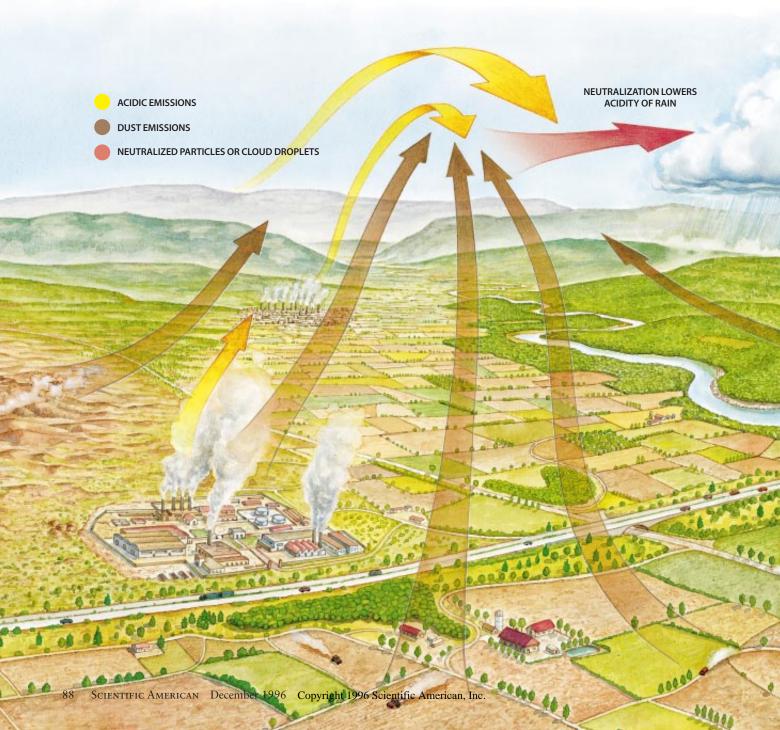
# Atmospheric Dust and Acid Rain

Emissions of acidic air pollutants have fallen dramatically. Why is acid rain still a problem? Atmospheric dust may be part of the answer

by Lars O. Hedin and Gene E. Likens

or the past several decades, scientists have been studying acid rain and how it affects the environment. As the harmful consequences of acidic air pollutants became increasingly clear, governments in North America and Europe began to regulate emissions of these compounds. Countries in the European Union enacted a variety of laws to control the release of sulfur dioxide and nitrogen oxides; the Clean Air Act imposed similar regulations in the U.S. Policymakers expected these reductions to rejuvenate forests, lakes and streams in many regions. In some respects, the issue seemed wrapped up.



But the problem of acid rain has not gone away. Why is the rain falling on parts of Europe and North America still acidic, despite tighter controls on pollution? And why do some natural ecosystems—in particular, forests—show levels of damage from acid rain greater than scientists originally predicted?

Recent findings suggest that acid rain is a much more complex phenomenon than previously thought. Results from several studies point to the unexpected but critical role of chemicals in the atmosphere known as bases, which can counteract the effects of acid rain by neutralizing acidic pollutants. We have

found that all the attention given to acidic compounds in the atmosphere has obscured the fact that emissions of bases have also decreased. A number of factors seem to be diminishing the level of these atmospheric bases and in the process aggravating the ecological effects of acid rain. Ironically, among these factors are some of the very steps that governments have taken to improve air quality.

Acids and bases are measured by what is known as the pH scale: solutions with a pH of less than 7 are acidic; those with a pH greater than 7 are basic; those with a pH of 7 are neutral. Common acids around the home include vinegar, orange

juice and beer; ammonia, baking soda and antacid tablets are all bases. Most of the bases in the atmosphere can be found in airborne particles referred to as atmospheric dust. These dust particles are rich in minerals such as calcium carbonate and magnesium carbonate, which act as bases when they dissolve in water.

