

A National Program for Assessing the Problem
of Atmospheric Deposition (Acid Rain)

A Report to the Council on Environmental Quality



NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

A research program sponsored by the
Association of State Agricultural Experiment Stations
of the North Central Region • NC-141

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The National Atmospheric Deposition Program was organized by the North Central Region of the State Agricultural Experiment Stations to access the magnitude of the atmospheric deposition of both beneficial and injurious substances and to determine the effect of these substances on terrestrial and aquatic ecosystems. With the cooperation of a number of federal agencies and state and private organizations, the program is undertaking efforts to:

Establish an atmospheric deposition monitoring network to determine spatial and temporal trends in the supply of beneficial nutrient elements and injurious substances in precipitation and dry particulate matter in various regions of the United States;

Determine the relative importance and contribution of precipitation, dry particulate matter, aerosols, and gases to the total atmospheric deposition in various states and regions; and

Coordinate research on the effects of changes in atmospheric deposition on: (a) the productivity of agricultural crops, forests, rangelands, wet lands, and surface waters; (b) the health and productivity of domestic food animals, wildlife and fish; and (c) corrosion of metals, painted surfaces, masonry, and materials in machinery or structures.

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A NATIONAL PROGRAM
FOR ASSESSING THE PROBLEM OF ATMOSPHERIC DEPOSITION
(ACID RAIN)

A Report to
The Council on Environmental Quality

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NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

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U.S. Forest Service;
U.S. Geological Survey;
Agricultural Research and Cooperative Research Divisions,
U.S. Department of Agriculture;
Department of Energy;
Illinois State Water Survey;
Environmental Protection Agency;
Canadian Atmospheric Environment Service;

and other private or publicly supported universities and research agencies in the United States and Canada.

Many other suggestions were made by scientists in the Swedish and Norwegian research programs on acid precipitation.

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I. EXECUTIVE SUMMARY

Issues Statement

Acid rain is a dominant feature of man-induced change in the chemical climate of the earth. This change is particularly evident in rural and urban areas throughout eastern North America and in many urban areas in the western United States. It has already been recognized as a major environmental problem in northern Europe and Japan.

Precipitation in the eastern United States has a mean annual pH between 4 and 4.5. The natural lower limit of precipitation pH is 5.6 (due to atmospheric CO₂). Current values represent as much as a fifty-fold increase in precipitation acidity on an annual basis. Increasing numbers of individual storms produce rain with pH ranging between 3.0 and 3.6. This observed increase over the natural system is due primarily to combustion of fossil fuels. Specifically, the gases SO₂ and NO_x are emitted during fossil-fuel combustion and are oxidized in the atmosphere to sulphuric and nitric acids that, in turn, are scavenged by precipitation.

Regional deposition of acid substances in rain and snow is only a part of the general phenomenon of atmospheric deposition. Other injurious substances also are being dispersed by wind and deposited on food and fiber crops, range lands, surface waters, and residential and other areas in many parts of the United States. Some other substances are toxic metal ions, including lead and mercury, and injurious organic substances of many sorts. They too are deposited in rain and snow and in the particulate matter--aerosol and larger particles--that are dispersed over the land when it is not raining or snowing.

Air emissions of many sorts add to both the beneficial and injurious substances dispersed in the atmosphere. These include emissions from industrial processes; municipal waste disposal; certain intensive agricultural and forestry operations (such as, use of pesticides and herbicides, burning of agricultural and forest residues, disposals of animal wastes, etc.); automobiles, trucks, and home-heating plants. Atmospheric processes lead to extensive mixing and to chemical and physical interactions and transformations of atmospheric particles, aerosols, and gases. The increasing use of tall stacks at power plants results in emitted materials and their reaction products being dispersed further afield by meteorological processes and being introduced into the biosphere by deposition at distances of hundreds or even thousands of kilometers from the original emission sources.

Thanks largely to research efforts in northern Europe and Canada, the effects of strong acids and many other substances on fish and other aquatic organisms are becoming much better understood. The effects are generally catastrophic for fish--particularly in southern Sweden and Norway, eastern Canada, and in the northeastern United States. By contrast, effects on commercial and urban forests, agricultural crops, wetlands, and our system of National Parks are largely unknown. Ignorance of these effects on terrestrial ecosystems in the United States is profound because our programs of research on atmospheric deposition have been both inadequate in scope and very poorly coordinated.

This report, prepared at the request of the Council on Environmental Quality, has two objectives: (1) To assess the present scope of available knowledge about atmospheric deposition and its effect on agricultural lands, forests, ranges, parks, surface waters, and aquatic life in the United States; and (2) to recommend a coordinated program of research and monitoring necessary to serve as a basis for the intelligent management of atmospheric emissions and for the amelioration of the adverse effects of atmospheric deposition on plant and animal life. Such a coordinated program is essential to insure that the continuing economic development of the United States, especially with regard to a national energy policy, is environmentally sound.

Background

Acid precipitation is a major environmental problem on both sides of the Atlantic Ocean. It is considered the primary environmental threat in the Scandinavian countries and a source of marked concern to other northern European countries and Canada. In the United States, acid precipitation is one of two major environmental problems recognized by the President's Council of Environmental Quality.¹ The increasing acidity of precipitation (Figure 1) has already caused measurable damage to aquatic ecosystems and has the potential for longer-term injury (over decades) to forest ecosystems; it can severely impoverish sensitive soils and degrade the natural ecosystems so important to human welfare. The continuing, unchecked environmental degradation caused by acid precipitation could reach a stage where the damage to natural ecosystems would be irreversible.

Several earlier reviews of the acid-precipitation problem in North America (see text for references) have agreed on both the need for research and the area of necessary research. The time has come to stop talking and to implement a comprehensive and well-coordinated program of research and monitoring. The United States already lags well behind other nations (including Canada, Norway, and Sweden) despite the severe threat posed by acid precipitation to large areas of this country.

Terms of Reference

This document recommends a coordinated program of research and monitoring on the effects of atmospheric deposition in the United States.² Research programs are, therefore, proposed to determine:

¹The other is the build-up of atmospheric carbon dioxide with its long-term potential for profound climatic alteration.

²The processes that lead to atmospheric deposition (emission, transformation, and transport in the atmosphere) are the subject of a separate document prepared by A. P. Altshuller. The title and table of contents of that report are given in the Appendix.

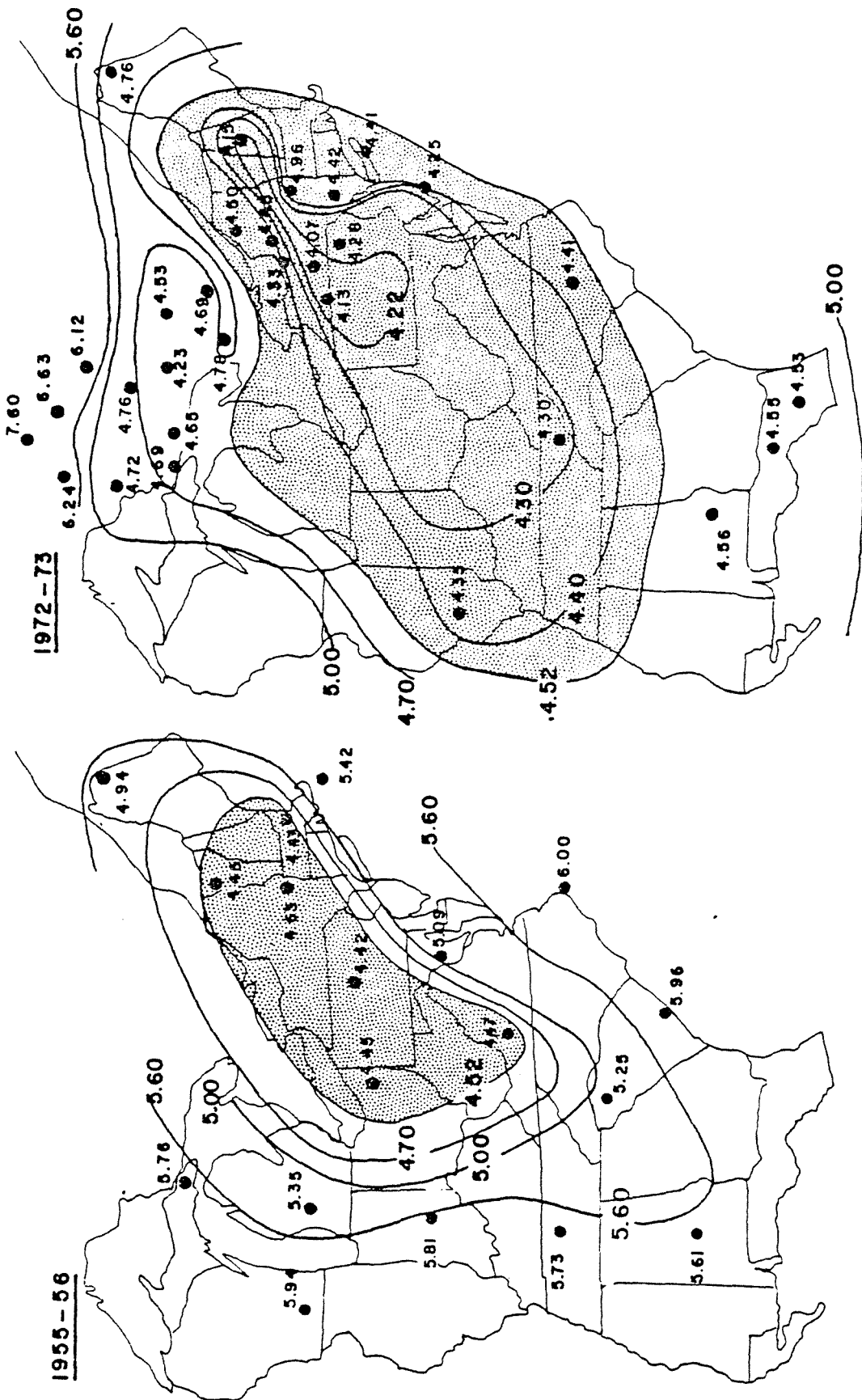


FIGURE 1 THE WEIGHTED ANNUAL AVERAGE OF pH OF PRECIPITATION IN THE EASTERN UNITED STATES IN 1955-56 AND 1972-73. (LIKENS, 1976)

1. The magnitude of atmospheric deposition (acids, organic substances, metals, and nutrients) in the United States; and
2. its subsequent effects on lakes, streams, wetlands, forests, agricultural lands, and other ecosystems; and
3. the importance of these effects to the welfare of the people of the United States.

This document covers atmospheric deposition and the nature and magnitude of its effects for all four types of substances (acids, metals, organics, and nutrients); however, the recommended research is "weighted" towards acid deposition. The recommended research on metals, organic substances, and nutrients is weighted towards determining the amounts of deposition because our knowledge of these substances is less complete.

Reliable research will give no "quick-and-easy" solutions to the problems of atmospheric deposition because lakes, forests, and agricultural and range ecosystems are complicated communities of organisms. The amount of time required to answer the key questions will vary from months to years. Key questions on the sensitivity of species, lakes, and soils to acidification can be answered relatively easily compared to the long-term questions of ecosystem stress and alteration. These differences in time, energy, and funding level are reflected in the diversity and duration (over 10 years) of the recommended research projects (Table 1).

Our research recommendations are the result of extensive reviews of past and current research on the phenomena and effects of atmospheric deposition. The ranking of the recommended research (Table 2) is based on factors relative to the specific effect:

1. What is the extent of available knowledge?
2. What is the potential impact?
3. Is the effect transient or cumulative?
4. Is the impact ecological, economic, or recreational?
5. What is the significance of the impact?

Overview of Research Needs

Four general types of research are recommended: (1) The measurement of spatial and temporal trends in atmospheric deposition, (2) calibrated watershed studies, (3) biological effects studies, and (4) economic assessment and criteria development. To succeed, the proposed research program must have a long-term commitment by the funding agencies. Specific aspects of each of the four areas are outlined below.

TABLE 1

Recommended Research Program

Annual Budget

Measurement of Atmospheric Deposition		\$ 2,600,000
1. Determine spatial and temporal variations in atmospheric deposition	\$ 1,200,000	
2. Determine nature of acid inputs to ecosystems	200,000	
3. Develop improved methods for measurement of dry deposition	700,000	
4. Determine mesoscale variability of atmospheric deposition	200,000	
5. Determine magnitude of atmospheric deposition of trace substances (e.g., metals and organics)	300,000	
Calibrated Watershed Program		2,680,000
(Analysis of Chemical linkages between atmospheric/terrestrial/aquatic ecosystems.)		
1. Chemical mass balance of elements		
2. Mobilization of nutrients and toxic substances in soils		
3. Experimental manipulation of ecosystems		
Biological Effects Program		3,100,000
(Analysis of effects on physiological functions, organisms and ecosystems.)		
1. Agriculture	1,000,000	
2. Forestry	900,000	
3. Wetlands and aquatic ecosystems	1,200,000	
Economic Assessment and Criteria Development		550,000
1. Estimate of current losses	200,000	
2. Identification of vulnerable organisms, soils and ecosystems	250,000	
3. Criteria for action	100,000	
	TOTAL:	<u>\$ 8,930,000</u>

TABLE 2
Project Priorities and Annual Costs

Projects	Priority			Totals
	High Number	Medium Number	Low Number	
Monitoring	6	6	4	\$2,690,000
Calibrated watershed studies	8	16	6	2,680,000
Biological effects research	14	19	14	3,100,000
Economic assessment and criteria development	4	5	2	550,000
Totals	31	36	27	\$8,930,000

National Measurement of Trends in Atmospheric Deposition

A national network of 50 to 100 sites designed to determine the composition, distribution, and magnitude of atmospheric deposition must be established to:

1. Provide information on spatial and temporal trends and
2. support research programs on the effects of atmospheric deposition.

Data from this monitoring network must be integrated with data from other research programs on effects and atmospheric transport and transformation.

Such a program began in July 1978 with support mainly from the State Agricultural Experiment Stations.³ However, a larger basis of support is required to insure the necessary continuity and scope of this program. An Interagency Coordinating Committee should be established to make budgetary and program-management decisions. It should include representatives from the National Oceanic and Atmospheric Administration (NOAA), the Environmental Protection Agency (EPA), the Department of Energy (DOE), the U.S. Geologic Survey (USGS), the Fish and Wildlife Service, the Forest Service, the Science Education Administration of the U.S. Department of Agriculture (USDA), and the National Science Foundation (NSF). A committee of scientists from the numerous disciplines who are directly involved in the NADP should review research needs and give advice on research plans and directions.

Calibrated Watershed Program

Large-scale field experiments must be conducted on four to six carefully selected, natural ecosystems that include both aquatic and terrestrial components. These integrated studies of acid-precipitation effects on whole ecosystems will be established on existing calibrated watersheds consisting of linked ecosystems (of lake and watershed) across the United States.

The program will determine:

1. The fluxes of materials deposited from the atmosphere through ecosystems;
2. the influence of these materials on ecosystem structure, function, and development;

³The program, originally designated NC-141 (North Central Regional Project on Atmospheric Deposition), is now called the National Atmospheric Deposition Program (NADP). It will include research on monitoring as well as the biological and other effects of atmospheric deposition.

3. the interactions among the terrestrial, wetland, and aquatic components making up the watershed units.

Most experiments necessary to determine the effects of atmospheric deposition on ecosystems will be performed within these first two programs. The NADP will provide data on spatial and temporal trends of atmospheric deposition. The Calibrated Watershed Program will provide a series of calibrated natural environments in which to assess the effects of atmospheric deposition. Diverse laboratory and field studies on biological effects, regional studies on economic assessment, and criteria development may also be associated with the NADP and the Calibrated Watershed Program.

Research on whole ecosystems is critical for the understanding of the effects of atmospheric deposition on real systems. These ecosystems provide a natural integration with the complex processes that control the responses of biogeochemical systems to changes in the composition of atmospheric deposition. Furthermore, research should be on linked ecosystems (i.e., terrestrial-wetland-aquatic) because the effects of atmospheric deposition in one cause effects in the others.⁴

Biological Effects Program

This program should consist of a systematic series of tests on the specific effects of atmospheric deposition on a wide range of biological systems. The overall program should include experiments on algae, grasses, herbaceous and woody plants, agricultural crops, forest trees, range vegetation, soil microorganisms, soil fauna, fish, and wildlife. Specific studies should include experiments on soil microbial processes, fish physiology and reproduction, plant and animal parasites and pathogens, microbial symbionts, plant growth and development, litter decomposition, foliar uptake of nutrients and toxic elements in precipitation, availability of nutrients and toxic elements in soil. Some of the studies should also emphasize specific physiological, nutritional, morphological, anatomical stress tolerances, and various ecological processes and relationships. Many of these experiments should be relatively short term, although some may be of intermediate duration (3 to 5 years). Most of the studies should be aimed at the identification of specific life forms, life stages, physiological processes, and ecological relationships that are sensitive to prevalent or anticipated types of atmospheric deposition. Some of the experiments should be conducted within one or more of the calibrated watershed studies; but many others will be independent studies in greenhouses, growth chambers, field plots, or experimental forests, wetlands or ponds, and lakes.

⁴See Section III of this report, Effects of Acid Deposition upon the Outputs from Terrestrial Ecosystems and Aquatic Ecosystems, by E. Gorham and W. McFee.

Economic Assessment and Criteria Development

Soon after the Calibrated Watershed and Biological Effects Programs are underway, analyses should be undertaken to assess the probable economic, environmental, aesthetic, ecological, and other impacts of the known and suspected effects. These estimates will need to be continuously updated and refined as new knowledge of both beneficial and detrimental influences of atmospheric deposition become better known. These assessments ultimately should be useful in the preparation of environmental impact statements and in the development of incentive systems or regulatory systems for altering the amounts, concentration, timing, and chemical nature of emissions.

Program Management

Initially, the research program must be fairly broad with a substantial diversity of specific goals. As more detailed information is obtained about effects, the scope of the research will be more closely focused on the most fruitful fields of further research and proven areas of national concern. Highest priority initially should be given to the establishment of an adequate monitoring network to provide a data base for determining temporal and spatial trends and to identify particularly sensitive biological systems. High priority should next be given to the establishment of the Calibrated Watershed Program. Although some areas of inquiry will require further study and others will be replaced, emphasis will continually be given to the most promising ideas and the investigators proven most competent.

The large-scale, integrated studies of ecosystems will use some calibrated watersheds (both natural and managed) presently established in different regions of the United States; but other new, calibrated watersheds will need to be set up to include both lakes and wetlands within their boundaries. (When new watersheds are calibrated, considerable additional funding will be required both for start-up and maintenance.) Such large-scale studies might be funded jointly by two or three federal agencies. The United States Department of Agriculture already manages calibrated watersheds suitable for study and is active (through the NADP) in the measurement of atmospheric deposition. It is also concerned with effects of atmospheric deposition on crops, forests, ranges, and wildlife. The United States Department of the Interior (USDI) also does a good deal of work on hydrology and water quality through the USGS. In addition, the U.S. Fish and Wildlife Service could become involved in studying and assessing the ecological effects of acid deposition. Similarly, the participation of NOAA in the World Meteorological Organization (WMO) precipitation-chemistry network is an indication of their interest. The DOE is currently funding a regional precipitation chemistry network for the eastern United States, as part of the Atmospheric Power Production Pollution Study. This program should be continued, strengthened, and interfaced with the NADP. In addition, DOE has (through its Environmental Measurement Laboratory) a long history of active programs on the magnitude of atmospheric deposition.

The basic research aspects of the total large-scale program would be most efficiently funded through the National Science Foundation (NSF), which has the major federal mission for such research. As evidence for this, it supported for a long time a large, successful program at Hubbard Brook Experimental Forest where atmospheric deposition research has played an important role. NSF has also provided stable funding for well-established research programs, for periods of many years, and yet has been flexible enough to allow the freedom necessary to pursue basic research in whatever directions turn out to be most fruitful.

A program on biological effects, oriented towards complementary research grants on a scale of about \$10,000 to \$100,000 each, will investigate specific aspects of atmospheric deposition and its physiological and ecological effects. These studies may be done within the calibrated watersheds or in laboratories; greenhouses; or experimental ponds, streams, fields, or forests. Small-scale field and laboratory experiments aimed at acquiring an understanding of chemical and biological mechanisms will also play an important role in this complementary research program. The available funds will be awarded in open competition after peer review but with the stipulation that proposed projects must clearly complement or supplement the large-scale programs of the Calibrated Watershed Program.⁵ These complementary research grants could also be funded by any of the agencies already mentioned (USDA, NOAA, USDI, DOE, NSF, EPA), depending on their mission orientation or their basic research potential. At first, a wide diversity of projects should be funded; as increased knowledge permits better focusing on specific objectives, the diversity of funded projects should decline. In addition to involvement of federal agencies, industry and state agencies are also currently involved in research on the phenomena and effects of atmospheric deposition. They should, therefore, be encouraged to participate in this program in an integrated manner with the federal agencies.

International Aspects

Increased atmospheric deposition and its effects are international problems. Atmospheric motions do not heed national boundaries and thus the emissions of acid precursors (SO_2 , NO_x), metals, and organics in one country can severely effect the ecosystems in another. Because intensive international cooperation on atmospheric deposition research is mandatory, we recommend the following programs:

1. An International Exchange Program of scientists, research-agency administrators, and policy makers: Individuals of one country should spend time in the laboratories and agencies of other countries to learn and to teach.

⁵Such auxiliary projects have been valuable to the research program at Hubbard Brook Experimental Forest.

