Acid Lakes from Natural and Anthropogenic Causes

Ruth Patrick, Victoria P. Binetti, Steven G. Halterman

Summary. Lakes may be acid because of natural ecological conditions or because of anthropogenic activities. Apparently there has been a recent increase in acidity of many lakes in the northeastern United States. Factors that may be contributing to this increase include the use by utilities of precipitators, sulfur scrubbers, and tall stacks; the use of petroleum; and methods of combustion of fossil fuels.

Naturally occurring acid lakes have been known in several areas of the United States for more than a century. In recent years, some lakes have apparently become more acid, and this increase in acidity has been correlated with anthropogenic causes.

Naturally occurring acid lakes fall into two groups. The first are those that form in areas of igneous rock or in areas where the substrate is largely sand. These lakes are typically small, and the water has low conductivity. The carbonate-bicarbonate buffering capacity is weak and, as a result, the lake water is very susceptible to the effects of carbon dioxide. Such lakes often have a *p*H of 5.6 to 5.7, and they are very vulnerable to changes in *p*H. Many lakes of this type that have become more acid in recent years are located at high elevations.

The second group of naturally acid lakes occupy similar geological substrates, but over time they have accumulated considerable organic matter. Peat and bog plants are commonly associated with such lakes. Often they have a *p*H of 4.5, and their *p*H may be as low as 3.4.

The causes of this low *p*H vary, but small amounts of sulfate may be largely responsible, although the organic acids also contribute. The free sulfate radical may result from sequestering by the bog plants, such as *Sphagnum*, of the alkaline-earth metals associated with this radical (*1*). There is evidence that *Sphagnum* growth is favored by increased acidity (*2*). The sulfate radical and reduced sulfur compounds may be produced by biological activity in the sediments. Anaerobic conditions result in reduced sulfur compounds. Because of the large amount of organic acids and their salts (humates) associated with this second group of acid lakes, the heavy metals that are soluble under low *p*H conditions are mostly chelated by the humates, and they do not become toxic to many forms of aquatic life. Specialized floras and faunas have developed in such lakes and streams (*3*). They support species that have not been found in lakes and streams with a nearly neutral *p*H (circumneutral) that have recently been made acid.

Records at the Academy of Natural Sciences of Philadelphia indicate that naturally acid lakes and ponds associated with peat and *Sphagnum* have existed since the 1860's (*4–6*) in New England and New Jersey. Similar shallow lakes and ponds are also found in the southeastern states (*7*). The existence of the acid conditions of these lakes over a long period of time can also be documented by the vegetation of the watershed where one finds acidophilous trees 50 to 100 years old.

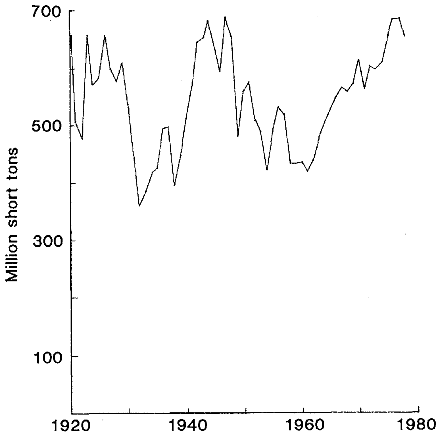

Fig. 1. United States coal production from 1920 to 1978 (*12, 13*).

Lakes with a *p*H of 3.4 to 4.5 contain many kinds of algae, particularly desmids and diatoms, a fair number of crustaceans, and some aquatic insects. The fish are not as diversified as in circumneutral lakes, but various characteristic fish are found. For example, the acid lakes of New Jersey contain the *Sphagnum* sunfish (*Enneacanthus obesus*), the blue-spotted sunfish (*E. gloriosus*), the yellow bullhead (*Ictalurus natalis*), the pirate perch (*Aphredoderus sayanus*), and the swamp darter (*Etheostoma fusiforme*) (*8*). These waters have apparently never supported significant natural populations of fish commonly found in circumneutral waters.

