INTERREGIONAL AIR POLLUTANT TRANSPORT: THE LINEARITY QUESTION

Extended abstracts from the Inaugural EURASAP Symposium, 22–24 April 1986, Budapest, Hungary

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Executive Summary

This report contains extended abstracts from an international meeting held in Budapest, Hungary. Its main subject is the question of proportionality and linearity between emissions and deposition/airborne concentration of air pollutants including sulfur, nitrogen, oxidants, and acidity. Session topics (which serve here as section headings) included analysis of measurements, ammonia and its implications for linearity, modeling with emphasis on chemistry, simplified approaches to the linearity issue, and results from long-range transport models. Linearity was found to be strongly dependent on the distance between emitters and receptors, the averaging time of pollutants, and the form of deposition.

Foreword

Considering the enormous amount of research conducted in Europe on air pollution, there is a need to promote and facilitate communication among scientists working on these problems. The European Association for the Science of Air Pollution (EURASAP) addresses this need. I was pleased that IIASA could not only host EURASAP's founding executive committee meeting in October 1985, but also organize its inaugural symposium in April 1986. This report is a record of this symposium. We are indebted to Dr. Ernö Meszaros and the Institute of Atmospheric Physics in Budapest for helping to make this meeting a success as well as Dr. Bernard Fisher at the Central Electricity Generating Board of the UK for reviewing the manuscript of this report.

R.E. MUNN
Leader, Environment Program
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About EURASAP

The European Association for the Science of Air Pollution (EURASAP) is a newly formed organization whose purpose is to provide a forum for coordination and communication between scientists throughout Europe on air pollution studies and their applications. It is our intention to organize specialized informal colloquia and workshops on selected topics for scientists with suitable expertise, and to encourage such other activities as may be appropriate to the advancement of the science and control of air pollution.

The benefits are intended both for research scientists and those implementing air pollution control measures, and the exchange of ideas between scientists with different areas of interest and expertise will be emphasized.

The initial Committee includes: Dr. H.M. ApSimon (UK), Dr. P. Bessemoulin (France), Dr. P. Builtjes (Holland), Professor A. Eliassen (Norway), Professor W. Klug (Germany, F.R.), Dr. J. Kretzschmar (Belgium), Professor E. Meszaros (Hungary), Dr. J. Pretel (Czechoslovakia), Dr. J. Pruchnicki (Poland), and Dr. F.B. Smith (UK).

This committee is supplemented by national correspondents in the different countries. The Association will actively cooperate with other national and international bodies involved in atmospheric chemistry and air pollution. Such links have already been established.

A regular newsletter provides advance notice of EURASAP activities and other meetings on air pollution science in Europe made known to the Association, brief summaries of EURASAP meetings, and news of European research — particularly work in progress or planned.

This inaugural meeting, a very successful beginning toward achieving our objectives, was attended by some 40 scientists from a wide range of European countries. We are very grateful to IIASA and Hungarian hosts for their impeccable organization and hospitality in making this meeting both enjoyable and scientifically successful.

Helen ApSimon
Chairman, EURASAP

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Introduction

The linearity question is of equal interest to those engaged in either scientific or policy work. To the atmospheric scientist, it is an important consideration in justifying simplications in their models; to the environmental policy analyst, it is crucial for estimating the amount of pollutant emissions that must be removed to reach a particular environmental objective. But when two professions address the same question, terminology can become confused. It is worthwhile, then, at the outset of this report to clarify the meaning of "the linearity question". In this publication, it generally refers to the relationship between a change in pollutant emissions and a change in deposition or concentration at another location. (The pollutants we are concerned with in this report are sulfur, nitrogen, oxidants, and acidity.)

The specific policy interest in this relationship is whether an $x\%$ reduction in emissions would yield an $x\%$ reduction in deposition or concentration. This, for the record, is proportionality, not linearity. Mathematically, proportionality is expressed:

$$Y = AX \tag{1}$$

where Y is pollutant deposition or concentration, X is emissions, and A is a proportionality constant. Under most circumstances the deposition or concentration Y will not only be affected by the emissions X, but also by other sources of either anthropogenic or natural origin. These sources may either be identified emitters or unidentified "background" contributors. If we call these additional sources B, we can compute deposition or concentration Y as:

$$Y = AX + B \tag{2}$$

If B is greater than zero, a reduction in emissions X will *not proportionally* reduce deposition or concentration Y, but will nevertheless *linearly* reduce it. The policy interpretation of linearity is that a steady decrease in emissions X will cause a steady decrease in deposition or concentration Y down to some level B. Strictly speaking, the linearity question asks whether relationship (2) holds for a particular emitter–receptor pair.

As is pointed out in this report, it is rather important to specify the time and space scales of interest when inquiring about linearity. For example, an emitter–receptor pair may be nonlinear over short times and distances, but linear when longer-term averages are of concern. Also the type of pollutant is important.

For instance, wet sulfur deposition may have a nonlinear relationship to emissions, whereas total deposition could be linear.

Contributors to this report address both the linearity and proportionality questions. Their approaches to these questions vary considerably: some examine historical air and precipitation data, others study the agents of nonlinear atmospheric processes such as ammonia, and still others use theoretical models with simple or complicated chemistry. Having examined the linearity question from so many different perspectives adds weight to the general conclusions of the meeting presented in the next section.

Summary and Findings

In the first session, devoted to analysis of measurements, attention was given to historic trends of sulfate in Scandinavian precipitation. An upward trend was found from 1955 to about 1975 with a total increase of about 50%. However, a negative trend of about 30% was observed from 1975 to 1983. Such a downward trend was not observed for nitrate and NH_3 in precipitation. Generally speaking, these temporal patterns agree with the estimated pattern of SO_2 emissions, though changes in measurement and analytical techniques obscure trends somewhat. An extensive analysis of measured SO_2 and SO_4 concentrations did not clearly reveal the same behavior over the whole of Europe.

Several speakers stressed that the term "background concentration" should always be clearly defined. Often the term is meant to indicate background concentrations at the edge of the area under consideration — for example, Europe, a specific country, or a city. This concentration should clearly be distinguished from the term "natural background", which is the concentration level in the case when all anthropogenic influences can be neglected. In connection with the first type of "background" precipitation quality, it was estimated that 15% of precipitation sulfate in Europe comes from outside Europe.

The second session, ammonia and its implications for linearity, showed the growing interest outside the Netherlands and the United Kingdom in the role that ammonia plays in aerosol formation and acid deposition. The transformation of SO_2 to $SO_4^=$, which is mainly controlled by H_2O_2 and O_3, could be enhanced by the presence of ammonia and could lead to nonlinear behavior between sulfur emissions and deposition over short distances. The emission density of ammonia, more than about 80% arising from livestock wastes, differs considerably over Europe, ranging from a few hundred to about 4000 kg per annum per km^2. The incorporation of ammonia in long-range transport models is showing promising results.

Modeling with emphasis on chemistry, the third session, contained some contributions devoted to photochemistry. On urban as well as on interregional scales, the relation between hourly O_3 concentration and emissions of NO_x and nonmethane hydrocarbons is far from proportional. It was emphasized that, ideally, acid deposition and photochemistry should be treated together. With respect to acid deposition of SO_2, calculations show that wet depositions are more disproportionate to emissions than dry depositions, mainly owing to the role of H_2O_2. Related calculations showed that the relationship between airborne sulfur and wet sulfate deposition may be particularly disproportionate in polluted areas.

The same point was clarified in the fourth session, devoted to simplified modeling approaches to the linearity issue. Model calculations of annual SO_2 averages showed that wet deposition requires a longer distance to become approximately proportional to emissions than dry deposition. Total deposition was calculated to be approximately proportional to emissions for a distance of more than 200–600 km downwind of three types of plumes — isolated, diffusive, and composite. Substantial disproportionality in wet deposition can occur over shorter distances. Therefore, SO_2 emission and total sulfur deposition are proportional on a European scale, but not so on the smaller scale of, for example, a single European country. Calculations with other dispersion models showed similar trends. If ecological effects result from total sulfur deposition, then the relation between effects and emissions will be more proportional than in the case in which these effects are caused by wet sulfur deposition alone.

The last session focused on results from long-range transport models. Calculations carried out with the EMEP trajectory model showed that a nonlinear wet deposition coefficient produced no significant nonlinearities between sulfur emissions and total (wet plus dry) deposition over one year. Uncertainty due to nonlinearity of the wet deposition coefficient was found to be the same or less than uncertainty due to a $\pm$ 20% error in model parameters. Interregional calculations carried out in the United States supported the hypothesis that a linear source–receptor relation exists for total S- and N-deposition over periods of about a year. Calculations for Europe with a trajectory puff model, including different sensitivity runs, are in progress.

Based on recommended findings presented to the meeting by W. Klug, the editors of this report summarize the conclusions of the meeting as follows:

(1) Linearity between emissions and deposition strongly depends on the distance between emitter and receptor, the averaging period, the constituent (acidity, oxidants, sulfur, and so on), and the form of deposition (e.g., whether total deposition is considered or wet deposition alone).

(2) Observations of SO_2 and $SO_4^=$ neither strongly support nor contradict the linearity of sulfur emissions and deposition over long time scales (season or longer) and large space scales (a few hundred kilometers).

(3) Model calculations show that the relationship between wet deposition of sulfur and emissions may be nonlinear close to sources ($\ll$ 500 km) and approximately linear far from sources ($\gg$ 500 km) over long time scales ($\geq$ one year).

(4) It is expected that the relationship between photooxidants and their precursors is nonlinear over both episodes and one year. Sulfur and nitrogen species may also be nonlinearly related to emissions on the episodic time scale.

(5) It is known that nitrogen behavior in the atmosphere involves nonlinear processes. Nevertheless, the relationship between nitrogen emissions and deposition over a one-year, or longer, time scale may be linear.

PART I.

Analysis of Measurements

1. Trends in Sulfate in Scandinavian Precipitation Agree with Trends in European SO_2 Emissions (short summary)

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Sulfate concentration in precipitation at a number of Scandinavian stations has been analyzed for temporal trends. The data extend back to 1955, although the quality of the data is highest during the period 1972–1985. Most stations show an increase in sulfate concentration between the late 1950s and the early 1970s by about 50%, in reasonable agreement with the increase in total European SO_2 emission during the same period.

A detailed analysis of data from 12 Swedish stations between 1972 and 1985 shows a decrease at all stations. At nine of these stations the trend is significantly negative at 90% confidence level. The average decrease during the 14-year period is about 30%. This number is consistent with the reported decrease in SO_2 emission in Sweden and in several other European countries, taking into account the present estimates of transboundary fluxes of sulfur compounds.

2. On the Proportionality of Atmospheric Sulfur Emission/Deposition

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The proportionality of pollutant emission/deposition was investigated empirically by analyzing historical trends in pollutant emission and air concentration and precipitation quality data for the same representative territory of Europe, for the last quarter century. During this timespan three major monitoring programs (EACN, OECD, EMEP) were carried out, which furnished data of reasonable quality for this assessment. This study deals only with wet deposition, which can be monitored more reliably than dry deposition.

Historical data of anthropogenic sulfur emission were reported in the literature. According to these data, emissions increased at the beginning of the 1950s. The rate of increase slowed down during the 1970s. As it turned out, different emission values were reported for the very same time period, owing to (1) the number of countries considered, (2) uncertainties of statistical data on emissions and its spatial distribution. For these reasons, emission values had to be normalized. Emission data sets reported were uniformly extended for 28 European countries, west of longitude 30 °E. Based on these normalized data, a reference emission value was assigned to each monitoring period, for the years 1956, 1974, and 1980. These data showed that the sulfur emission grew 4.4% yr^{-1} in the first phase, and 2.0% yr^{-1} in the second one. From 1956 to 1980, an overall 103% increase was found.

Average annual concentrations and frequency distributions of the concentrations for sulfur dioxide in air and sulfate ion in precipitation were determined in two different ways. In first case primary (reported) data have been used. In the second approach primary data were analyzed as concentration patterns for the same reference territory of Europe. Data were read at 126 grid points (200 × 200 km grid distance), then yearly averages were calculated for the periods of 1954–1959, 1973–1974, and 1978–1982.

Spatial distributions of the concentrations of sulfur dioxide and sulfate ion, based on normalized data, are presented. Very high yearly-averaged SO_2 values were found for the 1950s, with maxima of 30 μg S m^{-3} over Central Europe and

Great Britain. For 1973–1974, the highest value dropped to 15 μg S m^{-3}; for 1978–1982 to 11 μg S m^{-3}. SO_4^{2-} values had smooth patterns with maxima of 2.00 mg S l^{-1} for 1954–1959 and 2.55 mg S l^{-1} in the period 1978–1982.

Temporal distributions are initially represented by cumulative frequencies of SO_2 and SO_4^{2-} for primary and normalized data, during the same reference periods. Approximately log-normal distributions were obtained, excluding data of SO_2 for 1978–1982 that are atypical.

Mean concentrations of SO_2 were 9.6, 5.3, and 5.1 μg S m^{-3} for primary data, and 9.8, 5.1, and 4.3 μg S m^{-3} for normalized ones, in the different periods. Mean concentration of SO_4^{2-} were 1.12, 1.03, and 1.38 mg S l^{-1} for primary data, and 1.09, 1.12, and 1.18 mg S l^{-1} for normalized data, for the periods mentioned above.

We concluded that it is hard to demonstrate the generally assumed proportional relationship between the rate of emission and concentration and precipitation data. Moreover, the relationship is obscured by changes in sampling and analytical techniques, especially by the considerable increase of height of sources in case of SO_2. However, it seems well-based to conclude that, during the latter three decades in Europe, sulfur emissions increased by 4.3% yr^{-1}, SO_2 concentrations showed no increase; and the ratio between changes in sulfur emission and sulfate ion concentration has been, at most, 2:1.

3. On the "Natural" Acid Deposition and the Possible Consequences of Decreased SO_2 and NO_x Emission in Europe

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The aim of this paper is to find relationships between the wet (D_w) or total deposition (D) and the emission (Q) of a given region. By using the results of several box models for different regions or continents for sulfur compounds (SO_2, SO_4^{2-}), good empirical relationships were found between D_w/Q or D/Q and Q:

$$\log(D_w/Q) = -0.697 \cdot (\log Q) - 0.137 \qquad r = 0.96 \quad n = 17 \tag{3.1}$$

$$\log(D/Q) = -0.415 \cdot (\log Q) + 0.037 \qquad r = 0.92 \quad n = 14 \tag{3.2}$$

Although these relationships may be questioned theoretically, these good correlations nevertheless suggest that the ratio of deposition and emission strongly depends on the emission of a given region.

For oxidized nitrogen compounds, the ratios of D_w/Q and D/Q are nearly constants, i.e., D_w/Q and D/Q do not depend on Q in either global or regional scale. For nitrogen compounds (NO_x, HNO_3, NO_3^-), the following equations were determined:

$$D_w/Q = 0.4 \quad \text{and} \quad D/Q = 1 \tag{3.3}$$

Assuming that the formulas (3.1), (3.2), and (3.3) are valid for Europe we have calculated the natural level of deposition as well as the effects of an increase or decrease of S and N emission.

In *Figure 3.1* we depict the average European dry and wet depositions (in equivalent units) as a function of emissions. This figure represents the case when the European emissions of N and S oxides change proportionally. Dry deposition is a nearly linear function of Q; while wet deposition, especially at higher emission levels, depends less on the emission. At lower emission levels the importance of dry deposition is continuously decreasing, compared with that of wet deposition. If we reduce the European S and N emissions to their natural levels, dry deposition would become practically negligible, but wet deposition remains considerable (24 meq. m^{-2} yr^{-1}). This figure corresponds to an acidity of pH = 4.5 — which is acidity expected if sulfur and nitrogen compounds washed out by precipitation remain as acids in precipitation water.

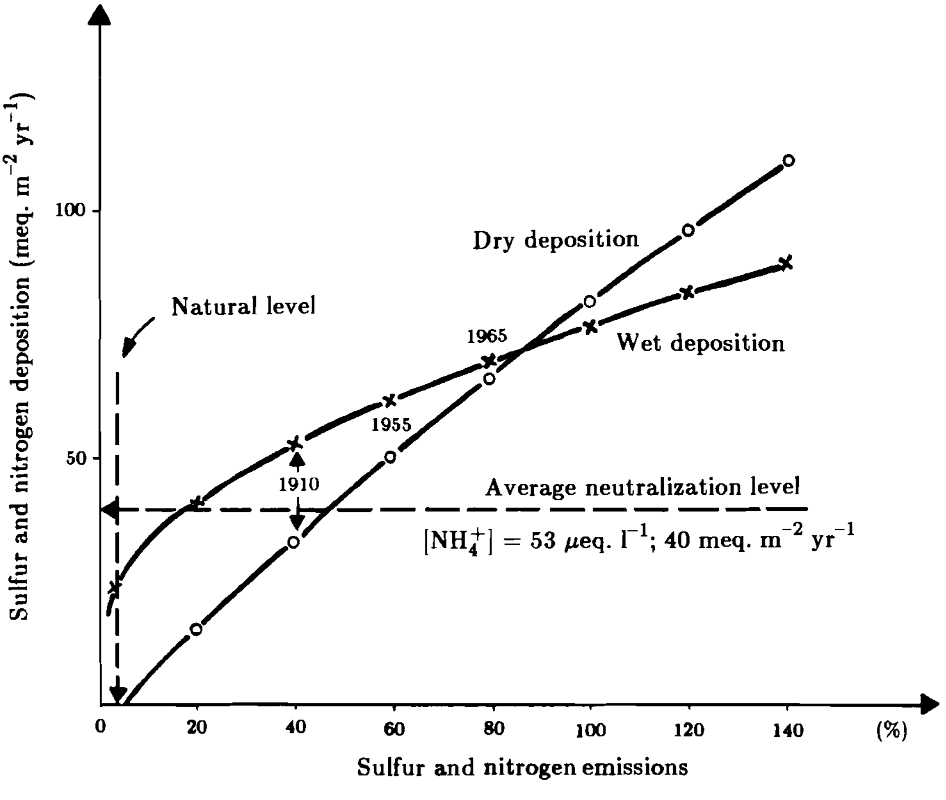

Figure 3.1. Relationship between sulfur plus nitrogen deposition and sulfur plus nitrogen emissions. Case I: sulfur and nitroten emissions changed proportionately.

Ammonia is a common neutralizing compound in the atmosphere. During neutralization ammonium is formed, with an average concentration in European precipitation of 53 μeq. l^{-1}. This figure corresponds to D_w = 40 meq. m^{-2} yr^{-1} wet deposition, which is higher than the calculated "natural" wet acid deposition. Atmospheric ammonia can neutralize not only the acids of natural origin, but also approximately 20% of man-made emission. We have to suppose, of course, that during the decrease of S and N emissions the flux rate of ammonia remains the same, an assumption supported by direct measurements. This means that in Europe we cannot speak about "natural" acidity of precipitation. Before industrialization, pH was probably controlled by atmospheric CO_2 at a level of pH ≈ 5.7.

Figure 3.2 displays the case when sulfur emission changes while NO_x emission remains at the present level. From this figure we can estimate what would happen if all the countries in Europe decreased their anthropogenic sulfur emissions by 30% (in which case the total sulfur emission would decrease by practically the same percentage). According to *Figure 3.2*, the average acidity of precipitation water in Europe would decrease by 8%, which would not solve the problems associated with acid rain (e.g., in lower Scandinavia). At the same time, dry deposition (and the atmospheric concentration of pollutants) would drop by 20% on average. We could also expect a total deposition decrease of only 14%. However, the export from Europe to the oceans and to other continents would be substantially (-64%) lower.

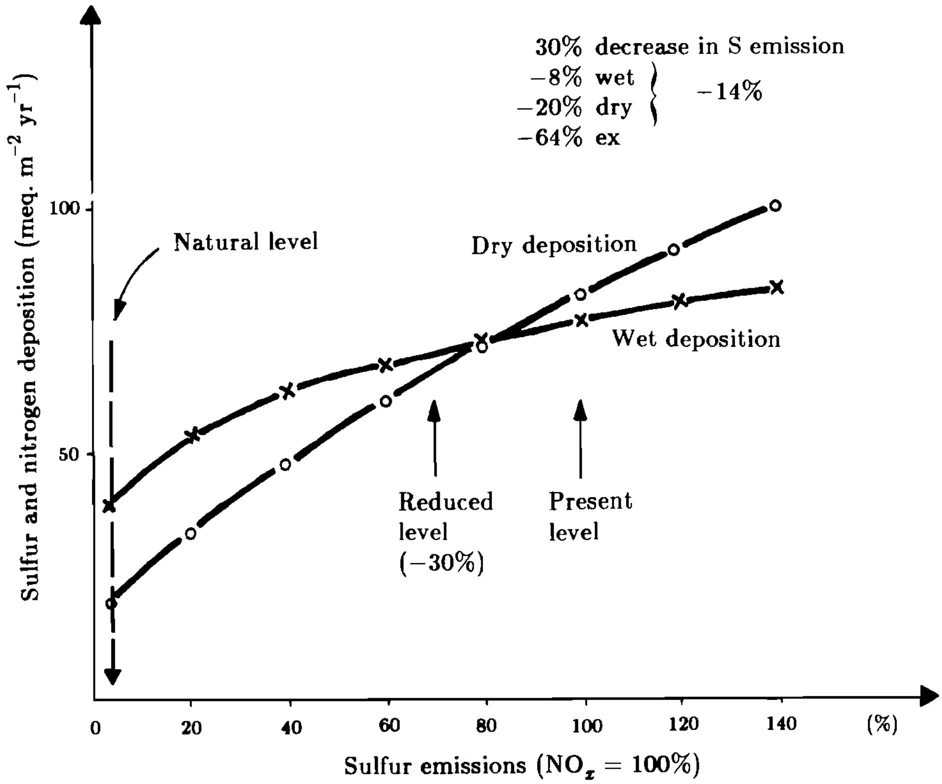

Figure 3.2. Relationship between sulfur and nitrogen depsition and sulfur plus nitrogen emission emissions. Case II: nitrogen emissions held constant but sulfur emissions changed.

4. Background Levels of Air and Precipitation Quality for Europe

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Background pollution may be defined, from the policymaking standpoint, as the initial condition from which the emission control strategy for a given area or region has to start. The measured or calculated value of background pollution includes contributions from natural sources and distant unidentified anthropogenic sources. While continental or regional background pollution contributes only 10–20% of the measurable average pollutant concentration in continental-scale simulations, the role of hemispheric background pollution is 30% to 70% greater. Clearly, the importance of background pollution increases when one moves from local to continental scale.

Assumptions of a model of background pollution

(1) Background pollution is receptor-oriented.
(2) Polluting processes (e.g., a regional plume) are source-oriented.
(3) Background pollution from a larger-scale pollution process is superimposed on the polluting effect of a smaller-scale process.
(4) Average emission density from local to global scales decreases several order of magnitude.

Generalized definition [Szepesi (1974, 1980, 1986)]

Air pollution originating from a larger-scale pollution process that takes place around or outside a more intense but smaller-scale process is called background pollution. The pollutant concentrations originating from the larger-scale process are superimposed on the more intense effect of the smaller-scale process. By following this principle global, hemispheric, continental, and regional background pollution can be defined.

Background precipitation quality

The concept of background pollution applies to precipitation quality as well as air quality. However, a distinction has to be made between sub-cloud and in-cloud transport and scavenging processes. That is, pollutants that escape from the mixed layer to the free atmosphere are transported as continental, hemispheric, and later as global background pollution. They are then usually removed by precipitation, which is superimposed on the effect of smaller-scale local pollution processes. This background pollution originating from larger-scale polluting processes includes both natural trace constituents and anthropogenic ones originating from very long-range transport. Based on this reasoning, we assumed that a multi-parameter regression analysis of long-term measured data would be capable of distinguishing between contributions from sub-cloud and in-cloud scavenging processes.

Results of multi-regression analysis

(1) For air and precipitation quality management, the contribution of background pollution must always be clarified and taken into account properly.

(2) Climate variability might have a significant interannual effect on the amount and spatial distribution of background pollution. This variability may increase, e.g., from the global to regional scales.

(3) Close correlation was found by multi-regression analyses between precipitation quality and gaseous or particulate species data. For continental Europe higher correlation was found than for Central Europe. The relationships were weaker for Northern Europe and especially for Southern Europe.

(4) When the relationships of precipitation quality with emission density were analyzed, poorer correlations and too-high background values were found.

(5) Some 67% of SO_2 over Europe originates from continental-scale anthropogenic sources.

(6) About 15% of precipitation sulfate over Europe comes from hemispheric background pollution.

(7) Only 18% of anthropogenic sulfur emission (22.5 Mt S y^{-1}) is wet deposited over Europe (west of 30°E).

(8) If some man-made sources over the whole continent are omitted, the hemispheric background concentration must be increased. This increased hemispheric background value is, e.g., 0.385 mg (SO_4^{2-}-S) l^{-1}.

