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General Report

ATMOSPHERIC PATHWAYS OF SULPHUR COMPOUNDS

Prepared by
MONITORING AND ASSESSMENT RESEARCH CENTRE of the
SCIENTIFIC COMMITTEE ON PROBLEMS OF THE ENVIRONMENT,
INTERNATIONAL COUNCIL OF SCIENTIFIC UNIONS

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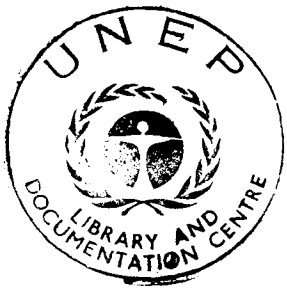
Atmospheric Pathways of Sulphur Compounds

by D. M. Whelpdale*

A General Report (1978)



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PREFACE

The pollution of the atmosphere by oxides of sulphur is a problem that has been continually growing since the Industrial Revolution and is now no longer confined to city areas alone. Due to the increasing use of fossil fuels to generate electricity, the quantities of sulphur oxides emitted to the atmosphere have increased several times over in the last 20 to 30 years. This is the main factor in atmospheric sulphur oxide pollution, other significant contributions coming from smelters and heavy industry.

It has been known for some time that sulphur oxides and particulates in air are associated with human health problems, particularly various types of lung disease, although the exact causal relationships are not well understood. Because of various acute pollution episodes – particularly those in London during the early 1950s during which the death rate increased markedly above average – programmes were initiated to clean up the air in large cities in many countries. As a result, at the present time the sulphur dioxide and sulphate particulate content of the air in many cities is being monitored and there are a number of programmes under way to investigate the correlation between exposure of humans and the incidence of lung disease.

On the assumption that the global consumption of energy will increase markedly during the next two or three decades, and that much of this additional energy is likely to be produced from the burning of coal, it would appear that total emissions of sulphur oxides into the atmosphere will continue to increase unless preventive action is taken. Although much of this increased emission may be from outside major cities or other areas of high population density, the total quantities of sulphur compounds involved are sufficient to cause concern with respect to atmospheric pollution on a regional scale.

This report broadly reviews the atmospheric transport of sulphur compounds on a regional scale. It lists estimates of present global emissions and summarizes present knowledge concerning transport models needed to estimate and predict sulphur oxide transport up to distances of several thousand kilometres. The report notes that present knowledge about these processes is insufficient for making adequate estimates of fluxes or for predicting the outcome of severe episodes. Although a number of monitoring and research programmes, both national and international, have been implemented or are planned, there is still a great dearth of monitoring data on concentrations and deposition rates in many areas of the globe. The report highlights these gaps in our knowledge and proposes monitoring and research studies that would go some way to providing the information required.

Bernard J. O'Brien
Director

1.0 Introduction

1.1 Purpose of Review

This review was prepared as a contribution to the UNEP* total assessment of sulphur oxides and related compounds. Emphasis has been placed on the regional-to-continental scale aspects of the atmospheric pathways of sulphur dioxide (SO_2) between emission sources and receptors.

The adverse effects of atmospheric sulphur compounds are best known on the local scale, in urban and industrial situations. Human respiratory ailments are known to be associated with atmospheres containing high concentrations of sulphur dioxide and sulphates (EPA 1975). Direct damage to certain agricultural crops and forest species, damage to property and buildings, and corrosion of materials also result from high SO_2 levels.

On the regional scale, atmospheric sulphur is the major contributor to the acidity of precipitation. Damage caused by the surface loading of SO_2 and acid precipitation is best documented in the case of freshwater ecosystems, where acidification of lakes and rivers has resulted in reductions in fish populations and species diversity in parts of Europe and North America. Soil chemistry changes are also occurring and decreases in forest productivity are suspected.† In the atmosphere itself, elevated particulate sulphate levels extending over large regions are becoming a concern from a human health point of view, particularly in the United States (EPA 1974). On the other hand, in areas of sulphur-deficient soils, such as portions of the Canadian prairies, atmospheric inputs of sulphur compounds, and other nutrients, have a beneficial effect.

Effects on climate are difficult to document or predict; however, concern is being expressed regarding the possible influence of small sulphate particles on the regional and global climate (Bolin and Charlson 1976) because of their effect on the radiative balance of the earth and their function as cloud condensation nuclei.

In this review, the topic is first placed in the context of the global biogeochemical sulphur cycle, and specific substances and scales of interest in the atmospheric sulphur cycle are discussed. In the second section, the atmospheric pathways of sulphur compounds are examined

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* United Nations Environment Programme

† For a discussion of the effects of acid precipitation, see *Ambio* **5**, 5-6, 1976.

by describing the various chemical and physical processes that make up the pathways. A brief description of sources and receptors of sulphur oxides is included to complete the atmospheric sulphur cycle. The third section deals with global and regional levels and trends, and the atmospheric sulphur budget. Current, large national and international programmes which are investigating aspects of the atmospheric behaviour of sulphur are then reviewed in section four. The last section summarizes the current state of our knowledge; this leads to a brief discussion of knowledge gaps, and future monitoring and research needs.

1.2 The Global Sulphur Cycle

In order to describe and quantify the movement or cycling of substances through the natural environment, global biogeochemical cycles of the substances are constructed. Such models are composed of a series of reservoirs – the atmosphere, hydrosphere, lithosphere, and biota – and transfers between these reservoirs. Here, only the atmospheric reservoir is discussed: the behaviour of sulphur oxides within the atmosphere, and the links with other reservoirs, emission sources and sinks.

Sulphur is a substance, like carbon dioxide, whose man-made component in the atmosphere is sufficiently large to interfere significantly with its natural cycle. Figure 1 (Granat, Rodhe and Hallberg 1976) is an informative diagram of the global sulphur cycle, showing the man-made sulphur transfers between reservoirs added to the natural ones. On the global scale it is indeed difficult to separate the effects of natural and man-made contributions; however, in many of the more industrialized parts of the world the man-made portion dominates. This review is concerned primarily with those situations.

1.3 Atmospheric Sulphur Compounds

Compounds of sulphur found in the atmosphere include the following: sulphur dioxide, sulphur trioxide, sulphate-containing compounds such as sulphuric acid and ammonium sulphate (and many others), hydrogen sulphide, methyl mercaptan, dimethyl sulphide, dimethyl disulphide, and other organic forms.

Sulphur dioxide accounts for the largest portion (~95 per cent) of man-made sulphur emissions. The oxidation reactions of SO_2 all lead to the formation of sulphates in times of the order of days, depending on the ambient meteorological conditions and the other substances present.

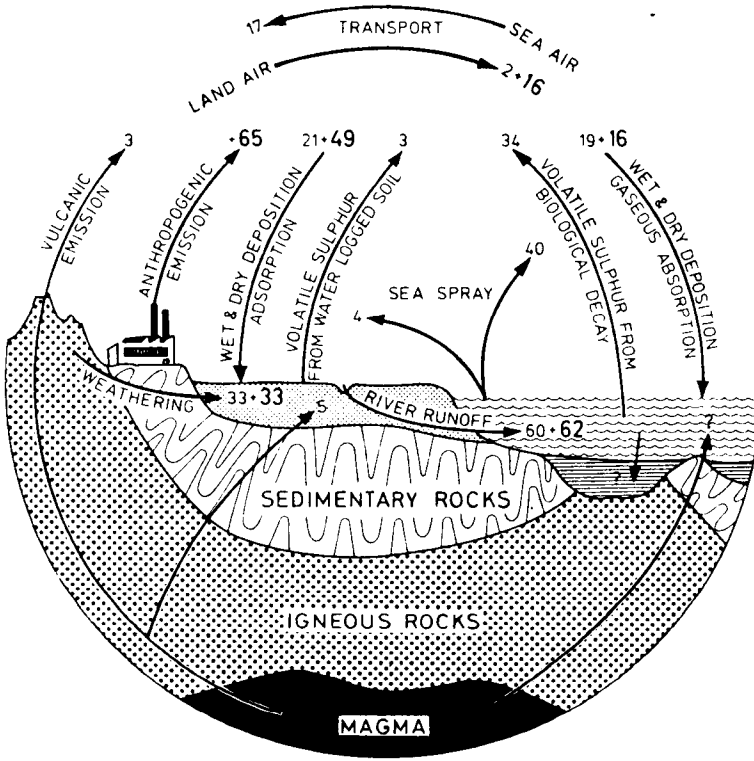

Figure 1. The global sulphur cycle; the fluxes shown are in Tg yr^{-1}*. Small type denotes the transfers as estimated to have prevailed before man had a significant influence on the sulphur cycle. The bold figures give estimates of what man has added by various activities. (Reprinted from *Ecological Bulletins/NFR22*, R. O. Hallberg in Granat *et al.* 1976).