2. An International Advisory Committee to coordinate the national research programs in different countries.⁶

Further Information

A more detailed summary of established facts and research recommendations, and a more fully annotated review of the current knowledge of atmospheric deposition and its effects are given in Section III:

1. The Phenomena of Atmospheric Deposition, James Galloway, p. 31 to 36.
2. Effects on Aquatic and Wetland Ecosystems, Eville Gorham, p. 37 to 45.
3. Effects on Vegetation, Ellis Cowling, p. 46 to 63.
4. Effects on Soils, William McFee, p. 64 to 73.
5. Effects of Acid Deposition upon Outputs from Terrestrial to Aquatic Ecosystems, Eville Gorham and William McFee, p. 74 to 82.

⁶The existing Canadian/United States Research Consultation Group on the long-range transport of air pollutants could serve in this role. Also, the United States/Canada Joint Commission, which is currently considering whether to become concerned with acid deposition and its effects, might provide sponsorship for further international cooperation.

II. RESEARCH RECOMMENDATIONS

Introduction

This report assesses and ranks the research needed to more fully understand the effects of atmospheric deposition on our environment (Tables 1 and 2). Acid deposition is given the greatest attention because we already know enough about it to realize that its effects are quite serious. Unfortunately, our state of knowledge about atmospheric deposition of organics, nutrients, and metals is so limited that it is not possible to make more than a preliminary assessment. Therefore, this assessment strongly recommends more research in these areas because of the potential for a multitude of effects over large regions.

Processes that occur before deposition (i.e., emissions, atmospheric-reaction mechanisms, and transport) are subjects unto themselves and are being covered in a separate study (see Appendix). However, one aspect of the "predeposition" processes is important to stress: atmospheric contamination. Changes in the composition of atmospheric deposition (acids, metals, organics, or nutrients) are regional rather than local because anthropogenic processes occur over a multistate area. The associated effects of these changes will not be seen in one or two isolated ecosystems but rather in many systems over a wide area. This is a new concept of the effect of man and his environment and poses important questions about abatement and control.

One ramification of contamination by atmospheric deposition on a regional scale is that a primary transfer mechanism of the biogeochemical cycle has been changed. It is, therefore, necessary to consider all aspects of the biogeochemical cycle. Because the concept of linkages should be used (effects of atmospheric deposition on terrestrial ecosystems cause effects on aquatic ecosystem, etc.), it is mandatory to investigate the effects of atmospheric deposition on many ecosystems. Effects in one area influence effects in another area.

This document is an assimilation of previous works (NAS 1975, Braekke 1976, Dochinger and Seliga 1976, MBG 1976, NAS 1978) from the viewpoint of scientists currently working in the field of the effects of atmospheric deposition on aquatic and terrestrial ecosystems. Most of the recommendations herein have been made before (if not specifically, then at least generally). We strongly believe that now is the time to begin a comprehensive research program on the phenomena and effects of atmospheric deposition.

Atmospheric Deposition

To understand the effects of atmospheric deposition on aquatic and terrestrial ecosystems, one must first understand the input processes. The following summary of current knowledge about the phenomena of atmospheric deposition is divided into two areas, each followed by recommendations for future research.

Collection of Atmospheric Deposition

A. Facts

1. There are two general processes, wet and dry.
2. Although the composition of wet deposition is influenced by a variety of complex atmospheric processes, it can be collected easily as rain and snow.
3. Methods are available for the collection and analysis of inorganic compounds at specific sites.
4. Procedures for the collection and analysis of wet deposition at several sites (i.e., a network of sampling sites) have received less attention. The spatial and temporal variability of the sampling fields is large and there are limitations as to the types of samples that can be collected and analyzed on a network basis.
5. The removal of material from the atmosphere by dry deposition is important. Depending on the physical and chemical properties of the atmosphere, the relative magnitude of dry deposition can be greater than wet deposition.
6. Collection of dry deposition is difficult because of the variety of depositional processes (dry fallout, aerosol impaction, gaseous absorption).
7. Dry deposition has been measured in three ways:
 - a. collection in a container open to the atmosphere,
 - b. estimation of dry deposition flux from particle size and micrometeorological parameters,
 - c. estimation from the construction of atmospheric or watershed budgets.

All methods have inherent difficulties; there is substantial discussion on the relative merits of each one.

8. The spatial and temporal variability of dry deposition is large and mostly unknown.
9. The magnitude of the rate of dry deposition is dependent on a variety of parameters, including particle size and composition (or gaseous composition), wind speed, morphology of the receiving surface, temperature, humidity, etc. Each parameter can be variable in space and time, making the measurement of dry deposition rate difficult.

B. Research recommendations (see Table 3)

1. General deposition. Extensive research is required from deposition (wet and dry) networks:
 - a. How well does the specific composition of atmospheric deposition determined at one site represent the deposition in the region?
 - b. What limits do the collection methods place on interpretation of data?
 - c. What ancillary tools can be used to analyze data (i.e., trajectory analysis)?
 - d. How should fog and mist be collected?
 - e. What is the best method to determine the deposition of trace metals and organic compounds?
2. Dry deposition. The basic questions about collection techniques for dry deposition are still unanswered:
 - a. What is the relative importance of dry fallout, gaseous absorption, and aerosol impaction in dry deposition?
 - b. What are the most suitable instruments to measure the components of dry deposition?
 - c. What factors (related to depositional mechanisms) influence the spatial variability of the depositional and composition fields?
 - d. What are the errors associated with the use of depositional velocity to calculate dry deposition rates?
 - e. Are effects of dry deposition cumulative or episodic? Do we need a data base with intense time resolution or are annual loadings adequate?
 - f. Dry deposition occurs on vegetative surfaces. Little is known whether this deposition is passive or if the plant has an active role to determine dry deposition rates to the vegetation. Research is needed to determine:
 - (1) What is the magnitude of the particle load trapped and retained by plant surfaces?
 - (2) What are the portions of the deposit which can be washed off of the surface by wet deposition?
 - (3) How much of the wet- and dry-fallout elements are retained in plant tissue?

TABLE 3: DEPOSITION STUDIES

Characteristics of Research Recommendations

[1] Measurement of deposition	Level of Knowledge*	Potential Impact*	Transient vs. Cumulative	Class of Impact			Type of Study			Time Required (years)	Basic or Applied	Priority*†	Funding Level (\$1,000's)	Number of Projects
				Ecological	Economic	Recreational	Monitoring	Calibrated Watershed	Ancillary					
Wet	H													1
Dry	L													3
[2] Magnitude of deposition														
Spatial and temporal trends	M						M		10+	A	H	1,200		2
[3] Nature of the acids	M						M		2	B	M	200		2
[4] Nature of the organics	L						M		2	B	M	200		2
[5] Mesoscale variation	M						M		2	B	M	200		1
												2,600		11

*L = Low, M = Medium, H = High;

† Priority applies to at least first project in each category. Subsequent projects usually of lower priority.

- (4) What is the magnitude and role the plant-surface exudates and precipitates in throughfall composition?

Magnitude of Atmospheric Deposition

A. Facts

1. Ecosystems removed from local influence of anthropogenic activity can receive a large portion of their elemental inputs from atmospheric deposition.
2. Historically, the concentration of anthropogenic organics (pesticides, PCB, PAH) in precipitation has been zero or close to zero.
3. Historically, the concentration of trace metals in precipitation has been low due to the nonvolatile nature of metals.
4. Historically, the concentration of hydrogen ion in precipitation has been $\leq 2.5 \mu\text{eq}/\ell$ ($\text{pH} \geq 5.6$).
5. Currently, the concentration of metals, organics, and acids in precipitation in some remote areas of the U.S. is more than an order of magnitude higher than has historically existed.
6. Increases are due to increased combustion of fossil fuels and related industrial activities.
7. The atmospheric deposition of nutrients (N, P, K, S, etc.) has increased with increasing anthropogenic activity. This increase certainly fertilizes some ecosystems (southeastern forests [S], oligotrophic lakes [N, P]).
8. In 1955, only the northeastern U.S. was receiving acidic wet deposition. By 1975 most of the eastern U.S. was receiving acidic wet deposition. The same trends in deposition are unavailable for some nutrients, all metals, and all organics because of the lack of a historical data base.

B. Research recommendations (see Table 3)

1. Temporal and spatial trends
 - a. Determine spatial and temporal trends in amounts of various nutrient elements and injurious substances in precipitation and dry deposition in various regions of the United States. Special attention should be given to the macronutrients (N, P, K, Ca, Mg, S), micronutrients (Fe, Cu, Co, Mn, Mo, and B), and trace substances, such as other metals, and natural and anthropogenic organic compounds.

2. Nature of acids. Based on stoichiometry, acid precipitation is caused by a 2-1 mixture of H_2SO_4 and HNO_3 with a slight contribution from HCl . However, because there are nonacid compounds of SO_4 , NO_x , and Cl in the precipitation, stoichiometry only gives a general^x indication of the relative importance of H_2SO_4 , HNO_3 , and HCl as causative agents of acid precipitation:
 - a. Improve collection and analysis techniques for gases (HNO_3 , HCl) and aerosols.
 - b. Improve the use of isotopic tracers ($\text{N}^{14}/\text{N}^{15}$, $\text{O}^{16}/\text{O}^{18}$, $\text{S}^{32}/\text{S}^{34}$) to determine sources for the SO_4 and NO_x species found in acid precipitation.
 - c. Determine the HNO_3 , H_2SO_4 , and HCl concentrations in the atmosphere and in precipitation in urban, rural, and remote areas.
3. Mesoscale variability of atmospheric deposition. The beginning of NC-141 is an important step in creating a national network to measure trends in precipitation composition. However, because of its limited scope, each station will have to represent about 80,000 km. Therefore, the composition of precipitation measured at each collection site will have to be extrapolated over large areas. There are obvious limits to the use of data in this way. Research is needed to determine what the exact limits are.

Effects of Atmospheric Deposition on Aquatic Ecosystem

A. Facts

1. In certain regions of the United States, precipitation passes through the soil with little alteration to the type and amount of dissolved substances. In such regions, the chemical quality of surface waters is primarily determined by the chemical quality of precipitation.
2. Acidity of lakes and streams is increasing because of increasing acidity of atmospheric deposition.
3. Input of S and N to lakes and streams is increasing.
4. Inputs of heavy metals and diverse organic molecules, some of which are known to be toxic, are increasing.
5. Input of metal cations from terrestrial soils (e.g., Ca, Al, Fe) is increasing because of acidity.
6. With marked acid deposition, diversity and productivity of most communities of aquatic plants and animals decrease although individual tolerant organisms may increase. Direct effects upon many fish species and entire aquatic food chains have been well documented. Some fish species have, in fact, disappeared from many thousands of lakes.

7. In some cases, species replacements (which may be self-accelerating) have profound effects on the nature of aquatic communities of plants and animals.
8. Changes in aquatic communities can, in turn, have a major effect on the cycles of elements in aquatic ecosystems, including those which are important in limiting productivity (P, N) and those which are especially toxic to organisms (Al, Hg, Cu, Zn, Ni, Pb).
9. Many aquatic ecosystems are known to be particularly sensitive to acid deposition, notably those on the igneous rocks of the Precambrian shield.

B. Research recommendations (see Table 4)

1. Determine seasonal pattern of inputs from acid deposition on to aquatic ecosystems on spatial and temporal bases, particularly with regard to associated heavy metals and organics. Release from snowmelt is particularly important (see Section III).
2. Determine the extent of the synergism and antagonism of various components of acid deposition, of materials released from surrounding soils by acid deposition.
3. Make year-round studies of effects of acid precipitation on sediment/water interactions and the cycles of nutrient elements (P, N) and toxic elements (heavy metals, organics), particularly with regard to microbial mediation of these cycles. Effects on speciation, sorption, and solubility should be included.
4. Determine and study the effects on organisms living in or on the surface film at the air/water interface (the "neuston"). This community has great potential as an early-warning system because both heavy metals and organics from air pollution concentrate strongly there, and acid deposition will have its greatest effect there before neutralization.
5. Conduct detailed seasonal studies of effects on ecosystem productivity at all trophic levels, concurrently with studies of species interactions (predator/prey, host/parasite, symbionts).
6. Conduct lab and field studies of the physiological effects of acid deposition on specific organisms, with special attention to effects on growth, development, and reproduction. Adaptation to an acidified environment also needs investigation, including methods of detoxication. Overall indices to physiological stress should be identified (e.g., life-span shortening, lowered fertility).

TABLE 4: AQUATIC ECOSYSTEMS

Characteristics of Research Recommendations

Characteristics of Research Recommendations	Level of Knowledge*	Potential Impact*	Transient vs. Cumulative	Class of Impact			Type of Study			Time Required (years)	Basic or Applied	Priority*†	Funding Level (\$1,000's)	Number of Projects
				Ecological	Economic	Recreational	Monitoring	Calibrated Watershed	Ancillary					
[2] Synergism and antagonisms of H+ with other effects and problems	L	M	E						A	5	B	H	200	4
[3] Element cycling	M	M	E	C					C	2-5	B	L	100	2
[4] Surface-film biology as an indicator	L	M	E	T					A	2	B	H	50	1
[5] (a) Ecosystem productivity	L	H	E	C	\$	R			C	10	B	M	100	3
[5] (b) Species interactions	L	H	E	C	\$	R			C	10	B	L	150	3
[6] Physiological effects on organisms	L	H	E	T					A	2	B	L	100	3
[7] Biotic impoverishment	M	H	E	C	\$	R			C	10	B/A	L	20	1
[8] Stratigraphic studies	L	?	E						C	2	B	M	40	1
[9] Ecosystem manipulation	L	?	E						C	10	B	H	200	2
[10] Aquatic-terrestrial linkages	L	?	E						C	10	B	H	200	3
[11] Worst-case studies	M		E		\$				A	2-10	B/A	L	100	2
[12] Characterizing sensitivity (indices)	L		E			R			A	2	B/A	M	20	1
[13] Ameliorating effects, restoration	M		E						C	2	B/A	L	100	1
[14] Beneficial effects	L	M	E	T	\$				C	2	B/A	L	50	1
[15] Effects on human water supplies	L	H		C	\$				A	5	B/A	M	100	1
[16] Economic losses	L				\$				A	2	A	H	50	1
[17] Criteria for action	L		E		\$				A	2	A	H	50	1
													1630	31

*L = Low, M = Medium, H = High;

† Priority applies to at least first project in each category. Subsequent projects usually of lower priority.

7. Set up a long-term monitoring program to measure the effects of acid deposition upon species replacement, biotic impoverishment (losses of species or of particular races of species), and ecosystem stability. The frequency of severe episodic pollution, as well as the general trends must be measured in conjunction with the determination of effects.
8. Make stratigraphic studies to elucidate some of the long-term effects of acid deposition, especially those of species replacement and biotic impoverishment. Fossils of diatom, cladocerans, and chironomids are likely to be particularly useful.
9. Develop useful dose/response curves for species and ecosystems, over a range of species and ecosystem vulnerability through experimental loading of acid deposition applied in varying amounts to selected lakes and streams.
10. Through integrated programs on a watershed (catchment) basis, study effects on aquatic ecosystems as they are linked to those on surrounding terrestrial ecosystems which are major sources of inputs. Mass-balances of the materials in atmospheric depositions should be part of such integrated programs.
11. Particular attention should be focused on worst-case situations. These involve a combination of
 - a. Nearness to major pollution sources;
 - b. Inherent vulnerability, as in the case of dilute and poorly buffered waters on hard crystalline rocks (the Precambrian rocks of the Laurentian Shield). High rainfall and snowpack buildup are also important because they imply severe leaching of soils, high atmospheric deposition by rain-out and washout, and--in the case of heavy snowpack--the possibility of severe episodic pollution at the time of snowmelt. Soil contents of toxic heavy metals, which could be mobilized by acid deposition, may also be a factor in vulnerability.
12. Further develop and refine indices of ecosystem vulnerability, such as Conroy's calcite-saturation index, taking into account the above-mentioned factors of climate, soil mineralogy, and chemical composition. Morphometric factors that control flushing rate, such as mean depth of lake and drainage-area/lake-area ratio, ought to be incorporated. Order in the hydrologic network will be important. Presence of sensitive species should also be considered. Likelihood of urban/industrial development might also be assessed.
13. Investigate means of countering or ameliorating the injurious effects of acid deposition.
14. Investigate whether slight amounts of acid deposition may have beneficial effects on lakes (addition of N, Ca, etc.).

15. Determine the influence of atmospheric deposition on the chemical quality of surface waters used as sources of drinking water in various regions of the United States.

Effects of Acid Deposition on Wetland Ecosystem

A. Facts

1. Very little attention has been paid to effects on wetlands.
2. The waters of Sphagnum bogs in the United Kingdom are more acid near urban/industrial areas.
3. Around metal smelters, severe biotic impoverishment has been observed but not measured.
4. Sphagnum species are excellent collectors of heavy metals and have been observed to be much richer in lead and cadmium in southern Fennoscandia than in northern regions far from sources of air pollution.

B. Research recommendations (see Table 5)

1. Initiate broad surveys (chemical and biological) in wetlands along transects away from known sources of acid deposition.
2. Make an intensive study of peatlands with waters below pH 5.6 and, in particular, on Sphagnum bogs whose surfaces receive only atmospheric precipitation and no water which has percolated through mineral soil. These are the most vulnerable ecosystems.
3. Further attention should then be directed to several points mentioned in consideration of aquatic ecosystems (see bracketed items 3, 5, 7, and 9 to 12).

Effects of Atmospheric Deposition on Vegetation

A. Facts

1. Major damage to crops in many regions of the United States is caused by the dry deposition of toxic gases, aerosols, and particulate matter. Sulfur dioxide, ozone, oxides of nitrogen, fluoride, hydrogen chloride, and photochemical oxidants cause the most serious economic damage nationwide. This impact can alter the species diversity, growth, and productivity of many terrestrial ecosystems.
2. Two of these toxic gaseous pollutants are converted in the atmosphere to strong mineral acids--sulfur dioxide to sulfuric acid and oxides of nitrogen to nitric acid. Both can cause economic damage to plants.

TABLE 5: WETLAND ECOSYSTEMS

Characteristics of Research Recommendations	Level of Knowledge*	Potential Impact*	Transient vs. Cumulative	Class of Impact			Type of Study			Time Required (years)	Basic or Applied	Priority†	Funding Level (\$1,000's)	Number of Projects
				Ecological	Economic	Recreational	Monitoring	Calibrated Watershed	Ancillary					
[1] (a) Impact surveys, chemical	L	H	C	E			C	A	2	B	M	40	2	
(b) Impact surveys, biological	L	H	C	E	\$		C	A	2	B/A	M	80	4	
[2] Impact on sphagnum bogs, methodology				E	\$			A	2	B/A	H	60	1	
[3] Effects on element cycling within wetlands	L	H	C	E			C	A	2	B	L	90	3	
[5] (a) Effects on wetland productivity	L	H	C	E	\$		C	A	2	B/A	M	120	3	
(b) Effects on species interaction	L	H	C	E	\$		C	A	5	B/A	M	120	3	
[7] Biotic impoverishment	L	H	C	E	\$		C	A	10	B/A	M	30	1	
[9] Developing experimental approaches				E			C	A	2-10	B	H	200	3	
[10] Methods of studying ecosystem linkages				E			C		2-10	B	H	200	3	
[11] Studies of worst-case situations				E	\$			A	2	B/A	M	80	2	
[12] Development of sensitivity indices				E	\$			A	2	B/A	M	30	1	
												1050	26	

* L = Low, M = Medium, H = High.

† Priority applies to at least first project in each category. Subsequent projects usually of lower priority.

3. Direct and indirect damage to crops and forests have been reported in laboratory, greenhouse, and field experiments in which synthetic rain equivalent (in chemical composition and rate of deposition) to natural rains has been applied. These biological effects include the following:
 - a. Induction of necrotic lesions on foliar organs;
 - b. Loss of nutrients from plants due to excessive leaching from foliar organs;
 - c. Predisposition of plants to infection by bacterial and fungal pathogens;
 - d. Accelerated erosion of epicuticular waxes on leaf surfaces;
 - e. Interactions between acids in precipitation and gaseous air pollutants (such as SO₂ and ozone) leading to greater amounts of damage to foliar organs than that observed with acids in precipitation or gaseous pollutants acting alone;
 - f. Inhibition of nodulation in legumes leading to decreased efficiency of nitrogen fixation by symbiotic bacteria;
 - g. Accelerated leaching of essential nutrients from soils leading to nutrient improvement of soils;
 - h. Decreased uptake of nutrients by mycorrhizae of forest trees;
 - i. Reduced rates of decomposition of leaf litter leading to decreased mineralization of organically-bound nutrients;
 - j. Inhibition of reproduction of root-knot nematodes and germination and infection by fungal parasites and pathogens of plants;
 - k. Premature senescence of older leaves on crop plants and forest trees.
4. Despite this impressive array of specific biological effects of simulated rain, reliable evidence of economic damage to crops by injurious substances in naturally occurring atmospheric deposition has been reported only rarely--for example, the "russetting" of Golden Delicious Apples, formation of surface blemishes that degrade the market quality of the fruit. Other economic damage due to injurious substances in precipitation has been reported but the evidence for these effects is not unequivocal. The most economically important of these suggested effects is a 2-7% reduction in forest growth in Sweden between 1950 and 1965.
5. Natural rains cause leaching of various substances from foliar organs, including nutrient elements, growth hormones, carbohydrates, and other metabolites. Field exposure to acid rains has been shown to accelerate these natural leaching processes.

