Acid Rain on Acid Soil: A New Perspective

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Summary. Acid rain is widely believed to be responsible for acidifying soil and water in areas of North America and northern Europe. However, factors commonly considered to make landscapes susceptible to acidification by acid rain are the same factors long known to strongly acidify soils through the natural processes of soil formation. Recovery from extreme and widespread careless land use has also occurred in regions undergoing acidification. There is evidence that acidification by acid rain is superimposed on long-term acidification induced by changes in land use and consequent vegetative succession. Thus, the interactions of acid rain, acid soil, and vegetation need to be carefully examined on a watershed basis in assessing benefits expected from proposed reductions in emissions of oxides of sulfur and nitrogen.

Acid rain is widely considered one of our most serious environmental problems. In landscapes where hydrology and geochemistry do not allow complete neutralization of acid runoff, acid rain is thought to be acidifying lakes and streams, as well as mobilizing aluminum and other metals toxic to fish and plants. Nutrients are also thought to be depleted by acid rain, raising concern about large areas of productive forests located on soils that are strongly acid and low in nutrients. A gradual acidification and sterilization of our soil and water, particularly in parts of the Adirondacks, northern New England, southeastern Canada, and southern Scandinavia, is predicted.

From its inception, however, soil formation in humid temperature climates is an acidifying process, mediated by the classic factors of geology, climate, biology, topography, and time. Indeed, the factors thought to make landscapes sensitive to acid rain are those that develop some of the most acid soils in the world. The results of natural soil formation are those attributed to acid rain: leaching of nutrients, release of aluminum, and acidification of soil and water.

Landscapes have usually been assumed to act merely as net sinks for acid rain (*1*), but generation of acidity in soils has recently been recognized as an additional source. This is evident in reports of the Norwegian project on "Acid Precipitation—Effects on Forests and Fish" (the SNSF project), for example (*2–4*). However, acid rain is still considered principally responsible for regional acidification (*2–4*), because the increased flux of SO_4^{2-} in rain is thought to result in equivalent leaching of hydrogen ions and other cations. We believe that this assessment needs reexamination. Large amounts of humic acids are present in forested landscapes thought to be particularly sensitive to acid rain. The solubility of these humic acids is controlled by *p*H, and hence they effectively regulate both acidity and anion flux.

In this article we define acidity in relation to rain and soil, describe how soil formation can acidify soil and water as well as leach nutrients and aluminum, show how humic acids buffer soils, and finally discuss the impact of changing land use and consequent vegetational succession. We wish to show that natural soil formation is often more important than acid rain in determining the acidity of lakes and streams.

Acidity of Rain and Soil

Rain in equilibrium with carbon dioxide in the air has a *p*H of about 5.6. Rain at *p*H 4.6 is often said to be ten times more acidic, but this neglects the acidity of undissociated carbonic acid (H_2CO_3) normally present in rain. The strong acid necessary to reduce the *p*H of rain from 5.6 to 4.6 actually represents a twofold rather than a tenfold increase in total acidity (*5*).

The acidity of rain has also been expressed in terms of the amount of limestone, $CaCO_3$, that can be neutralized or leached from the soil (*6*), but the amounts that can be dissolved by rain at *p*H 5.6 are often ignored. An annual rainfall of 1 meter per hectare at *p*H 5.6 can dissolve 400 to 500 kilograms of $CaCO_3$ per hectare, depending on the values of the thermodynamic constants used (*5*). Rain at *p*H 4.6 can dissolve an additional 10 to 12 kg/ha, and rain strongly acidified to *p*H 4 can dissolve an additional 50 kg/ha or about 1 kiloequivalent per hectare. For comparison, managed agricultural soils in the northeastern United States may require limestone additions of 50 to 100 keq/ha per annum.

Measurements of acid in soil are somewhat analogous to measurements of acid in rain. With clay minerals and organic macromolecules acting as immobile anion phases, soils resemble weak acids, making a thermodynamic interpretation of soil *p*H uncertain. However, certain principles apply: increasing concentrations of neutral salt decrease the measured *p*H, whereas increasing dilution with water increases *p*H. This salt effect is significant in measuring acidification of runoff.

The exchange acidity of soil is the analog of the total acidity of rain and is defined in terms of hydrogen ions readily exchanged by neutral salts. Acid humus typically has an exchange acidity of about 1 eq/kg, which is about 10,000 times greater than its acidity expressed as *p*H. In mineral soils, much exchange acidity is produced by hydrolysis of ionic aluminum. Hence, at *p*H values that are typical of strongly acid soils, ion exchange sites on minerals are occupied primarily by ionic aluminum and some additional aluminum is complexed by organic matter, giving a total exchange acidity on the order of 1000 keq/ha.

Soil Formation

The more mature a soil is the more it differs from its parent material, although the degree of difference is strongly influenced by geology. In humid temperate climates soils are more acid than their parent materials; water percolating through freshly ground granite is alkaline (*p*H 8 to 9), but soils developed from granite are acid. There is sufficient acidification that mature soils developed even on limestone or marble can be acid (*7*).

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Although chemical oxidation of reduced elements in parent materials produces acidity, it cannot account for the extremely acid podzols and related peats found on granite-like rocks. Acidification of these soils is biological (*8*); hence, the soils are most acid at the surface, where most decomposition and leaching occurs.

The major sources and sinks of soil acidity are illustrated in Fig. 1. Initially, weathering of freshly exposed siliceous bedrock is rapid and bases such as calcium, magnesium, potassium, and sodium are leached (pathway 3d in Fig. 1). Acid is generated by the biological oxidation of carbon, nitrogen, and sulfur, much as acid rain is created by the burning of fossil fuels. Because the partial pressure of CO_2 in soils can be 100 times that in the air, potential weathering rates by H_2CO_3 are immense, although seldom achieved in nature. Reaction and removal of hydrogen ions favor continued dissociation to H^+ and HCO_3^- (pathway 2c). With time, rates of acid neutralization, weathering, and cation denudation decrease and acids accumulate. Little H_2CO_3 is consumed by mineral weathering; most of it is lost as CO_2 and H_2O (pathway 2c). This is reflected by the low bicarbonate alkalinity of runoff from watersheds with strongly acid soils.

