Volume 3 | Issue 2 Article 6

7-1985

The Thirsty Earth: Acid Rain - A Sour Drink

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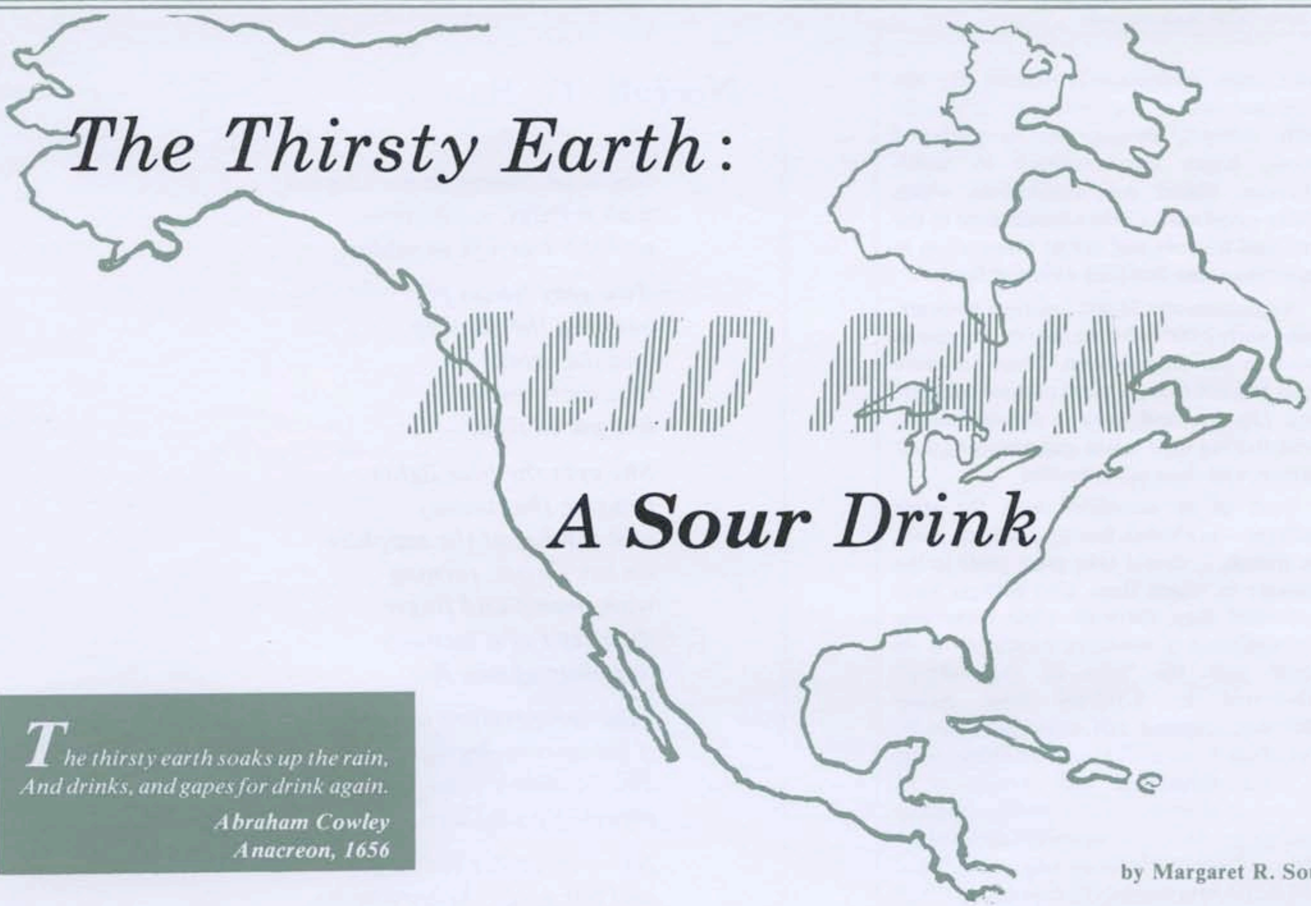
The Thirsty Earth:

ACID RAIN

A Sour Drink



> *The thirsty earth soaks up the rain,*
> *And drinks, and gapes for drink again.*
> ***Abraham Cowley***
> ***Anacreon, 1656***

by Margaret R. Souza

An irridescent halo of photochemical smog hangs over the city. Paint peels, flowers wilt and people struggle to breathe. Cause and effect are readily apparent.

