

CHAPTER 5

Effects of Acid Deposition on Tropical Aquatic Ecosystems

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5.1 INTRODUCTION

The relationship between anthropogenic activities atmospheric activity and environmental effects was first noted in Great Britain in the mid-nineteenth century (Smith, 1872). Since then, the phenomenon of acid deposition and its effects on aquatic ecosystems have been well documented in temperate regions in North America (NRC, 1986), Sweden (NSEPB, 1982) and Norway (Overrein *et al.*, 1980). These regions have an advanced industrial base (and the accompanying control technology) and aquatic ecosystems that are associated with young, recently glaciated soils or older, moderately weathered soils.

In few cases does our knowledge address the impact of acid deposition on tropical countries with emerging industrial bases and highly weathered soils. As a preliminary step to resolve this deficiency, this paper assesses the potential for acidification (defined as loss of alkalinity) of aquatic ecosystems in tropical areas. The chapter modifies current knowledge from temperate ecosystems to account for the special characteristics of tropical areas.

5.2 REVIEW OF CURRENT KNOWLEDGE

5.2.1 The Process of Acidification of Aquatic Ecosystems

For acidification of aquatic ecosystems by atmospheric deposition to occur, three conditions must be met. (1) the atmospheric deposition of sulfate, nitrate, or some other anion must increase; (2) the adjacent soils must not retain the anion that has experienced increased deposition; (3) the aquatic ecosystem must have a low alkalinity for acidification to result in biological damage. Aquatic ecosystems of this type are typically associated with acid soils.

The acidification of aquatic ecosystems is caused by an increased rate of deposition of any anion. The anion can be in the form of an acid or a salt. For example, if H_2SO_4 is deposited on an acid soil that does not retain sulfate, then the H_2SO_4 discharged from that soil to the aquatic ecosystem will result in acidification. Similarly, if increased amounts of CaSO_4 are deposited on the same soil, the sulfate discharged from the soil will be accompanied by Ca^{2+} and H^+ ions due to ion exchange reactions that occur in the soil between atmospheric Ca^{2+} and H^+ adsorbed on the soil. This phenomenon is termed the 'salt effect' and has been known to scientists for some time (Reuss, 1980, 1983; Reuss and Johnson, 1985). Thus, the most important atmospheric parameter in the acidification of aquatic ecosystems over the short term is not whether the deposition is acid, but rather the nature of the anion. If the anion is a 'mobile anion,' it can transport acidity from the acid soil to the aquatic ecosystem. The exact mixture of cations accompanying the mobile anion will reflect the cations in the initial deposition and the cations on the ion exchange sites in the soils adjacent to the aquatic ecosystem.

To this point, only two conditions have been addressed—increased deposition of an anion (as salt or acid) and the sensitivity of the aquatic ecosystem to acidification (the more acid the soil, the less the alkalinity of the aquatic ecosystem and the more likely the anion will mobilize H^+ from the soils into the aquatic ecosystems to neutralize the already low alkalinity).

A third condition speaks again to the soil but it addresses anion behavior as opposed to cation behavior. For increased deposition of an anion to acidify an aquatic ecosystem, it must not be retained by the soil. If it is retained, it will not mobilize H^+ from the soil into the aquatic ecosystem.

Table 5.1 Wet deposition of SO_4^{2-} to remote continental areas

	No. of samples	SO_4^{2-}			References
		Amount of Precipitation (cm)	Concentration ($\mu\text{eq/liter}$)	Deposition ($\text{g S/m}^2 \text{ year}$)	
East Africa	61	—	13	0.15	Rodhe <i>et al.</i> , 1981
Nigeria	—	—	8	0.11	Bromfield, 1974
Venezuela San Carlos	14	391	2.7	0.17	Galloway <i>et al.</i> , 1982
Brazil					
Amazon Basin	28	240	8.8	0.40	Stallard and Edmond, 1981
Lake Calado	59	200	3.8	0.12	Melack, unpublished data
Australia Katherine	120	112	4.7	0.064	Likens <i>et al.</i> , 1987

In summary, for aquatic ecosystems to be acidified by atmospheric deposition, increased atmospheric deposition of an anion must occur to an acid soil that does not retain the anion.

5.3 IMPACT OF ACID DEPOSITION IN THE TEMPERATE ZONE

This section discusses how the three conditions apply to aquatic ecosystems in temperate regions in the Northern Hemisphere and presents a model

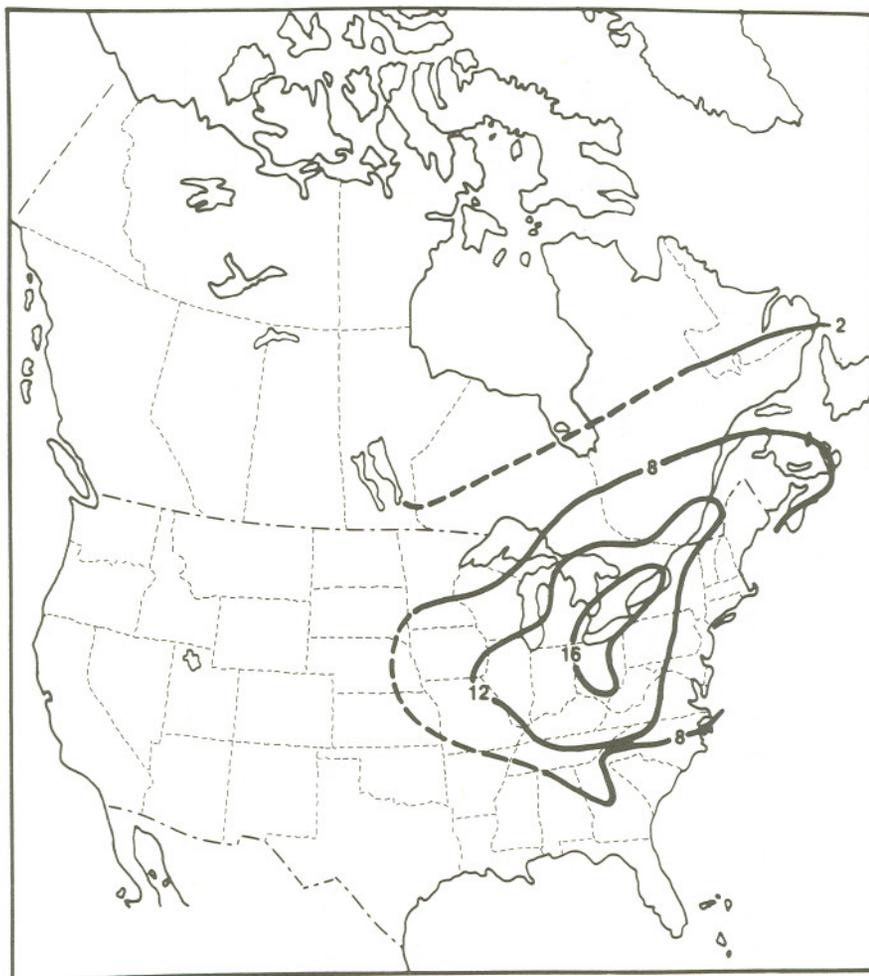


Figure 5.1 Enrichment factors for SO_4^{2-*} concentrations in North American precipitation in 1980 relative to remote areas (Galloway *et al.*, 1984) Copyright 1984, Science. Reprinted with permission. (* = excess, or non-seasalt SO_4^{2-})

that can be used to determine past, current and future responses of aquatic ecosystems to changes in atmospheric deposition.