6. Natural rains also cause weathering (erosion) of the protective waxes on the surface of foliar organs. Acid precipitation greatly accelerates these weathering processes and may increase the vulnerability of plants to drought and infection by biotic pathogens.
7. Natural rains have always contained small amounts of heavy metals and organic compounds. In recent years, however, much larger-than-expected amounts of various heavy metals and a vast array of volatile pesticides and other synthetic organic compounds have been added to precipitation and dry deposition in all regions of the United States. Very little is known about the effects of these substances on individual plants and terrestrial ecosystems.
8. Most natural ecosystems (forests, rangeland, grasslands, and wetlands) are deficient in nitrogen, phosphorus, and, sometimes, sulfur. These major nutrient elements are available in both precipitation and dry deposition. Furthermore, these and other essential elements dispersed in the atmosphere can be absorbed directly by foliar organs. Thus, atmospheric deposition makes an important contribution to the total nutrient supply of plants. This input is particularly important in natural ecosystems, such as forest, rangelands, grasslands, and wetlands, that are not fertilized.
9. Neutralization of strong acids in precipitation by ammonium will only temporarily alleviate the acidity of air and precipitation. Uptake of neutralizing ammonium ions will add to the acidification of ecosystems because a hydrogen ion will be released for each ammonium ion taken up by plants. Nitrification of the added ammonium will lead to further acidification.

B. Research recommendations (see Table 6)

1. Determine the quantitative contribution of atmospheric deposition, in general, and foliar absorption from precipitation, in particular, to the total nutrient budget of forest trees, range plants, various forage, grain, and horticultural crops.
2. Determine the extent of cuticular erosion by simulated and naturally occurring acid rains on various economic plants and their influence on drought hardiness and resistance to foliar pathogens.
3. Determine the pathways of absorption of nutrient elements by foliar organisms (direct absorption through cuticle, absorption through stomata, or through hyphae of fungi growing on leaf surfaces).
4. Determine the influence of atmospheric deposition on the content of heavy metals in selected fruit and vegetable crops.
5. Determine the influence of acid precipitation on both external and internal recycling mechanisms for conservation of essential elements in forest trees and other crop plants.

TABLE 6: TERRESTRIAL ECOSYSTEMS

Characteristics of Research Recommendations	Level of Knowledge*	Potential Impact*	Transient vs. Cumulative	Class of Impact			Type of Study			Time Required (years)	Basic of Applied	Priority*†	Funding Level (\$1,000's)	Number of Projects
				Ecological	Economic	Recreational	Monitoring	Calibrated Watershed	Ancillary					
[1] Contribution to nutrient budget of crops	L	H	C	E	\$		C		2	B	M	150	1	
[2] Cuticular erosion caused by acid	L	H	T	E				A	2	B	H	100	1	
[3] Pathways of plant uptake of deposition	L	M	C	E				A	2	B	H	100	1	
[4] Heavy metals in food supply	L	H	T		\$			A	2	A	H	50	1	
[5] Leaching of nutrients from foliage	L	H	T	E			C		10	B	L	200	2	
[6] Vulnerable life forms	L	H	T	E			C	A	2	B/A	H	200	2	
[7] Effects on ecosystem productivity	L	H	T	E	\$	R	C		10	B	M	800	4	
[8] Synergism and antagonisms in plants	L	M	T	E				A	2	B	M	200	2	
[9b] Damage to apples	M	H	T		\$			A	2	A	H	50	1	
[10] Snowmelt shocks to biota	L	M	T	E				A	2	A	H	100	2	
[11b] Effects on host-parasite interaction	L	M	T	E				A	2	A	H	200	2	
												2150	19	

*L = Low, M = Medium, H = High.

† Priority applies to at least first project in each category. Subsequent projects usually of lower priority.

6. Identify specific life forms, life stages, and life processes that are vulnerable to episodic inputs of injurious substances in precipitation or dry deposition. These vulnerable forms, stages, and processes could include germination of seeds and pollen of higher plants and germination of fungal spores.
7. Using an ecosystem approach, determine the impact of atmospheric deposition on plant productivity and species diversity in natural ecosystems, such as forests and natural grasslands.
8. Determine dose-response relationships for various injurious substances (gaseous pollutants, toxic organic compounds, and possibly heavy metals) in precipitation and dry deposition, both singly and in specific combinations. Particular attention should be given to the thresholds for direct injury by acid precipitation and synergistic interactions between acid precipitation and various gaseous pollutants, especially ozone and sulfur dioxides.
9. Determine the threshold concentrations of acids and other constituents of precipitation and dry deposition which cause such effects as (a) direct injury to foliage, (b) russetting of yellow Delicious apples, (c) inhibition of seed germination, and (d) other types of direct injury to crops, plants, and natural vegetation.
10. Determine the influence of acid substances and other constituents of snow on the survival and condition of plants and blue-green algae during periods of snowmelt. Damage to overwintering crops, like winter wheat, and to nitrogen-fixing blue-green algae and free-living bacteria should be given special attention.
11. Determine the effects of simulated acid rain on the susceptibility of agricultural crops and forest trees, insects and fungal and bacterial pathogens of agricultural crops and forest trees.

Effects of Atmospheric Deposition on Soils

A. Facts

1. Natural soil-formation processes in humid regions tend toward acidification; acid precipitation accelerates this process.
2. Soil acidification increases leaching of exchangeable plant nutrients; such as Ca, Mg, K, Fe, and Mn. It also increases the rate of weathering of most soil minerals.
3. Acidification reduces many soil microbiological processes; such as N fixation and breakdown of residues. The following processes, all of which are important in nutrient cycling and may be critical in some ecosystems, are known to be reduced by lowering soil pH:

- a. Nitrogen fixation by Rhizobium bacteria on legumes and by Azotobacter;
 - b. Mineralization of N from forest floors;
 - c. Nitrification of ammonium compounds;
 - d. Overall decay rates of forest floor material and, therefore, the rate of availability of stored nutrients.
4. Acidification reduces the availability of P to plants and increases the availability of phytotoxic elements, such as Al.
 5. Simulated acid rain increases the leaching losses of Al from the soil. This can cause an undesirable rise in Al in associated aquatic environments.
 6. Soils differ by orders of magnitude in their susceptibility to acidification. For example, moderately acid soils that are low in clay and organic matter will be subject to acidification much faster than well-buffered soils. Calcareous soils are unlikely to be affected by the acid but may be damaged by metal deposits.
 7. Amendments used on cultivated soils have a large effect on soil acidity and overshadow acid-precipitation influences. However, there are large uncultivated areas that have soils that are poorly buffered and susceptible, especially in forest and wilderness areas of the U.S.
 8. Heavy-metal deposition associated with acid precipitation, or independent of it, is potentially a problem to soil productivity. Toxic metals deposited on soils tend to accumulate; natural recovery of metal-contaminated soils is very slow. Limited areas near point sources have already accumulated phytotoxic levels of heavy metals.
 9. Significant quantities of plant nutrients; such as N and S, are being added to soil in dry deposition and precipitation. In some ecosystems these inputs may be important in the maintenance of the nutrient budget.
- B. Research recommendations (see Table 7)
1. Determine inputs of acids, metals, nutrients, and organic materials on a spatial and temporal basis. The background and trends over long periods and broad regions must be established in order to evaluate the impact of atmospheric inputs.
 2. Identify vulnerable soils
 - a. Identify soil subgroups or families that are vulnerable to acidification;

TABLE 7: SOILS

Characteristics of Research Recommendations

Level of Knowledge*	Potential Impact*	Transient vs. Cumulative	Class of Impact			Type of Study			Time Required (years)	Basic or Applied	Priority†	Funding Level (\$1,000's)	Number of Projects
			Ecological	Economic	Recreational	Monitoring	Calibrated Watershed	Auxiliary					
M	H		E	\$	R	A	A	2	A	H	50	1	
M	H												
M	M	C	E	\$		O	A	2-10	B	H	200	3	
L	M												
M	H	T/C	E	\$		C	A	2	B	H	500	4	
M	H												
M	H												
M	H	C				C	A	5	A	L	200	2	
L	H	C	E			C	A	10	B	H	100	1	
L	M	T/C	E			C	A	10	B	M	50	1	
M	H	C	E	\$		A	A	2	A	M	50	1	
M	M	C	E			A	A	5	B	M	100	1	
M	M	C	E			A	A	2	A	L	50	1	
L	H	C	E			A	A	2	A	M	50	1	
L	M	C				A	A	10	A	M	100	1	
											1500	18	

* L = Low, M = Medium, H = High

† Priority applies to at least first project in each category. Subsequent projects usually of lower priority.

- b. Identify soil regions that contain significant amounts of vulnerable soils. (This should then be compared to the results of 1.)
3. Determine the effects of acid deposition on vulnerable soils.
 - a. Determine the effects of acid on soil chemistry.
 - (1) Determine effects of acid on ion availability to plants and ion movement through soils. This is needed for plant nutrients as well as potentially toxic materials.
 - (2) Determine effects of acid on weathering of soil minerals.
 - (3) Determine effects of acid on translocation of organic materials in soils.
 - b. Determine the effects of acid on soil biota.
 - (1) Determine influence on nitrogen cycle through nitrogen-conversion organisms.
 - (2) Determine influence on population and activity of decomposing organisms.
 - (3) Determine influence on pathogenic organisms inhabiting the soil.
 - (4) Determine influence on mycorrhiza and other beneficial organisms.
4. Assess the negative and positive effects of acid precipitation on soils. Determine the potential economic loss due to reduced soil productivity.
5. Determine means to counter the effects of acid precipitation on soils. Evaluate alternative strategies for halting or reversing the acid effects from economic and biological/chemical standpoints.
6. Evaluate the ability of different soils to modify the chemistry of precipitation during its passage to aquatic systems.
7. Determine the difference in effects on surface-soil flora and fauna of input applied in short episodes of very acid rain versus more dilute applications of longer duration.
8. Identify areas that now or in the future are likely to receive damaging amounts of phytotoxic metals due to their proximity to sources and susceptibility to additional metal loading.
9. Establish criteria for toxic levels of metals in soils.

- a. Determine the interaction of precipitation acidity with metal availability and movement in soils.
 - b. Establish the relationship between metal toxicity and soil chemical characteristics.
10. Determine the potential effects of metal contamination on soil.
 - a. Assess the value of plant nutrients deposited on soils.
 - b. Determine the negative effects of metals on soils productivity.
 11. Determine what can be done to ameliorate the effects of metal contamination of soils.

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III. BACKGROUND DOCUMENTATION

THE PHENOMENA OF ATMOSPHERIC DEPOSITION

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Collection of Atmospheric Deposition

The ability to determine the effects of wet and dry deposition of substances on aquatic and terrestrial ecosystems is directly dependent on:

1. Identification of the important wet- and dry-deposition processes.
2. Quantitative determination of the deposition rates of each process.
3. Determination of the nature of the effect relative to the deposition process (i.e., cumulative, episodic, short-term, etc.).

The processes for removal of material from the atmosphere are complex and may generally be considered in two categories: wet and dry deposition.

The subcategories for the processes of wet and dry deposition are:

1. Wet deposition
 - a. Incident wet deposition--Water that gravitationally settles from the atmosphere to the surface of the earth.
 - b. Throughfall--Wet deposition that has passed through a leaf canopy.
2. Dry deposition
 - a. Dry fallout--Material that gravitationally settles out of the atmosphere. This material is $> \sim 10 \mu\text{m}$ in diameter and is primarily composed of fly-ash soil and sea-salt particles.
 - b. Aerosol impaction--Material that is too small to settle under the influence of gravity but, rather, is impacted onto surfaces. This material (e.g., $[\text{NH}_4]_2\text{SO}_4$, NH_4NO_3) is commonly $< \sim 10 \mu\text{m}$ and is usually formed by atmospheric gas-phase reactions.
 - c. Gaseous absorption--Gases that are absorbed by foliage or soils (e.g., SO_2 , NO_x , CO_2).

Bulk deposition is another term commonly used. It is defined as the material collected by a sampler open to the atmosphere at all times. It

includes all wet deposition, dry fallout, and some aerosol impaction and gaseous absorption.

After identifying the processes that deposit acidic materials, the relationship of the deposition processes to the ecological effects should be determined. In a general sense, two major categories of effects can be identified. Episodic effects are usually short term and generally result from high deposition rates of material on the receiving surface for short periods of time. Cumulative effects result from the accumulation of deposited material over long periods of time. An example of an episodic effect would be the effect on a leaf surface of a single rainfall having a pH of 2.5; whereas a cumulative effect would be the damage caused by the accumulation of acid from precipitation of pH 4.0 over a 12-month period. The elucidation of these different types of effects requires different approaches to the measurement of deposition and hence different solutions to sampling difficulties.

The difficulties in measuring wet and dry deposition vary considerably. Wet deposition is more easily collected because gravitational sedimentation is usually the single physical process that controls the rate of deposition. Dry deposition, however, comprises several complex processes (gravitational settling, aerosol impaction, and gaseous exchange) and it is difficult to select collection techniques which duplicate the capture by natural surfaces. Because of the relative ease of collection of wet deposition, development of the methodologies is more advanced. These advances are documented in reports from several investigations on collector design, choice of sampling period, sample stability, etc. (Granat 1974, WMO 1974, Berry et al. 1975, Galloway and Likens 1976, Galloway and Likens 1978a). The consensus of these reports is:

1. A wet-deposition collector should be of simple and rugged construction, able to withstand wide temperature and wind variations.
2. Due to the low ionic strength of wet deposition, collectors should be scrupulously cleaned.
3. Wet deposition should be collected separately from dry deposition because of the chemical and physical interaction between the two components.
4. Wet-deposition samples must be taken on an event basis if air-mass trajectory analysis is to aid in interpretation and if short-term effects of wet-deposition episodes on aquatic and terrestrial ecosystems are to be assessed. Chemical and biological changes may occur in the sample if it is not collected after each event. This is especially true in regions having a wet deposition with pH > 4.5.
5. Chemical preservation of wet deposition is difficult because of the possible contamination of such dilute samples. Rather, it is better to store the samples at low temperatures.

6. The composition of wet deposition can vary widely from one place to another. Consequently, any research or monitoring must allow for this inherent variability and care must be taken in placing collectors.

Difficulties that require further resolution through continuing research on wet deposition are:

1. Severe episodic effects (as opposed to cumulative) on aquatic and terrestrial ecosystems have been documented in laboratory and field studies (Dochinger and Seliga 1976a, Braekke 1976). However, these effects are quite dependent on the spatial and temporal variability of both the amount and composition of wet deposition. Therefore, further work is necessary to understand the relationship between episodic effects and the variability of the deposition and compositional fields of various constituents.
2. The effects of wet deposition on leaf surfaces in controlled environments have been documented (Shriner 1976). However, before these effects can be documented in the field, the physical and chemical interactions between individual drops and the leaf surface have to be investigated. For example, after a surface is moistened in the first part of a storm, do the following drops run off without interacting with the leaf? Similarly, what is the effect of the evaporation of droplets that have impacted on a leaf surface and, hence, the resulting concentration of ionic species there.
3. The composition of wet deposition is altered as it passes through the forest canopy, and therefore, it is necessary to realize that incident wet deposition will have a different effect on leaf surfaces than throughfall. To assess effects on leaves, it is necessary to determine how much of the canopy is exposed to incident wet deposition rather than throughfall.
4. The techniques for measuring throughfall composition are not as advanced as are those for collecting incident wet deposition. A variety of difficulties increase the sampling problem:
 - a. The spatial variation for throughfall composition is greater than for wet deposition; therefore, more intensive sampling networks are required. Currently, there are two techniques: The placement of individual collectors under the canopy, and the placement of integrating collectors under the canopy. The latter sampler is often a piece of plastic pipe cut in half lengthwise and placed horizontally under the canopy. The integrating nature of this collector eliminates some of the spatial variability in the composition of throughfall.
 - b. The prevalence of sample contamination by litter-fall requires constant attention.
5. The collection and measurement of the inorganic composition of wet deposition at specific sites has received extensive atten-

tion. Procedures for the collection and analysis of wet deposition at several sites (i.e., a network of sampling sites) has received less attention. The spatial and temporal variability of deposition fields is large and the types of samples that can be collected and analyses that can be performed on a network basis are limited (Karol and Myatch 1972; Granat 1974, 1976; Galloway and Likens 1978a; Gatz 1978). Research is needed to relate the program objectives to the spatial density of collectors required in a precipitation chemistry network.

6. The effects of the chemical constituents of fog and mist on vegetation are unknown. Fog and mist may contain much higher concentrations of contaminants than precipitation, but few collection methods are available and little research has been done on their effects.

7. Until recently, analysis of the transport of airborne contaminants was severely restricted by the lack of meteorological techniques for tracing air parcels. In an investigation of precipitation composition at a specific collection point, identification of the sources of given constituents is particularly difficult. To solve this difficulty, computer-generated back trajectories of air parcels have been used to relate source regions of gaseous emissions to acid-forming substances in precipitation (Cogbill and Likens 1974, Miller et al. 1978, Pack et al. 1978). These studies have employed trajectories that use winds averaged over a series of pressure levels. However, Danielson (1961, 1974) has shown that this type of trajectory computation can lead to completely erroneous results in some situations. Not only is vertical motion ignored, but the occurrence of a significant shear of the horizontal wind can cause serious errors. Therefore, research is required on the use of isentropic trajectory analysis that includes the effect of wind shear and vertical motion.

Substantial difficulties remain in the measurement of wet deposition. These difficulties, however, are slight when compared to those encountered in the measurement of dry deposition.

Dry deposition is a collective term that describes several processes, not associated with precipitation, that remove material from the atmosphere. As previously mentioned, the three main dry-deposition processes are dry fallout, aerosol impaction, and gaseous absorption. All three require different measurement approaches, each with their own inherent difficulties. A major difficulty is that, because the effectiveness of the deposition process depends to some extent on the nature of the surfaces (foliage, soils), an accurate, direct measurement of the transfer rate (i.e., dry deposition) would require duplication of the natural surface in the chosen collector. This is virtually impossible. The surface structures of foliage and soils are quite complex and unique. Therefore, direct measurements of dry-deposition rates are extremely difficult, and current indirect methods are of unknown accuracy. This inability to measure is critical and limits our understanding of the effects of dry deposition on aquatic and terrestrial ecosystems.

There are several techniques for estimating rates of partial or total dry deposition: Open buckets are exposed to the atmosphere during periods of no precipitation to collect whatever settles into them. The degree to which they collect aerosols by impaction and gases by absorption is unclear.

Dry deposition can also be estimated by determining the atmospheric concentration of the gas or particulate-constituent and then, using the deposition velocity, calculating the deposition flux. Difficulties of this approach are two-fold. First, the measurement of aerosol and gas concentrations (especially at ambient levels) is difficult; and secondly, experimental determinations of deposition velocities provide values that vary by factors of 2-3 (Fowler 1978). Current work in this area is being done within the MAP3S program of the Department of Energy and within the SURE program of the Electric Power Research Institute.

One of the largest receiving areas of dry deposition is vegetative surfaces. Therefore, it is critical that the interaction of atmospheric constituents with vegetation be more fully understood. Droppo and Hales (1974) reviewed the available methods of rate measurements for dry deposition; and, of the techniques, the micrometeorological methods have been the most extensively applied. However, a major deficiency of the previous work on dry deposition fluxes to vegetative surfaces is that most of the work has been done with grasses and little with forest canopies. Dry deposition on forest canopies has been indirectly measured by determining the changes in the precipitation composition as it passes through the forest canopy. However, because precipitation leaches material from leaf surfaces, this method usually gives an elevated estimate of dry deposition. More work in this area is needed.

Over the past 5 years, there have been several meetings and workshops on dry deposition:

WMO Expert Meeting, "Wet and Dry Deposition"; Toronto, Canada; November 1975;

NATO Meeting, "The Effect of Acid Precipitation on Vegetation Soil and Soil Biota"; Toronto, Canada; May 1978;

WMO Expert Meeting, "Dry Deposition"; Gothenburg, Sweden; April 1977;

EPRI Workshop, "Acid Rain"; Galloway, Scotland; September 1978;

U.S. Forest Service First International Symposium, "Acid Precipitation and the Forest Ecosystem"; Columbus, Ohio; May 1975.

The recommendations from those meetings were remarkably similar and are reflected in the recommendations of this report, specifically:

1. What is the relative importance of dry fallout, gaseous absorption, and aerosol impaction in acidic dry deposition?
2. What is the most suitable instrumentation to measure the components of dry deposition?

3. What factors (related to depositional processes) influence the spatial variability of the deposition and concentration fields?
4. What errors are associated with the use of deposition velocity to calculate dry deposition rates?

If we are to understand the effects of atmospheric deposition on aquatic and terrestrial ecosystems, substantial research on the measurement of dry deposition is mandatory.

Magnitude of Atmospheric Deposition

Atmospheric deposition is the transfer process between the atmosphere and the continents and oceans. Before the large-scale burning of fossil fuels and the associated industrial processes, the composition of atmospheric deposition was determined by natural biological (respiration, photosynthesis, nitrogen fixation, denitrification, etc.) and physical (aerosols generated by wind turbulence) processes that injected material into the atmosphere. From the marine sedimentary record it is evident that this natural component of atmospheric deposition has remained relatively constant over the last few million years. It is only in the last century that man's activities have changed the composition of atmospheric deposition. This change has the potential for severely affecting natural systems because terrestrial and aquatic ecosystems receive a large part of their material inputs from the atmosphere (Galloway and Cowling 1978). Thus they are quite sensitive to changes in the concentration of injurious and beneficial substances in atmospheric deposition. Among the substances that have increased in atmospheric deposition are hydrogen ions, metals, organic compounds, and nutrients. The magnitude of these changes is dependent on the geographical region and chemical constituents. The acidity of precipitation in large areas of North America and northern Europe has increased by more than an order of magnitude (Cogbill and Likens 1974, Braekke 1976).

Although it is known that the acidity of precipitation has increased, the relative contributions of the acids causing this increase (sulfuric and nitric) are not known. Until these are known, effective control measures will be difficult to establish. It is particularly important to understand what effect future national energy policies will have on the contributions of each of these acids to the acidity of precipitation.

The concentration of some metals in atmospheric deposition (e.g., Pb, Sb) has similarly increased in these areas (Galloway and Likens 1978b, Semb 1978). The concentration of some organics (pesticides, polychlorinated biphenyls and polyaromatic hydrocarbons) has increased orders of magnitude because, for the most part, there are no natural sources. All of these increases are due to anthropogenic activities.