(9) It is recommended the multi-regression analysis for NO_x be repeated when longer records of reliable particulate data are available.

5. Trend Analyses in the Time Series of Precipitation Acidity in Zagreb

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Metropolitan Zagreb, Yugoslavia's biggest industrial center, has nearly one million inhabitants, starting from about 250,000 inhabitants after World War II. The first measurements of the region's rainwater acidity were carried out 50 years ago, together with measurements of concentrations of several components suspended in daily rainwater samples. Several types of air chemistry research programs concerning pollutants in dry air and in precipitation in the post-war period were begun by different scientific and operational institutions in Zagreb. The data are only partly published in the open literature.

In 1967, the Institute for Physics of the Atmosphere of the Yugoslav Academy of Sciences and Arts in Zagreb began to measure precipitation acidity along with daily weather observations. The measurements were carried out first at three stations, and later two, becoming regular in 1969. Since 1974, the research has been conducted by the Geophysical Institute at the University of Zagreb. All measurements and research have been carried out by the same group of meteorologists, and the main approach to the problem has thus been meteorologically motivated. The first part of the pH data gathered since 1969 will be described here, emphasizing the quality of the annual mean values and the interannual variations of acidity.

Figure 5.1 shows the distribution of the stations: Zagreb-Grič (the city center, 45°49'N, 15°59'E, 157 m NN), Zagreb-Bijenik (north outskirts of the city), and Puntijarka (988 m high mountain top close to Zagreb).

During the first 11 years, measurements were taken regularly; lately, they have been carried out irregularly owing to limited technical facilities. Measurements were initially taken with a pH meter equipped with a glass and calomel electrode, produced by Iskra-Kranj. Since 1980, a pH meter with combined glass and calomel electrode has been used. Every scale reading was made with accuracy of 0.05 pH units, after the instrument pointer came to a rest. Water samples were collected with a polythene funnel in a 250 ml bottle from the same plastic material. The influence of the sample age on final results was analyzed.

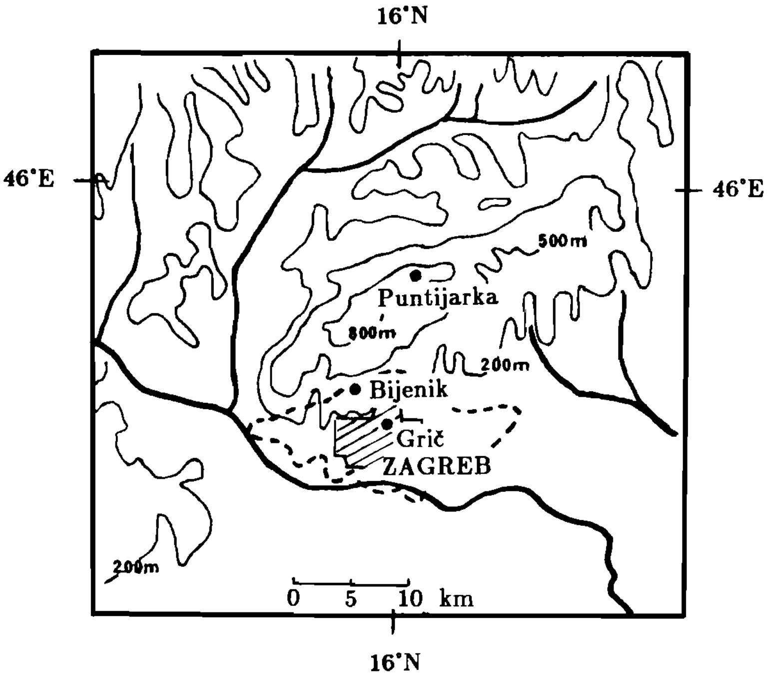

Figure 5.1. Location of precipitation acidity measurement stations in the Zagreb region.

Table 5.1 contains the weighted acidity mean values, together with extreme values, for the Zagreb-Grič station. The mean values were classified into four categories, according to sample age.

The precipitation in Zagreb is more acidic than the atmosphere when it is in equilibrium with atmospheric CO_2 (pH = 5.6).

The pH change from 5.3 to 4.9 or to 4.5 is lower than that measured in Western Europe. The trend toward the lower pH values in Zagreb data is seen both in extremes from year to year and in both stations. Minimum values decrease more steadily than maxima, but over a smaller range.

The values of mean pH derived from all the samples are somewhat higher than the values derived from fresh samples only. The differences, indeed, are not high, amounting to about 0.1 units at Grič and even less at Puntijarka. The amount is less than the observed interannual variation. In other words, the measured interannual changes are reasonable no matter how old the samples. *Table 5.1* also shows that in some years the number of fresh samples was 50% or less than the number of total samples, yet pH was close.

That natural acidity exceeds that emitted by Zagreb's urban environment leads to the conclusion that the region falls under the influence of acid pollution from distant pollution sources.

Table 5.1. Annual mean precipitation acidity values[a], derived from the daily samples for several sample age categories, Zagreb–Grič.

	Fresh samples		*Up to 3 days*		*Up to 7 days*		*All samples*										
Year[b]	$\overline{pH}$	N_0	$\overline{pH}$	N_3	$\overline{pH}$	N_7	$\overline{pH}$	N_T	N	$\frac{N_T}{N}$ (%)	RR_{pH}	RR	$\frac{RR_{pH}}{RR}$ (%)	pH_{min}	*S*	pH_{max}	*S*
1969	5.05	55	5.06	117	5.09	135	5.09	138	155	89	841	952	88	4.3	Wi	7.5	Wi
1970	4.98	18	5.06	66	5.01	90	5.11	109	153	71	953	1031	92	4.2	Wi	7.9	Su
1971	5.46	10	5.09	46	5.29	73	5.37	90	138	65	526	616	85	4.2	Wi	7.9	Su
1972	4.84	37	4.96	114	5.01	141	5.01	151	157	96	977	1062	92	3.9	Sp	8.4	Sp
1973	4.83	20	4.91	55	4.93	71	5.00	86	124	69	520	607	86	3.9	Wi	7.4	Su
1974	4.91	42	4.90	82	4.91	99	4.95	111	152	73	893	1085	82	4.3	Wi	8.5	Su
1975	4.80	36	4.89	70	4.92	76	4.98	90	136	66	558	745	75	4.1	Au	7.4	Sp
1976	4.90	40	4.94	76	5.00	84	5.01	86	146	59	580	819	71	4.0	Au	7.7	Au
1977	5.02	30	5.02	69	5.01	81	5.06	93	138	67	729	956	76	4.0	Sp	8.3	Su
1978	5.13	34	5.21	65	5.26	77	5.26	83	157	53	381	781	49	4.1	Su	7.3	Au
1979	5.01	37	5.22	69	5.18	83	5.19	95	148	64	762	915	83	4.4	Wi	8.2	Wi
1980	5.00	28	4.99	64	4.99	79	5.05	96	158	61	765	979	78	4.0	Wi	7.6	Wi
1981	5.26	2	5.28	11	5.28	19	5.28	25	134	19	231	899	28	4.5	Wi	7.0	Su
1982	4.85	14	4.78	46	4.89	58	4.86	70	130	54	601	799	75	3.9	Au	7.6	Su
1983	4.97	7	4.82	23	4.72	31	4.74	56	107	52	482	724	67	3.8	Wi	7.3	Sp
1984	4.24	12	4.25	32	4.32	46	4.49	83	147	56	609	938	65	3.7	Wi	7.5	Sp
1985	4.70	20	4.84	58	4.66	81	4.60	96	x	x	719			3.8	Wi	7.1	Au

[a]

$$\overline{\mathrm{pH}} = -\log \frac{\sum_i RR_i[\mathrm{H}^+]_i}{\sum_i RR_i}$$

N_0, N_3, N_7, N_T = Number of daily samples up to 0, 3, and 7 days old, and total samples.

N = annual total of rainy days with $RR \geq 0.1$ mm.

RR_{pH} = annual total of precipitation composed from the samples for which pH was measured (mm).

RR = annual total of precipitation (mm).

S = season.

[b] Values for 1980–1985 are preliminary.

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PART II.

Ammonia and its Implications for Linearity

6. Emissions of Ammonia and Their Role in Acid Deposition

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Ammonia emissions can play an important role in altering oxidation and deposition systematically on a regional basis. The dominant sources of ammonia are agricultural — mainly livestock wastes, with increased fertilizer applications now contributing a small proportion. An emission inventory prepared for England and Wales, with a 10 km grid resolution using 1981 agricultural census data, implies that some 300 kilotons of NH_3 were contributed per year, by the following sources:

Cattle	182
Sheep	62
Poultry	25
Pigs	19
Horses	2
Fertilizer	12
Total NH_3	302

Not only were there large variations across regions of the country, but diurnal and seasonal emissions also fluctuated widely:

December–February	56
March–May	97
June–August	73
September–November	75

Agricultural records suggest that emissions of ammonia probably increased by about 50% between 1950 and 1980 over Europe as a whole; but in some countries, such as the Netherlands and Belgium, emissions have at least doubled, whereas in others there is little change or even a slight reduction. Emission densities also vary considerably (see *Table 6.1*).

The reported emissions represent average fluxes, a meter or so above the ground, from fields with livestock or nitrogen applications acting as highly

Table 6.1. Trends in emissions of NH_3 from livestock (1950–1980).

Country	*Area* (10^3 km^2)	*Emissions* (10^3 tons) *1950*	*1960*	*1970*	*1980*	*% change* *1950–1980*	*Emissions* (tons per km^2)
Austria	83	49	53	56	61	24	.73
Belgium	30.5	40	57	67	75	88	2.46
Bulgaria	110	–	55	54	74	(34)	.67
Czechoslovakia	128	–	101	98	119	(18)	.93
Denmark	42.5	68	83	79	84	24	1.98
Finland	333	40	39	39	37	-7	.11
France	544	337	409	449	527	56	.97
Germany, F.R.	250	243	286	333	357	47	1.43
GDR	108	78	115	131	148	90	1.37
Greece	129	32	47	40	43	34	.33
Hungary	92	60	59	62	69	15	.75
Ireland	68	91	105	129	146	60	2.14
Italy	298	199	215	232	218	9	.73
Netherlands	41	54	77	100	127	135	3.10
Norway	324	29	28	25	26	-10	.08
Poland	313	159	213	256	310	95	.99
Spain	499	–	148	153	160	(8)	.32
Sweden	444	55	54	44	46	-16	.10
Switzerland	41	32	38	42	46	43	1.12
UK	244	236	321	336	366	55	1.49
Yugoslavia	253	140	149	137	132	-6	.52
Total Europe		2360	2850	3110	3450	46	

concentrated sources. The fate of such emissions, once they enter the atmosphere, is varied and complex, as shown in *Figure 6.1.* Much of the NH_3 will be transformed to NH_4, either by direct reaction with acidic species or by absorption within cloud droplets where uptake and oxidation of SO_2, in particular, are enhanced.

This has important implications for oxidation rates of SO_2, which can increase by an order of magnitude in mist and cloud. This has been observed in the Teesside smogs; and in experiments with aircraft monitoring the passage of sulfur emissions across the UK, after a very large deposition of sulfur was spotted over the cloud-capped hills of Wales, downwind of high ammonia-emitting regions.

Thus, although emitted in insufficient quantities to neutralize all sulfate and nitrate, ammonia can induce significant systematic and highly nonlinear concentrated deposition of acid species on a localized basis. On a seasonal basis, too, concentrations of sulfate in precipitation are higher over much of Europe in spring, which might be related to the peak in ammonia emissions in that season. Increases in ammonia emissions will likely expand the oxidation potential and wet removal of sulfur on an absolute basis, though it is difficult to confirm this from long-term trends that are subject to many simultaneous changes.

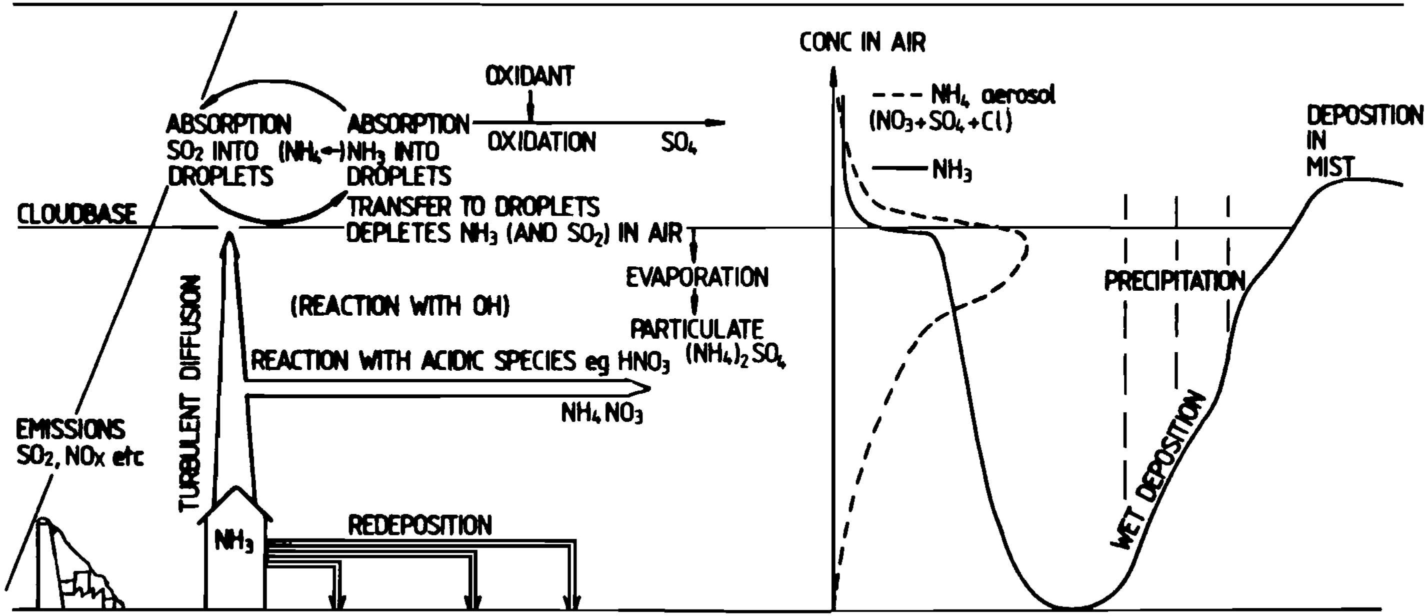

Figure 6.1. The fate of ammonia emissions into the atmosphere.

7. Ammonia Emission and Wet Deposition Flux of Ammonium in Europe

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Ammonia and ammonium are important atmosphere constituents, for which the atmospheric cycle is still poorly understood. Ammonia is the major acid-neutralizing substance in the atmosphere. However, both ammonia and ammonium are involved in the acid rain problem, because:

(1) Ammonia increases the pH of cloud water, thereby influencing the oxidation rate of sulfur dioxide.
(2) High atmospheric ammonia concentrations, i.e., in the vicinity of large cattle breeding areas or areas with intensive livestock breeding, cause direct damage to vegetation.
(3) There is evidence that dry deposited ammonia enhances the dry deposition rate of sulfur dioxide.
(4) In the soil ammonia and ammonium can be oxidized to nitric acid, thereby acidifying the soil.

We present here some materials that can be used for a better understanding of the atmospheric ammonia cycle.

Emission of NH_3

Our ammonia emission survey includes 26 European countries (of which the USSR is partly considered) plus Turkey. Ammonia emissions were estimated separately for three source types: domestic animals, fertilizers, and fertilizer (and related) plants. Emissions have been calculated using two grid systems: the IE-grid system with grid elements of 75 × 75 km^2 at 60°N; the EMEP grid system with grid elements of 150 × 150 km^2 at 60°N (Buijsman *et al.*, 1984). These emission data can thus easily be used in the modeling of the long-range transport of ammonia and ammonium (see Chapter 8 by Asman and Janssen in this Report).

The most important source of atmospheric ammonia is the decomposition of livestock wastes. Animal types considered include cattle, pigs, horses, sheep, and poultry. For some countries goats, mules, donkeys, and even camels have also been considered. The numbers of animals were taken from agricultural statistics, which, we assumed, would give the most spatially detailed information possible. Manure and N-production in relation to animal type and age (or weight) were derived from the information given by the Commission of the European Communities (1978), Nielsen (1984), and Sommer *et al.* (1984). Actual ammonia emissions were calculated by means of the factors proposed by Buijsman *et al.* (1985). Average N production and NH_3 emissions for different animals are shown in *Table 7.1.*

Table 7.1. N production and NH_3 emission by animals (kg N or kg NH_3 yr^{-1}).

Animal	*N production*[a]	*NH_3 emission*[a]
cattle	64	18
pigs	13	2.8
poultry	0.48	0.26
horses	34	9.4
sheep	12	3.1

[a] Average values, based on average age distribution within a category.

Ammonia emission from fertilizers was estimated by using the factors given by Fenn and Kissel (1974) and Fenn *et al.* (1981a, b). These factors range from 1% to 15% of the applied amount of nitrogen, depending on the fertilizer type. Fertilizer consumption data were taken from agricultural statistics. Ammonia emissions from fertilizer (and related) plants appeared to be of minor importance. We assumed emission factors for the different plants ranging from 0.8 to 15 kg NH_3 for each ton of produced substance. Ammonia emissions for some selected countries are given in *Table 7.2. Figure 7.1* shows the emissions in the IE-grid for the total area considered.

Table 7.2. Ammonia emission and emission densities in some European countries (kt NH_3 yr^{-1} or t NH_3 km^{-2} yr^{-1}).

Country	*Domestic animals*	*Fertilizers*	*Industrial sources*	*Total*	*Emission density*
Denmark	87	23	1	111	2.6
FRG	329	35	6	361	1.5
France	569	130	9	709	1.3
GDR	159	42	6	207	1.9
Hungary	83	42	4	130	1.4
Italy	252	101	7	361	1.2
Netherlands	128	12	8	148	3.9
UK	307	90	7	405	1.6
Europe	5241	1091	101	6432	0.8

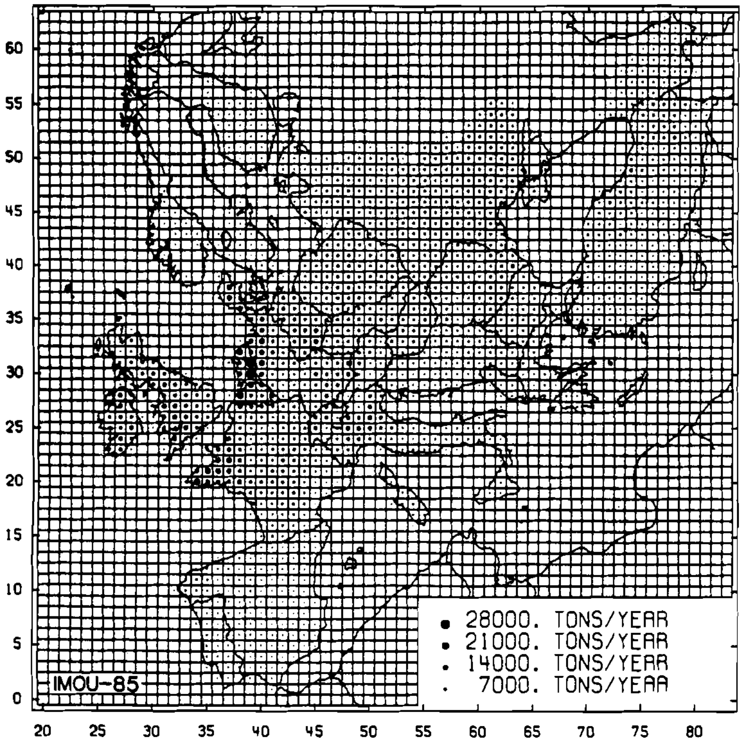

Figure 7.1. Anthropogenic ammonia emissions in Europe in 1982. Relative scale, IE-grid.

Wet deposition flux of NH_4^+

The wet deposition flux of NH_4^+ was estimated by using data on ammonium concentrations in precipitation for 216 measuring sites throughout Europe. We used information from two Europe-wide, six national, and ten local precipitation networks; and we required that at least one full year of measurements from each site. Unfortunately, several different kinds of measurement techniques were used: bulk or wet-only samplers, sampling periods from one day to one month, sample bottles protected against light, etc. On the basis of scarce experimental evidence, we have tried to make the available data comparable, using correction factors ranging from 0.75 to 1.21 (Buijsman and Erisman, 1986).

The resultant deposition field is shown in *Figure 7.2*. In the area bounded by latitudes 45°N and 65°N and by longitudes 10°W and 20°E, ammonia deposition amounted to approximately 1.9 Mt NH_4 yr^{-1}. On the one hand, this exceeds the value of 1.7 Mt given by Söderlund (1977); on the other hand, it is much lower than the 2.7 Mt value, which can be derived from EMEP data (EMEP/CCC, 1984).

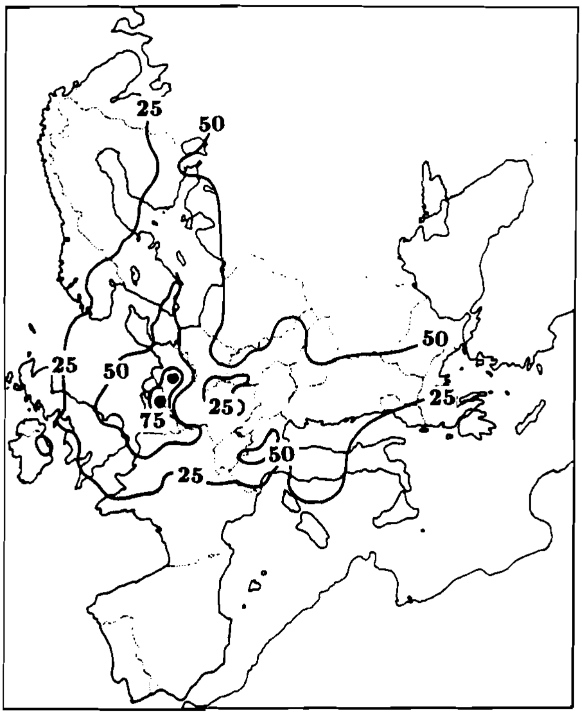

Figure 7.2. Wet deposition flux of ammonium in Europe (10^{-3} mol m^{-2} yr^{-1}).

Conclusions

At a minimum, our results highlight what is still missing from our understanding of the NH_3 cycle:

(1) Serious uncertainty still exists about real emission factors. Our estimate is probably a conservative one and could be at least 30% too low.

(2) Dramatic changes can occur in the ammonium concentration in precipitation after sampling, which seriously obscures realistic estimates of the wet deposition flux of ammonium.

In view of the foregoing we are currently unable to judge whether a change in ammonia emissions produces a linear change in ammonia deposition. As a rough estimate, the dry deposition flux of ammonia in the same area we considered for wet deposition flux could be approximately 1.0 Mt NH_3. This leads to the puzzling conclusion that the deposition in this area — about 2.9 Mt NH_3 — is nearly equal to the emission.

Acknowledgments

Great concern by the Air Directorate of the Netherlands Ministry of Housing, Physical Planning and Environment and by the Commission of the European Communities over the acidifying properties of NH_3/NH_4 made this research financially possible.

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8. A Long-Range Transport Model for Ammonia and Ammonium for Europe

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Many aspects of the atmospheric behavior of ammonia differ from the atmospheric behavior of sulfur dioxide. The emission of ammonia is caused by widespread and often discontinuous sources. Emission can occur from surfaces that also act as a sink at times. Once deposited, ammonia can be reemitted, depending on the airborne ammonia concentration and the ammonia concentration at the surface. As most ammonia is emitted from sources near ground level, measured ammonia concentrations can be influenced considerably by nearby emissions. As a result, the measured concentration is often not representative for a large area, which hinders verification of model results. Ammonia not only converts to relatively stable forms, as does, for example, sulfur dioxide, but the reverse reaction from ammonium to ammonia can occur as well. Very few measurements exist for ammonia and ammonium in the air, which makes it difficult to tune the model. Fortunately, the ammonium concentration in precipitation is measured at many stations, although these measurements are not always of good quality.

We applied a Lagrangian receptor-oriented model of the EMEP type (Eliassen, 1978). Values of the model's parameters were derived from a detailed numerical reactive diffusion model using K-theory, similar to PLUVIUS (Easter and Hales, 1984). Apart from the local dry deposition of ammonia, we introduced measures of additional local dry deposition of ammonium and effective dry deposition velocities. The product of the effective dry deposition velocity and the height-averaged concentration computed in the model gives the deposition rate. This deposition rate is equivalent to the product of the concentration at reference height (1 m) and the real dry deposition velocity. In this way we take into account a vertical concentration profile, which is caused by the fact that the deposition occurs at the earth's surface.

Table 8.1 shows the parameter values used in the model, where I is the rainfall rate (m s^{-1}). In *Figure 8.1* the *computed* ammonium concentrations in precipitation are shown (not including the background level of about 5 μ mole l^{-1}).

Table 8.1. Parameter values used in the model.

