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ACID DEPOSITION

S. E. Schwartz
Environmental Chemistry Division
Brookhaven National Laboratory
Upton, NY 11973

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ABSTRACT

The acid deposition phenomenon is a well documented example of the influence of industrial activities on atmospheric composition and precipitation composition. This phenomenon consists of emissions of sulfur and nitrogen oxides into the atmosphere, largely from fossil-fueled combustion, followed by transport, chemical transformation, and deposition to the surface. This deposition consists principally of deposition of sulfuric and nitric acids in precipitation (wet deposition) and deposition of gaseous SO_2, NO_2, and HNO_3 in the absence of precipitation (dry deposition). The acid deposition phenomenon is widely held to be responsible for deleterious effects on ecological systems, structural and ornamental materials, and visibility in the atmosphere. Because of the density of emission sources in eastern North America, it is not yet possible to specify precisely the contribution to deposition at particular receptor sites to particular emission sources. Present understanding of atmospheric transport velocities and rates of transformation and deposition processes suggest mean source-receptor distances of 500 to 1500 km. Regional emission densities in the Northeast United States substantially exceed standards that have been suggested to protect sensitive ecosystems. Recognition of the properties of the acid deposition phenomenon is explicitly noted in prospective legislation in the United States.

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Stephen E. Schwartz
Environmental Chemistry Division
Brookhaven National Laboratory
Upton, N.Y. 11973 USA

Introduction

Industrialization has brought many benefits to society. The labor of an individual is multiplied many times by utilization of energy resources other than his own muscles or those of animals. However, as we are increasingly coming to recognize, the earth's energy resources are limited, not only in and of themselves, but also as a consequence of the environmental effects of energy utilization. Premier Andreotti in his remarks quoted Professor Zichichi's observation that from the dawn of civilization man has lived with two great technological inventions, fire and the wheel. It goes without saying that our civilization has become what it is today in no small part because of these inventions. Yet each of these technologies has also become a major contributor to environmental pollution.

At first the environmental effects of energy technologies were only local, and solutions were based on this premise. The problem of air pollution from fires was solved by sending smoke up a stack. However, as global population increased, and as industrialization has increased at an even faster rate, we are reaching a situation where utilization of energy resources may be straining the capability of the environment to accommodate the associated pollutants. It is thus very appropriate that this session of the Seminars on Nuclear War, which have contributed so much in the past to calling attention to the dangers of modern war, turn its attention to some of the global hazards of industrial activity—appropriate because like the problems of war, the problems of industrial activities on the global environment can be resolved only by the community of nations. It is in this context that I wish to discuss the phenomenon of acid deposition.

Definition and Statement of the Problem

Acid deposition consists of delivery of acidic substances or precursors, principally sulfur and nitrogen oxides, acids, and salts, from the atmosphere to the earth's surface. These compounds (mainly the oxides) are introduced into the atmosphere in industrialized areas at rates that greatly exceed natural emission rates. Acid deposition thus consists principally of deposition of these emitted materials and the products of their atmospheric transformation processes. Deposition processes include delivery of material in precipitation (eddy transport followed by absorption, adsorption, adhesion, or other processes and commonly denoted "dry deposition") and by impaction of cloud or fog droplets. Because of atmospheric transport, acid deposition is generally displaced geographically from the emission source. A schematic diagram of the acid deposition phenomenon is given in Figure 1.

Acid deposition has been widely held to be responsible for deleterious effects on soils and aquatic ecosystems and, perhaps in conjunction with ozone and other factors, upon forests and certain

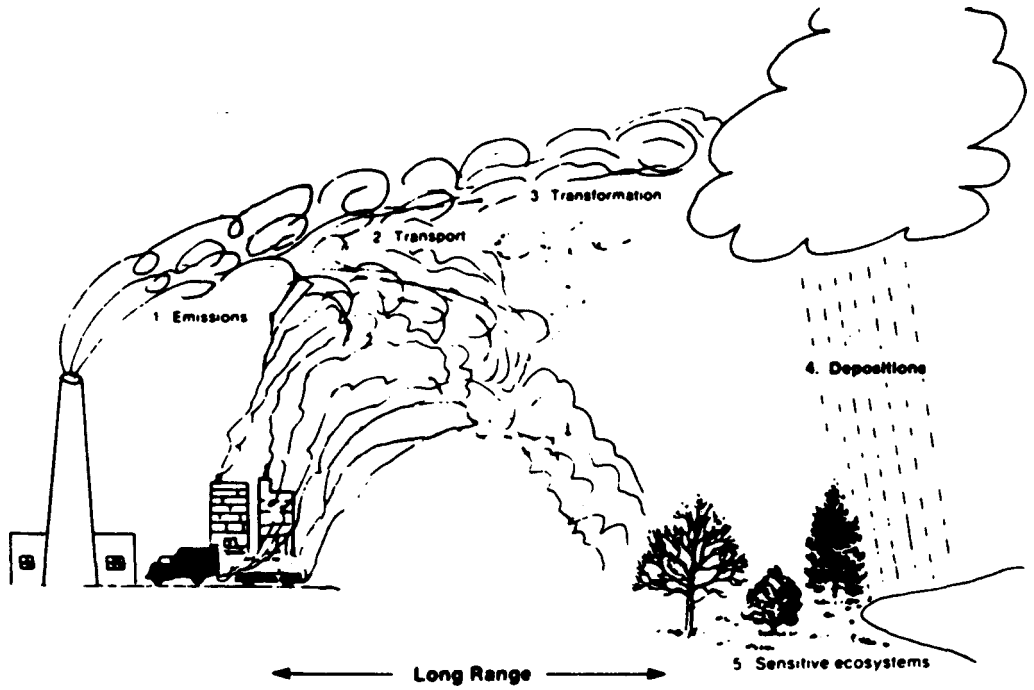

Figure 1. Schematic diagram of components of overall process of acid deposition.

cultivated crops. Acid deposition also contributes to the deterioration of structural and ornamental materials. Chronic exposure to gaseous and particulate acidic air pollutants at concentrations characteristic of industrialized regions can result in impairment of human physiological function and health. In view of the possible large social, economic, ecological, and aesthetic consequences of acid deposition, this phenomenon has become the subject of widespread concern. This concern is reflected in existing and pending legislation and regulation, the objective of which is to reduce acid deposition by reduction of emissions of sulfur and/or nitrogen oxides (1).

