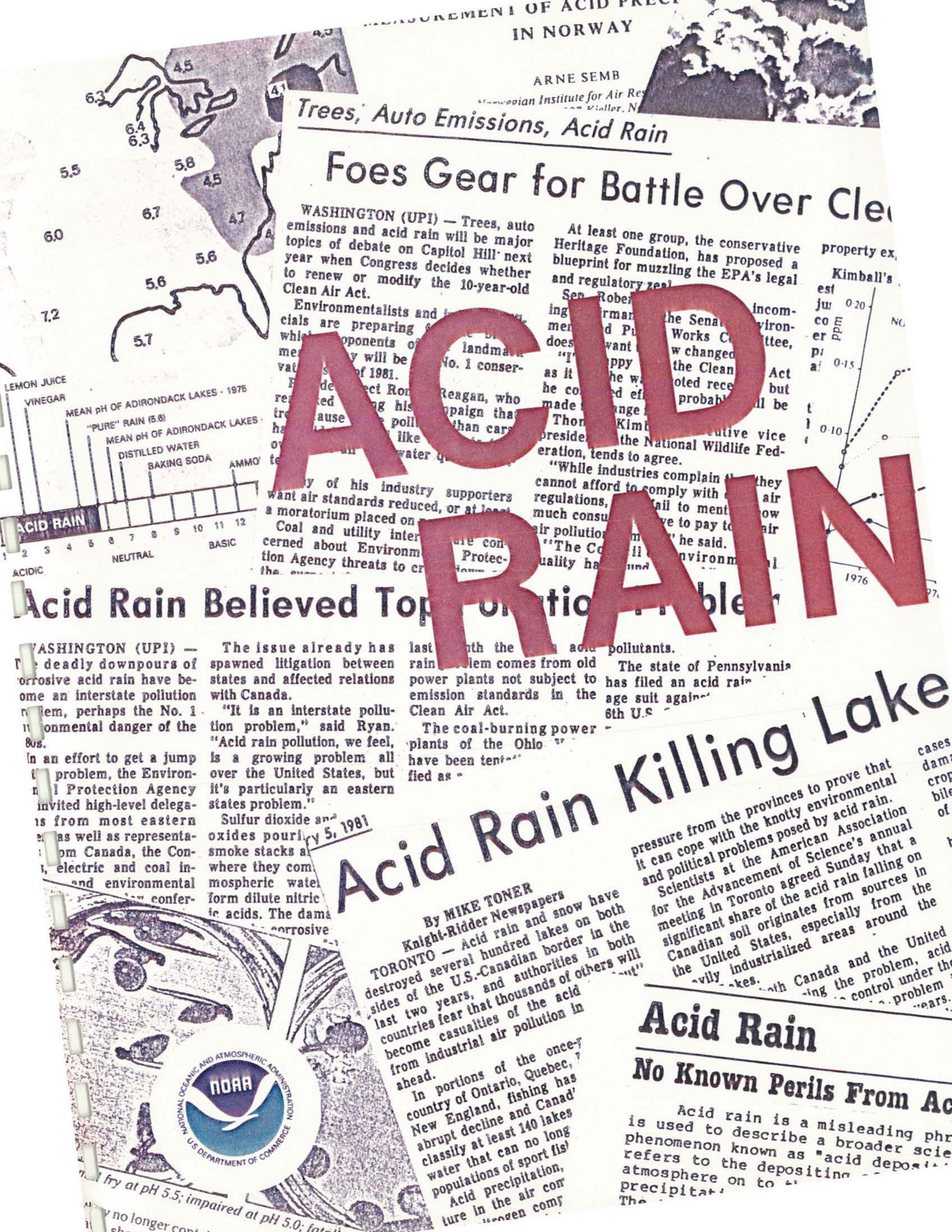
ACID RAIN



MEASUREMENT OF ACID PREC
IN NORWAY

ARNE SEMB
Norwegian Institute for Air Res

Trees, Auto Emissions, Acid Rain

Foes Gear for Battle Over Cle

WASHINGTON (UPI) — Trees, auto emissions and acid rain will be major topics of debate on Capitol Hill next year when Congress decides whether to renew or modify the 10-year-old Clean Air Act.

Environmentalists and cials are preparing which opponents of landma me y will be No. 1 conser- vat s of 1981.

de ect Ron Reagan, who re ted g his paign that tr ause poll than cars ha like o te water q

y of his industry supporters want air standards reduced, or at least a moratorium placed on

Coal and utility inter are con- cerned about Environm Protec- tion Agency threats to cr

At least one group, the conservative Heritage Foundation, has proposed a blueprint for muzzling the EPA's legal and regulatory zeal.

Sen. Robe ing rman he Sena viron- men d Pu Works C ttee, does want w changed

"I' ppy the Clean Act as it he w oted rece but he co d ef probab l be made nge

Thom Kimb utive vice presid the National Wildlife Fed- eration, tends to agree.

"While industries complain th they cannot afford to comply with air regulations, fail to ment ow much consu ve to pay t air pollution m " he said.

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Acid Rain Believed Top

WASHINGTON (UPI) — The deadly downpours of corrosive acid rain have become an interstate pollution problem, perhaps the No. 1 environmental danger of the 80s.

In an effort to get a jump problem, the Environ- Protection Agency invited high-level delega- s from most eastern as well as representa- m Canada, the Con- electric and coal in- and environmental confer-

The issue already has spawned litigation between states and affected relations with Canada.

"It is an interstate pollution problem," said Ryan. "Acid rain pollution, we feel, is a growing problem all over the United States, but it's particularly an eastern states problem."

Sulfur dioxide and oxides pouri smoke stacks a where they com mospheric wate form dilute nitric ic acids. The dama corrosive

last th the acid rain blem comes from old power plants not subject to emission standards in the Clean Air Act.

The coal-burning power plants of the Ohio have been tent fied as

pollutants.

The state of Pennsylvania has filed an acid rain age suit again 6th U.S.

Acid Rain Killing Lake

y 5, 1981

By MIKE TONER
Knight-Ridder Newspapers

TORONTO — Acid rain and snow have destroyed several hundred lakes on both sides of the U.S.-Canadian border in the last two years, and authorities in both countries fear that thousands of others will become casualties of the acid from industrial air pollution in ahead.

In portions of the once- country of Ontario, Quebec, New England, fishing has abrupt decline and Canad classify at least 140 lakes water that can no long populations of sport fis

Acid precipitation, ture in the air com nitrogen comp

pressure from the provinces to prove that it can cope with the knotty environmental and political problems posed by acid rain.

Scientists at the American Association for the Advancement of Science's annual meeting in Toronto agreed Sunday that a significant share of the acid rain falling on Canadian soil originates from sources in the United States, especially from the heavily industrialized areas around the kes.

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Acid Rain

No Known Perils From Ac

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NOAA
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
U.S. DEPARTMENT OF COMMERCE

A NOAA PROGRAM PLAN

FOR

ACID RAIN RESEARCH

March 1981

CONTENTS

SUMMARY

Request: NOAA requests $5,400,000 and ten positions to conduct research and monitoring in the atmospheric aspects of the acid rain issue. The first part of this request, $1,900,000 and two positions, has been approved and is in the FY82 budget. The request for additional support reflects the increased acid rain research and Federal leadership roles mandated to NOAA by recent legislation, which was enacted after NOAA's FY82 request. To meet these added responsibilities, NOAA requests an additional $3,500,000 and eight positions in FY83.

Acid Rain: High acidity precipitation is occurring in the northeastern United States and neighboring parts of Canada, as well as numerous other U.S. and worldwide locations. In many of these regions, lakes are found to be acidified and frequently to be devoid of fish. Some of these areas are downwind of copious man-made emissions of compounds that can form acids during their transport and dispersion. From this, it has often been inferred that industrialization has caused the acid rain "problem". Furthermore, there is mounting concern that the fish kill may be only one facet of a problem whose deleterious effects could extend to other natural plant and animal life, agriculture and livestock, soils and minerals, structures, and public health. Such concerns have often evoked arguments for immediate and extensive restrictions on man-made emissions of suspected acid precursors.

However, there are a growing number of observations that are not consistent with this man-caused/environment-damaged picture of acid rain. Lake acidification can occur for reasons other than acid rain. Furthermore, increasing trends in the emissions of suspected acid precursors have not always caused increased downwind acidity. There is presently no definitive explanation for the acid precipitation observed in remote, relatively non-industrial locations. No changes in the natural terrestrial ecosystem have been unequivocally attributed to acid

rain. Simulated acid rain in controlled environments has produced damage in some plants, but increased acidity has proven to be beneficial to other plants. Such uncertainties have made it clear that any rational decisions about the necessity and nature of ameliorative and/or regulatory actions regarding acid rain <u>must</u> be preceded by a much better understanding of its many complex facets.

<u>Urgency</u>: There are many reasons why a resolution of the acid rain issue is urgently needed. If indeed man's activities are causing a rapidly increasing rainfall acidity that is producing widespread, serious, and perhaps irreversible aquatic and terrestrial damage, then to do nothing will lead to severe environmental consequences. On the other hand, to reduce suspected acid precursor emissions drastically and immediately is an extremely expensive, disruptive, and restrictive imposition on the nation's industry, particularly at a time when economic recovery is considered a high priority. It would be unwarranted to incur such a high cost without the need being quite certain. The reality of the acid rain threat also influences the nation's energy policy, since some of the alternatives to foreign oil could exacerbate acid precipitation. The acid rain controversy has been elevated to an international level by the possibility that a large fraction of the acid materials deposited in Canada may originate from sources in the United States.

<u>Legislation</u>: In view of the potential seriousness of acid rain, the economic consequences of possible ameliorative actions, and the lack of key information required to make urgently needed rational decisions, Congress recently passed new legislation, the "Acid Precipitation Act of 1980" (Title VII of the "Energy Security Act of 1980", PL 96-294). This Act calls for a comprehensive ten-year Federal acid rain research program, which is summarized in the recently prepared <u>National Acid Precipitation Assessment Plan</u>. The <u>National Plan</u> groups the acid rain

information needs into nine research categories -- natural sources, man-made sources, atmospheric processes, deposition monitoring, aquatic impacts, terrestrial impacts, materials impacts, control technologies, and assessment and policy analysis -- and assigns Federal responsibilities in each category.

The Act has mandated NOAA's strong involvement in the acid rain issue. NOAA is one of the three co-chairs of the Interagency Task Force on Acid Precipitation. The National Plan has identified NOAA research responsibilities in three categories: natural sources, atmospheric processes and deposition monitoring. In the first two categories, NOAA has been assigned to serve as the lead agency and has responsibility for overseeing and coordinating all Federal research activities in each of these two categories. Lastly, in response to the Memorandum of Intent signed in 1980 by the United States and Canada, NOAA is also deeply involved in many of the technical committees that are studying trans-border air pollution problems.

NOAA Research Plan: NOAA became active in acid rain research in 1972, when the WMO/EPA/NOAA acid deposition monitoring network began. A year before the enactment of the "Acid Precipitation Act of 1980", NOAA recognized acid rain as an emerging national issue and proposed that its support be increased by $2,600,00 and five positions to expand its acid rain research. Part of this request, $1,900,000 and two positions, was approved and is in the FY82 budget. However, since then the situation has changed markedly for NOAA. Acid rain has become a major controversy, and the responding legislation has required that NOAA play a considerably enlarged role in Federal acid rain research activities. In response, NOAA proposes a new multi-organization* research program that will meet the NOAA responsibilities identified in the National Plan. The basis of the program is NOAA's demonstrated expertise in atmospheric and oceanic research. The present proposal incorporates the original

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* AL, AOML, ARL, PMEL, EDIS, OWRM, and CIRES

FY82 program and adds the complementary research, beginning in FY83, that reflects the expanded role required of NOAA in the National Plan.

Specifically, the part of the present program that will begin in FY82 is essentially unchanged from that proposed prior to the National Plan. When grouped by NOAA's research-category responsibilities, the major components of that research are:

FY82	Natural Sources (1/$600K)	- survey measurements, predominantly land-based sources
	Atmospheric Processes ($600K)	- long-range trajectory studies - acid global-circulation measurements - aerosol and cloud chemistry measurements
	Deposition Monitoring and Specialized Measurements (1/$700K)	- global- and national-trend measurements - establish initial atmospheric research sites - develop dry-deposition measurement methods

This research, with its emphasis on evaluating land-based neutral sources of acid precursors, transport processes, and deposition measurements, will make an important contribution to the Federal acid rain research effort. However, the National Plan specifies a much broader NOAA effort. For example, NOAA has the major share of the responsibility for assessing the role of natural sources, which implies a more-encompassing and intensive effort, particularly the need to examine potential aquatic sources. Furthermore, the FY82 research plans were made prior to the National Plan's having assigned NOAA major research responsibilities in the important area of acid-forming transformations. Hence, those original plans did not include major laboratory, field, and modeling studies aimed at understanding these chemical processes. To fill these gaps, it is proposed that, in FY83, NOAA's support be increased by $3,500,000 and eight positions for additional acid rain research that has the following principal program components:

FY83	Natural Sources (2/$1,300K)	- regional and local source-strength determinations, including both terrestrial and aquatic sources
	Atmospheric Processes (3/$1,200K)	- laboratory chemical-transformation measurements - chemical-transformation modeling
	Deposition Monitoring and Specialized Measurements (3/$1,000K)	- validative chemical-transformation measurements at atmospheric research sites - general field application of dry deposition instruments.