Symbol	*Explanation*	*Parameter value*
V_1	Dry deposition velocity for NH_3	8.0×10^{-3} m s^{-1}
V_{1e}	Effective dry deposition velocity for NH_3	5.6×10^{-3} m s^{-1}
V_2	Dry deposition velocity for NH_4^+	1.0×10^{-3} m s^{-1}
V_{2e}	Effective dry deposition velocity for NH_4^+	1.0×10^{-3} m s^{-1}
S_1	Scavenging ratio for NH_3	$5000.I^{-0.36}$ (mole m^{-3} prec)/(mole m^{-3} air)
S_2	Scavenging ratio for NH_4^+	$5000.I^{-0.36}$ (mole m^{-3} prec)/(mole m^{-3} air)
k	Pseudo first-order reaction rate NH_3 to NH_4^+	8.0×10^{-5} s^{-1}
α_1	Additional local dry deposition of NH_3	2.4×10^{-1}
α_2	Additional local dry deposition of NH_4^+	8.6×10^{-3}
β	Apparent part of the emission as NH_4^+	9.2×10^{-2}
h	Mixing height	800 m

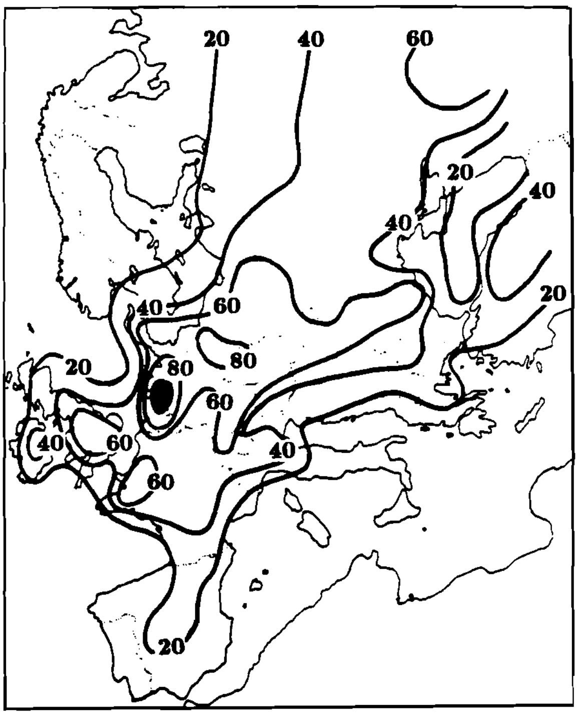

Figure 8.1. Computed ammonium concentration (micromole l^{-1}).

In *Figure 8.2* the *measured* ammonium concentrations are shown. In *Figure 8.3* the relation between computed and measured ammonium concentrations in precipitation is shown for average concentrations for 90 EMEP-grid elements. The correlation coefficient appears to be 0.73.

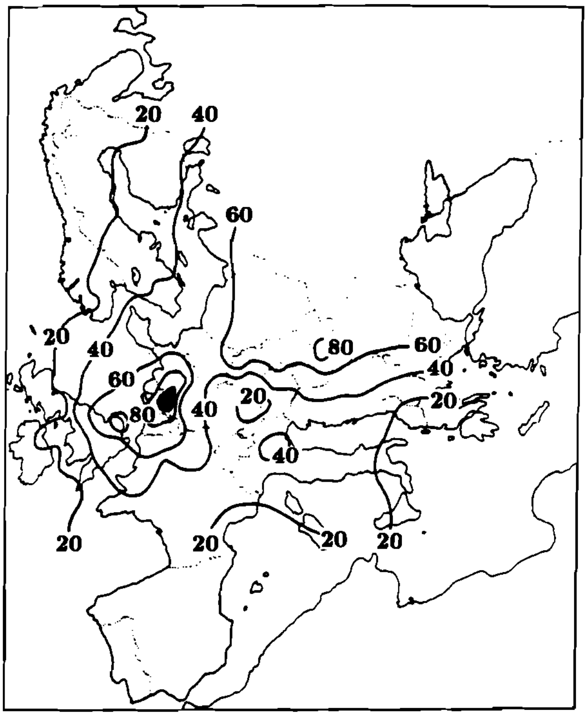

Figure 8.2. Measured ammonium concentration (micromole l^{-1}).

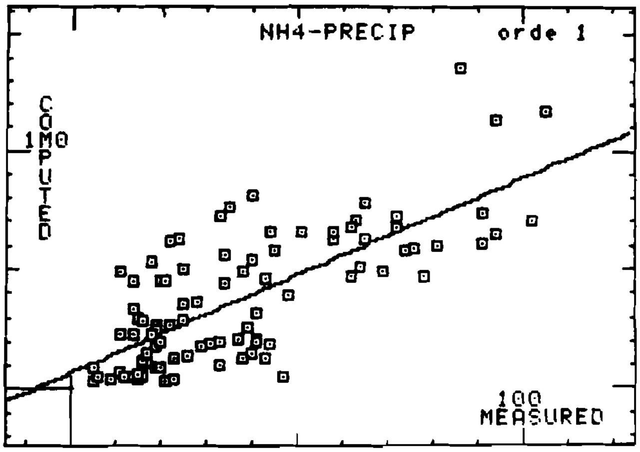

Figure 8.3. Computed versus measured ammonium concentrations (micromole l^{-1}).

Acknowledgment

The trajectories and precipitation fields were obtained from Prof. Dr. Eliassen and Dr. J. Saltbones, Norwegian Meteorological Institute (EMEP).

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PART III.

Modeling with Emphasis on Chemistry

9. Production of Nitric Acid in the Atmosphere under Various Conditions

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In the atmosphere transformations of nitrogen compounds are controlled by complicated nonlinear interactions. Therefore, only complex mathematical models can describe the relations between emission, concentration, and deposition.

We present here results from a model, which computes nitric acid production as a function of NO_x and hydrocarbon (HC) emissions, meteorological variables, and photooxidant chemistry. The model is applied to a hypothetical situation in which an air mass enters a city at 10:00 hours, remains for 2 hours, and continues over rural territory for an additional 18 hours. During this trajectory, the air parcel is assumed to be under a clear sky and to have daily variations of temperature and humidity similar to those typical of July in Budapest. We investigated the effect of eight different combinations of NO_x and HC emissions on nitric acid formation during this hypothetical meteorological situation. These combinations, or "scenarios", are shown in *Table 9.1.* For the urban calculations, conditions similar

Table 9.1. Factors assumed for the urban emission cases.

Case	*NO_x emission*	*Aliphatic HC emission*	*Aromatic HC emission*
A	1	1	1
B	1.5	1	1
C	1	1.5	1
D	1	1	1.5
E	1.5	1.5	1
F	1.5	1	1.5
G	1	1.5	1.5
H	1.5	1.5	1.5

to Budapest were used; for the rural calculations, "typical" European background conditions were used.

Figure 9.1 compares nitric acid production for the 20-hour simulation period resulting from emission cases C, D, and G with reference case A. In all these cases, NO_x emissions are held constant. The production of nitric acid is seen to be strongly dependent on HC emission. *Figure 9.2* shows results for cases E, H, and F compared to reference case B. Again, NO_x emissions are held constant, but at a higher level than in *Figure 9.1*, and again HC emissions have an important influence on nitric acid production.

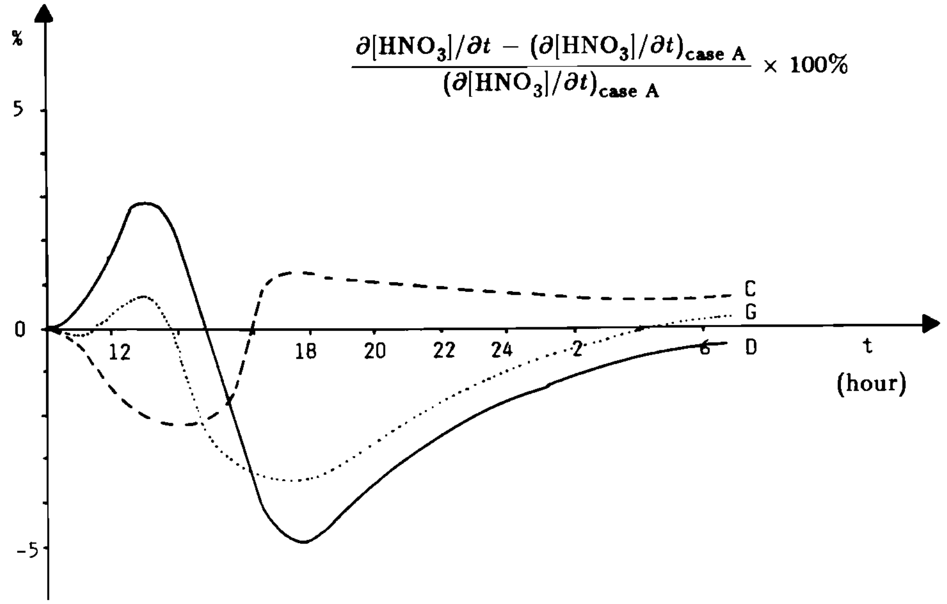

Figure 9.1. Relative changes in the rate of nitric acid production of emission cases C, D, and G, compared with reference case A.

In *Figure 9.3* the overall relative reaction rate for nitrogen oxide–nitric acid transformation is presented for cases A, B, and background conditions as a function of time. The overall relative rate of nitric acid production is seen to vary in a wide range, depending on the general composition of the atmosphere. This implies that there is no linear relation between the rate of the nitric acid production and the nitrogen oxide concentration. The time dependence of the relative transformation rate is also significant. Since the production rate and the concentration of nitric acid are influenced by the hydrocarbon emission, we believe that no overall relative transformation rate for general use in the transport models of nitrogen compounds can be recommended, at least for the case studies.

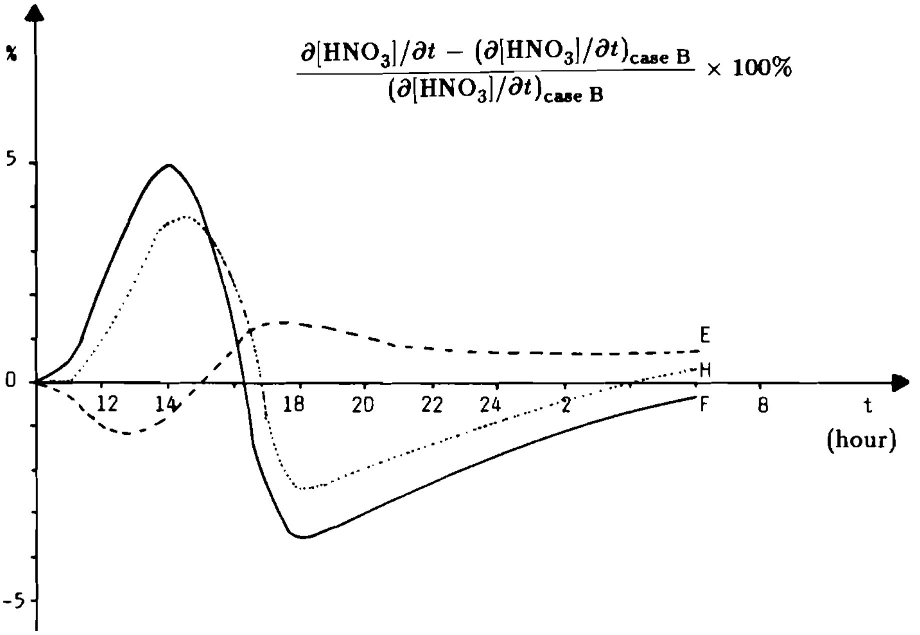

Figure 9.2. Relative changes in the rate of nitric acid production of emission cases E, F, and H, compared with reference case B.

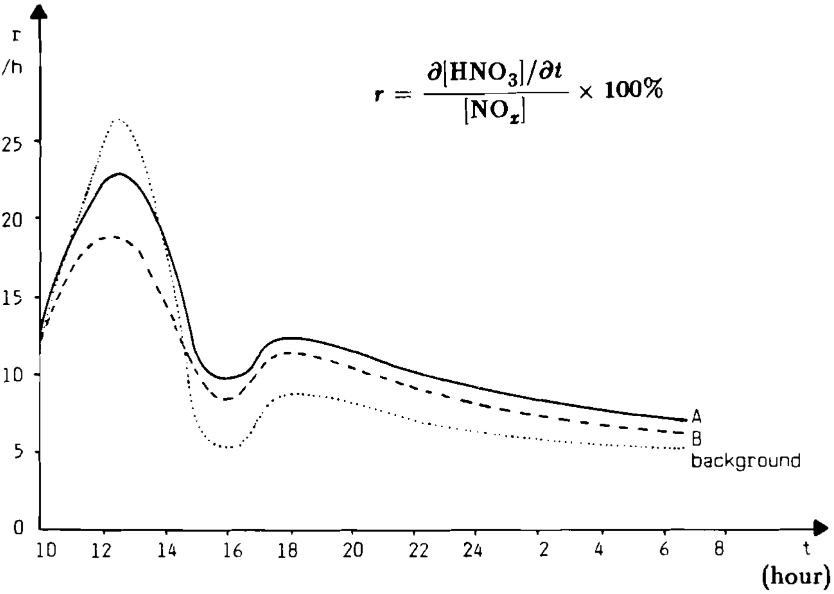

Figure 9.3. The overall relative reaction rate of $NO_x \rightarrow HNO_3^=$ transformation for three cases.

10. Chemical Aspects of the SO_2 Proportionality Issue

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Atmospheric oxidation of sulfur dioxide plays a crucial role in determining the pattern of sulfur deposition as both the dry deposition velocities of sulfur dioxide and sulfate aerosol and their wet removal efficiencies differ markedly.

Under dry conditions, the major oxidation route is via reaction with the hydroxyl radical [equation (10.1)]. SO_2 is not a significant sink for OH and, hence, sulfate production and sulfur deposition are proportional to atmospheric SO_2 concentration and to SO_2 emissions.

$$SO_2 + OH \longrightarrow HSO_3 \xrightarrow{O_2} SO_3 + HO_2 \tag{10.1}$$

The solubility of SO_2 in water is low and, for substantial removal by wet deposition, oxidation to sulfate must occur [equation (10.2)].

$$SO_2 \rightleftarrows H^+ + HSO_3^- \xrightarrow{\text{oxidant}} 2H^+ + SO_4^{2-} \tag{10.2}$$

The main routes for sulfate production in water droplets involve hydrogen peroxide and ozone.

For oxidation by hydrogen peroxide, the rate of depletion of gaseous SO_2 is given by equation (10.3):

$$\frac{d}{dt}[SO_2]_g = -k[H_2O_2]_g\,[SO_2]_g \tag{10.3}$$

This reaction is a major sink for H_2O_2 and, as the replenishment of oxidant is slow, the SO_2 oxidized is limited to an amount equivalent to the initial H_2O_2 concentration. Under most circumstances in Europe, SO_2 concentrations greatly exceed those of hydrogen peroxide and, hence, substantial nonproportionalities in wet deposition would be expected from this route.

The rate of SO_2 depletion via oxidation by ozone in water droplets is given by equation (10.4). As H^+ concentrations depend on the amount of sulfate produced, the rate of removal is markedly nonproportional.

$$-\frac{d}{dt}[SO_2]_g = \left[\frac{k_1}{[H^+]} + \frac{k_2}{[H^+]^2}\right][SO_2]_g[O_3]_g \qquad (10.4)$$

Nonproportional kinetics do not necessarily produce nonproportional long-term average wet deposition, however. If the rates are such that most of the SO_2 is removed during the timescale of the precipitation event, reductions or modest increases in airborne concentrations will result in a different temporal behavior during a given event, but will produce an overall removal that is proportional to the airborne concentrations. As the average wet deposition at a given receptor reflects the mean concentration of an ensemble of events, this could also be proportional to airborne concentrations.

A simple model has been developed to investigate some of the parameters influencing the efficiency of wet removal of airborne sulfur and the proportionality of wet deposition for air quality conditions representative of the range of situations in Europe.

Physical model

A simple model of average conditions in a precipitation system was adopted, equivalent to a closed vessel containing the airborne species and liquid water (defined by liquid water content) from which solution could be withdrawn (equivalent to precipitation) and fresh water added (equivalent to condensation).

The calculations considered a parcel of air initially filling a 1-km boundary layer that is mixed instantaneously and uniformly with a 3 km of air in the free troposphere. This defined the initial conditions in the precipitation system, which was subject to no further external influences. Liquid water content (LWC) was assumed to be instantly established and to remain constant during the event. The assumption of complete homogeneity in the system allowed the concentration losses due to precipitation to be treated as a first-order process with a rate constant equal to (condensation rate)/LWC.

A liquid water content of 0.44 g m^{-3} and a condensation/precipitation rate of 6.3×10^{-5} g m^{-3} s^{-1} were adopted. These values are typical for a synoptic scale updraft of 0.1 m s^{-1}. A timescale of 20,000 s was assumed, corresponding to 5 mm of precipitation during an event.

Chemical model

Airborne species considered were SO_2, sulfate, nitrate, ammonium, and the oxidants ozone and hydrogen peroxide. Sulfate and nitrate were taken to be in the initial form of acid and ammonium in the form of NH_3. These species were assumed to dissolve instantly in the atmospheric liquid water.

It was assumed that hydrogen peroxide reacted instantly to form an equivalent amount of sulfuric acid. Oxidation by ozone was presumed to be governed by equation (10.4), where k_1 and k_2 are composites of the Henry's Law rate constants for SO_2 and O_3. Loss of dissolved species was expressed as a first-order process with rate constant 1.4×10^{-4} s^{-1}.

The equations for the rate of chemical conversion and loss from the system form a set of first-order ordinary differential equations, which were solved using a Gear algorithm.

Model inputs

Composite rate constants k_1 and k_2 are inversely temperature-dependent, and a mean temperature of 273 K was assumed. While this may be high for winter conditions, this is compensated for by the time spent in the unreactive ice phase at lower temperatures.

Mean "summer" (April–September) concentrations of ozone and hydrogen peroxide in the boundary layer of 2.2×10^{-9}M (50 ppb) and 2×10^{-11}M (0.5 ppb), respectively, were assumed. These are compatible with measurements and modeling studies for European conditions. The same mixing ratios were assumed for free tropospheric air, and "winter" concentrations were taken to be half the "summer" values.

Input concentrations of sulfur species HNO_3, and NH_3 for three types of air quality — remote, "average" European, and high NH_3 — were derived from EMEP data, over the period 1978–1982, for sites N1, A2, and H5, respectively.

The frequency distributions of total airborne sulfur concentrations in the boundary layer are shown in *Figures 10.1–10.3* for winter, and *Figure 10.4* shows the summer values for site A2. H5 and A2 show similar distributions with significant contributions of daily averages higher than 20 ppb, whereas the N1 distribution moves to significantly lower concentrations. Summer distributions also move to lower concentrations. It was assumed that the airborne SO_4^{2-}/total S ratio for each site is independent of total S concentration, and mean values, derived from EMEP data, for "summer" and "winter" are shown in *Table 10.1.*

A mean "background" concentration of sulfate in rain of 12 μM was assumed, and this was converted to an initial concentration using the model deposition constant. A value for background nitrate and ammonium was derived from EMEP low-concentration data, and the NO_3^-/SO_4^{2-} and NH_4^+/NO_3^- ratios are also shown in *Table 10.1.* The background values were subtracted from EMEP data to obtain information on possible relationships between initial airborne S, HNO_3, and NH_3 in the boundary layer. Expressions derived from statistical analyses for each site and season are shown in *Table 10.1.*

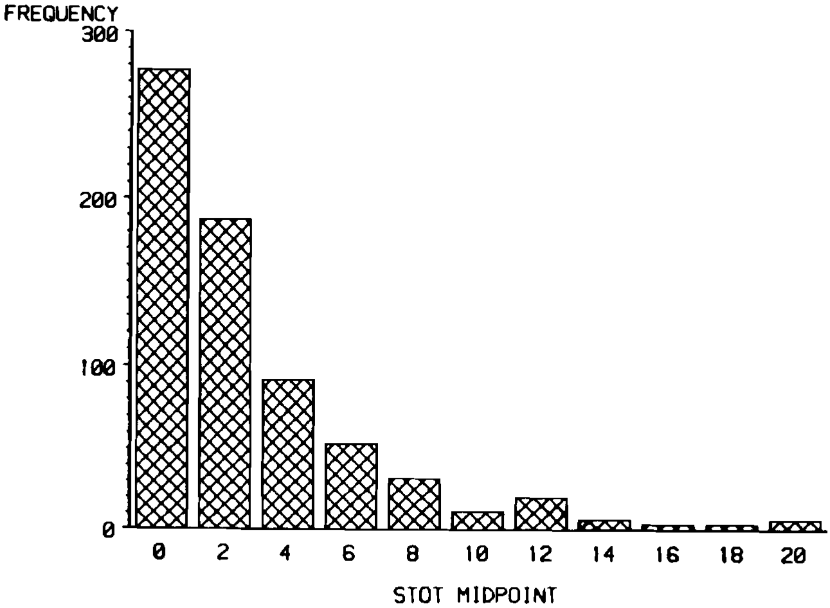

Figure 10.1. Frequency distribution of total airborne sulfur (nM/100), Site N1, winter.

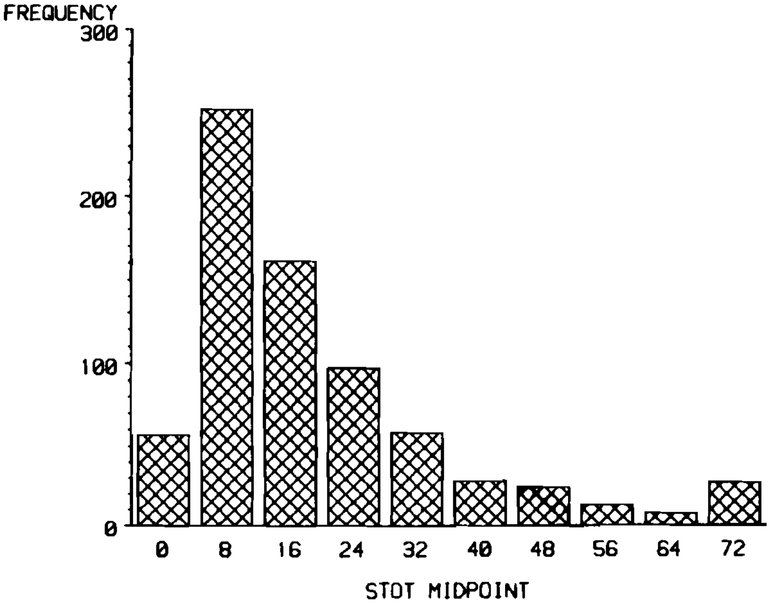

Figure 10.2. Frequency distribution of total airborne sulfur (nM/100), Site H5, winter.

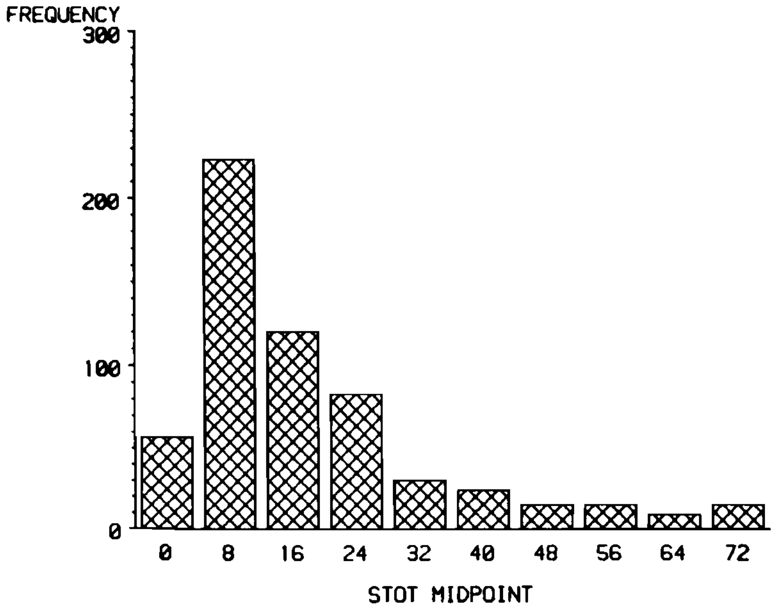

Figure 10.3. Frequency distribution of total airborne sulfur (nM/100), Site A2, winter.

