Acid Deposition: Unraveling a Regional Phenomenon

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Because sources of sulfur and nitrogen oxides distributed broadly across eastern North America have greatly overlapping zones of influence, it is difficult to determine detailed relations between emissions and the resulting acid deposition. Although substantial progress has been made in the past decade in understanding the pertinent atmospheric processes and in describing them in numerical models, because of the complexities of these processes and the wide range of the time and space scales involved, credible source-receptor relations for regional-scale acid deposition are not yet at hand. Consequently, near-term strategies for reducing acid deposition should be based on considerations other than detailed atmospheric source-receptor relations, but with confidence that regional deposition will be reduced equivalently to any reduction in regional emissions.

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 ("wet deposition" or familiarly "acid rain"), in the absence of precipitation (eddy transport followed by absorption, adsorption, adhesion, or other processes and commonly denoted "dry deposition") and by impaction of cloud or fog droplets. In view of the possible large social, economic, ecological, and aesthetic consequences of acid deposition (*1–12*), this phenomenon has become the subject of widespread concern. This concern is reflected in existing and pending legislation and regulations to reduce acid deposition by reducing emissions (*13*).

Research on acid deposition and how to reduce it with the fewest political, social, and economic costs can be divided roughly into research on emissions, atmospheric processes, and effects. The goal of emissions research is determining the rates and spatial distributions of emissions of acidifying substances and the means and costs of reducing these emissions.

Research in atmospheric processes is investigating the relations among (i) rates and spatial distributions of emissions of acidifying substances, (ii) atmospheric concentrations and spatial distributions of these substances and their atmospheric transformation products, and (iii) rates and spatial distributions of deposition of these materials. The goal of this research is a description of how atmospheric concentrations and deposition fluxes would change in response to changes in emissions.

Effects research is the study of the consequences of atmospheric concentrations and deposition rates of acidic and related substances on human health, artificial structural and ornamental materials, cultivated crops, and natural terrestrial and aquatic ecosystems. The goal of this research is the development of standards for concentrations and deposition that are suitable for protecting human health and the general welfare from adverse effects of acid deposition.

In this article, I 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. The impetus for this research derives largely from the effects of acid deposition. United States government standards pertinent to acid deposition have been restricted to atmospheric concentrations as distinguished from deposition fluxes. Annual average concentration standards are 1.2 μmol m^{-3} for SO_2 and 2.1 μmol m^{-3} for NO_2 (*14*). Consideration of effects of acid deposition on freshwater aquatic systems has led to suggestions for a deposition standard of 10 to 20 kg SO_4^{2-} wet deposition per hectare per year (10 to 20 mmol m^{-2} per year) (*5, 7, 9, 15*). Such a standard is expressed in terms of wet deposition only, mainly because dry-deposition fluxes have not been monitored and we thus lack knowledge of the magnitudes of the fluxes. The proposed deposition standards are made with the assumption that the wet- and dry-deposition fluxes are comparable, which suggests that a standard for total sulfur deposition might be 20 to 40 mmol m^{-2} per year (*16*). A corresponding standard for nitrate deposition has apparently not been proposed, but presumably it would be comparable in acid equivalents to the proposed standard for sulfur deposition, that is, 40 to 80 mmol m^{-2} per year. Such deposition standards might differ from location to location, reflecting the different sensitivities to acid deposition of soils with different buffering capacities.

If standards for atmospheric concentration or deposition flux are exceeded for present emission rates, then to meet these standards emissions must be reduced or perhaps redistributed. However, it is not immediately evident what sources should be reduced and by what amount. There are multiple solutions to this problem because the concentration at or deposition to a particular receptor site is the aggregate of contributions from multiple sources. Therefore, the problem is one of determining sets of changes in emission rates and distributions, any of which can be expected to meet various existing or prospective standards for concentration and deposition of acidic and related substances. This information can be used to determine optimal strategies for reducing acid deposition (*18–20*).

In this article, I focus on sulfur and nitrogen oxides and their oxidation products, as these substances are the predominant contrib-

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utors to acid deposition in industrialized regions of North America and Europe (*21, 22*). These substances contribute also to other air pollution problems. Nitrogen oxides are a key precursor to the formation of ozone (O_3) (*23–25*). Sulfate aerosol derived from SO_2 emissions is a major cause of visibility reduction on urban and regional scales (*26–29*) and may influence microphysical and optical properties of clouds (*30, 31*). Reductions in emissions of sulfur and nitrogen oxides would ameliorate these problems as well, and therefore policy decisions concerning emissions reductions must also take these considerations into account.

In characterizing acid deposition, much attention has been focused on free acidity, expressed either as the molar concentration of H^+ or as *p*H. However this emphasis may be misleading. Free acid concentration is a misleading parameter because of partial neutralization by ammonia and windblown soil. Also, *p*H is an inherently misleading measure of acid concentration because at low *p*H substantial changes in H^+ concentration are masked by only slight changes in *p*H, whereas at high *p*H, slight changes in H^+ concentrations are exaggerated when expressed as *p*H. Expressing acid deposition in terms of *p*H would also diminish the apparent accomplishment of any program of emissions reduction. As Lodge has noted (*32*), "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 *p*H of precipitation to increase by 0.3."

Historical Background

Acidification of precipitation was recognized as a local air pollution problem well over a hundred years ago (*33–35*). Smith, on the basis of measurements in Great Britain from the 1840s to the 1870s, observed that SO_4^{2-} concentrations in rain were greater in more densely populated locations and inland, especially near large coal-burning plants (*36*). Cohen and Ruston reported that annual deposition of SO_4^{2-} in precipitation at a number of stations, in the vicinity of Leeds, England, in about 1910, varied from 80 to 400 mmol m^{-2} (*37*). Gorham, again in England, called attention to rain with H^+ and SO_4^{2-} concentrations as great as 100 μM (*38*) and reported that acidities of water standing in bog pools were highest near industrial areas (*39*).