Atmospheric dust particles originate from a combination of sources. Fossil-fuel combustion and industrial activities, such as cement manufacturing, mining operations and metal processing, generate particles that contain bases. Construction sites, farms and traffic on unpaved roads also contribute. Sources such as forest fires and erosion caused by wind blowing over arid soils with little vegetation are considered natural yet can still be linked to human activity.

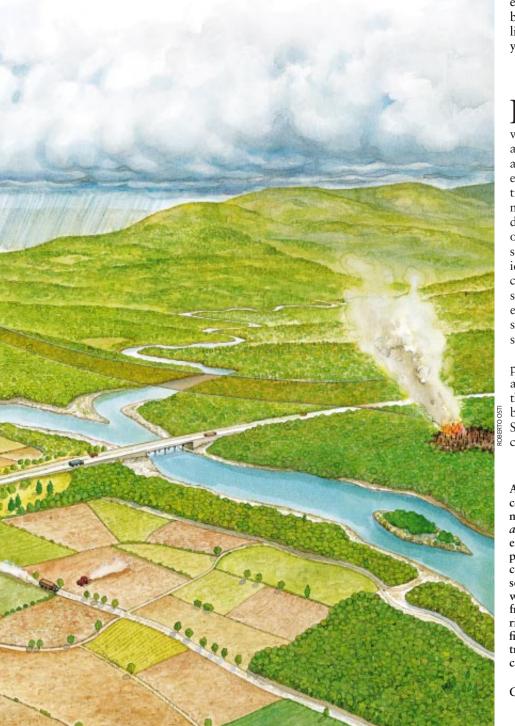
# A Natural Antacid

In the air, dust particles can neutralize Lacid rain in a manner similar to the way antacids counteract excess acid in an upset stomach. In a sense, when an acid and a base combine, they cancel each other out, producing a more neutral substance. Neutralization in the atmosphere takes place as dust particles dissolve into acidic cloud-water droplets or combine directly with acidic gases such as sulfur dioxide or nitrogen oxides. These reactions also generate socalled base cations-a term used to describe the positively charged atoms of elements such as calcium and magnesium that arise when mineral bases dissolve in water.

In addition to lowering the acidity of precipitation, atmospheric base cations also neutralize acid rain once they reach the ground—although the chemistry is a bit different than in the atmosphere. Small particles of clay and humus (decayed organic matter) in soil bear nega-

ATMOSPHERIC DUST (brown arrows) contains chemicals known as bases, which neutralize the acidic air pollutants (yellow arrows) that cause acid rain. Industrial emissions, agricultural processes, such as plowing, and traffic on unpaved roads contribute to atmospheric dust. Natural sources include forest fires and erosion by wind. Acidic pollutants derive primarily from the burning of fossil fuels in factories, cars and homes. An additional benefit of dust particles is that they deliver nutrients to forests; unfortunately, dust can cause health and environmental problems.

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tive charges and thus attract positively charged cations, such as calcium and magnesium; as a result, soils contain a natural store of base cations attached to these particles. As acidic rainwater drains into the ground, the base cations give up their places to the positively charged hydrogen ions found in acids, which bind more tightly to the soil particles. Because these particles sequester hydrogen ions, the acidity of the water that flows through the soil stays low. In some soils the process becomes more complex: acid rain triggers the dissolution of toxic aluminum ions that also displace the base cations.

As long as the soil has an abundant supply of base cations, this buffering system, known as cation exchange, protects forests from the harmful effects of acid rain. But the natural reserves of base cations can become depleted if soils that are naturally poor in bases are exposed to acid rain over decades, as has been the case in regions of Europe and North America. In these areas, hydrogen ions and aluminum ions have displaced a large part of the available base cations in soils, allowing levels of aluminum to rise and leaving the soil highly acidic. Furthermore, such acidified soils can no longer protect downstream ecosystems from acid rain: waters that drain these forests carry both acids and aluminum into streams, lakes and rivers.

Dust particles may serve one other important role. Elements such as calcium and magnesium, as well as sodium and potassium—all of which can be found in mineral dust—are essential nutrients for most plants. Acid rain not only dislodges these elements from clay and humus particles, from which plants get most of their nutrients, it also washes them into rivers and streams, depleting the ecosystem of its store of minerals.