Granted that acid deposition is responsible for deleterious effects on the environment, it is not immediately apparent to what extent and how emissions of sulfur and/or nitrogen oxides must be reduced in order to achieve a specified reduction in deposition or the extent to which deposition must be reduced in order to achieve a specified decrease in deleterious effects. In principle, acid depoeition can be controlled to any arbitrary specified extent by control of the emissions of precursors, but substantial control can be achieved only at great expense, and with concomitant political, economic and social consequences. For this reason it is desirable to develop optimum strategies for reduction in acid deposition. However, development of such strategies requires a high level of understanding of the acid deposition phenomenon.

Scientific and technological questions on acid deposition and how to reduce it with the fewest political, social, and economic costs can be divided roughly into questions on emissions, atmospheric processes, and effects. Developing the understanding necessary to answer these questions has set the agenda for research on acid deposition over the past decade. This research can be divided roughly into the following three categories:

- Emissions - What are present and historical rates and spatial distributions of emissions of substances responsible for acid deposition? What means are achievable for reducing such emissions, and at what cost, taking into account both economic and social factors?

- Atmospheric processes - What are the relations between the rates and spatial distributions of emissions of substances responsible for acid deposition, the atmospheric concentrations and spatial distributions of these substances and their atmospheric transformation products, and rates and spatial distributions of deposition of these materials to the earth's surface? How would atmospheric concentrations and deposition fluxes change in response to changes in emissions? By what strategies of reductions in emissions might specific standards for concentrations or deposition be achieved?

- Effects - What are the consequences of present atmospheric concentrations and deposition rates of acidic and related substances on human health, on artificial structural and ornamental materials, on cultivated crops, on natural terrestrial and aquatic ecosystems, and on the optical and radiative properties of the atmosphere? How would these consequences change in response to changes in concentrations and deposition? What standards for concentrations and deposition are suitable for protecting human health and the general welfare from adverse effects of acid deposition?

In this article, I briefly describe the state of research into the atmospheric component of the acid deposition phenomenon. The geographical focus of this review is eastern North America, but many of the considerations developed here are applicable also to other regions. For a more complete description see Ref. 2. That article also contains an extensive set of references to all aspects of research on the acid deposition phenomenon. For a more extended account of recent research and current understanding of the acid deposition phenomenon, attention is called to the recent four volume interim assessment of the causes and effects of acid deposition published by the United States Acid Precipitation Assessment Program (NAPAP), Ref. 3. An update of this report is expected to be published in 1990. For an excellent account of the developing perception of acid deposition as an environmental problem with a large-scale geographical range of influence see Ref. 4.

While this article focuses on the atmospheric component of the acid deposition phenomenon, it is important to note that any impetus for reducing acid deposition, and in turn emissions, must ultimately derive from consideration of the effects of such deposition. The objective therefore of effects research is to determine the response of various receptors that are actually or potentially susceptible to harm from acid deposition (ecosystems, materials, human populations) as a function of deposition or concentration. This information, in principle, serves as the basis for setting standards for deposition or concentration, the satisfaction of which would reduce deleterious effects to a specified level or would provide a specified margin of safety below the threshold for the onset of such effects. These standards may take various forms: concentration or deposition flux (of the several substances of concern) not to exceed specified values for specified averaging periods. Examples of such standards are the U.S. National Ambient Air Quality

Standards (5), which are set to protect the public health and general welfare. Such standards to date have been restricted exclusively to concentrations in air, as opposed to deposition fluxes. The standard for SO_2 specifies that concentrations are not to exceed (more than once per year) 1300 $\mu g\ m^{-3}$ (500 ppb; 20 μ mol m^{-3}) for a three-hour period; 365 $\mu g\ m^{-3}$ (140 ppb; 5.6 μ mol m^{-3}) for a 24-hour period; or 80 $\mu g\ m^{-3}$ (30 ppb; 1.2 μ mol m^{-3}), annual average. The corresponding standard for NO_2 is 100 $\mu g\ m^{-3}$ (53 ppb; 2.1 μ mol m^{-3}), annual average. For small-particle aerosol mass (less than a nominal 10-μm aerodynamic diameter) the standards are 150 $\mu g\ m^{-3}$ for 24 hours and 50 $\mu g\ m^{-3}$ annual average. Promulgation of a further standard, for acidic aerosol, is under consideration (6). Consideration of effects of acid deposition on freshwater aquatic systems has led to suggestions of a deposition standard of order 10 to 20 kg $SO_4^=$ wet deposition per hectare per year (10 to 20 m mol $m^{-2}\ yr^{-1}$) (7-9). This standard, which is expressed in terms of wet deposition only, in view of uncertainty in dry deposition fluxes, assumes a comparable dry deposition flux, suggesting that a standard for total sulfur deposition might be 20 to 40 m mol $m^{-2}\ yr^{-1}$. A corresponding standard for nitrate deposition does not appear to have been proposed, but presumably such a standard would be comparable in acid equivalents to the proposed standard for sulfur deposition, i.e., 40 to 80 m mol $m^{-2}\ yr^{-1}$. Such deposition standards might differ from region to region, reflecting different sensitivities to acid deposition due to differing soil buffering capacities.

Given one or more standards for concentration or deposition flux that are exceeded for present emission rates, it is clear that these rates must be reduced or, perhaps, redistributed in order to satisfy the standards. However, it is not immediately evident how this is to be achieved, i.e., what sources are to be reduced and by what amount. Finding the solution to this problem is a major objective of the atmospheric science component of acid deposition research. It should be emphasized, however, that there is not a unique solution to this problem. In fact, there are multiple solutions, since the concentration at or deposition to a particular receptor site is the aggregate of contributions from multiple sources. Therefore, the problem facing the atmospheric science community is one of determining sets of changes in emission strengths and distributions, any of which can be expected to satisfy various standards for concentration and deposition of acidic and related substances. This information, together with considerations of achievability, cost, cost distribution over different sectors of the economy and over different geographical regions, and international relations can then be used by policy makers to determine optimal strategies for achieving desired reductions in acid deposition.

While the focus of this article is on acid deposition and on the atmospheric concentrations of the responsible sulfur and nitrogen species, it should be noted that these substances are implicated also in distinct but related air pollution issues. Specifically, nitrogen oxides are identified as a key precursor to the formation of ozone, itself a major pollutant on urban and regional scales. Sulfate aerosol derived from SO_2 emissions is a major component of total submicrometer aerosol contributing to visibility reduction on urban and regional scales (10). Both ozone and visibility are explicitly considered within NAPAP, in recognition of the inherent connection of these phenomena with acid deposition phenomenon.