Evidence that acid deposition was a regional phenomenon was presented by Rossby and Egnér, who measured the ionic composition of rain and atmospheric aerosol at a network of stations in Sweden in the 1950s and suggested that episodes of regionally high aerosol-sulfur concentrations were related to air-mass circulation that transported material from the interior of the Eurasian continent (*40*). Subsequently, Odén (*35*) demonstrated that high acid deposition was a regional phenomenon on an annual basis in Sweden and in Western Europe by presenting contour maps showing large areas of low annual *p*H. He also noted that annual *p*H decreased with time from the mid-1950s to the late 1960s at several stations in Sweden. Odén observed that the composition of precipitation of individual storm events depended on the trajectory of airflow preceding the event; trajectories over southern England, the Benelux countries, or central Europe were associated with precipitation enriched in dissolved acid, sulfur, and nitrogen in comparison to those directly from the North Atlantic. This work received widespread attention from both the scientific community and the general public (*33*), and acid rain has since remained a major environmental issue in Europe.

Awareness that acid deposition was an environmental concern was later in coming to North America than to Europe. Although Junge and Werby (*41*) published maps of SO_4^{2-} and NO_3^- concentrations in precipitation in the mid-1950s showing slight maxima in the northeast United States, deposition was mostly attributed to natural sources. It was not until the analysis of these and later data by Likens and colleagues in the early 1970s (*42*) that a pattern of increased acid deposition in the northeastern United States relative to the rest of the country was recognized. On the basis of prevailing winds, these investigators suggested that much of the acidity in this region originated in industrial areas of the Midwest. Despite these and a few other U.S. and Canadian studies dealing with precipitation composition and the effects of acid deposition (*43*), much of the North American research throughout the 1970s on atmospheric transport and transformation of sulfur compounds continued to be motivated more by concerns over atmospheric concentrations of SO_2 and aerosol SO_4^{2-} (as agents of human health impairment upon inhalation) than by concerns over the effects of the deposited material on aquatic or terrestrial ecosystems (*44*).

Once the importance of acid deposition was recognized in North America, there was a rapid and large response in the research and political communities. Networks were established to measure systematically precipitation composition (*45, 46*). The U.S. Acid Precipitation Act of 1980 led to initiation of the National Acid Precipitation Assessment Program, a 10-year research effort to examine causes, effects, and mitigation of acid deposition (*8*). Also in 1980, the United States and Canada began negotiations to limit acid deposition resulting from transport across the border (*5a*). Recognition of the severity of the acid deposition phenomenon together with increased funding has resulted in an enormous amount of research (*2, 4, 6–9, 18, 19, 22, 27, 47–51*).

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. Because of their chemical properties 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) (*52*). 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 nonuniform. 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. 1) 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 considerable short-range structure with local values well in excess of average emission fluxes. Long-time average atmospheric concentrations and wet deposition fluxes (Fig. 2) 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 (Figs. 1 and 2) 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. Lovett *et al.* (*56*) reported impaction fluxes at a high elevation forest of 280, 160, and 240 mmol m^{-2} per year for SO_4^{2-}, NO_3^-, and H^+, respectively. On the basis of concentrations in cloud and fog water at a network of sites in the northeast United States, Weathers *et al.* (*57*) suggested that deposition by such impaction may be widespread throughout the region.

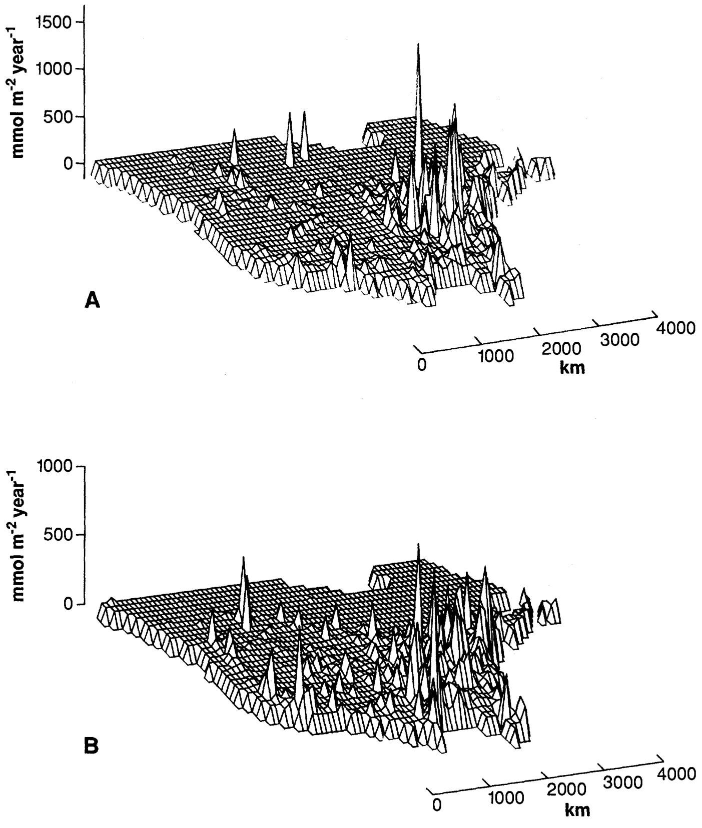

Fig. 1. Spatial distribution of emissions of (**A**) sulfur oxides and (**B**) nitrogen oxides in the United States and Canada (south of 60°N, that is, the southern boundary of Yukon and Northwest Territories), gridded according to 1° latitude by 1° longitude (~85 km by 111 km) cells. The actual structure is much greater than indicated, since a substantial fraction of the material is emitted from point sources and cities. Data are for 1980 (*53*).