* Tg, teragram is equal to 10^{12} grams, or 10^6 metric tons.

Sulphur trioxide is emitted with SO_2 in amounts of a few per cent of the SO_2. It combines very rapidly with water to form sulphuric acid.
Sulphate-containing compounds are the end-products of atmospheric oxidation reactions of SO_2. They may exist as components of hydrometeors, as solid or liquid particles, or in liquid films on solid particles. The principal compounds are sulphuric acid, ammonium sulphate and other sulphate salts. Sulphate aerosols larger than approximately 1 μm* are generally produced by mechanical processes, while the vast majority, those below 1 μm and predominantly in the 0.1 to 1 μm range, are generated by gas-to-particle conversion reactions.
Hydrogen sulphide is formed primarily from the natural decay of vegetation on land, marsh lands and in the oceans. In air, hydrogen sulphide is probably oxidized to SO_2 within hours.

Relatively little is known about the organic compounds. They are primarily from natural sources, and emissions of dimethyl sulphide, along with hydrogen sulphide may be important in the global sulphur budget. Granat *et al.* (1976) have reviewed the available data for these substances and found that little information is available on their natural concentrations, emissions, the extent of man-made contributions, their atmospheric decay rates, and whether SO_2 is an intermediate product.

For the purpose of this review, sulphur dioxide and sulphate in its various forms, are of prime interest.

1.4 Distance Scales

Pollution situations can be grouped conveniently, if somewhat arbitrarily, into four distance scales: local, regional, continental, and global†. If a distance of the order of 10 kilometres is characteristic of the local situation, then an increase by an order of magnitude for each subsequent scale is appropriate. Our interest here is in the two intermediate cases, regional and continental – i.e. over distances of approximately a hundred to several thousand kilometres.

Local pollution problems associated with cities or major point sources

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* μm, micrometre is equal to 10^{-6} metres.

† Much confusion exists in the use of these terms and the associated distance scales, particularly for "regional". The terms are used in this report as defined in the text.

arise primarily from high ambient pollutant concentrations and from large pollutant deposition rates to soils, vegetation and other receptors. On this scale, adverse effects can usually be directly related to the offending emission sources and, in turn, improvements are relatively easy to achieve by reducing emissions from these sources.

Not all pollution is removed from the atmosphere near sources, however, and what remains gives rise to the regional-to-continental scale sulphur problems that are currently of such great scientific and socio-economic interest. The average residence time of pollution sulphur is usually between one and five days, depending on the climate of a region. This means that most sulphur will be removed from the atmosphere within this time following its emission and, correspondingly, within a transport distance of a few hundred to a few thousand kilometres from its source. The main concern on this scale is the damage caused by deposition of acidic sulphur compounds at the Earth's surface. Although individual sources cannot usually be identified, major emission areas, such as the heavily industrialized Ruhr Valley or British Midlands, can be, and thus control and remedial actions are quite feasible. These regional-to-continental scale problems are particularly significant because large, ecologically and economically important geographic areas may be adversely affected, and because, in most parts of the world, the existence of political boundaries within these distances makes the problem that of one country polluting another.

On the global scale, the impact of man-made sulphur compounds is not as well documented nor understood as it is for smaller scales. As noted earlier, there is some concern about the influence of sulphate particles on climate; however, this topic is not pursued here.

2.0 Atmospheric Pathways

2.1 Sources of Atmospheric Sulphur

Over the past several years estimates of natural and man-made sulphur emissions have been made for global sulphur budget calculations. Table 1 lists some of these values along with the percentage of total emissions for which man is responsible. On a global basis, fossil fuel combustion accounts for 75 to 85 per cent of man-made sulphur emissions, and industrial processes such as refining and smelting account for the remainder (Robinson and Robbins 1972; Friend 1973).

Table 1. Emissions of sulphur into the atmosphere (Tg S yr^{-1}).

Reference	Natural emissions	Man-made emissions	Percentage man-made of total
Eriksson (1960)	280	40	13
Junge (1963)	230	40	15
Robinson and Robbins (1972)	90	64	42
Kellogg *et al.* (1972)	92	50	35
Friend (1973)	108	65	38
Granat *et al.* (1976)	35	65	65

Natural emissions include those from volcanoes, and biological decay over land and ocean; sea spray* is not included because most of it returns directly to the oceans. These estimates have large uncertainties, particularly in the case of natural emissions, where the magnitude of biological decay emissions is adjusted to make budgets balance. The relative importance of man-made emissions (last column) is seen to be increasing as estimates are refined. The most recent figures of Granat *et al.* (1976) are based on the formulation of a pre-industrial sulphur budget which suggests that natural emissions of volatile, reduced sulphur compounds are substantially less than previously assumed. It is clear that man-made emissions account for a significant portion of total sulphur emissions into the atmosphere, even on a global scale.

However, global totals such as these do not provide the required detail for the study of smaller-scale problems. Both natural and pollutant atmospheric sulphur sources are distributed irregularly over the Earth. Volcanic emissions are sporadic, but may be very significant when eruptions occur, as compared with their annual average value. An assessment of the distribution of biological sources of hydrogen sulphide and dimethyl sulphide is rather difficult in view of the little information available. It is currently believed that marshy areas and tidal flats, which are quite restricted geographically, are the main source areas for these compounds. The geographical distribution of pollutant sources is better known and corresponds closely to the degree of

* The annual production rate of sea spray sulphur is estimated to be 44 Tg S yr^{-1}; 90 per cent of this is assumed to return directly to the oceans, and 10 per cent is assumed to be transported over land.

industrialization in various regions of the world. Kellogg *et al.* (1972) estimate that 93.5 per cent of SO_2 pollution is produced in the Northern Hemisphere, and the remaining 6.5 per cent in the Southern Hemisphere.

Evidently then, it becomes essential to look at emissions and budgets on a scale smaller than global. Rodhe has done this in detail in Granat *et al.* (1976) for north-western Europe. This region*, an area of about one per cent of the Earth's surface, accounts for an estimated 13 Tg S yr^{-1}, approximately 20 per cent of the global total. Natural emissions here are estimated to be not likely to exceed five per cent of the pollution emissions (OECD 1977), or less than one per cent of the natural global emissions (using figures of Granat *et al.* 1976). In regions such as this and eastern North America, where man-made emissions completely dominate the natural ones, regional rather than global budgets provide more insight into the nature and magnitude of the sulphur problem.

Emission inventories are now being constructed in many parts of the world as a first step in looking at large-scale pollution problems. They are painstaking to construct; it is difficult to obtain the desired resolution in time and space. This is because data are often not readily accessible in the form desired, or often not available at all. It is then necessary to resort to emission factors, basing emissions on population and industrial productivity. The best inventory compiled to date on this scale is that of the OECD† Long-Range Transport of Air Pollutants Programme (Semb 1978). A second, of comparable complexity, is being assembled for eastern North America.

2.2 Processes

2.2.1 Introductory Remarks

After a pollutant has been injected into the atmosphere its behaviour is completely governed by the physical and chemical environment (e.g. wind speed, solar radiation, neighbouring chemical species) in which it finds itself. The series of processes which it undergoes – turbulent diffusion, photo-oxidation, scavenging by precipitation, etc. – define its pathway through the atmosphere. Although much is known qualitatively about individual chemical and physical processes, and even quantitatively in some cases, the real difficulty lies in quantifying the composite pathway.

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* The area bounded by the latitudes 45°N and 65°N, and by the longitudes 10°W and 20°E.