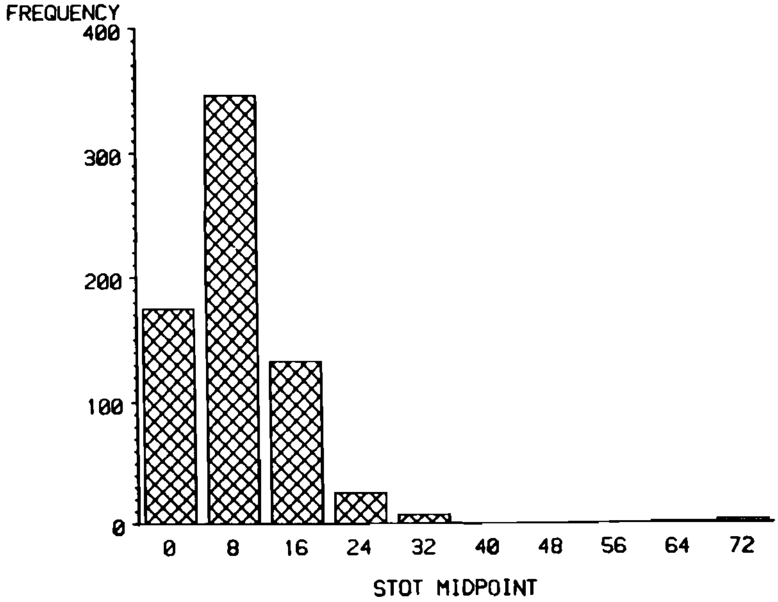

Figure 10.4. Frequency distribution of total airborne sulfur (nM/100), Site A2, summer.

Table 10.1. Airborne concentration relationships.

Site	*Season*	$\frac{SO_4^{2-}}{Total\ S}$	$\frac{HNO_3}{Total\ S}$	NH_3/M
Background		1.0	0.9	$0.6\,[HNO_3]$
N1	Summer	0.60	0.9	$1.2\,[HNO_3] + 1.1 \times 10^{-11}$
N1	Winter	0.45	0.9	$[HNO_3] + 1.4 \times 10^{-11}$
H5	Summer	0.29	0.7	$0.96\,[HNO_3] + 8.9 \times 10^{-11}$
H5	Winter	0.21	0.4	$1.5\,[HNO_3] + 8.1 \times 10^{-11}$
A2	Summer	0.43	0.6	$[HNO_3] + 3.3 \times 10^{-11}$
A2	Winter	0.29	0.6	$0.71\,[HNO_3] + 5.3 \times 10^{-11}$

Model calculations were performed for the input conditions in *Table 10.1* and also for cases where initial S and HNO_3 were halved.

Results and discussion

Sulfur dioxide removal efficiency as a function of initial boundary layer airborne sulfur concentration for the six cases considered is shown in *Figure 10.5.*

For N1 and A2, substantial inefficiency is predicted for airborne concentrations > 2 ppb. SO_2 removal efficiency is much higher in summer than in winter for N1 and A2. This reflects the effects of higher oxidant levels and a more favorable neutralizing capacity ($NH_3 - HNO_3$) for summer conditions, which allow a greater conversion to produce the same pH. The small seasonal difference for H5 is due to the more favorable neutralizing capacity in winter.

Total sulfur removal efficiency as a function of airborne sulfur is shown in *Figure 10.6.* Higher conversions of SO_2 and higher initial sulfate fractions for summer conditions produce substantial seasonal differences for N1 and A2. For H5, which had lower sulfate fractions and smaller seasonal differences in this fraction, efficiency shows less seasonal variation.

Overall efficiencies of SO_2 and total S removal for the airborne concentration distribution in each case are shown in *Tables 10.2*, *10.3*, and *10.4* for N1, H5, and A2, respectively. The predicted efficiencies for N1 are particularly high owing, in part, to the high weighting of low-concentration events; and the low values for H5 and A2 are the significant result of occasions of very high airborne sulfur to the mean airborne sulfur.

The long-term average compositions for the input frequency distribution, which are equivalent to mean precipitation composition, are also shown in *Tables 10.2–10.4* together with precipitation-weighted mean concentrations derived from the EMEP data set. A comparison of these results indicate that concentrations produced by the model are reasonable. It is also interesting to note the significant charge imbalance in the measurement data.

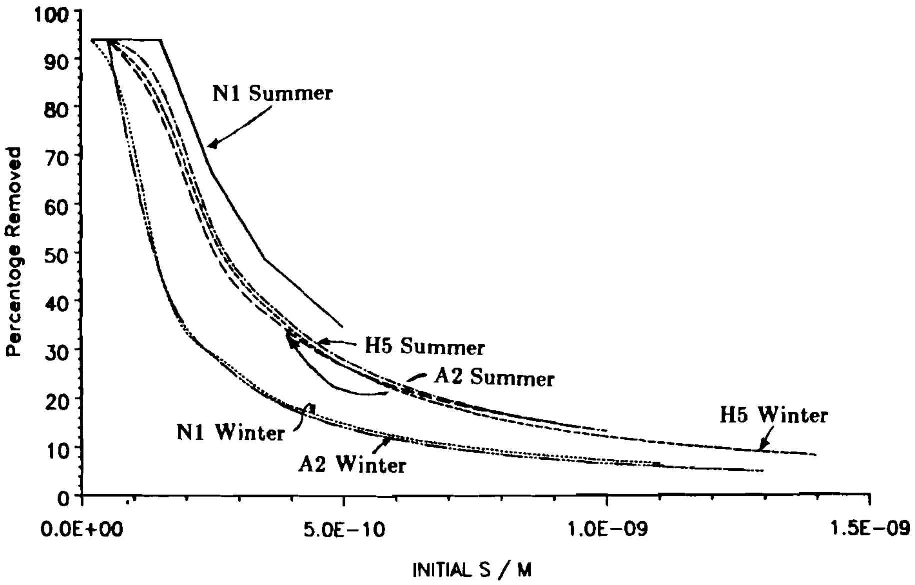

Figure 10.5. Sulfur dioxide removal efficiency.

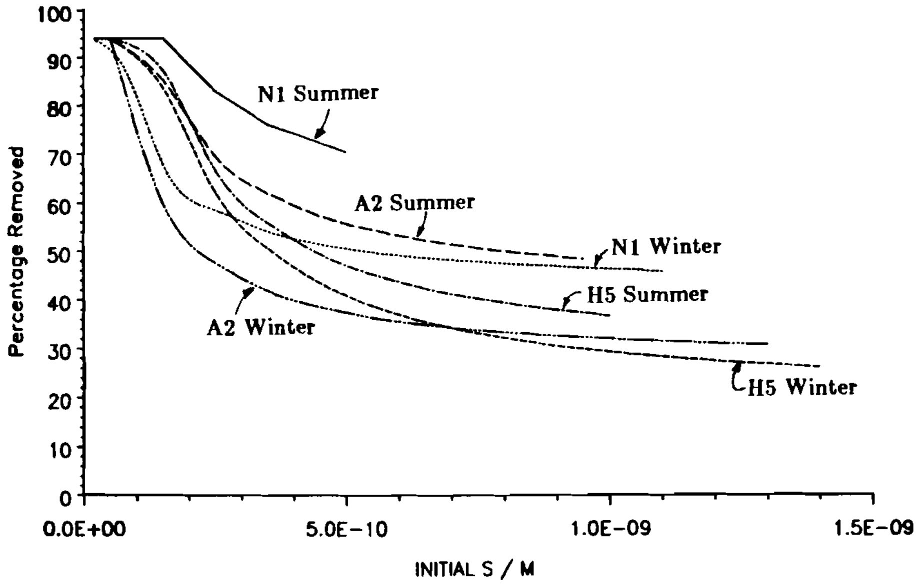

Figure 10.6. Sulfur removal efficiency.

Table 10.2. Mean solution compositions and overall removal efficiencies for the input S distribution for case N1.

		Concentration (μM)				*Efficiency* (%)	
Season	*Input*	H^+	SO_4^{2-}	NO_3^-	NH_4^+	SO_2	*Total S*
Summer	Measured	75	40	36	42		
Summer	Original	42	24	22	27	88	91
Summer	$\frac{1}{2}$ S	31	18	22	27	93	94
Summer	$\frac{1}{2}$ (S + HNO_3)	26	18	19	27	93	94
Winter	Measured	64	32	40	40		
Winter	Original	45	25	27	33	45	67
Winter	$\frac{1}{2}$ S	34	20	27	33	65	78
Winter	$\frac{1}{2}$ (S + HNO_3)	26	20	19	33	68	80

Table 10.3. Mean solution compositions and overall removal efficiencies for the input S distribution for case H5.

		Concentration (μM)				*Efficiency* (%)	
Season	*Input*	H^+	SO_4^{2-}	NO_3^-	NH_4^+	SO_2	*Total S*
Summer	Measured	29	62	58	107		
Summer	Original	35	46	50	109	41	56
Summer	$\frac{1}{2}$ S	15	34	50	109	66	74
Summer	$\frac{1}{2}$ (S + HNO_3)	7	38	31	109	84	87
Winter	Measured	36	57	40	101		
Winter	Original	34	55	57	134	20	35
Winter	$\frac{1}{2}$ S	17	46	57	134	46	56
Winter	$\frac{1}{2}$ (S + HNO_3)	13	55	34	134	64	70

Table 10.4. Mean solution compositions and overall removal efficiencies for the input S distribution for case A2.

		Concentration (μM)				*Efficiency* (%)	
Season	*Input*	H^+	SO_4^{2-}	NO_3^-	NH_4^+	SO_2	*Total S*
Summer	Measured	39	55	52	64		
Summer	Original	73	46	41	61	41	64
Summer	$\frac{1}{2}$ S	46	33	41	61	66	78
Summer	$\frac{1}{2}$ (S + HNO_3)	32	33	26	61	68	79
Winter	Measured	30	64	72	77		
Winter	Original	91	53	76	;92	12	35
Winter	$\frac{1}{2}$ S	58	37	76	92	21	42
Winter	$\frac{1}{2}$ (S + HNO_3)	31	39	44	92	27	46

The effects of halving airborne S and S + HNO_3 on S removal efficiency are illustrated in *Figures 10.7* and *10.8* for sites H5 and A2 in winter. (Note that the reduced S concentration efficiencies are plotted against the original airborne S.) The efficiency changes for H5 are substantially greater than for A2 as the higher ammonia concentrations provide a greatly enhanced neutralizing capacity at the reduced sulfur levels — changes which are further increased by nitric acid reductions.

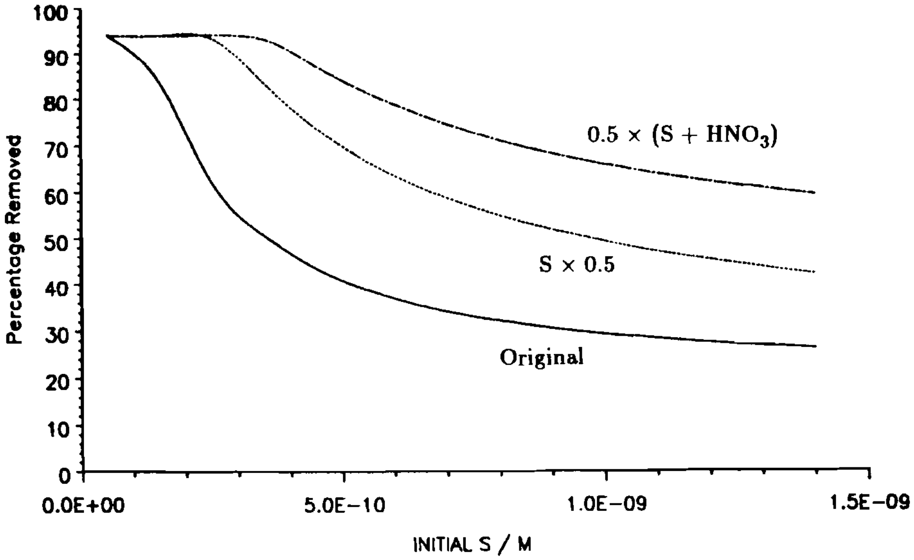

Figure 10.7. Sulfur removal efficiency, Site H5, winter.

The long-term average solution compositions for the reduced concentrations scenarios, together with mean SO_2 and total S removal efficiencies, are also shown in *Tables 10.2–10.4*. For N1 under summer conditions, the predicted nonproportionality of wet sulfate deposition is due entirely to the invariant "background", whereas, for winter conditions, the nonproportionality is increased by a more efficient SO_2 removal at the reduced concentrations. For H5, the higher neutralizing capacity produces a greater contribution of SO_2 efficiency changes to the nonproportionality, particularly in winter when no decrease in sulfate deposition is predicted for a halving of SO_2 and HNO_3 concentrations. Similar but less pronounced effects are predicted for A2. The relationship between mean H^+ and airborne concentrations is a complex function involving neutralizing capacity; and in high-ammonia situations, the relationship between airborne sulfur and acidity can be close to proportional.

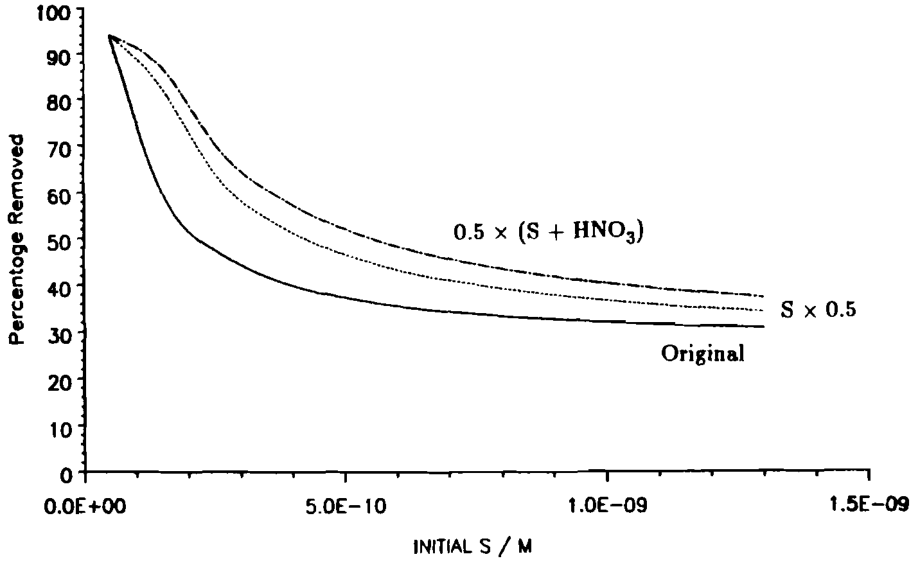

Figure 10.8. Sulfur removal efficiency, Site A2, winter.

Thus, in polluted areas of Europe, significant chemically induced nonproportionalities between airborne sulfur concentration and wet sulfate deposition might be expected. For more remote areas, particularly under summer conditions, the chemical component of nonproportionality may be lower and the background contribution to nonproportionality may predominate.

11. Nonlinear Processes in Acid Deposition and Photochemistry

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Chemical transformations in the atmosphere are nearly always—in a chemical sense—nonlinear. Thousands of different species exist in the atmosphere, anthropogenic as well as from natural origin, so it is unlikely that a completely linear chemical transformation can take place.

The word nonlinear, however, is often used in air pollution studies in a slightly misleading way to indicate that the relationship between a certain emission and its contribution to the concentration is disproportional — in other words, that an $x\%$ decrease in emissions will not lead to a $x\%$ decrease in the contribution to the concentrations. Thus defined, even the emission of a completely inert species from a stack described by a Gaussian plume model could lead to "nonlinearity" in case an emission reduction is combined with a volume rate or exit temperature change (change of emission conditions). In that case the relation between emission and ground-level concentration at a certain downwind location would be "nonlinear". Note that the contribution of the emissions of different sources to the higher percentile concentrations is, in general, nonadditive and, in this sense, also "nonlinear". In the following some remarks will be made about "true" nonlinearity in acid deposition and photochemistry, i.e., nonlinearity that is *not* due to changes in atmospheric transport of the pollutants.

Nonlinearity in acid deposition

Nonlinearity in acid deposition is, to a large extent, due to wet, aqueous phase chemistry. The final problem in acid deposition is the amount of free ions, H^+, in the water and in the ground. From model calculations it appears that on an annual basis the emissions of SO_x, NO_x, and NH_3 will, in a nearly linear way, lead to dry deposition of these species. Acidification then takes place due to rainfall and further conversion in the water and the ground. (It is also clear that in principle rainfall itself is a kind of "nonlinear" process: there are locations with more and with less rain and, consequently, more or less wet deposition.) The main cause of nonlinearity is the conversion of the primary emissions to $SO_4^=$, NO_3^- and NH_4^+. At some distance from the source, the converted fraction depends on the levels of OH-radicals, O_3, NO, and VOC concentrations encountered in transit.

Since chemical conversion is a more important removal mechanism for NO_x than for SO_2, the NO_x concentrations exhibit a more nonlinear behavior. (It can be expected that in general large nonlinearities occur when the influence of deposition is small relative to the influence of conversion.) In this way, an emission reduction of SO_x, NO_x, and NH_3 could, at a certain location, lead to a less-than-proportional reduction of $SO_4^=$, NO_3^-, and NH_4^+ concentrations, and of free ions. This effect will be more pronounced during acid deposition episodes than for long-term averages. Obviously, in the long range, all emitted SO_x, NO_x, and NH_3 must finally be deposited somewhere, but it is important where this deposition take place, in a more or less sensitive area, or within or outside certain country borders.

Nonlinearity in photochemistry

Photochemistry is governed by the emission of NO_x and reactive hydrocarbons (VOC, volatile organic compounds). In the air, owing to chemical reactions and photolysis, secondary pollutants occur, such as O_3 and PAN. The efficiency with which these pollutants are generated depends strongly on the VOC/NO_x concentration ratio.

Current concentration levels in the air over parts of Europe and North America are such that, owing to the ratio of VOC/NO_x concentrations, a reduction of NO_x emissions could lead to no reduction or even an increase in hourly O_3 peak concentrations during episodes. Calculations have been carried out using a two-layer trajectory model, the so-called MPA model (Measuring/Modeling Program Aerosols) for the EMEP area with Dutch receptor points. The calculations covered five different episodes. The results showed that the VOC/NO_x ratio can vary strongly, not only between different episodes, but also in the course of a particular simulation. Differences in this ratio between the two layers occurred frequently, because wind shear transported the two layers over different source areas, and also because the VOC emissions, in contrast to NO_x emissions, occur exclusively close to the ground. Consequently, it is necessary to study a representative set of episodes in order to characterize nonlinearities.

Figure 11.1 gives an overview of the results averaged over the five episodes (van den Hout *et al.*, 1985; de Leeuw and v.d. Hout, 1985). From this graph it is clear that an $x\%$ VOC emission reduction will in general lead to a $0.5 \times x\%$ peak O_3-concentration decrease. A decrease of up to 60% in NO_x emissions showed hardly any influence. In the so-called PHOXA project (PHotochemical Oxidants and Acid Deposition Model Application) preliminary calculations have been carried out recently by SAI, USA, using a Eulerian grid model covering a large part of Northern Europe; see, for example, *Figure 11.2*. It is expected that more detailed and quantitative results with respect to the relation between NO_x and VOC emissions and O_3 peak concentrations will shortly be available from this study.

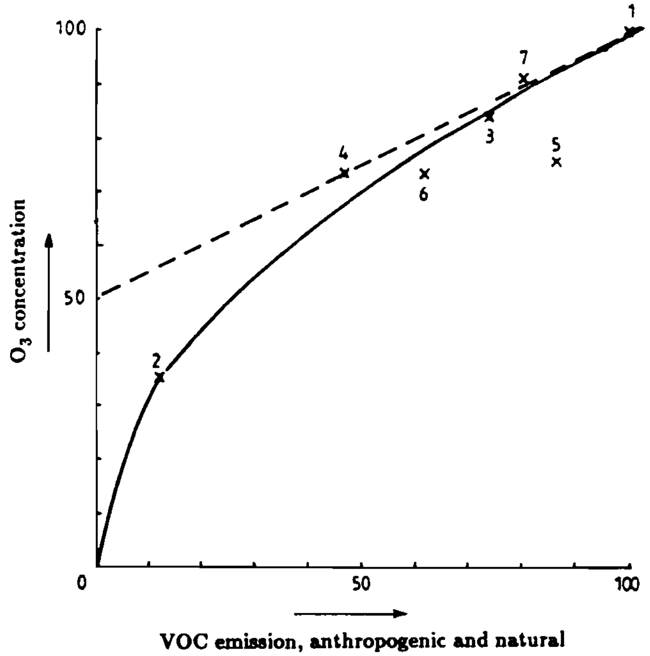

Figure 11.1. Indication of the effect of VOC emission reduction; numbers refer to different strategies.

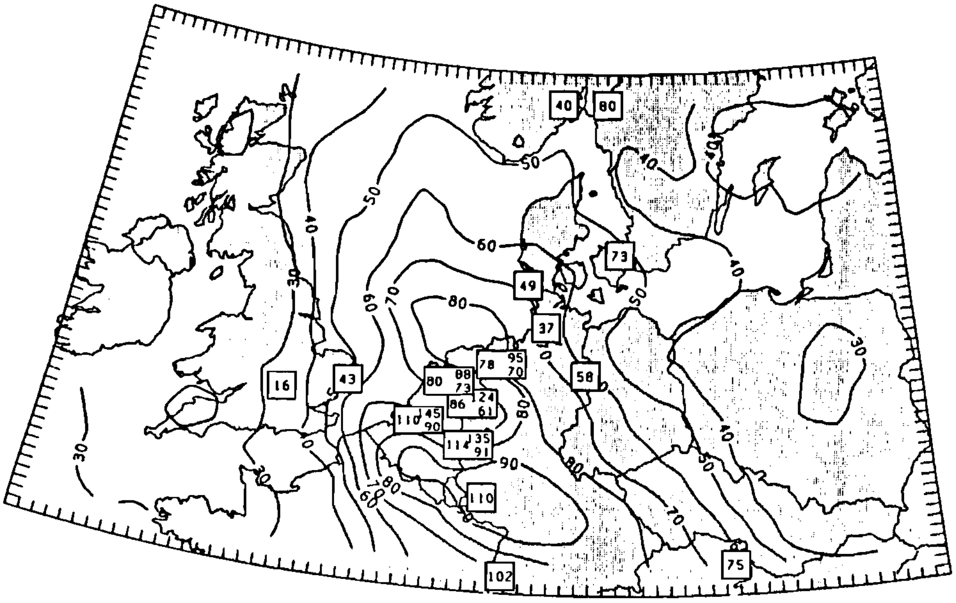

Figure 11.2. Hourly averaged predicted mixed-layer O_3 concentrations (ppb) with inserted observations, for hour ending 1200 on 26 July 1980.

References

de Leeuw, F.A.A.M. and van den Hout, K.D. (1985) Modeling of photochemical episodes, presented at CEC-COST 611 Meeting, Bilthoven, September.

van den Hout, K.D. *et al.* (1985) *Volatile Organic Compounds in Relation to Dutch Air Quality*, TNO Report CMO 85/03 (in Dutch).

PART V.

Results from Long-Range Transport Models

12. The Response of Long-Term Depositions to Nonlinear Processes Inherent in the Wet Removal of Airborne Acidifying Pollutants

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Important nonlinear processes are inherent in the in-cloud oxidation and removal by rain of acidifying species on the dry, wet, and total depositions of these species averaged over a long period, such as a year or longer. Because of the immense difficulties in providing the correct input data, no attempt is made here to represent the highly complex nature of these nonlinear processes in any exact sense. Instead a simple parameterization is used to convey the correct spirit of these nonlinearities, sufficient to determine the qualitative response of long-term depositions.

Equations are formulated and solved that model the fate of a primary pollutant, such as sulfur dioxide, emitted from a source. The equations, being stochastic in nature, can simulate the overall behavior appropriate to a large ensemble of situations. They include the effects of transport, plume growth, dry deposition, oxidation, exchange between "dry" and "wet" regions, intermediary additional sources, and the parameterized wet deposition referred to above. The results strongly indicate that the related total (wet plus dry) depositions downwind from a particular source at any receptor beyond a few hundred kilometers are always approximately proportional to the magnitude of the source emission. This conclusion has marked relevance to the discussion on how best to reduce environmental damage.

Closer into the source, however, marked nonproportionality is sometimes evident, and any reductions in the emission will result in a significantly less than proportional reduction in the total deposition. Precise details then relate to the nature of the nonlinear processes involved and cannot be predicted by the simple parameterized form used in this paper.

The model

The basic equations are reasonably familiar, being four in number and representing the conservation of sulfur dioxide and of sulfate in wet and dry regions (see, for example, Smith, 1981). The only essential difference is that, for an isolated plume, account has to be taken of the changes in concentration arising from plume growth with downwind distance. A more subtle difference, but one that is the very essence of this paper, is the nature of the wet removal terms by which the rainout of sulfur dioxide and sulfate are represented in the equations. As already indicated, these terms, unlike in Smith (1981), are nonlinear in character, and their implications are explored in this analysis.

Because of the nonlinear nature of the wet removal terms, it is impossible to find exact analytical solutions to the equations. Consequently, resort is made to an approximate method, summarized in *Figure 12.1*. A single source and its subsequent depositions are studied, assuming that the emissions at source take place over a long period under both dry and wet conditions. Simplifying the meteorology to the extent of assuming a constant wind speed and constant mixing depth, the initial air concentrations are the same in both dry and wet periods (in *Figure 12.1*, this means $C_0 = D_0$). Considering the emissions purely in terms of sulfur dioxide, the deposition velocity is taken to be that of SO_2 and is given a constant value of 1 cm s^{-1}.