In characterizing acid deposition, much attention has been focused on free acidity, expressed either as the molar concentration of H^+ or as pH. However, in the context of acid deposition, this emphasis on free acidity may be misleading in several respects. To be sure, the emitted sulfur and nitrogen oxides, when further oxidized in the atmosphere produce the strong acids sulfuric and nitric acids that raise the concentration of free acidity in precipitation. However, the actual free acid concentration is subject to considerable variability because of partial neutralization due to ammonia and wind-blown soil constituents that would be present in the atmosphere irrespective of emissions of the anthropogenic sulfur and nitrogen oxides. This neutralization alters the perception of the anthropogenic influence on precipitation composition; consequently, sulfate and nitrate concentrations are a much more robust indicator of such influence than is free acidity.

As regards the quantity pH, it should be pointed out that this variable can be a misleading measure of acid concentration, since at low pH, substantial changes in H^+ concentration are masked by only slight changes in pH, whereas at high pH, slight changes in H^+ concentration are exaggerated when expressed as pH. Expressing acid deposition in terms of pH would have the effect of diminishing the apparent accomplishment of any program of emissions reduction. As James Lodge has noted (11), "If whatever control strategy is hit upon is successful in cutting the acidity in half, an evil conspiracy of the chemists will only allow the pH of precipitation to increase by 0.3," observing further that the public and, for that matter, many technical people do not "really have a gut feeling for the simple fact that the logarithm of 2 is 0.3." Since a two-fold decrease in emissions of sulfur and nitrogen oxides in northeastern North America would require an enormous societal commitment and would constitute an enormous achievement, one would wish for psychological reasons if nothing else, to see the results of such a reduction expressed linearly rather than compressed on a logarithmic scale.

The foregoing discussion serves as the context for considering the atmospheric component of the acid deposition phenomenon. I now briefly review some of the findings of that research that are most salient from a policy perspective.

Conservation of Matter

The law of conservation of matter, or "Newton's law of air pollution," applies to the acid deposition phenomenon: what goes up must come down. Sulfur and nitrogen oxides emitted into the atmosphere are necessarily returned to the surface of the earth. One can thus, for a specified time-average emission rate, immediately specify the resulting total time-average deposition rate, albeit not the spatial pattern nor the chemical form nor the mode of deposition. Comparison of the average emission flux in a given geographical region with proposed standards for deposition flux gives the ultimate rollback of emissions necessary to achieve such standards. For example, total annual emissions in Ohio (an area of 107,000 km^2) are 2.4×10^6 metric tons SO_2 per year (3.8×10^{10} mol per year) and 1.0×10^6 metric tons nitrogen oxides (reckoned as NO_2) per year (2.2×10^{10} mol per year) (3). The resulting average emission fluxes, 360 mmol m^{-2} per year for sulfur and 210 mmol m^{-2} per year for nitrogen, would exceed suggested standards for deposition fluxes by factors of 10 to 20 for sulfur and 3 to 5 for nitrogen. The same calculations for the entire northeastern United States (the region

bounded by and including North Carolina and Tennessee on the south and the Mississippi River on the west; area 1.5×10^6 km^2) yield an average emission flux for sulfur of 130 mmol m^{-2} per year and for nitrogen of 120 mmol m^{-2} per year, still substantially greater than suggested deposition standards.

These calculations have unavoidable implications. If there is no net export of material, then the proposed standards for acid deposition are substantially exceeded even if deposition is uniformly distributed over the region, and all the more so if deposition is non-uniform. Proposed standards can be met only by substantial reduction in emissions or by net export of emitted sulfur and nitrogen compounds. These calculations establish the necessity of understanding the spatial distribution of acid deposition as governed by the spatial distribution of sources and by atmospheric processes.

Geographical Distributions of Emissions and Deposition

Emissions of sulfur and nitrogen oxides (Fig. 2) are quite high in the northeast United States and southeast Canada relative to the rest of the continent. Emission density patterns in this region have

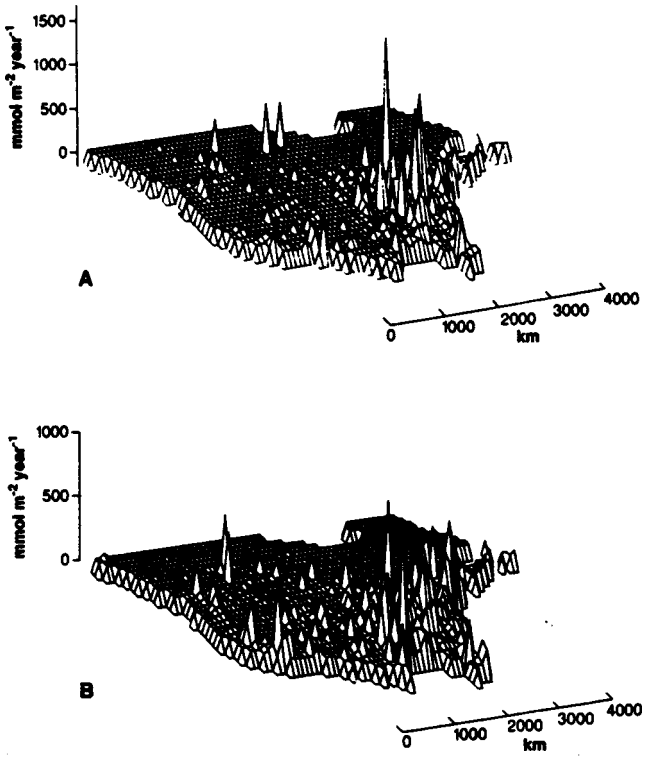

Fig. 2. Spatial distribution of emissions of (A) sulfur oxides and (B) nitrogen oxides in the United States and Canada (south of 60°N, that is, the southern boundary of Yukon and Northwest Territories), gridded according to 1° latitude by 1° longitude (~85 km by 111 km) cells. The actual structure is much greater than indicated, since a substantial fraction of the material is emitted from point sources and cities. Data are for 1980. From Ref. 2.

considerable short-range structure with local values well in excess of average emission fluxes. Long-time average atmospheric concentrations and wet deposition fluxes also are elevated in eastern North America; however to the extent they are known, spatial distributions of average concentrations and deposition fluxes are substantially broader and less structured than those for emissions. The key features of acid deposition as a regional phenomenon are a pattern of high emissions distributed throughout a region coupled with mean atmospheric transport distances that are sufficiently large that time-average distributions of atmospheric concentrations and deposition from different sources substantially overlap, but sufficiently small that these distributions remain peaked in the region of emissions.