† Organisation for Economic Co-operation and Development.

In this section the individual processes are briefly discussed, along with the meterological factors which affect them. Then, the task of modelling these processes is examined.

2.2.2 Transport and Diffusion

In very simple terms, pollutants are carried along, or transported, through the atmosphere by the mean wind, and mixed, or dispersed, by turbulent fluctuations in the wind. Because travel times in the atmosphere for the distance scales of interest (hundreds to thousands of kilometres) may last from one to several days, the synoptic scale of meteorological motion is most relevant, although the meso- and micro-scale phenomena also have an important role to play.

The vertical structure of the lower troposphere is important to pollutant transport. Wind speed increases with height as the effect of surface roughness diminishes. Thus, the higher a pollutant's effective injection height (stack height plus plume rise), the greater the transport wind speed it experiences. On the average, atmospheric temperature decreases with height above the surface; however, the actual variation of temperature above the surface, at a given time and place, defines the stability of the atmosphere, and thus the amount of vertical mixing. Pollutants emitted into an unstable atmospheric layer are mixed throughout the layer; on the other hand, pollutants emitted into a stable atmospheric layer are mixed very little in the vertical.

The structure of the near-surface layer – the planetary boundary layer – experiences a diurnal variation which affects pollutant transport and diffusion. At night, surface long-wave radiation cools the near-surface air and causes the formation of a ground-based stable layer, or inversion. Pollutants emitted into this layer undergo little mixing or dilution, while those emitted above it may be slowly mixed through a large depth of the atmosphere above the ground-based inversion without reaching the surface. In the morning, as solar radiation heats the surface and causes convective mixing, the stable layer is eroded from below and pollutants mix through progressively greater depths of the atmosphere, frequently up to one or two kilometres, depending on the time of year and meteorological conditions. The following night, the cycle is repeated – pollutants well-mixed from the previous day remain above the newly formed surface inversion, and new pollutants are injected into the lower stable layers. Although this picture is rather simple and pertains primarily to fair-weather conditions in non-polar, continental areas, it does indicate the complexity of the atmospheric

processes controlling pollutant behaviour and the difficulty in modelling these processes.

Pollutants are mixed or dispersed through the lower atmosphere by turbulent diffusion, vertical wind shear, and precipitation processes. Turbulence is generated both mechanically (e.g. interaction with the surface, changes in surface roughness, and wind shear) and thermally (e.g. convective motions from solar radiation heating the underlying surface). The larger the scale and intensity of turbulence, the more efficient the mixing. Wind shear – the change in wind direction with height – causes a spreading of pollutants in the horizontal. In some situations, for example, in the case of rain falling through an SO_2 plume, precipitation can cause a vertical redistribution of pollutants.

Frequently, for lack of time and space resolution in meteorological and pollutant measurements, one resorts to envisaging the transport as occurring at the speed of the mean wind in a layer through which the pollutants are assumed to be uniformly mixed.

Pollutants can be transported over large distances under a variety of meteorological conditions. Plumes emitted into a stable atmosphere undergo little vertical or horizontal diffusion and can travel intact for several hundred kilometres before being dispersed or incorporated into cloud. Figure 2 (Munn 1976) shows such a narrow, coherent plume observed by satellite over Ontario, Canada. On the other hand, when emissions from diverse sources over a broad area accumulate in stagnating air associated with anticyclonic conditions of eastern North America or western Europe, the pollutants become well mixed by day-time convection, and are slowly transported in the southerly flows to the west of the high pressure centres, to affect areas several hundreds of kilometres across for a couple of days at a time. A related transport situation is responsible for many of the episodes of excessive sulphate and hydrogen ion deposition in Scandinavia. The air in stagnant anticyclonic conditions over Europe becomes heavily polluted and is then drawn into a frontal area of a depression running along the northern edge of the anticyclone. Only modest rainfall at the front is needed to produce relatively large depositions.

2.2.3 Transformation

The chemistry of sulphur dioxide in the atmosphere is complex. There are many possible gas-phase reactions (homogeneous reactions) and reactions involving liquid droplets and solid particulates (heterogeneous reactions) by which SO_2 may be transformed into sulphate. In turn, several factors – temperature, amount of sunlight, concentrations of

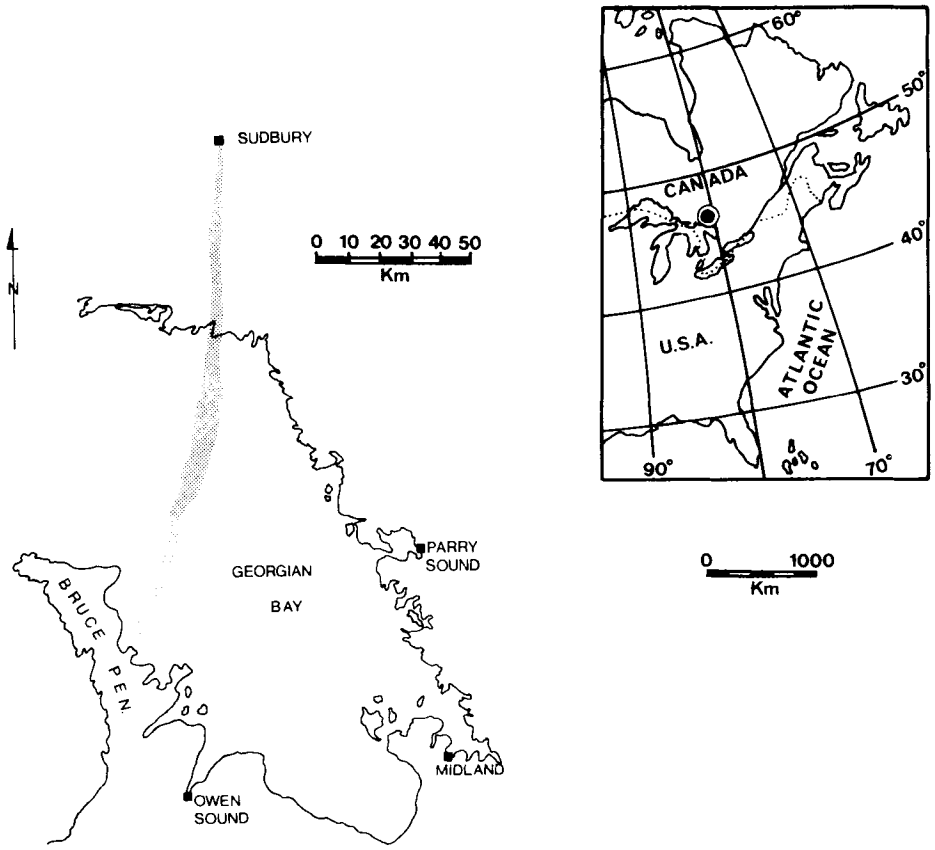

Figure 2. Tracing from ERTS photograph, showing the outline of a plume from the 381 m nickel smelter stack at Sudbury, Ontario, crossing Georgian Bay, 1040 EST, September, 1972 (Munn 1976). The inset shows the map location in central Ontario, Canada.

other substances (particularly water and aerosols) – influence the rates of oxidation. A knowledge of these transformation processes and rates is very important in order to be able to predict the concentrations of the various species along the transport path. Both the effectiveness of removal from the atmosphere and effects on receptors are governed to a large extent by the physical and chemical state of the sulphur-containing compound. Unfortunately, the various reaction rates are not well established for clean-air conditions, that is, away from urban atmospheres and plumes.

Reaction rates* for gas-phase oxidation of SO_2 range from a few tenths of a per cent to a few per cent per hour. For the western European summer, Eggleton and Cox (1978) suggest values of 0.5 to 5% hr^{-1} in sunlight, depending on the degree of pollution of the atmosphere, with the lower figure relating to clean air. Calvert, Fu Su, Bottenheim and Strausz (1978) also find rates up to 4% hr^{-1} in sunny, summer, urban conditions. The most important mechanisms are those involving the oxidation of SO_2 by other short-lived pollutants which have been photochemically generated (Eggleton and Cox 1978). The direct photo-oxidation of SO_2 is not important. Because these reactions are dependent on solar radiation, their importance decreases significantly in winter-time and at night.