Dry deposition cannot be directly monitored (*46, 58*). Fluxes determined with passive collectors (for example, plates or coated surfaces) are questionable because such collectors do not adequately simulate the aerodynamic, chemical, and biological properties of actual surfaces in the ambient environment (*58, 59*). Mass balance methods, at the level of individual leaves, trees, or watersheds, are confounded by large and variable retention of sulfur and nitrogen by biological materials and soils (*60*). To estimate dry deposition fluxes, I take 0.3 cm s^{-1} (1×10^5 m per year) as a representative average deposition velocity for SO_2 (*17*) and multiply this value by concentrations such as those shown in Fig. 2A. The SO_2 dry-deposition fluxes suggested by this calculation range from less than 16 to greater than 125 mmol m^{-2} per year (*61*). Such estimates (*63*) 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. In one storm (22 to 24 April 1981), for example, acid concentrations were high (>100 μeq per liter) in the first rain samples obtained at stations from Ohio to New York (*64*). High concentrations of aerosol sulfate at times have extended across New York state (~500 km) (*65–67*); such episodes are frequently associated with air transport to upstate New York from the southwest or occasionally from the south or southeast. A widespread, highly acidic cloud and fog (H^+ concentration 80 to 160 meq per liter) was observed to extend from Maine to Virginia during a several-day period in August 1984 (*68*). A sustained stagnant high-pressure system that covered much of the eastern United States preceded this event and evidently permitted the accumulation of high concentrations of acidic materials over the entire region.

Studies of haziness provide additional evidence of the regional nature of acid deposition. Patterson *et al.* (*28*) 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 (*69*).

High concentrations of aerosol SO_4^{2-} at nonurban sites are often associated with trace metals (*66, 67, 70, 71*) or soot particles (*67*) characteristic of emissions from coal- or oil-fired combustion sources in different geographical regions. Although the stability of such regional "signatures" and the quantitative attribution of SO_4^{2-} aerosol to different source regions on the basis of association with these tracers of opportunity are controversial (*72*), 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 qualitative indication of regional-scale transport of SO_4^{2-}.

Several workers have attempted to determine the influence of local sources on precipitation composition and thereby ascertain the relative contributions of locally emitted material and imported material to wet deposition. Dasch and Cadle (*73*) showed that annual average concentrations of SO_4^{2-}, NO_3^-, and H^+ at Warren, Michigan (7 km north of Detroit), and at a rural site 66 km farther north were essentially identical. Similarly, Chan *et al.* (*74*) were unable to detect any influence of SO_2 emissions from a large nickel smelting plant in Sudbury, Ontario, on monthly average SO_4^{2-} concentration in precipitation. These studies suggest that even in the vicinity of major urban or point sources, the cumulative contribution to long-term wet deposition of imported material dominates over the local contribution. Local sources can have a discernible influence on precipitation composition on an event basis, however, as shown by comparisons of composition upwind and downwind of point sources or urban regions (*75*).

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 (*76*). Concentrations of aerosol SO_4^{2-} and H^+ in precipitation measured at Bermuda (1100 km from North America) are substantially greater under conditions of airflow from North America than from the south or east (*77, 78*). Similar results have been obtained for nonsea salt (NSS) SO_4^{2-} in precipitation in the eastern North Atlantic (*79*). 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 (*80*). However deposition of acidic species in these remote sites is much lower than in eastern North America. For example, at Bermuda, recent annual wet deposition for NSS SO_4^{2-}, NO_3^-, and H^+ was 11, 22, and 7 mmol m^{-2} per year, respectively (*81*). 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 (*82*).

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. However, 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 (*83, 84*). 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 (*85*). 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 400 km per day (*87*). Emitted SO_2 and NO and their atmospheric oxidation products are thought to have mean residence times of ~1 to ~3 days (*88–89*), indicating mean transport distances of ~400 to ~1200 km.

Several studies have attempted to determine, in source-free regions, the decrease with transport distance of the concentrations of specific acidic substances in precipitation or in surface level air. Summers and Fricke (*90*), using measurements of surface air concentrations at stations in eastern Canada as a broad plume of material was advected northeastward, obtained characteristic decay distances (a decrease in concentration by $1/e$) in the absence of precipitation of 480 km for SO_2, 1280 km for SO_4^{2-}, and 540 km for total nitrate (HNO_3 plus particulate NO_3^-). Decay distances inferred from decreases in precipitation concentrations were 1700 km for SO_4^{2-} and 1100 km for NO_3^-. Whelpdale *et al.* (*80*) inferred a decay distance for SO_4^{2-} of 2400 km from the decrease in SO_4^{2-} concentration in precipitation with distance over the North Atlantic.

Interpretation of these measurements is not straightforward. Decrease in concentration with distance can be due not only to removal of material by deposition but also to dilution or dispersion as lateral or vertical mixing occurs with air that has lower concentrations, leading to an overestimate of the removal rate. Decreases in concentrations at the surface may also lead to an overestimate of total removal rates if some of the material is isolated from the surface, for example, by inversions. The presence of small natural or anthropogenic sources may diminish the apparent removal rate, as may production by chemical reaction. Furthermore, in the case of nitrate, the removal rate depends strongly on the distribution between gaseous HNO_3 and aerosol NO_3^-. For these reasons, empirically measured decay distances should at best be viewed as valuable semiquantitative indicators of the mean transport distance.

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 (*51*).

Atmospheric Processes

Understanding processes that govern the transport and transformation of acidic and related substances in the atmosphere, and the deposition of these materials to the surface, is necessary to formulate physical simulation models of the acid deposition phenomenon and to gain insight into the processes that govern source-receptor relations for acid deposition (*2, 4, 6–8, 48, 51*).