Because a long-term record is essential to quantify trends in atmospheric deposition, a National Atmospheric Deposition Program (NADP) must be formed.

Coupled with the need to develop the NADP is the need for continuing research on the program design relative to the program objectives. For example, how dense should it be? What should the sampling frequency be?

In summary, it is crucial to understand the processes of atmospheric deposition and their spatial and temporal variability in order to understand their effects on our environment.

THE EFFECTS OF ACID PRECIPITATION UPON AQUATIC AND WETLAND ECOSYSTEMS

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Introduction

Deposition of acid from the atmosphere, with consequent severe effects upon aquatic ecosystems, is by now a well-known phenomenon (Dochinger and Seliga 1976a). Both sulfuric and nitric acids are involved, and hydrochloric acid may be a much more local source in certain circumstances (Gorham 1976). Deposited along with the acids are many other toxins, including acid sulfate particles, heavy metals, and a variety of hydrocarbons, as well as nutrients such as nitrogen, potassium, calcium, and probably phosphorus (Gorham 1976, 1978; Lunde et al. 1976; Henriksen and Wright 1978).

All these pollutants may exert a wide range of effects upon organisms and ecosystems, particularly oligotrophic ecosystems. There is a strong likelihood of both synergistic and antagonistic interactions. These have been little investigated, although it appears that metal toxicity may increase with increasing acidity. Atmospheric deposition not only provides very significant inputs to aquatic ecosystems of both toxins and nutrients (with the former generally exerting a predominant influence), but the acids which are generally abundant may also have indirect effects upon the toxicity of other ecosystem inputs (e.g., soil-derived metals, such as aluminum and several trace metals) and upon the availability of certain nutrients through weathering and biological activity (e.g., N, P, K, Ca, etc.). Biotic effects begin with those upon individuals and species and range from acute and chronic toxicity to impairment or failure of reproduction, lessening of genetic diversity within species, and the possible extinction of rare and endangered biota. Effects upon communities of plants and animals include lowered production and lessened diversity, which in turn may lead to a decrease in ecosystem stability.

Effects Upon Chemical Budgets and Cycles

Direct effects are well known, with many aquatic ecosystems (both rivers and lakes) exhibiting increases of acidity exceeding an order of magnitude. Losses of Ca, Mg, and Al from small watersheds (catchment basins) have also been directly related to inputs of hydrogen ions (Gjessing et al. 1976), and southern Scandinavian waters are known to have become enriched in salts in recent years, probably for this reason (Malmer 1976).

Heavy metal inputs have also increased significantly, particularly where the major sources of acid deposition are metal smelters such as the large Sudbury complex in Canada (Gorham 1976). Such inputs may come directly from the atmosphere and also through increased leaching of impacted soils. Inputs of aromatic hydrocarbons, and of nutrient elements such as nitrogen, are associated in particular with combustion of fossil fuels.

Short-term storage of pollutants in snow pack can increase significantly the toxic impact of acids upon aquatic biota at the time of snow-melt. Long-term storage in sediments may, in contrast, provide a significant degree of detoxication, particularly for associated heavy metals. Sediment/water interactions are of vital importance in this respect and have been little investigated.

Seasonal studies of acid input, neutralization, and output are urgently needed, particularly as some impacted waters show a significant rise in pH under ice in winter (J. R. Kramer, private communication). The impact of acid deposition upon budgets (inputs, outputs, storage) of associated heavy metals, organic toxins, and nutrients also deserves thorough investigation. Long-term monitoring of annual and seasonal deposition over decades is of special importance in order to assess (a) trends in deposition and (b) the frequency of severe, episodic pollution which can have major impacts upon biota (e.g., fish kills).

In situations of severe acidification, studies of effects upon the stability of soil minerals and on the formation and breakdown of clay minerals are badly needed. Effects have been hypothesized under severe acid attack (Norton 1976) and under less severe attack over long periods of time (Malmer 1976).

It is also of great importance to establish the effects of changes in acidity upon the speciation and upon the sorption and desorption by clays and organic matter, of toxic and nutrient elements in sediments. The degree to which deposition of various elements and organic molecules may saturate the various systems in lakes and streams may sequester them from the biota also requires investigation. Effects of increasing acidity upon the ability of organisms to take up or exclude various toxic or nutrient elements and to degrade organic pollutants deserve increased attention.

Acidity may have an impact upon productivity, and hence upon a variety of chemical cycles, by determining the balance between bicarbonate and free carbon dioxide in solution, with bicarbonate very scarce below pH 5 and strongly predominant at pH 8. Aquatic plants differ in their ability to use the bicarbonate ion for photosynthesis (Moss 1973), so that this balance may be of considerable importance.

Effects Upon Aquatic Communities

All of the diverse communities of lakes and streams may be affected by acid deposition and associated phenomena. Although a good deal of work has been done on the impact of acid deposition upon aquatic communities, much of it has consisted of general regional surveys, with little detailed seasonal study over a period of years. Such detailed studies are now urgently needed and should focus upon ecosystem structure, function, and diversity. The nature and complexity of the food web, productivity at all trophic levels, decomposition rates, and interactions between predators and prey, parasites and hosts, and associated symbionts all deserve attention. Gene-pool depletion within species, actual losses of species themselves, and species replacement are each an important aspect of ecosystem diversity to be investigated, specially insofar as they influence ecosystem stability.

Such studies may also be accompanied by physiological studies upon specific organisms important in the communities. Little has been done except on certain fishes (Leivestad and Muniz 1976, Leivestad et al. 1976), and even in their case much remains to be learned. Laboratory and field studies of the metabolic effects of acid deposition (with its associated inorganic and organic components) should be an important part of future research programs. The major focus ought to be upon growth, development, and reproduction, with attention given to limits of tolerance and also to the ways in which organisms either adapt to the pollutants or detoxify them.

Neuston

The organisms inhabiting or living upon or beneath the surface film are likely to be specially affected by atmospheric deposition, in particular because many inorganic and organic pollutants become concentrated there, often to levels that are orders of magnitude greater than those in the bulk water beneath (Wangersky 1976). The first impacts of acid deposition, before and during neutralization, will also be felt there. So far little or no work has been done on this community, despite its obvious suitability as an early-warning system for airborne pollution.

Phytoplankton

Several investigations (Stokes et al. 1973, Almer et al. 1974, Conroy and Keller 1976, Conroy et al. 1976, Wright et al. 1976) have shown a decrease in both algal biomass and species diversity with increasing levels of acidity in lakes, as well as a lowered rate of primary production (Conroy et al. 1976, Kwiatowski and Roff 1976). In this way the base of the food chain is impoverished both qualitatively and quantitatively.

Zooplankton

The same sort of impoverishment is exhibited by the zooplankton of acid lakes in Sweden and elsewhere (Almer et al. 1974, Dickson et al. 1975, Sprules 1975, Hendrey and Wright 1976, Leivestad et al. 1976). Little is known of how far this is a direct result of acidification or an indirect result of decreased biomass and diversity of phytoplankton. Both types of effect might be anticipated.

Nekton

Effects upon fish are large and of special interest to humans, as fish are a source of food and recreation. The fish populations of thousands of lakes in northern Scandinavia and eastern North America have become severely depleted in recent years owing to progressive acidification (Jensen and Snekvik 1972, Beamish et al. 1975, Dickson 1975, Leivestad et al. 1976, Wright et al. 1976, Schofield 1976, Trojnar 1977). Some fish disappear below pH 6, and many disappear below pH 5. Associated problems include inhibition of gonad development (Beamish 1976), and osmoregulatory

dysfunction (Dickson 1975, Wright and Snekvik 1977). Sudden fish kills have resulted from sudden drops in pH (Leivestad and Muniz 1976). Metal toxicity may also be a significant factor.

Littoral Organisms

The diversity of aquatic macrophytes is greatly decreased in lakes near the Sudbury smelters, where associated heavy metals may have a greater effect than sulfuric acid pollution (Gorham and Gordon 1963). In Sweden, acidification has led to progressive, autocatalytic "oligotrophication" of some lakes where communities dominated by Lobelia and Isoetes have been replaced by Sphagnum-dominated communities (Grahn et al. 1974, Grahn 1976). This may reduce the cycling of cations such as calcium which are strongly adsorbed by the Sphagnum. It may, in addition, reduce the cycling of the limiting nutrient phosphorus, which is also strongly taken up by Sphagnum and probably adsorbed to an increasing degree by sorptive complexes in soils and sediments as pH declines (Gorham 1976).

Takeover by Sphagnum has not been observed in North America, where, however, mats of Drepanocladus fluitans and Leptodictyum riparium can cover lake bottoms (Gorham and Gordon 1963) and deserve investigation in this context.

Grahn et al. (1974) also observed accumulation of organic debris and mats of fungal hyphae in some acidified lakes, presumably because of an inhibition of bacterial activity. The effect of such developments upon nutrient cycling must be profound and merits detailed study.

Benthos

Bottom-living organisms, both littoral and profundal, may also be affected directly and indirectly by materials deposited from the atmosphere. Changes in benthic algae have been observed in Sweden, where acidification favors the filamentous genera Batrachospermum and Mougeotia (Grahn et al. 1974). Benthic invertebrates are less diverse in acid lakes (Hendrey and Wright 1976, Leivestad et al. 1976, Conroy et al. 1976), with the important amphipod Gammarus absent from lakes below pH 6.0 and snails absent below pH 5.2 (Okland 1969a,b; Dickson 1975). Effects will vary with the season and with the stage of development of the organism. According to Bell (1971), insect emergence may be influenced by sublethal levels of acidity, and those emerging very early in spring will be most susceptible to the pulses of acid input owing to snowmelt (Hagen and Langeland 1973, Hultberg 1976). Where predatory fish are killed, Gyrinidae and Corixidae may become more abundant (Grahn et al. 1974).

Effects upon benthic invertebrates will ramify to produce effects on other organisms; particularly if the species affected are important components of the food web, significant grazers on algae and macrophytes, or major detritus feeders (Hendrey et al. 1976) active in the recycling of limiting nutrients. Some benthic invertebrates prefer detritus which has been "conditioned" by prior microbial attack. If the microbes responsible for such "conditioning" are inhibited by low pH, secondary effects will be observed upon the invertebrate fauna and have not been studied.

Partial Users of Aquatic Habitats

Organisms which use aquatic environments for a part of their life cycle may be seriously affected by acid deposition, as, for example, the amphibian Ambystoma (Pough 1976), which utilizes small pools for breeding. Animals such as the moose, which appears to depend for a sufficient supply of sodium upon aquatic macrophytes (Botkin et al. 1973, Jordan et al. 1974), will be affected if acid or heavy metal deposition inhibits the production of such plants. Birds also search streams and the littoral zones of lakes extensively for food, and their diet may in consequence be affected by any factor influencing the distribution and productivity of aquatic organisms. Such secondary dietary effects have not been examined.

Effects Upon Wetland Communities

There is no study known to the writer of the effects of acid deposition upon wetland ecosystems, although much is known of the distribution of organisms in relation to natural pH gradients. Accumulation of airborne heavy metals by bog mosses (e.g., Sphagnum fuscum, S. magellanicum) has been extensively documented (Rühling and Tyler 1971; Pakarinen and Tolonen 1976a,b), and the acidification of bog waters near urban and industrial centers has been described (Gorham 1958a), but there has been no study of the ecological effects upon the bog ecosystem. (Completely "dead" peat bogs have been observed by this author in the vicinity of Sudbury, where pollution from both acid and heavy metal is extreme.) Presumably a progressive decline in both biotic diversity and productivity occurs as increasing saturation of the peat exchange complexes by hydrogen ions makes biological uptake of metal cations and ammonium (and perhaps phosphate as well) more difficult. Direct and secondary effects upon invertebrate and vertebrate animals may be anticipated but are essentially unknown, as are effects upon bacteria and fungi--which must be presumed vital to the breakdown of organic detritus, the formation of peat, and the recycling of limiting nutrient elements such as nitrogen, phosphorus, etc.

Associated inputs of nutrients (NH_4 , NO_3 , K, Ca, S, and possibly P) could have beneficial effects upon wetlands, many of which are extremely impoverished in this respect, but these are likely to be outweighed by the harmful influence of greater acidity along with higher levels of other inorganic and organic toxins.

It is noteworthy that certain kinds of wetlands are inhabited by a great diversity of orchids, which are among the most widely protected rare plants. Such habitats deserve special consideration for preservation.

The impact of acid deposition should first be examined by regional biological and chemical surveys along transects away from major points or regional sources. Particular attention should be paid to peatlands whose surfaces are wholly or partially isolated from the mineral soil so that they are strongly influenced by atmospheric deposition. The waters of such peatlands are usually below pH 5.6 and may go below pH 4.0. They have little capacity to neutralize inputs of strong acids so that they are especially sensitive to impact.

Further work upon wetlands should follow the recommendations outlined for aquatic ecosystems. One specific recommendation might be to investigate the growth of certain species of peat-forming Sphagnum mosses in relation to acid deposition on bogs fed solely by atmospheric precipitation. Growth might be studied also in relation to the deposition of toxic heavy metals, which these mosses accumulate quite effectively, and of nutrients. Inputs of the growth-limiting nutrient nitrogen (and perhaps phosphorus) are increased by atmospheric pollution and may counterbalance in some degree the toxic effects of acids and heavy metals.

Sphagnum samples, collected from specific sites on a broad regional basis, could also be archived for eventual study of temporal changes in heavy metal accumulation (cf, Rühling and Tyler 1969, 1971).

Effects Upon Humans

Effects upon human users of aquatic and wetland ecosystems may be rather diverse and may involve food supply in at least two ways. Where fish populations decline because of acid deposition, the loss may be obvious (Beamish 1976). Where acid deposition leads to contamination by excessive heavy metals, whether airborne or derived from soils subjected to a stronger degree of acid leaching, the effect upon humans may be less obvious. There is at least a suggestion that elevated mercury levels in fish may sometimes be a result of such acidification (Landover and Larsson 1972, Brouzes et al. 1977), which deserves further study. The possibility of contamination of water supplies by airborne aromatic hydrocarbons, which include potential carcinogens, has not been studied.

Acidification of water supplies is another potential cause of harm, leading to corrosion of metals from household plumbing systems. Soft water has been related epidemiologically to cardiovascular problems, perhaps through effects upon heavy metals (Bierenbaum 1976).

Yet another effect is less easily measured: Lakes and wetlands are used extensively for recreation, whether it be fishing, bird watching, or canoeing and hiking. Anything which degrades these habitats will, therefore, contribute in some degree to a loss of recreational potential, however hard this may be to assess.

Recovery from Impact

Recovery may be brought about in two ways: by elimination of the pollution or by amelioration of its impact. So far only the latter has been studied, at least in natural ecosystems. Liming has been attempted in Sweden (Andersson et al. 1974) and at Sudbury, where both acidity and heavy metal pollution are exceptionally severe (Scheider et al. 1975). Addition of nutrients has also been employed at Sudbury (Scheider and Dillon 1976). Long-term treatment and follow-up will be required to assess adequately the results of such treatment, which ameliorates the impact of both acidity and heavy metal pollution, because the metals are more readily sequestered in biologically unavailable forms at neutral or alkaline pH.

In some cases, restocking by tolerant species may be a practical means of avoiding the worst results of acid deposition and should be tested. Restocking of the original species may also be a necessary accompaniment of liming.

Rating of Ecosystem Sensitivity

It has long been known that the sensitivity of ecosystems to alteration by atmospheric deposition is related to the capacity of rocks and soils to supply bases capable of neutralizing acids and to supply other soluble elements to soil solutions and lake waters (Gorham 1958b, 1961; Gorham and Gordon 1960, 1963; see also Wright and Lysholm 1975). Recently a calcite saturation index (CSI) was developed (Conroy et al. 1974, Kramer 1976) to provide a quantitative estimate of a lakes resistance to acidification. It is the logarithm of the degree of saturation of a water body by CaCO_3 and is defined as follows:

$$\text{CSI} = \text{p}(\text{Ca}^{2+}) + \text{p}(\text{Alk}) - \text{p}(\text{H}^+) + \text{pK},$$

where $\text{p}(X) = -\log_{10}(X)$, $\text{pK} = +2$, (Ca^{2+}) is given as mol/l, and (Alk) and (H^+) are given as eq/l. In waters saturated with CaCO_3 , $\text{CSI} = 0$; if supersaturated, $\text{CSI} < 0$. A CSI index < 1 indicates that acid deposition is unlikely to cause acidification, whereas an index of 1-2 may indicate some susceptibility. An index between 2 and 3 indicates danger, and an index of more than 3 suggests that acid loading will very likely be deleterious. Such sites are usually oligotrophic to begin with, lying on hard rocks such as the Precambrian Shield. Galloway and Cowling (1978) have mapped the distribution of sensitive areas in North America.

The calcite saturation index measures only the neutralization capacity of lake or stream water, which reflects many other factors involved in determining a lakes sensitivity to acid deposition. For example, where adjacent soils are thin and coarse-grained, their neutralization capacity will be low. Soils also may differ considerably in their contents of toxic heavy metals capable of mobilization by acid deposition.

Climate may be involved, with areas subject to heavy rainfall receiving specially large atmospheric inputs by rain-out and wash-out. Heavy snow pack may lead to unusually severe episodic pollution during the spring melt. The ratio of precipitation to evaporation may also be important as a determinant of the rate at which water flushes through a lake or stream as well as of the degree to which soils have been leached naturally. Lake morphometry may also be significant in determining flushing rate, with mean depth and ratio of drainage area to lake area as the major factors. Depth may also determine whether acid rain in summer reaches the profundal sediments, which it will do only if the lake is unstratified. This may have great importance for the profundal benthos. Stream and lake order may likewise be very significant, with headwater streams and lakes usually subjected to the greatest impact because of high rainfall, shallower and more heavily leached soils, and difficulty of upstream recolonization.

Another geographic factor to be taken into account is the likelihood of future urban/industrial development close to the site. Probability estimates for such development ought to be incorporated into ratings of ecosystem sensitivity, which depends not only upon intrinsic vulnerability but also upon extrinsic factors affecting the degree of atmospheric deposition to which ecosystems will be liable.

Finally, the nature of the biota may be significant insofar as the balance between sensitive and tolerant species may affect ecosystem stability.

Methods of Study

It is important to recognize that investigation of the effects of acid deposition and associated phenomena requires a diversity of approaches. Field surveys are of great importance, particularly along transects away from point sources when these can be identified. Experimental manipulation of natural lakes and streams, as in the Experimental Lakes Area under study by the Fisheries Research Board of Canada in western Ontario, will probably provide the most useful quantitative dose/response curves for both species and ecosystems and also the best assessment of synergistic and antagonistic interactions, which so far have received far too little attention. Artificial ponds and streams may also be useful. They will, however, require supplementation by laboratory studies, including the establishment of artificial microcosms, because experiments in nature are expensive in both money and personnel. Simulation studies will also be useful once sufficient data become available to make modelling reasonably feasible. Experiments are needed over a range of pollutant loadings to systems of widely varying vulnerability. It may be of considerable importance, for example, to examine the impact of heavy-metal inputs where the accompanying acids are neutralized as well as where they are not.

Long-term monitoring will be vital to the success of ecological assessment. It is clear from the Swedish experience (Odén 1976) that some effects may take decades to become clearly evident, to the degree that cause-and-effect relationships may be assigned with any confidence. In particular, it is only by such long-term study that the subtle, indirect effects of acid and metal deposition upon ecosystem metabolism and ecosystem succession will become apparent. Unfortunately, after such a time, some effects may well have become irreversible.

Stratigraphic studies of lake sediments and peats can provide a retrospective view of long-term ecosystem changes to complement monitoring into the future. Siliceous diatom frustules can indicate the severity of impact by a shift in the balance of acidophilic and acidophobic species and in the balance of species characteristic of eutrophic and oligotrophic habitats. Cladoceran carapaces and the head capsules of larval chironomids can provide similarly useful biological information in lake sediments. Stratigraphy will also indicate chemical changes consequent upon the deposition of heavy metals and organic pollutants (Müller et al. 1977).

There should be a strong research focus upon worst-case situations where cause-and-effect relationships can be established most readily and convincingly. Finding such situations will be greatly assisted by going through the sensitivity-rating process described earlier.

Wherever studies are made, they will be most rewarding if combined and integrated with studies on adjacent terrestrial habitats. Linkages between ecosystems are of very great importance (Likens and Bormann 1974, Hasler 1975, Hynes 1975) and are particularly important for lakes and streams that receive major inputs of both inorganic and organic materials from the surrounding watersheds. In the case of inorganic materials, acid deposition is likely to increase leaching inputs to aquatic ecosystems. On the other hand, by retarding terrestrial litter decomposition, inputs of organic matter may be decreased. Such a reduction of decomposition may also act to retard the release of nutrients to streams and lakes by litter recycling. Wherever possible, therefore, entire watersheds should be the units for study.

Priorities for Future Research

Although all ecological aspects of acid deposition require further investigation, some are deserving of especially high priority. Among these (and not necessarily in order of preference) are:

- (a) Organic toxins accompanying acid precipitation;
- (b) Synergism and antagonism of acids, metals, organic toxins, and nutrient elements;
- (c) Wetland communities (effects upon species composition and productivity);
- (d) Neuston communities (ditto) as early indicator systems;
- (e) Biotic impoverishment (loss of species);
- (f) Genetic impoverishment (loss of races, ecotypes, etc.);
- (g) Effects upon microbial metabolism and the cycles of elements, including nutrients as well as toxins;
- (h) Effects upon ecosystem stability, including subtle indirect effects of pollutants, alone and in combination, that lead to species replacement;
- (i) Chemical and biological stratigraphy of lake sediments and bog peats;
- (j) Integration with terrestrial studies on a watershed basis.