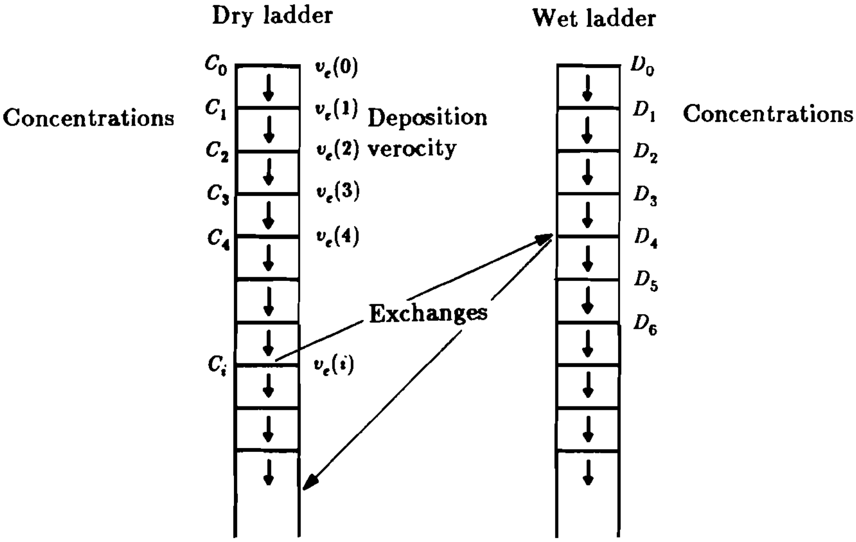


Figure 12.1. Concept of model calculations.

In the first time step, the airborne concentration as it advects downwind falls, owing to dry deposition, to plume width growth (where this is relevant), and may increase if the air flows over new sulfur dioxide sources. As a result, the concentration changes from C_0 to C_1. Some conversion of sulfur dioxide to sulfate has also taken place, and this lowers the effective deposition velocity in the second time step. Exactly the same changes are taking place on the dry ladder, except that a bigger fall in concentration can be anticipated as a result of rainout. Consequently, D_1 is significantly smaller than C_1. The magnitudes of the concentrations C_i and D_i at the ith time step can be evaluated very simply, and this is the first step in the computer program that is used to study the question of proportionality between emissions and depositions.

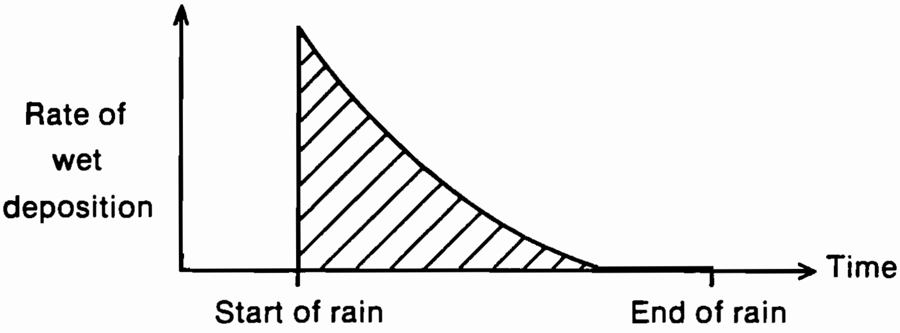
The amount of sulfur on both the dry and wet ladders is initially defined by the emission and by the fraction of time the source is within dry conditions, compared to wet conditions. However, in later time steps allowance has to be made for the advection of boundary-layer air, carrying the pollution from dry regions into wet, and vice versa. These exchanges are known only statistically, but that does not matter because the model itself is a statistical presentation of the fate of sulfur emissions from the source. The statistical exchange rates are defined by two time scales, taken from Rodhe and Grandell (1972). The time scales are eight hours (the average time spent in wet regions), and 40 hours for dry regions. At each time step, then, a multiple exchange between "rungs" on the two ladders takes place so that a defined fraction on one ladder at one rung is transferred to a rung on the other ladder at a concentration that is as nearly the same as possible. The exchange means that, as time proceeds, the emission is no longer held on a single rung on each ladder, but rather on an increasingly large number of rungs. To limit the number of rungs the program must cope with, a finite number is chosen in which the concentration associated with the lowest rung is so small that material arriving on this rung is not passed any further down, thereby invoking a small and, it is hoped, negligible error. Another small error arises because, on exchanging material between one ladder and the other, there is no way of ensuring that proper account is made of the different mix of SO_2 to SO_4 in the incoming air and what is assumed at that rung.

Table 12.1 summarizes some of the parameter values used in the model. Not shown in the next section is the result of a rather thorough sensitivity study, which looked in detail at the response of the deposition values to changing the parameter values. For good physical reasons this study showed that, while the magnitudes of the depositions varied as some of the parameters were changed, as one would expect, the implications regarding proportionality were hardly affected at all. The model turns out to be extremely robust. The reason for this robustness can be seen in *Figure 12.2*. Consider the middle footprint, the shape of which depends on the

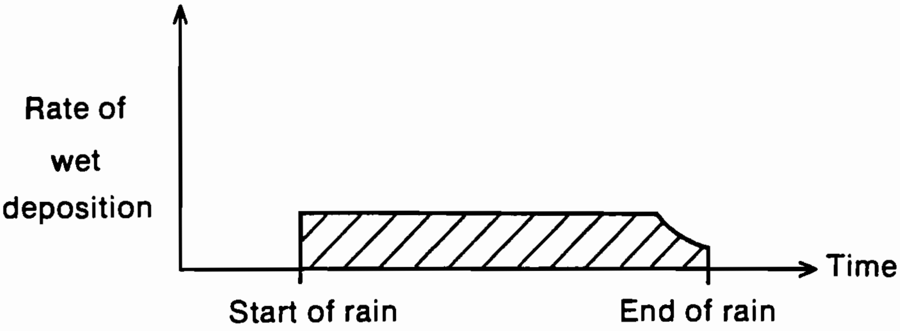
Table 12.1. Parameter values used in the model.

Parameter	*Value*
Wind speed	Constant ≈ 10.4 m s^{-1}
Mixing depth	Constant = 800 m
Rate of rain (in wet periods only)	0.34 mm h^{-1}
Time step	15 mins
Wet and dry periods	Experienced with statistical time scales of 8 and 40 hours, respectively
Dry deposition velocities	1 cm s^{-1} for SO_2 0.2 cm s^{-1} for SO_4
Emissions	Uniform and steady over 150 × 150 km EMEP grid square
Nonlinear rainout	Removal rate in rain $\propto \frac{C}{1+\epsilon C}$ where C = concentration ϵ = nonlinearity parameter

(*a*) Proportional model in which rain persists long enough to remove most airborne material.



(*b*) Nonproportional model in which rain persists long enough to remove most airborne material.



(*c*) Nonproportional model in which rain does *not* persist long enough to remove most airborne material.

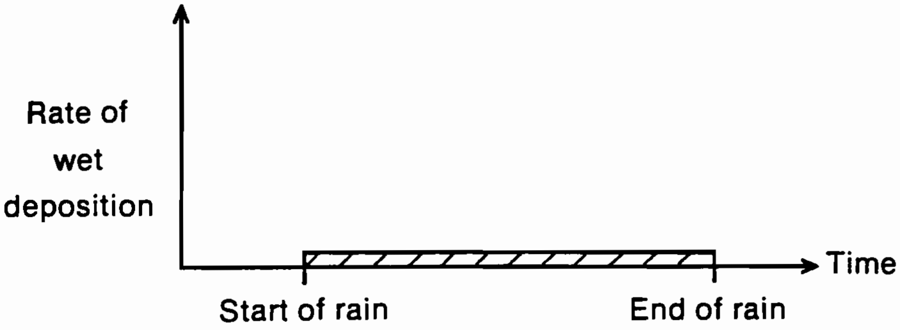


Figure 12.2. Three possible “footprints” of wet deposition during a rain event.

detail of the nonlinear processes involved in wet removal. Therefore, on any one occasion when a receptor *R* is being affected, what it receives in wet deposition depends on where it is relative to the footprint. Provided *R* is sufficiently far away from the source, over a large number of rain events it will appear in a wide variety of positions within the footprint, and effectively integrate the whole footprint, which in turn must be equated to the constant emission. The long-term depositions thus become independent of the details of the nonlinear processes. It is only much nearer to the source, where the whole footprint cannot be sampled, that these processes become very evident.

Results

Figure 12.3 shows the three types of plumes that we considered. The first is a very wide diffuse plume coming from a large number of small sources. Typical concentrations in such a plume are about 30 μg m^{-3}. The second plume is from an isolated large source, such as a modern power station. The initial concentration may be as high as 1000 μg m^{-3}, but because of plume growth (which is assumed linear in time in the model) the concentration drops rather quickly. The third plume comes from a group of large sources, such as those that can be found in the north Midlands of the UK, as shown in the figure. Here the average concentration could be 600 μg m^{-3} and will fall much more slowly since plume growth will not be very important over the distances of concern.

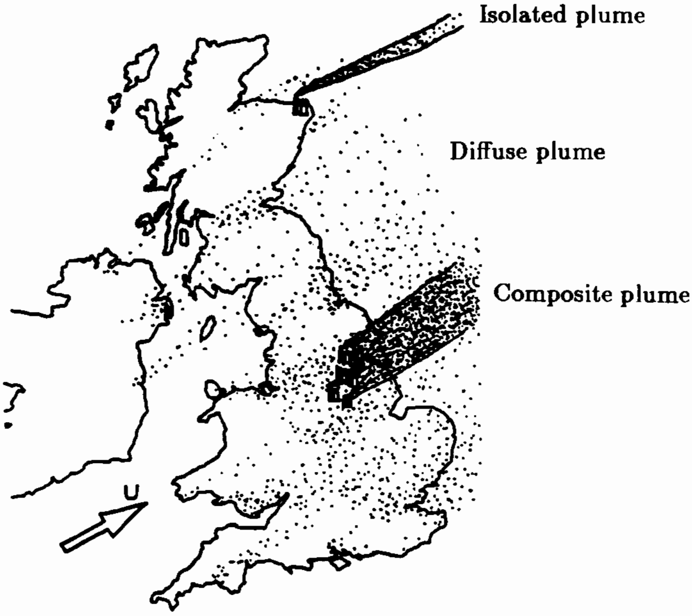


Figure 12.3. Three types of plumes analyzed.

The model is used to explore the response of the long-term downwind deposition fields to halving emissions at source. Depositions are said to be "approximately proportional" to emissions if a 50% reduction in source strength produces a reduction in deposition at a receptor in the range 40 to 60%.

Figure 12.4 shows the deposition response of the first diffuse plume to halving emissions. As can be seen, for dry, wet, and total deposition the relationship is approximately proportional beyond 400 km, and in fact very soon becomes such that enhanced benefits are achieved by cutting emissions.

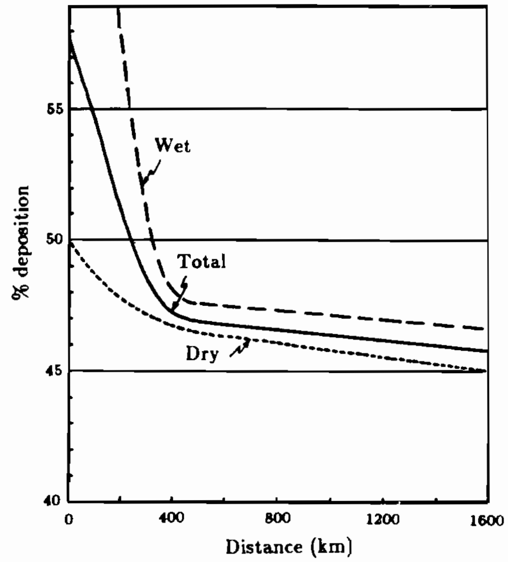


Figure 12.4. Response of deposition to halving emissions in a diffuse plume.

Figure 12.5 shows very similar results for the expanding power station plume. In slight contrast, *Figure 12.6* shows the response for the third, or composite, type of plume. Here the dry and the total depositions are approximately proportional at all distances, but because of the high concentrations in the plume the nonlinear effects persist for a very large distance, and the wet deposition is suppressed and makes a relatively small contribution to the total deposition. Thus, even where nonlinear processes are important in the wet deposition, the overall influence remains negligible.

Table 12.2 summarizes the results.

In conclusion, beyond a few hundred kilometers from a source area, the nonlinear effects of cutting emissions are rather small, at least on the long-term depositions. The effect on the magnitudes of *episodes* has yet to be explored. Since episodes can have very significant effects on the ecosystems in sensitive areas, we cannot claim that modest reductions in emissions will necessarily eliminate damage in such areas.

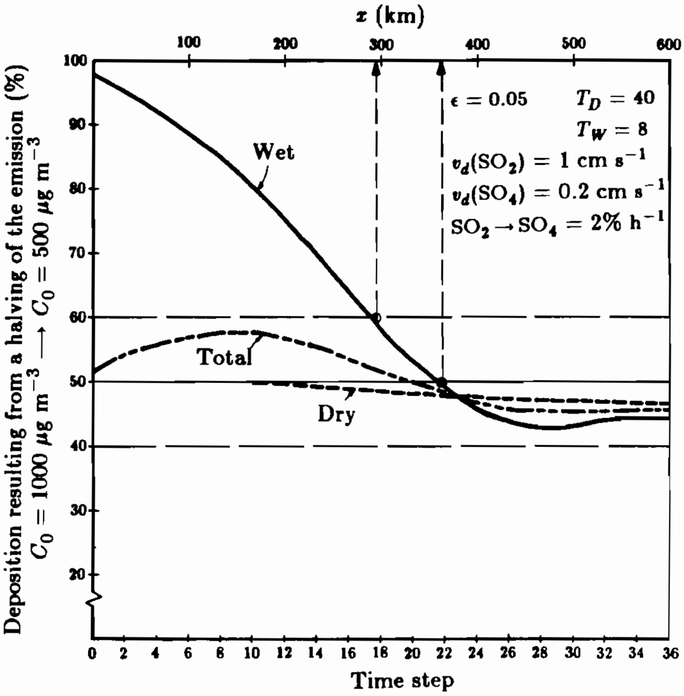


Figure 12.5. Response of deposition to halving emissions in an expanding plume.

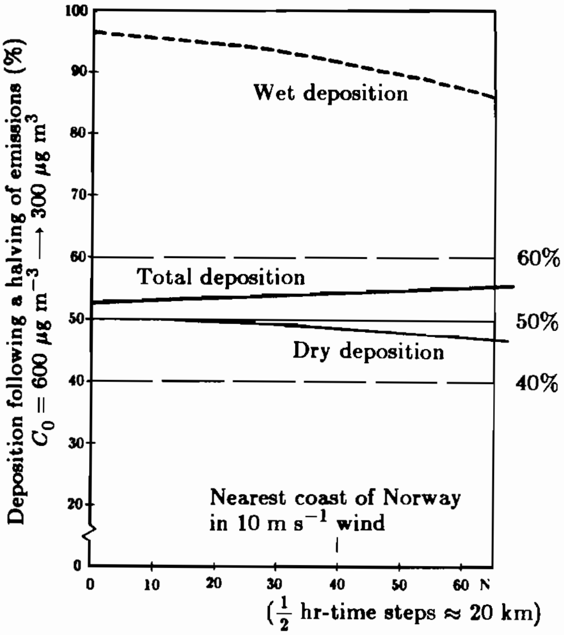


Figure 12.6. Response of deposition to halving emissions in a composite plume.

Table 12.2. Summary of results: the distance *d* beyond which deposition is "approximately proportional" to emission. (Distance from East Midlands source area to sensitive lakes of S. Norway is about 800 km.)

Source type	*Intermediary sources**		*Values of* d *for:* *Wet deposition*	*Total deposition*
(A) Broad dispersed source	No		300 km	250 km
	Yes	(a)	150 km	50 km
		(b)	> 2000 km	50 km
(B) Single isolated large point source	No		500 km	200 km
	Yes	(a)	values not currently available:	
		(b)	probably similar to (A)	
(C) Composite plume from cluster of large sources	No		3000 km	0
	Yes	(a)	1400 km	0
		(b)	> 2000 km	0

*(a) Intermediary source strength unaltered when initial source strength is reduced.
(b) Initial and intermediary source strengths are reduced by same proportion.

References

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13. Dependence of Sulfur Deposition on Emissions and its Variation with Distance

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This paper reports on two interlinked studies of the proportionality or otherwise of long-term (annual) sulfur depositions and emissions. At the time of writing, the second study is unpublished, whereas the first study has been fully described elsewhere (Mitchell and Williams, 1985). Therefore, given limited space, only a summary of the first study is given here, while the second is covered in somewhat more detail.

The first study introduces novel rainfall statistics into a well-known simple Lagrangian model developed by Smith (1985). Except for the treatment of rainfall, the model used is exactly as described by Smith (1985) and will not be detailed here. Nonlinear effects are accounted for by a parameter ϵ applied to the wet deposition term. The effect of ϵ on long-term (i.e., annual) depositions (total, wet, and dry) along a line of 15 grid squares, each 150 km in length and lying parallel to the constant mean wind, is examined. Smith's rainfall treatment was based on the wet/dry region concept of Rodhe and Grandell (1972), developed from an analysis of the statistical properties of the duration of wet and dry periods viewed as a Markov process. The Smith model thus treats long-period rainfall statistics in an averaged way. We were interested in examining the effects on Smith's conclusions of using actual rainfall data.

The method adopted treats rainfall on a day-to-day basis, integrating the transport equation for each day for a year and averaging the 365 results. The rainfall total in each grid square was set equal to 700 mm yr^{-1} (following Smith), and the rainfall rate in each square was determined as shown in *Table 13.1.* The daily rainfall pattern at Eskdalemuir in southern Scotland in 1983 was chosen as the base case for calculating rainfall rates in each square. [Sensitivity analyses based on rainfall patterns from other sites and/or years have been performed (Mitchell and Williams, 1985).] For the first of the 365 simulations, square 1 uses January 1, 1982 (i.e., D_1) of the Eskdalemuir rain data. For the same simulation, square 2 uses a day, D_2, chosen at random from within 2 days of D_1, square 3 uses $D_2 \pm 2$ and so on. Having fixed the start day for each square, the rainfall rates for subsequent simulations were determined by incrementing the appropriate start day by 1 (*Table 13.1*). The results can be shown to be insensitive to the choice "±2".

Table 13.1. Daily rainfall data scheme.

Day of model run (1–365)	*Grid square*	*Day of Eskdalemuir 1982 rainfall data set used in grid square*
1	1	1 January = D_1
	2	$D_1 \pm 2 = D_2$*
	3	$D_2 \pm 2 = D_3$
	$\vdots$	$\vdots$
	15	$D_{14} \pm 2 = D_{15}$
2	1	$D_1 + 1$
	2	$D_2 + 1$
	3	$D_3 + 1$
	$\vdots$	$\vdots$
	15	$D_{15} + 1$

* D_2 is chosen at random from within ±2 days of 1 January in a cyclic sense, i.e., from within 1–3 January 1982 and 30–31 December 1981.

Several of the scenarios modeled by Smith (1985) have been repeated and the effects of this alternative treatment for rainfall examined. Only a subset of the conclusions described in detail by Mitchell and Williams (1985) are summarized here, namely, those of most relevance to this symposium.

The results of the model agreed, broadly speaking, with those of Smith (1985). They show that for relatively long downwind distances (> 1000 km) and for averaging times of a year or more, a given percentage reduction in emissions leads to a similar percentage reduction in total (i.e., wet plus dry) deposition. Indeed, the results show that, at these long downwind distances, there is a possible enhanced benefit in deposition reduction such that a 50% reduction in emissions leads to a reduction in depositions (total, wet, or dry) of ~55%. In the near field (~300–500 km), where air concentrations are relatively high, nonlinear effects are still in evidence.

The second study also analyzed measurements taken at Eskdalemuir, which is located some 300–500 km from the major industrialized regions of the United Kingdom (UK) (*Figure 13.1*). Daily measurements of precipitation composition, aerosol sulfate, and sulfur dioxide (SO_2) have been made at the site by Warren Spring Laboratory (WSL) since 1978, as part of the European Monitoring and Evaluation Programme (EMEP). In this study, attention focused on the annual time series for the wet deposition (corrected for marine contribution), dry deposition and total deposition of sulfur at the site over the period 1978–1983, as determined from the measurements and the variation of these time series with wind direction. The aim of the ongoing work is to investigate whether the decrease in anthropogenic

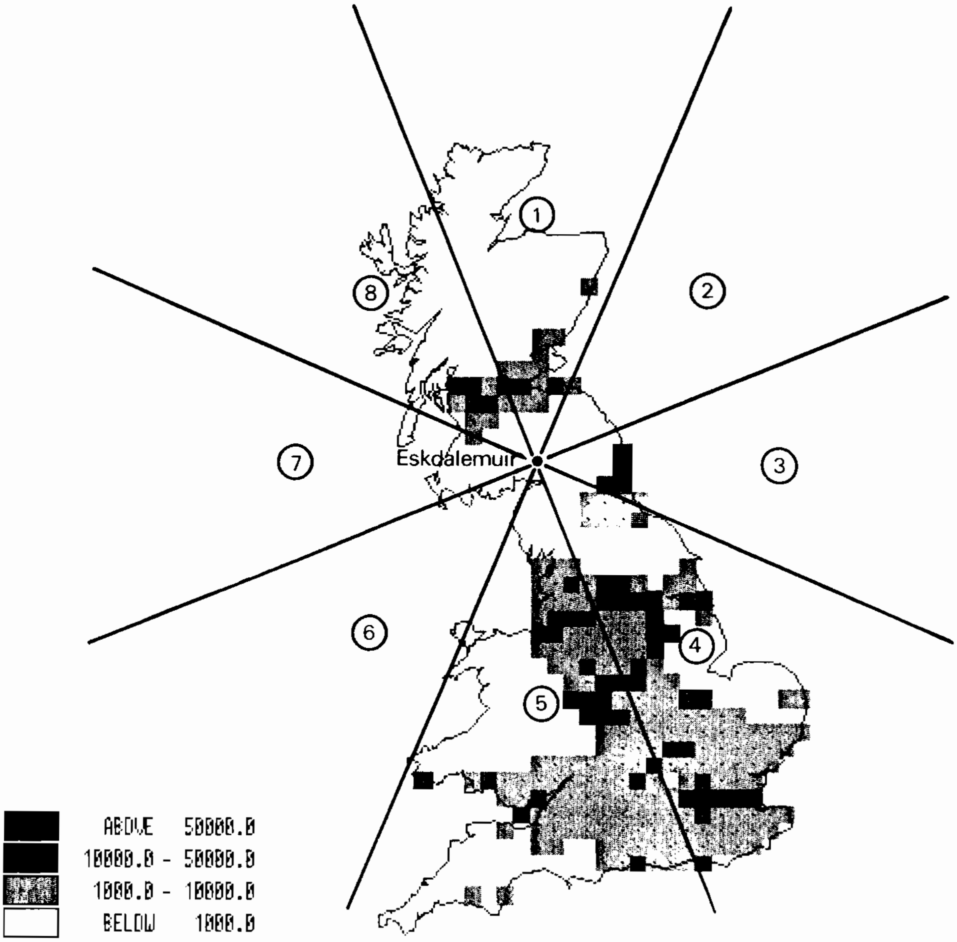


Figure 13.1. UK emissions of SO_2 (tons), 1983, and EMEP sectors at Eskdalemuir.

emissions of SO_2 from the UK over the same period is reflected in the measurements, although it is recognized that a period of six years is too short for reliable determination of trends over time.