Regional scale transport. A key element in modeling acid deposition on regional scales is the description of 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, that is, for up to 4 or 5 days or more. Models have been developed that use routinely measured wind and temperature fields to describe transport on a regional scale [for example, (*91*); see (*22, 92, 93*)], but suitable data to test these models have been lacking. Recent studies (*94*) involving the intentional release of known quantities of inert perfluorocarbon compounds (tracers) capable of detection for distances up to thousands of kilometers from the release point have now permitted such tests. In one study, gases were released at ground level at either Dayton, Ohio, or Sudbury, Ontario, when forecast trajectories were expected to transport the material to a network of monitoring sites that extended from Pennsylvania to southeastern Quebec. Comparison of measured and calculated trajectories (*95*) suggested that the flow corresponding to the low to middle boundary layer (~950 mb) 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. The experiments were, however, conducted for only a limited set of synoptic conditions (in large-scale anticyclones and behind cold fronts). Data from this sort of experiment are needed for evaluation of model performance in more complex meteorological situations. Such information, to distances as great as 3000 km, should be forthcoming (*96*).

Chemical reactions. Atmospheric reactions, by changing the physical and chemical properties of the emitted materials, greatly affect removal rates and hence exert a major influence on source-receptor relations. Sulfur dioxide, the anhydride of a weak acid, is subject to fairly rapid dry deposition (~1 to 3 days) to vegetation and to moist, basic surfaces (*17*). It is not dissolved to great extent in cloud water or rainwater (*97*) and is thus not substantially removed from the atmosphere in precipitation, unless it is oxidized to the much more soluble sulfate species. This oxidation may occur in the gas phase, initiated by OH free radical (*98*) (Table 1, reaction 1), or in cloud water by H_2O_2 (reaction 2) or O_3 (reaction 3). Atmospheric H_2SO_4 may be neutralized in part by NH_3 and other basic materials such as carbonates. Because of their low vapor pressure, H_2SO_4 and SO_4^{2-} salts are present almost entirely as aerosol particles. These particles are readily and efficiently incorporated into cloud water (*99*), and as such are subject to wet deposition; however, aerosol particles are only slowly removed from the atmosphere by dry deposition, on account of their low diffusion coefficients (*58, 62*).

Nitric oxide is nearly insoluble in water and is unreactive in solution; therefore, little if any NO is dry deposited to the surface or oxidized by reactions in cloud water. Nitric oxide is oxidized on a time scale of hours to NO_2 by reaction with O_3 (reaction 4) or by other secondary photochemical reactions involved in the formation of O_3 and other oxidants (reaction 5). Nitrogen dioxide also is only weakly soluble in water and not highly reactive in solution at concentrations characteristic of the ambient atmosphere (*100*). However, it is apparently subject to dry deposition to vegetation (*17*), perhaps by oxidation of lipids or phenolic compounds (*101*). Nitrogen dioxide can be further oxidized by gas-phase reaction with OH (reaction 6); NO_2 can also be oxidized at night by reaction with O_3 to form NO_3, which can subsequently form N_2O_5 and HNO_3 (reaction 7) (*102*). Nitric acid, in contrast to H_2SO_4, is quite volatile (*103*). It is also highly soluble in cloud and rainwater (*89*), and because it readily adsorbs or absorbs onto material surfaces, it is also subject to rapid dry deposition (*17, 59*). In clear air nitric acid may be taken up by aerosol particles, provided that there is sufficient basic material to neutralize the acid (*103*); aerosol NO_3^- is much less subject to dry deposition than is HNO_3 vapor. Some atmospheric NO_2 reacts to form organic nitrates including peroxyacetylnitrate [$CH_3(CO)O_2NO_2$ (PAN)]. Organic nitrates may serve as reservoir species that can contribute to long-range transport of atmospheric nitrogen species (*104*).