Taken together, the above set of program components constitutes a balanced, complementary, and comprehensive research program plan to provide the acid rain information needs assigned to NOAA. As reflected in the <u>National Plan</u>, NOAA's decade of experience in meteorology, chemistry, and oceanography is considered a key part of the research program needed to address the acid rain issue. The research proposed and the resources requested herein will allow NOAA to meet its responsibilities in this national effort. The results will impact directly on possible future regulatory actions, energy strategies, and foreign policy.

INTRODUCTION

Acid rain is one of today's most widely publicized environmental controversies (e.g., see cover). The issue was raised by the discovery in the 1950s that high-acidity rainfall was occurring in northern and western Europe. Later it was recognized that a similar situation exists in the northeastern United States and the neighboring parts of Canada, and, in recent years, acid precipitation has been documented at numerous other locations in the United States and around the world. There is now growing conjecture that acid rain is due to man's activities and there is mounting concern that this deposition of acid materials may have severe environmental and economic consequences. However, the large number of uncertainties that currently surround the acid rain phenomenon preclude any rational decisions regarding the necessity and nature of potentially expensive ameliorative and/or regulatory actions. In short, there are unresolved fundamental questions:

- Do we have an acid rain problem?
- If so, how much of the problem is caused by man?
- What can we do about it?
- How much time do we have?

The controversy raised by these questions has focused considerable attention on acid rain -- its causes, processes, extent, and effects.

A. ACID RAIN PHENOMENON

The salient features of the formation and deposition of acid materials are summarized schematically in Fig. 1. The process is initiated by the injection of sulfur-, nitrogen-, and chlorine-containing compounds into the atmosphere by a variety of man-made and natural

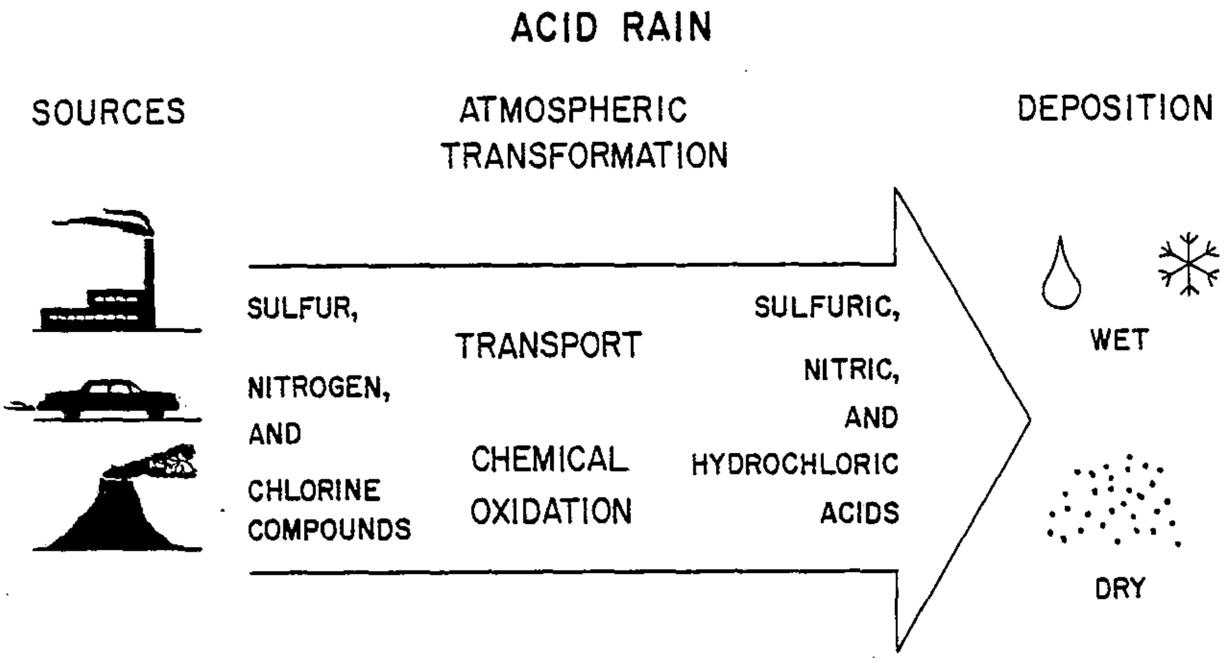

Figure 1. A schematic representation of the atmospheric phase of the acid rain phenomenon.

sources. The vast majority of these emitted compounds -- SO_2 (sulfur dioxide); NO and NO_2 (nitric oxide and nitrogen dioxide, which are denoted jointly as NO_x); and H_2S (hydrogen sulfide) -- are not strong acids. However, during their dispersal and transport by winds, these precursors undergo complex chemical transformations with various atmospheric species to form materials containing three major acids: sulfuric, H_2SO_4; nitric, HNO_3; and hydrochloric, HCl. These acidic materials are deposited on the earth's surface via several mechanisms. The atmospheric residence time between emission and deposition (i.e., the time available for chemical transformation) may be hours or months, depending on the nature of the source, the chemicals emitted, and the prevailing meteorological conditions. In the latter case, the receptor area where the acidic materials are deposited may be thousands of miles from the source of the precursors of these materials.

The extent and complexity of the acid rain phenomenon are given in more detail in Fig. 2. Many of man's activities are known to produce large quantities of materials that can potentially form acidic materials. The burning of fossil fuels in the United States releases millions of tons of SO_2 and NO_x into the atmosphere each year. The largest U.S. source of SO_2 emissions is coal-fired power plants; whereas, the man-made production of NO_x is believed to be about equally divided between such stationary sources and transportation. Detailed quantitative estimates have been made not only of the magnitude of these emissions, but also of their temporal trends and geographic distributions. Figure 3 shows the emission rates estimated for the last four decades and the projected rates through the year 2000. Both SO_2 and NO_x show increasing emission rates up to the present. Although the amount of coal burned is expected to increase in the future, the improved ability to capture these materials at the source is expected to limit the emission-rate increases. This is not the case for NO_x, the emissions of which are projected to increase substantially in the coming years. Figure 4 gives the estimated current emission-rate densities of the sum of SO_2 and NO_x for the continental United States. The heavily populated industrial corridor from Illinois to New York accounts for a large fraction of these materials.

A variety of natural emissions contain compounds that can be precursors of acidic materials. Some of these, such as wildfires and

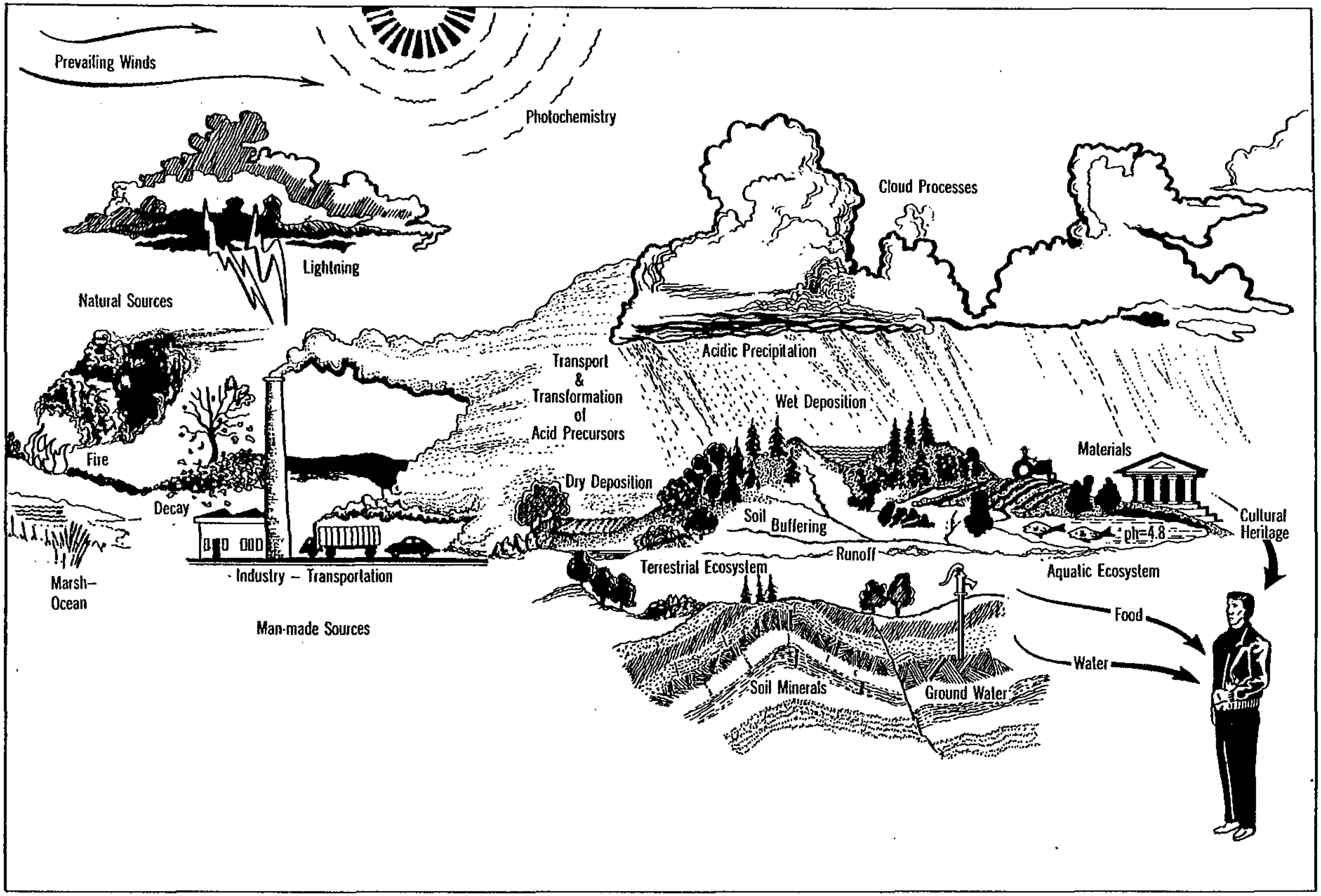

Figure 2. Acid rain -- its possible sources, transports, transformations, depositions, and effects.

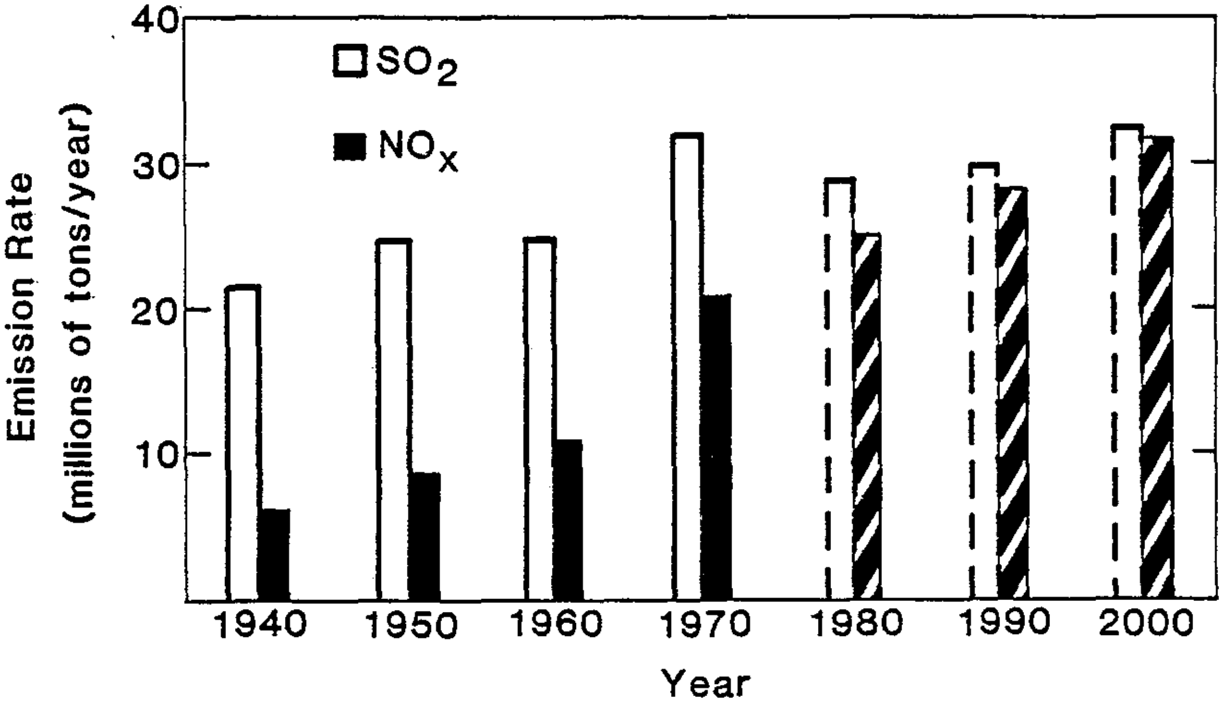

Figure 3. Trends in the national SO_2 and NO_x emissions since 1940 (EPA, 1978a,b; DOE, 1980).

lightning, can add to the NO_x burden. Furthermore, biological activity in soils, marshes, estuaries, and biologically productive areas of the world's oceans, contribute a variety of sulfur compounds, — e.g., H_2S (hydrogen sulfide), COS (carbonyl sulfide), and $(CH_3)_2S$ (dimethyl sulfide) — that can be acid precursors. Several sources of chlorine-containing compounds, like volcanic aerosols and oceanic CH_3Cl (methyl chloride), are known. In addition, there are natural sources of alkaline materials, such as windblown dust, that could tend to neutralize the effects of acidic materials. In contrast to man-made emissions,