A wilderness lake once teeming with aquatic life is crystal clear. The majestic trees of a remote forest are turning brown. A more insidious environmental agent is implicated, acid rain.

These two phenomena, although different on the surface, are closely related in origin. Both are the products of an industrial, urbanized society with its dependence upon the combustion of fossil fuels for the energy it consumes in ever increasing amounts.

England, the birthplace of the industrial revolution in the late eighteenth century, was the first country to experience both smog and acid rain on a grand scale. It had long been suspected that the pollution from the coal fires of London was causing more than a foul smell. Respiratory problems and the damage to vegetation, fabrics and to iron and stone structures had been linked to the burning of coal. By the mid-nineteenth century, scientists had detected both sulfuric and nitric acids in the air and the term 'acid rain' had been coined. A simple solution to the problem was devised. Factories were equipped with taller smokestacks, the ambient air became cleaner and the problem was apparently solved. However, it became absolutely clear that the problem had not been solved when, in 1952, thousands of people in the British Isles died as a result of the 'killer fog'. Even taller stacks were built in response to this crisis.

> ***. . . depletion of . . . natural buffers . . . is converting this once robust earth into an increasingly fragile one.***

In 1972, Sweden presented a report to the United Nations Conference on the Human Environment notifying the world community that not only had the acid rain problem not been solved by building taller and taller stacks, some as tall as the Empire State Building, but that these very stacks built to prevent acid rain formation had caused it to expand from a local, urban problem to one of global dimensions.

Acids in the Environment

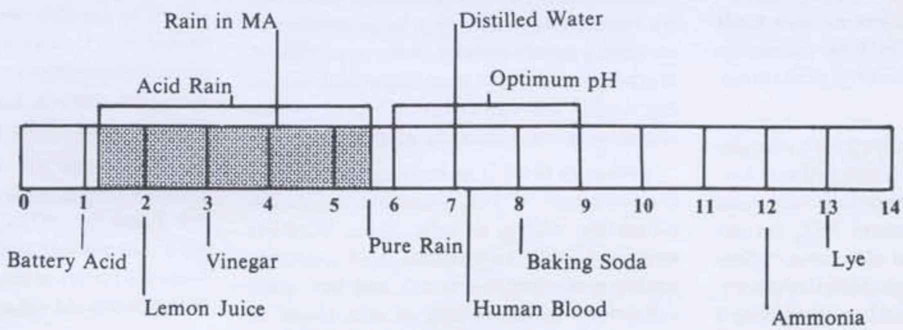
Acid rain is a general term which refers to both wet and dry deposition of acidic substances from the air onto the earth's surface. Thus, it includes all forms of precipitation as well as the settling out and washing out by precipitation of fine solids (particulates) and liquid droplets (aerosols).

There are a large number of naturally occurring acidic substances. Acetic acid, a weak acid commonly known as vinegar, is responsible for the characteristic sour taste of pickles. Carbonic acid, another weak acid, produces the pleasant, sparkling taste of a carbonated beverage. In contrast, stomach acid (hydrochloric acid), a strong acid of about the same concentration as vinegar, produces the decidedly unpleasant, sour and burning sensation associated with heartburn. Since the two acids primarily responsible for acid rain, sulfuric and nitric, are strong acids, it is not surprising that this most sour drink is having a serious and detrimental effect on the earth.

Natural unpolluted rain, unlike distilled water, is not neutral but is slightly acidic. This acidity is produced when the slightly soluble atmospheric gas, carbon dioxide, dissolves. Acid rain is frequently 20 to 100 times more acidic than unpolluted rain not only because pollutants dissolve to form strong rather than weak acids but also because these pollutants are considerably more soluble in water than is carbon dioxide.

The acidity of water is conveniently quantified using the pH scale (Figure 1). On this scale the pH of distilled water is 7, that of unpolluted water is 5.6 and that of the rain falling in Massachusetts averages 4.2. Two characteristics of the pH scale are important to note. First, pH decreases as acidity increases. Second, the scale is based on powers of 10, that is, each decrease of 1 pH unit represents a ten-fold increase in acidity. Thus, rain in Massachusetts is 25 times more acidic than unpolluted rain.

