



## Project Summary

# Regional Acid Deposition: Models and Physical Processes

**This report presents the results of a 10-month study on the current status of research on fundamental concepts and physical processes relevant to regional acid deposition modeling. The role of models in environmental assessment is described first. This is followed by a review of existing models in a chapter designed to establish a reference framework for the bulk of the report. Most, if not all, of the principal concepts in model construction and evaluation are discussed. After extensive discussions of state-of-the-art regional meteorological modeling and the chemistry of acid generation in the troposphere are presented, the discussion focuses on the development of a new generation of acid deposition models. Based on the topics reviewed, the desirable features of a comprehensive model are described with emphasis on components needing great improvement or omitted in present models. These features include emissions data, detailed acid rain chemistry, cloud processes, dry deposition, model validation, and sensitivity analysis.**

***This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

### Introduction

Although the acid rain phenomenon has been recognized for the past 100 years, important features of the acid rain problem are new: (a) quantitative questions are perceived that must be answered to fully understand the essential chemical and meteorological processes, and (b) mathematical models and

field- and laboratory-measured programs are available to investigate these questions. Similarly, now available are reasonably logical and mature formulations of relationships between ecological systems (and physical structures) and acid deposition that can be investigated quantitatively. Also, as noted above, public awareness of the potential effects and probable causes of acid rain is new, as is the understanding that some kinds of pollution traverse political boundaries.

The bulk of the report examines the full range of meteorological and chemical processes that are involved in the overall phenomenon that is, the production and deposition of acidified rain, snow, fog, and mist, and the dry deposition of acid anhydrides over important inhabited regions, such as the east central United States and Canada. Particular attention is given to issues in the study of acid rain through mathematical models. Although the scientific questions dictate the kinds of field measurements, laboratory experiments, and model development to be undertaken (all of which are necessary), particular interest is in how to develop and employ credible models. A *credible model* is defined as one built on basic physical and chemical processes that can test hypotheses and guide the design and assessment of field measurement programs; its ultimate use is for predicting acid deposition rates and source-receptor relationships and for reliably estimating the effects of emission control strategies.

### The Physical Picture

To understand and model the acid rain phenomenon one must recognize a wide range of physical and chemical processes and their interactions. Briefly, these are (a) emissions of materials that cause and regulate acidity in precipitation and deposition,

(b) meteorological motions that transport and dilute the emitted substances laterally and vertically, (c) the various physical and chemical transformations that alter the physical phase and chemical properties (e.g., valence or oxidation state) of the emitted substances, and (d) the meteorological factors and surface adhesiveness that lead to deposition of the transformed substances. Less recognized than the above processes are those properties of the Earth's surface that control the rate of uptake of dry materials (e.g., gaseous  $\text{SO}_2$  and/or airborne particles).

Because the principal acids in precipitation are sulfuric ( $\text{H}_2\text{SO}_4$ ) and nitric ( $\text{HNO}_3$ ), most concern is with sulfur and nitrogen emissions. However, the hydrocarbons and their oxidation products are important reactants in the chemistry which ultimately leads to  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . Estimates of anthropogenic emissions of  $\text{SO}_2$  (mostly from coal- and oil-burning electrical power plants and metal-smelting plants) and of  $\text{NO}_x$  (mostly  $\text{NO}$  and  $\text{NO}_2$  from high temperature combustion processes, including those in auto and truck engines and power plants) are reasonably reliable for the world's industrialized countries. Much less credible, but probably less important, are estimates of natural emissions of organic sulfur gases and of natural  $\text{NO}_x$  compounds. Natural sources of gaseous  $\text{NH}_3$  and particulate  $\text{NH}_4^+$ , gaseous hydrocarbons, airborne mineral dusts, and lightning-produced  $\text{NO}_x$  must also be estimated reliably. Minor contributions to precipitation acidity from  $\text{HCl}$  and organic acids are often negligible.