A layer of humus eventually forms which often lies over bleached mineral soil. Earthworms and other organisms that mix litter with mineral soil are now absent, and microbial populations have changed. Production of simple organic acids is slight, but production of partially oxidized humic acids of high molecular weight is favored (*9*). These humic acids more strongly acidify their environment than the final oxidation products of CO_2 and H_2O. The increased acidity decreases the solubility of humic acids (*10*), and enhances their accumulation. The rate of mineral weathering is now exceedingly low, most organic acids are lost as CO_2 and H_2O, and the upper mineral soil is a highly weathered siliceous residue resistant to acid weathering. This process is known as podzolization, and soils with distinctive bleached horizons are known as podzols.

It is often thought that acid humus accumulates because organic matter decomposes slowly. This is clearly true where thick peat develops under sparse vegetation. It is not true for the productive forests on podzolized acid soils in the Northeast, southeastern Canada, and Scandinavia (*11*), where concern about acid rain is greatest.

Formation of mature podzol soils from freshly exposed materials is measured in thousands of years, because the capacity of the parent material to neutralize acid is great relative to rates of weathering. For example, the potential for neutralization of acids by the parent material at Hubbard Brook in New Hampshire is nearly 21,000 times greater than the yearly inputs of acid rain and 11,000 times greater than the estimated rate of mineral weathering (pathways 3a to 3d in Fig. 1) (*12*). In addition, the aluminum oxides in the parent material neutralize acid in water (pathway 3c) when the *p*H is below 5 and serve as an enormous sink against acidification (*13*).

Although some preferential flow occurs in soils, so that not all ion exchange sites can react equally with leachate, the time scale of weathering allows distinctive soil horizons to develop parallel to the earth's surface rather than surrounding vertical channels of preferential flow. Given the rate of soil formation, or even the 100 or more years said to be necessary for significant leaching of cations by acid rain (*14*), strong acidification of mineral soil is generally restricted to the upper soil profile. In addition, the earth's surface is not stable: erosion, tree throw, frost heaving, and soil creep constantly expose new and less weathered mineral material. Although the amounts of soil moved are small, the corresponding resistance to acidification is large. Only where weathering can keep pace with disturbance do we see mature, albeit heterogeneous, soil development.

Acidification of Soil and Water

Because cation exchange reactions are rapid, hydrogen ions in acid rain could rapidly acidify soil by depleting exchangeable base nutrients. If increases in H^+ in acid rain (ΔH) leached nutrient cations (ΔM) from soils on a charge-equivalent basis (that is, $\Delta M/\Delta H = 1$), strongly acid soils would be highly susceptible to acidification because of their low nutrient content. However, the ability of hydrogen ions to remove nutrient cations from soils more acid than *p*H 5 is low; that is, $\Delta M/\Delta H \ll 1$ at the mean *p*H of present-day acid rain (*15*). Conversely, base nutrient cations are efficiently retained. Data on acid soils and acid rain in areas of concern around the world show that, on average, the proportion of bases to acid in the rain is usually equal to or greater than that in the strongly acid forest soils on which the rain falls (*15–17*).

Artificial leaching experiments, some

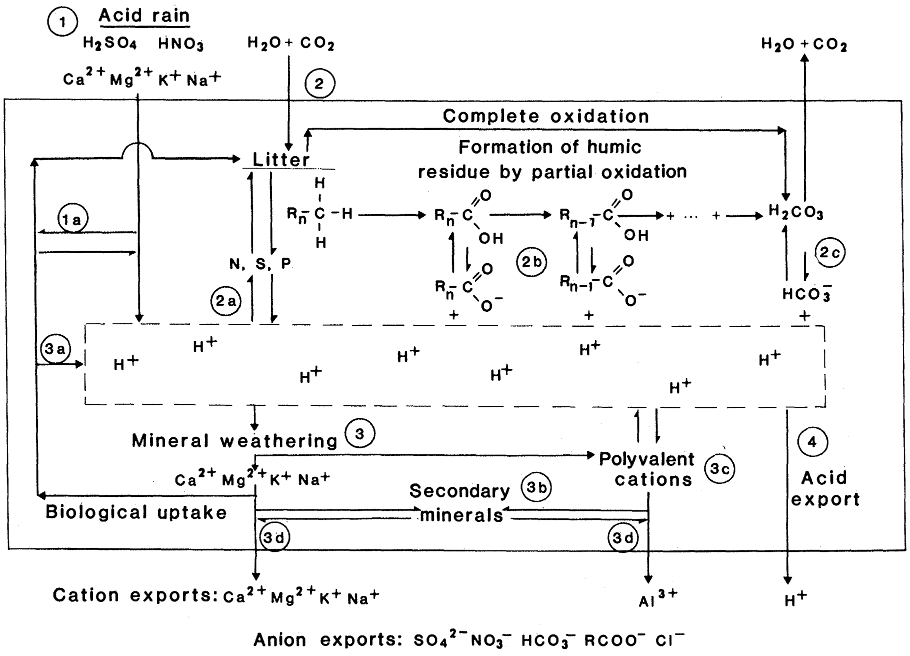

Fig. 1. Major sources and sinks of acidity in soil. Acid rain (1) is a source of acidity, but its composition may be altered before reaching the soil (1a). Although biological processes (2) are net sources of acidity, this obscures the fact that they serve as a substantial sink in acid soils through the production of weak organic acids (2b), which are ultimately converted to CO_2 and H_2O (2c). Mineral acids (2a) can be cycled rather tightly, with some sulfur and nitrogen lost to the atmosphere and some sulfur and phosphorus converted to solid phases. Weathering of minerals (3) generally consumes acid in excess of cation export (3d), as secondary minerals (3b) and hydrolysis products of aluminum, iron, and manganese (3c) accumulate in soil. Aggrading vegetation results in net cation uptake (3a) and can contribute to acidification. Rain which is less acid than the soil solution can also be acidified by hydrolysis (3c). Cation (3d) and acid (4) export is charge-balanced principally by anions shown at the bottom.

of which have lasted up to 5 years, verify that acid rain at *p*H 4 or higher is inefficient in replacing base cations from podzols and related acid soils (*2–4, 18*). As soil *p*H increases above 5, base cations are replaced more efficiently. Thus, the less acid soils with low cation exchange capacity developed on coarse siliceous materials are actually more susceptible to acidification (*15*). Little research has been conducted on the impact of acid rain on such soils (*19*).