Figure 1, pH Scale



Most plants and animals experience optimum growth and reproduction at a pH somewhere between 6.0 and 9.0. Detrimental effects are observed in many species if the pH of the water in their environment falls below 6. This optimum pH range (6-9) is above the pH of unpolluted water (5.6). These more alkaline conditions result from the neutralization of rain by reaction with alkaline substances in the atmospheric, terrestrial and/or aquatic environments. For example, as a droplet of rain falls to the earth it may strike an alkaline dust particulate, gas molecule or aerosol droplet and be partially neutralized; it may be further neutralized after striking the ground as it percolates through and reacts with the soil and finally, it may be still further neutralized by reaction with substances in the ground water, stream or lake into which it flows.

The presence of these alkaline substances in the environment accounts for the earth's ability to respond to and diminish the destructive effects of acid rain. It is the depletion of these natural buffers by the continual assault of rain 20 to 100 times more acidic than normal which is converting this once robust earth into an increasingly fragile one.

Sources of Acid Rain

In New England and most other regions east of the Mississippi, sulfuric acid is the major constituent (62%) of acid rain. The concentration of nitric acid is about half this amount (32%) and hydrochloric acid is usually present in minor amounts (6%). In contrast, the nitric acid concentration in Los Angeles is about twice that of sulfuric acid although in most regions west of the Mississippi the sulfuric acid concentration is equal to (1:1), or somewhat larger than (1.4:1), the nitric acid concentration.

Both sulfuric and nitric acids occur naturally in the atmosphere. Sulfur containing compounds which react to form sulfuric acid are emitted from erupting volcanoes, the bacterial decomposition of organic matter and sea spray. Compounds of nitrogen, the precursors of nitric acid, result primarily from chemical reactions occurring during lightning storms and in the soil.

These natural sources produce a measurable (background) concentration of these acids. Since these sources are globally distributed, however, their contribution to the annual average acidity varies little from region to region.

Man-made sources, on the other hand, tend to be concentrated in urban areas within the Northern Hemisphere. Sulfuric acid forms primarily from sulfur oxides (SO_x), mostly sulfur dioxide (SO_2), emitted during electrical generation (62%), industrial processing (18%) and industrial fuel combustion (13%). Nitric acid precursors are nitrogen oxides (NO_x), primarily nitric oxide (NO) and nitrogen dioxide (NO_2), emitted from fossil fuel combustion in transportation (39%), electrical generation (34%) and industrial manufacturing (19%).

Measured on a global scale, man-made sources are estimated to account for 41% of the total atmospheric sulfur and from 6% to 50% of the total atmospheric NO_x. Since these sources are not uniformly distributed, they may contribute as much as 80 or 90% of the total acidic pollutants in some regions such as Sweden and the Northeastern United States, thereby causing the precipitation to be highly acidic in these regions.

Fluctuations in the relative amounts of sulfuric and nitric acids can be correlated with human patterns of fuel consumption.

The amount of sulfuric acid in the atmosphere is maximum in the winter when electrical generation peaks, while the amount of nitric acid reaches a maximum in the summer when traffic levels peak. The abnormally high concentration of nitric acid in Los Angeles obviously results from the freeway traffic.

The emission of SO_x can be reduced by burning fuels with lower sulfur content, for example, by replacing high-sulfur eastern coal with low-sulfur western coal, oil or gas. SO_x emissions increased 46% from 1940 to a peak value in 1970 after which a slight decrease has been noted. This decrease can be directly correlated with the switching by electrical utilities from coal to oil and gas and with the installation of flue gas disulfurization (FGD) scrubbers on the smokestacks of coal fired burners in response to emission standards set in the Clean Air Act of 1970.

Most of the FGD technology used in the United States is based on the reaction of SO_x with limestone and/or lime. This emission control device is capable of reducing SO_2 emission from coal fired burners by 75-90% but the solid by-product (calcium sulfite) is not marketable and presents a serious waste disposal problem.

If high-sulfur coal is to be burned, it may be cleaned prior to burning. Since sulfur is present in coal primarily as iron pyrite (fool's gold) which like gold is very dense, it can be partially removed by an operation similar to that used in panning for gold:

pyrite settles out when a mixture of crushed coal and water is mechanically shaken.

Since the oxides of sulfur cannot be prevented from forming during combustion, sulfur must be removed either prior to combustion or after conversion to the oxides as in scrubbing. Nitrogen oxides, on the other hand, can be prevented from forming by adjusting the conditions under which the fuel burns. Furthermore, the oxidation process can be reversed and NO_x can be converted into the harmless major constituent of air, nitrogen, N_2.