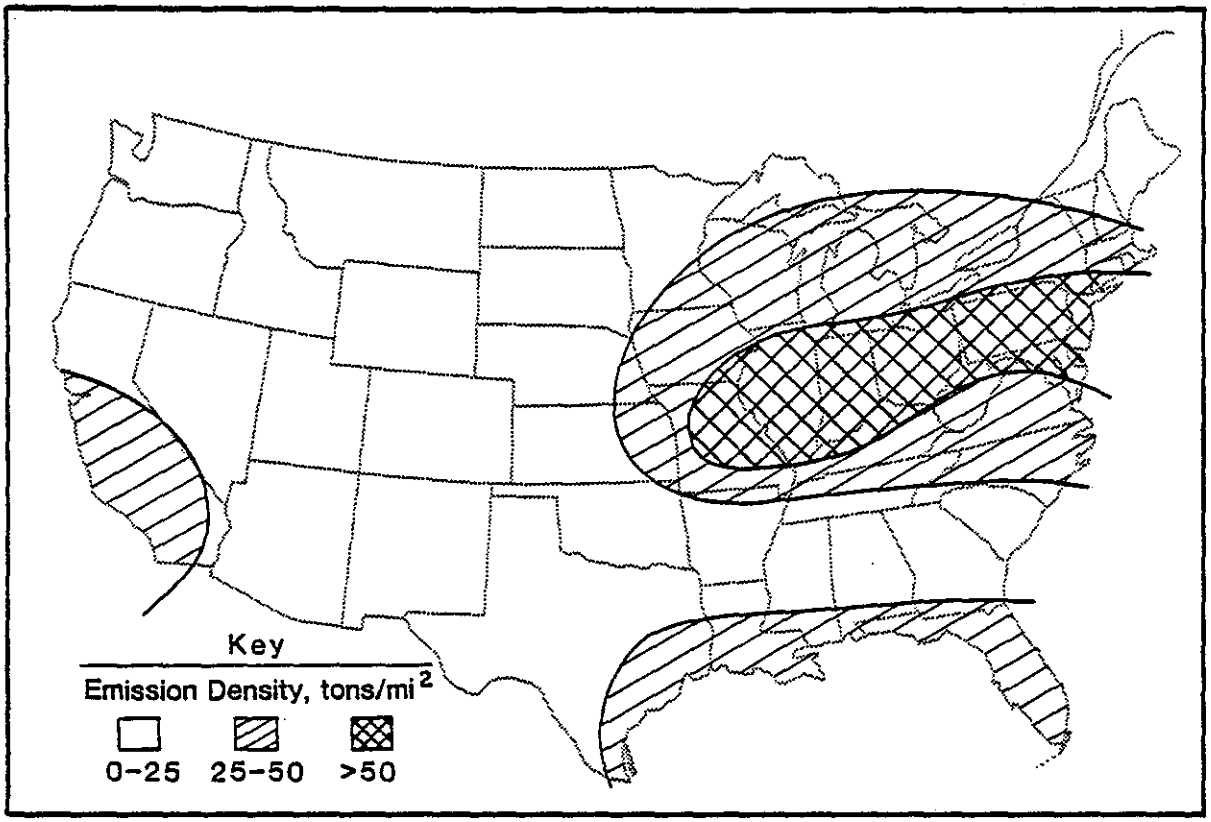

Figure 4. Approximate characterization of annual combined SO_2 and NO_x emission density (EPA, 1980)

which tend to be localized and recognizable, natural emissions of acid precursors and alkaline materials tend to be widely distributed and more difficult to characterize.

The altitude at which the emissions are injected into the atmosphere is suggested to be a factor in their role in acid deposition. Tall stacks have been used increasingly to avoid local deposition of the emitted materials. However, the goal of wider dispersal is necessarily accompanied by longer residence times and hence by potentially greater time available to chemically transform the SO_2 and NO_x emissions into acidic materials. Furthermore, with less loss of materials to the ground in the immediate vicinity of the source, there is more airborne material available for possible chemical transformation into acid compounds.

Because the lower atmosphere is a dynamic, constantly varying system, it is an exceedingly complex task to trace the movement of pollutants from the point of their emission to the place where they are deposited. There are, however, general patterns of air movement. Most of the United States experiences prevailing winds from the west. This prevalence is shown in Fig. 5, which traces some of the most frequent general storm-track patterns. As the low-pressure centers move toward the east, Gulf coast or Atlantic coast moisture is supplied to the storm. Because of this moisture supply and the convergence of many storm tracks across the eastern states, this region experiences relatively high rainfall. Thus, the northeastern states and southeastern Canada tend to receive rainfall from storms that typically have crossed the high-emission pollution corridor shown in Fig. 4. These are the storms that have the greatest potential for uptake of SO_2 and NO_x emissions and hence the greatest potential for becoming acid laden.

During the transport period, the sulfur-, nitrogen-, and chlorine-containing materials may be converted into acids by chemical reactions with atmospheric species, the conversion processes being referred to as oxidation and the atmospheric species responsible for the reaction being the oxidants. The extent of acid formation in the atmosphere depends not only on the concentrations of the precursor species, but also on the

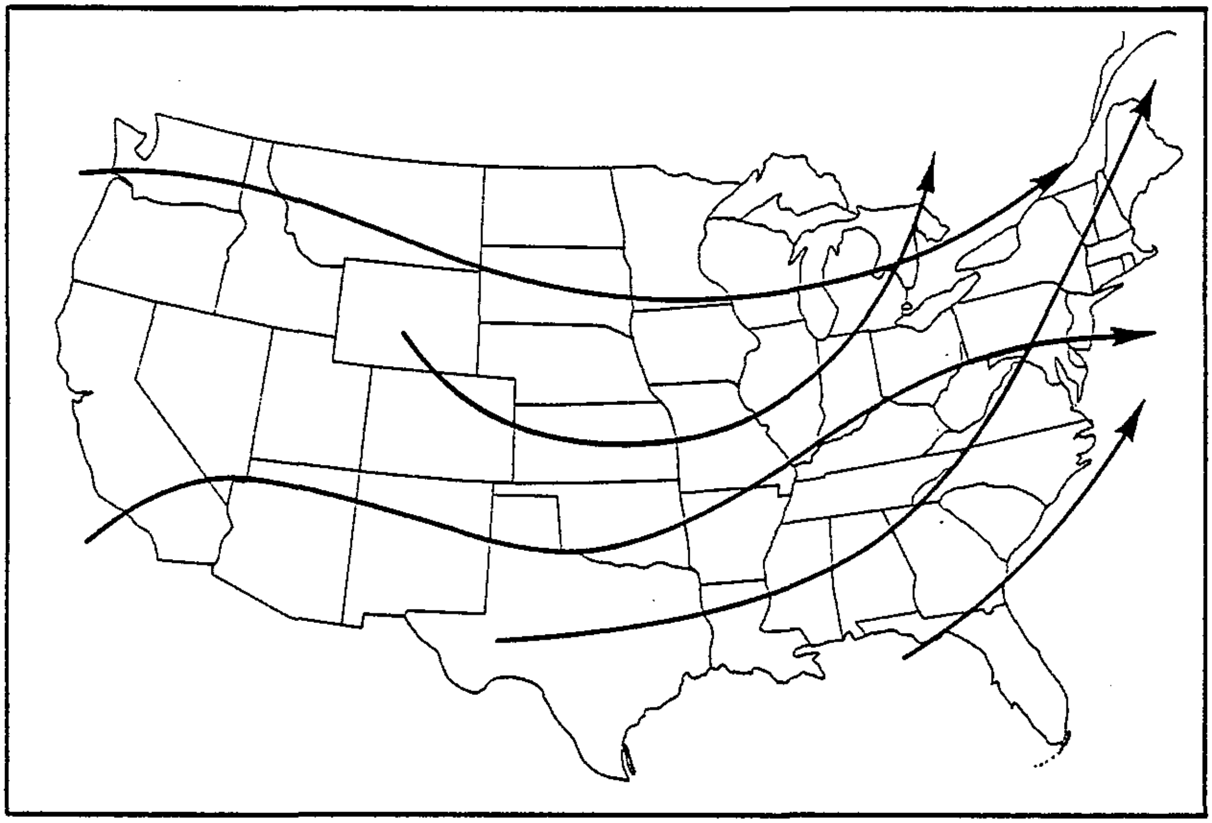

Figure 5. Frequent routes of storm centers (DOE, 1980).

concentrations of the various oxidants -- like OH (hydroxyl) and HO_2 (hydroperoxyl) radicals -- whose sources are other chemical and photochemical processes involving many different trace constituents. The oxidizing processes include gas phase (homogeneous) and surface and liquid phase (heterogeneous) reactions, the latter involving solid and liquid aerosols. Because most of these processes depend strongly on concentrations, temperature, humidity, and solar radiation, the time of conversion of the precursors to acidic materials varies greatly in complicated ways.

The processes that remove the acid materials are as varied as those that can form them. Rainout begins with the condensation of cloud water vapor on nuclei, many of which are believed to be sulfur-containing particles. During the subsequent droplet growth, soluble gases are absorbed, chemical changes occur, and the drop descends to the ground. Washout may occur as the drops sweep through the pollutant-laden air beneath the cloud. Similar processes may involve snow, hail, or fog. Furthermore, many of the acidic materials may be deposited on the earth's surface without precipitation occurring, i.e., dry deposition. The rates of this less-obvious removal process are highly variable, depending strongly on the nature of the surface, turbulence, and windspeed.

The most common past measure of the acid materials being deposited in a given area is the acidity of the rainfall occurring there. The acidity of a solution such as rain is expressed in terms of its pH, where a change of one pH unit is a factor-of-ten change in acid concentration. Figure 6 shows the pH scale and gives several examples. Distilled water is considered neutral at a pH of 7. "Pure" rain is slightly acidic, pH = 5.6, due to the natural formation of carbonic acid in the raindrop by the absorption of atmospheric CO_2 (carbon dioxide). Carbonic acid is a weak innocuous acid that has been and will be present in rain irrespective of other natural or man-made inputs. Consequently, acid rain is generally considered to be precipitation with pH values less than 5.6.

Figure 7 shows that precipitation with pH $\leq$ 5.6 is occurring in the eastern United States and on the west coast. These data reflect the measurements made by the WMO/EPA/NOAA network in 1974-1975. Unfortunately,

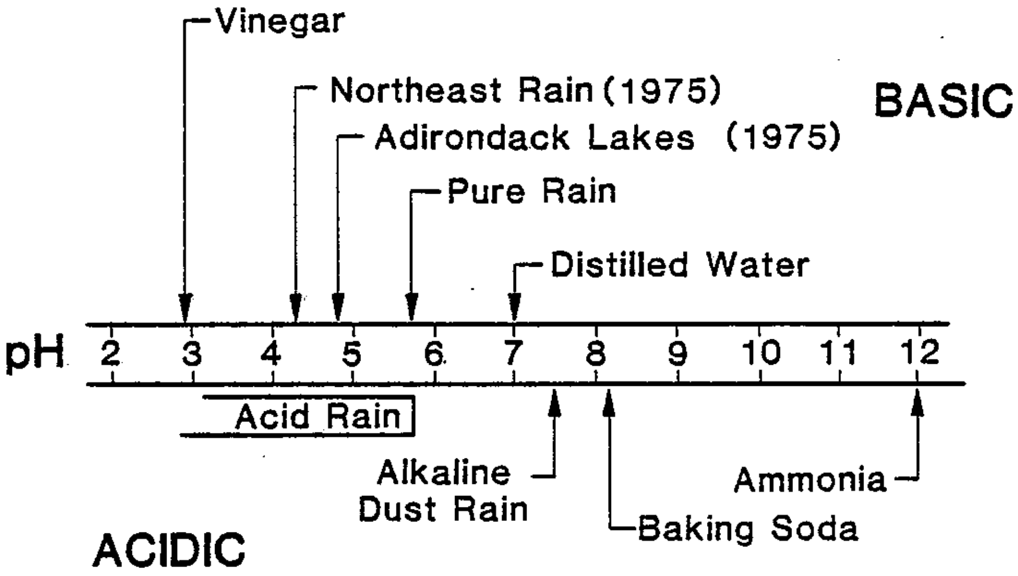

Figure 6. The pH scale with representative examples (EPA, 1979).

there has been no single acid precipitation monitoring network that has operated continuously in the United States over the past two decades. Hence, it is not straightforward to examine past long-term trends. Attempts to do so have to rely on a large amount of direct and indirect past information related to acid deposition. Figure 8, which is based on one such compilation, compares the estimated pH contours for 1955 to those twenty years later. This comparison has been widely cited as evidence that the acidity of rainfall in the northeast has increased sharply over this period and that acid precipitation has spread westward and southward.