Recent research has focused on obtaining improved description of

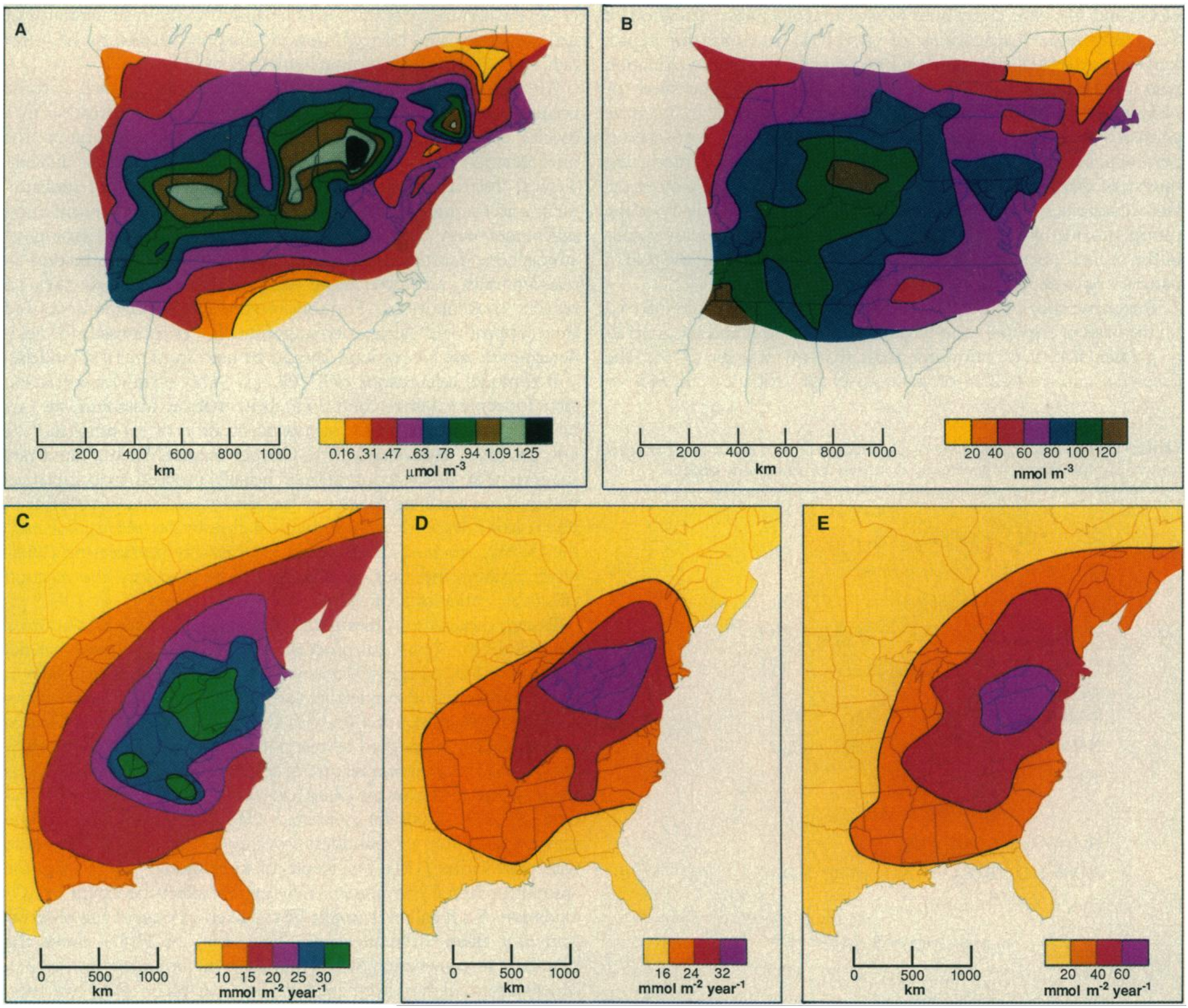

Fig. 2. Spatial distributions of atmospheric concentrations and wet deposition of acidic species in eastern North America. Monthly (9 January to 10 February 1978) mean atmospheric concentrations of (**A**) SO_2 and (**B**) SO_4^{2-}, as contoured from a network of 54 sites selected to minimize influence of local sources (*54*). Similar distributions but with somewhat lower SO_2 and higher SO_4^{2-} concentrations were obtained in other seasons. Annual (1984) deposition flux for (**C**) SO_4^{2-}, (**D**) NO_3^-, and (**E**) H^+ in precipitation, adapted from (*55*). Deposition patterns for other years are similar (*8*).

rates of gas-phase (*105–107*) and to a greater extent aqueous-phase (*97, 107–109*) atmospheric reactions; the greater emphasis on aqueous-phase reactions reflects an increased recognition of their importance and, until recently, a less-advanced capability for describing these reactions than gas-phase reactions. The approach to this problem is typically iterative, involving field measurements, laboratory experiments, and numerical modeling. The importance of a reaction may be inferred initially from field measurements. Laboratory experiments are necessary to determine rate coefficients, solubilities, mass transfer properties, and other properties required for evaluation of reaction rates. Box models (zero-dimensional systems of ordinary differential equations) allow important reactions to be identified over a wide range of conditions. One-, two-, and three-dimensional calculations allow spatial variability, mixing, dry deposition, and cloud and storm processes to be coupled to chemical reactions and permit detailed comparison with field measurements.

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 of the formation of oxidants, especially H_2O_2 and O_3, that contribute to the aqueous-phase oxidation of SO_2. Box-model calculations of gas-phase reactions for representative situations suggest that peak gas-phase daytime oxidation rates are ~1 to 5% per hour for SO_2 and ~10 to 50% per hour for NO_2 (*105*). A number of field studies [for example (*23*)] have consisted of time series measurements of gaseous and aerosol species pertinent to acid deposition, together with numerical modeling, mostly of clear-air processes. These studies suggest that a more-or-less accurate description is at hand of the gas-phase chemistry of the nitrogen-oxide-hydrocarbon-ozone system. However, many details of the organic chemistry need to be elucidated, including the role of natural organics and formation of peroxides.

The occurrence of in-cloud oxidation reactions had been inferred on the basis of regional mass-balance considerations and the generally greater acidity of rainwater than that of clear air (*110*). The occurrence in particular of aqueous-phase oxidation of SO_2 in clouds by H_2O_2 and, to a lesser extent, by O_3 (*111*), has been confirmed with model calculations and field measurements. Daum *et al.* showed that the acidity of cloud water in nonurban locations is commonly much greater than would be expected simply by dissolution of soluble aerosol species and nitric acid present in clear air and demonstrated that H_2O_2 and SO_2 are essentially mutually exclusive in nonprecipitating, liquid-water, stratiform clouds; this observation suggests that reaction has proceeded to completion in such clouds (*112, 113*). 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 (*114*). In contrast, under conditions of low H_2O_2 concentration in winter, the composition of cloudwater is essentially that which would be expected simply from dissolution of sulfate and nitrate aerosol and nitric acid gas present before cloud formation (*115*). Field measurements suggesting SO_2 oxidation by O_3 have been reported (*116*), but the interpretation of these results has been questioned (*117*). Recent field studies suggest that oxidation of NO_2 by reaction 7 (Table 1) may contribute substantially to the acidity of wintertime stratiform clouds (*118*); the occurrence of this reaction pathway in moist subsaturated air had previously been inferred from the disappearance of the NO_3 free radical at night at high relative humidities (*119*).