Some of the modifications to the combustion process which result in reduced NO_x emissions by preventing its formation include reducing the amount of air available during combustion, installing special low-NO_x burners, and lowering the combustion temperature. The injection of ammonia into the combustion chamber or the installation of selective catalysts in the stack remove NO_x by convertiing it to nitrogen. Perfection of these technologies can virtually eliminate NO_x emissions from stationary combustion sources.

Nitrogen oxide emissions increased steadily (273%) from 1940 to a peak in 1973. Fuel conservation associated with the energy crisis may account for the temporary reduction in these emissions, which are again rising. Since fuel combustion for transportation accounts for a large fraction of man-made NO_x, control of automobile emissions should significantly reduce nitric acid formation.

Most cars are now equipped with a single-stage catalytic converter which reduces carbon monoxide and hydrocarbon emissions but, unfortunately, increases NO_x formation. A more effective but also more expensive and complex two-stage catalytic converter in which a second chamber containing a ruthenium oxide catalyst converts NO_x to N_2, is currently being installed on some new cars. Others are equipped with a less efficient single-stage converter system in which exhaust gases are recycled, allowing the engine to be operated at lower air concentrations and at lower temperatures thereby reducing NO_x emissions.

Trends in SO_x and NO_x emissions have been studied at the Brookhaven National Laboratory. The decreases in emissions of SO_x from all sources and of NO_x from transportation projected between 1975 and 1990 may not be realized or may be less dramatic than expected due to the relaxation of emission standards. The EPA has chosen to apply clean air standards on the basis of the average emission of the entire fleet of cars produced by a given manufacturer or of an entire industrial complex rather than to enforce standards on each car model or each smokestack.

Transformation, Transport and Deposition

Once sulfur and nitrogen containing compounds have been emitted into the atmosphere from both natural and man-made sources, they may undergo many complex reactions prior to deposition. For sulfuric and nitric acids to be formed, most of these compounds must undergo further oxidation by reaction with any of a large number of oxidizing agents present in the atmosphere. It is believed that the most important oxidizing agents are the constituents of photochemical smog, especially ozone.

Although there is general agreement that the reduction of SO_x emissions would decrease the acidity of rain, some scientists believe that the concentration of oxidizing agents is the limiting factor and that more reductions in the acidity of rain could be achieved by altering the mixture of gases in smoke plumes than by concentrating efforts exclusively on reducing SO_x emissions.

The pH of rain in a given region is determined by three factors: the rate at which SO_x and NO_x are oxidized to the acids, the effectiveness of the neutralization of acidic pollutants by natural buffers and the amount of acidic pollutants emitted in that region and transported into it from other regions.

The rate of oxidation is negligible in pure air, slow at background concentrations of pollutants and relatively rapid in polluted air. Thus, the more polluted the air is, the more acidic the rain becomes. An increased rate also results as temperature and solar radiation increase: acids form most rapidly in the summer and rates are maximum in the mid-afternoon. The presence of particulates also increases the rate of acid formation. Certain metal compounds such as vanadium pentoxide adsorbed on the surface of soot particles catalyze the oxidation; oxidation should occur faster near the point of emission before soot particles have settled out. Finally, oxidation occurs faster when the reactants are dissolved in water droplets: thus, acid rain forms faster when the humidity is high and the dew point is also high.

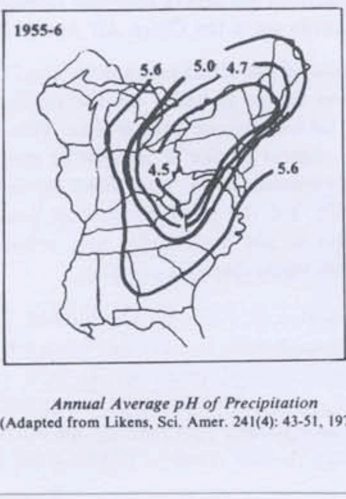
Both ammonia, which is emitted into the atmosphere during forest fires, during volcanic eruptions and as a waste product of microbiological metabolism, and dust particles, which enter the atmosphere from alkaline soils, are capable of neutralizing acids and raising the pH of rain. Alkaline soils have been shown to emit more ammonia than do acidic soils. Regions in which soils are alkaline and much dust is generated as a result of low rainfall and/or agriculture as the main land use are expected to have rain of relatively low acidity.