Bicarbonate alkalinity is the principal measure of the ability of lakes to resist acidification. In highly siliceous watersheds with acid soils where rates of mineral weathering by H_2CO_3 are low, inputs of HCO_3^- per unit drainage area are also low. Lakes in such watersheds with small ratios of drainage area to lake area could be acidified by acid rain falling directly on them. Little change in *p*H will occur until 80 to 90 percent of the bicarbonate has been neutralized (*20*). One lake in Canada that occupies about 40 percent of an entire watershed has apparently been directly acidified by acid rain (*21*). However, this direct acidification is usually considered a minor factor relative to acid runoff (*2–4, 20, 22*).

Alpine-like lakes and streams in granitic terrain are believed to be especially vulnerable, particularly where there is little mineral soil and permeable geologic material to neutralize runoff from acid rain. Also, the relatively steep and short slopes of these landscapes minimize infiltration and time of contact with neutralizing minerals. The granitic shield and similar areas of eastern North America and northern Europe also have large proportions of extremely acid peats with only small amounts of weatherable minerals (*1, 20, 23–26*). Because these peats often border lakes and streams, they can exert a disproportionately large influence on water chemistry (*25, 26*). For example, acid peats cover 24 percent of a watershed in southernmost Norway, and 62 percent of the drainage flows through them (*26*).

The factors thought to make these landscapes sensitive to acid rain also limit neutralization of runoff acidified by acid soil. The thin and rocky soils that develop on these areas naturally produce such thick humus that they are often classified as organic soils (*17, 24, 27–31*), and they have a lower *p*H than the thicker soils downslope (*27, 31–33*). This topographic gradient in soil chemistry and other properties, where the upland soils are "leaky" and act as A horizons and the lower-lying sites act as B horizons, is known as a geochemical soil catena (*34*). Thus, a gradient in stream acidity paralleling a soil catena in mountainous areas should not be surprising, although it is not always evident. Such gradients have been observed at Hubbard Brook and other mountainous watersheds in the northeastern United States, but the acidification has been attributed entirely to acid rain (*35, 36*).

The interim report of the SNSF project attributed acid runoff solely to acid rain (*1*). This evoked criticism from other Scandinavian scientists, who noted that the amounts of acid in soils are enormous relative to that in rain and that runoff from acid soils will be acid regardless of the *p*H of rain (*37, 38*). They suggested that in such watersheds, runoff from heavy rains and rapid snowmelts is acidified because a greater proportion is in contact with the most acid surface soil horizons. Thus, hydrologic factors can make rapid runoff significantly more acid than runoff from gentler rains or slower snowmelts, which percolate to a greater depth and more slowly through less acid subsoil and geologic materials. In short, the effects of acid rain were said to be confused with those of acid soil (*37, 38*).

A later report of the SNSF project acknowledged that soils can act as both sources and sinks for acid and that the effects of acid rain were not clearly expressed even in watersheds as small as 10 ha (*39*). Accordingly, "minicatchments" ranging in size from 0.003 to 0.026 ha were established. Because of their small size, shallow soil, and large areas of exposed bedrock (46 to 74 percent), these catchments represent a worst case where the effects of acid rain should be most evident (*39*).

On average, runoff in the minicatchments was twice as acid as the acid rain, and the *p*H of the runoff was correlated with soil *p*H. Only for the heaviest rains in the smaller basins was the *p*H of rain found to measurably affect the *p*H of runoff (*39*). There was essentially no difference in acidity between the snowmelt from a snowpack at *p*H 4.3 and that from a snowpack neutralized to about *p*H 7 (*40*). Artificial rain at *p*H 3.85 acidified runoff by 0.2 to 0.4 *p*H unit, but it was concluded that further studies were needed to determine whether such acid rain can measurably acidify runoff in larger watersheds (*41*).

Although it has been demonstrated that acid soils can acidify runoff, it is still contended that acid rain is the major factor in the acidification of leachate and runoff. We believe that this is due to a number of misconceptions. One of them concerns anion leaching. As we noted earlier, hydrogen ions in acid rain at *p*H 4 or greater are inefficient in exchanging bases and thereby in acidifying strongly acid soils. Accordingly, most of the hydrogen ions in rain are thought to remain in solution and move through the soil accompanied by sulfate as the principal anion (*2–4, 20, 22, 42*). Sulfur in rain generally exceeds the nutrient requirements of forests, and humic materials coat aluminum and iron oxides that might otherwise immobilize sulfate by anion fixation (*1, 2–4, 20, 42, 43*). Thus, most of the H_2SO_4 falling on these soils is thought to move through them, causing increased cation leaching proportional to the increased flux of SO_4^{2-}. Similarly, acid peats are considered to offer little resistance to acidification of runoff by acid rain (*1, 2–4, 20, 26*).

However, the anion leaching theory has a major flaw. Watersheds considered to be most sensitive to acid rain have soils that are strongly acid and rich in humus, and their chemistry is not one of simple ion exchange. Humic materials act as weak acids; they dissolve in water and color and acidify it. The solubility of humic materials is a function of *p*H: the more acid the water, the less is dissolved (*10*). Sulfate apparently does not react strongly with humic materials, but the added H^+ in acid rain hinders their dissociation and decreases their solubility (*10*). The response is analogous to that of an inorganic system containing an excess of a sparingly soluble solid phase. Thus, additions of H_2SO_4 in rain should increase the flux of SO_4^{2-} and decrease the flux of organic anions with little or no measurable change in *p*H (*44*). Organic acids that accumulate are fated to be oxidized to CO_2 and H_2O.