Although the liquid-phase oxidation of SO_2 has been extensively studied under a variety of experimental conditions, there is still considerable disagreement in the literature concerning the rates of reaction. Uncatalyzed† oxidation is thought to be relatively unimportant in the atmosphere, compared with other possible liquid-phase reactions (Beilke and Gravenhorst 1978). Catalyzed oxidation in the presence of metals (e.g. iron, manganese) is important in urban plumes and perhaps urban fogs where their concentrations are sufficiently high, but probably not in cleaner, rural air. Liquid-phase oxidation involving the strong oxidizing agents ozone and hydrogen peroxide may also be very important; however, reaction rates and atmospheric concentrations, respectively, for these two substances are not sufficiently well known. The effect of atmospheric ammonia is to retard the increase in acidity of the solution resulting in further dissolution and liquid-phase oxidation

* Reaction rate refers to the rate at which a substance is consumed (or created) in a chemical reaction.

† A catalyst is a substance which enhances the rate at which a chemical reaction occurs, without being used up itself. Thus, an uncatalyzed reaction is one which proceeds in the absence of such a substance.

of SO_2. It is also important in the final transformation of sulphuric acid to ammonium sulphate. In summary, the liquid-phase oxidation reactions are generally thought to be of comparable importance to the gas-phase reactions.

There are a variety of measurements which indicate that SO_2 is both adsorbed and oxidized on the surface of solid particles. Carbon is believed to be a particularly effective surface in this regard. No rate data are available, however, and the importance of these reactions to overall conversion of SO_2 to sulphate aerosol in the atmosphere cannot be assessed. This mechanism could be significant in stack plumes.

The oxidation of SO_2 in plumes is governed by both chemical and dispersion processes which cannot be considered independently. Under certain atmospheric conditions plume reaction rates may be controlled by the rate of mixing of ambient air into the plume. After long plume-travel times, chemical processes are likely to become the dominant rate-limiting factor. The relative importance of homogeneous and heterogeneous reactions is often difficult to determine. Field measurements in plumes over distances of a hundred or more kilometres typically yield reaction rate values of a few tenths to approximately 4% hr^{-1} (Lusis and Wiebe 1976; Husar *et al.* 1978).

The oxidation of reduced natural sulphur compounds could make a significant contribution to atmospheric SO_2 concentration, particularly in regions of large natural and small man-made emissions. What is known of their reaction rates, and the place of SO_2 as an intermediate in their transformation schemes, is thus of considerable interest. Hydrogen sulphide and other organic sulphides can be oxidized to SO_2 by ozone, and by photo-oxidation processes involving the hydroxyl radical* and atomic oxygen (Eggleton and Cox 1978). The ozone reaction is probably unimportant in the atmosphere, and that involving the hydroxyl radical most important. Estimated reaction rates for the latter reaction are in the range of 2 to 12% hr^{-1}.

2.2.4 Deposition

Pollutants are removed from the atmosphere by a number of deposition processes: during dry periods by sedimentation, surface adsorption, and impaction; and during precipitation by in-cloud and below-cloud scavenging. The relative importance of these processes depends both

* A radical is a group of atoms which occurs in the molecules of a number of compounds, and which remains unchanged through many chemical reactions. The hydroxyl radical consists of one hydrogen atom and one oxygen atom.

on the climate of a region and on the physical and chemical properties of the specific compounds present. The important deposition processes are known, relatively well understood, and have been measured in the laboratory and under certain field conditions; however, modelling them realistically still poses considerable difficulty.

Direct surface uptake of sulphur dioxide is the most important dry removal process for atmospheric sulphur. Turbulent motions bring the gas into contact with the Earth's surface where it is adsorbed, dissolved or undergoes chemical reaction. The uptake may be limited either by the efficiency of the gas-phase transfer to the surface, or by the resistance imposed by the underlying surface. The oceans, other non-acidic moist surfaces, some crops and forest species at certain growth stages are good sinks; whereas dry, snow-covered surfaces and acid soils, for example, are less efficient.

Dry deposition of sulphate particles is much less important than that of SO_2. Sulphate particles are predominantly in the sub-micrometre range, and their removal by gravitational sedimentation is slow. Scavenging by forests is thought to be an effective deposition mechanism, but little quantitative information is yet available.

Dry deposition measurements are very difficult to make. Several approaches are currently used in the field – primarily, specialized micro-meteorological measurement techniques, chemical tracer experiments, and plume budget studies. These various techniques give comparable results (Garland 1978), namely, that dry deposition typically accounts for the removal of atmospheric sulphur at rates up to a few per cent per hour. On the basis of a rather limited number of such specialized measurements at selected locations, dry deposition processes are parametrized (see section *2.3.2*) and removal rates applied to large areas of the Earth's surface.

Deposition by precipitation is the result of both in-cloud and below-cloud capture of SO_2 and particulate sulphate. In-cloud processes include sulphate particles serving as condensation nuclei, coagulation, and diffusional uptake of SO_2. Below-cloud processes include interception of particles by falling drops and diffusional uptake of SO_2. In-cloud scavenging processes are more important in clean air, i.e. where SO_2 levels below the clouds are low.

Sea salt can contribute significantly to precipitation-sulphate levels in the marine environment. Measured sulphate concentrations at coastal sites can be corrected for the effects of sea spray deposits by applying the sea water sulphate/sodium ratio to measured sodium concentration

in precipitation at these sites. The "excess sulphate" values so determined are commonly used.

Wet deposition is, in general, much more easily measured than is dry deposition – several precipitation chemistry networks exist in various parts of the world for the routine measurement of wet deposition. Sulphur deposition, usually in sulphate form, is determined from measurements of sulphate concentration in precipitation samples and precipitation amount. Typically, the removal rate for particulate sulphate is of the order of 40 per cent per hour, and for SO_2, an order of magnitude less. The overall efficiency of wet removal depends on many factors: precipitation type, intensity, duration, frequency, the relative amounts of SO_2 and sulphate present, and the size distribution of particulate sulphate. Parametrization of wet removal processes is based on man measurements, made under a variety of meteorological conditions; yet, it still poses one of the most difficult modelling problems.

Wet and dry deposition appear to be of comparable importance, on an annual basis, over those large areas where measurements and calculations have been made. Dry deposition is more important closer to source regions where concentrations are higher, and, in principle, it goes on all the time. On the other hand, wet deposition occurs only periodically. Garland and Branson (1976) have estimated that, over the United Kingdom, the dry deposition of sulphur is approximately 2.3 times the wet deposition on an annual basis. Rodhe, in Granat *et al.* (1976), found the dry deposition over western Europe to be in the range of 0.7 to 1.4 times the wet deposition. In regions where major emission sources are more distant, such as Scandinavia, Dovland, Joranger and Semb (1976) have shown that wet deposition is more important than dry. For southern Norway in particular, where orographic precipitation contributes very significantly to the wet deposition, wet deposition is approximately 2.5 times the dry deposition.

2.3 Modelling

2.3.1 Modelling Approaches

Classical diffusion models are of very limited applicability for distance scales of the order of 100 kilometres, and they are inapplicable for scales of the order of 1000 kilometres. Over such scales, the basic assumptions of steady-state conditions and homogeneous flow break down because of diurnal variations in planetary boundary layer properties, meso-scale circulations such as sea-breezes and orographic lifting, and migrating synoptic-scale high and low pressure systems. Instead, for problems of

this scale, a variety of modelling approaches are being used – trajectory analysis, box models, statistical formulations, and three-dimensional, time-dependent air quality models.

These models serve three main purposes :

1. interpretation of field measurements
   (e.g. meteorological explanation of severe pollution episodes, source identification, data interpolation between measuring sites) ;
2. computations of fluxes and fields
   (e.g. annual pollutant loadings, transboundary fluxes) ;
3. prediction
   (e.g. potential episodes of acid rain, scenarios for various source-receptor configurations, long-term loadings).

Although prediction is the ultimate objective of model development and application, the other two uses are extremely important by-products.