The major man-made sources of SO_x and NO_x in the U.S. are located in states abutting or lying to the east of the Mississippi. Approximately 50% of the emissions from these sources originate in the highly industralized Ohio River Basin.

All regions of the U.S. except Florida and the Gulf States are influenced by the prevailing Westerly winds, as is dramatically illustrated by satellite weather monitoring presented on TV newscasts. Pollutants emitted into the atmosphere are transported by these winds to regions northeast of the source through most of the year.

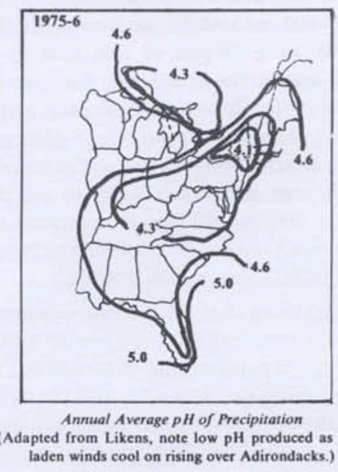
The average pH of precipitation in the Eastern U.S. is presented for 1955-6 in Figure 2 and for 1975-6 in Figure 3. It can be seen that the pH generally rises as distance from the center of the Ohio Valley increases. If the threshold value (the pH at which rain

Figure 2



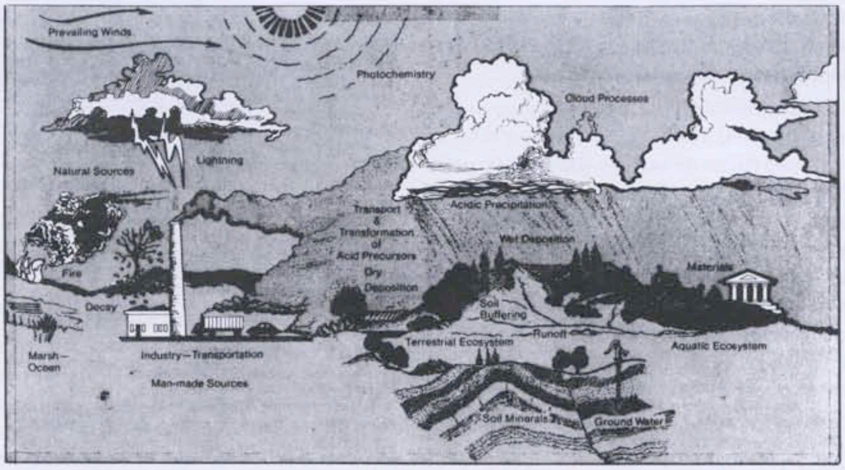
Annual Average pH of Precipitation
(Adapted from Likens, Sci. Amer. 241(4): 43-51, 1979)

Figure 3



Annual Average pH of Precipitation
(Adapted from Likens, note low pH produced as acid laden winds cool on rising over Adirondacks.)

Figure 4



Schematic of Acid Rain - from sources to areas of impact
Reprinted from The Interagency Task Force on Acid Precipitation. "National Acid Precipitation Assessment Plan." June 1982, p. 21

starts to have a destructive effect on sensitive areas) is taken to be 4.6, it can be seen that the area at potential risk, which encompassed parts of Ohio, Pennsylvania, New York, West Virginia and Virginia in 1956, had spread by 1976 to the entire Eastern U.S., except for the most southern tip of Florida.

Yet, acid rain has not damaged these areas equally. Some areas are very sensitive to acid damage while other regions, such as the midwest with its alkaline soils and bedrock, are not. Scandinavia, the northeast United States and eastern Canada are extremely sensitive for a number of reasons. First, they are downwind of both highly industrial regions and regions in which air stagnates and acids accumulate. Second, acids are not effectively neutralized because soils are thin and acidic and emit little ammonia. Third, these regions are densely forested and little fertilizer dust is present to neutralize rain. And fourth, these regions have a high annual rainfall and a large number of annual episodes of rain which lead to a high accumulation of acidic substances as the rain cleanses them from the air. New England, for example, averages 40-49 inches per year and precipitation occurs on an average of 120-150 days.

In addition, the importance of local sources of air pollution must not be ignored. Residual oils, the major fuels used in New England, contain vanadium compounds which catalyze acid formation. But according to 1982 data, the New England region (which has few industries or coal burning utilities) contained 5.3% of the U.S. population and contributed only 2.6% of the total NO_x and 2.4% of the total SO_x. Under the leadership of the New England Governors, further steps are being taken to reduce this local pollution.