With the exception of early work in the 1950s by Hans Egnér of Uppsala Agricultural University in Sweden and Eville Gorham of the Freshwater Biological Association laboratory in England, scientists have not paid much attention to the idea that the atmosphere can be a major source of base cations found in soils. Scientists have traditionally thought that the slow dissolution of minerals and rocks in deeper parts of the soil replenished base cations, in a natural process called chemical weathering.

But recent findings, including our own studies, are now revising the general view of how bases enter soils and how forests depend on atmospheric inputs of minerals and nutrients. In some forests the atmosphere actually appears to be the main source of base cations. These new results suggest that many forests are more sensitive to changes in atmospheric chemistry than scientists once believed.

# Less Dust, More Damage

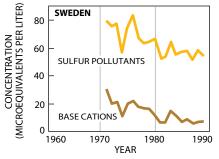
7 fforts to reduce emissions of acidic air pollutants offered encouraging results at first: levels of atmospheric sulfur, for instance, have dropped dramatically over the past three decades in much of Europe and eastern North America. The two of us became concerned, however, that policymakers and scientists alike might be neglecting the role of atmospheric bases in their attempts to evaluate whether these reductions in sulfur compounds have benefited the environment. Considering the significance of basic chemicals to both forest growth and the prevention of acid rain, we decided to investigate whether levels of atmospheric dust have also changed over time in response to lower emissions imposed by new regulations.

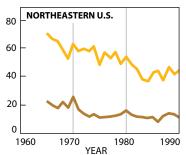
Regulations to limit emissions of dust

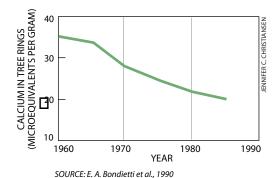
were enacted because, as scientists have known for some time, microscopic particles suspended in the air can cause a range of health problems when inhaled; they also degrade visibility and contribute to a host of other environmental problems. Governments in North America and Europe have for over 20 years designated acceptable air-quality standards for particulate matter; these regulations were quite distinct from those focusing on acidic pollution. (Atmospheric dust from other sources appears to have dropped off as well: Gary J. Stensland and Donald F. Gatz of the Illinois State Water Survey have found that emissions of particles containing bases have fallen in response to less traffic on unpaved roads.)

Working together with European scientists, we began by evaluating the longest records of precipitation chemistry that can be found in eastern North America and western Europe. By measuring base cations dissolved in snow and rainwater, we can keep track of the levels of mineral bases in the atmosphere and monitor the input of these base cations into forest ecosystems. Our findings were startling: we discovered that atmospheric bases have declined at unexpectedly steep rates during the past 10 to 30 years. The longest existing North American record, collected at the Hubbard Brook Experimental Forest in New Hampshire, showed a 49 percent drop in atmospheric base cations since 1965.

On the other side of the Atlantic we found that the longest-running high-quality European record, from the forested area of Sjöängen in southern Sweden, showed a 74 percent decrease in base cations since 1971. Our analyses of several other records confirmed with few exceptions that atmospheric bases have declined precipitously across extend-







Note: microequivalents are used to measure quantities of acids and bases.

PARALLEL DECREASES in acidic sulfur pollutants and the base cations that neutralize them cancel out much of the expected benefit from reducing acidic pollutants. The authors' studies in Sweden and the U.S. provide evidence for these trends. In ad-

dition, other studies have shown that levels of the base cation calcium have decreased in the trees of a New Hampshire forest over the past several decades; such decreases in essential nutrients further weaken forests.

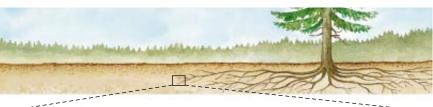
ed areas of Europe and North America.

