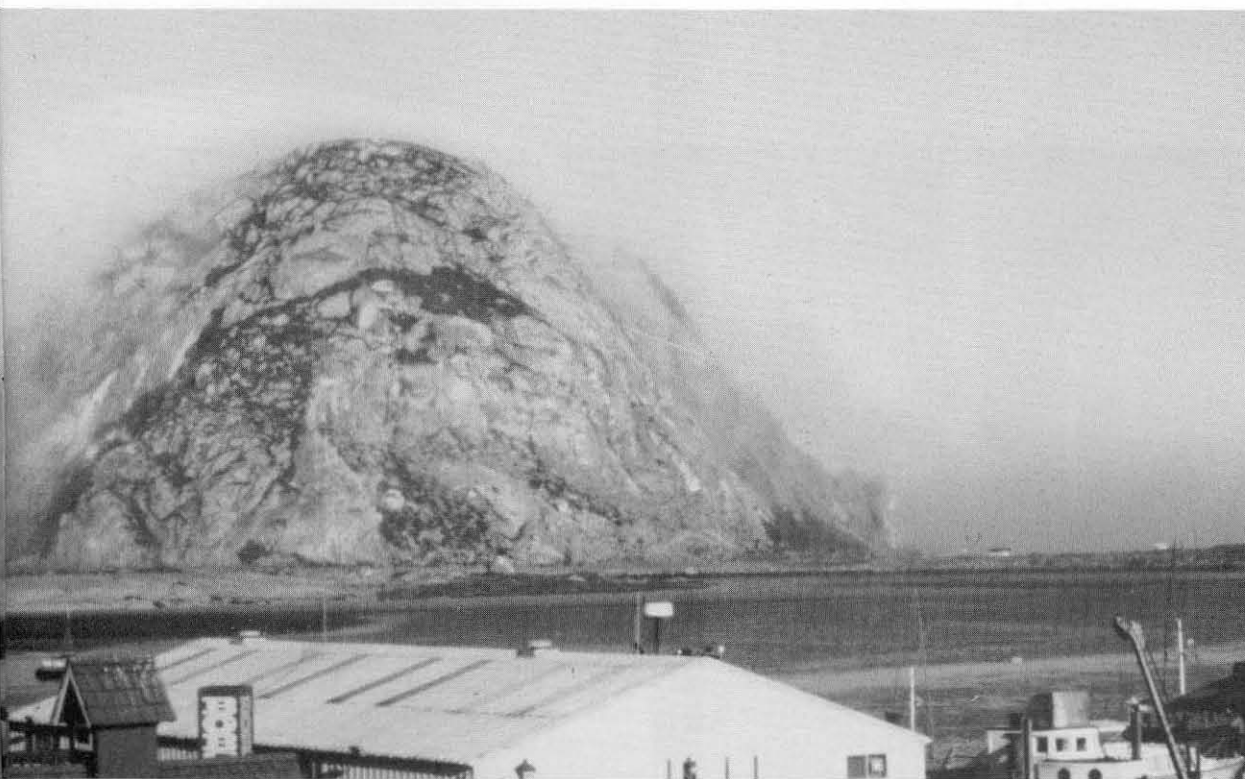
eral decline in acidic concentration. The reason for this is that a certain portion of the fogwater droplets reach the earth by deposition. Oil recovery operations in Kern County release sulfur dioxide and nitrogen oxides that are converted to sulfate and nitrate. In addition to these ions, ammonia and hydrogen ion dominate the chemical composition of haze aerosol in the valley. When temperature inversions are associated with relatively high humidity, the valley turns into a continuous-flow, stirred-tank reactor that acidifies the fog formed under these conditions. However, the valley fog, which ranges from 30 to 70 microns in droplet diameter, slowly settles out of the atmosphere over time by conventional



sedimentation. This results in an overall removal of acidity from the atmosphere during the course of a fog event in the Central Valley.

The measurements of fog we've taken in southern California show a pH in the domain of roughly 3 to less than 2. Since acidity is a function of time in any fog event, the pH values used to compare a number of locations must have been obtained at approximately the same point in time during the course of a fog. The most extreme event observed in southern California was a relatively light, evaporating fog at Corona del Mar, during which the pH reached a low of 1.7 — an acidity equivalent to that of some common toilet bowl cleaners. This fog was about 1,000 times more acidic than the typical acid rain in southern California and about 10,000 times more acidic than relatively pure rainfall. Its nitrate concentrations were quite high; they were found to be roughly three times the sulfate. This ratio seems to hold for the Los Angeles area as a whole. Mt. Lee (known for the Hollywood sign), though not as highly concentrated as Corona del Mar, was also quite acidic: pH 2.2. Upland had relatively low pH values and slightly higher concentrations, resulting in an acidity approximately 100 times higher than typical acid rain. And at Henninger Flats in the San Gabriel Mountains, the cloudwater main-





*Fog forms as a density-stratified flow over Morro Rock. Morro Bay was found to have relatively clean fog.*

tained an average pH of approximately 2.8 over three years.

Acid fog is not the only kind of fog we've measured. In Ontario, California, we observed a basic fog of pH 7.6 downwind from a cattle feedlot, where the hydrolysis of urea to yield ammonia and carbon dioxide helps to neutralize potential acidity. But such basic fogs--and their requisite conditions--are anomalies in southern California. One midnight on San Nicolas Island, 60 miles due west of Los Angeles, we found a relatively clean fog of pH 5.7; by the end of the night, the pH had dropped to 3. An analysis of the wind trajectories indicated that on that day the air mass was coming straight down the Santa Barbara Channel over the offshore oil operations. As a result, the fog that night had a very different chemical signature from fogs observed in either the Los Angeles basin or the San Joaquin Valley (that is, sulfate dominated nitrate by a ratio of two to one).

Relatively clean fogs have also been observed. Despite the tendency to think of the northeast as being relatively dirty, that region's fog was found to be comparatively clean at ground level. In fact, one of the cleanest sites we have studied was in Albany, New York, where the acid concentrations were a mere fraction of what they are in the Los Angeles area. Morro Bay had relatively clean fog, while in northern California, Point

Reyes showed the influence of the San Francisco air mass: its fog was routinely acidic, but did not contain levels and concentrations of acidity as high as in fog farther south.

Through the phenomenon of occult precipitation, acid fog may take its toll on southern California's environment in unsuspected ways. The extensive damage suffered by trees on the San Gabriel and San Bernardino mountain slopes may be a partial consequence of the intercepted cloudwater in a pH range of 2 to 3. It's hard to say that this damage is directly due to acid deposition; on the other hand, it's hard to believe that an entire tree bathed in water of about pH 2.5 will fare well. Recent research at UC Riverside has documented the damaging effects of water at this pH on a variety of plant surfaces.

Although we have made significant advances in our understanding of aqueous-phase atmospheric chemistry over the last three years, much research lies ahead. The complexity of the acidic deposition problem is enormous, and no easy solution is readily apparent. In a few more years we hope to have greater insight into the chemistry and physics of cloud acidification. At that point there may be a more fundamental basis for implementing specific pollution control strategies to reduce the inherent problem of acidic deposition and, in particular, acid fog. □