Under conditions of low *p*H, many chemicals are in a reduced state and exert an oxygen demand. As a result, the O_2 content of naturally acid lakes or those where increased acidity is caused by human activities is often much less than in circumneutral lakes.

A comparison of recently compiled data with data collected between 1920 and 1940, or even between 1950 and 1960, indicate that many lakes in New Hampshire and New York have become more acid (*9–14*). Many of these lakes contain peat and *Sphagnum* and have considerable aquatic life. Because methods of determining *p*H or acidity have varied, it is often difficult to state precisely how large the changes are, but for some of these lakes, data indicate a trend toward reduced *p*H and alkalinity. The fossil record of diatoms and pollen will have to be examined to establish trends over time.

When we examined the activities that are associated with acid rain, which is often correlated with increased acidity of lakes, several facts became apparent. The amount of coal produced and used over this period of time has varied (Figs. 1 and 2) (*15, 16*), but the amount produced and used in the 1920's and 1930's and in the middle 1940's in the United States is not very different from the amount produced and used today. The amount of anthracite coal burned has always been a small fraction of the total amount burned—approximately 11.5 percent before 1950 but declining to less than 1 percent by 1975 (*16*). It is difficult to obtain exact data for the amount produced and used in the corridor that would affect the northeastern states, but our data show a pattern similar to that

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for the entire United States. For example, the amount of coal burned in the corridor affecting the Northeast has increased at about the same rate as the amount of coal burned in the nation as a whole since 1960. This is based on the increase in coal-fired generating capacity in the corridor (*17*).

The dominant users of coal have changed since 1920 (Fig. 3). The use of coal for transportation has practically disappeared, whereas the use by industry has recently shown a slight decline and the use by electrical utilities has steadily grown.

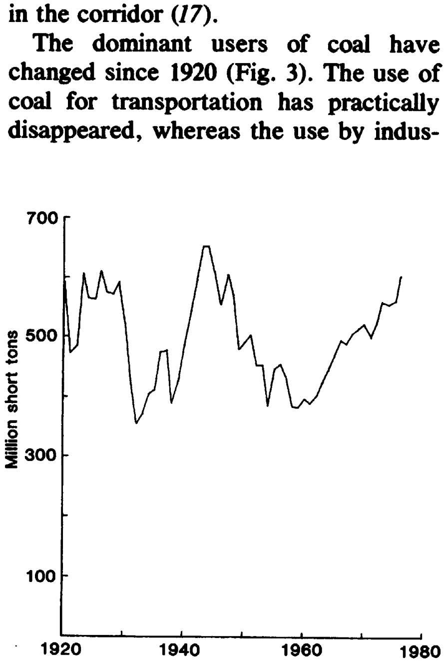

Fig. 2. United States coal consumption from 1920 to 1976 (*12, 13*).

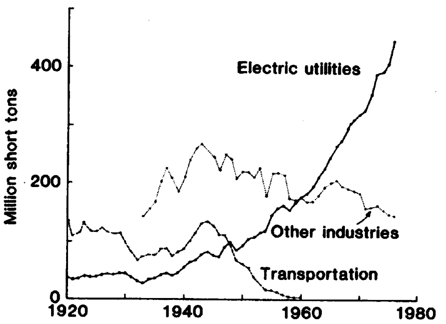

Fig. 3. Nationwide coal consumption by electric utilities, by other industries, and in transportation (railroads) from 1920 to 1976 (*13*).

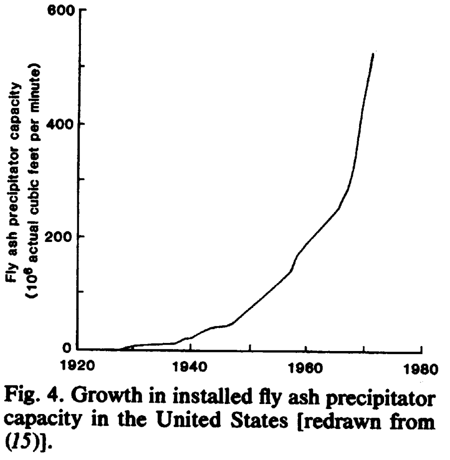

Fig. 4. Growth in installed fly ash precipitator capacity in the United States [redrawn from (*15*)].