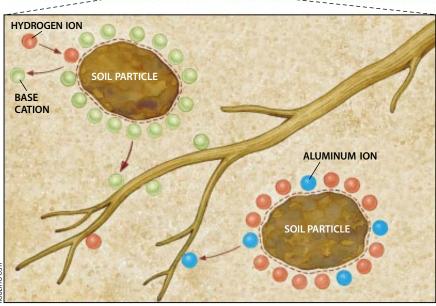
But have these cuts in atmospheric bases been strong enough to counteract—or even nullify—the expected environmental benefits of reductions in acidic emissions? Our research indicates that this indeed has been the case. We found that the decline in bases has often mirrored the downturn in atmospheric sulfur, at rates sharp enough to offset a large part of the drop in sulfur compounds. For example, we found that the decrease in base cations canceled out between 54 and 68 percent of the reductions in atmospheric sulfur in Sweden and up to 100 percent at some locations in eastern North America [see illustration on opposite page]. These trends mean that declines in bases have kept the atmosphere sensitive to acidic compounds despite reduced emissions of these chemicals. When we began this work, we certainly did not anticipate that reductions in one form of pollutants—dust particles—would be found to decrease the success of reductions of another pollutant, sulfur dioxide.

The numerous sources of dust particles and the often sketchy information on emissions of particulates make it difficult to determine why these sharp reductions in atmospheric bases have occurred. We do know that new and cleaner industrial techniques, developed in accordance with regulations on the release of particulate matter, have been an important factor. For example, improved combustion efficiency and the practice of scrubbing particles from smokestacks have curtailed particulate pollution associated with the burning of fossil fuels. Evaluating the contribution of more diffuse sources of dusttraffic, agricultural methods and wind erosion, for instance—has been more difficult. But our studies suggest that the decline in dust particles mainly reflects changes in human behavior as opposed to natural variations.

#### A Major Source of Nutrients

Scientists have watched for years as calcium, magnesium and potassium levels have dropped in forest soils around the world. For example, Leif Hallbäcken and Carl Olof Tamm, both at Uppsala Agricultural University in Sweden, have documented losses of 56 to 74 percent of the available cations in Norway spruce forests over the past 60 years. Other reports show similarly dramatic losses of base cations in England, Ger-





BASE CATIONS (*green*) in soil provide nutrients for plants, which absorb the chemicals through their roots. Typically, base cations attach themselves to particles of humus or clay (*left*). But when acid rain falls on the soil, hydrogen ions (*red*) from the rain displace the base cations, which are then washed away. Over time, the hydrogen ions, together with aluminum ions (*blue*) released from the soil as a result of acid rain, can build up on particles (*right*). Not only do hydrogen and aluminum displace essential nutrients, but they interfere with the plant's biochemistry; aluminum in particular can be toxic.

many and the U.S. Several recent studies of ailing forests show that the precipitous loss of base cations can be a key factor in the phenomenon of forest decline. Ernst-Detlef Schulze and his colleagues at the University of Bayreuth have argued that depletion of magnesium in soils has played a significant role in the dwindling of spruce forests in the Fichtelgebirge of Germany. Although their evidence is less clear, researchers at Oak Ridge National Laboratory in Tennessee, led by Samuel B. McLaughlin, have found that the slowdown in growth of red spruce trees in the southern Appalachian Mountains correlates with lower availability of calcium in soils. Interestingly, small-scale experiments involving fertilization of some forests with base cations, particularly calcium and magnesium, have ameliorated damage in the sugar maple forests of Quebec, for instance, and in Norway spruce and silver fir forests of Germany and France.

Reports such as these made us wonder whether certain soils are suffering not only because of continued exposure to acid rain but also because they do not receive enough base cations from the atmosphere. Scientists can now pinpoint the origin of base cations and trace their movements through forest ecosystems by looking at the natural isotopes of the element strontium (determined by evaluating the number of neutrons in the nucleus of a strontium atom), which can be used as a tracer for calcium. Strontium atoms that derive from the bedrock and those that come from the atmosphere tend to exist as different mixtures of isotopes. This technique has illustrated that atmospheric dust is in fact a critical source of mineral ions in many forest ecosystems.