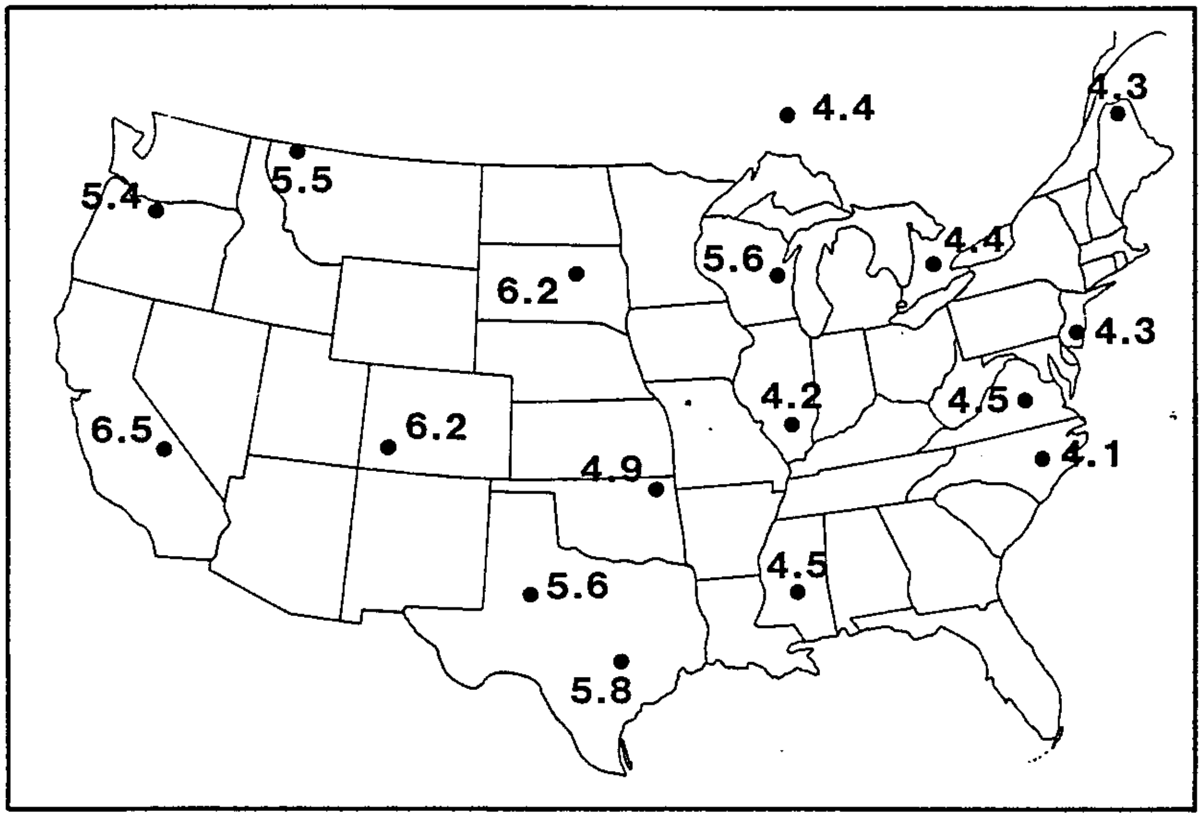

Figure 7. Precipitation-amount weighted mean pH at WMO/EPA/NOAA stations for 1974-1975 (DOE, 1980).

Naturally, such reports have created the impetus to understand the potential effects of acidification on the environment and have generated concern that these effects could be deleterious. Most of the information available at present are the impacts of increased acidity on the aquatic environment, particularly fresh water organisms. The increasing acidity of lakes and the corresponding decrease in fish populations are very well documented. Figure 9 shows an example of how a group of Adirondack lakes have changed in twenty-five years. In the 1930s, only

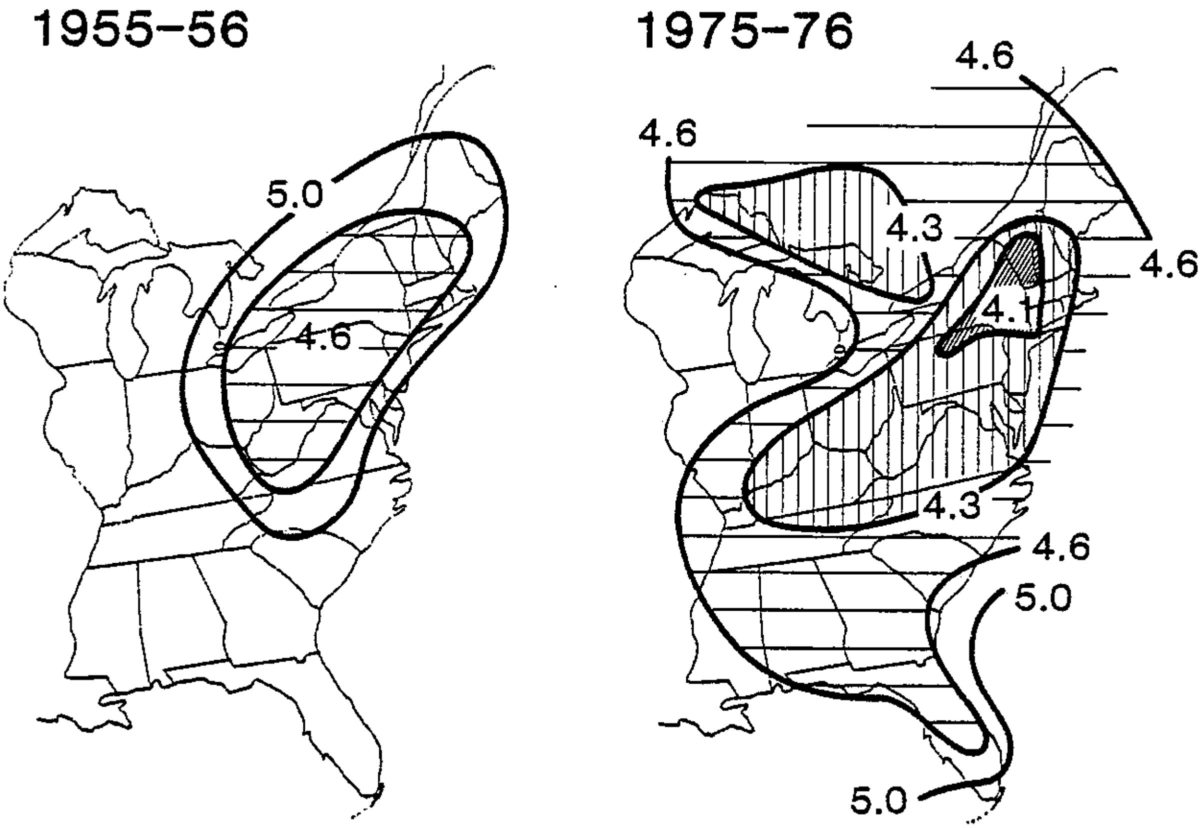

Figure 8. Deduced weighted annual average pH of precipitation in the eastern United States in 1955-1956 and 1975-1976 (after Cogbill and Likens, 1974; Likens _et_ _al_., 1979).

a few percent of these lakes had pH values less than 5.0 and had no fish; whereas, in 1975, this acidic fish-barren fraction had risen to about 50%. Laboratory studies have clearly shown that many species of fish cannot reproduce in water whose pH is less than 5.0.

Deleterious, as well as some beneficial, effects of acidification on the terrestrial environment (e.g. vegetation, soils, structures, and human health) have been proposed, but are considerably less well docu-

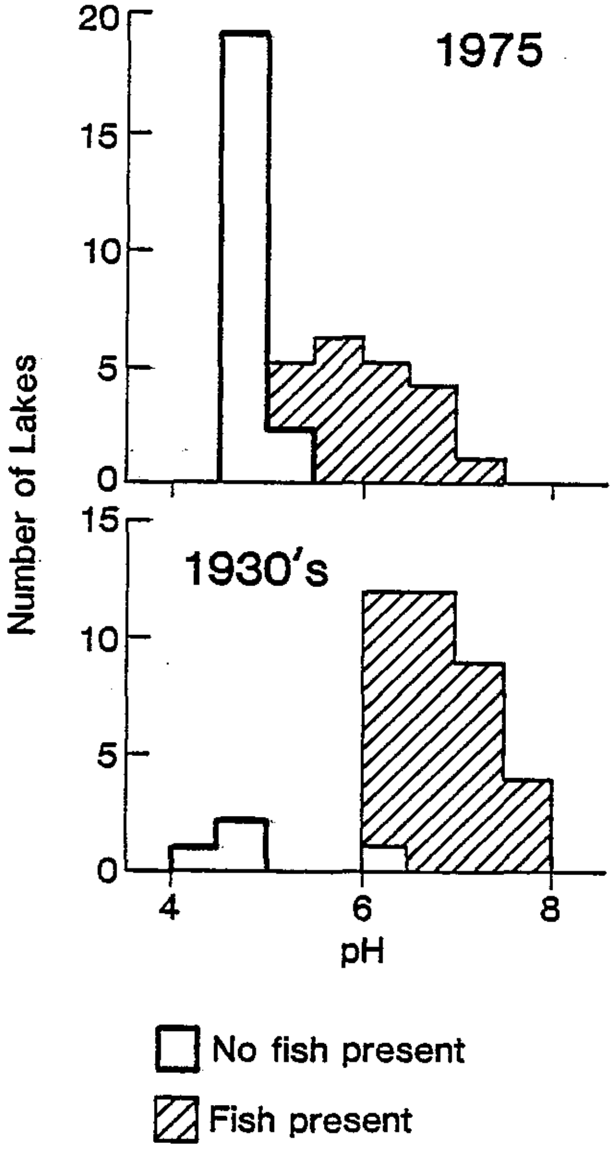

Figure 9. Frequency distribution of pH and fish population status for high-elevation Adirondack lakes surveyed in the 1930's and again in 1975 (Schofield, 1976).

mented than aquatic effects. The potential terrestrial impacts are varied, as the following examples show. The damage to crops exposed in a controlled environment to simulated acid rain was observed for some types of plants, but some other types registered positive results. Elevated acidity in soil may cause a larger release of heavy metals to plants, which could indirectly pose a threat to livestock, as well as humans. High acidity rainfall promotes corrosion of metals and weathering and cracking of limestone, potentially contributing to loss of structural strength.

B. URGENCY

The results contained in the previous figures are representative of those that have caused the current national concern about acid rain. Namely, the bulk of the man-made emissions of the acid precursors are from geographic areas (Fig. 4) over which many storms pass (Fig. 5) on their way to precipitation regions where acid rainfall is observed (Fig. 7) and where high-acidity, fish-barren lakes are found (Fig. 9). It has been frequently inferred from this that the Adirondack fish died as a result of lake acidification caused by acid rain whose source was SO_2 and NO_x emissions from the upwind industrial corridor. Furthermore, man-made emissions of suspected acid precursors have increased in recent decades (Fig. 3), just as there are indications that the acidity of northeastern rainfall has increased over this period (Fig. 8). From this, it has also often been inferred that the United States has largely created its (and perhaps some of Canada's) acid rain "problem", of which the fish kill could only be one facet, by the industrialization occurring during recent decades. Furthermore, based on projected emissions, it is feared that the situation will necessarily worsen, producing perhaps irreversible losses, in the years ahead as population and energy consumption increase. This is the acid rain picture that is often discussed as a possible "worst case" in the scientific literature. It is also the picture that is frequently circulated widely by the media. Lastly, it is the picture that has evoked arguments for immediate and extensive restrictions on man-made emissions of suspected acid rain precursors. A pivotal question is raised:

- Is this man-caused/environment-damaged acid rain picture correct?

There are many reasons why an answer to this question is urgently needed:

> Environmental. If indeed man's activities are causing a rapidly increasing rainfall acidity that is producing mounting widespread, serious, and irreversible aquatic and terrestrial damage, then to do nothing will lead to severe environmental consequences.
>
> Economic. On the other hand, to reduce suspected acid precursor emissions drastically and immediately is an extremely expensive, disruptive, and restrictive imposition to place on the nation's industry, particularly at a time when economic recovery and growth is considered a high national priority. To incur such a cost without its need being very certain would be folly.
>
> Energy. In order to reduce the United States' dependence on foreign oil, alternative energy options are being considered. Accompanying many of these options, like increased coal usage, is the possible threat of increased acid rain. The reality of that threat is crucial input to major energy-policy decisions.

> _International Relations_. The possibility that the acid materials deposited in Canada may originate from sources in the United States, and vice versa, has elevated the acid rain controversy to an international level. Harmonious relations require that the uncertainties surrounding this phenomenon be resolved and appropriate action taken.

With the increased scrutiny given acid rain during the last year or so, it has become evident that the understanding of this phenomenon is quite far from being complete. Thus, despite its urgency, the above question cannot at present be reliably answered.

C. INFORMATION NEEDS

It is now recognized that any rational decisions about the necessity and nature of ameliorative and/or regulatory actions regarding acid rain must be preceded by a much better understanding of its many complex facets: sources, transport, transformation, deposition, trends, aquatic and terrestrial impacts, and economic consequences. In each of these areas, there are many questions that need to be answered and many conflicts between results that need to be resolved. The list is long, too long to be summarized here. It should suffice to use a few examples to illustrate the types of information needs that exist in the various sectors of the acid rain issue.

- Acid precipitation has been detected in extremely remote regions of the world. What is the origin of this acidity: local natural processes or unusually long-range transport of man-made materials?

- Although prevailing circulation patterns are known, detailed individual trajectories are imperfect. How reliably can source location be linked to receptor area?
- Present transport models account for the sulfur chemistry with empirical relations, rather than reaction-rate information. How much does the crudeness of these approximations impair the reliability of the predictions?
- Measurements have addressed primarily the acidity of wet deposition. What is the magnitude of dry deposition?
- Long-term trends of precipitation acidity have been based on data obtained using methods now considered outmoded, gathered at different sites for different time periods, and include varying amounts of wet and dry deposition. How reliable are the trends (Fig. 8) deduced from these early results?
- While it is certain that the low pH of lakes prevents many species of fish from reproducing, rainfall may not be the only way that acids enter lakes. How important are acid products from nearby natural terrestrial sources?
- It has not yet been possible to observe or measure changes in the natural terrestrial ecosystem that can unequivocally be attributed to acid precipitation. How reliable is it to infer effects and deduce magnitudes from the results of simulated acid rain in controlled artificial ecosystems?
- In agronomy, the liming of farm land has been used successfully to offset the effects of acidification from fertilizers. How effective in the long-term are the similar procedures being used on some lakes?