EFFECTS OF ACID PRECIPITATION AND ATMOSPHERIC DEPOSITION
ON TERRESTRIAL VEGETATION

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Summary

Acid precipitation is an important threat to the health and productivity of terrestrial vegetation in many parts of the United States. But acid precipitation is only one special feature of the general impact of the atmosphere on the biosphere of the earth. In recent decades, human activities (mainly increased combustion of fossil fuels) have greatly increased total emissions and deposition of beneficial nutrient elements and injurious substances (such as strong acids) from the atmosphere. Projected increases in the use of fossil fuels, and especially in the use of coal, will add still further to the total burden of beneficial and injurious substances deposited on vegetation and soils from the atmosphere. The purpose of this brief paper is to assess the status of our limited knowledge of the effects of present emissions and projected increases in emissions from combustion of fossil fuels on the vegetation of the agricultural, forest, range, and urban lands of the United States.

Acid Precipitation as Part of a General Phenomenon
of Atmospheric Deposition

Most plants take up nutrients from the atmosphere as well as from the soil solution. This capacity is especially important in natural ecosystem such as forests and rangelands where nutrients from other sources are scarce and where fertilization is not a normal management procedure. But this capacity also increases the vulnerability of terrestrial plants and animals to injury by acid substances and other toxic ions in the atmosphere and in precipitation.

Forest and rangelands cover a larger fraction of the total land area of the United States than all other uses of land combined. For this reason, terrestrial vegetation, soils and surface waters are the primary deposition sites for precipitation and airborne particulate matter of all types. Trees develop very large canopies of leaves and branches that extend high into the air. Thus, forests and range plants provide an extremely large surface for deposition and potential assimilation of both beneficial nutrient elements and injurious substances dispersed in the atmosphere.

Airborne substances that influence terrestrial plants and animals include: sea spray from ocean and large lakes; dust resulting from wind erosion of soil as well as from volcanic and cosmic sources; gases such as carbon dioxide, ammonia, sulfur dioxide, hydrogen sulfide, methane, etc., released from decomposing organic matter and volcanoes; biogenic particles,

such as spores, hyphal fragments, bacteria, and pollen; particulate matter, aerosols, and gases produced by wild fires and controlled burning of agricultural, residential, and commercial heating and transportation operations.

Combustion of fossil fuels is the largest anthropogenic source of airborne substances. Some of these substances include beneficial nutrient elements; others are injurious to terrestrial plants and animals.

Many of these atmospheric trace constituents are at least partially soluble in water and can thus be absorbed or assimilated by plants when precipitation is intercepted by vegetation. In a typical forest, an average raindrop washes over three tiers of foliage before it reaches the soil. Since some of the substances dissolved in precipitation are beneficial while others are injurious to plant and animal tissues, the net effect of atmospheric trace constituents can be beneficial or injurious depending on the chemical composition of the precipitation, the duration and intensity of precipitation episodes, the species and genetic characteristics of the plant on which the precipitation is deposited, and the physiological condition, structure, phenology, and stage of maturity of the organism.

Direct injury to vegetation is most likely when a particularly vulnerable life form (for example, lichens) is exposed at a particularly vulnerable life stage (for example, early stages of reproduction or before formation of cuticle on leaves or fruit), and is growing in a poorly buffered environment (for example, sandy soils) during a season of the year when acid precipitation is most likely (for example, spring rains).

Rain and snow change in chemical composition within, as well as between, precipitation events. In cold climates, acid substances accumulate in the snowpack where they are released in concentrated form with the first melt water and thus cause very sudden increases in acidity of surface soils, vegetation, and surface waters. Thus a given plant may be subject to beneficial atmospheric influences at one time and to negative influences at another time within a given day, month, growing season, or the years of its development in the case of perennial plants and animals. Even a given molecular species, such as sulfur or nitrogen dioxide, may be absorbed and utilized as a beneficial nutrient at one concentration in the atmosphere. At another, higher concentration, even on the same day, the same substance may be absorbed and found to be toxic or even injurious to the very same plant.

Herbaceous and perennial plants are subject to changes in atmospheric deposition within a given growing season. Trees, on the other hand, persist for many years or even decades in the same environment; they are subject to very long-term changes in the chemistry of the atmosphere and precipitation.

The effects of acidic precipitation on plants is only one facet of the much longer subject of atmospheric/plant/soil interactions. Acidity in precipitation should be understood as a reflection not only of the amounts of substances yielding hydrogen ions (such as sulfuric, nitric, hydrochloric, and organic acids) but also of the total ionic balance between all the other cations and anions dissolved in precipitation.

For all of the above reasons, it is difficult to assess the effects of acid substances in precipitation in isolation from the general chemistry of precipitation. Also, the effects of a given "acid rain" or a prevailing condition of "acid rains" are very complex, are variable in time, and involve significant interactions that are only partially understood. Thus, these effects are not easily resolved into simple generalizations.

Potential Effects of Acid Precipitation on Vegetation

A partial list of theoretical effects of acid precipitation on vegetation was developed earlier by Tamm and Cowling (1976) and is reproduced in Table 8. The effects are classified as either direct or indirect, although most direct effects will have many indirect consequences as well. A decreased rate of growth would be the expected consequence of most of the effects postulated in Table 8 but unequivocal evidence of significant growth effects have yet to be demonstrated in agricultural, forest, or range ecosystems. Specific biological effects that have been proven to occur in at least one experimental plant are marked with an asterisk (*) in Table 8.

The Availability of Essential and Injurious Elements

The growth and productivity of plants is determined by the availability of fifteen elements that are essential for growth and a few that are toxic to plants. Among the essential elements, carbon, hydrogen, and oxygen are rarely limiting. The major fertilizer elements--nitrogen, phosphorous, and potassium--are often limiting. Sulfur, calcium, and magnesium are sometimes limiting as well as the so-called micronutrients --iron, copper, zinc, manganese, molybdenum, and boron.

Some elements are both essential and injurious to plants. For example, small amounts of sulfur and large amounts of nitrogen are needed for synthesis of protein, nucleic acids, and other substances in plants but gaseous sulfur and nitrogen oxides and sulfuric and nitric acid aerosols are injurious to plants at very low concentrations. Similarly, excess amounts of the micronutrient elements can injure plants. Atmospheric fluoride is toxic to plants at 25-50 ppm. Aluminum is the most abundant potentially toxic element in soils. Its availability (and thus its toxicity) is influenced greatly by the acidity of soils, which in turn is influenced by the abundance of acid precipitation. Estimates of the threshold concentrations for detectable injury or economic damage by air pollutants, including NO_2 , SO_2 , O_3 , and precipitation require substantial additional research with a great variety of plants and conditions of exposure.

Many factors (i.e., genetic composition, biotic and other abiotic stress factors, dose of pollutant, and pollutant combinations) affect the impact of acid precipitation and other pollutants on terrestrial plants and animals. Variation in any one factor can result in variation in the nature and magnitude of pollutant effects. This is shown simplistically in Figure 2.

Table 8. Potential Effects of Acidic Precipitation
on Terrestrial Vegetation

Direct Effects

*1. Damage to protective surface structures such as cuticle.

Damage to surface structures may occur due to accelerated erosion of the cuticular layer that protects most foliar organs. It also could result from direct injury to surface cells by high concentrations of sulfuric acid and other harmful substances that are concentrated by evaporation or adherence of soot particles on plant surfaces.

*2. Interference with normal functions of guard cells.

Malfunction of guard cells will lead to loss of control of stomata and thus altered rates of transpiration and gas-exchange processes and possibly increased susceptibility to penetration by epiphytic plant pathogens.

*3. Poisoning of plant cells after diffusion of acidic substances through stomata or cuticle.

This could lead to development of deep necrotic or senescent spots on foliar organs including leaves, flowers, twigs, and branches.

*4. Disturbance of normal metabolism or growth processes without necrosis of plant cells.

Such disturbance may lead to decreased photosynthesis efficiency, altered respiratory patterns, and intermediary metabolism, as well as abnormal development or premature senescence of leaves or other organs.

*5. Alteration of leaf- and root-exudation processes.

Such alterations may lead to changes in populations of phyllosphere and rhizosphere microflora and microfauna, including nitrogen-fixing organisms.

*6. Interference with reproduction processes.

Such interference may be achieved by decreasing the viability of pollen, interference with fertilization, decreased fruit or seed production, decreased germinability of seeds, etc.

7. Synergistic interaction with other environmental stress factors.

Such reinforcing interactions may occur with gaseous sulfur dioxide, ozone, fluoride, soot particles, and other air pollutants as well as drought, flooding, etc.

Table 8.--Continued

Indirect Effects*1. Accelerated leaching of substances from foliar organs.

Damage to cuticle and surface cells may lead to accelerated leaching of mineral elements and organic substances from leaves, twigs, branches, and stems.

2. Increased susceptibility to drought and other environmental stress factors.

Erosion of cuticle, interference with normal functioning of guard cells, and direct injury to surface cells may lead to increased evapotranspiration from foliar organs and vulnerability to drought, air pollutants, and other environmental stress factors.

*3. Alteration of symbiotic associations.

Changes in leaf- and root-exudation processes and accelerated leaching of organic and inorganic substances from plants may affect the formation, development, balance, and function of symbiotic associations, such as mycorrhizae, nitrogen-fixing organisms, lichens, etc.

*4. Alteration of host-parasite interactions.

Resistance and/or susceptibility to biotic pathogens, parasites, and insects may be altered by subjecting plants to any environmental stress. Acid precipitation may increase the susceptibility of plants to these injurious agents, alter their capacity to tolerate disease or injury, or alter the virulence of pathogens. The effects of acidic precipitation may vary with the following: the nature of the pathogen involved (whether a fungus, bacterium, mycoplasma, virus, nematode, parasitic seed plant, insect, or multiple-pathogen complex); the species, age and physiological status of the host; and the stage in the disease cycle in which the acidic stress is applied--for example, acidic rain might decrease the infective capacity of bacteria before infection and increase the susceptibility of the host to disease development after infection.

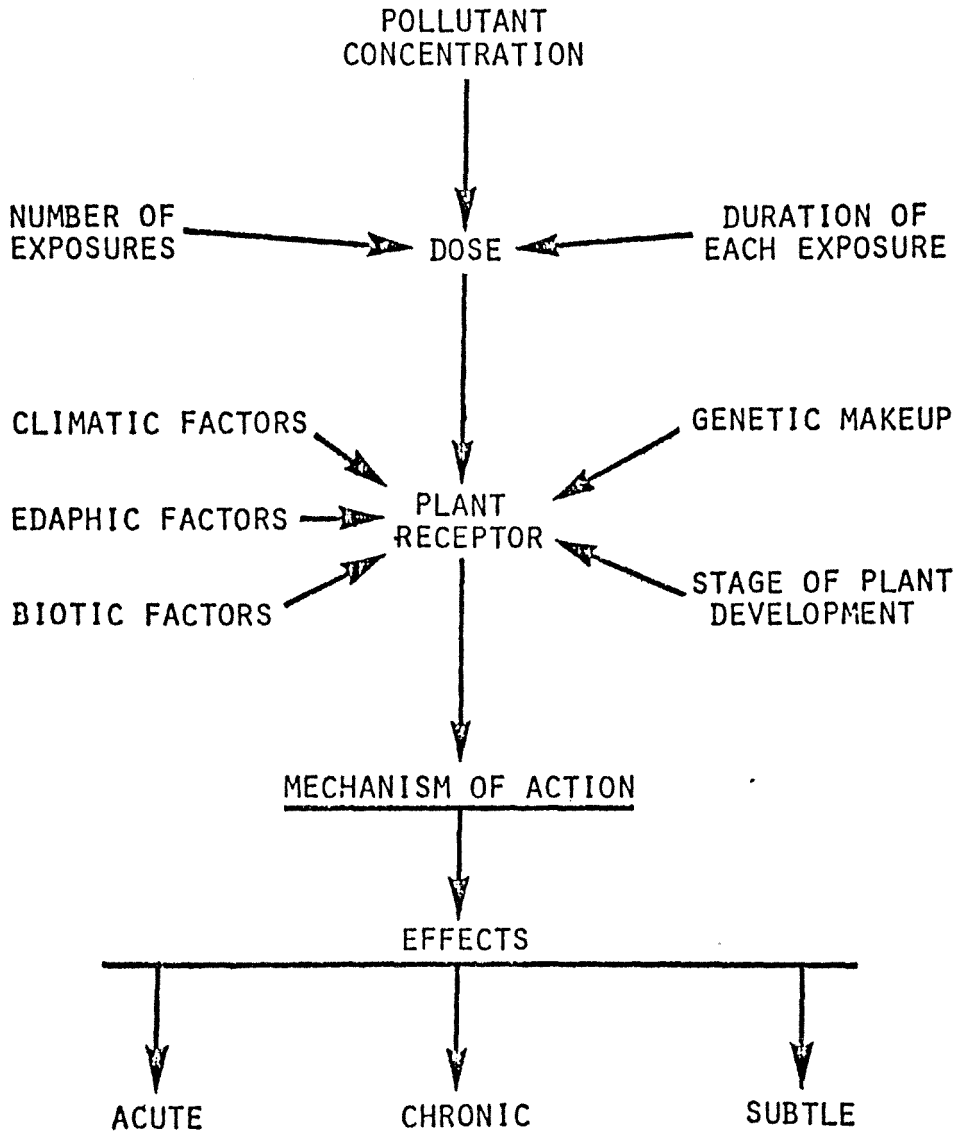


Figure 2. Conceptual model of factors involved in air-pollution effects on vegetation (Heck *et al.* 1977).

Previously, it was believed that the essential and potentially toxic elements listed in the first paragraph of this section were taken up by plants almost entirely from the soil solution. Now, it is recognized that airborne gases, particulate matter, and aerosols significantly augment the supply of both essential and injurious elements. All of the substances listed above can be taken up readily through foliar organs as well as by absorption from the soil solution (Tamm 1958, Wittwer and Bukovac 1969).

Much larger amounts of essential nutrients are required for sustained-yield agriculture than for sustained-yield range management or hardwood or softwood forestry. This is true in rangelands because biomass yields are very low and in forests because the parts of trees that usually are harvested--the wood and bark of tree stems--contain very much less of the most essential elements than the seeds and fruits that are commonly harvested in agriculture. This is a major reason why fertilization is so common in agriculture and so rare in forestry and range management. In some forested regions, atmospheric deposition alone is more than adequate to permit harvesting of crop after crop of trees without fertilizing the forest. This is much less likely to remain so as more and more of the nutrient-rich branches, foliage, and roots of trees are harvested in so-called "whole-tree chipping" and other modern harvesting practices.

Plant life as we know it would be impossible without atmospheric sources of carbon for photosynthesis, nitrogen for biological fixation and protein synthesis, oxygen for respiration and synthesis of carbohydrates, and water for transpiration of plants. All of the essential and injurious substances listed above are present in the gaseous, particulate, and aerosol emissions from the combustion of fossil fuels. All of the vast amounts of these emissions into the atmosphere eventually return to the surface of the earth where they are deposited on vegetation and soils by one of four major processes: 1) precipitation of dissolved, suspended, or absorbed substances in raindrops and snowflakes; 2) deposition of wind-blown dust and particulate matter; 3) impaction of aerosols; and 4) absorption of gases.

Many scientists believe that acid rain and snow are deposited directly onto soils where acid substances could be neutralized in well-buffered soils or by applications of lime. This is true on some agricultural lands, specially after harvest, but is not true in forests, rangelands, or even on most agricultural lands during the growing season. Most raindrops are intercepted by the foliage of plants where substances dissolved in the rain can induce various physiological changes before reaching the soil. In a mature forest, for example, rain will wash over three tiers of foliage before reaching the soil. Most forests and rangelands in the United States are rarely fertilized and almost never limed to neutralize excess acidity. Furthermore, forests cover about half the total land area of the United States and develop very large canopies of leaves and branches that extend high into the air. Thus, forests provide a very large surface for deposition and assimilation of all the beneficial and injurious substances dispersed in the atmosphere and deposited as precipitation (Tamm 1958, Wittwer and Bukovac 1969, Tamm and Cowling 1976).

Sources and Amounts of Beneficial and Injurious Substances

There are three major reasons why agricultural, forest, and aquatic biologists are becoming increasingly concerned about atmospheric transport and deposition of both nutritionally beneficial and potentially injurious substances:

1. Vegetation, soils and surface waters are the primary deposition sites for precipitation and airborne particulate matter of all types;
2. Atmospheric deposition constitutes an important source of nutrients and potentially injurious substances that effect the productivity and stability of agricultural, forest, and aquatic ecosystems;
3. Human activities are steadily increasing the amounts and variety of substances dispersed in the atmosphere (Odén 1968, Bolin et al. 1971).

Recent increases in the deposition of substances on terrestrial vegetation are due mainly to increases in combustion of fossil fuels in industrial enterprises, residential heating, transportation, and agricultural operations. Previously, it was believed that most of these materials fell out of the atmosphere near the site of emission. Now it is recognized, particularly with increased use of tall stacks in power plants, that atmospheric processes can lead to extensive mixing and both chemical and physical interactions and transformations of atmospheric particulates, aerosols, and gases. Furthermore, these substances and their reaction products are dispersed by meteorological processes and finally enter the biosphere in fields of deposition that extend hundreds or even thousands of kilometers from the original sources of emission. The recent fallout of radioactive materials in the eastern United States as the result of atomic explosions in the Peoples Republic of China provides a dramatic reminder of the long-distance transport and deposition of pollutants (Cowling and Wood 1976).

The amounts of various substances introduced deliberately or inadvertently by man into the biosphere of the earth are becoming so large that man is becoming a major force in the biogeochemistry of the earth (Kovda 1975). This is shown in Table 9 which contains a tabulation of data on annual output of fertilizers, industrial dusts, garbage and other urban wastes and by-products, mine refuse, and discharges of aerosols and gases mainly from the combustion of fossil fuels. All these categories of matter are becoming comparable in magnitude to the discharges of dissolved and suspended substances in all the rivers of the world, the annual yield of photosynthetic products, or the cycling of inorganic elements in the earth as a whole. Anthropogenic emissions into the atmosphere are also very large, as shown in Table 10. Most gases, carbon oxides, and aerosols result from the combustion of fossil fuels. A very large part of these global emissions were produced in the United States.

TABLE 9
Biogeochemical and Technological Forces
in the Biosphere of the Earth

Biosphere Components	Tons per Year
Biogeochemical Processes:	
Yield of Photomass	1×10^{10}
Cycle of Inorganic Elements	1×10^{10}
River Discharges:	
Dissolved Substances	3×10^9
Suspended Substances	2×10^{10}
Anthropogenic Sources:	
Output of Fertilizers	3×10^8
Industrial Dust	3×10^8
Garbage, Urban Wastes and Byproducts	2×10^{10}
Mine Refuse	5×10^9
Aerosols and Gas Discharges	1×10^9

[SOURCE: Kovda 1975]

TABLE 10
Anthropogenic Emissions into the Atmosphere

Type of Emission	Tons per Year
Dust	2.5×10^8
Gases (mainly SO ₂ , HC, and NO _x)	6.5×10^8
Carbon Oxides (CO + CO ₂)	2.0×10^9
Aerosols	1.0×10^9

[SOURCE: Kovda 1975]

Note: Doubling about every 7-10 years.

If the United States is to so greatly augment the amounts of substance dispersed in the atmosphere and deposited into the biosphere of the earth, it is essential that we should measure the amount and chemical form of the deposited matter and understand the biological consequences of that deposition. Regrettably, in the United States our understanding of these processes is very fragmentary. Fortunately, however, more extensive measurements of atmospheric deposition and its biological consequences have been made in Europe, where an atmospheric-deposition network has been maintained since the late 1940 s (Odén 1968).

The European Air Chemistry Network began in Sweden and has gradually spread to include most of western Europe and parts of eastern Europe, including Poland and the Soviet Union. Since the mid-1950 s, a network of about 100 stations has made monthly measurements of changes in the chemistry of precipitation. The substances analyzed at most of these stations include the following major cations and anions: NH_4 , Na, Ca, K, Mg, SO_4 , NO_3 , PO_4 , Cl as well as pH, conductivity, and titratable acidity and alkalinity. These data have shown various long-term trends. For example, the amount of nitrate nitrogen in precipitation (an important fertilizer element) increased markedly in many parts of Europe during the fifteen years between 1955 and 1970. Nitrate nitrogen helps plants grow. Thus, the nitrogen added in precipitation probably increased yields of agricultural and forest crops.

But not all the substances detected in precipitation were beneficial. Long-term trends of injurious sulfate and hydrogen ions also were detected from 1955-1970. The latter changes were attributed to strong acids formed in the atmosphere, mainly from oxides of sulfur and nitrogen produced during combustion of fossil fuels. More recent data show that these trends of increasing acidity are continuing although the relative contribution of sulfuric and nitric acids is changing.

Changes in the Chemistry of Precipitation in the United States

Some monitoring of the chemistry of precipitation has been carried on in the United States (Feth et al. 1964, Lodge et al. 1968). A few of these studies provide excellent and reliable information about the acidity of precipitation. But most studies in this country have suffered from three major shortcomings:

1. The data were collected for a limited land area--typically only a single point or a few points in one or two states (Gambell and Fisher 1966);
2. The data were collected for very limited periods of time--typically only one or two years;
3. Very few direct measurements of pH have been made.

There is only one location in the United States--at the Hubbard Brook Experiment Forest in New Hampshire--where the acidity of rain has been measured directly and consistently for as long as ten years. The longest term national monitoring program was operated by the National Center for Atmospheric Research for six years, from 1960 to 1966 (Lodge et al. 1968).