5.3.1 Atmospheric Deposition

The deposition of sulfur and nitrogen to eastern North America has increased dramatically due to fossil fuel combustion (NRC, 1986). The magnitude of the increase can be estimated by comparing the average concentrations of SO_4^{2-} and NO_3^- in wet deposition from remote parts of the world (Table 5.1) to concentrations throughout eastern North America (Figures

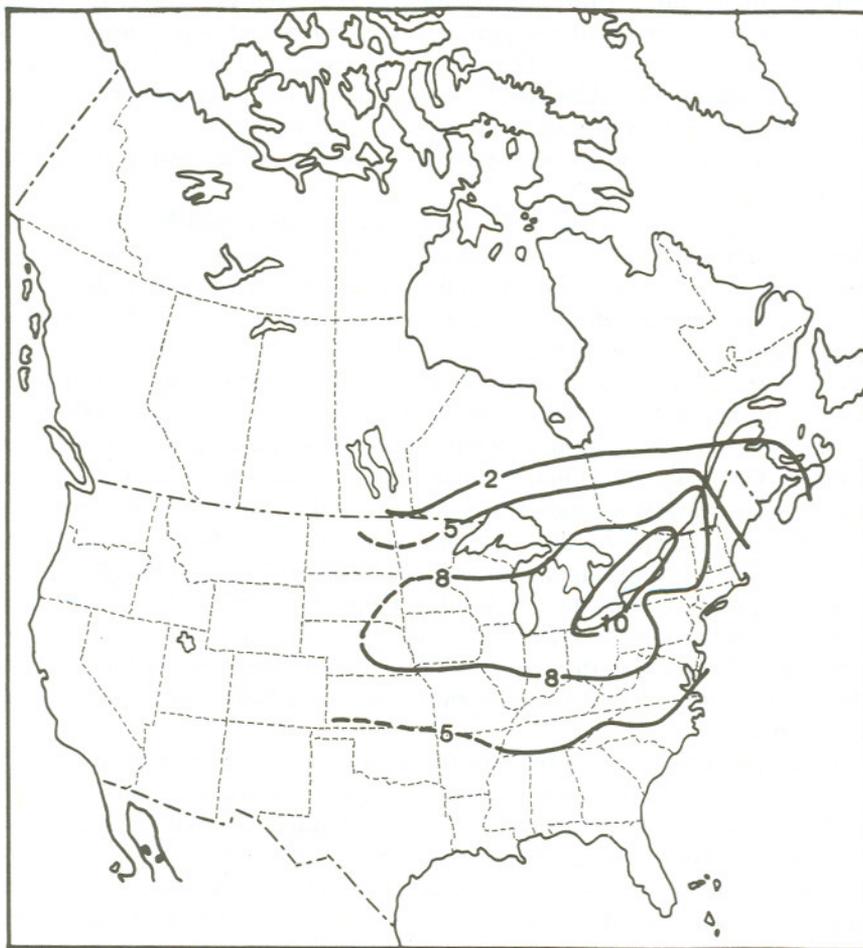


Figure 5.2 Enrichment factors for NO_3^- concentrations in North American precipitation in 1980 relative to remote areas (Galloway *et al.*, 1984)

5.1 and 5.2). The results show that the degree of enrichment of SO_4^{2-} and NO_3^- in North American wet deposition relative to remote areas is about an order of magnitude.

5.3.2 Sulfate Adsorption in Soils

Sensitive aquatic ecosystems that receive increased sulfate deposition are located throughout eastern North America. However, acidification has only been extensively documented in aquatic ecosystems of the northeastern United States and southeastern Canada (NRC, 1984, 1986). In the southeastern United States, acidification of aquatic ecosystems proceeds at a much slower rate, even though the area receives as much acid deposition and has low alkalinities (Figure 5.3). The reason for this different behavior is that soils in the southeastern United States have the ability to retain atmospheric sulfate and prevent its release to streams. The process providing this ability is sulfate adsorption; it provides temporary protection against acidification of aquatic ecosystems.

The adsorption of sulfate on a soil can be characterized by a Langmuir isotherm that relates the sulfate concentration in the soil solution to the amount of sulfate on the soil. As sulfur is added to a soil-water system, it is partitioned between the two in proportions determined by the shape of the isotherm. The shape of the sulfate isotherm can be characterized by two functions: E_{max} , the maximum amount of sulfate that the soil can absorb; and C , the half-saturation concentration. The very large E_{max} values of tropical soils relative to eastern North America (Johnson *et al.*, 1979; Gebhardt and Coleman, 1974) may indicate that tropical aquatic ecosystems are well protected against increased deposition of sulfur. However, the degree of protection will depend on the value of C , the half-saturation concentration, as well as E_{max} . For example, a soil with an E_{max} value of 40 meq/kg and C of 500 meq/m³ will respond in a similar manner to changes in sulfur deposition as a soil with an E_{max} of 8 meq/kg and a C of 100 meq/m³. Thus, to completely characterize the sensitivity of aquatic ecosystems to increases in sulfate deposition, complete details on the sulfate adsorption characteristics are required.

The impact of sulfate adsorption on stream acidification is illustrated in Figure 5.4 for regions of low sulfate adsorption (northeast United States) and moderate sulfate adsorption (southeast United States). In this figure the vertical arrows represent atmospheric deposition of sulfur (as sulfate); the horizontal arrows represent discharge of sulfate from the soils to the streams. The width of the arrow reflects the rate of deposition or discharge. The large box represents the soil reservoir; the dotted box within the large box represents the magnitude of the sulfate adsorption capacity of the soils. The smaller the box, the smaller the sulfate adsorption capacity. In the figure,

note that the rate of sulfur deposition is the same for the northeastern and southeastern United States. Also note that the soils in the northeast have a much smaller sulfate adsorption capacity than the soils in the southeast. This is due to the greater age and more highly weathered nature of the soils in the southeast.