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

	Gas phase	
	$SO_2 + OH \xrightarrow{M} HOSO_2$	(1)
	$HOSO_2 + O_2 \longrightarrow SO_3 + HO_2$	
	$SO_3 + H_2O \xrightarrow{M} H_2SO_4$	
Net:	$OH + SO_2 + O_2 + H_2O \rightarrow H_2SO_4 + HO_2$	
	Aqueous phase	
	$SO_2 \overset{H_2O}{\rightleftarrows} HSO_3^- + H^+ \rightleftarrows SO_3^{2-} + 2H^+$	
	$HSO_3^- + H_2O_2 \xrightarrow{H^+} SO_4^{2-} + H^+ + H_2O$	(2)
	$SO_3^{2-} + O_3 \longrightarrow SO_4^{2-} + O_2$	(3)
	Gas phase	
	$NO + O_3 \longrightarrow NO_2 + O_2$	(4)
	$NO + HO_2\ (RO_2) \longrightarrow NO_2 + OH\ (RO)$	(5)
	$NO_2 + OH \xrightarrow{M} HNO_3$	(6)
	Gas phase followed by aqueous phase	
	$NO_2 + O_3 \longrightarrow NO_3 + O_2$	(7)
	$NO_3 + NO_2 \overset{M}{\rightleftarrows} N_2O_5$	
	$N_2O_5 + H_2O(l) \longrightarrow 2H^+ + 2NO_3^-$	
Net:	$2NO_2 + O_3 + H_2O(l) \rightarrow 2H^+ + 2NO_3^- + O_2$	

Although field studies can, in favorable situations such as those noted above, provide evidence for the increase or decrease in a species' concentration that can be ascribed to in-cloud reaction, the interpretation of such data in terms of specific reactions is difficult. Typical fluctuations in atmospheric concentrations and measurement uncertainties usually preclude measurements of concentration differences with the precision necessary to determine extents of atmospheric reactions (*120*) and thus preclude determination of reaction rates, and even more the dependence of such rates on reagent concentrations. For this reason, rate expressions derived from appropriate laboratory experiments, as opposed to field-determined rate expressions, should be used in numerical models.

Box-model calculations (*97, 109, 111, 121*) of in-cloud reaction rates for representative conditions show that the instantaneous rate of SO_2 oxidation by H_2O_2 at a concentration of 40 nmol m^{-3} (1 ppb gas-phase equivalent) is ~10% per minute. Such a rapid rate suggests that the reaction should usually proceed to completion within cloud lifetimes. Moreover, because of acid catalysis the rate of this reaction is nearly independent of cloudwater *p*H. In contrast, the O_3-SO_2 reaction rate strongly decreases with increasing cloudwater acidity, and thus as sulfuric acid is produced the reaction effectively shuts itself off.

Recent modeling studies (*122, 123*) of in-cloud reaction coupled with cloud microphysical processes and dynamics suggest that the reaction of SO_2 with H_2O_2 reaction proceeds much more rapidly in both stratiform and convective clouds, provided that both species are present, than the reaction with O_3. In situations where SO_2 is in excess, H_2O_2 is exhausted by reaction, consistent with observations (*113*). Another common feature of several calculations is that acid is concentrated at the lowest cloud levels, also consistent with observation (*50, 112*). Updrafts associated with convective clouds induce upward transport of boundary-layer pollutants, again consistent with observation (*124*). The results of some models suggest that the amount of lateral entrainment may greatly affect the extent of SO_2 oxidation. Such an effect might be expected in view of the observation that there is frequently a "reservoir" of H_2O_2 above the boundary layer, whereas SO_2 is mostly in the boundary layer (*125*). Much attention has been paid to aqueous-phase SO_2 oxidation reactions because the extent of these reactions might not be linearly proportional to initial SO_2 concentrations and because these nonlinearities might in turn influence the linearity of the overall source receptor relation for acid deposition (*123, 126*).

Dry deposition. Substantial progress has been made in the past two decades in understanding turbulent transport in the surface layer of the atmosphere, in measuring material fluxes through this layer, in relating these fluxes to concentration gradients, and in inferring fluxes from field data (*46, 58–60, 62, 63, 127, 128*). Micrometeorological techniques to measure dry deposition flux directly or to infer this flux from vertical concentration gradients can be applied only under rather restricted conditions of meteorological situation, fetch, and surface uniformity. However, under suitable conditions, surface resistances characteristic of various types of vegetation and surface conditions can be measured; the surface resistance is the quotient of the concentration of the depositing material immediately adjacent to the surface divided by the deposition flux. This resistance, which is considered a robust and transferable measure of the dry-deposition rate, can be used together with measured or modeled concentrations of depositing species and micrometeorological parameters to estimate dry-deposition fluxes (*17, 63, 127*).

For gases such as SO_2, NO_2, and O_3 with a dry-deposition rate substantially less than the turbulent-transfer rate, uptake is controlled largely by chemical, biological, and biochemical processes at the surface. For example, leaf geometry, stomatal aperture and factors that control it, and the solubility and reactivity of the gases in intercellular fluids in the substomatal cavity are probably dominant influences on the rate of dry deposition to plants (*60, 129*). Because dry deposition of gases is a major acid deposition mechanism, gaining an understanding of these processes is particularly needed. The role of plants as active participants in the deposition of pollutant gases, much as they are active participants in CO_2 uptake, should be distinguished from the effects of gaseous air pollutants on vegetation. This distinction has been epitomized as "Ask not what the pollutants are doing to the plants; ask rather what the plants are doing to the pollutants" (*130*).

Regional Scale Physical Simulation Modeling

Maps such as those shown of the distribution of emission fluxes, atmospheric concentrations, and deposition fluxes provide little direct information for developing strategies to reduce acid deposition at specific receptor sites. What is needed is the set of source-receptor relations (SRRs) linking emissions (as a function of location) to deposition (also as a function of location). An appealing approach for obtaining SRRs is by means of physical simulation models—numerical descriptions of all of the component processes of the acid deposition phenomenon: emissions, transport, chemical and physical transformations, and dry and wet deposition. This approach is especially attractive from a regulatory perspective because it extends the promise of providing source attribution of deposition and responses to changes in rates and spatial distributions of emissions.