Whether the key emissions are anthropogenic or natural, they are injected into the atmosphere at or near the Earth's surface, usually within the planetary boundary layer. Accordingly, boundary layer meteorology is at the core of the acid rain problem. The physics of turbulence and convection, diurnal variation in surface heating, terrain geometry, and surface and boundary layer hydrology exert strong control over the initial dispersion of the emitted substances. Further, during the time these substances spend in the boundary layer, their physical environment (e.g., temperature, pressure, humidity, available sunlight) and proximity to surfaces and to other pollutants such as aerosol particles control the rate and type of chemical transformations that occur. These chemical transformations differ markedly from those that normally occur above the boundary layer in the free troposphere. Perhaps only one important acid precursor or regulator,  $\text{NO}_x$  from lightning, does not begin its atmospheric life in the boundary layer, although background tropospheric ozone is central to all tropospheric chemistry.

In dirty or clean air, in the boundary layer and above, chemicals react with each other. The precise rates and types of reactions depend strongly on the local pressure, temperature, available sunlight (both direct and scattered), the presence of liquid and vapor  $\text{H}_2\text{O}$ , and on the production of photochemical oxidants (like ozone and peroxyacetyl nitrate co-reactants). The discussion is organized into categories of homogeneous reactions (gaseous and liquid) and heterogeneous processes and by principal categories of chemical species. Key considerations include the exact rates of transformation (oxidation) of  $\text{SO}_2$  and  $\text{NO}_x$  into  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , respectively, the major pathways of transformation, and the essential controlling agents.

In an oxidizing atmosphere such as that of the Earth, the oxidation of  $\text{SO}_2$  and  $\text{NO}_x$  to  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  is inescapable, given enough time in the atmosphere. In characterizing regional acid deposition, however, one must determine what fraction of a region's total emissions is oxidized and deposited within the region and what fraction of the total is transported long distance (at high altitudes, for example) for eventual deposition onto territories hundreds or thousands of kilometers from the sources. That is, a credible description and model of this physical system must include quantitative treatment of material transport and transformation above the boundary layer. Similarly, the factors that limit the rate of surface deposition and uptake of gases (dry deposition) must be treated quantitatively. These factors include nearground turbulence, the condition and type of the surface (e.g., vegetation, soils), and the chemical stickiness and reactivity of the relevant substances on the surfaces.

### Existing Models and Components of Models

Two distinct types of models used are defined, described, and compared for studying long-range transport of air pollutants: Eulerian grid models and Lagrangian trajectory models. Also, because of different goals and problems facing air pollution meteorologists and chemists, it has been useful to develop and employ distinctly different models for air quality modeling (AQM) and acid deposition modeling (ADM). For ADM, it is concluded that the three-dimensional nature of the problem and the importance of simulating with adequate generality specific source distributions and eventual control strategies require an Eulerian framework.

Although ADM has improved the understanding of the acid rain problem, a number of phenomena have not yet been

fully treated largely because the ADM field is relatively new. Reasonably well-based treatments of each phenomenon have been attempted, but the best available mathematical parameterizations have not been coupled within one model. Individual models tend to be strong in one respect, but very weak in others. A number of fundamental weaknesses that are widespread, or even ubiquitous, can be mentioned. For example, existing acid deposition models do not allow for mixing of pollutants above the boundary layer. Similarly, no recognition is given to different types of precipitation (rain, snow, dew, etc.) or to the temperature and pH that characterize precipitation scavenging and acid formation. No cloud-chemical processes have been considered, nor have fundamental (or elementary) chemical reactions been treated with sufficient detail. Instead, linear overall transformation rates have been employed. (For example, the conversion rate of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  has been set equal to  $x\%$  per hour without regard to mechanisms or controlling factors, although seasonal dependence of  $x$  is sometimes permitted.) No published model has included reasonably complete chemical reaction schemes, and nitrogen oxides are usually omitted entirely. Similarly, dry deposition of pollutants has been simulated with fixed deposition velocities; and dependences on winds, surface topography, moisture, and vegetation types have been ignored. Sub-grid-scale inhomogeneities in emissions, transport, chemical reaction types and rates, and deposition have not been included. Few data and the use of nonmechanistic model parameterizations have led to more model "tuning" than is desirable. Consequently, much verification of ADM work is required.