Figure 5.3 Regions in North America containing lakes and streams that are sensitive to acid deposition. Shaded areas represent regions where bedrock is granitic or metamorphic with a low base supply. The isoline of pH 4.6 represents the annual average precipitation pH for 1980 (after Critical Assessment Review Papers, 1983)

If a sulfate reservoir in Figure 5.4 is filled, the soils become saturated with sulfate, and inputs (atmospheric deposition) equal outputs (discharge to soils). This is illustrated by the northeastern United States where satura-

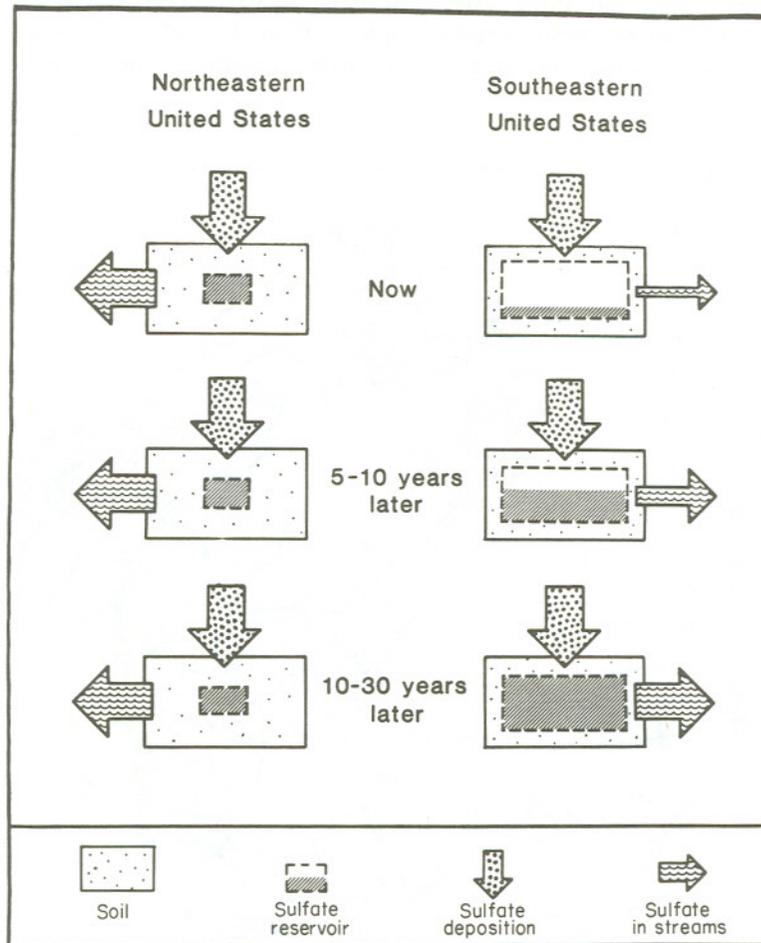


Figure 5.4 Response of soils to increased SO_4^{2-} deposition

tion of the sulfate adsorption capacity is caused by decades of past deposition. It is different in the southeastern United States. Although the amount of historical sulfur deposition has been essentially the same as in the northeast (NRC, 1986), the amount of sulfur discharged from the soils to the streams is substantially smaller than that deposited from the atmosphere because southeastern soils have a much larger sulfate adsorption capacity. However, as is evident from the figure, the sulfate capacity becomes saturated in southeastern soils as time progresses, and the amount of atmospheric sulfate released to the streams increases as a function of time. At the end

(10–30 years later), when the sulfate adsorption capacity is saturated, the inputs equal the outputs of sulfur.

5.3.3 Sensitivity of Aquatic Ecosystems

The spatial distribution of aquatic ecosystems with low alkalinity in North America is illustrated in Figure 5.3 together with an isopleth showing where the annual average pH of precipitation is less than pH 4.6. These sensitive aquatic ecosystems are primarily found in mountainous areas underlaid by granitic or metamorphic bedrock. The soils associated with this type of landscape are typically well drained and acid.

5.3.4 Estimating the Impact of Acid Deposition on Aquatic Ecosystems

5.3.4.1 Model Development

To determine the impact of changes in atmospheric deposition of sulfur on aquatic ecosystems, the relationships between atmospheric deposition and sulfate adsorption must be explored. Once the projected sulfate adsorption status of the soils is addressed and estimates of sulfur flux through the soils are made, it must then be determined whether the sulfate is accompanied by protolytic (H^+ , Al^{n+}) or non-protolytic (Ca^{2+} , Mg^{2+} , Na^+ , K^+) cations. The former will result in the acidification of aquatic ecosystems, the latter will simply increase their ionic strength. To determine the mixture of protolytic and non-protolytic cations, knowledge of ion exchange reactions, weathering reactions, hydrologic pathway and elemental uptake by forests must be obtained. With this many processes, each with their own time constants, the issue quickly becomes complex. As a tool to address this complexity, a simple model has been developed for use in eastern North America. The model, Modelling Acidification of Ground Water In Catchments (MAGIC), was developed as part of the Shenandoah Watershed Study (SWAS) by Jack Cosby, Richard Wright, George Hornberger, and this author. This section describes the model and draws extensively from a previous publication about the model (Cosby *et al.*, 1985a).

MAGIC assumes that atmospheric deposition and processes occurring in the soil are responsible for the observed surface water chemistry in a catchment. Alkalinity is generated in the soil water by the formation of bicarbonate from dissolved CO_2 and water:



The free hydrogen ion produced reacts with an aluminum mineral, such as gibbsite, in the soil:



Generally, the cation exchange sites on the soil matrix have a higher affinity for the trivalent aluminum cations than for divalent or monovalent base cations. An exchange of cations between the dissolved and adsorbed phases results in



where X denotes an adsorbed phase and BC^+ is a base cation.

Although we choose to represent exchange processes using aluminum-based cation interactions (Equation 3), the formulation is mathematically equivalent to exchange equations based on hydrogen ion/base cation interactions. The combination of a base cation (Equation 3) with bicarbonate (Equation 1) produces alkalinity (e.g. $\text{Ca}(\text{HCO}_3)_2$).

When the solution is removed from contact with the soil matrix and exposed to the atmosphere—that is, when water enters the stream channel—the CO_2 partial pressure of the solution declines. Carbon dioxide partial pressure in soils is commonly one to two orders of magnitude higher than atmospheric CO_2 partial pressure. However, the solution is no longer in contact with the soil matrix, so the cation exchange reactions no longer occur. The alkalinity and base cation concentrations are unchanged as water enters the stream channel.

If the exchangeable base cations in the catchment soils become depleted, less aluminum is exchanged from the soil water (Equation 3) so that the Al^{3+} concentration is higher and the base concentrations are lower in the water entering the stream channel. Less adsorption of aluminum by the soil also decreases soil and surface water alkalinity, producing low stream pH.

In this model the concentration of exchangeable base cations in the soil (the base saturation of the soil) is the major factor controlling the alkalinity (or acidity) of soil and surface waters. The process of acidification is controlled by the rate at which the base saturation of the soil changes. This in turn is affected by the rate of resupply through weathering of base cations from primary minerals and the rate of loss through leaching of base cations from the soil.