Models can be classified as being one of two types – either event or statistical/climatological. Event, or episode, models describe or predict, often on a real-time basis, occurrences of elevated pollution levels and associated meterological conditions which are of interest because of their short-term, deleterious effects. On the other hand, statistical or climatological models enable routine computations to be made and compiled for seasonal, annual, or several-year periods in order to look at longer-term concentration/deposition trends and pollutant loadings.

Trajectory analysis is primarily an interpretive tool : air parcels are followed forward in time from a source or backward in time from a receptor to investigate source-receptor relationships. Trajectories are often based on 850 mb or geostrophic winds and are typically computed for three or four days, although Pack, Lovelock, Cotton and Curthoys (1977) describe the use of five- to ten-day trajectories over the Atlantic. Rodhe, Persson and Akesson (1972), Prahm, Torp and Stern (1976), and Whelpdale (1978), as well as many others, have used back trajectories from receptor sites to distinguish between source and non-source regions (or directions) of sulphur pollutants.

Several of the long-range transport models are based on trajectory computations. Eliassen (1978) and Eliassen and Saltbones (1975, 1976) have used trajectory box models and simple Lagrangian dispersion models to calculate concentration and deposition fields, and decay and transformation rates of sulphur compounds over the OECD study region in western Europe. Prahm *et al.* (1976), Nordø (1976), Szepesi (1978) and others have used various forms of the trajectory-based models to compare their computed concentration and deposition

values with measured values during episodes of elevated pollutant levels. Using a statistical approach, long-term average sulphur concentration and deposition fields have been computed for the north-eastern United States by Sheih (1977) and for western and central Europe by Fisher (1975). Johnson, Wolf and Mamcuso (1977) have made similar computations for western Europe using a trajectory "puff" model. Bolin and Persson (1975) used a statistical formulation of the basic transfer equation to compute wet and dry deposition fields of sulphur over western Europe.

Models used in the OECD Long-Range Transport of Air Pollutants Programme (OECD 1977) give a good indication of the status of long-range transport model development and application. Annual mean concentration and deposition fields of the type shown in Figures 3 and 4 have been calculated for western Europe using these models, and have been shown to compare favourably with measured patterns. Figures 3 (a) and 3 (b) compare computed and measured wet deposition fields for 1974. Some minor differences exist but, in general, the model calculations show very good agreement with the measured fields. Figure 4 (a) is the computed dry deposition for the same region and year, and Figure 4 (b) is the total deposition field, the sum of those shown in Figures 3 (a) and 4 (a).

In addition, these models have been used to compute annual amounts of sulphur deposited in one country as a result of that emitted in others, with an estimated accuracy of ± 50 per cent. When used to describe pollution episodes over western Europe they reproduce main features of the fields, and calculated concentrations during episodes usually agree with measured values within a factor of two.

In general, models become more suitable for episode application as the physical and chemical processes are more realistically incorporated, and as computational accuracy is increased (see, for example, Prahm and Christensen 1978). Most models of the above types, at this stage of their development, appear to be more appropriately used for statistical/climatological compilations than for episode description (Ottar 1976).

2.3.2 Process Modelling

Parametrization or modelling of the chemical and physical processes which govern the behaviour of atmospheric sulphur compounds, is still at a relatively early stage of development in long-range transport models. Advances are most urgently required in the modelling of chemical transformations and wet removal processes.

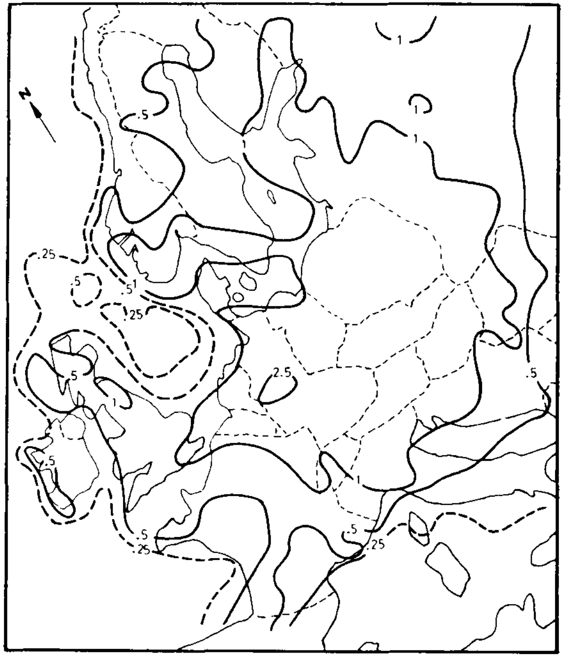

Figure 3 (a). Calculated sulphur wet deposition pattern in western Europe for 1974 (OECD 1977). Unit: g S m^{-2}*.

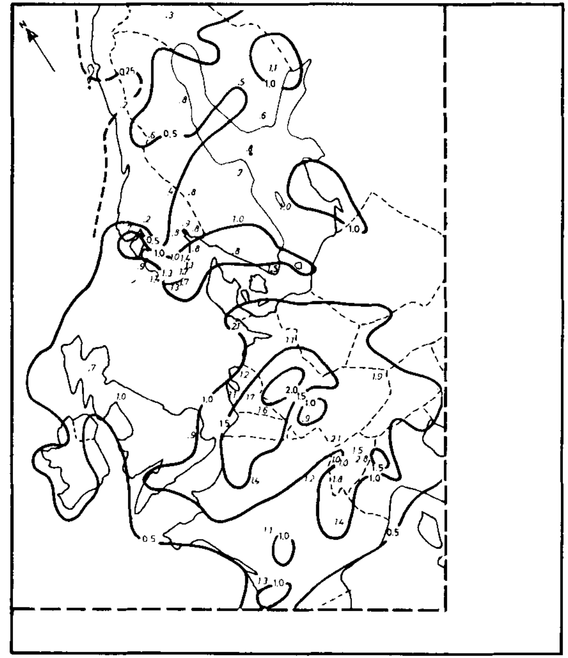

Figure 3 (b). Measured wet deposition field for 1974 (OECD 1977). Values at measuring stations are in italics. Unit: g S m^{-2}.

* grams of sulphur per square metre.

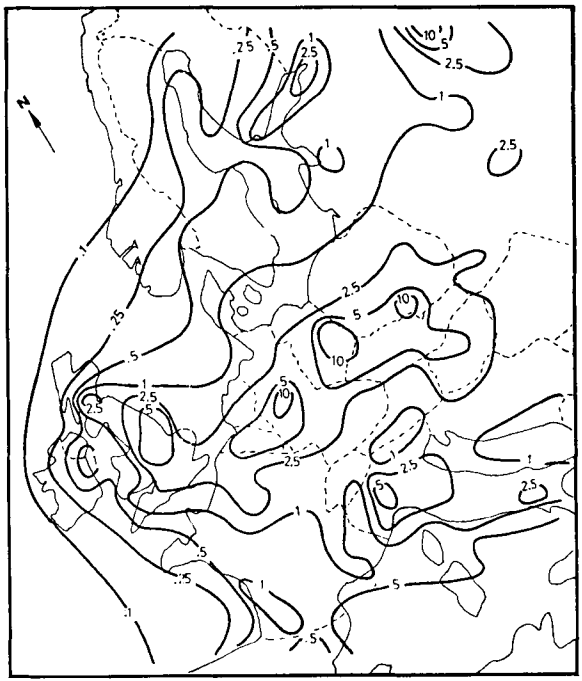

Figure 4 (a). Calculated sulphur dry deposition patterns in western Europe for 1974 (OECD 1977). Unit : g S m^{-2}.