The challenge of this task may be appreciated by envisioning eastern North America, an area of about 2500 km by 2500 km, gridded into cells of 250 km by 250 km. This results in some 100 cells, each of which is in principle both a source and receptor of acid deposition. The SSR is the contribution of each source to acid deposition at each receptor; the number of partial contributions to acid deposition (elements of the source-receptor matrix) that must be determined is thus of order 10^4. Although some decrease in this number might be gained with aggregation, substantial aggregation degrades the geographical specificity needed for policy application. Restricting attention to a subset of the matrix elements also leads to major dissatisfaction. If only a subset of sources is considered, the magnitude of contributions at a receptor site from small nearby sources or of cumulative contributions from numerous distant sources cannot be assessed; comparison of modeled and measured deposition also is precluded. If only a subset of receptors is considered, the benefit of reduced deposition at receptors not considered resulting from reduced emissions at a particular source cannot be taken into account in policy analysis.

Numerical models for describing regional scale acid deposition may be classified broadly into three categories: statistical, Lagrangian, and Eulerian (*92, 131, 132*). In the statistical approach, frequency distributions of transport trajectories and reaction and deposition rates are coupled in order to obtain concentration and deposition fields associated with individual emission sources. Input rate data can derive from laboratory measurements or from field measurements of residence times or transport distances. The method is well suited to generating multiyear averages of the deposition fields necessary for climatological representativeness. However, the method encompasses only a rudimentary treatment of the atmospheric processes involved.

Lagrangian models permit more detailed treatment of chemical and physical processes 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 carried out as long as desired to build up a climatologically representative deposition field. This information is of immediate application in developing strategies to reduce acid deposition. However, the calculation must be repeated for each source under examination, and therefore a large number of calculations is required to determine the source attribution of a large proportion of deposited material at receptor sites of interest.

Depending on the treatment of the atmospheric chemistry, Lagrangian models may or may not be linear; that is, the concentration or deposition field attributable to any source does or does not scale linearly with 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 SRR. Furthermore, chemical interactions among materials derived from multiple sources that would occur in the real world as puffs that disperse and merge into one another, cannot be included in linear models. The magnitude and significance of these inaccuracies are not known. The linear approach, however, gives rise to a major simplification in policy applications because 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 1982, a joint U.S.–Canadian Work Group reviewed eight statistical and Lagrangian regional-scale models and compared modeled concentrations and deposition from model to model and with observation. Mean transport trajectories were substantially different from model to model, and considerable variation was found in absolute values of wet, dry, and total sulfur deposition to nine particular receptors attributed to various sources, although the ranking of such sources was similar from model to model. The Work Group concluded that it was "encouraging" that the models were "able to reproduce the right order of magnitude of the large time- and space-scale features of the wet sulfur deposition fields" (*133*). A more recent jointly conducted comparison of 11 linear statistical and Lagrangian models (*134*) concluded that most of these models reproduced fairly well the shape and magnitude of regional patterns of seasonal wet sulfate deposition. There was, however, considerable variation from model to model and between models and field measurements in the structure of the spatial wet deposition patterns. Agreement with seasonal-average surface concentrations of SO_2 and SO_4^{2-} at four Canadian stations (the only such data available for comparison) was mostly within a factor of 2. No model to model comparisons of source attribution were presented.

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 program that generates these quantities from observational data. Initial chemical fields must also be specified. The model 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. Cloud- and storm-related transport and reaction as well as clear-air processes are readily accommodated. This approach is thus well suited to examine quite complex chemical mechanisms that could result in substantial nonlinearities between emissions from various sources and their deposition fields.

In practice, the Eulerian approach presents major conceptual and practical problems. Foremost among these are subgrid phenomena and artificial diffusion. Because of limitations in computational capabilities, present models (for example, *132, 135*) are restricted to fairly large grid sizes, typically 80 km by 80 km in the horizontal; materials present in each cell are immediately "dispersed" throughout the entire cell. Such dispersal can lead, for example, to fictitious reactions between species that are thus artificially mixed. The magnitudes of these artifact effects are not yet known. A further disadvantage is that in the model as in the real world, mixing of material from multiple sources makes it 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 different sources were "tagged," but in view of the already 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 (*136*). Another major problem with the Eulerian approach is that of carrying out enough model runs to obtain climatologically representative results.

Despite the difficulties and resource requirements inherent in the Eulerian approach, the U.S. National Acid Precipitation Assessment Program (NAPAP) is directing most of its regional scale modeling efforts to an Eulerian model (*132*). This policy is based in large part on the belief that the best way to characterize the SRR is by means of a scientifically based model that allows for demonstrated nonlinearities in atmospheric chemical processes (*137*).

A large effort is now under way to obtain field measurements that will permit the accuracy of models to be evaluated (*138*). These measurements include a ground network for long-term surface measurements of concentrations and wet deposition of acidic species. An important aspect of this model evaluation consists of aircraft measurements of sulfur and nitrogen species, oxidants such as O_3 and H_2O_2, and other modeled species such as PAN that will permit a much more stringent test of the models than can be obtained solely from surface measurement of sulfur and nitrogen species.