The mean wet deposition flux of SO_4^{2-} in the northeastern United States is a factor of 4 or 5 less than the mean emission flux of SO_2 in the region; this difference indicates that material is removed from the atmosphere by dry deposition or by export from the emission region, or both. Even so, wet deposition fluxes exceed suggested standards over much of eastern North America. Impaction of fog or cloud droplets also can contribute substantially to acid deposition at least locally, at exposed sites.

Since dry deposition cannot be monitored with confidence, it is necessary to estimate the dry deposition flux from ambient atmospheric concentrations of the depositing species. Such estimates (e.g., 12) indicate that on an annual basis, dry deposition exceeds wet deposition in near-source regions and is comparable to wet deposition farther from the region of highest emission density. Dry deposition is thus a major component of regional acid deposition.

The regional nature of the acid deposition phenomenon is exhibited also on the basis of short-term measurements. For example, high concentrations of aerosol sulfate at times extend across New York state (~500 km) (13,14) frequently in association with air transport to upstate New York from the southwest or occasionally from the south or southeast.

Studies of haziness provide additional evidence of the regional nature of acid deposition. Patterson et al. (15) showed that five widespread several-day episodes of enhanced haziness during a single month were associated with high concentrations of aerosol SO_4^{2-} throughout the eastern United States. Satellite photographs also indicate that such haze episodes can develop and extend over large parts of the eastern United States (16).

High concentrations of aerosol SO_4^{2-} at nonurban sites are often associated with trace metals or soot particles characteristic of emissions from coal- or oil-fired combustion sources in different geographical regions (14-17). The association of SO_4^{2-} in upper New York State and New England with tracers characteristic of the midwest or the mid-Atlantic seaboard is a strong indication of regional-scale transport of SO_4^{2-}.

Measurements of concentrations of acidic constituents in air and precipitation at remote locations provide additional evidence that these substances can be transported for large distances. Concentrations of aerosol SO_4^{2-} and H^+ in precipitation measured at Bermuda (1100 km from North America) are substanitially greater under conditions of airflow from North America than from the south or east (18). Similar results have been obtained for nonsea salt (NSS) SO_4^{2-} in precipitation in the

eastern North Atlantic (19). As far as 4000 km from North America, precipitation associated with flow from North America has 10 to 80% greater NSS SO_4^{2-} concentrations than the mean precipitation (20), although to be sure, deposition of acidic species in these remote sites is much lower than in eastern North America. Estimates of the fraction of North American emissions exported off the continent by the prevailing winds based on aircraft measurements of concentrations and climatological wind speeds are 25 to 35% for sulfur oxides and 15 to 25% for nitrogen oxides (21).

In sum, there is abundant observational evidence that acid deposition is a regional phenomenon in eastern North America. Its regional extent is due both to the broad distribution of emissions and to transport of emitted materials and their oxidation products, which results in spreading of deposition patterns relative to the emissions patterns and overlap of deposition patterns from multiple sources within this region. Nonetheless, despite this spreading, deposition remains highest near regions of greatest emission density.

Scale of Transport

A key measure of the source-receptor relation for acid deposition is the mean transport distance, $\bar{x}$, the distance of travel between source and receptor averaged over emitted molecules. This quantity defines the region of influence of a particular source, and is a measure of the dilution of the deposition flux attributable to a single source. One approach to estimating $\bar{x}$ is from the transport velocity and the mean residence time of the emitted material, as inferred from rates of removal processes. Calculations of climatologically averaged transport distances in the mixed layer of the atmosphere suggest that the median transport velocity is about 500 km per day (22). Emitted SO_2 and NO and their atmospheric oxidation products are thought to have mean residence times of ~1 to ~3 days (23), indicating mean transport distances of ~400 to ~1200 km.

Acid deposition is not the only tropospheric air pollution phenomenon characterized by transport scales of several hundred to several thousand kilometers. Combustion-generated soot and transition metals, pesticides, smoke from forest fires, and radionuclides from the fire at the Chernobyl nuclear power plant have been shown to have similar transport scales (24).

Atmospheric Processes

A principal means of determining source-receptor relations for acid deposition is by use of physical simulation models. Such a model consists of a numerical description of the various component processes that comprise the acid deposition phenomenon--emissions, transport, transformation, wet and dry deposition--all incorporated in a numerical computer code. Of course such models must necessarily embody numerous assumptions and approximations. Nonetheless, it is a premise of this approach that there be a one-to-one mapping of processes that occur in the real world to processes that are simulated in the model. It is a further premise of the approach that for the models to accurately evaluate source receptor relations or to accurately predict the consequences of a particular change in emissions, the models must accurately represent the processes that occur in the real world. For this reason it is desired to gain an accurate understanding of these processes. This desire has motivated much of the research into the atmospheric processes pertinent

to acid deposition. Key findings of this research are briefly summarized here. For more extensive reviews see Refs. 2, 3, 7, and 24-29.

Regional Scale Transport. A key element in modeling acid deposition on regional scales is describing the transport of material during the residence times of these species in the atmosphere or until the material has been advected out of the domain of interest, i.e., for time periods up to four or five days or more. Numerous models have been developed to use routinely measured surface and vertical wind and temperature fields to describe transport on a regional scale (e.g., 30; for reviews see 31-33), but until the past few years there have been few opportunities to test these models. However, newly developed capabilities for such studies (34) involving the deliberate release of known quantities of inert perfluorocarbon compounds (tracers) capable of detection at low concentrations at distances thousands of kilometers from the release point have permitted such tests. The first such study, the Cross Appalachian Tracer Experiment (CAPTEX-83), consisted of releases either at Dayton, Ohio, or Sudbury, Ontario, in situations when forecast trajectories were expected to transport the material to a network of monitoring sites that extended from Pennsylvania to southeastern Quebec. This experiment demonstrated the capability to detect plumes of tracer material at distances up to 1100 km, and travel times of up to 24 hours. Comparison of modeled and measured trajectories (35) suggests that a wind flow corresponding to the low to middle boundary layer is most appropriate for simulating the transport of boundary-layer pollutants. For travel times of 24 hours (mean transit distance 800 km) the typical separation of modeled and measured plumes was about 200 km. It should be noted, however, that the experiments were conducted over only a very limited set of synoptic conditions--within large-scale anticyclones and behind cold fronts. More realizations of this sort of experiment are needed to evaluate model performance in more complex meteorological situations. Considerable information of this sort, and to greater distances, should be forthcoming from the recently conducted Across North America Tracer Experiment (ANATEX) (36).