D. LEGISLATION

In view of the potential seriousness of the acid rain phenomenon, the economic consequences of possible ameliorative actions, and the lack of key information needed to make rational decisions, Congress recently passed new legislation, the "Acid Precipitation Act of 1980" (Title VII of the "Energy Security Act of 1980", PL 96-294). The purposes of this Act are:

> "1. To identify the causes and sources of acid precipitation;
> 2. To evaluate the environmental, social and economic effects of acid precipitation; and
> 3. Based on the results of the research program established by this subtitle and to the extent consistent with existing law, to take action to the extent necessary and practicable (A) to limit or eliminate the identified sources of acid precipitation, and (B) to remedy or otherwise ameliorate the harmful effects which may result from acid precipitation."

The Act calls for a comprehensive ten-year program of research and evaluation and for recommendations of remedial and ameliorative actions, where required. In order that this program be a coordinated Federal research effort, the legislation establishes an Interagency Task Force on Acid Precipitation, which has the mission of developing and implementing a National Acid Precipitation Assessment Program. The Task Force's recently prepared *National Acid Precipitation Assessment Plan* is a description of the research program.

The *National Plan* analyzes the current understanding of the acid rain phenomenon, identifies the information needed to fill the gaps in our understanding of the phenomenon and its consequences, proposes the research required to obtain that information, and outlines the management and coordination necessary to utilize the understanding gained to make recommendations for a rational course of action. The _National_ _Plan_ incorporates the results of previous Federal planning and research efforts. Furthermore, it calls for communication and cooperation with relevant non-Federal (state and local governmental agencies, universities, industry, private contractors, and research institutions) and international agencies or groups who are active in acid rain research.

The _National_ _Plan_ groups the needed acid rain information into nine key research categories. For each category, three types of information are presented. First, the research tasks are specified and assigned priorities. Second, the agencies involved in the research category are identified and their involvement subdivided into two levels: "participating" -- an agency with direct involvement and with major research activities that are integral components of the task, and "contributing" — an agency not directly involved but with activities that nevertheless are significant contributions to the task. Third, a lead agency is designated and charged with the responsibility of overseeing and facilitating program planning and coordinating the research activities with the other Federal and non-Federal acid rain efforts. Table 1 summarizes the nine research categories and the agency involvements.

E. INTERNATIONAL AGREEMENTS

In response to both United States and Canadian concern regarding transborder air pollution, in general, and acid rain, in particular,

Table 1. Summary of National Acid Precipitation Assessment Plan

	Agencies*		
Research Category	Lead	Participating	Contributing
Natural Sources	NOAA	NOAA	EPA, DOE, DOI, NASA NSF, TVA
Man-Made Sources	DOE	DOE, EPA	TVA
Atmospheric Processes	NOAA	DOA, DOE, DOI, NOAA, TVA	DOE, EPA, NOAA, NSF, TVA
Deposition Monitoring	DOI	DOA, DOE, DOI, NOAA, TVA	DOA, DOE, DOI, EPA, TVA
Aquatic Impacts	EPA	DOA, DOI, EPA, TVA	DOE, DOI, EPA, HHS, NSF, TVA
Terrestrial Impacts	DOA	DOA, DOI, EPA, NSF, TVA	DOE, EPA, HHS, NSF
Materials Impacts	DOI	DOE, DOI, EPA	
Control Technologies	EPA	DOE, EPA	TVA
Assessment and Policy Analysis	EPA	DOA, DOE, DOI, EPA, NOAA	DOE, DOS, HHS, NOAA, NASA, NSF

*The Appendix contains a list of acronyms.

both governments signed a Memorandum of Intent in August 1980. The Memorandum notes that the two countries have set a high priority (a) for research that will provide a scientific understanding of long-range transport of air pollutants and resulting environmental effects and (b) for developing and implementing policies and technologies to combat such effects.

F. NOAA RESEARCH PLAN

NOAA (Air Resources Laboratory, ERL) became active in acid rain research in 1972, when, in cooperation with WMO and EPA, monthly precipitation sample collection and analysis was instituted at ten regional sites in the contiguous United States to provide information on national acid-precipitation trends. In addition, NOAA later provided support to establish the first of several remote world-wide sites that, in cooperation with local investigators, will furnish data on the possible global spread of acid rain. Lastly, a year before the enactment of the "Acid Precipitation Act of 1980", NOAA recognized acid rain as an emerging national issue and proposed that its FY82 annual budget be increased by $2,640,000 and that its staff be augmented by five positions to support expanded acid precipitation research. Part of this request, $1,900,000 and two positions, was approved and is in the FY82 budget.

However, since then, the situation has changed considerably for NOAA. The acid rain issue has become one of the major environmental controversies of the day and it impacts national energy strategy, as well as foreign policy. In response to this issue, recently enacted legislation has called for a Federal acid research program in which NOAA is required to play prominent research and leadership roles.

Specifically, the National Acid Precipitation Assessment Plan stipulates that NOAA has acid rain research responsibilities in three of the nine major categories listed in Table 1:

- natural sources
- atmospheric processes
- deposition monitoring.

By being designated as a "participating" agency in each category, NOAA is required to conduct major research programs aimed at information needs in these areas. Furthermore, the National Plan assigns NOAA to be the lead agency in the first two of these categories. The overseeing and coordinating role implied by the lead-agency designation requires that the level of NOAA's research involvement be such that the relevant NOAA laboratories be fully abreast of the developments in each of these research fields.

Along with these research responsibilities, NOAA is required to take a leadership role in the Federal acid rain research program. Namely, NOAA is to provide a Director of Research who will oversee all Federal acid research planning and the implementation of a balanced, coordinated program. To assist in the preparation of the mandated _National Acid Precipitation Assessment Plan_, NOAA was called on to provide members and an Executive Secretary of the Interagency Task Force responsible for the _National Plan's_ preparation. NOAA will also furnish chairmen for the technical working groups for the two research categories for which it has been designated as lead agency (i.e., natural sources and atmospheric processes) and will provide members of other working groups. In addition to these _National Plan_ leadership roles, NOAA has provided a chairman and members of the Coordination Committee organized to fulfill the initial planning required by the Canada-United States Memorandum of Intent regarding research aimed at understanding transborder air pollution.

Therefore, in response to the intensified acid rain issue and the considerably enlarged NOAA research role mandated by the ensuing legislation, NOAA proposes a new multi-organization research program involving four Environmental Research Laboratories,

Aeronomy Laboratory
Atlantic Oceanographic and Meteorological Laboratories
Air Resources Laboratory
Pacific Marine Environmental Laboratory,

as well as

Environmental Data and Information Service
Office of Weather Research and Modification
Cooperative Institute for Research in Environmental Sciences

The basis of the program is a coordinated application of NOAA's demonstrated expertise in atmospheric and oceanic research. The objective is to remedy the principal deficiencies in the current understanding of the three acid precipitation research categories that are designated in the National Acid Precipitation Assessment Plan as the areas in which NOAA's responsibilities lie. The present proposal incorporates the original FY82 program and adds the complementary research, beginning in FY83, that reflects the expanded role required by NOAA in the National Plan.

Specifically, the part of the present program that will begin in FY82 is essentially unchanged from the research proposed prior to the National Plan. The FY82 Federal budget presently allocates $1,900,000 to the following major components of that research, which, when grouped by NOAA's research-category responsibilities, are:

FY82	Natural Sources	- survey measurements, predominantly land-based sources
	Atmospheric Processes	- long-range trajectory studies - acid global-circulation measurements - aerosol and cloud chemistry measurements
	Deposition Monitoring and Specialized Measurements	- global- and national-trend measurements - establish initial atmospheric research sites - develop dry-deposition measurement methods

While it is clear that these program components are certainly within NOAA's present research responsibilities, it is also clear that the National Plan specifies a much broader NOAA effort in these categories, particularly the first two. For example, Table 1 shows that Federal natural-source research is largely represented by NOAA alone. This responsibility implies a more-encompassing and intensive effort, particularly the need to assess potential aquatic sources. Furthermore, some of the principal uncertainties in the acid rain phenomenon are the atmospheric chemical transformations that form the acidic materials. Since NOAA's original FY82 acid rain research plans were made prior to the National Plan's having assigned major responsibilities to NOAA in this area, these FY82 plans did not include major laboratory, field, and modeling studies aimed at understanding these chemical transformations. At the present, however, this would be a serious omission. To fill these gaps, it is proposed that, in FY83, NOAA's annual budget be increased by $3,500,000 and that its staff be augmented by eight positions for acid rain research with the following principal program components:

FY83	Natural Sources	- regional and local source-strength determinations, including both terrestrial and aquatic sources
	Atmospheric Processes	- laboratory chemical-transformation measurements - chemical-transformation modeling
	Deposition Monitoring and Specialized Measurements	- validative chemical-transformation measurements at atmospheric research sites - general field application of dry deposition instruments.

Taken together, the above set of program components constitute a balanced, complementary, and comprehensive research program plan to provide the acid rain information needs assigned to NOAA in the *National Plan*. The details of these research tasks -- their objectives, procedures, time schedule, and resource requirements -- are given in the sections below. Although each program component is discussed separately, it should be clear that they are, in fact, strongly interrelated parts, all involving many similar research tools, methods, platforms, and measurements by more than one Laboratory.

As reflected in the *National Plan*, NOAA's scientific expertise is considered a key part of the research program needed to address the acid rain issue. The research proposed and the resources requested herein will allow NOAA to meet its responsibilities in this national effort. The results will impact directly on possible regulatory actions, energy strategies, and foreign policy.

OVERALL PROGRAM OBJECTIVES

In response to the pressing need to understand the acid precipitation phenomenon and to fulfill the legislated obligations in this regard, the NOAA research program has the following overall objectives:

- To develop instruments and techniques that have sufficient sensitivity and versatility to make field measurements of the ambient concentrations of acidic and relevant alkaline materials, as well as their precursors and oxidants.
- To conduct a coordinated program of measurements using these and existing instruments and techniques at selected geographic areas and under a range of environmental conditions to determine the production and transformation rates, ambient concentrations, deposition rates, and long-term trends of chemical species that are involved in acid deposition.
- To identify and quantify natural sources of acidic and alkaline materials, as well as their precursors, that contribute to acid deposition and to obtain a global budget.
- To perform laboratory studies of chemical reactions that involve the acid materials, their precursors, oxidants, and relevant alkaline chemicals and to determine the reaction rates.
- To model acid-forming, acid-buffering, transport, and deposition processes, using the above measurements as input or as validation, with the goal of predicting the severity of acid deposition.
- To participate in and coordinate with other international, national, state, or private research programs on acid precipitation, when appropriate, in order to expedite scientific understanding of the problem and recommendations, if necessary, for a proper course of ameliorative action.

PROGRAM COMPONENTS

Described here are the specific tasks that will be done to accomplish the above proposed research objectives. Although grouped here by the research categories of the National Plan in which NOAA's responsibilities lie (i.e., natural sources, atmospheric processes, and deposition monitoring) these tasks involve atmospheric field measurements, laboratory measurements, and theoretical modeling, all of which form an interrelated and mutually supportive set, as indicated schematically in Fig. 10. All of these tasks are in the set assigned the highest priority in the National Plan.

Each of the research-category sections below are subdivided into scientific background, objectives, research strategy, and program plan.

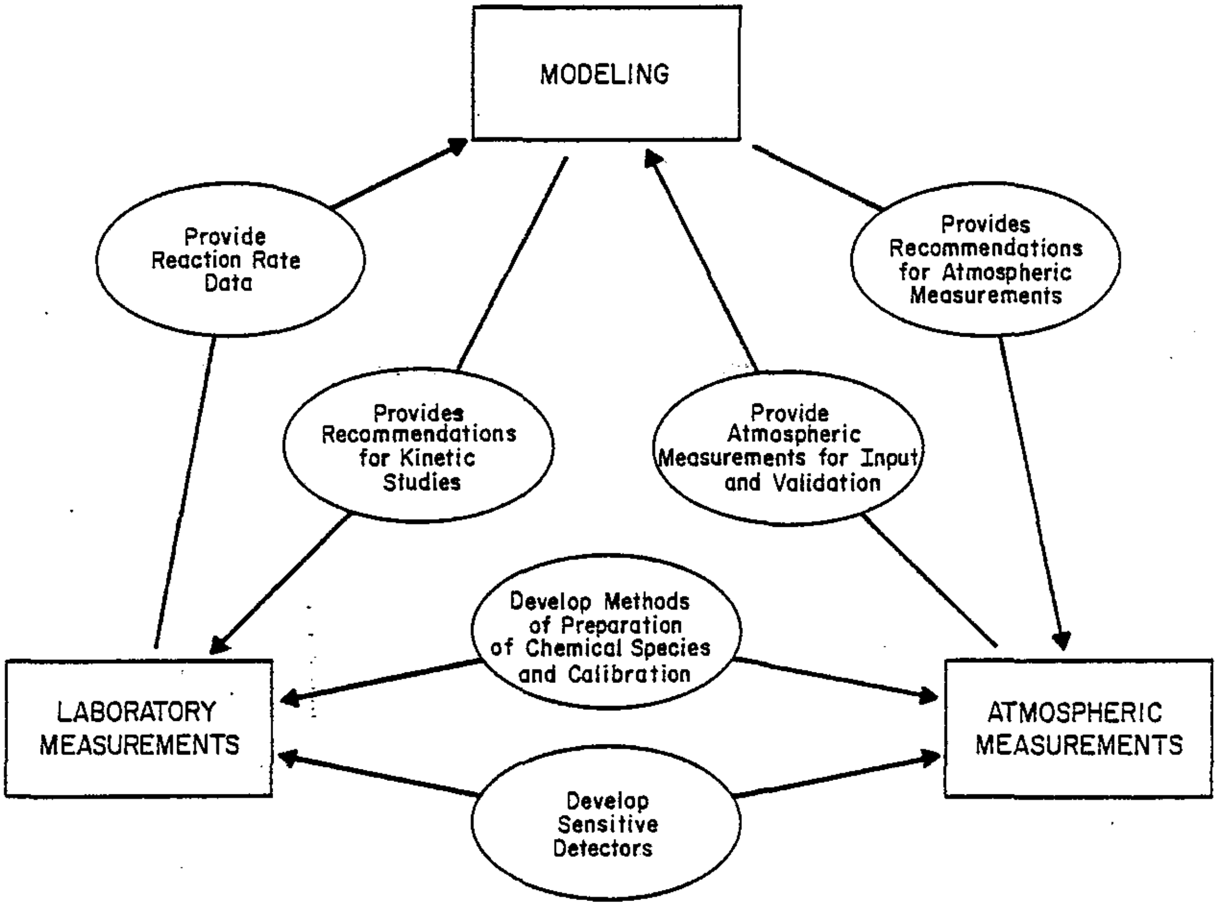

Figure 10. The interrelated components of the acid rain research program.