Using fragmentary bits of information, obtained indirectly and in limited areas and periods of time, Dr. Gene Likens and one of his graduate students at Cornell University (Cogbill and Likens 1974) managed to calculate the probable changes in average acidity of rainfall in various parts of the eastern United States from 1955-1973. As shown in Figure 3, precipitation in a large portion of the eastern United States was less than pH 5.6 in 1955-56; the zone of greatest acidity (lowest pH) was generally consistent with the zone where sulfur emissions were high--parts of Ohio, Pennsylvania, West Virginia, New York, and New England. By 1973, however, the area with an average pH of rain below 4.5 had extended to include parts of Missouri, Arkansas, Mississippi, Alabama, Georgia, South Carolina, Virginia, Kentucky, Illinois, Michigan, and further north into New England and Canada. Essentially, it embraces most of the area east of the Mississippi River. Individual rainstorms with pH values between 2.1 and 3.6 have been reported in New York, Illinois, Indiana, New Hampshire, Massachusetts, and North Carolina--in some cases many hundreds of kilometers from major sources of air pollution (Likens 1976).

The relative contribution of sulfate and nitrate to the total acidity of precipitation apparently changed markedly during the years since 1964-65. At Hubbard Brook, New Hampshire, the ratio of sulfate to nitrate changed from 83:15 in 1964 to 66:30 in 1974. During this same decade, total input of hydrogen ions increased by 36%. Thus, most of this increase appears to be due to increased deposition of nitric acid.

Effects of Acid Precipitation on Terrestrial Ecosystems

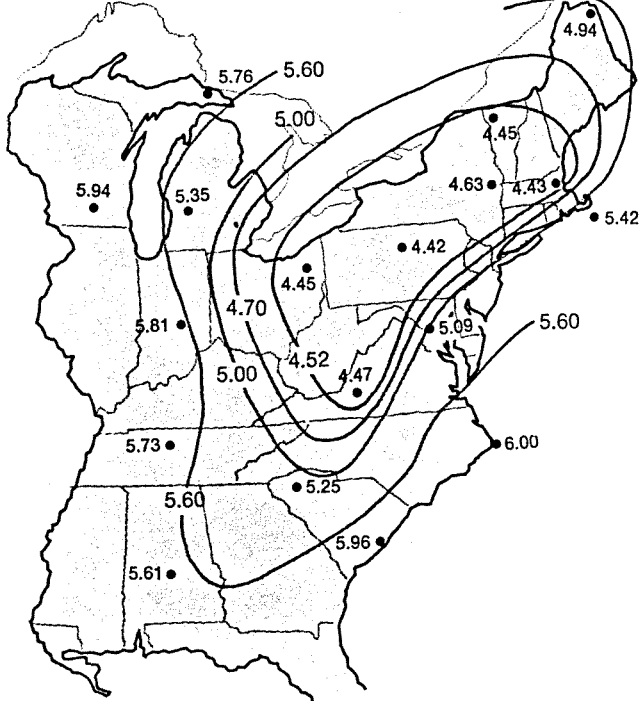
Research on the changing chemistry of precipitation and its effects on terrestrial and aquatic ecosystems has been conducted in Europe since about 1955 and in North America mainly since about 1966. Several publications are worthy of special notice in this connection. The pioneering researches by Eville Gorham, first in England, later in Canada, and most recently in the United States, dealt with effects on lake waters, aquatic vegetation, terrestrial vegetation, and human health (Gorham 1958b, 1976). Svante Odén 1968). In 1971, Bolin and his co-workers completed the Swedish Case Study's contribution to the United Nations' Conference on the Human Environment (Bolin et al. 1971). In 1972, the Norwegian government established a special Manhattan-style research project called Acid Precipitation: Effects on Forests and Fish, with an annual budget of 10,000,000 Norwegian Kroner (U.S. \$2,000,000). This huge project started with two specific objectives:

1. To establish, as precisely as possible, the effects of acid precipitation on forests and freshwater fish;

Acidity of precipitation has increased markedly in the eastern U.S. . . .

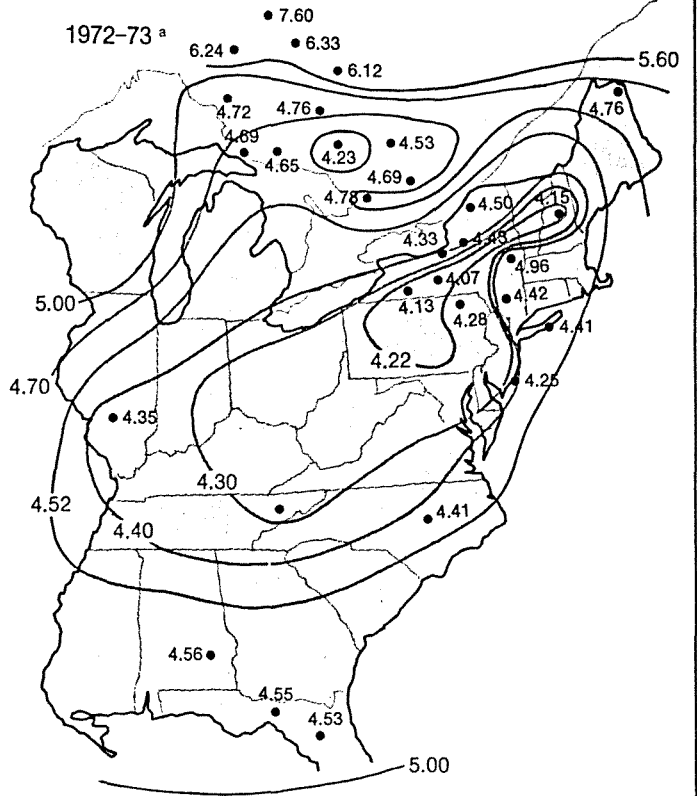
Average pH of annual precipitation

1955-56



Source: C. V. Cogbill and G. E. Likens

1972-73^a

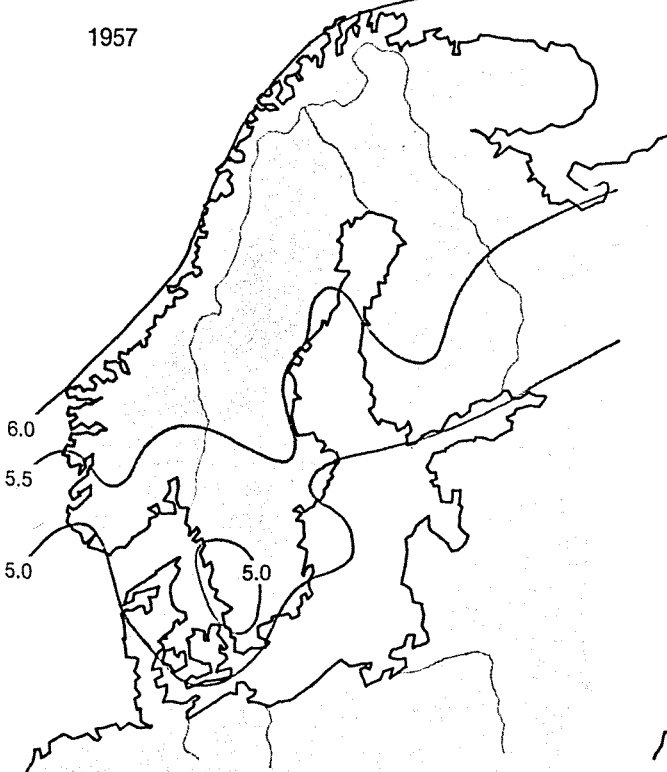


^a Data from Oak Ridge, Tenn., for 1973-74; data from Tallahassee, Fla., for 1974-75; and from Gainesville, Fla., for 1976. Source: Various, including C. V. Cogbill, Thomas Burton, Patrick Brezonik, and Gray Henderson

. . . and in Scandinavia during the past two decades

Average pH from 12 monthly samples

1957



Source: Svante Odén

1970

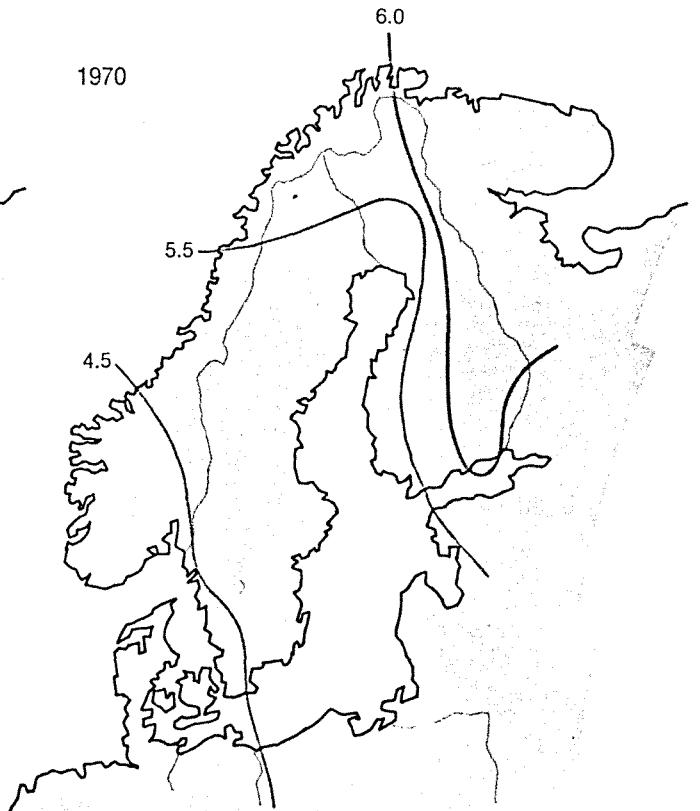


Figure 3. (From Likens 1976).

2. To investigate the effects of air pollutants on soil, vegetation, and water to the extent required to support the primary objective.

The first International Conference on Acid Precipitation and the Forest Ecosystem was held at Ohio State University at Columbus in May of 1975 (Dochinger and Seliga 1976a). In June of 1976, an International Conference on Effects of Acid Precipitation was held at Telemark, Norway, and the major papers assembled for this meeting published by Braekke (1976) and in a special issue of Ambio (1976). In November, 1976, Gene Likens published his summary report in Chemical and Engineering News (Likens 1976). In May 1978, a NATO Advanced Research Institute on Ecological Effects of Acid Precipitation was held at Toronto, Canada. In September, 1978, the Central Electricity Generating Board in England will host an international symposium on the biological effects of acid precipitation. The proceedings of these last two meetings are scheduled for publication in 1979.

The effects on terrestrial ecosystems generally have been less well documented than those on populations of freshwater fish and other aquatic organisms. Nevertheless, certain definite effects have been reported. The most striking of these effects was the development of peat moss (Sphagnum sp.) as a submarine, rather than a terrestrial plant, in acidified lakes and streams in Sweden. Dense mats of Sphagnum and an apparently parasitic aquatic fungus develop on the bottom of these lakes in water as deep as 18 m. This growth induces oligotrophication (opposite of eutrophication)--a self-accelerating process that leads to a substantial nutrient impoverishment of lake waters.

Analyses of forest growth in southern Sweden from 1896 to 1965 showed a 2% to 7% decrease in growth between 1950 and 1965. Johnsson and Sundberg (1972) "found no good reason for attributing [this] reduction in growth to any cause other than acidification." Similar attempts to quantify possible effects on growth of forests in the United States have been inconclusive.

Other reports given at the meetings in Columbus, Ohio, and Telemark, Norway, indicated that:

1. Forest canopies filter out sulfur and hydrogen ions from precipitation (Mayer and Ulrich 1976, Knabe and Günther 1976);
2. Acidity of bark and development of cuticular features, such as the frequency and size of stomata, can be used as biological indicators of sulfur pollution and acidification (Sharma 1976); for example, pH values of 2.2 to 4.7 were reported in the bark of several species of trees in Poland (Grodzinska 1976);
3. Vegetation developing in recently formed sandy soils or glacial-outwash areas is more vulnerable to the effects of acidic precipitation than vegetation growing in older, well-buffered soils of high clay content and consequently large base-exchange capacity (Tamm et al. 1976, Frink and Voight 1976);

4. Before reaching the soil, acidic substances in precipitation can induce direct changes in the physiology of foliar organs (Tamm and Cowling 1976);
5. After reaching the soil, these substances can also induce changes in root function and the availability of essential cations (Frink and Voight 1976);
6. Ammonia combines with sulfate ions in the atmosphere and tends to neutralize atmospheric acidity. When the ammonia is absorbed by plants, however, both the ammonia and the released sulfate ions contribute to the total acidification of agricultural and forest ecosystems (Odén 1976).

Simulated "rain" acidified with sulfuric acid has been reported to:

1. Induce direct injury to foliage of pines, birch, and mosses (Shriner 1976, Wood and Bormann 1974, Tamm et al. 1976);
2. Induce symptoms similar to those caused by certain other pollutants and biotic pathogens (Wood and Pennypacker 1976);
3. Induce poorer germination of spruce seeds (Abrahamsen et al. 1976);
4. Accelerate leaching of nutrients from foliage (Wood and Bormann 1974, Abrahamsen et al. 1976) and from soil (Abrahamsen et al. 1976, Wiklander 1973/74);
5. Inhibit decomposition of leaf litter from the forest floor (Abrahamsen et al. 1976);
6. Increase erosion of epicuticular waxes on oak and bean leaves (Shriner 1976);
7. Decrease uptake of nitrogen by endomycorrhize of sweetgum seedlings (Haines and Best 1976);
8. Inhibit reproduction of root-knot nematodes (Shriner 1976);
9. Inhibit development of bean rust and production of telia by the oak-leaf-rust fungus, Cronartium fusiforme (Shriner 1976);
10. Inhibit or stimulate development of halo blight in bean seedlings depending on the time in the disease cycle during which the simulated "rain" was applied (Shriner 1976);
11. Inhibit nodulation and fixation of nitrogen by Rhizobium in bean and soybean seedlings (Shriner 1976).

As yet unknown constituents of precipitation have been shown to induce "russetting"--brown blemishes that cause Yellow Delicious apples to be degraded for marketing (Kender, personal communication).

With the exception of this latter effect on apples, the possible economic consequences of the various biological effects listed above are not known. Nevertheless, the variety of biological influences that have been observed suggests that:

1. Much more research is needed to evaluate the ecological and possible economic influences of changes in the acidity and other chemical properties of precipitation;
2. A well-coordinated network to measure long-term changes in the chemistry of air and precipitation is needed in rural and urban areas throughout North America.

Based on a general analysis of effects reported to date Heck et al. (1977) offered the following generalization about relative vulnerability of vegetation to acid precipitation:

1. Freshwater fish are more vulnerable to acute acid shock than freshwater vegetation;
2. Aquatic vegetation is more vulnerable than terrestrial vegetation;
3. Herbaceous vegetation is more vulnerable than wood vegetation;
4. Plants growing in recently formed sandy soils or glacial-outwash areas are more vulnerable than plants growing in well-buffered soils of high clay content and consequently large base-exchange capacity;
5. Reproductive stages are more vulnerable than vegetative stages;
6. Plants growing in natural ecosystems are more vulnerable than plants growing in agroecosystems, where liming and other fertilization practices are common;
7. Coniferous forests are more vulnerable than hardwood forests;
8. Plants growing in regions of high rainfall are more vulnerable than desert plants.

Previous Analyses of Research Needs on the Effects of Acid Precipitation

In 1975, the National Academy of Sciences' Committee on Atmospheric Sciences published its report on Atmospheric Chemistry: Problems and Scope (NAS 1975). In May 1975, a workshop to define future needs for research on acid precipitation was held immediately following the First International Symposium on Acid Precipitation and the Forest Ecosystem. The recommendations of this workshop were published by Dochinger and Seliga (1976b). In May 1977, the Director of the Norwegian Special Project on Acid Precipitation--Effects on Forests and Fish provided an updated analy-

sis of research needs on acid precipitation as perceived from the standpoint of knowledge of acid-precipitation effects in Scandinavia. (SNSF 1977). In December 1975, the Federal Interagency Advisory Committee on Water Data impaneled a Working Group on Precipitation Quality to determine "information needed on chemistry of precipitation in the United States and to recommend appropriate measures for supplying the necessary data" (Kennedy 1977). In September 1977, the congressionally mandated "Committee of Nine" responsible for regional research in the Agricultural Experiment Stations of the United States approved plans for establishment of a long-term interagency research project entitled, "Chemical Changes in Atmospheric Deposition and Effects on Agricultural and Forested Land Surface Waters in the United States" (CSRS 1977).

In each of these major studies, needs for research on the changing chemistry of precipitation and its ecological effects were analyzed. A remarkable degree of similarity in initial research recommendations is evident in all of these reports:

1. Establish a permanent network to continuously monitor changes in the chemistry of precipitation and
2. Coordinate this long-term monitoring program with research to determine the sources, transport, and transformation of pollutants, the meteorology of their dispersal and deposition, and the nature and magnitude of their ecological effects on agricultural land, forested land, rangelands, urban lands, and surface waters in the United States.

The initiative for establishment of such a monitoring and research network has already been taken (CSRS 1977). What it needs now is adequate financial and formal interagency support. In creating this plan, scientists in the various State Agricultural and regional Forest Experiment Stations (SAES and FES) of the Department of Agriculture (USDA) joined together with scientists in other pertinent units of the United States Geological Survey (USGS), National Oceanic and Atmospheric Administration (NOAA), the Environmental Protection Agency (EPA), the Tennessee Valley Authority (TVA), the Department of Energy (formerly ERDA), the National Science Foundation (NSF), and the National Aeronautic and Space Administration (NASA) as well as with publicly and privately supported colleges and universities in the United States and Canada. The result is an integrated interagency plan for research with the following specific objective as outlined in the project plan itself:

Objective: In cooperation with federal, state, and private research agencies, to conduct research on atmospheric deposition and its effects on agricultural and forest lands and surface waters. This will be accomplished by:

1. Establishing a National Atmospheric Deposition Program (NADP) to determine spatial and temporal trends in the supply of beneficial nutrient elements and potentially injurious substances in precipitation and dry particulate matter deposited in various regions of the United States.

2. Determining the relative importance and contribution of precipitation, dry particulate matter, aerosols, and gases to the total atmospheric deposition in various states and regions of the United States.
3. Developing optimum procedures for collecting precipitation (regularly timed sampling and event sampling) and dry particulate matter (open containers, air-filtration collectors, and biological collectors).
4. Determining the stability of certain constituents of precipitation during the collection, transport, and storage prior to analysis.
5. Investigating the transport and transformations of atmospheric constituents.
6. Organizing and coordinating research in the SAES, FES, and other research institutions and agencies on the effects of changes in atmospheric deposition on: a) the productivity of agricultural crops, forests, rangelands, wetlands, and surface waters; b) the health and productivity of domestic food animals, wildlife, and fish; and c) the corrosion of metals, painted surfaces, masonry, and other materials in machinery or structures.

To accomplish these objectives, an interdisciplinary team of research scientists and a network of precipitation collection sites (NADP) is now being established by the State Agricultural Experiment Stations (SAES), the USDA Forest Service, and other cooperating agencies.

Current Priorities for Future Research

The following eleven items represent research required to assess the phenomenon of acid precipitation and determine its effects on agricultural, forest, range, and urban vegetation in the United States:

1. Determine spatial and temporal trends in the amounts of various nutrient elements and injurious substances in precipitation and dry deposition in various regions of the United States. Special attention should be given to the macronutrients (H, N, P, K, Ca, Mg, S) and micronutrients (Fe, Cu, Co, Mn, Mo, and B).
2. Determine the quantitative contribution of atmospheric deposition, in general, and foliar absorption from precipitation, in particular, to total nutrient budget of forest trees, range plants, various forage, grain, and horticultural crops.
3. Determine the extent of cuticular erosion by simulated and naturally occurring acid rains on various economic plants and their influence on drought hardiness and resistance to foliar pathogens.

4. Determine the pathways of absorption of nutrient elements by foliar organisms (direct absorption through cuticle, absorption through stomata or through hyphae of fungi growing on leaf surfaces).
5. Determine the influence of atmospheric deposition on the content of heavy metals in selected fruit and vegetable crops.
6. Determine the influence of acid precipitation on both external and internal recycling mechanisms for conservation of essential elements in forest trees and other crop plants.
7. Identify specific life forms, life stages, and life processes that are vulnerable to episodic inputs of injurious substances in precipitation or dry deposition. These vulnerable forms, stages, and processes could include germination of seeds and pollen of higher plants, germination of fungae.
8. Using an ecosystem approach, determine the contribution of atmospheric deposition to plant productivity and species diversity in natural ecosystems, such as forests and natural grasslands.
9. Determine dose-response relationship for various injurious substances in precipitation and dry deposition, both singly and in specific combinations. Particular attention should be given to the thresholds for direct injury by acid precipitation and synergistic interactions between acid precipitation and various gaseous pollutants, especially ozone and sulfur dioxides.
10. Identify the constituents of precipitation and dry deposition which cause russetting of Golden Delicious apples.
11. Determine the influence of acid substances and other constituents of snow on the survival and condition of plants and blue-green algae during periods of snow melting. Damage to over-wintering crops, like spring wheat, and nitrogen-fixing blue-green algae and free-living bacteria should be given special attention.

EFFECTS OF ACID PRECIPITATION AND ATMOSPHERIC DEPOSITION ON SOILS

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Summary

The natural acidification of humid-region soils is accelerated by acid precipitation. This is generally detrimental to productivity because plant nutrients are lost, soil exchange capacity is reduced, availability of P to plants is reduced, and solubility of Al is increased. The process is relatively slow but possibly damaging within a few decades on acid, uncultivated soils that are either shallow, low in clay and organic matter, or both. In agricultural areas, the effects of fertilization and liming will far exceed the direct effects of acid precipitation on the soil and thus make them essentially undetectable.

Attention should be focused on soils that are poorly buffered and not in agriculture. There, the effect of acid may not only upset the fragile nutrient cycle, it may cause the soil to release levels of Al damaging to aquatic systems.