Moreover, in certain regions, where soils tend to be damaged by acid rain or naturally low in base cations, most of the calcium appears to come from the atmosphere rather than the bedrock. For instance, we have determined that in unpolluted forests of Chile, the dominant tree species, the southern beech, feeds on calcium that originates almost exclusively in the atmosphere.

These observations suggest that many forests depend quite heavily on the atmosphere for a supply of mineral bases; the drops in atmospheric base cations have therefore led to a slower replenishment of critical bases and nutrients in forest soils. Of course, natural levels of atmospheric dust have always varied, but usually across centuries or millennia. Studies conducted by Paul A. Mayewski and his co-workers at the Univer-

sity of New Hampshire on ice cores from Greenland indicate that the amounts of dust and calcium in the atmosphere have been strongly affected by climate variations over the past 20,000 years. In the coldest and driest global climates, high levels of calcium and dust prevailed, whereas wetter and warmer periods saw low concentrations. Analysis of modern trends, from around 700 A.D. to the present, suggests that current quantities of dust are relatively low compared with conditions during the past 20,000 years. One notable exception was the

Dust Bowl, the extended drought of the mid-1930s in the western U.S.

# **Remaining Questions**

As scientists have discovered the importance of bases in the atmosphere and, more recently, the link between emissions of atmospheric dust and nutrients in the soil, they have begun to paint a new picture of how forests respond to atmospheric pollution. This emerging view suggests that the effects of acid rain are more complex than

expected and that the damage caused by the pollution is more serious than predicted. For instance, the widely quoted conclusion from the 1990 National Acid Precipitation Assessment Program (the most recent evaluation of the problem of acid rain by the U.S. government), that there was no clear evidence linking acid rain to forest damage, no longer seems tenable.

It is entirely feasible that continuing



SANDSTORM in the Sahara Desert can scatter dust particles around the globe. Studies in Amazon forests have turned up dust that originated in the Sahara, more than 3,000 miles away.

acid rain, in combination with limited supplies of base cations, could produce environmental conditions to which many plant species, particularly in sensitive ecosystems, have never been exposed in the course of their evolution. Consequently, predicting how they will respond over the next several decades will be extremely difficult. And effects may not be limited to plants. Jaap Graveland and his colleagues at the University of Groningen, have noted that certain birds, such as the great tits of the Netherlands produce thinner, more fragile eggs in

forests that have been heavily damaged by acid rain and have low stores of calcium in the soil.

What can we do about acid rain and atmospheric dust? Suggestions range from the improbable to the feasible. After the publication of one of our recent papers, a reader wrote proposing that forests might be saved by a hot-air balloon campaign to drop calcium-rich particles from the skies—a costly and

impractical solution. Deliberate increases in the release of particulates are also unrealistic and would set back progress in airpollution control by decades. One reasonable suggestion, however, is to reduce emissions of acidic pollutants to levels that can be buffered by natural quantities of basic compounds in the atmosphere; such a goal would mean continued reductions in sulfur dioxide and nitrogen oxides, perhaps even greater than those prescribed in the 1990 Amendments to the Clean Air Act in the U.S.

The ecological dilemma of atmospheric dust will very likely be with us for some time: base cations take years to build up in soils, and it may take decades or more for forests to recover their depleted pools of nutrients, even if levels of acidic air pollution continue to fall. In the meantime, researchers and governments must develop careful strategies not only for monitoring the current health of forests but also for predicting their stability in the next century and beyond. Simple solutions do not always work in complex ecosystems.

# The Authors

LARS O. HEDIN and GENE E. LIKENS have worked together for more than a decade, examining how acid rain affects forest and aquatic ecosystems. Hedin is an assistant professor in terrestrial biogeochemistry in the section of ecology and systematics at Cornell University. In addition to his research on base cations, Hedin studies nutrient cycles in unpolluted temperate and tropical forests. Likens is director of the Institute of Ecosystem Studies in Millbrook, N.Y. He has published extensively on the topic of acid rain and on how human activities impact the environment.

# Further Reading

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