Such a buffering mechanism helps explain why acid rain does not increase cation leaching in strongly acid soils at rates equivalent to deposition (*18, 45*). Rates of cation export from watersheds in the northeastern United States, Canada, and Norway which are thought to be sensitive to acid rain are remarkably low (*1, 35, 46–49*). Investigators at Hubbard Brook found it perplexing that the rate of cation export from the watershed was unusually low and apparently not enhanced by acid rain (*49*). Johnson (*35*) reported that "geologically, no excessive chemical weathering activity [as measured by cation export from watersheds] can be attributed to acid rain over the northeastern United States."

Other researchers state that the strong acids in acid rain result in equivalent leaching of cations (*1, 46–48*), but this conclusion is not supported by their own data. For example, rates of loss of cations in rivers in Canada are lowest where inputs of acid rain are highest (*47*). If the assumption of equivalent leaching were strictly applied to Norwegian data there should be no net loss of cations without acid rain, because net losses of cations are equivalent to inputs of acid in acid rain (*1, 48*).

The organic acid buffering mechanism also offers an alternative explanation of the observation that humic-colored lakes in Scandinavia are becoming clearer, an effect previously attributed to precipitation of humic acid by iron and aluminum dissolved by acid rain (*50*).

Leaching of Aluminum

The presence of aluminum ions in solution in soil and water at *p*H 5 or less has been considered evidence of dissolution of aluminum by acid rain (*1, 43, 51*). Even though it has long been known that large amounts of soluble aluminum are present in acid soils, the discovery of leaching of soil aluminum by acid rain (*43*) has been described as a principal and historic contribution (*52*). The discovery was based on the observation that there is considerably less aluminum mobilization in "pristine" sites in New Mexico and Washington than in "polluted" sites at Mount Moosilauke in New Hampshire. This is not surprising, however, since the soils in New Mexico and Washington are naturally less acid than those in New Hampshire (*53*).

There is a further misconception that aluminum leached from the A horizon of podzols is normally immobilized in the B horizon, and hence that aluminum in leachate which has moved through the B horizon must have been dissolved by acid rain. Such movement of aluminum out of soils is implicit in the concept of the geochemical soil catena (*34*). Some aluminum is leached and may appear in surface waters, as shown in 1930 by Joffe and later by others (*54, 55*). Indeed, at the sites in Washington examined by Ugolini and co-workers (*53*) one-third to one-half of the aluminum from the A horizon remains in solution in the B horizon. Aluminum does not appear in nearby spring water because it is precipitated as the water moves through fractured basic andesite bedrock. In New Hampshire, on the other hand, the water moves rapidly over solid bedrock, and hence aluminum appears in adjacent spring water.

The belief that aluminum ions in water result from acid rain is supported by the idea that all aluminum leached from organic-rich soils is complexed by organic anions. In humic-rich soils at *p*H 4.5 to 5, humic materials do complex most of the aluminum, as shown 50 years ago (*56*). However, aluminum complexation decreases dramatically as the *p*H decreases below about 4.5. Likewise, the solubility and mobility of complexed aluminum decrease as acidity increases (*10, 57*). Accordingly, ionized aluminum should be expected in water draining from organic-rich soils at *p*H 4 or less. This may also help explain why more aluminum is leached from the upper soil horizons at the Washington sites at *p*H 4.5 to 4.7 than at the New Hampshire site at *p*H 4 (*43, 53*).

Basic cations in rain may also promote exchange of ionized aluminum from acid soil into leachate and runoff. Indeed, the data from the snowmelt study mentioned earlier suggest that sodium in the neutralized snowpack replaced aluminum on exchange sites, which increased the concentration of aluminum in runoff for several weeks to about twice that in corresponding runoff from the snowpack with *p*H 4.3 (*40*). Acid rain may also increase the concentrations of base cations in forest throughfall. For example, about 90 percent of the hydrogen ions in acid rain at Hubbard Brook are neutralized in the northern hardwood canopy during the growing season; *p*H 4.1 rain becomes *p*H 5.0 throughfall (*58*). Although these leached nutrient cations are apparently taken up by the forest (*59*), the effects on aluminum chemistry are not known. Future studies should be carefully designed so that ion exchange by neutral salts (the salt effect) is not confused with dissolution of aluminum by acid (*60*).

Effects of Changing Land Use

Both regional acid rain and drastic changes in land use are associated with societal and technological evolution. Earlier, the exploitation of temperate forests was widespread and highly destructive. The remaining forests of western Europe all show the influence of man (*61*). The extensive heaths of Great Britain, Scandinavia, and northern Europe are the consequences of earlier and careless land use (*62*). Several thousand years of burning, grazing, and cutting caused severe erosion, which helped to create the unusually thin soils and low treelines of the uplands and low mountains of southern Norway (*2, 38, 63*). Many of these practices were transported to eastern North America with the arrival of the Europeans more than three centuries ago.

Fortunately, the temperate forests in Europe and North America were sufficiently resilient that they are now recovering. In New England, the volume of standing wood has increased by about 70 percent between 1952 and 1976 (*64*). Worldwide, temperate forest regrowth is so great that it may influence the global carbon cycle (*62, 65*). Given the effects of vegetation on soil acidification, there is little doubt that recovery of landscapes from earlier disturbance can result in increasingly acid surface soil horizons and thickening and acidification of forest floors.

In the 1920's, Salisbury (*32*) demonstrated that successional change and forest recovery from previous exploitation were responsible for widespread acidification of British landscapes; the upper slopes, with their acidophilic vegetation, were shown to be undergoing the greatest acidification. Large-scale recovery of forests in New England stimulated early studies in Connecticut. Red pine planted in 1900 on abandoned corn and tobacco fields developed a forest floor with a *p*H of about 3.8 (*66*). Other plots were established in 1926 and 1927 in 20- to 40-year-old hardwood stands and have been protected from cutting and burning. Our measurements show that today hardwoods have acidified the forest floor at one site from about *p*H 5.5 to 3.9 and the underlying mineral soil from *p*H 5.1 to 4.6 (*67*). At another site there was almost complete mortality of oak from drought and defoliation. Basal area declined from 30.5 m^2/ha in 1957 to 4.6 m^2/ha in 1977. Here, we found that the *p*H of the forest floor had actually increased from 3.8 to 4.2 (*67*).