Leaching of base cations is affected mainly by the concentrations of strong acid anions, such as SO_4^{2-} , NO_3^- , Cl^- , and F^- , in the solution moving through the soil. If these increase in concentration, there must be an equivalent increase in cation concentration to maintain a charge balance. Initially, these additional cations are derived from the exchangeable base cations in the soil. As the base saturation declines, aluminum and hydrogen ions become increasingly important in maintaining the ionic charge balance, and the soil and surface waters become acidified.

The time scales of surface water acidification and the time lags between onset of deposition and surface water responses are complex functions of the interactions of the soil processes. It is not possible to determine these scales and lags analytically from a knowledge of the rates of the individual processes. The nonlinear interactions of these processes can be understood only through a series of speculative simulation experiments. When reasonable estimates of the rates of the processes, derived from field and laboratory studies, are used, MAGIC can be used to examine at least the orders of magnitude of the response times of catchments to acid deposition.

5.3.4.2 Model Application

To illustrate the use of MAGIC, a hypothetical catchment is constructed with characteristics similar to White Oak Run, Shenandoah National Park, Virginia in the southeast United States. White Oak Run (515 hectare) has one major perennial tributary, hillslopes are steep, and soils thin and rocky. White Oak Run is covered with second growth mixed chestnut and white oak forest. It is underlain by early Cambrian quartzites and shales (Weaverton, Hampton and Erwin formations); quartz and sericite are the dominant minerals in bedrock with minor orthoclase (Schwab, 1970, 1971; Gathright, 1976). Soils are formed from underlying bedrock and are generally similar throughout the two watersheds. A thin A horizon (0–5 cm in depth) overlies a B horizon, which grades into saprolite to 60–100 cm. Color and texture are uniform through the B horizon, although there are chemical and mineralogical changes with depth. Soils are silty or silty clay loams, and are classified as Hapludults, Dystrochrepts, and Udorthents (Hockman *et al.*, 1979; USDA Soil Conservation Service).

Soil chemistry reflects the aged, highly weathered soils in White Oak Run; soils are acidic and base saturation averages 2%. Soil mineralogy is dominated by quartz and dioctahedral mica (sericite) at the base of the profile, with the mica weathering to a 10–14 'dioctahedral vermiculite' at the top of the B horizon. In the A horizon, mica has collapsed to 10.5. Minor kaolinite is present throughout the column, probably formed from orthoclase in bedrock. Values for the sulfate adsorption capacity ($E_{\max} = 8$ meq/kg) are similar to values used by Cosby *et al.* (1984, 1985b, c).

A square wave (on-off) sulfur deposition sequence was used as input to the model. The deposition square wave was constructed using currently measured atmospheric deposition at White Oak Run for the "on" portion of the sequence (Cosby *et al.*, 1985b, c). Estimated background atmospheric deposition at White Oak Run was used for the "off" position (Cosby *et al.*, 1985b, c; Galloway *et al.*, 1982).

In this model, background deposition is initially in a steady state. After 20 years the deposition is assumed to increase within 1 year to currently

observed levels and remains 'on' at this level for 120 years. The deposition then decreases to background levels and remains 'off' for the next 140 years.

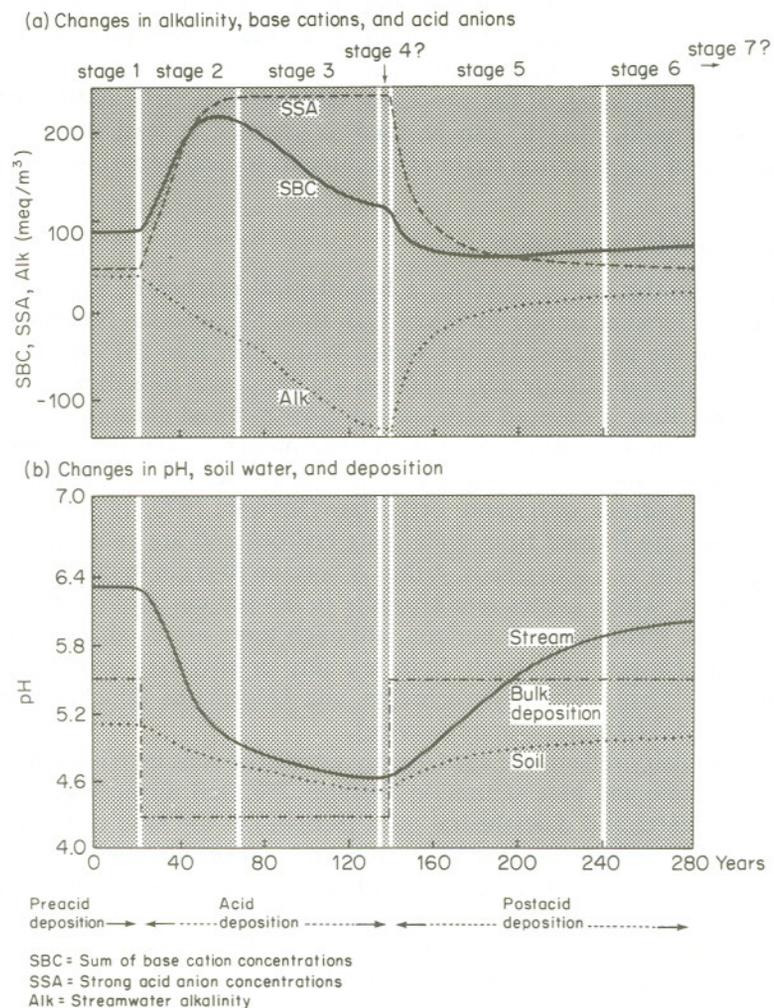


Figure 5.5 Predictions of the model MAGIC for a square wave increase in the acidity of bulk deposition. Reprinted with permission from Cosby et al., *Environmental Science and Technology*, 19, 1144–1149. Copyright (1985) American Chemical Society

The results of the modeling experiment (Figure 5.5) are divided into the stages of acidification and recovery proposed by Galloway *et al.* (1983) as a convenient means of comparing the time scales of changes in water quality.

Stage 1—Preacidification

This is the steady state prior to the increase in atmospheric deposition of sulfur, represented by the first 120 years of model output. Recovery of the hypothetical catchment after deposition ceases is assessed by the rate at which the water quality variables return to preacidification levels.

Stage 2—Undersaturated sulfur adsorption capacity

During this stage there is a lag in the increase of strong acid anion concentrations (SSA in Figure 5.5, principally SO_4^{2-}) as the soils adsorb the atmospherically derived sulfur. As anion concentrations slowly increase, base cation and protolytic cation concentrations increase and the latter cause alkalinity to decrease (Figure 5.5). Given the sulfur adsorption characteristics of the model catchment, 40–50 years must elapse before stream sulfur concentrations stop increasing and the catchment can achieve a sulfur input–output steady state. In this hypothetical catchment the alkalinity is depleted ($\text{Alk} \leq 0$, Figure 5.5a) after approximately 20 years. The rate of supply of base cations from soil cation exchange reactions reaches a peak after approximately 30 years, as indicated by the plateau and downward turn in base cation concentrations. The response time for the initial acidification of the catchment is 20–40 years.

