To Catch a Cloud

State University of New York at Albany

The silo-like building on the summit of Whiteface Mountain in the Adirondacks houses a variety of experiments and monitoring equipment for studying clouds.

By IVARS PETERSON

WHITEFACE MOUNTAIN, N.Y. — On a clear day, an observer on top of Whiteface Mountain can see down into Lake Placid or as far as Montreal's distant towers more than 70 miles away. For scientists who work at the silo-like field station perched on this Adirondack peak, however, the attraction is the view when the mountain is shrouded in clouds. Their interest is focused on the intricate chemical interactions within the water droplets that make up a cloud and in the air carrying the cloud. They poke their probes and collection gear into the surrounding mists to monitor minute quantities of contaminants and to study the origins of acid rain.

Acid rain formation seems simple. A variety of sources, both natural (including volcanoes, forest fires and sea spray) and man-made (such as fossil fuel combustion and industrial processes), emit sulfur and nitrogen oxides. These substances react in the atmosphere to form fine sulfate and nitrate particles, which in solution become sulfuric and nitric acid. During this process, the pollutants may travel hundreds of miles over several days, falling out of the sky as dry particles or in rain, snow, hail or sleet. Acid clouds that envelop mountaintops and acid fogs that seep through city streets also deposit potentially harmful chemicals. At Whiteface Mountain, researchers have found that clouds can be 10 times more acidic than the rain reaching the ground, and they wonder about the effects of such clouds on mountainside vegetation.

The effects of acid rain are not well understood. In North America, damage to aquatic life and changes in water and soil chemistry are becoming increasingly evident in sensitive regions such as the Adirondacks. Recent speculations link forest damage and decreased crop yields to acid rain (SN: 6/5/82, p. 373). Volker A. Mohnen, director of the Atmospheric Sciences Research Center of the State University of New York at Albany, which runs the Whiteface Mountain facility, says sensitive ecosystems are showing unmistakable signs of stress because their ability to tolerate the continuous influx of sulfur and nitrogen compounds appears to be decreasing.

Combatting the effects of acid rain requires the control of emissions from sources that burn fossil fuels. Mohnen says the key challenge facing atmospheric scientists is establishing the links between various sources and deposition in particular areas. Only then can scientists develop an effective way of reducing acid rain deposition in sensitive areas. Finding these source-receptor relationships requires considerable knowledge of the transport and transformation of sulfur and nitrogen oxides and other pollutants.

Yet, as research continues, scientists

An important part of acid rain formation seems to involve the chemical processing factory inside a microscopic cloud droplet

are becoming increasingly aware of the complexity of the atmospheric and chemical processes involved. The pollutants are all part of a highly interactive, coupled system, in which the concentration of one pollutant may depend on the concentration of others present in the same air mass. At the same time, researchers are learning that chemical reactions within clouds and inside cloud droplets, rather than just in the air in bright sunlight, may contribute significantly to acid rain formation.

Pever V. Hobbs of the University of Washington in Seattle recently looked at sulfate production in natural clouds. He and his colleagues made airborne measurements of how much sulfate was in the air flowing into one end of a cloud and the sulfate concentration in the air coming out of the cloud. Their results, soon to be published, show that in the five or ten minutes that air takes to pass through the type of cloud they studied, the amount of sulfate doubles.

"For the first time, we have an actual measure of the rate of production of sulfate in the atmosphere through cloud reactions," Hobbs says. "We find that the rate is extremely high."

But clouds evaporate, leaving particles behind. These particles may themselves fall to the ground or become the nuclei for new cloud droplets further downwind. Jeremy Hales of Battelle Northwest Laboratories in Richland, Wash., says there are "two extremely pressing and large unknowns." One is the efficiency of cloud droplets in scavenging particles and gases like sulfur dioxide from the atmosphere. The other is the chemistry that goes on inside a cloud droplet once the material gets in.

Catching tiny cloud droplets, either from aircraft or at ground level, isn't easy; about a million droplets make up a single raindrop. Analysis is difficult, too. Contaminants that may play important roles in cloud chemical reactions are often present in concentrations of less than one part per billion.

Several pioneering efforts in detecting and analyzing cloudwater have begun at Whiteface Mountain in recent years. Sophisticated "catch buckets" have replaced the fine filaments and spiderwebs used in earlier days to capture cloud droplets. At Whiteface, the acidity of clouds is now monitored continuously, and samples of collected cloudwater are analyzed regularly. These field measurements play an important role in deciding which ones of many possible droplet chemical reactions are dominant under different conditions.