While soil properties and effects of changing land use vary from site to site and are even heterogeneous within sites, some general relations are evident. Land use and forest management studies in North America and northern Europe reveal that disturbance under conifers affects acidity and depth of humus more than similar disturbance under hardwoods (*28, 29, 54, 68, 69*). Likewise, the greater the disturbance, the greater the effect. Mixed hardwood-conifer forests are intermediate, but their response to disturbance tends to resemble that of conifers (*28, 29, 54, 68–70*). Thus, as Salisbury (*32*) concluded, recovery from earlier disturbance will have its greatest effects on the upper slopes—that is, on strongly acid soils rich in organic matter.

In the northeastern United States, the most severe changes have occurred in the spruce-fir forests of northern New England and on the steep slopes of the Adirondacks, where acid rain is thought to be particularly harmful. By the early 1900's essentially all the spruce-fir forests had been clear-cut for pulp, except for a small fraction of the forest in the Adirondacks which was preserved (*30, 71–73*). The original spruce-fir forests were very resistant to fire (*72, 74*), but lumbering was often followed by severe fires that largely or completely destroyed the thick forest floor (*28–30, 73, 75*).

The more intense a forest fire, the greater the effects on depth and acidity of the forest floor. Organic acids are oxidized and lost to the atmosphere, leaving alkaline ash on the soil (*28, 29, 54, 68, 69*). In managed spruce forests in Scandinavia, where controlled burning reduced the depth of humus by only 1 cm, the *p*H of the remaining 4 cm of humus rose 2 to 3 units. After 50 years the original depth of humus was restored, as was the original *p*H of 4. The *p*H of the upper mineral soil was still elevated by about 0.2 *p*H unit (*69, 76*).

The depth of the forest floor under undisturbed stands of spruce and fir on the upper slopes of the Adirondack, White, and Laurentian mountains commonly exceeds 30 cm and the *p*H is less than 3.5 (*27–31*). Diebold (*28*) showed that in the Adirondacks, fire in spruce-fir slope forests is more destructive to the forest floor than in other forest types (*28, 29, 68, 69, 75*). On the average, the depth of the forest floor up to 30 years after burning was reduced by 30 cm. The thinner and less acid forest floors of the lower slopes and valleys were reduced by 5 to 13 cm (*27–31*).

On the steeper slopes of the White Mountains the depth of the forest floor ranges from discontinuous to 5 to 10 cm (*77*), suggesting widespread destruction of the original forest floor. The depth of the forest floor may also be reduced in the absence of fire; in cutover but unburned Adirondack spruce forests the floor averages about 5 cm in depth (*78*).

The effect of cutting and burning on the *p*H of the forest floor on the steep slopes of the Adirondacks has apparently not been determined. In the various forest types of the lower slopes and valleys, Young [in (*68*)] showed reductions in the depth of the forest floor from both cutting and burning that were similar to those reported by Diebold (*28*). The *p*H of the forest floor averaged about 4 in undisturbed stands, but under stands that were cut or burned the average *p*H was about 5 when measured 20 to 50 years after disturbance. The *p*H of the mineral soil averaged about 0.7 unit higher under disturbed stands.

Maturation of forests also influences hydrology. As the depth of humus increases, the amount of water percolating into the subsoil may decrease (*79*). Runoff can become more acid not only because of the increasingly acid humus, but also because of the increasing proportion of near-surface runoff. Also, snowpacks last longer under older forests, making episodic flushes more likely during periods of warm weather or rainfall (*80*). The devastating effects of spring snowmelt may be more severe in part because of changes in hydrology and chemistry induced by changes in the forest.

Although the effects of forest disturbance and recovery are variable, it is apparent that recovery results in increasingly acid soil horizons and thickening organic horizons (*28, 29, 54, 68, 69*). Accordingly, water moving through such soil should also become more acid, and the proportion of ionized aluminum to organically complexed aluminum may also increase (*57*).

Thus, mountainous areas of the northeastern United States are not pristine environments that are acted on only by acid rain. These landscapes, which were disturbed in the past, are undergoing the soil formation process that produce the greatest increases in natural soil acidity.

The idea that changing land use and consequent vegetational succession are largely responsible for acidification of soil and water in southern Norway was first advanced by Rosenqvist (*38*). Forest recovery in southernmost Norway has been dramatic: the volume of standing wood increased by more than 70 percent during the period 1927–1928 to 1964–1973. Rosenqvist proposed that this large-scale recovery of forest and the reversion of land to acid heath and forest was producing large areas of increasingly acid soils. As an illustration, he showed that the exchange acidity of surface humus under a 90-year-old spruce forest on an abandoned Norwegian farm was equivalent to the strong acids in about 1000 years of rain of 1 m per year with *p*H 4.3. He proposed that these increasing amounts of increasingly acid humus and mineral soil (*81*) are acidifying runoff in watersheds where there is incomplete neutralization of acids by mineral weathering (*38, 63*).

The final report of the SNSF project acknowledges that changes in land use and consequent vegetative succession have long been known to acidify soil and will in general affect the alkalinity and *p*H of rivers and lakes (*2–4*). Nevertheless, it considers changes in land use to be a minor factor and concludes that the observed increases in sulfate in runoff and presumed equivalent increases in leaching of hydrogen, aluminum, and other cations are responsible for most of the observed increases in acidity (*2–4*).

We believe that the effects of changing land use and vegetative succession cannot be dismissed on the basis of studies performed to date. Further, the hypothesis that increased deposition of acid and sulfate is causing equivalent leaching and acidification is theoretically unsound and is not supported by direct observations. Natural processes of acidification must be more carefully considered in assessing benefits expected from proposed reductions in emissions of oxides of sulfur and nitrogen.