Chemical Reactions. The principal emitted species responsible for acid deposition, the gases sulfur dioxide, SO_2, and nitric oxide, NO, are ultimately oxidized in the atmosphere or subsequent to deposition to the strongly acidic high oxidation state acids, sulfuric acid, H_2SO_4, and nitric acid, HNO_3. From the perspective of total acid deposition the nature and extent of atmospheric transformations of these substances are unimportant. However, by changing the physical and chemical properties of the emitted materials, these transformations play a major role in determining the means by which these substances are removed from the atmosphere and the rates of these removal processes and hence exert a major influence on the source-receptor relationship.

The reactions thought to be of greatest importance in the atmospheric oxidation of SO_2 and nitrogen oxides are listed in Table 1. As indicated in the table, reactions may take place in the gas phase or in aqueous solution, rainwater or, more importantly because of the greater time available for reaction, cloudwater. Recent research has focused on obtaining improved description of the rates of these reactions. Model calculations for representative situations suggest peak gas-phase daytime oxidation rates due to reaction initiated by OH free radical of about 2% hr^{-1} for SO_2 and 10 to 50% hr^{-1} for NO_2 (37). NO_2 can also be oxidized at night by reaction with O_3 to form NO_3, which can

Gas phase

$$SO_2 + OH \xrightarrow{M} HOSO_2$$
$$HOSO_2 + O_2 \longrightarrow SO_3 + HO_2 \quad (1)$$
$$SO_3 + H_2O \xrightarrow{M} H_2SO_4$$

Net: $OH + SO_2 + O_2 + H_2O \rightarrow H_2SO_4 + HO_2$

Aqueous phase

$$SO_2 \overset{H_2O}{\rightleftarrows} HSO_3^- + H^+ \rightleftarrows SO_3^{2-} + 2H^+$$
$$HSO_3^- + H_2O_2 \xrightarrow{H^+} SO_4^{2-} + H^+ + H_2O \quad (2)$$
$$SO_3^{2-} + O_3 \longrightarrow SO_4^{2-} + O_2 \quad (3)$$

Gas phase

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (4)$$
$$NO + HO_2\ (RO_2) \longrightarrow NO_2 + OH\ (RO) \quad (5)$$
$$NO_2 + OH \xrightarrow{M} HNO_3 \quad (6)$$

Gas phase followed by aqueous phase

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
$$NO_3 + NO_2 \overset{M}{\rightleftarrows} N_2O_5 \quad (7)$$
$$N_2O_5 + H_2O(l) \longrightarrow 2H^+ + 2NO_3^-$$

Net: $2NO_2 + O_3 + H_2O(l) \rightarrow 2H^+ + 2NO_3^- + O_2$

Table 1. Important atmospheric oxidation reactions of sulfur and nitrogen oxides. M represents any molecule; R represents an organic group. From Ref. 2.

subsequently react to form N_2O_5 and HNO_3. Accurate description of the gas-phase reaction system is important not only because of the direct reactions of the sulfur and nitrogen oxides, but also because oxidants, especially H_2O_2 and O_3, produced by secondary photochemical reactions contribute to the aqueous-phase oxidation of SO_2.

The importance of in-cloud oxidation reactions is increasingly becoming recognized. Such reactions had been inferred on the basis of regional mass-balance considerations and the generally greater acidity of rainwater than that of clear air. The occurrence of aqueous-phase oxidation of SO_2 in clouds by H_2O_2 and, to a lesser extent O_3, suggested initially by Penkett (38), has been confirmed by model calculations which are based on laboratory-determined solubilities and kinetic rate coefficients, and by field measurements. Because of acid catalysis, the rate of SO_2 oxidation by H_2O_2 is nearly independent of cloudwater pH (39). The instantaneous SO_2 oxidation rate in clouds for representative conditions by H_2O_2 at a concentration of 40 n mol m^{-3} (1 ppb gas-phase equivalent) is of order 10% min^{-1}. Such a rapid rate suggests that the reaction should commonly proceed to completion within cloud lifetimes, exhausting the concentration of the limiting reagent. The ozone reaction, in contrast to the SO_2 reaction, exhibits a strong decrease in rate with increasing cloudwater acidity, and thus as sulfuric acid is produced the reaction effectively shuts itself off. In contrast to SO_2, NO_2 does not appear to undergo appreciable aqueous-phase oxidation, largely because of its low solubility (39).

Persuasive evidence of the importance of in-cloud reactions is becoming available from field measurements. Daum et al. (40) showed that the acidity of cloudwater in non-urban locations is commonly much

greater than would be expected simply by dissolution of soluble aerosol species and nitric acid present in clear air. These investigators also demonstrated that H_2O_2 and SO_2 are essentially mutually exclusive in non-precipitating liquid water stratiform clouds (that either SO_2 or H_2O_2 is present, but not both) indicative that reaction has proceeded to completion in such clouds, consistent with cloud lifetimes and evaluated reaction rates (40). A recent study involving the intentional release of SO_2 into a cloud has provided unambiguous evidence for depletion of ambient H_2O_2 on a time scale of minutes (41). Other recent field studies suggest that the oxidation of NO_2 initiated by O_3 may be contributing substantially to the acidity of wintertime stratiform clouds (42).

Dry Deposition. Substantial progress has been made in the past two decades in understanding the turbulence structure of the atmospheric boundary layer, in measuring material fluxes through this layer, in relating these fluxes to concentration gradients, and to inferring fluxes from monitoring data (43). However, for gases such as SO_2, NO_2, and O_3, which are taken up by the surface at less than the maximum rate controlled by turbulent transfer, i.e., for which there is a substantial surface resistance, such understanding remains little more than a phenomenological description of the controlling surface resistance. This is unfortunate, since an understanding of the chemical, biological, and biochemical processes that control this deposition would greatly enhance the confidence that can be placed in models of dry deposition. Since dry deposition of gases appears to be the major sink for acidic pollutants, gaining such an understanding is all the more important. For dry deposition to plants for example, this understanding would require consideration of leaf geometry, stomatal aperture and factors that control stomatal opening, and the solubility and reactivity of these gases in intercellular fluids within the substomatal cavity. For an example of a study that is pointing in this direction, see Ref. 44.

Regional-Scale Physical Simulation Modeling

In order to develop strategies to reduce acid deposition at specific receptor sites, it is necessary to apply source receptor relations (SRRs) that link emissions (as a function of location) to deposition (also as a function of location). Perhaps the intellectually most satisfying approach to obtaining SRRs is by means of physical simulation models—numerical description of the acid deposition phenomenon as the sum of its component processes: emissions, transport, chemical and physical transformations, dry and wet deposition. This approach appeals to the reductionist view of physical science: Study and understand all the component pieces of the phenomenon, and understanding of the whole phenomenon will follow. This approach is attractive also from a regulatory perspective, since it extends the promise of providing a highly differentiated description, including responses to various scenarios of changes in rates and spatial distributions of emissions.