Stage 3—Saturated sulfate adsorption capacity

Concentrations of anions reach a new steady value as the soil sulfate adsorption sites are filled and the dissolved–adsorbed sulfate equilibrium is reestablished. The flux of high concentrations of anions through the soil continues to deplete the store of exchangeable base cations. Even though the catchment reaches a steady value of sulfate in 45 years (stage 2), base cation concentrations continue to decline for an additional 55 years. The response time of continued acidification of the catchment—when it is no longer accumulating sulfur from atmospheric deposition—is at least 50 years.

Stage 4—New steady state at the higher level of atmospheric deposition

Base cation concentrations should return to preacidification levels because at steady state these are controlled only by the primary mineral resupply rate. Stage 4 is not achieved in this example. However, the rates of change of base cation concentrations and alkalinity decrease markedly near the end of stage 3 and appear to approach asymptotic values by year 140 of the simulation. This hypothetical catchment's response to an approximately ten-fold increase in sulfur deposition required about 100 years to complete.

Stage 5—Supersaturated sulfate adsorption capacity

This stage begins when deposition decreases to the initial low level. The rate of decline of streamwater anion concentrations will depend on conditions in

the soil because sulfate adsorbed by the soil must be flushed from the system. As the anion concentrations decrease, the base cation concentrations will also decrease, and alkalinity will begin to increase as fewer hydrogen and aluminum ions are needed to balance the strong acid anions. The acidification and recovery curves produced by MAGIC are notably asymmetric. The recoveries estimated by the model are initially rapid but become progressively slower. The model shows a return of strong acid anion concentrations to preacidification levels by year 280, and stage 5 lasts approximately 100 years. Desorption of the SO_4^{2-} accumulated in the soil takes nearly twice as long as the initial adsorption.

Stage 6—Recovery of soil base saturation

After the anions have returned to their preacidification levels, there is a further lag in the recovery of base cation concentrations and alkalinity. Until the soil base saturation has returned to preacidification levels, recovery of stream base cation concentrations and alkalinity will not be complete. The recovery process appears to take approximately twice as long as the initial acidification. Recovery time for this hypothetical catchment is 150–200 years.

Stage 7—Return to preacidification steady state.

This stage in the conceptual model of Galloway *et al.* (1983) is achieved only after an additional 80 years of simulation beyond that shown in Figure 5.5.

The simulated responses of the pH of streamwater and water that come into contact with the soil matrix—soil water (Figure 5.5b)—are also asymmetric. However, the magnitude of the changes in soil water pH is much smaller than the corresponding changes in surface water pH. Soil water and streamwater pH response times are measurable in decades. As with the other water quality variables, the recovery of pH takes much longer than the initial depression.

This example shows that the aquatic ecosystem of this catchment responds to acidification over a long period (decades) and requires a longer time to recover once acid deposition is terminated. The degree of response (e.g. amount of acidification) and the long time scales are the direct result of the three conditions for acidification: (1) the input of the acid, (2) the soil sulfate adsorption capacity, and (3) the alkalinity of the aquatic ecosystem and the acidity of the soils. The actual values selected for these three conditions are characteristic of the southeastern United States. They are not characteristic of tropical areas. The next section discusses the three acidification conditions with respect to tropical areas and applies the model MAGIC to determine the response of tropical aquatic ecosystems to variations in sulfate adsorption capacity.

5.3.4.3 Cautionary Note

This model is a relatively simple mathematical description of the interaction of several processes affecting acidification phenomena. The model's simplicity makes it easy to understand conceptually (Galloway *et al.*, 1983) and to set parameters (Cosby *et al.*, 1985a, b, c). However, due to its simplicity, the model may not be immediately usable in all areas. For example, the hydrological module has only one reservoir, the sulfate reduction process is ignored, and mineral weathering rates might not be constant as is assumed. Despite these problems, the model is useful as a tool for understanding the general response of aquatic ecosystems to change in the rates of atmospheric deposition.

5.4 ACIDIFICATION OF TROPICAL AQUATIC ECOSYSTEMS

5.4.1 Atmospheric Deposition

The first of the three conditions that must be met for acidification of aquatic ecosystems to occur is increased deposition of a mobile anion that will facilitate a transfer of protolytic cations from the soil to the aquatic ecosystem. The potential anions are sulfate, nitrate, chloride, and fluoride. In addition to natural sources, their sources are a combination of fossil fuel combustion, agricultural burning and roasting of minerals. Of these anions, nitrate can generally be eliminated from consideration due to its efficient utilization by terrestrial ecosystems. Exceptions are in cases where the ecosystem is limited by a different element or where the passage of water through the ecosystem is too fast to allow efficient nitrate uptake.

Chloride increases in atmospheric deposition would be of special concern, as Cl^- usually is not absorbed by soils. Increased rates of atmospheric deposition would be reflected rapidly in increases of surface water concentrations.

In the case of fluoride, substantial quantities are emitted to the atmosphere during the roasting of clays. This is of special concern in developing countries, where bricks are common construction materials. Fluoride however, is tightly absorbed by soils (Sanchez, 1976) and thus the impact of increases in atmospheric deposition of fluoride on aquatic ecosystems might be prevented or significantly delayed due to soil adsorption.

Based on past experiences in North America, sulfate and nitrate are the most likely mobile anions to increase their rates of atmospheric deposition. However, since nitrate is effectively taken up by the terrestrial ecosystem, sulfate is the primary anion that causes long-term regional acidification of aquatic ecosystems in temperate regions (NRC, 1986). Therefore, the rest of this chapter will use sulfate as an example to illustrate the impact of the increased deposition of an anion on aquatic ecosystems.

In the absence of historical data, the magnitude of the increase in atmospheric deposition of sulfur species can be estimated with data from remote areas of the world unaffected by anthropogenic activities. The limited data on the concentrations of sulfate in wet deposition in remote areas (Table 5.1) show that concentrations range from 2.7 to 13 $\mu\text{eq/liter}$ with a median value of 5.8 $\mu\text{eq/liter}$. The sources of the sulfate most likely are atmospheric oxidation of reduced sulfur gases released from soils and vegetation. However, as mentioned previously, total wet and dry deposition of sulfur species must be considered. Using the data in Table 5.1, together with the available data on dry deposition rates, wet and dry deposition rates of sulfur to remote continental areas are estimated to be 0.2 and 0.1 $\text{g/m}^2/\text{year}$, respectively (Figure 5.6) (Galloway, 1985). These average fluxes vary considerably. For dry deposition, the variability is due to uncertainties in atmospheric concentrations, uncertainties in deposition velocities, and limited data. For wet deposition, the variability is due to spatial differences in precipitation rates and limited data on precipitation concentrations of sulfate in remote continental areas.