A. NATURAL SOURCES

While studies have concentrated on man-made sources of acid precipitation for good reasons, there is very little information available on natural sources. Yet an assessment of the relative importance of natural and man-made sources is a key step in essentially all pollution problems, since the target of regulatory actions can obviously only be the latter. The National Plan assigns considerable responsibility to NOAA in the assessment of the role of natural sources: first, as the lead agency and secondly, utilizing NOAA's field-measurement experience and abilities as a key part of the Federal acid rain effort in this research category (Table 1).

Scientific Background

Several natural sources of acid precursors have been suggested. The terrestrial and marine biosphere is thought to be a very significant source of sulfur compounds. These biogenic emissions are probably much larger than non-biogenic sulfur sources like volcanos and thermal springs (Cullis and Hirschler, 1980). The natural sources of nitrogen compounds that could contribute to acid precipitation have been much more difficult to identify and characterize. Lightning is one of the few natural sources of NO_x that has been estimated (Dawson, 1980; Hill et al., 1980). Ammonia may contribute to acid precipitation in complicated ways: as an alkaline agent that may increase the pH of rainfall (Likens et al., 1979) or, via atmospheric reactions, it may form NO_x (McConnell, 1973), which can lead to a decrease in pH. Most ammonia sources are thought to be of natural origin, primarily the decay and decomposition of organic matter. Natural chlorine sources include volcanic gases and CH_3Cl (methyl chloride), the latter from presumed oceanic sources (Singh *et al.*, 1977).

Numerous global budgets have been estimated for sulfur compounds (Cullis and Hirschler, 1980). Most place natural emissions larger than man-made; however, the reverse can be true in polluted areas of the eastern United States (Galloway and Whelpdale, 1980). The uncertainties in global budgets could be as large as factors of two to four. The nitrogen and chlorine budgets are even more difficult to assess. Even though their emissions are weak, natural sources are significant in budgets because they are often distributed across large areas. However, the low concentrations imply that the examination of these sources cannot generally be carried out using the standard, commercially available instruments that are routinely used to monitor the considerably stronger industrial and/or urban emissions near their sources. Consequently, the research that is required to locate and characterize many of the natural sources of acid rain will primarily entail the design, construction, and deployment of new high-sensitivity instruments and techniques directed toward identification and quantification at selected locations.

1. Oceans

Objective: To identify and quantify natural acid rain precursors produced in the oceans.

Research Strategy: Measure the flux direction and magnitude of the significant acid-related gases from biologically distinct classes of marine areas, whose regional distribution can be estimated. The flux from each class and the regional distribution of the classes will yield an estimate of the flux distribution.

Program Plan

The flux of a given species will be determined using the stagnant film boundary model (Broecker and Peng, 1974), which relates the flux to the known diffusivity and the concentrations of the species in the surface mixed layer and the air above the surface. Internal checks can be made on the derived flux by comparing it to *in situ* production rates estimated using standard thermocline models and subsurface measurements. To adequately assess these mixing and transfer processes, the density structure of the surface and the near-surface ocean will be defined via continuous-recording salinity-and-temperature depth sensors.

The target species are the reduced sulfur compounds (e.g., CH_3SH, CH_3SCH_3, $CH_3S_2CH_3$, COS, etc.), low molecular weight halogenated compounds (eg., CH_3Cl) and the odd-nitrogen species (e.g., NO_x). Gas collection, preconcentration, sorbtion, and stripping techniques will be used in conjunction with gas chromatography, mass spectroscopy, and chemiluminescence (Zafiriou and McFarland, 1980) to identify the acid-related materials and to measure the concentrations required.

To define the biological activity that accompanies the flux determination, measurements will be carried on plant chlorophylls, nutrients, and the inorganic-to-organic carbon rates, as well as estimations of the fixation of inorganic sulfur and subsequent release of organic sulfur compounds by marine organisms. It is these parameters that will be used in developing simple correlations between fluxes and classes of biological activity, from which regional and global budgets can be estimated. The field measurements will be supplemented with culture studies to ascertain whether the gases are of bacterial origin or arise primarily from the activities of phytoplankton.

The regions to be studied are those characterized by high biological productivity. Representative large-scale areas include the Peruvian upwelling, tropical divergences, seasonal coastal upwellings, and the high-latitude productive areas of all oceans. The first such study will be the cruise of the NOAA RESEARCHER near the Yucatan Peninsula in the spring of 1982, which will be a multidisciplinary investigation of sulfur chemistry in the marine boundary layer.

The oceanic observations will be made from NOAA Class I or II research ships, frequently in coordination with other NOAA programs. These instrumented vessels can furnish all of the required support meteorological and hydrographic data and can provide laboratory and deck space and quarters for up to 25 scientists. The fact that these ships have been used extensively in the performance of both climate and environmental marine programs indicates their suitability for a large-scale research program such as that outlined above.

2. Land

Objective: To identify and quantify the emission rates, geographical distribution, and temporal variations of sources of acid-related materials on land.

Research Strategy; Categorize the significance of the numerous possible natural sources of acid precursors and related alkaline materials from reliable earlier studies or new survey measurements of local concentrations of the relevant species. For the most significant sources, establish the flux magnitudes from measurements of the atmospheric gradient of the species or by new flux-sensing instrumentation. With estimates of the occurrence of the source types and the flux measurements from each type, emission distributions will be obtained.

Program Plan

The first step of the proposed research plan is an inventory of the suspected likely natural sources of materials that could contribute to acid precipitation, with an emphasis on the estimated strength, geographical distribution, emitted compounds, and the likelihood that these compounds are transformed into acid or alkaline materials. The inventory will build on the previous sulfur estimates, of which there are many. The nitrogen and chlorine estimates will necessarily be crude, since much less is known regarding these natural sources.

Based on the likely importance revealed by the inventory, survey field measurements will be made at appropriate locations within the United States with existing instruments and techniques, or those developed for that purpose. The ambient concentrations will be an indication of the potential significance of each type of source. Chamber methods (Aneja et al., 1979) and bagging techniques (Holdren et al., 1979) can provide accompanying rough estimates of the flux. Furthermore, the dry-deposition instruments discussed in Sec. C-3 below can also yield flux information.

Where justified, eddy-correlation (Lenschow et al., 1980) and gradient (Priestly, 1959) techniques can also be used to obtain improved values of the flux from the source area. The former method requires very fast response instruments (e.g., ≤ 0.1 sec, typically an optical response time), which will pose challenges for many of the species sought. The gradient method relates the altitude profile of the species to concurrent eddy-diffusivity (momentum-transfer) data. Both methods can involve aircraft or tower instrumentation.

In addition to those molecules listed in Sec. 1 above, potential acid-related compounds examined will include aerosols and dust particles (Mamane and Pueschel, 1980) and ammonia. Likely areas where measurements will be made include marshes and swamps, high-wind erosion regions, biologically active farmland, geological emission sites, and spontaneously ignited coal seams. Information about the emissions from semi-random events, such as lightning, forest fires, or volcanic activity, will depend on likely occurrence during longer-term measurement programs with broad aims, such as the research sites discussed in Sec. C-2 below.

B. ATMOSPHERIC PROCESSES

As noted in the National Plan, the processes whereby the acid materials are formed during transport are one of the major areas of uncertainty in the acid precipitation phenomenon. Yet it is clear that without an understanding of these transport and chemical-transformation processes no quantitatively reliable source/receptor, emission/deposition model could be constructed. A proper assessment of the acid rain problem requires such models.

Because of their complexity, a detailed understanding of the transport and acid-forming processes entails a research effort that is beyond the resources of a single agency. Nevertheless, NOAA's expertise in this research field is the basis for potentially major contributions to the understanding of this important part of the acid rain phenomenon, as indicated by NOAA being selected as the lead agency for this research category in the National Plan (Table 1). The program components discussed below build on that proficiency.

1. Transport

Scientific Background

The lower atmosphere is a constantly changing system, as winds, storm motion, and temperature cycles demonstrate. Consequently, it is an exceedingly difficult task to accurately simulate the path of pollutants from their points of injection to the region of their deposition by a storm system that may have developed over several days. Major simplifications in the structure of the atmosphere must presently be made if trajectory models are to be manageable. These simplifications often include rudimentary treatment of features like wind shear, turbulence, convection, thermal layering, and boundary conditions (Fahien, 1980). Thus, the goal of trajectory model improvements is to replace these simplifications with progressively more accurate representations.

Objective: To improve the prediction of the transport and dispersion of conserved substances by air motions.

Research Strategy: Test the model improvements by comparing the predictions to field measurements of released tracers.

Program Plan

The existing trajectory model (Heffter, 1980) will be augmented in two ways. The first is to utilize a broader-input meteorological data base. More wind data for the United States and Canada will be routinely acquired. The second is to improve the present treatment within the model of air movements over irregular terrain (such as in the vicinity of mountains and coastal areas) and to add vertical spreading as one of the dispersive mechanisms of air pollutants.

Tracer releases will test the improved model's reliability at the 1000 km range. In recent years, several suitable tracers have been developed and the present tests may be conducted with tracers released for other applications. It will be necessary to conduct tracer tests under a variety of weather conditions, seasons, and release heights. While this field work will provide validation, the improvement of the trajectory model is the main output of the research task. The transport prediction capability will provide support for other phases of the problem, such as locating likely upwind sources of observed anomalously high concentrations of chemicals.

2. Global Circulation Measurements

Scientific Background

Acid precipitation is now being observed in areas that are far from industrialized regions (Miller and Yoshinaga, 1981). It is important to the understanding of the global aspects of the acid rain issue (e.g., the political implications) to determine whether this acidity is due to unsuspected local natural sources or due to very long-range transport from the distant industrial areas. The basis for inquiry along these lines is a set of remote-area measurements that are free from obvious local large natural sources (like volcanos) and that are made over a sufficient time to identify changes that could arise from seasonal circulation patterns. When coupled with improved long-range transport model predictions (Sec. B-1 above), these data can make a major contribution to understanding the global dispersion of acidic materials.

Objective: To obtain data on the composition of precipitation in remote areas, determine the characteristics of the acidity or alkalinity at the sites, and infer the processes that control the observed composition.

Research Strategy: Establish sites in remote areas of the world, measure the precipitation composition with on-site and continental-based laboratory analyses), and establish trends and sources.

Research Plan:

In 1979, NOAA provided support to the University of Virginia to establish initial cooperative remote sites for precipitation chemistry measurements throughout the world (Galloway *et al.*, 1981). The site selection criteria are:

(1) technically qualified personnel
(2) no local pollutant sources
(3) at least 100 km from industrial areas
(4) meteorological instruments available
(5) rapid access to a postal system
(6) precipitation of ≥ 50 cm/yr.

Seven sites have been established: Amsterdam Island, Alaska, Argentina, Australia (2), Bermuda, and Venezuela. Additional sites are planned at South Africa, India (2), Chile, Brazil, Mexico, and Peru. In addition to precipitation collection, aerosol measurements will be done in order to confirm the initial indications that sulfuric acid from particles is a major contributor. After preliminary measurements on site, the samples will be returned to the University of Virginia for analysis, where network-accepted procedures are used. Particular emphasis will be placed on the prevention of sample alteration during transit. If acid precipitation occurs in these remote areas, as the preliminary results indeed indicate, the potential sources of these materials will be examined using trajectory models and by inferences drawn from the chemical composition of the precipitation.

3. Chemical Modeling

Scientific Background

In the assessment of the acid rain phenomenon and in considering a possible course of action, models are a basic tool, since they are the major means of establishing source/receptor relations and examining in advance the effects of new sources of pollution. Current acid rain transport/photochemical models can only be regarded as preliminary since they involve very tentative assumptions and major chemical simplifications

(Ferguson and Machta, 1981). Most of these models use highly parameterized representations of the transformations and depositions of SO_2 and $SO_4^=$ (sulfate). Furthermore, all but a few of the existing models have neglected NO_x sources, transformations, and depositions. Without a better representation of such mechanisms, models cannot provide an insight into how the complex, interrelated acid rain phenomenon functions as a whole.