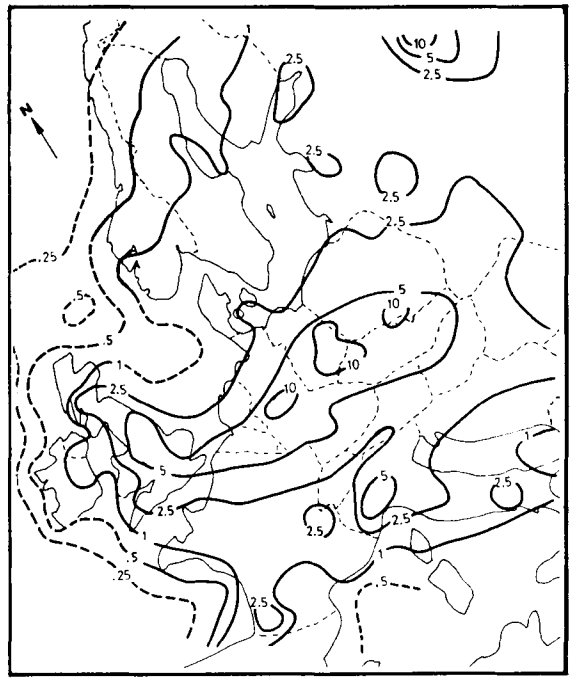

Figure 4 (b). Calculated sulphur total deposition pattern for 1974 (OECD 1977). Sum of Figures 3 (a) and 3 (b). Unit : g S m^{-2}.

The oxidation of SO_2 to sulphate is usually assumed to be a first order decay process*, with different decay rates sometimes being specified for in-plume, urban, regional, and background conditions. Few determinations of SO_2 to sulphate transformation rates are available over distances of hundreds to thousands of kilometres, and in those that are available (e.g. Lusis and Wiebe 1976) it is usually not possible to specify the reactions responsible for the decay of SO_2. Nevertheless, such data are exceedingly important because they permit the "composite" transformation process to be modelled. Transformation rates of approximately 1% h^{-1} in long-range transport models provide results that are consistent with measured values (Prahm *et al.* 1976; Eliassen and Saltbones 1975). Further refinement will require that the chemistry be specifically modelled, including reactions with other substances, catalytic effects, and the dependence on humidity.

Wet removal is included in models either as part of a general first-order decay term along with dry deposition, or as a discontinuous process occurring during precipitation periods only. The latter approach is more refined, but requires information on the areal extent, duration, and intensity of precipitation events. Improvements in the modelling of wet deposition will require a better understanding of physics and chemistry of the scavenging processes.

Dry deposition is normally estimated by assuming that the pollutant flux† to the surface is proportional to the concentration just above the surface. This of course requires computed or measured surface concentration fields of SO_2 and sulphate. A better knowledge of the dependence of the proportionality constant on surface characteristics and atmospheric stability would improve our ability to estimate dry deposition. In statistical long-range transport models (e.g. Eliassen and Saltbones 1975) a general decay term incorporating both wet and dry removal, with a value of the order of 7% h^{-1}, gives results consistent with measured concentration fields.

Pollutants are either assumed to be uniformly mixed in the vertical up to the mixing height‡, or they are assumed to mix or diffuse upwards

* The rate of decrease of sulphur dioxide concentration is proportional to the sulphur dioxide concentration.

† The flux is the mass of pollutant crossing a unit area of a horizontal plane near the surface per unit of time.

‡ Mixing height can be thought of as the level to which pollutants are mixed in the lower atmosphere, often of the order of 1000 metres. For more rigorous definitions see Munn (1976).

at a constant rate. More sophisticated approaches attempt to model the diffusivity as a function of height. Constant mixing height values are often assumed in long-range transport model calculations, although on occasion actual values from radiosonde stations are used. Mixing height climatologies of the type prepared by Holzworth (1967) and Portelli (1977) in North America will provide valuable input to climatological models. Over long transport distances vertical wind shear and mixing are more effective in causing horizontal spreading of pollutants than is horizontal diffusion. The assumption is frequently made that pollutants are uniformly mixed through a box along the trajectory path.

In summary, improvements in the short-term predictive capabilities of long-range transport models and, as a result, in their statistical usage, will come with better insight into the chemical and physical processes taking place in the atmosphere, and in our ability to model them realistically.

2.4 Receptors

2.4.1 Characteristics

Receptors at the Earth's surface form the final part of the atmospheric portion of the biogeochemical sulphur cycle. Although not discussed in detail here, impacts on these receptors are most important, for they, along with effects on human health and climate, form the basis of our concern over man-made atmospheric sulphur. The quantity of sulphur deposited on, or taken up by, various receptors depends upon several factors: the amount of sulphur in its different chemical forms and physical states present in the overlying atmosphere; the state of the ambient atmosphere; and, for some processes, the physical, chemical and physiological characteristics of the surface. In turn, the impact on a receptor depends upon both the quantities of the various sulphur forms deposited and the susceptibility of the receptor to damage. The nature of the Earth's surface has little influence on deposition by gravitational processes, i.e. precipitation and sedimentation, but it does affect gas-phase deposition of SO_2 (by its pH, for example) and small-particle sulphate uptake (by surface roughness).

Oceans cover much of the Earth's surface and the relatively high pH* of ocean waters ($\sim$8) makes them excellent sinks for SO_2. However, because of the high ion content of ocean water, additions of man-made sulphur are unimportant from an ecological point of view.

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* Neutral pH is 7; the pH of "clean" rain is 5.7.

The many types of vegetation, including cultivated crops, have wide ranges of characteristics which influence sulphur uptake (e.g. physiological state, surface wetness, roughness) and of susceptibility to damage (Knabe 1976). Forests are of special interest because they are a potentially susceptible, economically important resource in northern temperate latitudes (Tamm 1976). SO_2 and particulate-sulphate deposition may be enhanced over and within forests, and precipitation composition is altered on passage through the forest canopy; however, only limited quantitative information is available about these phenomena and their specific effects.

SO_2 uptake is dependent upon soil pH and moisture content (Payrissat and Beilke 1975), and certain soils (e.g. podzolic) are susceptible to chemical change from atmospheric inputs (Malmer 1976). Freshwater lakes and rivers, and the aquatic biota they support, are also known to be susceptible to acidification from atmospheric sulphur (Wright and Gjessing 1976; Schofield 1976). Although snow-covered surfaces are inefficient receptors of gaseous- and particulate-sulphur compounds, the spring melt of the accumulated winter snow-pack can result in rapid, short-term inputs of high-sulphate, low-pH water to freshwater systems with resulting disastrous effects on fish.

2.4.2 Geographical Distribution

The above discussion indicates that continental receptors are more susceptible to damage by sulphur deposition than are oceanic ones. In addition, it is estimated that 75 per cent to 80 per cent of man-made sulphur is deposited on land (Kellogg *et al.* 1972; Granat *et al.* 1976). The Northern Hemisphere accounts for about 93 per cent of the global man-made SO_2 emissions and has approximately two-thirds of the Earth's land area. Thus most of the global man-made sulphur is deposited back onto the continental Northern Hemisphere, whereas a relatively small amount finds its way to land in the Southern Hemisphere. Little is known of deposition patterns or harmful effects in the Southern Hemisphere.

Within a given land mass, the relative location of sources and receptors, in association with the prevailing meteorological regime, determines the deposition patterns and effects. For example, portions of the north-eastern United States and eastern Canada, and parts of Scandinavia, which lie downwind of major source regions and which have poorly buffered lakes and soils, are experiencing the greatest impacts of pollution sulphur and, as a result, are the subject of intensive

scientific investigation at the present time (see section 4).

The question of transatlantic transport of sulphur from North America to Europe has been raised. Nyberg (1977) reports evidence of North American sulphur in precipitation samples collected over the Atlantic. In view of its relatively short atmospheric residence time (a few days), the travel distance involved, and the large emissions in Europe, the North American contribution to European concentration and deposition levels is expected to be very small, probably less than five per cent.

3.0 Sulphur in the atmosphere

3.1 Global and Regional Concentrations

Representative concentration values for SO_2, particulate sulphate, and sulphate in precipitation are given in Table 2 for rural Europe and North America, for the North Atlantic Ocean, and for clean global background areas. Although data are still sparse from remote locations, more and more high quality data are becoming available from national sampling networks and large projects in Europe and North America (e.g. the OECD Long-Range Transport of Air Pollutants Programme). Over continents concentrations vary a great deal, particularly for SO_2, depending on source and receptor proximity. Near sources and in cities SO_2 and particulate-sulphate concentrations can easily be an order of magnitude larger than those listed for rural areas. The influence of industrialized eastern North America can be seen over the North Atlantic where concentrations are elevated above global background values.