The sulfate concentration and deposition data from remote areas presented in Table 5.1 and Figure 5.6 can be compared with the data on precipitation chemistry from the case studies presented in this volume. This comparison can be used to determine the current impact of anthropogenic activities on precipitation composition. While anthropogenic activities cer-

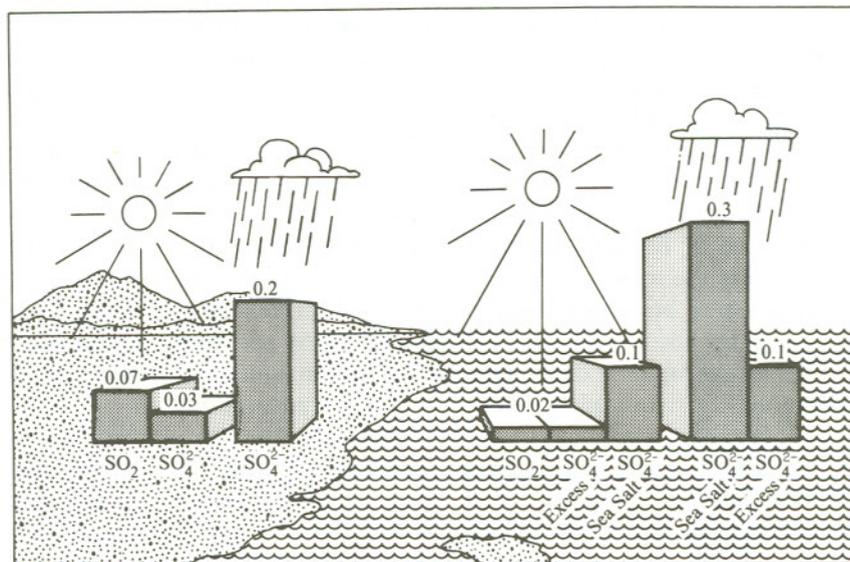


Figure 5.6 Wet and dry deposition rates of sulfur species to remote continental areas ($\text{g S/m}^2/\text{year}$) (Galloway, 1985)

tainly affect the urban areas of Venezuela, Sanhueza *et al.* (1987) indicate that the impact is less than in industrialized countries of the temperate region. The rural areas of Venezuela have levels of sulfate concentrations and depositions closer to, but still higher, in some cases substantially higher, than those observed in remote areas. At this time, due to the unknown natural variability of precipitation composition in remote areas, uncertainties in Venezuelan data caused by the sulfate method of chemical analysis (turbidimetry), and a limited number of samples from Venezuelan rural areas, it is impossible to determine the degree of impact that anthropogenic activities have on precipitation composition in rural Venezuela.

Ayers and Gillett (1988) summarize the data on precipitation chemistry for tropical Australia. They cite volume-weighted average (VWA) sulfate concentrations from seven data sets (three unpublished) during the period 1977–1985. The VWA concentrations range from 6.4 to 28.8 $\mu\text{eq/liter}$ with a median of 5.2 $\mu\text{eq/liter}$ and an arithmetic mean of 6.3 $\mu\text{eq/liter}$. As Ayers and Gillett discuss, the variability of the data is probably due to natural variations in the contributions from sulfate salts in soils and to SO_2 oxidation. Although the SO_2 sources are not specified, the concentrations of sulfate in precipitation are similar enough to remote areas (as discussed in Ayers and Gillett, 1988 and in Galloway, 1985) to exclude a substantial impact of anthropogenic activities on sulfate concentrations.

The case study on China presents little data on the composition of precipitation in tropical regions. However, the data presented for the subtropical region indicate that anthropogenic activities in urban and rural areas have a substantial impact on precipitation composition due to population density and combustion practices. Relative to remote areas of the world, precipitation in China is enriched in sulfate 14 to 80 times (Galloway *et al.*, 1987). This enrichment is larger than that between remote areas and the United States (Galloway *et al.*, 1984) and represents, as Zhao and Xiong (1988) discuss, a possible effect on ecosystems.

The combustion of fossil fuels is the primary source of increased sulfate in atmospheric deposition. The extent of the impact of fossil fuel combustion on atmospheric deposition is clearly dependent on the amount of fuel burned and on how the fuel is burned. The topic of fossil fuel combustion practices covers many areas. I discuss two: the removal of particulates from the combustion plume and the height of emission of the plume to the atmosphere. These topics are especially appropriate for tropical regions given the preponderance of developing countries.

If particulates are not removed from the plume by electrostatic precipitators or other devices, it is likely that the pH of the precipitation associated with the plume will be higher due to the alkaline nature of fly ash. However, this will not substantially reduce the potential for the atmospheric deposition to acidify aquatic ecosystems. Salts as well as acids can result in acidification.

In developing countries short stacks are commonly used. This practice results in greater spatial variability in precipitation composition. For example, according to the case study on southwestern China, the annual average pH of precipitation over an area of 0.5×10^6 km² varies from 4.2 to 6.2. In an equivalent area of eastern North America, the annual average pH varies from 4.1 to 4.4. The difference in spatial variability is due to differences in emission densities and stack heights. Two consequences of the increased spatial variability are that the rate of sulfur deposition in the local area of emissions is increased, and long-distance transport of the emitted material is limited. Thus, sulfur deposition will be variable over small scales, and the acidification of aquatic ecosystems will be more of a local and not regional phenomenon compared to countries with taller stack heights.

In summary, the available data on the composition of precipitation in tropical countries indicate a range of patterns, from composition unaffected by anthropogenic activities to composition severely affected. The following section addresses the state of knowledge on the other two conditions that need to be met for anthropogenic acidification of tropical aquatic ecosystems to occur.

5.4.2 Anion Adsorption Capacity of Tropical Soils

Sulfate adsorption in soils has been widely studied and has been associated with a variety of soil properties, including soil acidity (Chao *et al.*, 1964; Hingston *et al.*, 1967; Couto *et al.*, 1979; Johnson and Cole, 1980), iron and/or aluminum oxyhydroxide content (Chao *et al.*, 1964; Alymore *et al.*, 1967; Barrow, 1967; Haque and Walmsley, 1973; Johnson *et al.*, 1980), clay content (Neller, 1959; Haque and Walmsley, 1973; Johnson *et al.*, 1980), degree of soil weathering (Johnson and Henderson, 1979), and degree of exposure to acid precipitation, i.e. degree of sulfate adsorption saturation (Shriner and Henderson, 1978). Negative relationships between adsorbed sulfate (or sulfate adsorption capacity) and soil organic content have also been reported (Barrow, 1967; Haque and Walmsley, 1973; Couto *et al.*, 1979; Johnson *et al.*, 1980, 1982). These influences on the magnitude of sulfate adsorption capacity can be summarized by the statement that the older and more acidic the soil, the greater its sulfate adsorption capacity.