Effects of Acid Rain On The Environment

Acid rain is generally considered to be detrimental to the environment, the most well-documented damage being to fresh water ecology where extinction of acid sensitive species and disruption of the food chain have been observed.

Soft water or bicarbonate lakes and ponds are particularly susceptible to damage. The drainage from the water sheds of these fresh water bodies is over acidic igneous bedrock which is ineffective in neutralizing acidity, although the soil and litter layer may have limited buffering capacity. The buffering capacity of the waterbody itself is primarily due to the presence of bicarbonate ions formed as carbon dioxide dissolves. As hydrogen ions are introduced by acid run-off and precipitation (Figure 4) they react with biocarbonate ions and carbon dioxide is expelled into the air. (This same buffering system is primarily responsible for the ability of the blood to maintain a constant pH. Acids formed as waste products of metabolism are neutralized in the blood stream and CO_2 is carried to the lungs and exhaled. An excessive excretion of acids into the blood as a result of disease can cause acidosis and eventual death, just as depletion of the buffers in a fresh water body may cause its acid death.)

The health of a lake may be evaluated on the basis of its ability to neutralize acid influx, i.e., its remaining buffering capacity (alkalinity) (see Table 1). It has been estimated that a drop in pH is not detectable until 70% of the alkalinity has been depleted. Thus, if only pH is measured, as was a common practice in the past, considerable damage may have already been done before any change is detected.

As pH drops below 6, changes in the aquatic ecosystem occur at all levels of plant and animal life. Most fundamental are decreases in the number of species and in the size of the colonies of the lowest members of the food chain, zoo- and phytoplankton. Microbiological activity is also decreased, thus inhibiting the decomposition of organic debris on the lake bottom. This not only diminishes the amount of nutrients released into the lake due to decomposition but, as debris accumulates, the influx of both nutrients and buffers from the lake bottom is diminished. In addition, as pH drops certain species of acid sensitive plants are replaced by more tolerant species such as sphagnum moss. The growth of sphagnum is detrimental because it can choke out other vegetation; furthermore, it absorbs metal ions and discharges hydrogen ions in their place, thus creating a more and more acidic environment.

Decline in salmon populations was first linked to low pH in Sweden in 1926. A further decline in the number of species and the total fish population in Scandinavia, Canada and the U.S. has been noted over the past 60 years, with the most dramatic losses occurring in the last 20 years.

Table I
Sensitivity to Acid Precipitation

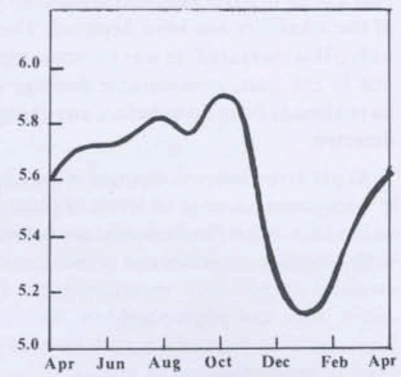
Sensitivity Category	Alkalinity (mg/l as $CaCO_3$)	Site, Plymouth County
Not Sensitive	20	Matfield River, E. Bridgewater*
Sensitive	10-20	Thirty Acre Pond, Brockton
Highly Sensitive	5-10	Carver Pond, Bridgewater
Endangered	2-5	Wampatuck Pond, Hanson
Critical	0-2	Lake Nippenicket, Bridgewater
Acidified	pH 5.0 or lower, 0	Snows Pond, Rochester

**Abnormally high alkalinity due to Waste Water Treatment Plant discharge*

***Note:** Interim Report of the Mass. Acid Rain Monitoring Program shows that of the 1200 water bodies tested; 70 are acid dead, 85% are sensitive and 35% are either endangered or critical.*

Two patterns of pH change can cause this drop in population. Snow melt and heavy rain in late winter and early spring can cause acid shock as large quantities of acid enter fresh water bodies when the ground is frozen (Figure 5). Alternatively, water bodies may experience a long-term gradual decline in pH.