On the global scale, Georgii (1978) has reviewed available data and presents the following generalized picture of the large-scale SO_2 and particulate-sulphate distributions. Near-surface continental SO_2 concentrations are greater than those over the ocean. High concentrations of industrially-produced SO_2 are confined to a relatively shallow vertical layer over the continents, which results in a steep vertical gradient in the one- to two-kilometre level, with concentrations falling to less than one $\mu g\ S\ m^{-3}$ near the tropopause. Sulphate concentrations also decrease in the vertical, but more slowly than SO_2 values. Mid- and upper-tropospheric sulphate concentrations are below a few tenths $\mu g\ S\ m^{-3}$. Granat *et al.* (1976) have critically examined past precipitation chemistry data and have concluded that sulphate concentrations in precipitation free from man's influence are of the order of 0.1 mg $S\ell^{-1}$ or less, lower than has previously been reported.

Table 2. Representative concentrations of SO^2 and sulphate in air and precipitation

Location	SO_2 concentration ($\mu g\ S\ m^{-3}$)	Particulate-sulphate concentration ($\mu g\ S\ m^{-3}$)	Excess precipitation-sulphate concentration ($mg\ S\ell^{-1}$)
Rural Europe	4–10*†‡	1–3*‡	1–2*¶
Rural North America	3–5‡§	1–3‡§	1–2°**
North Atlantic between 30° and 60°N	0.3–1.5‡	0.3–1‡	0.2–0.6††
Clean global background:			
ocean	0.5†	0.1–0.5¶	0.04¶
land	up to 1.7¶	0.1–0.5¶	0.1¶

* OECD (1977)
† Georgii (1978)
‡ Mészáros (1978)
§ Altshuller (1976)
¶ Granat *et al.* (1976)
° Summers and Whelpdale (1976)
** Lodge *et al.* (1968)
†† Nyberg (1977)

3.2 Global and Regional Budgets

Global budgets provide a means of assessing the magnitudes of fluxes and burdens in a biochemical cycle without having to explore details of the individual processes involved. The budget of Hallberg (Granat *et al.* 1976), for example, in Figure 1 identifies the pathways of sulphur compounds through the environment, and estimates the fluxes of both natural and man-made sulphur along these pathways. This shows, on a global basis, that man-made emissions are comparable to natural ones, and that the former dominate along some pathways. However, such global averages do not apply either to very clean areas or to heavily polluted ones.

In industrialized regions, man-made sulphur emissions far exceed natural ones, and thus pollutant budgets on this scale are of a quite different character. As noted earlier, the average atmospheric residence time of sulphur is a few days, corresponding to travel distances comparable to the extent of heavily-industrialized regions in eastern North America and Europe. In such cases regional budgets can provide an insight into the impact of man-made emissions. Rodhe (Granat *et al.* 1976) and Garland (1977) have both made such budget calculations for the same area of north-western Europe ; these are shown in Table 3.

Both authors estimate that approximately 60 per cent of the sulphur emitted in the region is deposited there, and that the remainder is exported. Rodhe estimates that wet deposition in the region is between 74 per cent and 150 per cent of the dry deposition ; whereas, Garland estimates it to be considerably lower, only 43 per cent of the dry. Both authors estimate the average residence time for atmospheric sulphur emitted in this region to be about two days.

Country budgets have been constructed for the U.K. (Garland 1977), for Sweden (Högström 1977), Hungary (Várhelyi 1978), and for countries participating in the OECD Long-Range Transport of Air Pollutants Programme (OECD 1977). As Rodhe (1978) notes, however, if horizontal fluxes into and out of smaller regions are large and not accurately known, the certainty with which the importance of emissions and depositions can be determined is greatly reduced.

3.3 Temporal Trends

Man-made sulphur oxide emissions to the atmosphere increased fivefold between 1900 and 1965 (Robinson and Robbins 1972). In the OECD study region the annual emission rates increased by about one half between 1900 and 1940 and then doubled to 25 Tg S yr^{-1} between

Table 3. Atmospheric sulphur budgets for western Europe
Units are Tg S y^{-1}

	Rodhe in Granat *et al.* 1976			Garland 1977		
	man-made	natural	total	man-made	natural	total
Source terms						
Emissions	13	? (<2)	13+	14	1–2	15–16
Import	1*		1			1
Loss terms						
Wet deposition†	4.1	0.5	4.6			2.7
Dry deposition	2.9–5.9	0.2–0.3	3.1–6.2			6.3
Export	4–7					5.0

* Estimated additional ~10% of total deposition is assumed to come from pollution sources outside area.

† Excess sulphur.

1940 and 1970 (OECD 1977). In the United States there was an approximate 60 per cent increase between 1940 and 1970 (Urone 1976). In spite of these large increases, there is little information available on trends in atmospheric concentrations.

The analysis of ice cores from different sites in the Northern Hemisphere is useful to reconstruct the impact of man's activities on the sulphur cycle. The observed sulphate in Greenland ice during the 1960s is about three times that of the last century. This difference is believed to be the result of man-made sulphur oxide deposition, but volcanism may also have been involved. Measurements of sulphate concentrations in the Antarctic snowpack (Delmas and Boutron 1978) for the time period 1950-1975 show no evidence of a man-made component although they do show the influence of the Mt Agung eruption in 1963. There is no trend evident, and the mean value is in essential agreement with one found at Byrd Station for the last 10,000 years. Thus, this very remote location has remained essentially uninfluenced by increased emissions of sulphur; although, as is well known, the same is certainly not the case for carbon dioxide.

In northern Scandinavia, sulphate deposition in precipitation has almost doubled over the two decades starting in 1955 (Granat *et al.* 1976) and at many stations in Europe annual means of sulphate concentrations in precipitation show upward trends between 1955 and 1975 (Granat 1978). Abrupt increases are evident at Scandinavian stations around 1960, with a subsequent levelling off. It is clear that precipitation concentration records alone, at one station or group of stations, do not closely reflect trends in emissions; in addition, changes in meteorological conditions and other deposition processes must be taken into account.

In an analysis of National Air Sampling Network data in the United States for the years 1963-1972, Altshuller (1976) found that non-urban sulphate concentrations increased several per cent per year during the period in six of seven geographical regions (the exception being several east coast sites which showed no clear trend), while non-urban sulphur dioxide values were low and showed no clear trends. Altshuller attributes these findings to long-distance sulphur oxide transport with chemical conversion of SO_2 to sulphates occurring over the range of hundreds of kilometres.

There is quite clearly a need for stable, long-term measurement programmes, particularly in the more heavily industrialized areas of the

* World Meteorological Organization.

globe where man-made emissions dominate, in order that the trends in concentration and deposition of atmospheric sulphur compounds may be established. The Regional Stations in the WMO* Background Air Pollution Network are expected to contribute to fulfilling this need.

4.0 Current programmes

4.1 Introduction

As a result of the increasing awareness of the extent and potential ecological significance of atmospheric pollution caused by industrial sulphur emissions, several countries have undertaken extensive programmes in both atmospheric and ecological fields to investigate and attempt to remedy such problems. In Europe, in particular, these efforts have often been co-ordinated under the auspices of intergovernmental organizations. Two major programmes of this kind are the Co-operative Technical Programme to Measure the Long-Range Transport of Air Pollutants, within OECD, and the Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe, within the ECE*. In North America, a number of regional programmes sponsored by national government agencies or departments are in progress.

The design and first results of many of these programmes were described in detail in the proceedings† of the International Symposium on Sulfur in the Atmosphere (ISSA), held in Dubrovnik, Yugoslavia, 7-14 September 1977. Thus, only a brief description is given here.

4.2 Co-operative Technical Programme to Measure the Long-Range Transport of Air Pollutants – OECD

The OECD programme began in July 1972 at the initiative of the Scandinavian countries after analysis of data from the European Air Chemistry Network showed that a central area of acid precipitation in Europe was expanding from year to year. The objective of the programme was to determine the relative importance of local and distant sources of sulphur compounds in terms of their contribution to the air pollution over a region, special attention being paid to the question of acidity in precipitation.