One chemist who studies potential reaction mechanisms is William L. Chameides at the Georgia Institute of Technology in Atlanta. Recently, he and Douglas D. Davis suggested that free radicals, reactive molecules with unpaired electrons, may be produced within clouds. Chameides says, "What we have proposed ... is that free radicals, which we know are important in the gas phase, also play a very important role ... in the aqueous phase of cloud drops."

Chameides and Davis report in the June 20 JOURNAL OF GEOPHYSICAL RESEARCH, "The mechanism involves the scavenging by and incorporation into cloud droplets of OH and HO_2 radicals from the gas phase during daylight hours; once dissolved in cloudwater these species can undergo rapid aqueous phase chemical reactions leading to the generation of H_2O_2 [hydrogen peroxide]."

The presence of hydrogen peroxide is important because it (along with ozone, O_3) provides the oxygen needed to transform sulfur and nitrogen oxides into sulfates and nitrates. "We've identified a new pathway for forming acidity," says Chameides. The proposed mechanism is somewhat speculative, he admits. "No one has measured the 'sticking coefficient' for free radicals like OH on a droplet of water." The molecule, he explains, could just bounce off instead of staying.

Another key measurement needed is hydrogen peroxide concentration. Hales says, "Our field measurements of hydrogen peroxide both in the rainwater and in the air around cloud systems are totally unreliable, and we have just begun getting an inkling in the last few years that they're as unreliable as they are."

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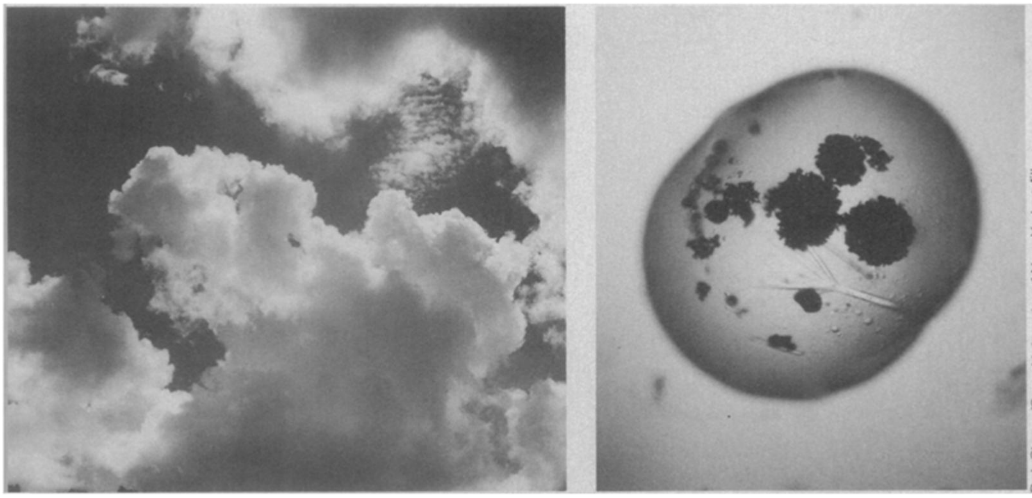
During a rainstorm at Whiteface Mountain, Tom Kelly of the Brookhaven National Laboratory takes readings from a highly sensitive detector for gaseous sulfur and nitrogen compounds.

Despite these questions, Mohnen and other researchers are excited about the proposed mechanism. Next year, Mohnen says, methods of studying photochemistry in clouds will be added to the instrumentation at Whiteface Mountain. Chameides says, "We're just beginning to scratch the surface in aqueous phase chemistry in the atmosphere. These free radicals could imply a broad spectrum of chemical processes that could go on and that could lead to generation of other species that we haven't thought about before."

Other research adds to the complications. Michael W. Holdren of Battelle's Columbus, Ohio, Laboratories found that organic nitrogen compounds such as peroxyacetyl nitrate (PAN) are prominent in the atmosphere, soluble in rainwater and may affect rainfall acidity. These compounds are among the photochemical



R. J. Cheng/State University of New York at Albany

Flyash trapped in cloud droplets may enhance acid rain production, says Roger J. Cheng of the State University of New York at Albany. He has demonstrated in the laboratory that flyash from electric power plants catalyzes the reaction of sulfur dioxide in water droplets to form sulfates. When flyash particles are injected into water drops (2 to 3 millimeters in diameter) exposed to sulfur dioxide, needle-like sulfate crystals appear (right). Cheng says this reaction is also probably implicated in marble deterioration and leaf damage.

products that make up smog. Holdren says, "Our field studies show that PAN is present in the atmosphere in concentrations that rival the concentrations of nitric acid and particulate nitrate." PAN decomposes in water to form nitrate, a component of acid rain.