<u>Objective</u>: To introduce detailed chemical transformations into acid rain transport, dispersion, and deposition models to better understand the acid rain phenomenon.

<u>Research Strategy</u>: Introduce and verify clean tropospheric chemistry through model calculations and measurements. Expand this to include photochemical pollutants at the regional level.

<u>Research Plan</u>

The first stage of the model development will be primarily the inclusion of gas phase, clean-air photochemistry into the transport and dispersion models described in Sec. B-1 above. Clean-air concentrations of NO_x, HNO_3, SO_2, O_3, CO (carbon monoxide), CH_4 (methane), and nonmethane hydrocarbons will be specified in the models. The concentrations of radicals, (e.g., OH and HO_2) and other reactive species, such as H_2O_2 (hydrogen peroxide) and CH_2O (formaldehyde), will be calculated (e.g., Liu, 1977; Liu <u>et al</u>., 1980). The treatment of the nonmethane hydrocarbon chemistry will follow the "lumped mechanism" of Hecht <u>et al</u>. (1974). Laboratory kinetic studies, described in Sec. B-4 below, will provide input information for reactive processes. At this stage of development, heterogeneous processes will be represented by simple parameterized linear removal of the soluble gases like H_2O_2, HNO_3, and H_2SO_4. The model calculations will be tested critically at selected atmospheric research sites, described in Sec. C-2 below, where simultaneous measurements of the critical species will be made and compared to predictions.

The second stage of the model development will be the addition of an aerosol chemistry for clean-air conditions. The physical processes and mathematical formulation of Turco et al. (1979) will be adopted. Precipitation scavenging and dry deposition of aerosols will be parameterized using information from the studies described in Sec. B-5 below. This model will also undergo field tests for validation. At this stage, the model can be used to examine the relation between sources of the acid precursors and resulting acid precipitation in clean continental regions.

In the last stage, pollution sources will be introduced at the regional level. The changes required in the model's homogeneous chemistry should be minor, but the heterogeneous reactions may need major modifications. By the time that this stage is developed, the laboratory studies of Sec. B-4 can provide considerable assistance in identifying and quantifying the important heterogeneous processes to be incorporated. Critical field measurements will be designed to test the validity of the model calculations. Continuous optimization of the computer code and the calculational methods will be carried out. The finished code should be extremely useful for investigating a wide variety of regional acid rain phenomena; e.g., source/receptor relationships, the effects of nonmethane hydrocarbon emissions on acid deposition, and the effects of projected increases in NO_x emissions. Only through such in-depth model calculations and field and laboratory measurements can the complex transformations and depositions of acid materials be evaluated.

4. Laboratory Chemistry

Scientific Background

The complex chemistry whereby natural and man-made nitrogen, sulfur, and chlorine compounds are converted to acidic materials is one of the major areas of uncertainty in the acid rain phenomenon. The rates at which the emitted compounds are converted to acids will be a factor in determining the distance from the source that the acids will appear in the atmosphere. A rigorous analysis of this problem would require accounting for every chemical species and chemical reaction that occurs in the atmosphere, but, fortunately, the problem can be reduced to a managable number of oxidants that presently appear to dominate atmospheric chemistry and hence figure strongly in acid formation. These include the molecules like OH (hydroxyl radical), RO_2 (peroxy radicals, where R represents a hydrogen atom or some organic radical), and O_3 (ozone) (Demerjian et al., 1974).

The present understanding of even the major reactions that involve these oxidants and that lead to acid formation is very poor. Similarly, the reactions that form these oxidants and the reactions that compete with acid formation are not well known. The following examples are indicative. The mechanism by which SO_2 is converted to sulfuric acid is not known beyond an assumed first step (Calvert et al., 1978). Atmospheric observations of the temporal behavior of NO_3 radicals (nitrogen trioxide), a very important member of the nitrogen oxide family, cannot be explained with our present knowledge of NO_3 chemistry (Noxon et al., 1980). Although it is known that enormous amounts of natural and man-made hydrocarbons are oxidized in the atmosphere, virtually nothing is known of the details, such as how these processes affect the balance of the OH, RO_2, and O_3 species. Lastly, in addition to these homogeneous processes, gas-particle, gas-droplet, and particle-droplet processes are frequently proposed as reaction pathways that could form acid materials, and reliable quantitative information on these heterogeneous processes is essentially nonexistent.

To understand the chemical transformations in the acid rain phenomenon, three types of laboratory kinetics measurements are required: (1) studies of the reactions that control the production and loss of the dominant reactants, (2) studies of the reactions that are responsible for the transformation of the original sulfur, nitrogen, and chlorine compounds to acids, and (3) studies of the heterogeneous processes that are responsible for the removal of acid molecules by aerosols, water drops, etc.

> Objective: To determine the rates and products of the reactions affecting acid-related sulfur, nitrogen, and chlorine compounds under appropriate atmospheric conditions.
>
> Research Strategy: Identify the key reaction pathways that involve the acid precursors and the major oxidants and use existing and newly devised techniques for measuring their rates and products.

Program Plan

A study of the atmospheric reactions of NO_3 will be initiated. This work will be directed toward identifying possible new loss mechanisms for NO_3. A part of this study will be to measure the reactivity of NO_3 with hydrocarbons.

The oxidation of NH_3 (ammonia) will be investigated. Although the first step, the reaction with OH is well known, the subsequent fate of the NH_2 radical produced is not well established. Ammonia is unusual because it has the potential to both neutralize acid species in solid and liquid particles and to form nitrogen oxides and ultimately nitric acid. The large known sources of NH_3 require that its role be clearly understood.

The reactive properties of other molecules, particularly the reduced sulfur compounds -- CS_2, COS, H_2S, etc. -- will be studied. In each case, measurements will be made to determine the rates and products of the key oxidation steps.

In the longer term, the heterogeneous loss of HNO_3 and H_2SO_4 on the surfaces of atmospheric particles and water drops will be examined. The rates of these processes probably depend on temperature, pH, and particle size, all of which will be varied in these studies. The needed information is the fraction of the collisions with the surface of the particle that result in the loss of the acid molecules.

In all of these studies, sensitive detectors for a variety of molecules are required, many of which already have been developed: laser magnetic resonance for OH (Howard and Evenson, 1974) and HO_2 (Howard, 1977) and tunable diode laser for HNO_3 (P. S. Connell and C. J. Howard, to be published, 1981). Other detectors will be developed as needed and will draw on this experience.

5. Aerosol and Cloud Processes

Scientific Background

The injection, formation, and transport of acid-related aerosols constitutes an important part of the acidic cycle in the atmosphere. The aerosols are not only important in the initial formation of the cloud, but they may be scavenged by droplets within the cloud (rainout) or below the cloud during the precipitation process (washout). Therefore, both the physical and chemical properties of the aerosol are important.

The processes occurring within the cloud are varied and complex. Typically, water vapor in the atmosphere is continually condensing, evaporating, and recondensing. Large volumes of air pass through the cloud stage this way and, if the air is pollutant-laden, the droplet size and acidity can be greatly altered. Thus, droplet acidity depends sensitively on the cloud processes, in addition to the gas-phase pollutant concentrations.

It is extremely difficult to quantify such processes via measurements and most models account for these processes only in a highly parameterized way. Even this type of accounting lacks experimental verification.

> Objectives: To obtain correlations between (a) aerosol size, composition, and origin and (b) cloud water acidity to determine useful relations for predicting the acidity of rainfall.
>
> Research Strategy: Perform airborne measurements of aerosols and cloud water acidity in widely different environments and at various distances downwind from

sources. Use the correlations from these observations to classify cloudwater or rainfall acidity by aerosol source, composition, and residence time.

Program Plan:

Aerosols and cloud-water acidity will be measured throughout the boundary layer in the vicinity (up to 100 km) upwind and downwind of locales of interest, including both man-made and natural aerosol emissions. Important man-made aerosol sources to be examined will include cities, power plants, smelters, refineries and surface mining operations, (e.g., Pueschel and Van Valin, 1978; Parungo et al., 1980). Natural sources of aerosols to be examined will be volcanos, wind-erosion dust, and sea salt.

Aerosol sizes and composition will be determined by microchemical spot techniques (Mamane and dePena, 1978), scanning electron microscopy and x-ray energy dispersive analysis (Parungo et al., 1978). Earlier studies (Barrett et al., 1979) have shown consistent correlations between drop size and the origin of the nucleating aerosol.

Cloud-water will be sampled with special collectors designed for that express purpose and the samples will be analyzed for pH and composition. Measurements made at various altitudes in the cloud will provide some insight into cloud processes as they relate to acidity.

Aerosol measurement below the cloud will indicate the potential for the increase of acidity by washout. Surface precipitation will accompany these airborne measurements, where feasible. Likely locations for such coordinated air-surface studies will be the atmospheric research sites discussed in Sec. C-2 below. Correlations and classifications between the aerosol, cloud-water acidity, and precipitation acidity measurements are highly likely to yield practical relations that can be incorporated into acid deposition models.

The measurements described above will also be used as surveys. For example, the natural aerosol "background" in remote areas will be studied. The aerosol characteristics will provide information about possible sources of acidity in these areas. These studies will utilize the results of separate characterization of source emissions. For example, as has been demonstrated with the measurements associated with the Mount St. Helens eruption (R. F. Pueschel, private communication, 1980) that large amounts of ejected material need not imply a potentially large contribution of acid precursors. The eruptions that were studied produced very little sulfate- and nitrate-containing material.

C. DEPOSITION MONITORING AND SPECIALIZED MEASUREMENTS

Although there are several precipitation-chemistry measurement stations and networks in operation now, there has been no one network that has operated continuously over the past two decades (DOE, 1980). Several precipitation collection and research networks have been started, only to be later terminated. Frequently, funding was not adequate or sufficiently long-term that instrument and technique reliability could be fully tested and cross-compared with others under the same conditions. The changing degree of support for acid-rain research essentially precluded the establishment of semi-permanent monitoring or research sites that could bring a variety of techniques to bear on all parameters of the problem.

With the benefit of hindsight and by recognizing clearly the importance of an assessment of the acid rain problem, the commitment implied in the National Plan rectifies the situation by establishing a "trends network" and by initiating a broad-based field-measurement program to gain a fundamental set of acid-related data. A three-tiered measurement structure was established. First, a Global Trends Network will involve a worldwide grid of remotely placed sites whose aim is to provide information on clean "background" levels and/or the influence of intercontinental transport patterns. Secondly, a National Trends Network will involve relatively remote sites that can examine long-term trends in acid precipitation in the United States. Lastly, a Research Support Network will be made up of special-study sites whose aim is to examine particular research problems related to locale, processes, etc.

This important and enormous monitoring/research effort, being coordinated by the Department of the Interior as the lead agency, involves the research conducted by several agencies, as shown in Table 1. NOAA's experience in monitoring and field research is recognized by the _National Plan_ as an important resource in this endeavor. In addition to the global remote-area sites described in Sec. B-2, the present research plan has three program components designed to utilize NOAA's expertise and to fulfill NOAA's part of the _National Plan_ in this regard.

1. National Precipitation Acidity Monitoring

Scientific Background

Since 1972, NOAA has collaborated with the World Meteorological Organization and the Environmental Protection Agency in maintaining a set of ten regional sites within the contiguous United States at which precipitation samples are collected. The locations are not near urban or industrial areas. Sample retrieval is weekly. The proximity of National Weather Service instruments provides supporting weather records. The chemical analyses of the samples are performed at the Illinois State Water Survey laboratories (Stensland, 1980). Under the _National Plan_, these monitoring sites will contribute to the National Trends Network and hence are intended for long-term (≥ 10 years) future operation. Their existing data sets and the experience gained over the past eight years at these sites will make them valuable members of that network.

Objective: To obtain precipitation chemistry data at relatively remote continental United States sites to determine national precipitation acidity trends.

Research Strategy: Upgrade the existing regional sites, both in quality and in number.

Program Plan

All of the existing sites and procedures will be reviewed to check their consistency with the protocols of the National Trends Network, as these become available. The location of several new sites will focus on regions of high current interest, such as those likely to be influenced in the future by urban and energy-production growth. Contracts will be let for site operation and sample analyses.

2. Atmospheric Research Sites

Scientific Background

In previous acid rain studies, there was seldom a coordinated set of meteorological, atmospheric-chemistry, and precipitation measurements made simultaneously at one site for extended periods. Without such information, it is impossible to interpret the complex interplay between acid precipitation sources, transport, transformations, and depositions. These data are the key to understanding the acid rain phenomenon in detail.

The National Plan specifies the need for a variety of such detailed, coordinated research efforts aimed at specific and special problems of selected urban areas, local events like volcanic eruptions, sites near new types of industrial processes such as the retorting of oil shale, and locations where special studies are being conducted on acid deposition effects. The research at such sites will be aimed at specific acid rain problems, which is an approach that is different from that of the larger-in-number and more-simply instrumented monitoring sites.

Objective: To provide a detailed understanding of the acid formation and deposition mechanisms.

Research Strategy: Establish two or three semi-permanent sites characteristic of continental regions. Furnish these sites with the complement of instruments needed to examine the major parameters in acid formation and deposition. Use the results to formulate and test models of these processes.

Program Plan

A major part of the NOAA program's acid-related atmospheric processes research will derive from orchestrated measurements made at specially selected and instrumented sites in the United States. The site selection will be based on three criteria:

(1) the representativeness of the meteorological, geographical, and acid precipitation region or the appropriateness to address a specific local problem,
(2) the availability of detailed meteorological support available,
(3) the proximity of existing NOAA facilities, if appropriate.