Highly weathered, acid soils are common in humid tropical regions. These characteristics, coupled with the lack of organic matter, result in soils with a large capacity for anion adsorption (Mekaru and Uehara, 1972; Sanchez, 1976; Uehara and Gillman, 1981; Gebhardt and Coleman, 1974; Barrow *et al.*, 1969). In a review of sulfate adsorption capacity (E_{\max}) of tropical soils, Sanhueza *et al.* (1988) cite a minimum value of 20 meq/kg and a maximum value of 60,000 meq/kg for a variety of soil types. Andepts appear to have

the largest values and Alfisols and Oxisols the lowest values. The importance of sulfate adsorption as a process to delay acidification of aquatic ecosystems in tropical regions is illustrated by the fact that in regions of southeastern United States, where delayed acidification of surface waters is documented, values of E_{\max} are only 5–10 meq/kg—substantially less than the values for tropical soils given above. As we will see in a latter section, the ability of tropical soils to adsorb anions can control acidification rates of tropical aquatic ecosystems in areas receiving increased atmospheric deposition of sulfate.

5.4.3 Sensitivity of Aquatic Ecosystems in the Tropics

Once the first two conditions have been met, the third condition for acidification of aquatic ecosystems by changes in atmospheric deposition requires that the aquatic ecosystems have low alkalinity. Such systems are commonly associated with highly weathered, acid soils. Tropical terrestrial ecosystems can have extremely acid soils due to their age, amount of rainfall, and other factors. In the tropics, 51% of the soils are highly weathered, leached soils (Oxisols, Ultisols, Alfisols) (Sanchez, 1976; Jordan, 1985). It is expected, therefore, that tropical regions can have an extensive distribution of low alkalinity aquatic ecosystems.

Many of the tropical case studies presented in this volume substantiate this expectation. In southern China, alkalinities of major rivers can approach 300 $\mu\text{eq/liter}$ indicating that substantially lower values are probable upstream (Zhao and Xiong, 1988). In Australia, the limited data available suggest that some aquatic ecosystems in the Northern Territory have alkalinities low enough (<200 $\mu\text{eq/liter}$) to be considered sensitive to acidification (Ayers and Gillett, 1987). The major rivers of South America have alkalinities that are among the lowest in the world (Sanhueza *et al.*, 1988). Alkalinities for entire river systems in the Orinoco basin of Venezuela can be less than 100 $\mu\text{eq/liter}$ and, as Sanhueza *et al.* state, the systems can be considered very sensitive to acidification.

In summary, tropical countries meet the three conditions of acidification of aquatic ecosystems: the composition of atmospheric deposition in tropical countries is beginning to change due to industrialization; the alkalinities of aquatic ecosystems over large regions are low enough to make the ecosystems susceptible to acidification; in some cases, acidification may be delayed or prevented by the high sulfate adsorption capacity of tropical soils.

Unfortunately, the data necessary to rigorously evaluate the three conditions are lacking, and more data are required before definite conclusions can be drawn. The first chapter of this volume presents suggestions on how the necessary data can be obtained.

5.4.4 Rates of Acidification of Tropical Aquatic Ecosystems

Although the available data are sparse, there is enough information to illustrate how changes in atmospheric deposition will affect tropical aquatic ecosystems.

The impact of acid deposition on tropical, relative to temperate, aquatic ecosystems is illustrated by using MAGIC to determine the response of three aquatic ecosystems associated with soils that vary in their ability to adsorb sulfate. The first aquatic ecosystem is associated with a soil with a low sulfate adsorption capacity ($E_{\max} = 0.5$ meq/kg), representative of the northeastern United States. The second aquatic ecosystem is associated with a soil having a moderate sulfate adsorption capacity ($E_{\max} = 8$ meq/kg), representative of the southeastern United States. A third aquatic ecosystem is associated with a soil having a high sulfate adsorption capacity ($E_{\max} = 40$ meq/kg). This value is common among tropical soils, but is probably too low to represent all tropical soils, since soils with values of E_{\max} in excess of 100 meq/kg are not uncommon (Gebhardt and Coleman, 1974; Rajan, 1979). In this simulation a value of $C = 100$ meq/m³ for the half-saturation concentration of the sulfate adsorption isotherm is used. The impact of this selection will be discussed later. In the simulation all three systems have identical characteristics (e.g. acid deposition sequence, soil characteristics) except for E_{\max} .

The atmospheric deposition sequence (Figure 5.7a) is a square wave. Sulfate deposition increases after an initial period of low deposition. The increased sulfate deposition remains constant for a period and then decreases back to initial conditions. The response of the sulfate concentrations of the three aquatic ecosystems to the increased sulfate deposition shows quite different behavior (Figure 5.7b). The aquatic ecosystem with low sulfate adsorption soils follows the atmospheric deposition sequence closely. Changes in deposition are quickly matched by increases in sulfate concentrations in the aquatic ecosystem. Lag times are only a few years. The aquatic ecosystem with moderate sulfate-adsorbing soils has larger lag times, on the order of decades. The aquatic ecosystem with high sulfate-adsorbing soils has a very long response time. Changes in sulfate deposition are not reflected in the sulfate concentration in the aquatic ecosystem for about a century (Figure 5.7b).

As the sulfate concentrations in the aquatic ecosystems increase, the pH decreases (Figure 5.7c). The magnitude of the decrease is dependent on the initial pH, the soil acidity, and the amount of primary mineral weathering. The more acid the soil, the greater the decrease in pH associated with a given increase in sulfate concentration.

From these three examples, it is evident that soils of moderate to high sulfate adsorption capacity will provide protection to aquatic ecosystems from increased deposition of sulfate for periods of at least decades. However, the