Figure 13.2 compares the annual time series for anthropogenic emissions of SO_2 expressed as sulfur (SO_2-S) from the UK (HMSO, 1984) between 1978–1983 with the corresponding time series for sulfur deposition and rainfall at Eskdalemuir. The time series for dry deposition has been calculated using a fixed deposition velocity of 5 mm s^{-1} for SO_2 (multiplied by the appropriate observed sector-averaged SO_2 concentration and number of observations). This velocity is at the lower end of the range of values (~5–8 mm s^{-1}) typically used to calculate regional distribution patterns of dry deposited sulfur, but it is considered appropriate for

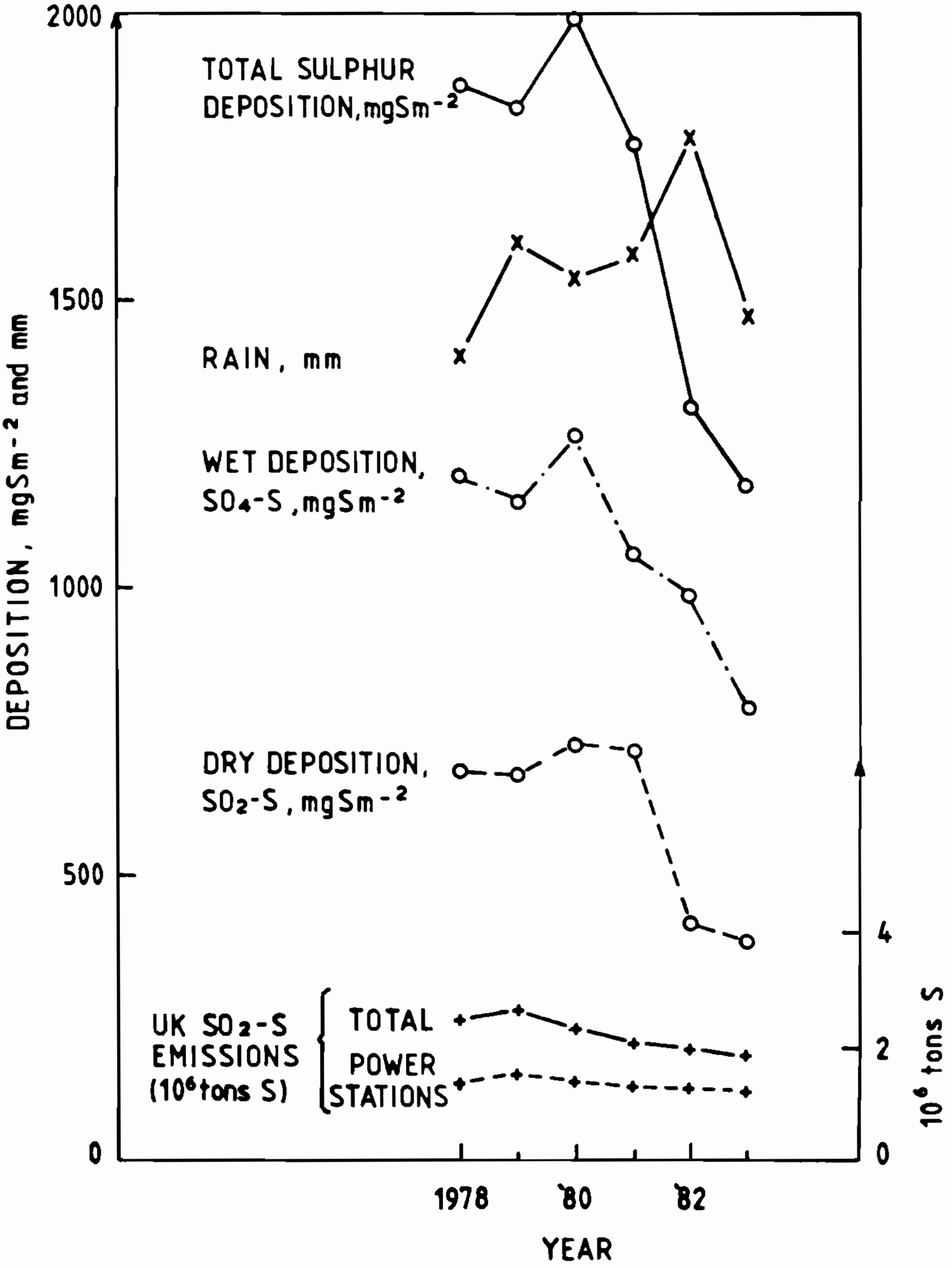


Figure 13.2. Eskdalemuir deposition time series: UK emissions of sulfur dioxide (expressed as sulfur), 1978–1983.

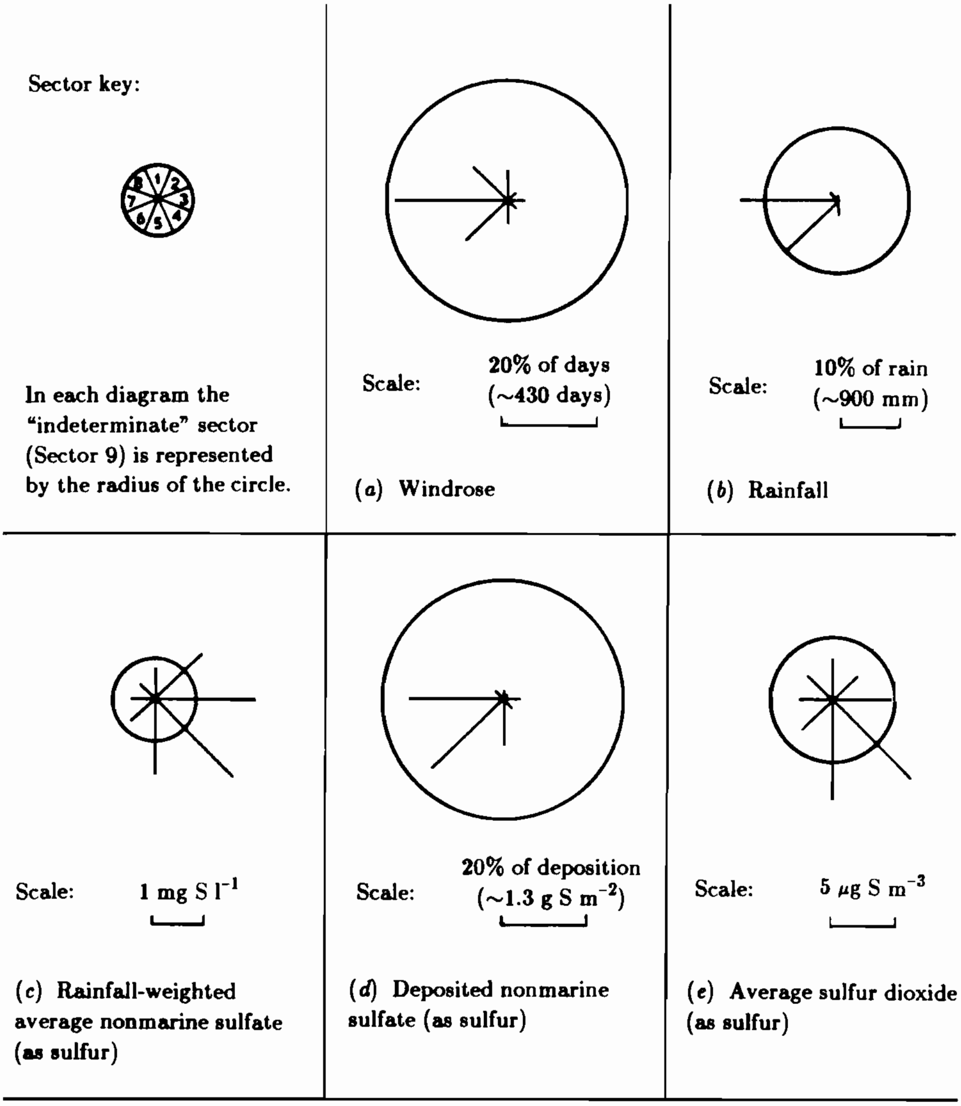
this particular site (Barrett *et al.*, 1983). Dry deposition of aerosol sulfate has been neglected because the Barrett research group considered its contribution less significant than that from SO_2. Over the period, total UK emissions of sulfur and emissions from power stations decreased by ~25% (from 2.51 to 1.85 Mt yr^{-1}) and ~10% (from 1.41 to 1.27 Mt yr^{-1}), respectively. Over the same period, total deposition of sulfur at Eskdalemuir and wet and dry deposition, separately, decreased by ~37% (from 1.88 to 1.18 g S m^{-2}), ~34% (from 1.20 to 0.79 g S m^{-2}) and ~44% (from 0.68 to 0.38 g S m^{-2}), respectively. However, obviously, these deposition time series are influenced not only by UK emissions, but also by changes in anthropogenic emissions of SO_2 from outside the UK and natural emissions. For example, estimates of the percentage contribution from UK emissions to wet deposition at the site are ~40–60% (Barrett *et al.*, 1983; Perrin, 1986).

To examine if the reduction in UK emissions is reflected in the measurements of sulfur deposition at Eskdalemuir, we have used the sector analyses provided by the Meteorological Synthesizing Centre (West) of EMEP. The measurements are assigned to angular sectors on the basis of isobaric, 96-hour back trajectories. Four trajectories are calculated per day. The criteria used to assign a sector to a particular day are detailed by Lemhaus *et al.* (1985). Each sector is 45° wide; sector 1 centered on magnetic north, sector 2 on northeast, and so on (*Figure 13.1*), with a ninth "indeterminate" sector assigned when the criteria are not satisfied. At Eskdalemuir, each of the sectors 1 to 8 can be regarded as being influenced by UK emissions of SO_2 (*Figure 13.1*). However, as is shown below, the sum of the contributions from sectors 1, 2, and 8 to the annual total (~5–15% and ~3–13%, respectively). Secondly, annual emissions of SO_2 from Northern Ireland are only a small proportion (~7%) of total UK emissions (e.g., ~0.17 and 0.15 Mt S in 1980 and 1982, respectively; Eggleston, personal communication). For these reasons, we focus on sectors 3, 4, and 5 as "UK sectors" (i.e., sectors influenced by UK emissions) and on sectors, 6, 7, and 9 as "non-UK sectors" (sector 9 in the sense that its pollution origin is unknown). It is also worth noting that annual emissions of SO_2 from Eire are relatively small — over the period 1979–1983 they decreased (OECD, 1985) from ~0.12 to 0.07 Mt S yr^{-1} — so that their influence on annual sulfur deposition (total, wet, or dry) at Eskdalemuir will be negligible.

Before looking at the deposition time series in the individual sectors, it is of interest to illustrate the wind, pollution, and deposition roses of some relevant parameters determined from the daily measurements and sector analysis. *Figure 13.3* shows the windrose, rainfall deposition rose, and pollution roses for sulfate concentration ($SO_4^{=}$-S) in rain, wet deposited sulfur, and SO_2-S concentration in air over the period 1978–1983. The corresponding roses for the individual years are similar. The main points to note are:

(1) The windrose for raindays (not illustrated) is similar to that for all days [*Figure 13.3(a)*].

(2) The majority of the rain (~80–90% on an annual basis) falls in non-UK sectors; in particular, a large proportion (~15–40%) falls in "indeterminate" sector 9 [*Figure 13.3(b)*].



(*a*) Windrose

(*b*) Rainfall

(*c*) Rainfall-weighted average nonmarine sulfate (as sulfur)

(*d*) Deposited nonmarine sulfate (as sulfur)

(*e*) Average sulfur dioxide (as sulfur)

Figure 13.3. Eskdalemuir, 1978–1983: (*a*) windrose and (*b*)–(*e*) pollution and deposition roses (see subcaptions).

(3) While the concentration of $SO_4^{=}$-S in rain is higher in UK sectors [*Figure 13.3*(*c*)], the proportion of measurements and amount of rainfall in these sectors is relatively small [~5–15% and ~5–10%, *Figures 13.3*(*a*) and *13.3*(*b*)]. Hence, the majority of wet-deposited sulfur (~65–80%) is attributable to

non-UK sectors [*Figure 13.3(b)*]. Approximately 20–45% of the wet deposition is attributable to sector 9.

(4) The concentration of SO_2-S is also higher in UK sectors [*Figure 13.3(e)*], but the proportion of measurements in these sectors is relatively small [~5–15% compared to ~65–75% in non-UK sectors, *Figure 13.3(a)*]. A large proportion of the measurements [~20–35%, *Figure 3(a)*] and of the dry deposition (~25–40%, not illustrated) is attributable to sector 9.

The fact that a large proportion of the wet and dry depositions is attributable to sector 9 obviously complicates interpretation of the deposition time series within each sector.

Figure 13.4 compares the annual time series for wet-deposited sulfur and rainfall in each sector. Although the changes in deposition frequently reflect those in rainfall, there are several important exceptions, for example, sector 6, 1982–1983; sector 7, 1978–1979 and 1981–1982. It is also clear that wet-deposited sulfur in each of the UK sectors (3, 4, and 5) does not show a trend with time. In particular, it does not reflect the decrease in UK SO_2 emissions over the period (*Figure 13.2*). Rather, the decrease in the total wet deposition over the period (*Figure 13.2*) appears to be largely due to decreases in non-UK sectors (6, 7, and 9). The time series for wet deposition, dry deposition, and total deposition of sulfur in each sector are shown in *Figure 13.5*. As for wet deposition, the dry and total deposition series in the UK sectors show no time trend. The decrease in total dry deposition toward the end of the period (*Figure 13.2*) appears to be due mainly to a decrease in sector 9. In the majority of sectors, wet deposition exceeds or is of the same order of magnitude as dry deposition. The main exceptions are sectors 1 and 8, reflecting the relatively small number of raindays and amount of rainfall along with the proximity of relatively large emissions of SO_2 in these sectors [*Figures 13.3(a)*, *13.3(b)*, and *13.1*]. Hence, the decrease in the total deposition of sulfur (*Figure 13.2*) primarily reflects a decrease in deposition in non-UK sectors.

We can conclude that a sector analysis of the annual deposition time series for sulfur at Eskdalemuir between 1978–1983 does not support a proportional relationship between UK emissions of SO_2 and sulfur deposition (wet, dry, or total) at this particular site and over this period. This is consistent with the results of the modeling study described above and the study by Smith (1985), both of which show that proportionality between long-term (e.g., annual) emissions and total or wet deposition of sulfur at such a remote site requires source–receptor distances of the order of ~1000 km.

Obviously, the current analysis has not taken into account several other factors that might also influence trends in the deposition time series. In particular, recent work (Davies *et al.*, forthcoming) suggests that climatic changes may affect precipitation composition on a yearly time scale. However, before attempting to quantify the implications of such influences for this work, given the magnitude of the sulfur deposition in the "indeterminate" sector, the priority will be to analyze the trajectories assigned to this sector in more detail.

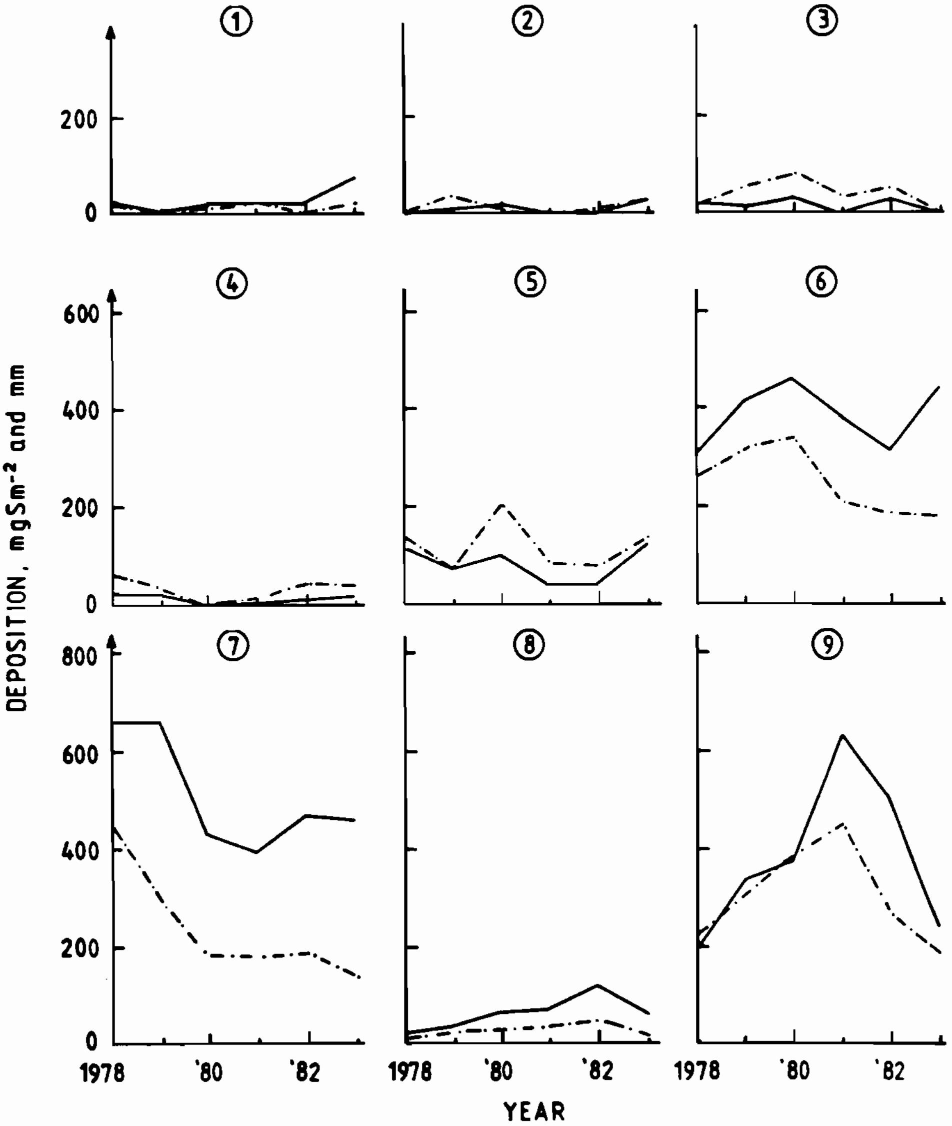


Figure 13.4. Eskdalemuir, 1978–1983: deposition time series/sector numbers appear in circles; the broken line = wet-deposited sulfur (mg S m^{-2}); the solid line = rainfall (mm).

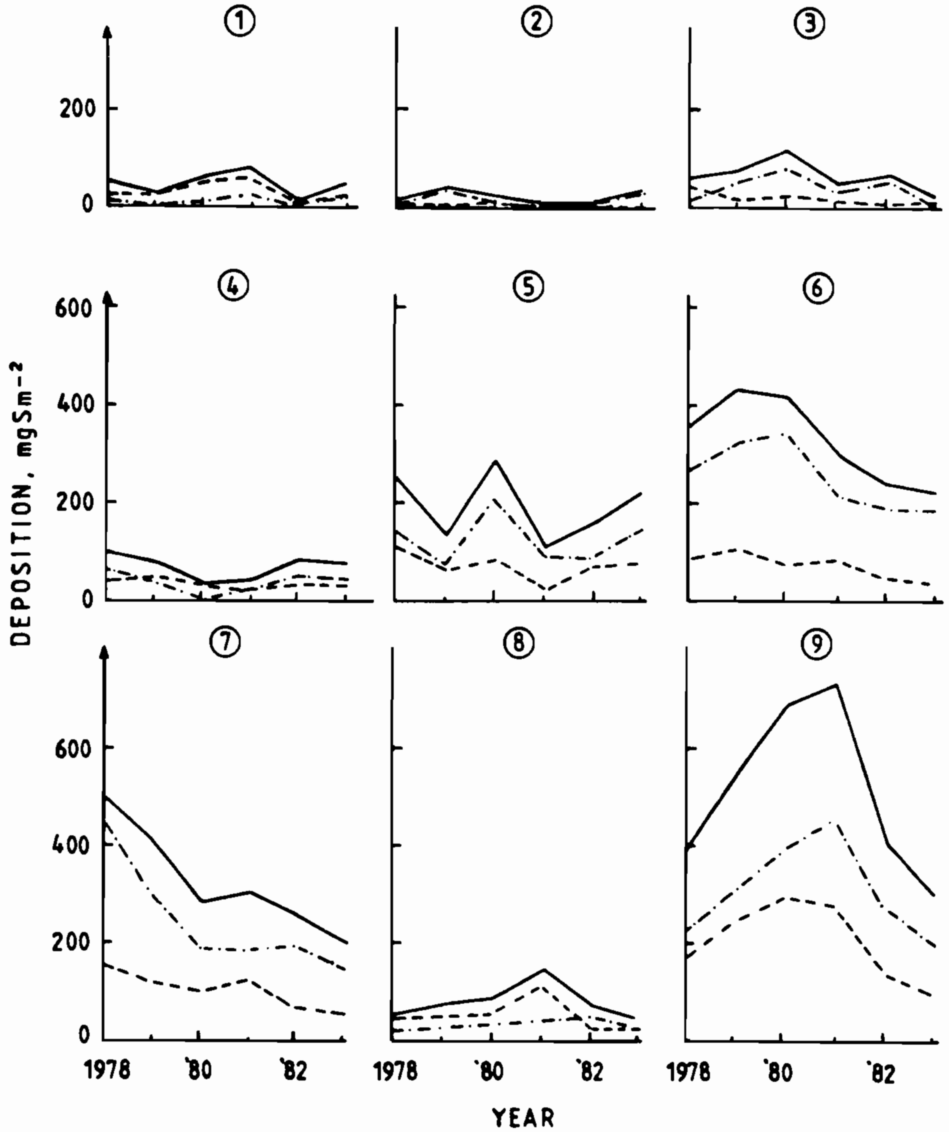


Figure 13.5. Eskdalemuir, 1978–1983: deposition time series/sector numbers appear in circles; the broken line with dots = wet, the broken line = dry, and the solid line = total deposited sulfur (mg S m^{-2}).

Acknowledgments

This work was supported by funding from the UK Government, Department of the Environment.

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14. The Influence of the Nonlinear Nature of Wet Scavenging on the Proportionality of Long-Term Average Sulfur Deposition

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Transport and deposition models are applied to air pollution problems for two purposes: from the scientific point of view, the goal is to improve understanding of the basic processes affecting the pollutant; while for regulatory purposes, models are often the only available means of relating cause and effect, and so establishing what controls should be applied to the cause in order to ameliorate a given effect.

These two aims are, to some extent, in conflict since, in order to obtain as much scientific information as possible about a given process, it is necessary to compare the results of a model sensitive to the formulation of that process with observation; whereas regulatory or predictive use of models requires that the model results depend only weakly upon the model's detailed formulation to minimize the effect of errors.

No direct comparison can be made between calculated source–receptor deposition relationships and observations. It is possible only to compare the deposition at a receptor from *all* relevant sources with model predictions, and use the derived bounds on model parameters suitable for reproducing the observations to calculate bounds on the source–receptor relationship.

An objective determination of parameter values for use in a long-term average transport model

When the aim is not simply to be able to reproduce observations, but to test the validity of chosen parameter values, it is not sufficient to specify parameter values *a priori*, since there will often exist a range of parameter values that yield at least as good a fit.

An alternative approach is to vary the parameters used in the model, and then to optimize the agreement between the set of calculations, $\underset{\sim}{C}$, and observations, $\underset{\sim}{O}$. The measure of agreement used is, to some extent a matter of choice, but it is *not* correct to use the popular correlation coefficient because it does not take into account any systematic scaling or offset errors. The choice used here will be among the simplest conceivable: the mean square difference between calculations at a monitoring site i, C_i, and the observation O_i, normalized by the variance in the observations. This will be denoted by M:

$$M = \sum_{\text{monitoring sites}} (C_i - O_i)^2/(O_i - \bar{O})^2$$

The process started by Fisher and Clark (1985) of optimizing the Fisher statistical model (Fisher, 1978) to fit European monitoring data has been extended to look at the wet deposition parameters in some detail. Other parameters have been kept the same as used by Fisher and Clark (1985), since these are very well constrained. The oxidant rate in dry conditions has been taken to be 1% h^{-1}, and the dry deposition velocity is assumed to be 8 mm s^{-1}. The model has been slightly improved by allowing rainfall probability to vary with wind direction using probabilities given by Klug (private communication), and by shortening the mean duration of wet (T_W) and dry periods (T_D) such that the sum is 61 h, which is more consistent with the data of Hamrud and Rodhe (1981). The results have been checked against the longer periods originally used and show no material difference in the conclusions below. The model results have been compared with EMEP results covering the four-year period, October 1977–September 1981.

Two wet deposition parameters exist in the model: Λ_4 describes the removal of SO_4^{2-} aerosol entering a rain period, while Λ_2 describes the oxidation of SO_2^4 to SO_4^{2-} in cloud followed by rainout, together with the direct wet removal of SO_2. For each, the efficiency of wet removal in the average rain event is given by $E = 1 - \exp(-\Lambda T_W)$. The value of M as a function of E_2 and E_4 is shown in *Figure 14.1*, together with the same function with the additional assumption that a background B equal to 0.32 mg S l^{-1} exists in rainfall. It is clear that the inclusion of this background constant significantly improves the agreement between calculations and observations. The best fit, however, still lies at the point $E_2 = E_4 = 1$, suggesting that wet deposition may still be underestimated.

Since the background is another arbitrary parameter in the model, it is possible to optimize the value through two assumptions: (1) that the background is a constant deposition at each site, and (2) that it is a constant concentration in rain so that the deposition is proportional to rainfall amount. The results shown in *Figure 14.1* make it clear that the latter assumption provides the better fit. However, the most notable feature is that variation in M with respect to E_2 and E_4 has been virtually eliminated. Instead, it was found that the optimized background (*Figure 14.2*) varies with assumptions concerning E_2 and E_4: the higher E_2 and E_4, the lower the background. Given that mean rainfall over the monitoring sites was 0.95 m a^{-1}, agreement between the estimated "background" values estimated using both methods is remarkably high.