The regional location of these sites will utilize several guides. For example, the Environmental Protection Agency has categorized regions of the continental United States by the consumption of fuel by stationary installations and by transportation (EPA, 1978b). Rainfall activity can also be divided into regions (ESSA, 1968). These divisions, as well as geographical differences, show the utility of a few sites whose measurements could be representative of the regional acid precipitation patterns.

The initial measurements that are considered to be essential to the mission of a regional site are severalfold. The key data set to be acquired involves real-time pH, conductivity, and on-site major-ion analyses of the precipitation collected. Complementing these will be a determination of the physical and chemical properties of the collected aerosols. A necessary supplement to the initial acid-related measurements will be meteorological support measurements (e.g., the NOAA PROFS network). These data will range from simple wind-parameter, temperature, and humidity measurements to solar radiation and vertical sounding (and perhaps radar observations) of weather patterns. As the sophistication and completeness of the assembled instrumentation increases, the information gained from these sites will be the fundamental input and validation of regional acid precipitation models.

The short-term atmospheric research sites will be focused on particular acid rain problems. The instrumentation will reflect the nature of the specified task. One of the immediate experiments will test the present understanding of the gas-phase relations between precursors and acids, like NO_x and HNO_3. Special events, like snowfalls, will be examined for relations between gas-phase and aerosol-phase acid-concentration changes and the acidity in the collected snow.

New instrument development will be a key feature of both the regional and special-purpose research sites. The initial emphasis will be on near real-time detectors for gas-phase acid materials, like HNO_3 and H_2SO_4, and major oxidants, like OH. After laboratory development, these sites will field-certify the instrument. Proven techniques will augment other sites' capabilities to measure the increasing number of acid rain parameters required to test the more and more sophisticated model predictions that will be part of the natural evolution of the national acid precipitation assessment effort.

3. Dry Deposition

Scientific Background

Until recently, wet deposition was considered to be the main mechanism whereby acid materials are deposited on the earth's surface. However, regional modeling studies and mass-balance calculations (Garland, 1978) have indicated that dry deposition of acid materials is probably of equal importance to wet deposition. Dry deposition of SO_2 has been studied in some detail (e.g., Whelpdale and Shaw, 1974). The parameter that is needed for model studies is the deposition velocity. Measured values range from 0.04 to 7.5 cm/sec with typical values being 0.1 to 2 cm/sec. Some of the variability may be differences between experimental techniques, but the data are probably reliable enough to indicate that the deposition velocity depends rather strongly on the nature of the surface. The deposition velocities of acid materials are unknown, largely due to the difficulty in detecting these materials in the gas phase.

Several approaches have aimed at the routine collection of dry acid deposition with buckets, plates, etc. All of these techniques may suffer from serious unknown flaws, and it is generally thought that there is presently no reliable way of accurately monitoring dry deposition of acid materials. This represents a major gap in the assessment of the acid deposition issue.

Objective: To develop reliable methods and detectors for measuring the dry deposition of acid materials and apply these to field measurements.

Research Strategy: With existing and newly developed detectors for acid materials, explore eddy-flux devices and gradient methods for determining dry deposition rates.

Several methods and devices for quantifying dry deposition rates will be explored. The first of these will be based on a method that has been used previously to measure vertical fluxes of carbon dioxide (Desjardins, 1972). Air samples for upward and downward moving air parcels are separately passed through different filters. The contents of the stored samples can be measured and related to the turbulent deposition rate. The same device can also be used to measure the evolution of acidic or alkaline materials from the earth's surface. This technique can be supplemented by other eddy-correlation, as well as gradient, methods (see Sec. A-2). Each method will be employed under a variety of surface and weather conditions to parameterize the deposition rates.

The eddy-correlation method requires a fast response detector for acidic materials (see Sec. A-2), which will have to be developed. The other methods mentioned above permit a slower response detector, and this will be the initial thrust of the investigation. For nitric acid, the filter-collector scheme (Huebert and Lazrus, 1979) provides a sufficiently sensitive detector. Other detection methods will be explored not only for nitric acid, but also sulfuric acid.

The initial field tests of the dry deposition instrumentation are likely to be at the atmospheric research sites described in Sec. C-2 above. A long-term goal is to develop the instrument for routine monitoring of dry deposition.

PROGRAM SCHEDULE

PROJECT	TASK	FY82	FY83	FY84
NATURAL SOURCES	Survey Measurements	━	━╸	
	Land	╺━	━	━
	Oceans, East		━	━
	West			━
ATMOSPHERIC PROCESSES	Transport	━	━	━
	Global Circulation Measurements	━	━	━
	Chemical Modeling			
	Clean-air processes		━	━
	Polluted-air processes			━
	Laboratory Chemistry			
	Chemical Reactions		━	━
	Gas-Aerosol Absorption			━
	Aerosol and Cloud Processes	━	━	━
DEPOSITION MONITORING AND SPECIALIZED MEASUREMENTS	National Trends Network	━	━	━
	Atmospheric Research Sites			
	Establish Site 1	━	━	━
	Site 2	╺━	━	━
	Site 3		━	━
	Dry Deposition			
	Development	━		
	Field Application	╺━	━	━

REFERENCES

Aneja, V. P., J. H. Overton, L. T. Cupitt, J. L. Durham, and W. E. Wilson, Direct measurements of emission rates of some biogenic sulfur compounds, Tellus, 31, 174-178, 1979.

Barrett, E. W., F. P. Parungo, and R. F. Pueschel, Cloud modification by urban pollution: A physical demonstration, Meteorol. Rdsch., 32, 136-149, 1979.

Broecker, W. S., and T. H. Peng, Gas exchange rates between air and sea, Tellus, 26, 21-35, 1974.

Calvert, J. G., F. Su, J. W. Bottenheim, and O. P. Strausz, Mechanism of the homogeneous oxidation of sulfur dioxide in the troposphere, Atmos. Environ., 12, 197-226, 1978.

Cogbill, C. V., and G. E. Likens, Acid precipitation in the northeastern United States, Water Resources Res., 10, 1133-1137, 1974.

Cullis, C. F., and M. M. Hirschler, Atmospheric sulphur: natural and man-made sources, Atmos. Environ., 14, 1263-1278, 1980.

Dawson, G. A., Nitrogen fixation by lightning, J. Atmos. Sci., 37, 174-178, 1980.

Demerjian, K. L., J. A. Kerr, and J. G. Calvert, The mechanism of photochemical smog formation, Adv. Environ. Sci., 4, 1-262, 1974.

Department of Energy. Acid rain information book, DOE/EV/10273-1, 1980.

Desjardins, R. L., A study of carbon dioxide and sensible heat fluxes using the eddy correlation technique. Ph. D. Thesis. Cornell University, Ithaca, N.Y., Diss. Abst. No. 73-341, 1972.

Environmental Protection Agency. National air pollutant emission estimates, 1940-1976. EPA-450/1-78-003, 1978a.

Environmental Protection Agency. National air quality, monitoring, and emissions trends report, 1977. EPA-450/2-78-052, 1978b.

Environmental Protection Agency. Research summary. Acid Rain, EPA-600/8-79-028, 1979.

Environmental Protection Agency. 1977 national emissions report. In: National emissions data system of the aerometric and emissions reporting system. EPA-450/4-80-005, 1980.

Environmental Science Services Administration. Climatic Atlas of the United States. U.S. Department of Commerce, Environment Data Services, Washington, D.C., 1968.

Fahien, R. W. Air pollutant dispersion modeling, in Coal Burning Issues, ed. by A. E. S. Green, (University of Florida Press, Gainesville) 1980.

Ferguson, H. L., and L. Machta, Atmospheric Modeling, Report of Work Group 2, Coordination Committee for the Fulfillment of the Requirements of the Memorandum of Intent signed on August 5, 1980, by United States and Canada, January 15, 1981.

Galloway, J. N., and D. M. Whelpdale, An atmospheric sulfur budget for eastern North America, Atmos. Environ., 14, 409-417, 1980.

Galloway, J. N., W. C. Keene, and G. E. Likens, Progress report: global precipitaton chemistry network, (University of Virginia, Charlottesville), January, 1981.

Garland, J. A., Dry and wet removal of sulphur from the atmosphere, Atmos. Environ., 12, 349-362, 1978.

Hecht, T. A., J. H. Seinfeld, and M. Dodge, Further development of generalized kinetic mechanisms for photochemical smog. Environ. Sci. Technol. 8, 327-339, 1947.

Heffter, J. L., Air Resources Laboratory's atmospheric transport and dispersion model, NOAA Tech. Memoran. ERL ARL-81, NOAA, 1980.

Hill, R. D., R. G. Rinker, and H. D. Wilson, Atmospheric nitrogen fixation by lightning, J. Atmos. Sci., 37, 179-192, 1980.

Holdren, M. W., H. H. Westberg, and P. R. Zimmerman, Analysis of monoterpene hydrocarbons in rural atmospheres, J. Geophys. Res., 84, 5083-5088, 1979.

Howard, C. J., Kinetics of the reaction of HO_2 with NO_2, J. Chem. Phys., 67, 5258-5263, 1977.

Howard, C. J., and K. M. Evenson, Laser magnetic resonance study of the gas phase reactions of OH with CO, NO, and NO_2, J. Chem. Phys., 61, 1943-1952, 1974.

Huebert, B. J., and A. L. Lazrus, Tropospheric measurements of nitric acid vapor and particulate nitrate, in Nitrogenous Air Pollutants, edited by D. Grossjean (Ann Arbor Science Publishers, Ann Arbor) pp. 307-315, 1979.

Lenschow, D. H., A. C. Delaney, B. B. Stankov, and D. H. Stedman, Airborne measurements of the vertical flux of ozone in the boundary layer, Boundary Layer Meteorol., 19, 249-265, 1980.

Likens, G. E., R. F. Wright, J. N. Galloway, and T. J. Butler, Acid Rain, Sci. Am., 241, 43-51, 1979.

Liu, S. C., Possible effects on tropospheric O_3 and OH due to NO emissions, Geophys. Res. Lett, 4, 325-328, 1977.

Liu, S. C., D. Kley, M. McFarland, J. D. Mahlman, and H. Levy, On the origin of tropospheric ozone, J. Geophys. Res., 85, 7546-7552, 1980.

Mamane, Y., and R. dePena, A quantitative method for the detection of individual submicro-meter size sulfate particles, Atmos. Environ., 12, 69-82, 1978.

Mamane, Y., and R. F. Pueschel, A method for the detection of individual nitrate particles, Atmos. Environ., 14, 629-639, 1980.

McConnell, J. C., Atmospheric ammonia, J. Geophys. Res., 78, 7812-7820, 1973.

Miller, J. M., and A. M. Yoshinaga, The acidity of Hawaiian precipitation. A preliminary report, Geophys. Res. Lett., submitted, 1981.

Noxon, J. F., R. B. Norton, and E. Marovich, NO_3 in the troposphere, Geophys. Res. Lett., 7, 125-128, 1980.

Parungo, F., E. Ackerman, H. Proulx, and R. F. Pueschel, Nucleation properties of fly ash in a coal-fired power plant plume, Atmos. Environ., 12, 929-935, 1978.

Parungo, F. P., R. F. Pueschel, and D. L. Williams, Chemical composition of oil refinery plumes in Los Angeles, Atmos. Environ., 14, 509-522, 1980.

Priestly, C. H. B., Turbulent Transfer in the Lower Atmosphere, (University of Chicago Press, Chicago) 1959.

Pueschel, R. F., and C. C. Van Valin, Cloud nucleus formation in a power plan plume, Atmos. Environ., 12, 307-312, 1978.

Schofield, C. L., Acid precipitation: Effects on fish, Ambio, 5, 228-230, 1976.

Singh, H. B., L. Salas, H. Shigeishi, and A. Crawford, Atmos. Environ., 11, 819-828, 1977.

Stensland, G. J., Precipitation chemistry trends in the northeastern United States, in Acid Rain, edited by T. Y. Toribara, M. W. Miller, and P. E. Morrow (Plenum Press, New York) pp. 87-104, 1980.

Turco, R. P., P. Hamill, O. B. Toon, R. C. Whitten, and C. S. Kiang, A one-dimensional model describing aerosol formation and evolution in the stratosphere: I. Physical processes and mathematical analogs, J. Atmos. Sci., 36, 699-717, 1979.

Whelpdale, D. M., and R. W. Shaw, Sulphur dioxide removal by turbulent transfer of grass, snow, and water surface, Tellus, 26, 196-205, 1974.

Zafiriou, O. C., and M. McFarland, Determination of trace levels of nitric oxide in aqueous solution, Anal. Chem. 52, 1662-1667, 1980.

APPENDIX

List of Acronyms

AL	Aeronomy Laboratory
AOML	Atlantic Oceanographic and Meteorological Laboratories
ARL	Air Resources Laboratory
CIRES	Cooperative Institute for Research in Environmental Sciences
DOA	Department of Agriculture
DOE	Department of Energy
DOI	Department of Interior
DOS	Department of State
EDIS	Environmental Data and Information Service
EPA	Environmental Protection Agency
ERL	Environmental Research Laboratories
HHS	Department of Health and Human Services
NASA	National Aeronautics and Space Administration
NOAA	National Oceanic and Atmospheric Administration
NSF	National Science Foundation
OWRM	Office of Weather Research and Modification
PMEL	Pacific Marine Environmental Laboratory
PROFS	Prototype Regional Observing and Forecasting Service
TVA	Tennessee Valley Authority
WMO	World Meteorological Organization