References and Notes

1. F. H. Braekke, Ed., *SNSF Proj. Res. Rep. FR 6/76* (1976).
2. L. N. Overrein, H. M. Seip, A. Tollan, Eds., *SNSF Proj. Res. Rep. FR 19/80* (1980).
3. D. Drabløs and A. Tollan, Eds., *Ecological Impact of Acid Precipitation*, (SNSF Project, Oslo, 1980).
4. H. M. Seip, *ibid.*, p. 358.
5. W. Stumm and J. J. Morgan, *Aquatic Chemistry* (Wiley-Interscience, New York, 1970), p. 161; R. M. Garrels and C. L. Christ, *Solutions, Minerals, and Equilibria* (Harper & Row, New York, 1965), p. 74.
6. G. E. Likens, F. H. Bormann, R. S. Pierce, J. S. Eaton, N. M. Johnson, *Biogeochemistry of a Forested Ecosystem* (Springer-Verlag, New York, 1977), p. 43.
7. H. A. Lunt, *Conn. Agric. Exp. Stn. New Haven Bull. 523* (1948); R. D. Krebs and J. C. F. Tedrow, *Soil Sci.* **83**, 207 (1957); D. M. J. Provan, R. Sorensen, J. Låg, *Meld. Nor. Landbrukshoegsk.* **48**, (No. 22) (1969).
8. S. Mattson, *K. Lantbrukshoegsk. Ann.* **5**, 261 (1938); H. Jenny, *Factors of Soil Formation* (McGraw-Hill, New York, 1941); P. W. Birkeland, *Pedology, Weathering, and Geomorphological Research* (Oxford Univ. Press, New York, 1974); N. van Breeman and R. Brinkman, in *Soil Chemistry*, part A, *Basic Elements*, G. H. Bolt and M. G. M. Bruggenwert, Eds. (Elsevier, New York, 1978), p. 141.
9. S. Mattson and E. Koutler-Andersson, *K. Lantbrukshoegsk. Ann.* **13**, 153 (1946); M. Schnitzer and J. G. Desjardins, *Can. J. Soil Sci.* **49**, 151 (1969).
10. M. H. B. Hayes and R. S. Swift, in *The Chemistry of Soil Constituents*, D. J. Greenland and M. H. B. Hayes, Eds. (Wiley-Interscience, New York, 1978), p. 281; K. Ghosh and M. Schnitzer, *Soil Sci.* **129**, 266 (1980); G. S. P. Ritchie and A. M. Posner, *J. Soil Sci.* **33**, 233 (1982). Most soil humic substances are in a solid or gel state. Polar functional groups and charged sites with their counterions will be strongly solvated in water. Electrostatic repulsion between like charges of dissociated groups is required for dissolution of humic fraction. Replacement of readily dissociated counterions by H^+ gives rise to contraction and precipitation of humic substances by reduction of charge repulsion between weakly dissociated carboxyl groups, enhanced hydrogen bonding, and expulsion of solvent from within the macromolecular humate structure.
11. L. G. Romell, *Soil Sci.* **34**, 161 (1932).
12. Acid to dissolve minerals is calculated from the average composition of Hubbard Brook geologic materials [N. M. Johnson, G. E. Likens, F. H. Bormann, R. S. Pierce, *Geochim. Cosmochim. Acta* **32**, 531 (1968)], assuming a 0.6-m slice weighs 8.82×10^6 kg/ha. The depth of 0.6 m is used since sola of well-developed soils in the Northeast are about 0.6 m. Acid-neutralizing capacity of Al is three times that of bases. Rates of acid deposition and mineral weathering were estimated by C. T. Driscoll and G. E. Likens [*Tellus* **34**, 283 (1982)].
13. N. M. Johnson, paper presented at the American Chemical Society National Meeting, Las Vegas, Nev., 28 March to 2 April 1982.
14. W. W. McFee, J. M. Kelly, R. H. Beck, *U.S. For. Serv. Gen. Tech. Rep. NE-23* (1976), p. 725. These authors stated that their calculations were based on simplifying assumptions that may not hold, namely that (i) hydrogen is the only cation in rain, (ii) replacement of basic cations

by hydrogen is complete ($\Delta M/\Delta H = 1$), (iii) no hydrogen is consumed by other mechanisms, and (iv) no basic cations are supplied by other mechanisms.