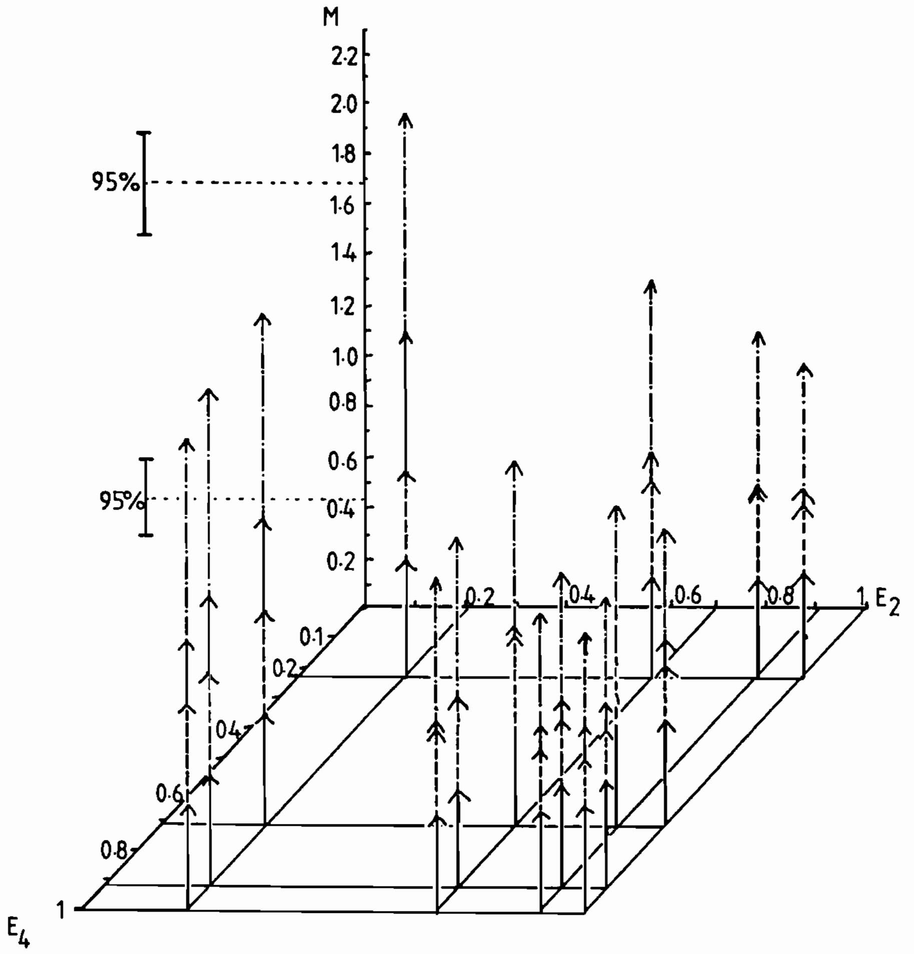

Figure 14.1. The quality of agreement (M) between model calculations and EMEP observations as a functions of wet removal efficiency of SO_2 (E_2) and sulfate aerosol (E_4). Top arrow refers to zero background. Lower arrows represent constant background, optimized deposition background, and optimized concentration background figures, respectively.

On the assumption that the monitoring sites comprise a small sample of all points over Europe, the 95% confidence limits on M have been estimated using the technique of bootstrapping (Efron, 1982). These vary from ±0.2 at high M values to ±0.15 at low M values, and at any point (E_2, E_4) this translates into an uncertainty in B. The overall conclusion, in the absence of other information, is that it is impossible to distinguish between different rainfall removal efficiencies unless the assumed "background" is constrained below some value, in which case the lower the required background, the higher the removal efficiency required to explain the observations. If background is constrained below about 0.4 mg S l^{-1}, then the

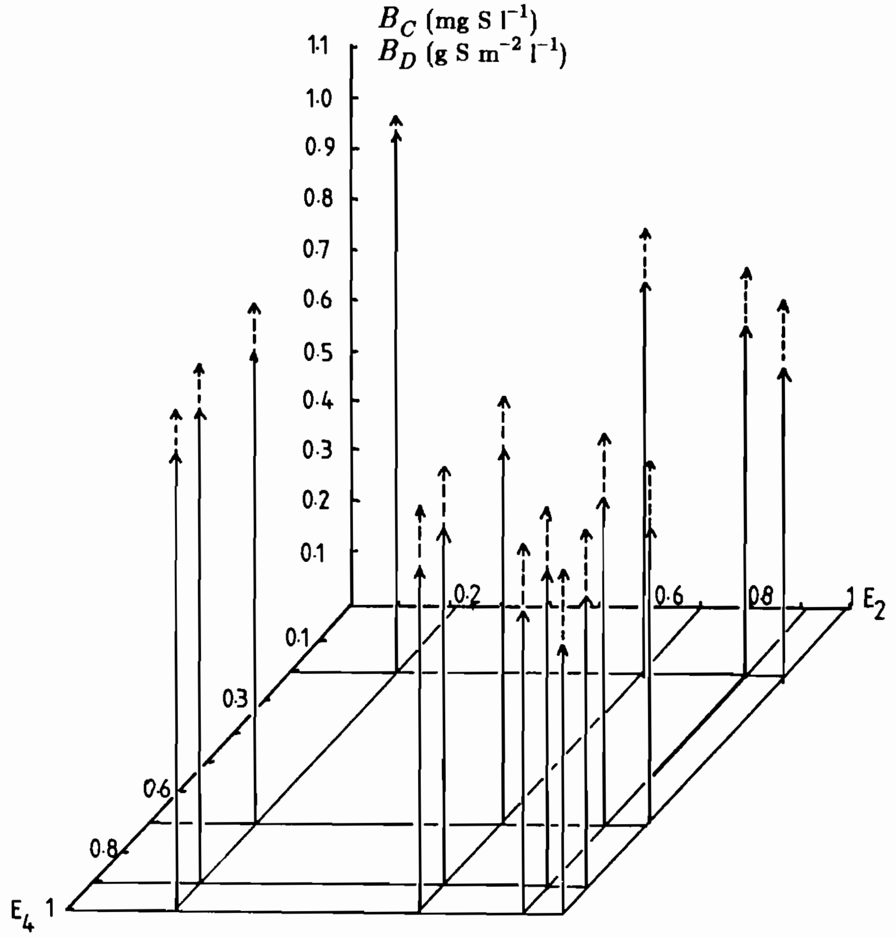

Figure 14.2. Top and lower arrows indicate the optimized value of background deposition (B_D) and background concentration (B_C), respectively, as a function of assumed wet removal efficiency of SO_2 (E_2) and sulfate aerosol (E_4).

average removal efficiency of SO_2 cannot be much below about 50% (although the sulfate removal efficiency is quite arbitrary).

Results of a nonlinear statistical model

Smith's (1985) model demonstrates that the proportionality of wet deposition and emissions is critically dependent on the efficiency of SO_2 wet scavenging. If most of the SO_2 from a source entering a rain system that passes over a receptor is, on average, removed by the system, then the wet deposition will be high and, on average, proportional to the source strength. Alternatively, if little is removed, on average, because of nonlinearities in the wet scavenging processes, then the wet deposition will be significantly less and not proportional to the source strength.

A modified version of Smith's model has been programmed, taking into account oxidation during dry conditions (assumed linear) and using a power law formulation of nonlinear wet scavenging based on the work of Cocks (private communication). The wet scavenging coefficient is assumed to vary as $[SO_2]^{-0.65}$, except at very low concentrations where it is assumed asymptotic to a constant, rapid, removal coefficient. The model equations may be written:

$$\begin{aligned}
\frac{\partial P_{2D}}{\partial t} &- \frac{\partial}{\partial c}(L_D c P_{2D}) &= -P_{2D}/T_D + P_{2W}/T_W \\
\frac{\partial P_{2W}}{\partial t} &- \frac{\partial}{\partial c}(L_W c P_{2W}) &= -P_{2W}/T_W + P_{2D}/T_D \\
\frac{\partial P_{4D}}{\partial t} &+ \frac{\partial}{\partial s}(S_D P_{4D}) &= -P_{4D}/T_D + P_{4W}/T_W \\
\frac{\partial P_{4W}}{\partial t} &+ \frac{\partial}{\partial s}(S_W P_{4W}) &= -P_{4W}/T_W + P_{4D}/T_D
\end{aligned}$$

where P_{2D} and P_{2W} are the probability density functions (PDFs) of SO_2 concentration (c) in dry and wet periods, and P_{4D} and P_{4W} are the PDFs of sulfate aerosol concentration (s). L_D, L_W, S_D, and S_W represent the total loss and production rates of c and s defined by:

$$\begin{aligned}
L_D &= V_d/a + \mathrm{d}\ln V/\mathrm{d}t + K_{ox} \\
L_W &= L_D + \Lambda_2(c) \\
S_D &= k_{ox} c - s\,\mathrm{d}\ln V/\mathrm{d}t \\
S_W &= S_D - \Lambda_4(s)
\end{aligned}$$

where V_d/a is the dry deposition loss rate, $\mathrm{d}\ln V/\mathrm{d}t$ is the rate of dilution, k_{ox} is the oxidation rate of SO_2 in air, and Λ_2 and Λ_4 are the wet scavenging coefficients. These equations have been solved numerically on a grid defined by the characteristic curves for four different source scenarios:

Case I: A 400 kt a^{-1} SO_2 source distributed uniformly along a line 150 km long, with no further dispersion. This may be regarded as the "base case" in that the initial concentration (in a 10 m s^{-1} wind) is only 10.6 $\mu g\ m^{-3}$, or about 3.8 ppb, so the results are likely to rapidly approach those of a "linear" model.

Case II: A 4 Mt a^{-1} SO_2 source distributed uniformly along a line 450 km long, with no further dispersion. This may be regarded as roughly approximating the UK plume in conditions where lateral dispersion has smoothed out any detailed plume structure. In a 10 m s^{-1} wind the initial concentration is 35.2 $\mu g\ m^{-3}$ (about 13 ppb).

Case III: A 400 kt a^{-1} SO_2 source initially spread along a line 10 km long, and spreading at a rate of 3 km h^{-1}. This may be thought of as approximating a small group of power stations. The initially concentration in a 10 m s^{-1} wind is 158.5 μg m^{-3}, or about 57 ppb.

Case IV: A 1.2 Mt a^{-1} SO_2 source spread along a line 50 km long, with no further dispersion. This roughly approximates the combined plume of central England, and has an initially concentration of 95.1 μg m^{-3} (about 34 ppb) in a 10 m s^{-1} wind.

Salient features of the results are shown in *Table 14.1*, which illustrates the distance at which a 50% emission reduction would lead to a 40% reduction in wet deposition and in the ratio of wet to dry deposition 700 km from the source in each case. These figures show that the relative levels of wet deposition may be significantly less for higher source strengths (i.e., those sources producing higher airborne concentrations at a given distance) and that wet deposition from major source conglomerations may be significantly nonproportional on a regional scale, the distance depending on source strength and meteorological conditions.

Table 14.1. The distance at which wet deposition becomes 60% for a 50% emission reduction, and the ratio of wet to dry deposition at 700 km, for different source and meteorological scenarios.

	Case			
Variables	*I*	*II*	*III*	*IV*
Distance at which 50% emission reduction leads to 60% wet deposition				
$v_d = 8$ mm s^{-1}, $u = 10$ m s^{-1}	170 km	480 km	500 km	720 km
$v_d = 1$ mm s^{-1}, $u = 10$ m s^{-1}	200 km	695 km	640 km	950 km
$v_d = 8$ mm s^{-1}, $u = 5$ m s^{-1}	165 km	340 km	325 km	350 km
$v_d = 1$ mm s^{-1}, $u = 5$ m s^{-1}	220 km	465 km	435 km	370 km
Ratio of wet to dry deposition at 700 km from source				
$v_d = 8$ mm s^{-1}, $u = 10$ m s^{-1}	0.41	0.36	0.38	0.27
$v_d = 1$ mm s^{-1}, $u = 10$ m s^{-1}	2.80	2.15	2.45	1.56
$v_d = 8$ mm s^{-1}, $u = 5$ m s^{-1}	0.66	0.58	0.67	0.49
$v_d = 1$ mm s^{-1}, $u = 5$ m s^{-1}	3.28	2.48	3.23	1.87

These results may be interpreted very simply. An approximate solution to the above equations may be obtained by integrating over the PDFs and applying a steady-state approximation, valid at travel times greater than about T. This leads to an estimated ratio of wet to dry deposition, given by

$$R = \bar{\Lambda}_2 T_W / ((1 + \bar{\Lambda}_2 T_W)\ v_D T_D / a)$$

in the absence of dry oxidation, where $\bar{\Lambda}_2$ is the concentration-weighted scavenging rate averaged over the distribution of airborne SO_2 concentration at a given travel time. The term $v_D T_D / a$ is clearly related to the average loss by dry deposition in dry periods, while $\bar{\Lambda} T_W / (1 + \bar{\Lambda} T_W)$ is equal to the efficiency of wet removal averaged over all durations of wet periods. If dry oxidation is included, an extra, but similar, term is introduced, relating the efficiency of sulfate aerosol removal. It is clear from this that close to the source, where $\bar{\Lambda} T_W$ is <1, the wet deposition will be reduced when compared with a linear model with efficient wet removal; but further away, as $\bar{\Lambda} T_W$ becomes greater than 1, the detailed behavior of $\bar{\Lambda}_2$ with respect to SO_2 concentrations becomes unimportant, and the wet deposition will respond in proportion to emissions.

Conclusions

These results demonstrate two major conclusions:

(1) The fact that a model using a given set of parameters is able to reproduce observations well does not, in itself, justify the formulation of the model or the parameter values used. In particular, if background wet deposition is regarded as an unknown adjustable parameter, then nothing can be objectively stated regarding the efficiency of SO_2 wet scavenging. If background is constrained below a value consistent with other observations (about 0.4 mg S l^{-1}), this implies an average removal efficiency greater than or about 50%.

(2) Applying recent results regarding nonlinear chemistry inside precipitation systems suggests that the efficiency of removal reasonably close to major sources (e.g., within 1000 km) may, on average, be rather less than 50%, implying that existing linear models overestimate their contribution to wet deposition, and that in this regime the response to a change in emissions would not be proportional to the emission change, while emissions from smaller sources would be efficiently scavenged. Given that observed deposition is a mixture of deposition from both behavior regimes, this is not in conflict with conclusion (1). The primary indicator of behavior is the concentration-weighted, event-weighted mean scavenging efficiency.

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PART IV.

Simplified Approaches to the Linearity Issues

15. Effect of Nonlinear Sulfur Removal Coefficients on Computed Sulfur Source–Receptor Relationships: Some Model Experiments

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The so-called "linearity question" concerned with long-range transport of sulfur in the atmosphere may be posed in a variety of ways. One way of particular interest to European policy analysis is to ask whether reductions or increases of annual total sulfur emissions in a particular country will result in a proportional increase or decrease of sulfur deposition at a receptor location some distance from the source country. This paper outlines a method to investigate this question, based on a Lagrangian long-range model of sulfur in Europe (Eliassen and Saltbones, 1983)

Method

As a first step, model parameters that reflect sulfur removal processes are assigned nonlinear functions of airborne SO_2 concentration. Next, mass balance equations for SO_2 and $SO_4^=$ are solved along a set of computed air trajectories for an entire year between a particular sulfur source country and receptor grid element. This yields annual total sulfur deposition at the receptor. Since there is a nonlinear term in the model equations, we repeat these annual computations for several levels of "background" (i.e., nonsource country) sulfur emissions.* Consequently, we obtain a range of receptor sulfur depositions for each level of source country sulfur emissions. This range reflects the possible deviation from linearity of the source–receptor relations due to assumed nonlinearity of coefficients.

This method is attractive because it provides insight into possible nonlinearity under realistic emission conditions and actual meteorologic situations.

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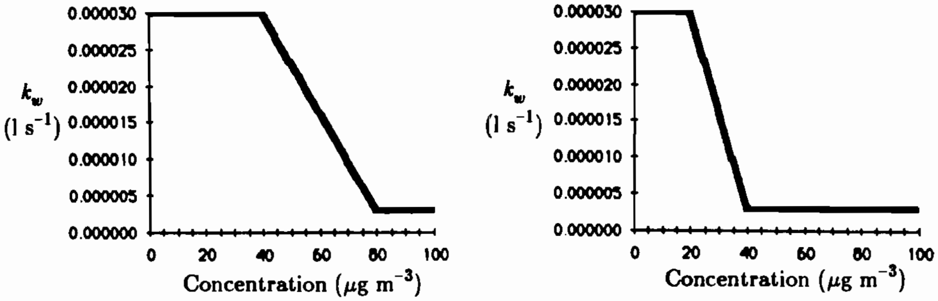
* In this paper we investigate the effect of emissions from a single country on deposition at a single receptor. Emissions from all other countries and from outside the European study area are called "background emissions".

Application

For the model experiments described in this paper, two source–receptor combinations were used because of the contrast in their meteorologic and geographic situations: German Democratic Republic (GDR)–Illmitz (eastern Austria), and United Kingdom (UK)–Roervik (southern Sweden). For this application the wet deposition coefficient (k_w) was made a function of SO_2 air concentration. This coefficient is, of course, a crude approximation of exceedingly complex physical and chemical removal processes occurring in the boundary layer. We assigned k_w the functional form given in *Figure 15.1*, which reflects so-called SO_2 "saturation" in the boundary layer. This saturation may result from the conversion of raindrop-absorbed SO_2 to $SO_4^=$ in rain with an attendant increase in raindrop acidity. Increased raindrop acidity shifts the sulfur species equilibrium in the raindrop toward $(SO_2)_{aqueous}$, thereby decreasing the absorption rate of $(SO_2)_{air}$ [*cf.* Barrie (1981)].

(*a*) Function 1 (*b*) Function 2



(*c*) Function 3 (*d*) Function 4

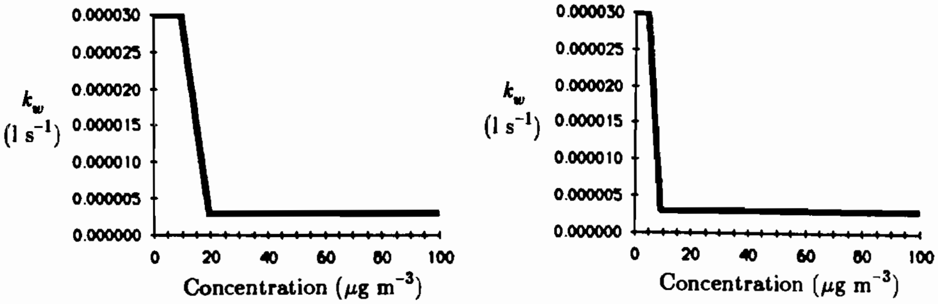


Figure 15.1. Assigned nonlinear k_w functions.

In this model experiment, four different functions of k_w were investigated (*Figure 15.1*). The maximum value of k_w was set equal to the EMEP value of 3×10^{-5} sec^{-1}.

Since k_w is assumed to be a nonlinear function of SO_2, it is necessary to investigate the effect of different levels of "background" (nonsource country) emissions. This was accomplished by running one-year model experiments for five different background emission levels: one corresponding to current emissions, two higher, and two lower. These scenarios are listed in *Table 15.1*. The country-scale emissions in this table were distributed to grid elements in each country according to the 1980 spatial distribution of these elements estimated by EMEP. Source country emission levels were varied in 20% increments above and below their 1980 values. Computations were based on the set of 1980 trajectories for the two source–receptor combinations. These trajectories were computed by the Pettersson method using meteorological data provided by EMEP-W.

Results

The deviation from linearity for the five emission scenarios and the two source–receptor combinations are presented in *Figure 15.2*. Results in these figures were obtained by using function 4, the"most nonlinear" of the functions in *Figure 15.1*, i.e., the function in which k_w decreases at the lowest SO_2 air concentration. At 100% of 1980 GDR sulfur emission levels, function 4 for k_w resulted in a 21–28% deviation of total sulfur deposition from the linear case, depending on the background emission levels. For the UK to Roervik combination, a deviation of 8% to 11% from the linear case was computed at 100% UK 1980 emissions, depending on the background (nonsource country) emission scenario.

The enhancement of deposition for the nonlinear cases, illustrated in *Figure 15.2*, may be attributed to the net effect of the k_w functions in *Figure 15.1* in reducing the "average" wet deposition rate compared to the original k_w value. A reduction of k_w increases travel distance of sulfur from the source countries. A compensating reduction of deposition should be computed at receptors closer to the source countries.

Figure 15.3 summarizes results from all four nonlinear k_w functions assuming a "current emission" background (nonsource country) emission scenario.

Results of these model experiments depend, of course, on the prescribed k_w function. In future model experiments, it will be helpful to increase the maximum value of k_w in these functions so that the "average" k_w for a one-year simulation will more closely resemble the original EMEP-W model k_w value. This would make comparison of linear and nonlinear cases more consistent.

Comparison with other parameter uncertainties

We can now compare the uncertainty owing to nonlinear k_w (*Figure 15.2*) with deposition ranges due to parameter uncertainty (*Figure 15.4*). These parameter uncertainty ranges were computed by first assigning uniform distributions to all EMEP model parameters (except the parameter describing background concentration in the wet deposition formulation). These distributions were then used to

Table 15.1. "Background" sulfur emission scenarios.

Country	*MPC*[a]	*CRP*[b]	*Current*[c]	*ECE,C*[d]	*ECE,TC*[e]
Albania	23	50	50	50	74
Austria	129	110	220	186	269
Belgium	285	203	403	430	639
Bulgaria	355	350	500	853	1 125
Czechoslovakia	601	1 085	2 550	1 353	1 701
Denmark	161	110	219	211	277
Finland	207	149	298	261	329
France	502	818	1 635	769	1 020
Germany, FR	847	640	1 600	1 498	2 355
Greece	99	175	350	188	310
Hungary	325	572	817	746	968
Ireland	77	88	218	170	296
Italy	729	1 330	1 900	1 449	2 427
Lluxembourg	15	15	24	37	63
Netherland	42	96	240	704	1 107
Norway	63	35	69	91	120
Poland	964	1 378	1 378	2 042	3 158
Portugal	27	85	85	50	76
Romania	429	1 000	1 000	916	1 135
Spain	498	1 878	1 878	1 086	1 841
Sweden	188	87	248	267	363
Switzerland	29	42	60	53	77
Turkey	108	250	500	216	393
USSR	3 640	5 833	8 375	7 393	10068
Yugoslavia	574	1 500	1 500	1 294	1 875

[a] MPC = Major Pollution Controls. RAINS model scenario [for description of RAINS, see Alcamo, *et al.* (1985)] assuming flue gas desulfurization of public power plant and industrial boilers and coal cleaning and fuel desulfurization of conversion and domestic sectors. For the year 2000.

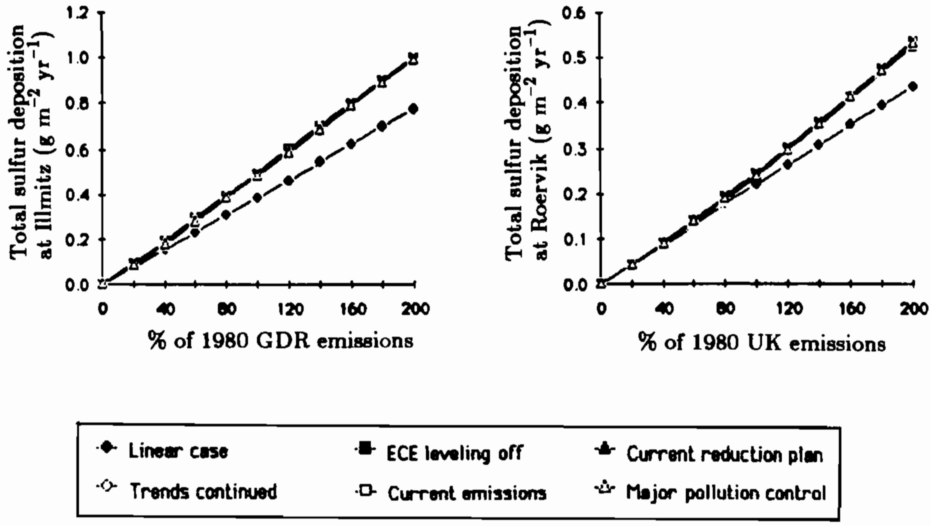
[b] CRP = Current Reduction Plans. Estimate for the year 2000 of emissions if countries implement their current sulfur reduction plans.

[c] Current = Estimated Current (1980) emissions. From Economic Commission for Europe (1985) and Organization for Economic Cooperation and Development (1985).

[d] ECE,C = Economic Commission for Europe (ECE), Conservation. RAINS model scenario based on an ECE energy conservation scenario in the year 2000 (ECE, 1983). No controls are assumed.