Scientists have also been measuring the composition of precipitation in remote areas of the world to try to estimate acidity before fossil-fuel combustion, to establish a natural background level. John M. Miller of the National Oceanic and Atmospheric Administration says the results show that rain is more acid than expected in these areas, and the causes and compositions depend on the location. In tropical, high-rainfall areas, organic acids such as acetic and formic acid make up a large portion of the acidity. On Amsterdam Island in the Indian Ocean, sulfates and sulfuric acid are the main contributors.

In a recent report on the first year of measurements, the authors state, "We believe there is no single natural pH [acidity] of precipitation applicable to the whole globe but rather several natural values, each unique to a region the size of a continent or an ocean." They speculate that if contributions from human activities were removed, the natural mean pH is probably greater than or equal to 5. This figure is less than the 5.6 pH expected if only carbon dioxide were dissolved in water, but much less acid than the rains that fall on the Adirondacks and elsewhere.

It's not just rain and snow that deposit sulfuric and nitric acid in sensitive ecosystems, although "wet" deposition may be the dominant one in areas far from pollution sources. The earth's surface is continually exposed to dry "fallout" of sulfur dioxide and nitrogen oxides, which are converted to sulfates and nitrates after deposition. Fine sulfate particles may also settle to the ground adding to the overall burden.

The amount of dry deposition may be as large as or greater than the amount of acid delivered by precipitation, although estimates of its magnitude are uncertain. Perry J. Samson of the University of Michigan at Ann Arbor, who works with mathematical models that try to reproduce what occurs in the atmosphere, says, "We need more information about dry deposition. It becomes very important when we're dealing with how we change sulfur dioxide emissions in order to change acidification."

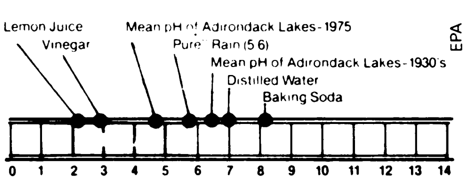
Moreover, precipitation acidity is affected by neutralizing agents in the air such as windblown alkaline dust or ammonia. One thing researchers can't do, Hobbs says, is collect cloud water without taking in dry particles that bombard and contaminate the drops during collection. What's needed is a device that collects dry particles and droplets separately, so that chemical analyses can be performed on both components for comparison. Hobbs says, "There's a lot of technology to be developed, as well as scientific ideas."

Chameides says, "The long-term need in this field is a very ambitious field measurement program." Most valuable would be programs in which all parameters are determined simultaneously under a variety of meteorological conditions, or sequential measurements in which a storm is followed across the continent. These are the kinds of data needed to improve and validate the models that have been constructed to link emission of pollutants and acid deposition.

Results of various models are beginning to be used to aid in drafting legislation. A year ago, a National Academy of Sciences study recommended a 50 percent decrease in acid deposition in sensitive areas. The current controversy, involving scientists and legislators, concerns whether a 50 percent reduction in sulfur dioxide emissions at midwestern coal-fired power plants will achieve this objective. Reductions in emissions would certainly help, most scientists agree, but by how much is uncertain. Many atmospheric scientists argue that too little is known yet about the transport and transformation of pollutants over long distances and that the models used are too simple to reflect the complex chemical processes taking place in the air and in clouds.

Chameides says, "I think it is clear that there are not going to be any simple answers. We have to analyze a very complex system before we can come up with a way to lick the acid rain problem." Samson, after examining the assumptions built into current regional deposition models, suggests that concurrent changes in both reactive hydrocarbon and nitrogen oxide concentrations must be considered when control strategies for reducing sulfate deposition are designed.

Whiteface Mountain is one place where researchers are beginning to untangle some of the complexities of acid rain formation. Some researchers are measuring the size of airborne particles and the sulfate-scavenging efficiency of clouds. Scientists from the Brookhaven National Laboratory on Long Island are testing sensitive instruments designed for airplanes to measure low concentrations of gas-phase sulfur dioxide, nitrogen oxides and ammonia. David Miller of the Desert Research Institute in Reno, Nev., collects cloudwater for chemical analysis. The results from his measurements will be compared to laboratory simulations of acid rain formation. These and other research projects complement one another, and the interactions among the scientists produce useful insights. Mohnen says, "For the first time, we've been able to bring the right group of equipment and personnel together, and all the marbles are beginning to fall into place." □



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The pH Scale

The pH scale measures hydrogen ion concentration. Acidic solutions have a pH less than 7, alkaline more than 7. Each unit decrease in pH represents an increase in acidity by a factor of 10. Thus, rain with a pH of 3 is 100 times more acidic than rain with a pH of 5.