Further research on the temporal and spatial patterns of acid deposition, the means of identifying vulnerable soils, and related aquatic systems is needed. Additional information is needed on the effects on soil biota and chemical processes to more adequately determine effects on productivity.

Metal contamination of soils is serious wherever it occurs. The more fertile, highly buffered soils are also the most effective filters for metals, retaining near the surface a high percentage of that added from the atmosphere. All soils will retain metals well above the toxic levels if annual input is high. Current research indicates such inputs are restricted to urban and industrial areas, but some affected areas extend 10-20 kilometers from the source and the possibility of extensive regions being adversely affected is no longer remote.

Research on regional patterns of deposition and on soil-metal-acid interactions is needed. Further information is needed on the effects on soil of chemicals and biological properties and on means to counter the negative effects.

Introduction

Soils are normally the recipients of wastes of all types in natural ecosystems, and their normal development is influenced by the nature of organic and inorganic inputs received. In recent decades, the influence of man upon soils has spread far beyond those lands that he tills to all those beneath the atmosphere he has contaminated. Acid precipitation and atmospheric deposition of metals are now widespread phenomena. Rain of pH

below 4.5 is a well-recognized problem in Scandinavia (Braekke 1976) and now is widespread in the eastern U.S. (Cogbill and Likens 1974). Deposition of potentially phytotoxic Ni, Cd, Zn, Cu, and Pb can be found in many areas of the U.S. and Europe, along with nutrient elements N, P, K, Ca, Mg, and innocuous materials, such as Na, Cl, and Si. Our soil resource provides the vast majority of our food and fiber, is usually the most stable part of terrestrial ecosystems, and is the slowest and most difficult to reclaim if lost or damaged. Therefore, any potential for wide-spread damage due to acid precipitation or other atmospheric contaminants is of the gravest concern.

Soil Acidification and Associated Effects

In those areas of the world where there is sufficient precipitation entering the soil to cause appreciable quantities of water to move through the solum, soils tend to lose basic cations as they age. Thus, most soils of the humid regions of the world are becoming more acid with time. This is part of the natural soil-forming process that is dominant in the non-irrigated, food- and fiber-producing areas of the world. There are exceptions, of course, such as areas where the soil is frequently renewed, as in floodplains, and when man is reversing or delaying this trend with amendments.

The slow acidification of humid region soils is accompanied by numerous related processes, most of which are detrimental from the standpoint of plant production. Therefore, any acceleration of this natural process is undesirable. If the incoming precipitation becomes more acidic, the soil acidification process is accelerated; but the process is extremely slow. Measurable effects may possibly occur after a few years where the soil is poorly buffered or where inputs are very high, such as in the Sudbury area of Canada (Hutchinson and Whitby 1976). More commonly, however, soil changes in response to current acid inputs will probably be measurable only after decades or centuries. The expected effects of acid precipitation on soils are summarized below from Reuss (1975), McFee *et al.* (1977), Norton (1976), Malmer (1976), and unpublished sources:

- 1) lowered soil pH
- 2) accelerated leaching of plant nutrients and other ions
- 3) accelerated weathering of soil minerals
- 4) changes in soil biota
- 5) reduction in organic matter decay rates and associated release of plant nutrients
- 6) reduction in nitrification
- 7) increased Al mobility and associated toxicity
- 8) reduced P availability to plants
- 9) increased mobility of some organic soil components

Acid precipitation entering the soil has three possible fates. (1) In drier regions and in some soils that are relatively young, the acid will be neutralized by reaction with free bases such as CaCO_3 and Na_2CO_3 . Acid precipitation added to these soils is not likely to be a problem and could be beneficial in some areas. (2) After incomplete reaction with soil minerals, the acid water may pass into the ground water in soils that are already quite acid and/or have low cation exchange capacity (CEC), e.g.,

sands with low organic matter content. (3) Most soils in the U.S. have appreciable cation exchange capacity. In these soils, acidic ions would enter into exchange reactions which to a large degree control the resulting pH of the soil. McFee *et al.* (1977) discussed the degree of pH shift expected in a typical midwestern soil and concluded that, if the pH of precipitation were 4.0 and the annual input were 100 cm, the reduction in soil base saturation due to acid precipitation could be 19% in 100 years, resulting in a pH shift downward of 0.6 units. It was further pointed out that this would occur only if there were no concurrent inputs of basic cations and the exchange of H^+ was complete. There are basic ion inputs, such as Ca^{++} and Mg^{++} , and the net acidifying effect is lessened by accompanying neutral salts (McFee *et al.* 1977).

Wiklander (1973/74) discusses the chemistry of soil acidification by acid precipitation, pointing out that it is basically a cation exchange reaction leading to lower base saturation and pH. The efficiency of the replacement is determined by soil properties as well as the pH of the precipitation and the concentration of other ions such as Ca^{++} , Mg^{++} , NH_4^+ , Na^+ and K^+ .

Reuss (1975) makes it very clear that acid precipitation on the order of pH 4.0 would play a minor role in determining soil pH in cultivated areas. He shows that the effects of natural N and S transformations in the soil are large by comparison. The potential acidifying effects of 100 kg of N per hectare applied as NH_3 far exceed that expected in precipitation in a period of several years. The potential acidity of fertilizers is discussed by Tisdale and Nelson (1975) and the influence of form of absorption by plants and relation to the whole soil ecosystem is discussed by Reuss (1975). It can be calculated that 10,000 cm of pH 4.0 rainfall (100 years at 100 cm per year) could be neutralized with an application of 10 metric tons of $CaCO_3$ per hectare (4.5 ton/acre). That is well within normal liming rates applied every 5-10 years in much of the eastern U.S. On lands in agriculture, where liming and fertilization are routine, we can conclude that the acid-precipitation effects on the soil itself are likely to be insignificant and go unnoticed because natural N and S transformations and soil amendments will have much larger impacts. However, in uncultivated, unfertilized areas that have low CEC, soil acidification may become significant even in areas far removed from sources. There is considerable concern in Norway and Sweden about the effects on shallow, poorly buffered soils. Field plots and lysimeter studies there indicated increased leaching of metal cations (Ficke 1977, Abrahamsen *et al.* 1976) and a reduction in base saturation and pH when H_2SO_4 was added.

Using physical chemical equilibria, Norton (1976) described the potential effects of acid rain on soils as a trend toward destabilization and solution of clay materials, loss of cation exchange capacity, increased rates of chemical denudation, and extensive podzolization. Iron and aluminum oxides and hydroxides may be dissolved and redox-sensitive elements (Mn, Ni, Co, Fe) become more susceptible to leaching. The leaching of Ca^{++} by acid rain has been examined by Overrein (1972), using a 40-cm profile of podzolic forest soil. He found only slight increases in leaching at pH > 4.0 on several soil types. Below pH 3.0, however, leaching loss increased rapidly; the effect was least in clay loam and greatest in sandy clay loam

and fine sand. Other lysimeter studies of the effects of acid precipitation on soils in Scandinavia have been conducted by Abrahamsen *et al* (1976) and Tamm *et al* (1976). Fisher *et al* (1968), in a study of the effects of atmospheric inputs at Hubbard Brook, NH, concluded that the overall effect of acid in precipitation is to leach base metal ions from watershed minerals.

The most significant work on Acid Precipitation and Soils in progress is a part of the SNSF-project (sur nedbdrs Virkning på Skog og Fisk) in Norway. This rather large project on acid precipitation has several participants looking at effects on soils. Abrahamsen and co-workers are continuing studies of effects on soil as well as on the vegetation. Preliminary results show a drop in soil pH in surface layers of poorly buffered podzols and no consistent effects on soil-fauna populations. They have expressed concern about the effect of increased leaching of Al from shallow, sandy soils upon streams and lakes. The results of other researchers in Scandinavia, such as Tamm (1976), Wiklander (1975), and Malmer (1976) have pointed out the following: (1) Soils are not all equally susceptible to effects of acid precipitation (2) Short-term effects on biota due to soil changes brought about by acid inputs are difficult to measure (3) Application of simulated acid precipitation increased leaching of cations but in an amount much less than the added cations (4) Acid rainfall treatments above pH 4.0 have not generally shown effects on soils in the limited time frame of experiments conducted so far (5) Decreased forest productivity has not been demonstrable thus far in natural conditions or under treatments with pH 4.0 or higher rain.

Tveite and Abrahamsen (1978) reported that simulated acid rain (dilute H_2SO_4) increased the growth of sapling scots pine after three years of application. Other workers have suggested that acid rain is the cause of reduced forest growth in certain areas and the initial stimulation may be short lived, since the acid application accelerates leaching of several plant nutrients from the soil (Wood and Borman 1977).

Tamm (1976) claims that decreases in forest growth due to acid precipitation have yet to be demonstrated, but soil organisms and biological processes have been shown to be sensitive. Crowther and Ruston (1911), in a three-year simulated acid-rain experiment, found that acidification lowered the total number of soil bacteria and that nitrifying and N-fixing organisms were more seriously affected than ammonifiers; this resulted in increased NH_4^+ and decreased NO_3^- in the soil. Denison *et al* (1976) found that dilute H_2SO_4 caused a decrease in nitrogen fixation in soil and litter in western Washington coniferous forests. It is well known that increased soil acidity generally reduces bacterial populations in favor of fungi.

It has been demonstrated quite dramatically that, when acid rain and air pollution are so severe that large areas, such as that in the copper-basin of Tennessee and Sudbury, Canada, lose most of their vegetation, the soils may be severely denuded, and the soils are apparently incapable of full recovery. Severe erosion has probably been the most damaging, but there is evidence of acidification also. As Hutchinson and Whitby (1976) put it, "These profound and damaging changes may be only indicative of

extreme local conditions and may be a harbinger of what can be anticipated in other acid rain areas."

In summary, we feel that soils in general are much more resistant to damage from acid precipitation than lakes and vegetation; however, the present acid inputs common over large areas in northern Europe and north-eastern U.S. are a hazard to those soils that have low total cation exchange capacity due to shallowness, low organic matter content, low clay contents, or combinations of these. We believe that a system of monitoring these effects in the field is needed and additional basic research should be performed on soil-acid interaction to enable prediction of future effects more accurately.

Soil Contamination by Atmospheric Deposition

Nutrients essential for plant growth (Table 11) as well as other substances are deposited on soils from the atmosphere (Wilson 1959) (Table 11). Annual inputs of N, P, K, Ca, and Mg are compared from two forest locations in Minnesota with data from Ontario, Michigan, and England in a paper by Verry and Timmons (1977). These values ranged as high as 8.5 kg/ha/yr (9.0 lb/A/yr) for Ca in Ontario to less than 0.1 kg/ha/yr (0.1 lb/A/yr) for P on some sites. These amounts are significant in natural ecosystems but represent a very small proportion of the total supply, less than 1% of that available in a typical soil and standing crop. Leaching losses are frequently of the same order of magnitude. The data of Tabatabai and Laflen (1976) indicate that in Iowa 6.3, 6.2 and 16 kg/ha/yr of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$, respectively, are added annually by precipitation. They concluded that this S input is a major source for crops in that region and Ohlrogge (1971) has expressed a similar view in Indiana. Obviously, the N input is a small portion of most crop needs but a significant contribution in a natural system. It is not uncommon in many areas of the world to find soils that appear to have insufficient supplying power for some essential elements yet produce plants with adequate levels of those same nutrients. Undoubtedly, there are many instances where the atmospheric deposition supplies the additional amount needed. In the case of the nutrients N, P, K, Ca, Mg and S, which are used in relatively large amounts by plants, we can look upon accumulation in soil from aerial deposition, in the amounts commonly reported, as generally beneficial or at worst insignificant. In the case of sulfur, and possibly nitrogen, the forms reaching plants may be damaging; but other than the acidifying effects already discussed, the levels accumulating in soils are not a problem.

The air also carries and deposits metals such as Pb, Zn, Cu, Cd, Ni, and Hg in quantities high enough to be of concern in some areas (Table 12). Zinc and copper are beneficial in small amounts, but like the others listed may become toxic to plants and soil organisms at higher levels.

Metal smelters are probably most notorious for spreading metals over the surrounding soils. In contrast to the values presented in Table 3, Buchauer (1973) reported soils contaminated with Zn, Cu, Cd, and Pb to the point that vegetation was severely affected (50,000 ppm Zn, 900 ppm Cd, 600 ppm Cu, 200 ppm Pb, or more in the A1 horizon) near a smelter in Pennsylvania and serious contamination extended 12-39 km. Hutchinson and Whitby (1976) reported heavy metal contamination within 8 km of the Sudbury smelters and Munshower (1972) cited the effects of smelters in Montana.

Localized metal contamination is not restricted to smelters. Lagerwerff and Specht (1970) demonstrated metal contamination of soils along highways, and Purves (1972) has convincing evidence of significant metal contamination by Zn, Cu, and Pb in urban and industrial areas of Great Britain. Parker *et al.* (1978) report 2400 ppm Zn, 460 ppm Pb, 120 ppm Cu, and 10 ppm Cd in the surface soils of the urban area in northwestern Indiana with lesser, but detectable, contamination extending into the rural countryside (Pietz *et al.* 1978). These Cd levels, for example, are higher than those reported to reduce growth of soybeans (Haghari 1973).

TABLE 11. BASIC CATIONS IN PRECIPITATION FROM SEVERAL LOCALES

Location	kg/ha/yr				
	Calcium	Potassium	Magnesium	Sodium	
England	3.5	1.4	2.2	17.0	Carlisle <i>et al.</i> (1966)
Indiana	6.9	1.2	-	2.6	Carroll (1962)
Minnesota	3.5	1.1	0.7	1.1	Verry and Timmons (1977)
North Carolina	5.0	2.3	1.1	4.4	Henderson <i>et al.</i> (1978)
New Hampshire	2.7	0.7	0.6	1.6	Fisher <i>et al.</i> (1968)
Ontario	8.5	0.7	3.0	0.8	Schindler and Nighswander (1970)
Oregon	5.0	0.2	1.0	1.8	Henderson <i>et al.</i> (1978)
Tennessee	14.2	3.4	2.2	4.0	Henderson <i>et al.</i> (1978)

TABLE 12. COMPARISON OF TRACE ELEMENT INPUT BY RAIN BETWEEN FOUR DIFFERENT AREAS (kg/ha/yr)

	Copper	Cadmium	Lead	Mercury	Nickel	Zinc
Average for 32 Stations in the U.S.*	.20	-	.30	-	.03	.89
Average for 8 Stations in Delaware*	.03	.08	.06	.001	-	-
Walker Branch Watershed Tennessee*	.23	.15	.24	.003	.09	.49
Urban NW Indiana†	.16	.008	.81	-	-	.98

* from Lindberg et al. (22).

† from Parker, McFee and Kelly (30).

TABLE 13. NORMAL SOIL LEVELS OF SELECTED TRACE METALS

Element	Average Range	Concentration	Source
Copper	2-100	31	Reuther and Labanauskas (1965)
Cadium	-	.06	Lisk (1972)
Lead	2-200	16	Brewer (1965)
Mercury	-	.03	Lisk (1972)
Nickel	5-500	100	Vanselow (1965)
Zinc	10-300	10	Chapman (1965)

It is clear that metal contamination of soils is taking place in many localities, but is it occurring over large areas in significant amounts? Soil sampling by Reiners *et al.* (1975) in remote areas of New Hampshire suggests that Pb, and perhaps Zn, may be accumulating. Lindberg *et al.*'s (1977) data from eastern Tennessee shows metal inputs of Cd, Mn, Pb, and Zn that are high enough to cause some soil accumulation but probably not to damaging levels. They cite data in comparison to their own from several areas, both rural and urban, that show higher rainfall inputs. Mills and Zwarich (1975), however, found little evidence of metal contamination of soils in rural areas of Manitoba and I found more in rural central Indiana.

Metals entering the soil from the atmosphere are likely to become exchangeable ions on the clay or organic exchange sites, be complexed by organic compounds, or remain or become insoluble. In any of these cases there is a strong tendency for the soil to hold the metals. Thus, only a small portion of that entering or accumulated moves through the soil. On sandy soils in northwestern Indiana, zinc has accumulated to 1071 kg/ha (2500 ppm in top inch) in the surface layers and continues to be deposited at the rate 0.98 kg/ha/yr, but only 0.15 kg/ha/yr is leaching through the profile (Parker *et al.* 1978).

In summary, metal contamination of soil by aerial deposition has reached localized damaging levels only near urban and industrial sources; however, there is enough evidence of long-range transport and deposition on soils that it should be considered a threat. Both acid inputs and metal inputs are occurring in many areas of the U.S., but we are not presently obtaining a systematic, long-term measure. We do not know the spatial trends over large areas nor the temporal trends over long time periods on the order of decades. This information is necessary if we are to adequately assess the risk to our soil resources.

Priorities for Future Research

1. Adequate regional monitoring networks.

At present we know there is acid precipitation in the U.S., but our knowledge of spatial and temporal trends is poor. We need standardized, regional, long-term input data for acidity, metals, and nutrients.

2. Fundamental investigations into interaction of acid with soil constituents.

Soils differ dramatically in their susceptibility to acidification and to other adverse effects of acid inputs. The soil's ability to hold added sulfur, its tendency to release aluminum, the stability of its exchange complex, and its resistance to pH change are all predictable to some degree from established principles. However, the reliability and accuracy of such predictions are not good. Much more research is needed, especially on the chronic effects of acid inputs.

Much of what is known of acid effects on microorganisms is based on isolated cultures, whereas the soil situation is an

interacting system of multitudes of species. Much more information is needed from soil cultures and field studies, specifically, the influence on organisms that are important in the N cycle.

Research is needed on the effects of atmospheric deposition on soil organic matter cycles. Models of nutrient cycling depend heavily on a knowledge of accumulation and decay rates of organic material and our present knowledge is sketchy. Soils are complex systems of organic and inorganic materials seldom, if ever, in true equilibrium. Therefore, theoretical approaches must be field tested, at least on small scale plant-soil models.

3. The interaction of acid precipitation and soil-metal availability and movement.

Numerous areas in the U.S. receive significant quantities of metal deposition from the atmosphere, and the use of soil as a disposal for sludge and other metal-bearing wastes is increasing. Since it is usually true that reduced pH increases metal mobility, the interaction of acid precipitation and movement of metal in the soil deserves more study.

4. Definition of toxic levels of metals in soils.

Total analysis of soils is seldom a useful measure of availability of plant nutrients or toxic elements to plants. The common extractants used in agriculture and forest soils diagnostic testing must be tested on potentially toxic metals. There is a need to establish critical levels of toxic substances and determine how they fluctuate due to soil properties or environmental conditions.

5. The influence of acidification on soil fauna and flora.

More emphasis is needed on examination of the thin layers of soil near the surface. The inhabitants of these layers should respond first to acidification and could provide an early warning of serious soil changes. Population changes in these layers will also result in changes in nutrient cycles due to their influence on initial decay of litter.

6. Terrestrial output to aquatic systems.

The vegetation and soil of the watershed exert a dominant influence on the water quality in an aquatic ecosystem. Studies of the interaction of atmospheric inputs to plants and soils with the quality of water draining from the soil is needed. What are the influences of cation exchange capacity and the nature of the exchange complex on the release of Al, the retention of S and the movement of metals to aquatic systems?

7. Classifying and mapping land areas most vulnerable to damage from atmospheric deposition.

Several factors are known that influence vulnerability. The existing knowledge of soil characteristics and plant and weather factors needs to be drawn together and vulnerability criteria established. This should then be used to map these areas such that they could be identified and compared with regions of high input. These area would then be the obvious places to intensify field research.

8. Influence of acid precipitation on soil weathering.

The acceleration of soil-mineral weathering and formation and destruction of clay minerals need to be understood in greater detail in order to evaluate the long-term hazard of acid precipitation to our soil resources.

EFFECTS OF ACID DEPOSITION UPON OUTPUTS FROM TERRESTRIAL TO
AQUATIC ECOSYSTEMS⁷

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Introduction

Linkages among ecosystems are receiving much attention currently (Likens and Bormann 1974, Hasler 1975) and are especially important for aquatic ecosystems, which serve as receptors for the diverse outputs of terrestrial ecosystems and are strongly affected by them. The influence of acid precipitation upon terrestrial outputs may be direct, where elements deposited from the atmosphere to the land pass over or through the soil to streams and lakes; or it may be indirect, where elements added in precipitation accelerate or retard the processes of soil weathering, leaching, and organic decomposition.

Components Of Acid Precipitation

The increasing acidification of streams and lakes in northwestern Europe and northeastern North America is a combined effect of acid precipitation falling upon the lakes and upon their drainage basins. In southern Scandinavia only a few lakes measured in the period 1920-1940 had pH levels below 5.5, whereas in 1974 about 40% of 155 lakes in southern Norway were below that level (Wright and Henriksen 1977). In both Norway and Sweden, declines in pH of 0.02-0.05 units/year have been recorded over recent decades (Gjessing *et al.* 1976, Wright and Gjessing 1976). In the Adirondack Mountains of the northeastern United States, 4% of the mountain lakes above 600 m elevation had pH values below 5.0 in the period before 1940, whereas in the mid-1970s 51% were below that value (Schofield 1976). The average pH decline was 0.05 units/year (Wright and Gjessing 1976). The balance between acid deposition directly on the lake surface and acid deposition transferred from the land has not been assessed. It will be

⁷To be included in the report of the NATO Advanced Research Institute's meeting on the Effect of Acid Precipitation on Vegetation, Soil and Soil Biota in Toronto, Canada, in May 1978.

determined not only by the ratio of drainage area to lake area, but also by the absorption of sulfur and nitrogen oxides and the impaction of acid droplets and particles upon terrestrial vegetation, and by the degree of neutralization occurring in the canopy and in the soil (Nihlgard 1970; Eaton et al. 1973).