The heavy reliance by NAPAP on the Eulerian modeling approach has been criticized by the Canadian Research and Monitoring Coordinating Committee for Acid Rain, who recently stated that NAPAP's "obsession with the development of an Eulerian model is inexplicable in scientific terms," and asserted that a hierarchy of methods is "available" to estimate SRRs, including pattern association, regional budget studies, trajectory sector analyses, tracers of opportunity, analysis of impact of emission changes and statistical and Lagrangian models (*139*). However, these approaches also have not yet yielded SRRs that can be employed with confidence. Moreover, because of the importance of nonlinear processes, they should be accounted for in the models. There even remains substantial uncertainty, by factors of 2 or more, in the most fundamental property of SRRs, the mean distance of transport of the emitted materials. This situation, which is a reflection of the complexity of the regional acid deposition phenomenon, calls for pursuit of SRRs by a variety of techniques that will, it is hoped, finally provide consistent results and thereby establish the desired scientific credibility.

Empirical Determination of SRRs

An alternative approach to determine SRRs is by empirical experiment (*140–143*). Although such an approach is attractive (*140*), there are major problems with the several experiments that have been proposed and with the approach in general (*141*). Passive tracers alone cannot mimic the acid deposition processes nor can reactive tracers or tracers of opportunity such as transition-metal ions. Mass-balance experiments, in which the depositional losses of sulfur and nitrogen species are inferred by ratio of their concentrations to those of coemitted passive tracers, would be subject to large uncertainties, as would experiments in which emissions of acidic species are deliberately increased or decreased. Experiments involving large-scale modulation of emissions would also be quite costly, and there are substantial technical constraints to achieving the necessary modulation. Experiments involving releases of stable low-abundance isotopes of sulfur or nitrogen oxides would require large quantities of these isotopes (tens of kilograms per single realization) in order to overcome the natural variability in isotopic abundances associated with existing emission sources; even then signal to noise would deteriorate rapidly with distance from the source (*142*). Experiments with the radioactive ^{35}S isotope appear technically feasible at emission rates that would result in ambient concentrations well within current standards (*143*); however, such intentional release of radioactive material may not be publicly acceptable. Beyond the above considerations, numerous realizations of these experiments would have to be carried out for a diverse set of meteorological conditions in order to obtain an accurate estimate of the long-time average deposition field corresponding to an individual source. The experiment would then have to be carried out for a representative distribution of source regions. For these reasons, empirical experiments would not appear to be viable approaches to determine SRRs for acid deposition.

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 a recent review of the effects of acid rain on freshwater ecosystems, Schindler (*9*) 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 (*9*), 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. The states would then be given a schedule by which to achieve this standard, say 10% of the required reduction per year for 10 years.

In the meantime, the atmospheric research community would 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 (*144*).

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84. In this definition, no assumption is made about the distribution of source-to-receptor distances; for an exponential distribution, the mean transport distance would equal the distance for an e-fold decrease. A fundamental problem inherent in this definition (W. G. N. Slinn, personal communication) is that a gaseous species for which dry deposition occurs at a rate less than that governed entirely by atmospheric mass transport (that is, for which there is an appreciable surface resistance) is temporarily removed from the atmosphere several times before being ultimately removed. It is this ultimate removal that is intended in the definition. In practice this imprecise definition is not a problem for atmospheric sulfur and nitrogen compounds. On longer time scales, however, there is a further problem regarding, for example, release of reduced sulfur compounds mediated by biological action upon sulfur previously deposited from the atmosphere.
85. The long-term average distance of transport for a given emitted substance is not a defined property of the substance, but might be expected to vary as a function of source location because of orographic effects or spatial variation of climate or chemical environment (*83*). Dependence of $\bar{x}$ on variables such as stack height might also be expected (*86*). However, such variations are probably relatively small, and thus $\bar{x}$ can be considered a robust property of the system that varies only slowly over the emissions domain. A distinct but related quantity is the deposition-weighted mean distance from a given receptor site to the sources of material depositing at that site (*83*). This is a useful quantity from a regulatory perspective because it provides a sense of how far away reductions in emissions might be expected to reduce deposition. In principle, however, it may exhibit large variation as a function of receptor location because local sources may dominate nearby deposition (*83*).
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Changing Composition of the Global Stratosphere

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The current understanding of stratospheric chemistry is reviewed with particular attention to the influence of human activity. Models are in good agreement with measurements for a variety of species in the mid-latitude stratosphere, with the possible exception of ozone (O_3) at high altitude. Rates calculated for loss of O_3 exceed rates for production by about 40 percent at 40 kilometers, indicating a possible but as yet unidentified source of high-altitude O_3. The rapid loss of O_3 beginning in the mid-1970s at low altitudes over Antarctica in the spring is due primarily to catalytic cycles involving halogen radicals. Reactions on surfaces of polar stratospheric clouds play an important role in regulating the abundance of these radicals. Similar effects could occur in northern polar regions and in cold regions of the tropics. It is argued that the Antarctic phenomenon is likely to persist: prompt drastic reduction in the emission of industrial halocarbons is required if the damage to stratospheric O_3 is to be reversed.

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OZONE IS FORMED IN THE STRATOSPHERE BY PHOTOLYSIS of O_2 to atomic oxygen (O),

$$h\nu + O_2 \rightarrow O + O \quad (1)$$

followed by

$$O + O_2 + M \rightarrow O_3 + M \quad (2)$$

Its chemistry can be described approximately by reactions 1 and 2 supplemented by

$$h\nu + O_3 \rightarrow O + O_2 \quad (3)$$

and

$$O + O_3 \rightarrow O_2 + O_2 \quad (4)$$

Interchange between O_3 and O by reactions 2 and 3 is rapid. It is convenient to consider O_3 plus O as a family, that is, odd oxygen. Reaction 1 provides the source of odd oxygen, the only important source identified to date for the stratosphere. Reaction 4 represents the sink. Reactions 2 and 3 serve to regulate the relative abundances of O_3 and O. Odd oxygen can be removed also by reactions catalyzed by trace quantities of hydrogen (H), hydroxyl radical (OH), and hydrogen superoxide radical (HO_2) (*1*). The dependence of the rate for reaction 2 on the density of the third body, M, ensures