The method of treating stack gases from the burning of coal has also changed. Although the first precipitator was installed about 1923, their real usage started about 1930; usage has greatly increased since 1950 and particularly since the mid-1960's (Fig. 4) (*18*). In 1975 all operating coal-burning power plants as well as new plants were required to control particulates, and the number of electrostatic precipitators greatly increased (*19*). The precipitators, which were used to capture fly ash, also removed the alkaline-earth metals that had interacted with the oxides of sulfur (SO_x) and of nitrogen (NO_x) produced by the combustion of fossil fuels.

Sulfur scrubbers came into use early in 1970 (Fig. 5) (*20*), and in 1978 they were required for all new generating plants that burned coal (*21*). The old plants, which emit an estimated 15 to 20 million tons of sulfur (*22*), were exempt from this regulatory requirement. In the scrubbing of sulfur, aerosols of sulfur are formed and emitted. For example, in a coal containing 2 to 3 percent sulfur, 90 percent of the sulfur is removed by scrubbing and about 8.2 percent goes out of the stack as an aerosol (*22*). The fine particulates in the aerosol are easily transported by the air.

The height of stacks at plants that burn fossil fuels has steadily increased, particularly after the mid-1960's (Fig. 6) (*23*). These tall stacks have been associated with acid precipitation because they introduce emissions into the atmosphere at elevations where they may be subject to transport over long distances. Since about 1975 a hotter combustion flame, which increases the amount of NO_x emitted, has often been used in the combustion of coal.

Although coal use has not increased significantly, there has been a great increase in the use of petroleum (Fig. 7) (*24*). The gases from oil-burning facilities are not controlled. They are very low in precipitates but contain varying amounts of SO_x and NO_x. Petroleum use in transportation has increased about 300 percent since 1940 and 179 percent since 1960 in the corridor believed to affect the northeastern United States (*25*). Many motor vehicles emit considerable NO_x and small amounts of SO_x.

In summary, it is evident that acid lakes may be produced naturally or by anthropogenic causes. Some naturally acid lakes are, according to the records, more acid today than formerly. Many lakes that contain humates support considerable aquatic life that has adapted to the acid conditions. The increase in acidity of these lakes in many cases has not greatly affected the aquatic life.

Some lakes recently made acid as a result of human activities may not have sufficient humates to chelate metals released in them and, as a result, conditions may exist that are toxic to most aquatic life. Such conditions have been

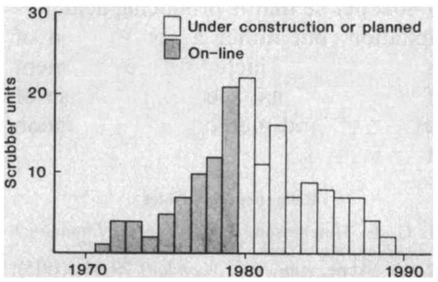

Fig. 5. Number of flue gas-desulfurization units installed at electric utilities each year in the United States (*17*).

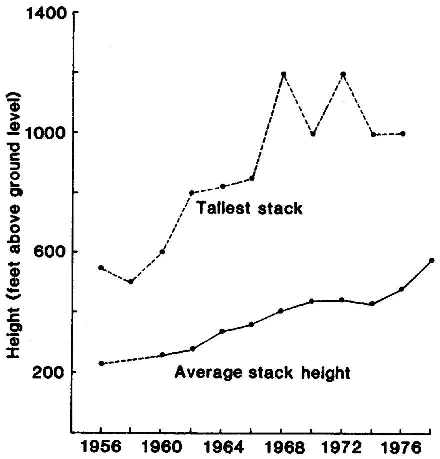

Fig. 6. Average stack height and tallest stack reported among power plants burning fossil fuels (bituminous, lignite, oil) included in biannual design surveys of new power plants, 1956 to 1978 (*20*).