Response of stream pH and $[SO_4^{2-}]$ to changes in atmospheric deposition

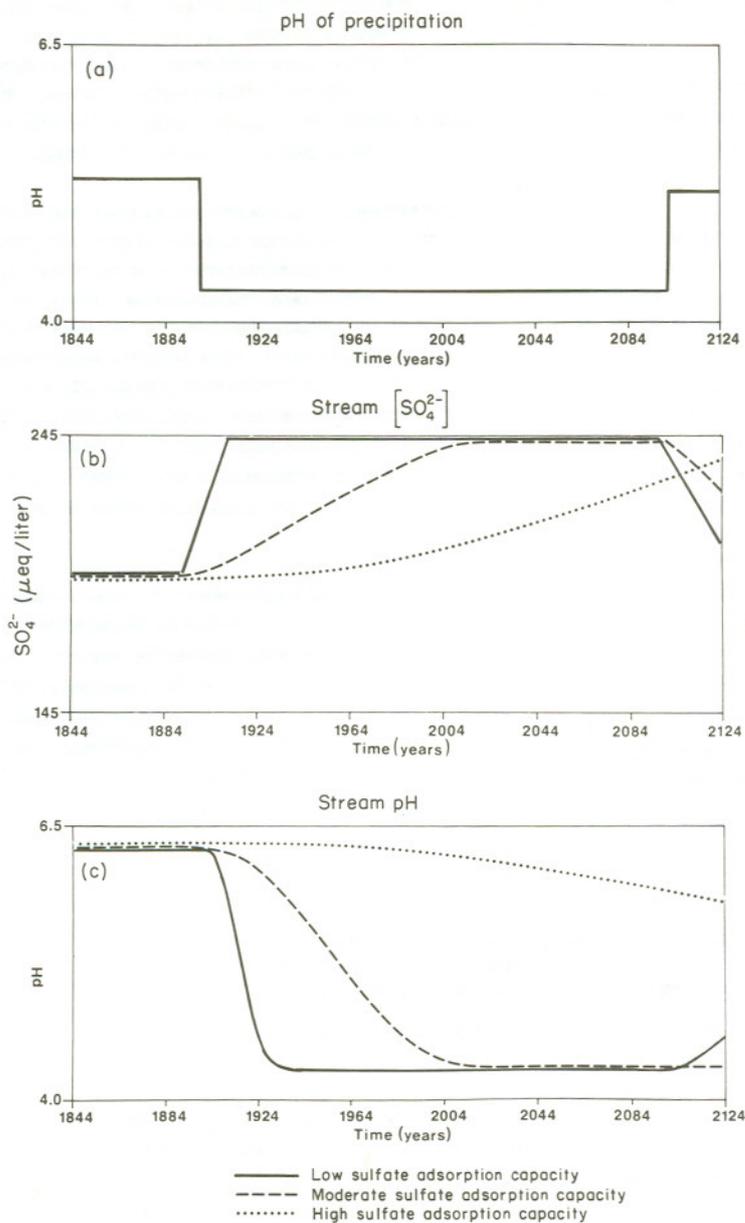


Figure 5.7 Changes in pH of three aquatic ecosystems, associated with soils having different sulfate adsorption characteristics, to changes in sulfate deposition

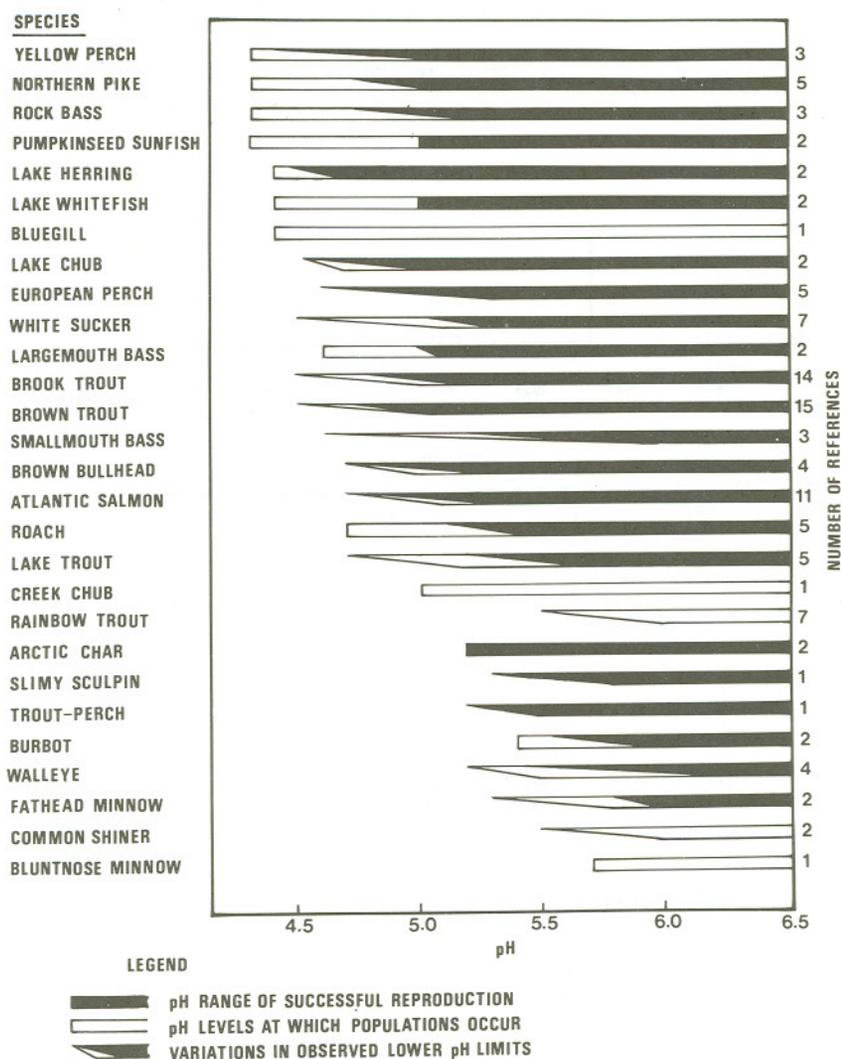


Figure 5.8 Initial estimates of relationships between acidity and fish response (Reproduced with permission from Critical Assessment Review Papers)

higher values of E_{max} in tropical soils will only provide long-term protection to aquatic ecosystems if the values of C (half-saturation concentration) are small ($\leq 100 \text{ meq/m}^3$). For a definitive determination of the impacts of sulfur deposition on a specific aquatic ecosystem, the soil associated with that ecosystem must be characterized.

The relative rates of three processes, atmospheric deposition, anion ad-

sorption and alkalinity generation, define the rate of chemical change. To complete the discussion of acidification of aquatic ecosystems, a fourth process—biological activity—must be considered. As the pH of an aquatic ecosystem decreases due to acidification, a host of biological changes occur, generally over very short time periods (within a year). These changes occur at all levels of the aquatic ecosystem from bacteria to fish, from plankton to macrophytes (Critical Assessment Review Papers, 1983). Over the past few decades an appreciable literature on responses of fish populations to pH changes has developed. As one would expect, not all species are affected to the same degree. Figure 5.8 illustrates the impact of pH changes on different fish species. There are several species that either cannot reproduce or survive in the pH range 5.5 to 4.5, which is characteristic of aquatic ecosystems acidified by changes in the composition of atmospheric deposition.

It should be noted that these data are from temperate regions. A similar data set is necessary for the biota of tropical regions.

5.5 CONCLUSIONS

The following points are offered in summary.

1. Acidification of aquatic ecosystems results from increases in the atmospheric deposition of a mobile anion to an acid soil. Of the possible anions, sulfate is a likely candidate.
2. The rate of acidification of the aquatic ecosystem is dependent on the rate of change in atmospheric deposition, the sulfate adsorption characteristics of the soils, and the acidity of the soil.
3. Aquatic ecosystems associated with acid soils of moderate to high sulfate adsorption capacity will acidify over the span of decades. Aquatic ecosystems associated with low sulfate adsorption soils will acidify more quickly.
4. Tropical soils are generally quite acid due to their age and humid environment. However, because of their acidity, the high concentrations of iron and aluminum oxy-hydroxides gives them a high sulfate adsorption capacity. In these types of systems, acidification of aquatic ecosystems may be extensively delayed after the onset of the mobile anion.
5. Once acidification of aquatic ecosystems occurs, biological changes are rapid and extensive.

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