Because of this appeal, substantial effort has been directed to the construction, execution, and evaluation of numerical models to describe regional scale acid deposition, as well as to research into the component processes. These models may be classified broadly into three categories: statistical, Lagrangian, and Eulerian. However, within each of the categories there are a variety of realizations, the differences among them reflecting differences in judgment of the practitioners in making the inevitable compromises necessary to achieve desired

objectives of spatial resolution and climatological accuracy within the constraints of available computing power.

Briefly, the statistical approach couples frequency distributions of transport trajectories, and reaction and deposition rates to obtain concentration and deposition fields associated with individual emission sources. Input rate data can derive from laboratory measurements or from field measurements such as residence times or transport distances. The method is well suited to generating multi-year average deposition fields necessary for climatological representativeness. A disadvantage is that the method encompasses only the most rudimentary treatment of the atmospheric processes involved.

The Lagrangian approach permits a considerably more detailed treatment of chemical and physical process and of wet and dry deposition as the air parcel into which the material has been introduced is advected across the region. The model directly and transparently yields the concentration and deposition fields that result from the emitted material. The calculation is repeated as long as is desired to build up a climatologically representative deposition field. This information is of immediate application in developing strategies to reduce acid deposition. A disadvantage of the approach is that the calculation must be repeated for each source under examination. This would potentially require a large number of calculations if it is desired to establish the source attribution of a large fraction of deposited material at receptor sites of interest; this information is necessary not only from a policy perspective but also in order to compare total modeled concentration or deposition with measured values, for purposes of model evaluation.

Depending on the treatment of the chemical milieu into which sulfur and nitrogen oxides are emitted, Lagrangian models may or may not be linear; i.e., the concentration or deposition field attributable to any source is or is not linearly proportional to the magnitude of emissions from that source. Because of nonlinear chemistry in both the sulfur and nitrogen systems a linear treatment inevitably introduces inaccuracy into the resulting source-receptor relation. A further inherent inaccuracy in this approach is that it does not countenance interactions among materials derived from multiple sources that would occur in the real world as puffs disperse and merge into one another. The magnitude and significance of these inaccuracies are not known. The linear approach, however, does give rise to a major simplification in using Lagrangian models for policy applications, since the concentration and deposition fields for a given source may be determined once and for all and simply scaled in proportion to the emission strength.

In the Eulerian approach, materials are conceptually emitted from all sources in the region into an atmosphere that is gridded three-dimensionally into cells. At successive time steps, the amount of each chemical species in each cell is increased or decreased as governed by chemical reaction rates, transport from and to adjacent cells, emissions, and deposition. Wind fields, clouds, and precipitation are prescribed by a meteorological program that generates these quantities from observational data. Initial chemical fields must also be specified. The approach evaluates the total deposition at each receptor site resulting from emissions at all sources, and automatically takes into account interactions of materials from multiple sources. The approach readily accommodates cloud- and storm-related transport and reaction as well as clear-air processes, and is thus well suited to examine quite complex chemical mechanisms that could result in substantial

nonlinearities between emissions from various sources and the deposition fields of materials emitted from those sources.

In practice, the Eulerian approach presents major conceptual and practical problems. Foremost among these is that of subgrid phenomena and artificial diffusion. Because of limitations in computational capabilities, even with modern high-speed computers, models to date (e.g., 45,46) are restricted to fairly large grid sizes, of order 80 km by 80 km in the horizontal; materials present in such grid cells are immediately "dispersed" throughout the entire grid cell. This can lead, for example, to fictitious reactions between species that are artificially mixed. The magnitudes of these artifact effects are not yet known. A further difficulty that arises with this approach is that since, in the model as in the real world, material from multiple sources is mixed, it is difficult to attribute the deposition at a given receptor to the individual contributing sources. In principle that could be achieved by repeated model runs in which materials from the several sources were "tagged", but in view of the intensive computational requirements of these models, this approach quickly becomes prohibitive. A similar problem arises in examination of the changes in deposition that would result from particular changes in emissions. Recently, however, solutions to these problems have been suggested that use stored concentration fields to obtain exact or nearly exact results without the need for repeated model runs (47). A further major problem with the Eulerian approach is that of carrying out enough model runs to obtain climatologically representative results.

In summary, at the present time it seems that no single approach to determining SRRs has yet been demonstrated as superior in all respects. This situation, which is a reflection of the complexity of the regional acid deposition phenomenon, calls not for criticism of alternative approaches to determining SRRs, but rather for pursuit of this information by a variety of techniques that will, it is hoped, finally obtain mutually consistent results and thereby establish the desired scientific credibility of these results.

Implications for Regulatory Action

Because of the large number of sources of sulfur and nitrogen oxides distributed broadly over eastern North America within their mutually overlapping distances of influence, it is difficult to attribute deposition at any given location to the contributing emission sources and thereby to develop strategies for reducing deposition to particular sites. Major efforts directed to obtaining the process-level understanding necessary to develop such strategies are under way and substantial advances have been made. However, verified, scientifically credible SRRs for acid deposition are not now available, and it seems unlikely that they will be available in the near future, especially if the U.S. National Acid Precipitation Assessment Program is not continued after 1990, as is now planned.

In recent review of the effect of acid rain on freshwater ecosystems, Schindler (8) concluded, "Clearly, we know enough about the effects of acid rain on aquatic ecosystems to make a strong case for regulating emissions of sulfur oxides," adding that "regional air pollution is much more severe than we believed in the past, and more comprehensive measures to control it are necessary to preserve the integrity of the biosphere." In the context of such calls for regulation of emissions, a question that is inevitably asked regarding source-receptor

relations for acid deposition is "Do we know enough to regulate?" Rather than attempt to answer that question directly, I reply with another question, which I consider equally valid, namely, do we know enough to emit? Every day, by maintaining the present pattern of emissions, our society is making a policy decision with regard to acid deposition.