15. L. Wiklander, *Grundfoerbaettring* **26**, 155 (1973/74); *Geoderma* **14**, 93 (1975).
16. F. J. Pearson and D. W. Fisher, *U.S. Geol. Surv. Water Supply Pap. 1535-P* (1971); S. Odén, *U.S. For. Serv. Gen. Tech. Rep. NE-23* (1976), p. 1; P. M. Vitousek, J. R. Gosz, C. C. Grier, J. M. Melillo, W. A. Reiners, *Ecol. Monogr.* **52**, 155 (1982).
17. J. S. Clayton, W. A. Ehrlich, D. B. Cann, J. H. Day, I. B. Marshall, *Soils of Canada* (Canadian Department of Agriculture, Ottowa, 1977), vol. 1.
18. A. O. Stuanes, in (*3*), p. 198; I. K. Morrison, *Can. For. Serv. Res. Notes* **1**, 6 (1981); L. N. Overrein, *Ambio* **1**, 145 (1972); W. H. Smith, *Air Pollution and Forests* (Springer-Verlag, New York, 1981), p. 187.
19. D. D. Richter *et al.*, in *Proceedings of the Second National Symposium on Acid Rain* (Greater Pittsburgh Chamber of Commerce, Pittsburgh, Pa., October 1982).
20. National Research Council, *Atmosphere-Biosphere Interactions: Toward a Better Understanding of the Ecological Consequences of Fossil Fuel Combustion* (National Academy Press, Washington, D.C., 1981).
21. P. J. Dillon *et al.*, *J. Fish. Res. Board Can.* **35**, 809 (1978).
22. New York State Department of Environmental Conservation, *Proceedings of the Acid Precipitation Research Needs Conference* (State University of New York, Syracuse, 1982).
23. N. S. Shaler, in *Tenth Annual Report of the United States Geological Survey* (Government Printing Office, Washington, D.C., 1890), p. 255; G. B. Rigg, *Bot. Rev.* **6**, 666 (1940); R. S. Farnham and H. R. Finney, *Adv. Agron.* **17**, 115 (1965).
24. F. H. Braekke, *Medd. Nor. Skogforsoeksves.* **36** (No. 11) (1981).
25. A. G. Everett, W. C. Retzsch, J. R. Kramer, I. P. Montanez, P. F. Duhaime, in *Proceedings of the Second National Symposium on Acid Rain* (Greater Pittsburgh Chamber of Commerce, Pittsburgh, Pa., October 1982).
26. F. H. Braekke, *Medd. Nor. Skogforsoeksves.* **36** (No. 10) (1981).
27. C. C. Heimburger, *Cornell Univ. Agric. Exp. Stn. Mem. 165* (1934).
28. C. H. Diebold, *Soil Sci. Soc. Am. Proc.* **6**, 409 (1941).
29. H. J. Lutz and R. F. Chandler, *Forest Soils* (Wiley, New York, 1946), p. 183.
30. H. J. Oostings and W. D. Billings, *Ecology* **32**, 84 (1951).
31. T. G. Siccama, thesis, University of Vermont (1968); H. L. Bohn, *Soil Sci. Soc. Am. J.* **40**, 468 (1976).
32. E. J. Salisbury, *J. Ecol.* **9**, 220 (1922).
33. E. T. Wherry, *Ecology* **4**, 395 (1923); S. A. Cain, *Bot. Gaz.* **91**, 22 (1931); L. F. Ohmann and M. F. Buell, *Bull. Torrey Bot. Club* **95**, 287 (1968); T. G. Siccama, *Ecol. Monogr.* **44**, 325 (1974); T. Troedsson, *Ann. Agric. Fenn.* **19**, 81 (1980).
34. M. A. Glazovskaya, *Trans. 9th Int. Congr. Soil Sci.* **4**, 303 (1968).
35. N. M. Johnson, *Science* **204**, 497 (1979).
36. N. M. Johnson *et al.*, *Geochim. Cosmochim. Acta* **45**, 1421 (1981).
37. J. Låg, in *Fresh Water on the Sea*, S. Skreslet, R. Leinebø, J. B. L. Matthews, E. Sakshaug, Eds. (Association of Norwegian Oceanographers, Oslo, 1976), p. 21.
38. I. T. Rosenqvist, *Sci. Total Environ.* **10**, 39 (1978).
39. H. M. Seip, G. Abrahamsen, E. T. Gjessing, A. Stuanes, *SNSF Proj. Int. Rep. IR 46/79* (1979).
40. H. M. Seip, S. Andersen, B. Halsvik, *SNSF Proj. Int. Rep. IR 65/80* (1980).
41. H. M. Seip, E. T. Gjessing, H. Kamben, *SNSF Proj. Int. Rep. IR 47/79* (1979).
42. D. W. Johnson, J. Turner, J. M. Kelly, *Water Resour. Res.* **18**, 449 (1982).
43. C. S. Cronan and C. L. Schofield, *Science* **204**, 304 (1979).
44. This hypothesis has been verified, at least in part, by J. G. McColl, B. A. Browne, and M. K. Firestone [in *Agronomy Abstracts* (American Society of Agronomy, Madison, Wisc., 1982), p. 178] and F. H. Chang and M. Alexander (*Soil Sci.*, in press), who showed that acid additions up to *p*H 3 do not measurably acidify leachate and generally decrease organic leaching. P. J. Isaacson and E. C. Krug (unpublished data) found similar buffering by organic acids.
45. G. Abrahamsen, in (*3*), p. 196; ______ and A. O. Stuanes, *ibid.*, p. 152.
46. J. N. Galloway, C. L. Schofield, G. R. Hendrey, E. R. Altwicker, D. E. Troutman, in (*3*), p. 254; J. N. Galloway, C. L. Schofield, G. R. Hendrey, N. E. Peters, A. H. Johannes, *ibid.*, p. 264.
47. M. E. Thompson, F. C. Elder, A. R. Davis, S. Whitlow, *ibid.*, p. 244.
48. R. F. Wright and M. Johannessen, *ibid.*, p. 250.
49. N. M. Johnson, R. C. Reynolds, G. E. Likens, *Science* **177**, 514 (1972).
50. B. Almer, W. Dickson, C. Ekström, E. Hörnström, in *Sulfur in the Environment*, part 2, *Ecological Impacts*, J. O. Nriaga, Ed. (Wiley-Interscience, New York, 1978), p. 271; W. Dickson, in (*3*), p. 75.
51. R. F. Wright *et al.*, *SNSF Proj. Res. Rep. FR 3/75* (1975); W. Dickson, *Verh. Int. Ver. Limnol.* **20**, 851 (1978).
52. E. B. Cowling, *Environ. Sci. Technol.* **16**, 110A (1982).
53. M. C. Hoyle, *U.S. For. Serv. Res. Pap. NE-260* (1973); F. C. Ugolini, H. Dawson, J. Zachara, *Science* **198**, 603 (1977); F. C. Ugolini, R. Minden, H. Dawson, J. Zachara, *Soil Sci.* **124**, 291 (1977); W. C. Graustein, thesis, Yale University (1981).
54. O. Tamm, *Northern Coniferous Forest Soils* (Scrivener, Oxford, 1950), p. 144.