Figure 5



Site: *Lake Nippenicket, Bridgewater, MA*
(Note acid shock resulting from January thaw)

Eggs and fish fry are particularly susceptible both to low pH and to fluctuations in pH. Acid shock which coincides with spawning and hatching is particularly damaging, especially if the pH drops below 5. Reduction of between 5-50% in viability of hatchlings can result in the eventual extinction of a species. A gradual decline in pH tends to adversely affect reproduction, spawning and development of gonads, leading to populations in which older, larger fish predominate. The most sensitive species, rainbow trout and salamanders, disappear as the pH drops below 6; plankton, crustaceans and shrimp start to disappear as the pH drops below 5 and virtually all fish and amphibians are gone and only a few acid resistant plants and invertebrates survive at a pH between 3.5 and 3.0.

The changes associated with acidification may be due directly to a change in pH, but the mobilization of toxic metals such as aluminum and mercury may also contribute. Aluminum compounds dissolved by acid rain produce gill damage, respiratory distress and death of fish at high concentrations and, if the concentration is low, they are absorbed into the blood and reduce the capacity of red cells to transport oxygen. Aluminum compounds also cause the precipitation of organic and inorganic materials from the water and may result in a decrease in nutrients, especially phosporus. And, as these materials precipitate, the water becomes increasingly transparent which favors the growth of sphagnum.

Swedish scientists have pioneered attempts to restore acid dead lakes by adding lime or limestone either directly to the lake or, preferably, by building limestone dams in feeder streams or by diverting these streams through limestone wells. Direct addition is of limited value unless it is repeated often, because the lime or limestone is deactivated as insoluble precipitates form on its surface. The return of fish and other vertebrates and invertebrates depends upon the concentration of toxic metal ions. If the concentrations are high, these species fail to survive even after a pH of 6 or above has been established. If concentrations are low, on the other hand, successful reintroduction has been reported.

Changes in the terrestrial ecosystem have not been traced to acid deposition as unequivocally as changes in fresh water have. However, evidence from laboratory studies suggests that this deposition causes disruption in nitrogen fixation and damage to the leaves of acid sensitive vegetation. From the study of tree rings, researchers in Sweden have concluded that the decrease in forest productivity since 1950 can be traced to acidification. A 50% reduction in the number of spruce trees in the Green Mountains of Vermont appears to be due to acid rain. Furthermore, it appears that nitric acid and its precursors NO_x rather than sulfuric acid and SO_x are primarily responsible for the destruction of forests. Since acidification increases the leaching of metal ions and other nutrients from the soil, the increased growth of acid resistant plants may be noticed in the short term. But toxic levels may be reached and nutrients may be depleted, leading to a long lasting and perhaps irreversible detrimental effect.

Buildings and works of art have also suffered from acid rain, which has accelerated the rates of metal corrosion and of the destruction of cement, plaster and limestone.

Finally, the potential damage to human health cannot be ignored. In addition to the obvious respiratory problems associated with the inhalation of acidic aerosols and particulates, the contamination of food and water supplies by toxic metals may present a hidden danger. Concern has been expressed about a possible link between the ingestion of aluminum and the faulty aluminum metabolism observed in Alzheimer's disease. This potential link, however, is purely speculative; dietary aluminum has not been shown, at this time, to cause the onset or to accelerate the progression of this disease. However, the potential accumulation of mercury in edible fish presents a serious threat as does the possible leaching of lead from old water pipes and of both lead and copper from home plumbing systems. Municipal water supplies have not been shown to contain these metals at levels above public health standards, but well waters and edible fish have not been widely tested.

Conclusion

The story of the acid rain problem in the United States has been a story of delay. Canada, which receives 4 to 5 times as much acid pollution from the U.S. as it transmits to the U.S., has been frustrated in its attempts to negotiate cooperative acid rain legislation. Public pressure has never been stronger for the solution of any environmental problem other than that of toxic waste disposal. Yet, no decisive action has been taken on the national level. Some propose that action be delayed until more is known or until better emission control devices are available. Although many uncertainties about the exact mechanisms of acid rain formation and environmental damage do exist, there is no question that damage is being done, that man-made sources are causing this damage, that preventive measures can be taken and that further delay can only exacerbate the problem.

The enjoyment of a warm summer shower, celebrated in many lyrics, cannot help but be tempered by the dire predictions for this *Thirsty Earth* if leaders of the industrial nations continue to ignore the legacy of this most sour drink.

Margaret Souza teaches organic chemistry at Bridgewater. She and Marilyn Furlong, a geographer at the college, are participants in the Acid Rain Monitoring Project coordinated through the University of Massachusetts. More than one hundred water bodies in Plymouth County, many of which are susceptible to acid rain damage, are currently being analyzed at Bridgewater in the second phase of this project.