Should the current policy of emissions continue at its present course until more definitive atmospheric source-receptor relations are available? Or, in recognition of concerns such as those noted by Schindler, should more stringent controls of emissions be initiated, despite present uncertainties in SRRs. In addressing this question, the phenomenological view of regional acid deposition is helpful. Regional average emissions in the northeast United States of sulfur oxides are 130 mmol m^{-2} per year and of nitrogen oxides 120 mmol m^{-2} per year. These average emission fluxes substantially exceed suggested standards for total (wet plus dry) deposition of perhaps 20 to 40 mmol m^{-2} per year for sulfur and 40 to 80 mmol m^{-2} per year for nitrogen. Thus, if there is a policy decision to reduce emissions to values such as these, for example, a 70% reduction for sulfur species and a 35% reduction for nitrogen species, then in view of the uncertainties in atmospheric SRRs, the decision of how to distribute these reductions should be made on a basis other than SRRs, but with confidence that every mole of sulfur or nitrogen oxides not emitted is a mole not deposited. Possible bases for such standards might, for example, be moles per kilowatt hour of electricity production, or moles per capita per year. States would then be given a schedule by which to achieve this standard.

In fact, the proposed legislation for control of acid deposition introduced by the U.S. administration (1) takes just such an approach. In this legislation, target emission rates are expressed on a basis of SO_2 emitted per heat content of fuel consumed. Two target levels are proposed, with effective dates of 1996 and 2001, and sources whose emissions exceed these targets must reduce their emissions to these target levels by these dates. Sources whose emissions are already below the target levels may not exceed their current levels. However, the legislation provides that emissions rights may be bartered or sold within states. The presumption is that such bartering will lead to a more efficient system. At present the exact target levels for emissions state by state or for the entire U.S. are not available. Figure 3 shows an estimate of total U.S. emissions, expressed as acid equivalents, for the 1996 and 2001 target years, compared to actual emissions in recent years, based on an initial analysis of the proposed legislation. However, the nature of the final legislation and the target emission levels still remain to be decided.

Whatever the final legislation, it would seem useful for the atmospheric research community to continue to work toward improvements in source-receptor relations and take advantage of the ongoing regional source-reduction experiment to devise improved emission strategies. This newly developed information, together with improved knowledge of effects of acidic pollutants, could be used to formulate mid-course corrections in achieving the desired deposition levels.

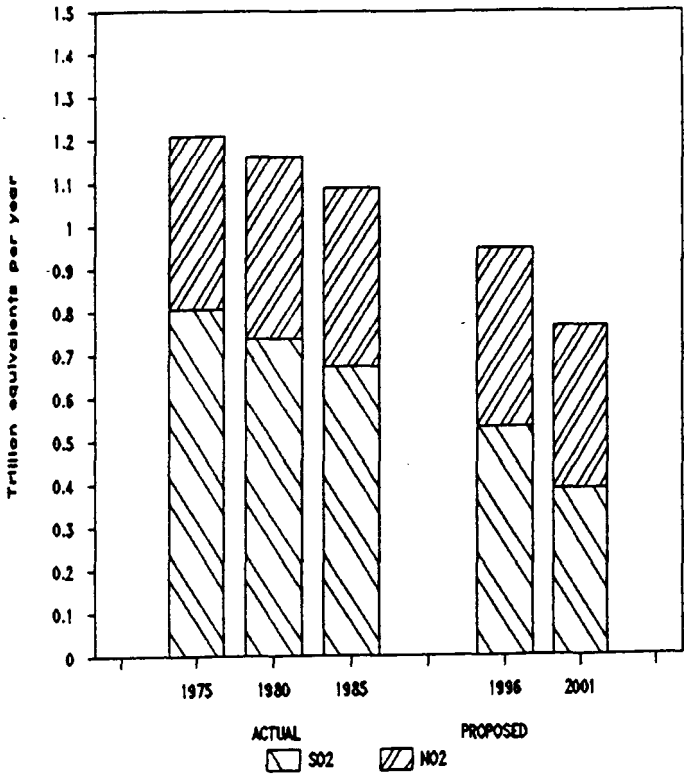

Figure 3. Actual (1975-1885) and proposed (1996-2001) emissions of sulfur and nitrogen oxides for total U.S. (48 contiguous states). Actual emissions, from Ref. 3; proposed emissions are based on an initial analysis of the proposed amendments to the clean air act (Ref. 1).

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References

1. Draft Bill "Clean Air Act Amendments of 1989," submitted by President George Bush to Congress, July 21, 1989.

2. S. E. Schwartz, Science **243**, 753-763 (1989).

3. National Acid Precipitation Assessment Program, Interim Assessment: The Causes and Effects of Acidic Deposition, 4 Volumes, C. N. Herrick, Ed. (U.S. Government Printing Office, Washington, DC, 1987).

4. E. B. Cowling, Environ. Sci. Technol. **16**, 110A (1982).

5. United States Code of Federal Regulations, Title 40 part 50, 1987.

6. Acid Aerosols Issue Paper, Report EPA/600/8-88/005a (U.S. Environmental Protection Agency, Research Triangle Park, NC, 1988).

7. U.S.-Canada Memorandum of Intent on Transboundary Air Pollution, Final Report (U.S. Environmental Protection Agency, Washington, DC; Atmospheric Environmental Service, Downsview, Ontario, 1983).

8. D. W. Schnidler, Science **239**, 149 (1988).

9. The state of Minnesota has set a standard for wet SO_4^{2-} deposition in sensitive areas of 11.5 mmol m^{-2} per year [Minnesota Pollution Control Agency, Rule 7005.4030 (1986)].

10. G. R. Cass, Atmos. Environ. **13**, 1069 (1979); R. B. Husar and D. E. Patterson, Ann. New York Acad. Sci. **338**, 399 (1980); C. S. Sloane, Atmos. Environ. **22**, 2033 (1988).

11. J. P. Lodge, Jr., paper presented at Workshop on Research Priorities and Criteria to Establish Factors which Govern Precipitation Chemistry, Lake Placid, NY, 11 to 15 October 1988 (Electric Power Research Institute, Palo Alto, CA).

12. A. Sirois and L. A. Barrie, Tellus **40B**, 59 (1988).

13. P. P. Parekh and L. Husain, Geophys. Res. Lett. 9, 79 (1982).

14. V. A. Dutkiewicz et al., Atmos. Environ. **17**, 1475 (1983; L. Husain et al., ibid., **18**, 1059 (1984); J. S. Webber, V. A. Dutkiewicz, L. Husain, ibid., **19**, 285 (1985).