The ADM and regional meteorological modeling (RMM) fields have a longer history and a greater data base than acid deposition modeling. Fortunately, AQM and RMM techniques and results are valuable for ADM development. For example, the experience and results of AQM researchers in dealing with large numbers of chemical reactions can be tapped. Schemes to classify and to reduce systematically the numbers of independent chemical reaction equations offer help to ADM. Also, methods of incorporating emissions into air quality models and the AQM emissions data base itself are largely applicable in ADM.

The relative maturity and quantitative nature of the RMM field can be of enormous benefit to those developing more general and realistic acid deposition models. Thus, overview of regional meteorological models is presented, history of their goals, methods, and capabilities is outlined; and the principal components of these models are identified.

Briefly, these are the mathematical or numerical aspects and the more physical features. In the former category, we review the essential features of the spatial grids in these models, the various numerical methods employed to solve the governing partial differential equations, the lateral boundary conditions, and the overriding need for adequate data analysis and data initialization. Each of these RMM components, as well as the main purposes of RMM, is closely related and applicable to the task at hand in ADM, namely to model accurately the dispersion and transport of pollutants.

Similarly, physical aspects of regional meteorological models that have been improved and tested will benefit ADM development. These physical aspects include the transport of heat, moisture and momentum at the Earth's surface, in the planetary boundary layer, and free troposphere, and the energy sources and sinks that govern the transports. Also included are phase changes of water and the interaction of radiation with clouds and the surface. Because these physical phenomena occur on many disparate spatial scales, including scales shorter than a model's grid spacing, parameterizations are necessary — for example, to relate the cumulative effect of subgrid-scale phenomena on the fluid flow to the model-resolvable scales of motion. We review parameterizations of surface processes, of planetary boundary layer processes, of condensation and evaporation processes, and of radiative effects of layered clouds in current models; and we identify strong indicators of profitable research.

Another important consideration in the field of RMM that will be directly useful in ADM is that of objective measures of model skill, i.e., the accuracy of model predictions. Several standard quantitative measures of forecast skill are reviewed and also summarize the state of the art of RMM's to forecast (precipitation, for example). RMM methods will serve as good preliminary guides for measuring objectively the ability of acid deposition models to forecast deposition patterns (say, annual totals) or deposition amounts in distinct events.

Because of the great potential for transferring methods and parameterizations from RMM to ADM, components of the former models have been reviewed in some detail. First, the need for objective analysis is recognized — irregularly spaced initial meteorological data must be transformed to provide initial conditions on a model grid. The techniques, quality, computational costs, and history of objective analysis methods are summarized, and several case studies are discussed. The related need for data initialization is discussed in similar detail.

General physical considerations, mathematical analysis, and experience with meteorological models can indicate general spectral and transient characteristics of data-caused noise. In specific applications (e.g., for a specific regional topography and synoptic situation), RMM provides sound theory and practical experience to guide the choice of initialization procedure. Accordingly, unneeded computational costs can be avoided. Because boundary conditions must be specified to solve differential equations, principal techniques used in RMM (spatial damping (or sponge) conditions, wave-radiation conditions) and bounded derivative schemes are reviewed with respect to various ADM applications. Numerical methods and mathematical principles for objective analysis, data initialization, and boundary conditions are also reviewed. Once again, the available general theory plus the experience of RMM researchers constitute a well-based foundation for ADM development.

On a more physical side, the essential RMM components mentioned above, surface physics and effects, planetary boundary layer physics and effects, and the thermodynamic and radiative physics and effects of clouds and precipitation are also reviewed. The methods and problems extent in the field of RMM are very close to those that will prevail in ADM.

## The Chemistry of Acid Generation in the Troposphere

The chemical phenomena and reaction sets in existing acid deposition models are far from complete for many reasons. An inadequate understanding of long-range transport of pollutants, whose importance has only recently been perceived by the public and its agencies, has prompted much ADM work to focus on the meteorological aspects of transboundary transport. Also incomplete and confusing until recently has been mechanistic information on the actual chemical processes that transform  $\text{SO}_2$  into sulfuric acid and  $\text{NO}_x$  into nitric acid. Further, the chemistry of acid generation is more complicated than that of regional chemical oxidants; the former involves gas-phase and aqueous reactions, while the latter is due to gas-phase reactions alone.