55. J. S. Joffe, *Proc. 2nd Int. Congr. Soil Sci.* **2**, 135 (1930); A. A. Rode, *Soil Science* (Department of Commerce, Washington, D.C., 1962), p. 155; L. Petersen, *Podzols and Podzolization* (DSR Forlag, Copenhagen, 1976); E. C. Krug, thesis, Rutgers University (1981).
56. S. Mattson and J. B. Hester, *Soil Sci.* **36**, 229 (1933).
57. K. Boratyński and S. Mattson, *K. Lantbrukshoegsk. Ann.* **7**, 63 (1939); J. van Schuylenborgh and M. G. M. Bruggenwert, *Neth. J. Agric. Sci.* **13**, 267 (1965); M. Schnitzer and E. H. Hansen, *Soil Sci.* **109**, 333 (1970); W. L. Hargrove and G. W. Thomas, *Can. J. Soil Sci.* **62**, 571 (1982).
58. J. W. Hornbeck, G. E. Likens, J. S. Eaton, *U.S. For. Serv. Gen. Tech. Rep. NE-23* (1976), p. 597. However, the effect of forest canopy on throughfall acidity is variable, ranging from nearly complete neutralization [Hornbeck *et al.*; D. W. Cole and D. W. Johnson, *Water Resourc. Res.* **13**, 313 (1977)] to no net neutralization (*43*) to concentrating acidifying substances in throughfall [B. Ulrich, in *Effects of Acid Precipitation on Terrestrial Ecosystems*, T. C. Hutchinson and M. Havas, Eds. (Plenum, New York, 1980), p. 255].
59. J. S. Eaton, G. E. Likens, F. H. Bormann, *J. Ecol.* **61**, 495 (1973).
60. W. L. Lindsay, M. Peech, J. S. Clark, *Soil Sci. Soc. Am. Proc.* **23**, 266 (1959); C. R. Frink, in *Acid Sulfate Soils*, H. Dost, Ed. (International Institute of Land Reclamation and Improvement, Wageningen, Netherlands, 1973), vol. 1, p. 131.
61. E. L. Stone, *Philos. Trans. R. Soc. London Ser. B* **271**, 149 (1975).
62. T. Bramryd, in *The Global Carbon Cycle: Scope Report 13*, B. Bolin, E. T. Degens, S. Kempe, P. Ketner, Eds. (Wiley, New York, 1979), p. 183.
63. I. T. Rosenqvist, in *Advances in Environmental Science and Engineering*, J. R. Pfafflin and E. N. Ziegler, Eds. (Gordon & Breach, New York, 1980), vol. 3, p. 56.
64. U.S. Forest Service, *Forest Statistics of the U.S., 1977* (review draft, 1978).
65. M. Clawson, *Science* **204**, 1168 (1979); T. V. Armentano and C. W. Ralston, *Can J. For. Res.* **10**, 53 (1980).
66. C. R. Frink and G. K. Voigt, *U.S. For. Serv. Gen. Tech. Rep. NE-23* (1976), p. 685.
67. H. W. Hicock, M. F. Morgan, H. J. Lutz, H. Bull, H. A. Lunt, *Conn. Agric. Exp. Stn. New Haven Bull. 330* (1931); Connecticut Agricultural Experiment Station, file data. Basal area is the sum of the cross-sectional areas of the trees per unit area of forest.
68. B. G. Griffin, E. W. Hartwell, T. E. Shaw, *Harv. For. Bull. 15* (1930); M. F. Morgan, *Am. Soil Surv. Assoc. Bull.* **12**, 49 (1931); H. A. Lunt, *Conn. Agric. Exp. Stn. New Haven Bull. 342* (1932); M. J. Plice, *Cornell Univ. Agric. Exp. Stn. Mem. 166* (1934); V. A. Young, *Ecology* **15**, 154 (1934); I. F. Ahlgren and C. E. Ahlgren, *Bot. Rev.* **26**, 483 (1960).
69. P. J. Viro, in *Fire and Ecosystems*, T. T. Kozlowski and C. E. Ahlgren, Eds. (Academic Press, New York, 1974), p. 7.
70. R. L. Donahue, *Cornell Univ. Agric. Exp. Stn. Mem. 229* (1940); T. H. Eaton and R. F. Chandler, *ibid. 247* (1942); A. F. Hough, *Soil Sci.* **56**, 19 (1943).
71. W. F. Fox, *U.S. Dep. Agric. Bur. For. Bull. 34* (1902); F. W. Very, *Science* **35**, 31 (1912); R. Marshall, *J. For.* **23**, 173 (1925); H. J. Oosting and J. F. Reed, *Am. Midl. Natur.* **31**, 182 (1944); R. C. Thompson, thesis, Syracuse University (1962).
72. A. K. Chittenden, *U.S. Dep. Agric. Bur. For. Bull. 55* (1905).
73. P. W. Ayres, *U.S. Dep. Agric. For. Serv. Circ. 168* (1909).
74. C. F. Korstian, *Ecol. Monogr.* **7**, 125 (1937); F. H. Bormann and G. E. Likens, *Pattern and Process in a Forested Ecosystem* (Springer-Verlag, New York, 1979), p. 201; T. J. Fahey and W. A. Reiners, *Bull. Torrey Bot. Club* **108**, 362 (1981).
75. R. C. Hawley and A. F. Hawes, *Forestry in New England* (Wiley, New York, 1912), p. 209; A. MacDonald, *J. For.* **23**, 457 (1925); L. S. Minckler, *ibid.* **43**, 349 (1945); H. I. Baldwin, *Bull. Torrey Bot. Club* **104**, 324 (1977).
76. Depth under comparable undisturbed spruce stands is about 10 cm.
77. M. C. Hoyle, *Rep. N. H. For. Notes* (Summer 1965).
78. J. Kittredge and H. C. Belyea, *J. For.* **21**, 784 (1923).
79. J. Låg and O. Einevöll, *Meld. Nor. Landbrukshoegsk.* **34**, 525 (1954); A. H. Knight, R. Boggie, H. Shepherd, *J. Appl. Ecol.* **9**, 633 (1972); R. Boggie and A. H. Knight, *Forestry* **53**, 179 (1980); J. F. Collins and E. Coyle, *J. Soil Sci.* **31**, 547 (1980).
80. H. W. Lull and F. M. Rushmore, *U.S. For. Serv. Northeast. For. Exp. Stn. Stn. Pap. 138* (1960); W. J. Schneider and G. R. Ayer, *U.S. Geol. Surv. Water Supply Pap. 1602* (1961); A. R. Eschner and D. R. Satterlund, *U.S. For. Serv. Res. Note NE-13* (1963); D. R. Satterlund and A. R. Eschner, *Water Resourc. Res.* **1**, 397 (1965).
81. In Scandinavia, spruce and pine growing on old farmland can acidify mineral soil from above *p*H 6 to about *p*H 4 within a few decades [W. Dickson, *Inst. Freshwater Res. Drottningholm Rep. 54* (1975)]. Similar rates of acidification have been reported under poplar and alder in the Netherlands [J. van der Burg and H. W. Kolster, *For. Abstr.* **44** (No. 2), 86 (1983)].