15. D. E. Patterson, R. B. Husar, W. E. Wilson, L. F. Smith, J. Appl. Meteorol. **20**, 404 (1981).

16. W. A. Lyons, Ann. N.Y. Acad. Sci. **338**, 418 (1980).

17. V. A. Dutkiewicz, P. P. Parekh, L. Husain, Atmos. Environ. **21**, 1033 (1987); K. A. Rahn and D. H. Lowenthal, Science **223**, 132 (1984); ibid **228**, 275 (1985); D. H. Lowenthal, K. R. Wunschel, K. A. Rahn, Environ. Sci. Technol. **22**, 413 (1988); D. H. Lowenthal and K. A. Rahn, ibid., p. 420; ibid., Atmos. Environ. **22**, 1829 (1988).

18. G. T. Wolff et al., Atmos. Environ. **20**, 1229 (1986); T. Jickells, A. Knap, T. Church, J. Galloway, J. Miller, Nature **296**, 55 (1982).

19. A. Nyberg, Q. J. R. Meteorol. Soc. **103**, 607 (1977).

20. D. M. Whelpdale, A. Eliassen, J. N. Galloway, H. Dovland, J. M. Miller, Tellus **40B**, 1 (1988).

21. J. N. Galloway and D. M. Whelpdale, Global Biogeochem. Cycles **1**, 261 (1987).

22. P. W. Summers and J. W. S. Young, paper presented at the International Joint Commission Symposium, Toledo, OH, 18 November 1987.

23. H. Rodhe, Atmos. Environ. **12**, 671 (1978); H. Rodhe and I. J. Isaksen, J. Geophys. Res. **85**, 7401 (1980); S. E. Schwartz, Tellus **31**, 530 (1979); J. A. Logan, J. Geophys. Res. **88**, 10785 (1983); R. G. Derwent, The Nitrogen Budget for the United Kingdom and North West Europe (Rep. ETSU R. 37, Atomic Energy Research Establishment, Harwell, 1986); S. Z. Levine and S. E. Schwartz, Atmos. Environ. **16**, 1725 (1982).

24. P. W. Summers, paper presented at Conference on Air Pollution in Europe: Environmental Effects, Control Strategies and Policy Options, Stockholm, Sweden, 26 to 30 September 1988.

25. Air Quality Criteria for Particulate Matter and Sulfur Oxides, Vols. 1-3, Report EPA-600/8-82-029a-c (U.S. Environmental Protection Agency, Research Triangle Park, NC, 1982).

26. The Acidic Deposition Phenomenon and Its Effects, Vols. 1 and 2, A. P. Altshuller and R. A. Linthurst, Eds., Report EPA-600/8-83-016a,b (U.S. Environmental Protection Agency, Research Triangle Park, NC, 1983).

27. J. Calvert, Chm., Acid-Deposition - Atmospheric Processes in Eastern North America (National Academy Press, Washington, DC, 1983).

28. J. Chamberlain, G. MacDonald, M. Ruderman, Overview of the Physical-Chemical Processes in the Formation of Acid Precipitation, Report JSR-82-301A (Mitre Corp., McLean, VA, 1983).

29. Ø. Hov, I. Allegrini, S. Beilke, R. A. Cox, A. Eliassen, A. J. Elshout, G. Gravenhorst, S. A. Penkett, R. Stern, Evaluation of Atmospheric Processes Leading to Acid Deposition in Europe, Air Pollution Research Report 10 (Commission of the European Communities, Paris, 1987).

30. J. L. Heffter, Air Resources Laboratory Atmospheric Transport and Dispersion Model (ARL-ATAD), NOAA Tech. Memo. ERL-81 (Air Resources Laboratory, Rockville, MD, 1980).

31. The OECD Programme on Long Range Transport of Air Pollutants, Organization for Economic Cooperation and Development (Paris, 1977).

32. A. Eliassen, J. Appl. Meteorol. **19**, 231 (1980).

33. R. A. Anthes, "Meteorological Aspects of Regional-Scale Air-Quality Modeling," in Advances in Environmental Science and Engineering, Vol. 1, J. R. Pfafflin and E. N. Ziegler, Eds. (Gordon and Breach, New York, 1979), pp 3-49.

34. G. J. Ferber, Cross-Appalachian Tracer Experiment (CAPTEX '83) Final Report, NOAA Tech. Memo. ERL ARL-142 (Air Resources Laboratory, Silver Spring, MD, 1986).

35. P. L. Haagenson, Y.-H. Kuo, M. Skumanich, N. L. Seaman, J. Climate Appl. Meteorol. **26**, 410 (1987).

36. R. Draxler, J. Heffter, B. Stunder, Across North America Tracer Experiment (ANATEX)--Comprehensive Plan (National Oceanic and Atmospheric Administration, Silver Spring, MD, 1985).

37. J. G. Calvert and W. R. Stockwell, Environ. Sci. Technol. **17**, 428A (1983).

38. S. A. Penkett, Nature Phys. Sci. **240**, 105 (1972); S. A. Penkett, B. M. R. Jones, K. A. Brice, A. E. J. Eggleton, Atmos. Environ. **13**, 123 (1979).

39. S. E. Schwartz, "Gas-Aqueous Reactions of Sulfur and Nitrogen Oxides in Liquid Water Clouds," in SO_2, NO, and NO_2, Oxidation Mechanisms: Atmospheric Considerations, J. G. Calvert, Ed. (Butterworth, Boston, 1984), pp. 173-208.

40. P. H. Daum, T. J. Kelly, S. E. Schwartz, L. Newman, Atmos. Environ. **18**, 2671 (1984).

41. G. P. Gervat et al., Nature **333**, 241 (1988).

42. W. R. Leaitch, J. W. Bottenheim, J. W. Strapp, J. Geophys. Res. **93**, 12569 (1988).

43. B. B. Hicks, M. L. Wesely, S. E. Lindberg, S. M. Bromberg, Eds. Proceedings of the NAPAP Workshop on Dry Deposition, Harpers Ferry, WV, 25 to 27 March 1986 (National Oceanic and Atmospheric Administration, Oak Ridge, TN, 1987); C. I. Davidson and Y.-L. Wu, in Acid Precipitation, Vol. 2, Sources, Emissions, and Modeling, D. C. Adriano, Ed. (Springer, New York, in press).

44. W. L. Chameides, Environ. Sci. Tech. **23**, 595-600 (1989).

45. J. S. Chang, R. A. Brost, I. S. A. Isaksen, S. Madronich, P. Middleton, W. R. Stockwell, C. J. Walcek, J. Geophys. Res. 92, 14681 (1987).

46. A. Venkatram and P. K. Karamchandani, P. K. Misra, Atmos. Environ. **22**, 737 (1988).

47. L. I. Kleinman, Atmos. Environ. **21**, 1219 (1987); L. I. Kleinman, Atmos. Environ. **22**, 1209 (1988).