Accordingly, the discussions and review of the chemistry of acid generation are focused at first on the essential chemistry itself rather than the chemistry in the existing ADM's. The main categories of the review are gas-phase reactions, aqueous-phase and heterogeneous processes, and photodissociative processes. Any credible ADM must

be based upon reaction mechanisms as opposed to depending completely on parameterizations of overall reaction or transformation rates.

For example, this simple parameterization in widespread use is inherently linear: The rate of production of  $\text{SO}_4^{=}$  is proportional to the gaseous  $\text{SO}_2$  concentration. In reality, the supply of chemicals that oxidize  $\text{SO}_2$  to  $\text{SO}_4^{=}$  might be limited in certain locations, and little or no  $\text{SO}_4^{=}$  production could take place even when large amounts of  $\text{SO}_2$  are available. Similarly, the  $\text{SO}_2$ -to- $\text{SO}_4^{=}$  conversion rate probably depends on the exact species that is accompanying the oxidation so that the rate  $x$  is not constant but varies with time. Analogous fundamental considerations apply to the conversion of  $\text{NO}_x$  to nitric acid, to the production of photochemical oxidants like ozone and peroxyacetylnitrate, and to the production of  $\text{SO}_2$  from biogenic organic sulfides, for example.

The main goal of the very detailed presentations is to identify from available research results the principal elementary reaction mechanisms and key species in the gas-phase, aqueous-phase, and heterogeneous reactions that cause and control acid generation. From a complex and encyclopedic list of chemicals and reactions, a smaller, more concise list of chemical variables and processes must be distilled to develop a tractable and useful ADM. From fundamental principles, laboratory data or photochemistry and kinetics, laboratory simulations of complex systems and field data, we can explain the essence of acid generation. These shortened lists of species and processes (elementary reactions when possible) will require further testing, such as zero-dimensional sensitivity calculations. In some cases, such as gas-phase species (i.e., hydrocarbons), the representative categories have been ground in AQM research previously, so only refinements will be needed for ADM development. In cases such as for solution-phase chemistry, achieving conciseness in the reaction list while still simulating the essential features and rates of reactions has not been accomplished, partly because the role of in-cloud chemistry in generating acids has been appreciated only recently.

Certain clear indications of how to proceed in ADM development do appear in the course of our review. For example, because all gas-phase processes that lead to  $\text{SO}_2$  oxidation are initiated by the gas-phase OH radical (in daylight, of course), the minimal reaction set for ADM must embody the major processes that control OH concentrations. Similarly, because of its role in  $\text{NO}_x$  chemistry and because it is a major source

of OH, tropospheric O<sub>3</sub> must be calculated accurately. In the liquid phase, it will be necessary to simulate behavior of O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, OH, HO<sub>2</sub>, NO<sub>3</sub>, and probably O<sub>2</sub><sup>-</sup> and N<sub>2</sub>O<sub>5</sub>. Fortunately, the fundamental data necessary in ADM development are forthcoming or are largely available already.

### Acid Deposition Model Development and Testing

Many of the issues that can arise in the design of a comprehensive model, i.e., one which includes coupled meteorology and chemistry, are discussed. The key meteorological and chemical processes that are identified earlier are stated more concisely, and certain other phenomena and practical considerations are introduced into the discussion. For example, the apparent importance of dry deposition of acidic gases and particles, the available methods for its measurement, the controlling physics and chemistry, and how ADM might treat dry deposition are discussed. Questions and facts are introduced concerning surface emissions of pollutants and natural sources of acid precursors and of those species that regulate acid generation. Other general features, components, and questions in ADM development are also reviewed and summarized, including model resolution, subgrid-scale processes and how to begin to treat them, mathematical and numerical techniques for large comprehensive models, special considerations coupling the laws of chemistry and physics, and issues in model validation and sensitivity analysis.

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*The complete report, entitled "Regional Acid Deposition: Models and Physical Processes," (Order No. PB 84-115 997; Cost: \$29.50, subject to change) will be available only from:*

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