Acid precipitation contains a variety of heavy metals particularly in the vicinity of metal smelters (Gorham 1976), and these too may be deposited directly in lakes or be transferred to them from the land. Concentrations of Pb and Zn in Norwegian lakes are distinctly higher in the south than in the central and northern parts of the country (Henriksen and Wright 1977), presumably owing to air pollution from industrial Europe.

In Lake Constance, Cd, Hg, Pb and Zn are enriched 3- to 4-fold in surface sediments, again most likely because of air pollution from coal combustion (Müller et al. 1977). In lake sediments in the northeastern U.S.A., Ag, Au, Cr, Ni, Pb, Sb and V exhibit increased rates of deposition in recent times, presumably for the same reason (Galloway 1977, Galloway and Likens 1977). In many instances, the balance between direct fallout on the lakes and transfer from the land is uncertain, because of unmeasured impaction and the possibility of enhanced acid leaching of heavy metals from terrestrial soils. However, in the case investigated by Galloway (1977, Galloway and Likens 1977) atmospheric deposition appears to be the predominant cause of recent enrichment in heavy metals, because other metals (Al, Fe, Ca, K, Mn) that might be expected to leach from acidified soils are not enriched in the same way.

Acid precipitation also contains a variety of plant nutrients, such as Ca, K, S, N, (Gorham 1958b) and possibly P (Gorham 1976). These likewise may be transferred from land to water, but in addition most are likely to be enriched by leaching from terrestrial soils upon which acids have been deposited.

Finally, acid precipitation contains a wide range of organic molecules, including alkanes, polycyclic aromatic hydrocarbons, phthalic acid esters, and fatty acid ethylesters, as well as a variety of commonly used industrial chemicals, such as polychlorinated biphenyls. These are reported from Norway in concentrations of one to a few hundred ng/l (Lunde et al. 1976). How much passes from land to water is unknown, but Müller et al. (1977) record enrichments of up to 50-fold for several polycyclic aromatic hydrocarbons in the recent sediments of Lake Constance.

In all the above-mentioned instances, there is an urgent need for mass-balance studies to determine the degree to which the acids, heavy metals, nutrients and organic molecules reaching aquatic ecosystems have originated from direct precipitation upon the lake surface, transfer from atmospheric deposition upon the land, or--in some cases--enhanced soil leaching due to acid precipitation. The most difficult requirement in determining chemical budgets is the accurate measurement of absorption and impaction of elements and molecules upon the vegetation canopy, and their subsequent transfer. In determining mass balance of some elements (N, S), gaseous emissions from soil may also be very difficult to assess. The problems are well illustrated by studies of the Hubbard Brook Experimental Forest (Likens et al. 1977).

An attempt to compare deposition with absorption plus impaction of hydrogen ions in a German beech forest (Mayer and Ulrich 1976) suggests that they are approximately equal (about 1 k equiv/ha/yr) and that about 40% of the total is buffered by the canopy. Litter decomposition produces a further substantial input of hydrogen ions (0.7 k equiv/ha/yr) to the mineral soil, but only a small amount (0.30 k equiv/ha/yr) escapes to seepage below the rooting zone. Assessments of this kind are, however, subject to many difficulties, particularly in measuring gaseous absorption and particulate impaction (Galloway and Parker, this meeting), so that the estimates can only be regarded as very approximate.

Materials Leached from Terrestrial Soils by Acid Precipitation

Acids deposited in precipitation may undergo three possible reactions. 1) In arid regions or where soils are young (as in recently glaciated areas), they will be neutralized by free bases such as calcium or magnesium carbonates in the soil. 2) Where soils have no free bases but an appreciable cation-exchange capacity, some hydrogen ions will replace metal cations on organic or inorganic exchange complexes. 3) Some hydrogen ions will also react to varying degrees with silicates or other minerals in the soil (cf. Burger 1969a,b; Kramer 1976, 1978), releasing soluble metal cations and silica and neutralizing some proportion of the acid. Hydrogen ions remaining after ion exchange and mineral weathering may be transferred in runoff of ground-water to aquatic ecosystems along with the metal cations and silica released by action of the acid. In small drainage basins on granitic bedrock, the output/input ratio of hydrogen ions ranges between 0.02 and 0.50 (Gjessing et al. 1976).

On agricultural lands, where liming and fertilization are routine, acid precipitation is readily counteracted by liming and its acid input is small compared to the potential acidity of N fertilizers and natural N and S transformations (Reuss 1975, Frink and Voigt 1976, McFee and Kelly 1977). Acid precipitation at pH 4 could lower the base saturation of a typical midwestern U.S. soil appreciably over 100 years and increase soil acidity by a few tenths of a pH unit (-0.3 pH unit indicates a doubling of acidity) if left unamended (McFee et al. 1977). In this way acid deposition accelerates the natural tendency of soils in humid climates, where precipitation exceeds evaporation, to lose metal cations by leaching and become more acid. Because natural soil acidification, though very slow, is generally accompanied by deleterious side effects (such as nutrient impoverishment and reduction in biological activity) any acceleration is generally viewed as undesirable.

That acid precipitation is neutralized to some degree by even poorly buffered soils is shown by recent Norwegian data (Wright and Henriksen 1977), which indicate that no lakes are currently quite as acid as the precipitation falling upon them, and more than 50% are less than half as acid as the precipitation. A comparison of the most dilute mountain lakes in the English Lake District with rain there of approximately the same ionic concentration, 150 μ equiv/l (Gorham 1978), reveals that the lake waters are 18 μ equiv/l lower in hydrogen ion and 0.21 μ equiv/l higher in Ca + Mg than the rain, presumably owing to ion exchange and weathering in the soils of the drainage basins.

How much of the recent increase in total ions present in south Swedish lakes and discharged by Swedish rivers (Malmer 1974,1976) can be ascribed to atmospheric deposition, and how much to the increased leaching consequent upon such deposition, has yet to be calculated. However, it has been shown that in small drainage basins on granitic bedrock the net losses of Ca + Mg + Al (between 10 and 90 k equiv/km²/yr) are directly related to the amounts of hydrogen ion input neutralized or retained in the watershed (Gjessing et al. 1976). Aluminum is very scarce in precipitation, and the high concentrations in strongly acid lakes of south Norway (>200 µg/l as compared to <20 µg/l in circumneutral lakes) must be due to acid weathering of aluminosilicates in the soils (Wright and Gjessing 1976) and displacement of Al ions into solution from cation-exchange complexes in the soil. A similar effect is evident in the Adirondack Mountains of the northeastern U.S.A. (Galloway 1977).

Experimental leaching of a forest podzol in field lysimeters, by simulated rain acidified with sulfuric acid over the pH range 6 to 2, revealed a distinct increase in output of Ca, Mg, K, and Al at each unit decrease in pH, most notably between pH 3 and 2 (Abrahamsen et al. 1976). Effects on a podzol-brown earth were less marked, particularly for K and Al, but other studies cited by the above authors have yielded opposite results. There are theoretical reasons for expecting non-calcareous, poorly buffered brown earths to be more affected by acid precipitation than already rather acid podzols (Malmer 1974, Wiklander 1974). The soils that will release the most basic cations in response to acid precipitation are the slightly acid soils with considerable exchange capacity (Wiklander 1973). These cations, Ca, Mg, K, etc., are seldom considered detrimental to the receiving stream. However, aluminum, which may be toxic to fish, may be leached from some soils and that becomes most likely in very acid soils that are rich in aluminosilicate minerals. Within the normal range of acidity in soils of humid regions (pH 8.2-4.0), the solubility of aluminum compounds such as Gibbsite, amorphous Al(OH)₃, and Kaolinite increases rapidly below pH 5.0 (Norton 1976). Some acid podzol soils are very low in Al-bearing minerals, but most contain Al that can be removed by acid leachate. Old, highly weathered soils are usually rich in Fe and Al oxides and are probably the most likely to release additional Al when treated with acid rain, but this has not been demonstrated.

Extrapolation of marked leaching effects at pH 3 and 2 to those of "normal" acid rain or near pH 4 is difficult, but, as Malmer (1976) has pointed out, over several decades precipitation at pH 4 may have an effect equivalent to less prolonged experimental leaching at pH 3. On the other hand, a problem with such research is our inability to accelerate all of the other processes that would occur over several decades. For example, during that period, the vegetation would cycle significant quantities of cation from deep in the soil to the surface. There would be inputs from the atmosphere of other materials, and weathering of rocks and minerals by other than acid processes would be proceeding. Moreover, as Bache (NATO 1978) has remarked, some effects of leaching at pH 3 might never occur at all at pH 4.

Near the metal smelter at Wawa, Ontario, acid precipitation has caused very severe leaching of Ca from the devastated forest soils (Gordon and Gorham 1963), with consequent enrichment of lakes in the area. Beyond

30 km downwind of the main smelter plume, lake concentrations of Ca are about 0.5 m equiv/l. At 12 km, where the forest is severely damaged by SO₂ fumigation, Ca is elevated to about 1.1 m equiv/l. It declines to about 0.75 m equiv/l close to the smelter, where the even heavier acid loading has, presumably, already leached away a good deal of the easily weatherable Ca from soil minerals.

Lake waters near the metal smelters of Sudbury, Ontario, are greatly enriched in Cu and Ni, which are smelted there (Stokes *et al.* 1973, cf. Gorham 1976). Although much of the lake input appears to come by atmospheric deposition (Hutchinson and Whitby 1974), the lake water mean for Ni (2400 µg/l) greatly exceeds the maximum concentration recorded in precipitation (830 µg/l), so that leaching of mine spoil seems a likely additional source.

Where acid rain is a result of SO₂ fumigations sufficient to devastate the vegetation, as at Sudbury (Gorham and Gordon 1960), severe soil erosion occurs and transfers large amounts of particulate matter to rivers and lakes. At Sudbury erosion has affected more than 1300 km², and river sediments approximately 80 km to the SW are high in Cu and Ni (Hutchinson *et al.* 1976). How far this is owing to transport of enriched sediment particles from the Sudbury area, and how far to sorption by local sediments of dissolved metal ions from Sudbury, is at present unknown, but sediment transport seems likely to be much more important.

The effects of acid precipitation upon mobilization of the plant nutrients N and P from the soil are little known at present. Nitrogen, especially, may be enriched in acid precipitation and can exert not only a fertilizing effect but also an acidifying effect (Reuss 1976). The Norwegian experiments (Abrahamsen *et al.* 1976) have shown no consistent effects of acid leaching with sulfuric acid upon N mobilization, and P was not investigated. In southern Norwegian lakes subject to enhanced acid deposition, P is seldom much enriched (Hendrey and Wright 1976) and may come from local point sources. Phosphorous chemistry in soils is complicated, but the P available for plant uptake is usually maximized in slightly acid to neutral soils. Apatite, one of the phosphatic minerals in soil, is weatherable by dilute sulfuric acid (Burger 1969a,b), but in very acid conditions secondary minerals of iron and aluminum phosphates form, reducing P availability to plants and presumably reducing leaching to aquatic systems. In alkaline soils with high Ca activity, P is immobilized as relatively insoluble calcium phosphates. Because of the importance of P as the chief limiting nutrient in fresh water (Schindler 1976) its transfer from land to water under the influence of acid deposition deserves more thorough investigation.

Transfer of organic matter from terrestrial to aquatic ecosystems may also be influenced by acid deposition. According to Schnitzer (this meeting), fulvic acids of low molecular weight change their structure and become more soluble as soils acidify, and can therefore be leached. Because fulvic acids form stable complexes with metal ions and interact with clay minerals, the transfer of these materials may also be affected (see also L. Peterson, NATO 1978).

The amount of nutrient elements leached from a soil may be greatly influenced by the rate and extent of microbial decay of organic materials and the conversion of inorganic forms. Most soil bacteria that have been studied show sensitivity to acidity, fungi to a lesser degree (Alexander, NATO 1978). Acid precipitation, through its influence on soil microorganisms, especially those inhabiting surface layers, is likely to influence the output of important nutrients.

Materials Retained in Terrestrial Ecosystems Under an Acid Precipitation Regime

Prominent among the materials prevented from reaching aquatic ecosystems by prior interaction with terrestrial ecosystems are in acids deposited from the atmosphere, which may be substantially neutralized--or exchanged for metal cations--in passing through plant canopies (Eaton et al. 1973) and through thin non-calcareous soils (Gjessing et al. 1976). In short term leaching experiments with sulfuric acid (Abrahamsen et al. 1976), which did not alter greatly the soil pH, not all the added SO_4 appeared in the leachate, possibly because of absorption. Over the long-term, acidification will itself lead to an increased capacity for absorption of anions such as SO_4 and PO_4 (Reuss 1975, 1976).

Heavy metals supplied from atmospheric sources or by acid leaching are likely to be trapped to some degree by vegetation, as shown in the element studies of accumulation in mosses by Rühling and Tyler (1969, 1971). They may also become bound to organic or clay exchange sites in the soil, or be complexed by organic molecules. They may also be retained in the soil if they are deposited as relatively insoluble particles. According to Parker et al. (1978), Zn has accumulated to 2500 ppm in the top 2.5 cm of a sandy urban soil in NW Indiana, U.S.A., and is being deposited at about 1 kg/ha/yr; but only 0.15 kg/ha/yr is leaching through the soil profile. In subalpine forests of New Hampshire, unexpectedly high concentrations of Pb have been observed in the soil humus layers, apparently accumulating from distant air pollution because of heavy precipitation combined with high winds and abundant plant surfaces for aerosol impaction (Reiners et al. 1975). The power of the soils to sequester heavy metals under various atmospheric loadings and at various pH levels deserves investigation by lysimeter experiments, such as those of Abrahamsen et al. (1976).

The supply of nutrient elements from terrestrial to aquatic ecosystems may be lessened as well as enhanced by acid deposition, with the balance between increase and decrease dependent upon the complex interplay of diverse biogeochemical processes and hence not well understood. If acidification retards litter decomposition on land, as it does to a modest degree in experiments in aquatic habitats (Leivestad et al. 1976), then recycling and leaching of several nutrient elements will be inhibited. Acidification is also likely to increase sorption of $\text{PO}_4\text{-P}$ by hydroxy-Fe complexes in the soil (Reuss 1975, 1976) and so inhibit its transfer to aquatic ecosystems. Acid deposition is likely to influence the N cycle in forest soils in diverse and opposing ways, and Tamm (1976) has proposed an interesting model with both negative and positive feedback loops as a basis for further investigation. In general, the expectation is that increased acidity will inhibit N cycling (and release to the forest biota or to aquatic ecosystems) by increasing immobilization of stable forms of N in the B horizon.

Retarded litter decomposition in a highly acid environment is likely to affect the export of organic molecules to aquatic ecosystems in ways difficult to predict. If decay is inhibited overall, export will decline; but if the production of colored "humic" substances is retarded less than their further decomposition, then acidification might well result in increased color of the waters percolating through soils to streams and lakes. As already noted, fulvic acids are especially likely to be affected.

If soil acidification is exceptionally severe, as for instance near the Sudbury metal smelters, the very nature of the organic matter in the soil may be changed owing to sulfonation of the previously carboxylated benzene rings of the "humic acids" (Hutchinson and Whitby 1977). Such altered molecules, which have an unusually low N content, will have greatly altered (and strengthened) capacities to bind metals, and so will retard their transport from terrestrial to aquatic ecosystems. Their influence upon soil weathering remains to be investigated, but could be pronounced.

The transfer of the diverse organic molecules found in atmospheric precipitation (Lunde *et al.* 1976) from land to water will presumably also be influenced by changes in soil structure and absorptive properties consequent on increasing acidification. However, the subject does not appear to have been investigated.

Factors Influencing the Response of Aquatic Ecosystems to Atmospheric Deposition

The vulnerability of aquatic ecosystems to atmospheric pollutants, either deposited directly or washed from the land, will depend upon a variety of climatic, geologic, topographic, morphometric, biotic and anthropogenic factors, most of which are equally important in determining the vulnerability of terrestrial ecosystems.

Chief among the climatic factors is the amount of precipitation available for rainout and washout of pollutants. Wind direction and wind speed are very significant as well (Gorham 1958b), and wind speed and humidity may both influence gaseous absorption and particulate impaction. Temperature is important insofar as it determines the balance between rain and snow. Snow appears to have a lower efficiency than rain for scrubbing various pollutants from the atmosphere (Herman and Gorham 1957, Gorham 1976; Fowler 1978). However, where it accumulates over the winter as snowpack, it may provide a sudden pulse of severe pollution to streams and lakes during spring thaw (Hultberg 1976), because the soluble materials are frozen out as intercrystalline brines and are washed out early in the melting process (Gorham 1958c). The ratio of precipitation to evaporation is yet another factor, determining the degree to which terrestrial soils are leached, influencing the rate at which precipitation passes through streams and lakes, and affecting the entrainment of dust particles to the atmosphere.

Geologic factors (including patterns of glaciation) are important in several ways. The areas most sensitive to acid precipitation are those with hard, crystalline bedrock and very little surficial soil, a large

part of Norway being a prime example. The water chemistry of streams and lakes draining such areas strongly reflects the chemistry of atmospheric precipitation (Gorham 1958b, 1961). Where the soil mantle is thicker, its texture, mineralogy, and organic content become very significant, and water chemistry is strongly influenced by soil chemistry (Gorham 1958b, Kramer 1978). Soils with free calcium carbonate (or other carbonates) are not susceptible to acidification, and non-calcareous soils are also relatively resistant if they are fine-textured, with clay and organic matter providing a high cation-exchange capacity and buffering to the soil against the effects of acid deposition. Soil minerals differ greatly in their response to acid weathering and in their content of carbonate impurities (Burger 1969a,b). They differ greatly as well in their content of heavy metals that can be mobilized by acid deposition.

Soil texture and structure will affect the pathways of water through the soil. Coarse soils with plentiful stones and boulders or with numerous old root channels, may allow rapid percolation and a very incomplete equilibration between water and soil (Troedsson 1955, Tamm and Troedsson 1957, Gorham 1958b). In this way streams and lakes may be acidified even where soil bases are theoretically sufficient to neutralize acid deposition, and effects upon streams and lakes may be more rapid than those upon terrestrial ecosystems.

Topography has considerable influence. Upland headwater lakes and streams, where soils are thin and precipitation is heavy, are especially susceptible to acidification. Lower in the hydrologic network, where soils are thicker, there is more likelihood of alkaline groundwater input. Topography further determines lake depth and the ratio of watershed area to lake area, both of which (along with precipitation and evaporation) determine the residence time of water in lakes.

Biotic factors must also be considered. The height, type and duration of leaf canopy have a significant effect upon gaseous absorption and particulate impaction from the atmosphere. The magnitude of transpiration, which varies with the plant cover, influences the ratio of precipitation to evaporation. Soil organisms also vary greatly in their sensitivity to acid deposition and will thus influence ecosystem response. For example, microorganisms that control the conversion of N and S forms in the soil are sensitive to changes in acidity and Abrahamsen *et al.* (1976) have shown changes in soil fauna numbers under acid treatments.

Anthropogenic factors must be taken into account. Spatial and temporal patterns of urban/industrial development play a minor role in determining the impact of acid deposition upon both terrestrial and aquatic ecosystems. The kinds of energy resources in use and the controls on atmospheric emissions greatly influence the nature and extent of atmospheric deposition. The degree of agricultural activity, such as liming and fertilization, will also have a substantial role in ameliorating the impact of acid deposition (Reuss 1975, Frink and Voight 1976), as may dustfall from windblown soil (Gorham 1976). Whether aquatic impacts can be ameliorated more effectively by liming drainage basins, or the lakes and streams themselves, has yet to be investigated and deserves experimental study.

Finally, natural episodic phenomena may be locally or temporarily significant. Forest fires, tornadoes, etc., may entrain into the atmosphere alkaline particulate material capable of neutralizing acid deposition. On the other hand, natural (and sometimes long-continued) fires in deposits of coal, lignite, or peat may cause acid deposition capable of severe degradation of adjacent ecosystems (e.g., the Smoking Hills of Arctic Canada, see Hutchinson, this meeting). Vulcanism may also be an important contributor to local acid rain (Bottini 1939).

Investigations of the complex effects of acid deposition upon aquatic ecosystems are best pursued by means of observations and experiments upon whole watersheds, because the vulnerability of lakes and streams to acid precipitation and its associated pollutants rests so largely upon the nature of the adjacent land and its biota. Integration of aquatic with terrestrial research programs should therefore be a matter of the highest priority for the future.

Such integration would also allow better comparison of differences in the rate at which acid deposition affects terrestrial and aquatic ecosystems. Present evidence indicates considerable effects upon sensitive aquatic ecosystems over a time scale of decades, whereas for comparable terrestrial ecosystems the time scale could well be an order of magnitude greater.

Conclusion

The following expression summarizes the measurements required for a thorough assessment of the effect of atmospheric deposition upon any elemental or molecular transfer from terrestrial to aquatic ecosystems:

$$P + I (\pm G) \pm B \pm S + E = O$$

where P = precipitation, I = particle impaction, G = gaseous absorption or emission, B = biomass retention or release, S = soil retention or release, E = erosion, and O = output from the terrestrial ecosystem. Biomass retention or release may be either short or long term, and involves the vegetation canopy, plant roots, and the organic portions of the soil, both living and non-living. Output may involve only stream outflow in sealed basins, but will include groundwater seepage in others. Where watersheds are not sealed by impervious bedrock, groundwater seepage may also have to be measured as an input factor in the above expression if an adequate mass balance is to be obtained.

Given the number of terms in the above expression (some encompassing diverse gains and losses) and the fact that only P and O are commonly measured, it is not at all remarkable that our understanding of the influence of acid deposition upon transfers from terrestrial to aquatic ecosystems is so incomplete.

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APPENDIX

Transport and Fate of Sulfur and Nitrogen
Containing Pollutants Related to Acid Precipitation

by

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