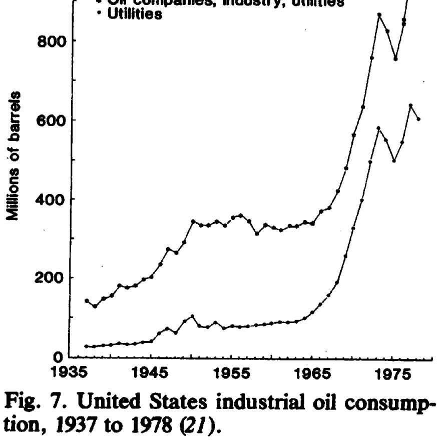

Fig. 7. United States industrial oil consumption, 1937 to 1978 (*21*).

observed by the senior author in Slippery Rock Creek in western Pennsylvania and in the headwaters of the Schuylkill River in eastern Pennsylvania where acid mine wastes enter circumneutral waters which are apparently very low in humates.

Several human activities produce SO_x and NO_x. The question is, which combination of these activities produces the most serious effects? From the data analyzed it appears that it is not the burning of coal per se that is producing acid precipitation, but rather a combination of many activities, including the treatment of stack effluents, the increased use of petroleum, and methods of combustion of fossil fuels.

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26. We thank the Environmental Assessment Council of the Academy of Natural Sciences for support of this work. We also thank C. L. Schofield of Cornell University, W. Lorenz and H. Elkins of the Sun Company, and R. Perhac of the Electric Power Research Institute for supplying us with information needed to carry out the research.

Transport of Energy in Muscle: The Phosphorylcreatine Shuttle

Samuel P. Bessman and Paul J. Geiger

The performance of muscle work was early recognized to be dependent on energy derived from chemical reactions within the tissue. In 1907, Fletcher and Hopkins (*1*) measured increased lactic acid in muscles fatigued to the point of rigor. Parnas and Wagner (*2*) showed that lactic acid was derived from muscle glycogen. Meyerhof (*3*, *4*) and his coworkers related lactic acid production to work done by the muscle.

Experiments on heat production, largely done by A. V. Hill (*5*) and his colleagues, revealed that the chemistry of the contraction itself was nonoxidative. Much later, in 1940, D. K. Hill (*6*) showed that oxygen was used only when contraction and relaxation were over. This "aerobic recovery heat" was virtually equal to the anaerobic work of contraction and relaxation. The initial heat of contraction was, however, much greater than could be accounted for by lactic acid formation.

The discovery of "phosphagen," that is, phosphorylcreatine, by Eggleton and Eggleton (*7*, *8*) and Fiske and Subbarow (*9*) supplied the answer to this question. Phosphorylcreatine was the first compound found to carry the "high energy" phosphate bond (*10*, *11*).

Meyerhof and Lohmann (*12*, *13*) quantified the energetics of phosphorylcreatine hydrolysis, and Lipmann and Meyerhof (*14*) showed that phosphorylcreatine breakdown during muscle activity was a reality, and not an artifact, by correlating contraction with the liberation of free creatine. Lundsgaard (*15*) observed phosphorylcreatine breakdown in contracting muscle poisoned with iodoacetate, which prevents lactic acid formation, and suggested that phosphorylcreatine was the energy donor for contraction, the role of glycolysis being to supply energy for resynthesis of the phosphorylcreatine (*16*, *17*). It was agreed that lactic acid formation was only indirectly related to muscle contraction. Phosphorylcreatine was thus established as the direct energy donor.

At this time, the discovery of adenosine triphosphate (ATP) complicated the picture (*18*, *19*). Meyerhof and Lohmann (*20*) observed the liberation of about 12 kilocalories per mole for each of the two terminal phosphates released from ATP by hydrolysis. Work in Englehardt's laboratory (*21*), amplified by Banga and Szent-Györgyi (*22*) and Straub (*23*), demonstrated that actomyosin contracts only upon addition of ATP. Lohmann

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