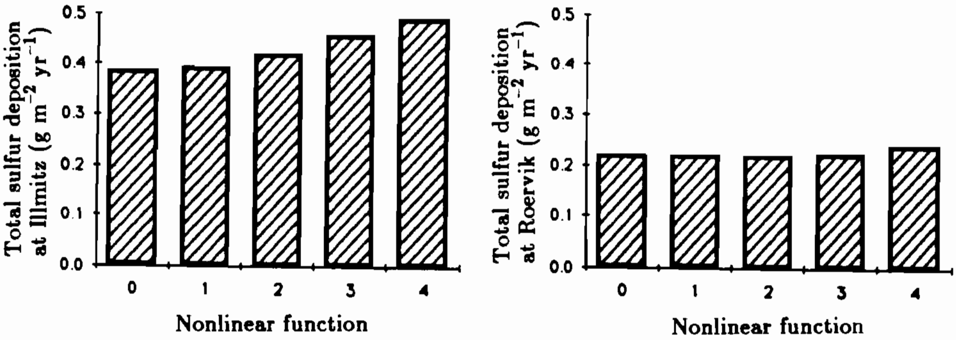
[e] ECE,TC = ECE, Trends Continued. RAINS scenario based on "trends continued" scenario of ECE (1983) in the year 2000. No controls are assumed.

compute total sulfur deposition by Monte Carlo simulation. The deposition ranges noted in *Figure 15.4* are the 90% confidence intervals (symmetric, two-sided) from the results of the Monte Carlo runs. Computations for ±20% and ±40% parameter uncertainty ranges are illustrated. The procedure for this analysis is described in Alcamo and Bartnicki (1985). For the GDR–Illmitz combination, the total deposition varied from -14% to +15% of the linearity case due to ±20% parameter uncertainty, as compared to +27% deviation due to a nonlinear k_w. For UK–Roervik, the deviation of total deposition due to parameter uncertainty of ±20% is -20% to +22% compared to a +10% deviation due to the nonlinear k_w.


(a) Transport from GDR to Illmitz (Austria)

(b) Transport from UK to Roervik (Sweden)

Figure 15.2. Computed deviation from linearity of two source–receptor combinations for nonlinear function 4.


(a) 100 GDR emissions.

(b) 100 UK emissions.

Figure 15.3. Computed total sulfur deposition for different k_w nonlinear functions including linear case (function 0), Current Emissions scenario.

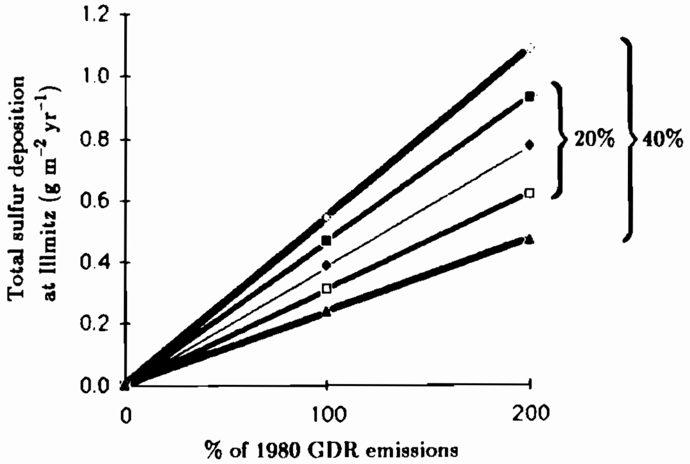


Figure 15.4. Computed total sulfur deposition uncertainty for ±20% and ±40% parameter uncertainty range: transport from GDR to Illmitz (Austria). (See *Figure 15.2* for symbol definitions.)

Summary and Conclusions

(1) The method presented here is a simple procedure for analyzing the effect of possible nonlinearity between country sulfur emissions and receptor total sulfur deposition. These computations are performed for realistic emission scenarios and actual meteorologic data. The method allows different uncertainties to be compared on the same time and space scales.

(2) The maximum deviation from linearity computed for all background emission cases (at 100% of the source countries' emission) is +28%.

(3) The deviation from the linearity case for the UK–Roervik combination is smaller than that for the GDR–Illmitz combination. This may be attributed to the absence of background emissions during air pollutant transport over the sea.

(4) Nonlinearity uncertainties were compared with other model parameter uncertainties. For the GDR–Illmitz combination, the nonlinear uncertainty as computed in this paper is of the same magnitude as that caused by a ±20% parameter uncertainty. For the UK–Roervik combination, nonlinearity uncertainty is much smaller than model uncertainty due to ±20% parameter uncertainty.

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16. Evidence of Linearity Effects in Modeling Sulfur and Nitrogen Oxides Transport and Deposition in Eastern North America

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In modeling annual averages of sulfate and nitrate in eastern North American precipitation, Fay *et al.* (1985, 1987) used a first-order linear model of transformation and deposition of the primary or secondary oxide species concentrations. The global rate constants and meteorological parameters of the model, assumed invariant in space, are determined empirically so as to minimize residuals in the comparisons of modeled and measured deposition rates. The model includes as intermediate variables the concentrations of primary and secondary species. Two types of measurements comparisons can be used to test the utility of the linearity model: a spatial comparison over a short time period and a long-term time trend at a single receptor.

Measurements made during the three-year period 1980–1982 at a set of 109 monitoring sites in eastern North America were used in the spatial comparison. The region, about 2500 km^2, enclosed the principal sources of emission and contained monitoring sites near the periphery at which low deposition rates were recorded, the ratio of maximum to minimum deposition rates being about 10. While different sampling periods were used throughout the network, the quality of the sample analysis was uniformly high. A comparison of the measurements with the model deposition rates is shown in *Figure 16.1* (*a* and *b*) for sulfate and nitrate, respectively. On average, the residuals are less than 20% of the mean values of the measured quantities. The residuals are approximately independent of the value of the deposition rate, perhaps reflecting a random component, such as measurement error.

It is significant that a linear model shows uniformly good agreement over such a large range of values of the deposition rates. According to the model calculations, most of the contribution to the deposition at a monitoring site comes from sources within 1000-km radius (Fay *et al.*, 1985). The sites having low deposition rates are

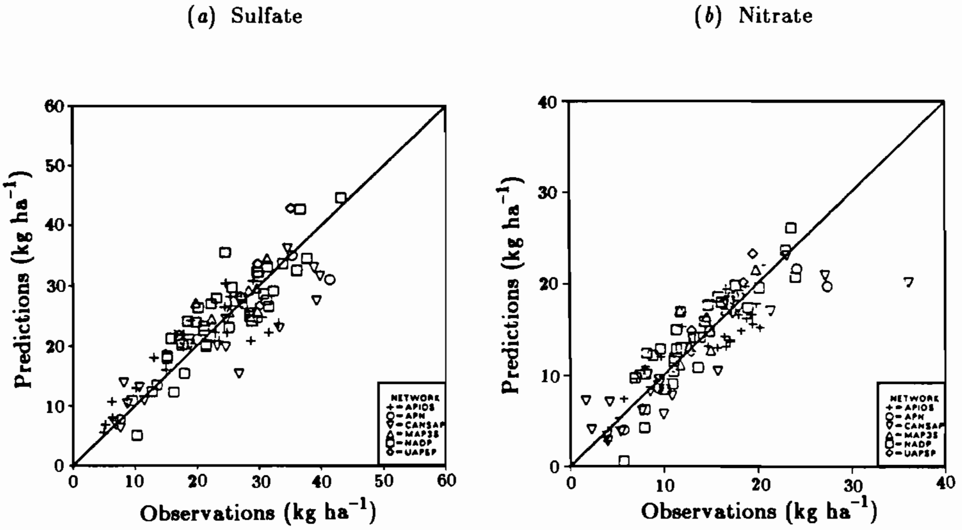


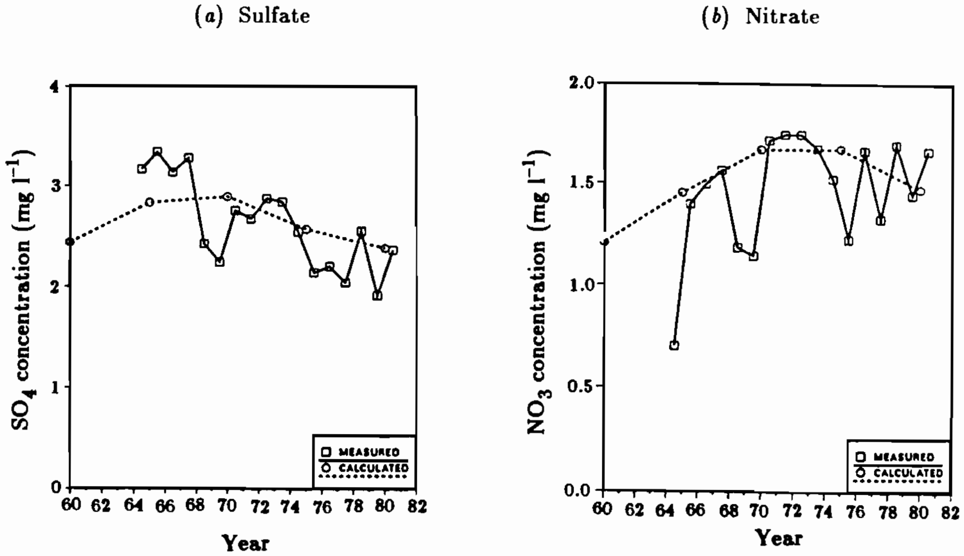
Figure 16.1. Computed versus observed concentrations in precipitation at 109 monitoring sites: (*a*) sulfate; (*b*) nitrate.

therefore sampled from regions where, on average, species concentrations are lower by about a factor of three than the source regions surrounding high-deposition rate sites. If the transformation or deposition rates were not approximately linearly dependent upon the species concentrations, then it would be difficult for a spatially uniform linear model to match the measurements over such large spatial regions having an order-of-magnitude range of species concentrations.

For sulfate (but not nitrate), there are significant differences in deposition rates between the summer half-year (October–March) and the winter half-year. A semiannual model of sulfate deposition shows that the linearity hypothesis applies equally well to the semiannual model (Golomb *et al.*, 1986).

A second comparison has been made with the measurements of annual average sulfate and nitrate concentrations in precipitation at Hubbard Brook, New Hampshire, for the period 1964–1980 (Fay *et al.*, 1985; 1987), shown in *Figure 6.2.* During this period the measured concentrations followed the trend of emissions from the source region affecting Hubbard Brook, which varied by about 30%. Because of the annual fluctuations in concentrations, probably caused by meteorological variability, close agreement with the measurements in any one year should not be expected. However, when averaged over several years, the comparison clearly shows that concentration trends follow the emission trends.

The different comparisons in both space and time presented above support the global linearity hypothesis as applied to modeling of the wet deposition throughout a large region affected by multiple sources, when averaged over periods of the order of a year.



(a) Sulfate

(b) Nitrate

Figure 16.2. Computed versus observed concentrations in precipitation at Hubbard Brook, New Hampshire: (*a*) sulfate; (*b*) nitrate.

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17. Heterogeneous and Nonconstant Homogeneous Transformation Rates in a Long-Range Transport Model for Sulfur Emissions

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We estimated long-range transport of sulfur emissions of Europe with the trajectory puff model MESOS, which is described in Halbritter *et al.* (1985). To calculate the concentrations of SO_2 and $SO_4^=$ in the air and dry and wet deposition of SO_2 and $SO_4^=$, the following parameters have been used:

(1) An average value of 1% h^{-1} over the whole year for the transformation from SO_2 to $SO_4^=$.
(2) A dry deposition velocity of 0.8 cm sec^{-1} for SO_2 and of 0.2 cm sec^{-1} for $SO_4^=$.
(3) For wet deposition, no distinction was made between washout and rainout processes. For wet deposition a time constant was used, which is proportional to rainfall rate. Values are 3×10^{-5} sec^{-1} for SO_2 and for $SO_4^=$ for a rainfall rate of 1 mm h^{-1}.

In contrast to other models (e.g., the EMEP model), MESOS uses a variable mixing height, dependent on time of day and time of season.

Modeling results for average values over the whole year are in good agreement with measurements, but there are differences for seasonal values; in addition, modeled wet deposition of SO_2 is much higher than wet deposition of $SO_4^=$, which conflicts with measurements. In the following, the results of some sensitivity tests, including modified assumptions for wet deposition and a variable transformation rate, are presented. So far, these calculations have only been performed for a single source — Hanover in the northern part of Germany, F.R. — for a stack height of 100 m with a heat output of 20 MW. Therefore, comparisons of modeling results with SO_2 and $SO_4^=$ measurements are not possible, but the results will give some insight into how seasonal and average annual values change.

Heterogeneous transformation and modified assumption for wet deposition

Concentrations of S (IV) in raindrops are described by the solubility equilibrium, which depends on temperature and pH value of raindrops (Beilke and Gravenhorst, 1978). A pH value of 4.5 and a temperature of 283 K give a time constant for SO_2 rainout of 1×10^{-5} sec^{-1} for a rainfall rate of 1 mm h^{-1} and a mixing height of 1000 m. Washout of SO_2, much lower than its rainout, is not considered in the modified calculations.

When clouds are present (data for cloud cover are given in the data base), heterogeneous transformation takes place in addition to homogeneous transformation. A cloud thickness of 500 m and a heterogeneous transformation rate of 5% h^{-1} within the clouds is assumed. During a rain event, most $SO_4^=$ present in clouds will be rained out (Fisher, 1982; Hegg *et al.*, 1984). For our calculations, we assume a value of 75%. No modifications were made for washout of $SO_4^=$. Some results include:

(1) Wet deposition of $SO_4^=$ makes up about 90% of total wet deposition, which is in good agreement with measurements (Davies, 1979).

(2) There are only small differences in total wet deposition as a sum over all directions. In *Figures 17.1* and *17.2*, the percentages of total wet deposition for different directions for a distance of about 300 km from the source are given for the summer months (April to September). For 1982 (*Figure 17.1*), there are large differences, giving higher amounts of wet deposition for the modified assumptions with trajectories going to the east. This is a result of enhanced $SO_4^=$ in air and of enhanced wet deposition with winds from westerly directions. For 1983 (*Figure 17.2*), the differences are very small.

(3) In *Figure 17.3*, the amount of SO_2 transformed to $SO_4^=$ up to a distance of 350 km from the source is given as a ratio of calculations with and without heterogeneous transformation. For all directions, this ratio is higher for January to March and October to December (winter) than for April to September (summer). The average values over all directions are 1.9 for summer and 2.2 for winter.

(4) Reduction of SO_2 concentration in the air with increasing distance from the source is more marked in the modified calculations. At a distance of 600 km from the source, we get a difference of 20% for the west–east direction and of 10% for the north–south direction. This again is the result of more clouds with winds from westerly directions.

Variable transformation rate

Measurements of concentrations in the air show that the ratio of SO_2 to $SO_4^=$ is higher in winter than in summer. According to Gillani *et al.* (1981), the homogeneous transformation rate for SO_2 depends on solar radiation. Therefore, calculations with a transformation rate depending on time of day, time of year, and on geographical latitude were performed. The rate was normalized such that for a

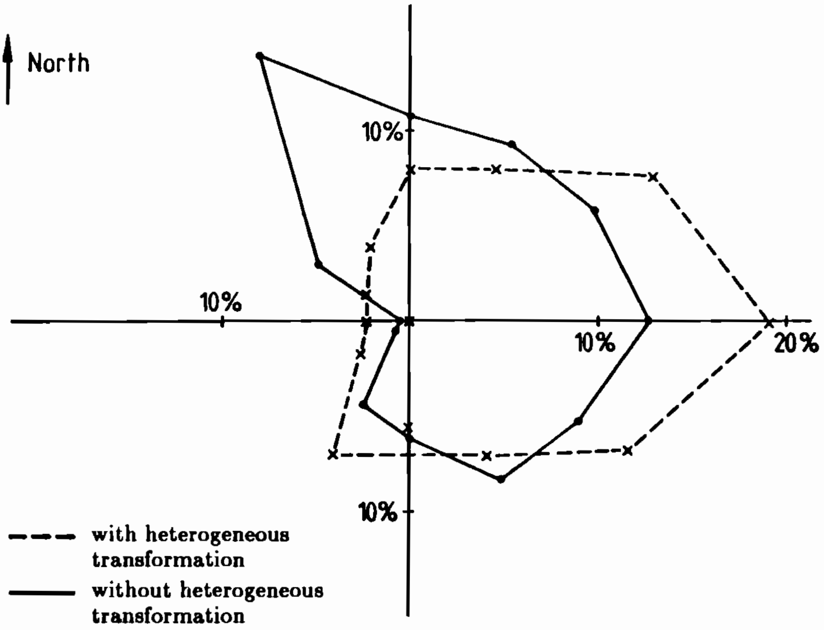

Figure 17.1. Percentage of total wet deposition in different directions 300 km from the source: summer 1982.

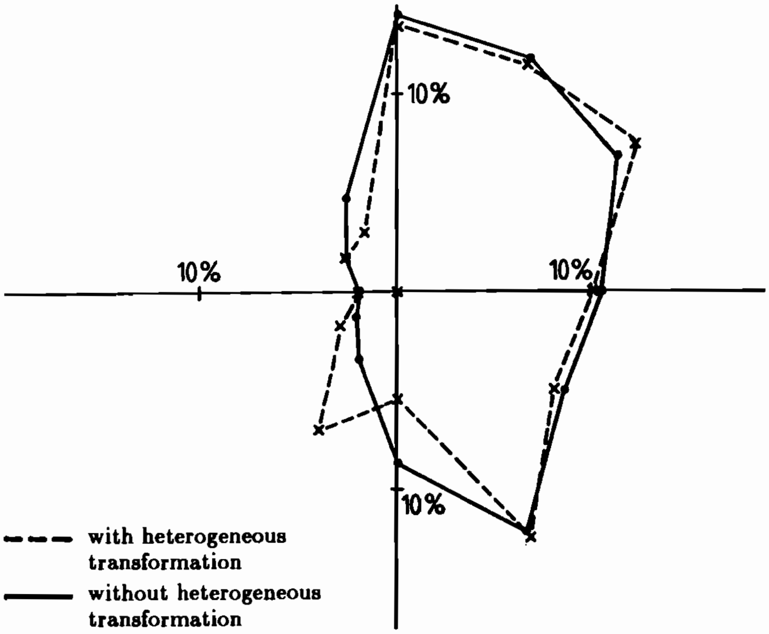

Figure 17.2. Percentage of total wet deposition in different directions 300 km from the source: summer 1983.

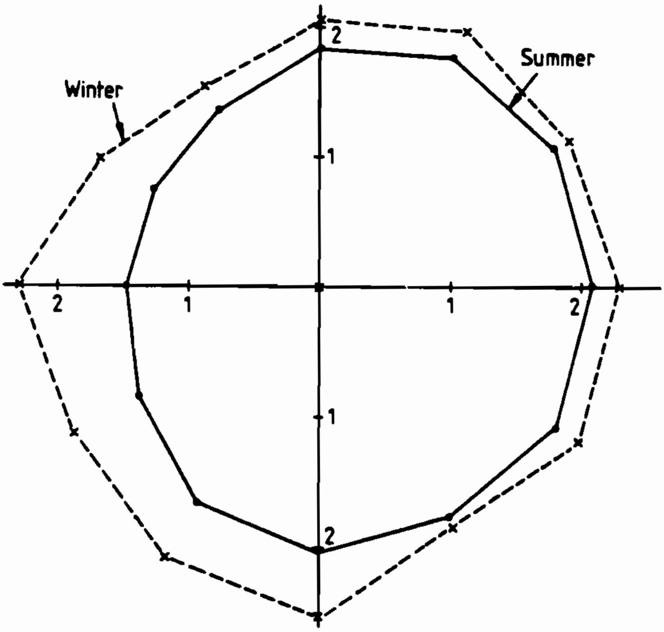

Figure 17.3. Amount of SO_2 transformed to $SO_4^=$ up to 350 km from the source; ratio of calculations with and without heterogeneous transformation.

latitude of 50° the average value over the whole year is 1% h^{-1}. *Figure 17.4* shows the amount of SO_2 transformed to $SO_4^=$, as a sum over all directions. At a distance of 600 km, the difference between variable and constant transformation rates is a factor of 1.3 in summer and of 0.6 in winter. Heterogeneous transformation yields the highest values. *Figure 17.5* shows the amount of ($SO_2/SO_4^=$) in the air as a ratio of winter to summer values. Values greater than 1 for a constant transformation rate result from different meteorological conditions. Higher values for a variable transformation rate (up to a factor of 2) are an indicator that the $SO_2/SO_4^=$ ratio in winter is higher than in summer, which agrees with measurements.

Conclusions

Calculations with the MESOS model were performed for one source, including heterogeneous transformation and a variable homogeneous transformation rate. The modified calculations yield better values for the contribution of wet deposition of SO_2 and $SO_4^=$ to total wet deposition, changes in the regional distribution of wet deposition, and changes in concentration values for different seasons. Further calculations should be done for different sources over Europe and for different sensitive parameters — e.g., heterogeneous transformation rate, rainout of $SO_4^=$, thickness of clouds — to verify the modified model, not only for average values over the whole year, but also for values for shorter time periods.

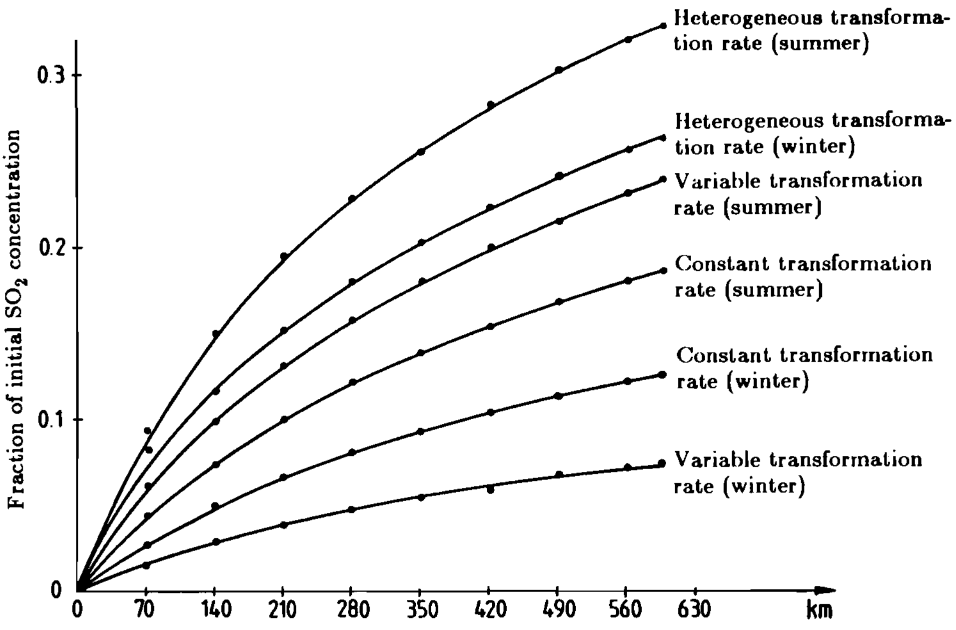

Figure 17.4. Amount of SO_2 transformed to $SO_4^=$; sum over all directions as a function of distance from the source.

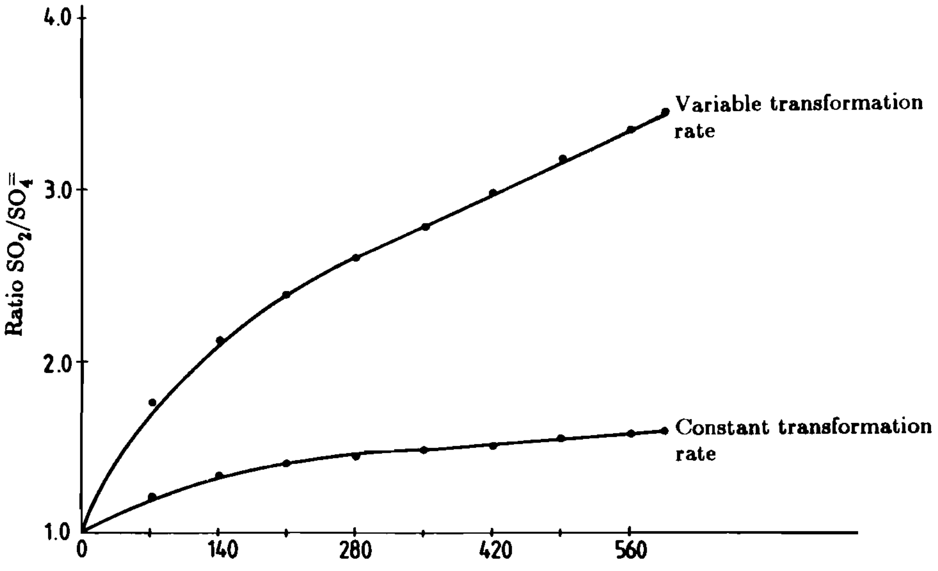

Figure 17.5. Amount of $(SO_2/SO_4^=)$ in the air; ratio of winter to summer as a function of distance.

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