Results of the programme confirmed that sulphur compounds do travel long distances (several hundred kilometres and more) in the atmosphere and showed that the air quality in any one European country

* Economic Commission for Europe.

† *Atmospheric Environment*, January 1978 issue.

is measurably affected by emissions from other European countries. A detailed description and results of the programme are available in OECD (1977), Ottar (1978), Semb (1978) and Eliassen (1978).

4.3 Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe – ECE

This programme grew out of a recommendation of the Conference on Security and Co-operation in Europe, "to develop through international co-operation an extensive programme for the monitoring and evaluation of the long-range transport of air pollutants. . . . ". It began in the latter half of 1977 and has as its main objective the provision of information to governments on the deposition and concentration of air pollutants, as well as on the quantity and significance of long-range transmission of pollutants and fluxes across boundaries. As described in the Programme Plan (ECE 1977), it consists of four basic components:

1. Sampling, measurement and chemical determination
2. Acquisition of emission data
3. Application and further development of transmission models
4. Evaluation of data and research

The programme is being conducted under the auspices of the United Nations ECE and forms part of the Global Environmental Monitoring System [GEMS] of the United Nations Environment Programme. The programme is being implemented with the co-operation of the World Meteorological Organization.

4.4 The WMO Background Air Pollution Network

In the late 1960s the WMO established a background air pollution network to assist specifically in studies of man's impact on climate. Since that time the goals of the programme have been broadened, making regional stations available for monitoring substances of interest to UNEP-GEMS, although not necessarily related to climate research. The network currently has approximately 115 stations in nearly 50 countries. The chemical constituents of precipitation, including sulphate, are determined at all stations and, in addition, measurements of SO_2 concentration and particle chemistry are recommended at baseline stations and regional stations with extended programmes.

To support their network operation, WMO has convened several technical meetings and workshops. Included have been a workshop on SO_2 sampling and analysis techniques at background levels, the Technical Conference on the Observation and Measurement of Atmospheric Pollution (TECOMAP, Helsinki 1973), an expert meeting

on Wet and Dry Deposition (WADEM, Toronto 1975), the Air Pollution Measurement Techniques Conference (APOMET, Gothenburg 1976), and an expert meeting on Dry Deposition (Gothenburg 1977).

Recently WMO member states in Europe have been asked to expand their activities on regional background air pollution monitoring to meet the requirements of the ECE programme (section 4.3).

4.5 The Canadian Long-Range Transport of Air Pollutants Programme.
This programme was established within the Canadian Department of the Environment in mid-1976 with the purpose of assessing the occurrence and effects of regional pollution and long-range transport of air pollutants in eastern Canada. Initially emphasis is on sulphur compounds and related substances, although some work on effects is being done for mercury and synthetic organics. The programme is multidisciplinary and includes source emission inventories, atmospheric dispersion modelling, pollutant concentration and deposition fields, and pathways and effects studies in aquatic and terrestrial ecosystems. The eventual goal is to evaluate the socio-economic costs of the pollution situation in order that any necessary regulatory action may be undertaken.

The initial objectives of the atmospheric programme are (i) to determine current, large-scale concentration and deposition fields for sulphur dioxide, and sulphate in particulates and precipitation; (ii) to determine the frequency and geographical extent of episodes due to long-range transport in the region; and (iii) to identify and determine the relative importance of local and distant sources of pollution.

Details of the programme and preliminary results are available in Whelpdale (1978).

4.6 The Multi-State Atmospheric Power Production Pollution Study (MAP3S) – USDOE*
The goal of this programme is to develop and demonstrate an improved, verified capability to simulate the present and potential future changes in pollutant concentration, atmospheric behaviour and precipitation chemistry resulting from pollutant releases to the atmosphere by large-scale energy conversion processes. In the initial three years, commencing October 1976, the study is focused on the effects of emissions from coal-fired electric power plants, particularly in the high-population, energy-intensive north-eastern quadrant of the United States. Details of the programme are outlined by MacCracken (1978).

* United States Department of Energy.

4.7 Sulphate Regional Experiment (SURE) – EPRI*

The purpose of the SURE programme is to define the relation between emitted primary pollutants (e.g. SO_2) and regional ambient concentrations of secondary products (e.g. sulphates). Emphasis is on identifying the contribution of the electric power industry to ambient sulphate levels in the north-eastern United States. The programme began in July 1977 and will continue for three years. Main elements of the programme are

1. a ground monitoring network of 54 randomly distributed stations throughout the north-eastern United States;
2. a programme of measurements of air quality using aircraft;
3. a detailed emissions inventory;
4. a modelling programme.

Details of the programme and results of the SURE design study are given by Perhac (1978).

4.8 North-Central Regional Project on Atmospheric Deposition – USDA†

The objective of this project, just about to get under way in the United States, is to conduct research on atmospheric deposition and its effects on agricultural and forest lands and surface waters. The basis for the project will be an atmospheric deposition network of about 40 stations, initially, to determine spatial and temporal trends in the supply of beneficial nutrient elements and potentially injurious substances in precipitation and dry particulate matter deposited in various regions of the United States. Details are available in Galloway and Cowling (1977).

4.9 Midwest Interstate Sulfur Transformation and Transport Project (MISTT) – USEPA‡

Project MISTT of the U.S. Environmental Protection Agency was designed to study the transformations of SO_2 to sulphate in polluted air masses undergoing transport. Pertinent chemical and meteorological parameters are measured with sufficient accuracy to permit their use in physical and mathematical models to derive rate parameters which characterize the transformation processes. Detailed results of studies to date are available in Wilson (1978).

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* Electric Power Research Institute.

† United States Department of Agriculture.

‡ United States Environmental Protection Agency.

5.0 Summary and recommendations

Man-made sulphur emissions are sufficiently large to interfere significantly in the global biogeochemical sulphur cycle. In heavily industrialized regions of the world, man's activity completely dominates the atmospheric sulphur budget.

Sulphur dioxide (SO_2) accounts for approximately 95 per cent of man-made sulphur emissions, while hydrogen sulphide and a number of organic forms comprise the natural emissions. Most atmospheric reactions lead to particulate sulphate-containing compounds as their end-products. The vast majority of these sulphate-containing aerosols are in the 0.1 to 1 μm size range.

The average atmospheric residence time of SO_2 in industrial regions is about one day. Thus, from the point of view of surface loading effects, the most acute sulphur pollution problems occur over distances from a hundred to a thousand kilometres. Damage resulting from deposition of sulphur compounds is already well documented in eastern North America and parts of Europe.

The current global emission rate of man-made sulphur is approximately 65 Tg S y^{-1} ; this is comparable to, and perhaps greater than, the rate of natural emissions. In eastern North America and western Europe, natural emissions are estimated to be less than five per cent of man-made ones.

- Governments should be urged to compile and make available data on man-made sulphur emissions ; special attention must be given to their temporal and spatial variations.
- Natural emissions of sulphur compounds require further investigation : specifically, species identification, location and source strength.

Atmospheric pathways of sulphur compounds are governed by the several processes they undergo between source and receptor. During the initial stages of travel, the vertical structure of the planetary boundary layer and its complex diurnal behaviour control pollutant dispersal. Transport over distances of hundreds to thousands of kilometres is influenced primarily by synoptic scale motions and can occur under a variety of meteorological conditions. Plumes emitted into a stable atmosphere undergo little vertical or horizontal diffusion and can travel intact for several hundred kilometres before being dispersed or incorporated into cloud. On the other hand, when emissions from diverse sources over a broad area accumulate in stagnating air associated with anticyclonic conditions over eastern North America or western Europe,

the pollutants become well mixed by day-time convection and are slowly transported in the southerly flows to the west of the high pressure centres. Similarly, over Europe during stagnant anticyclonic conditions, air becomes heavily polluted and is drawn into a frontal area of the depression running along the northern edge of the anticyclone. Only modest frontal rainfall is needed to produce relatively large pollutant depositions.

Details of many of the transformation and deposition processes in which sulphur compounds are involved are reasonably well understood qualitatively, but major difficulties still exist in realistically modelling them and their space and time variations. The homogeneous and heterogeneous transformation processes are of comparable overall importance, and typical transformation rates are 1–2% h^{-1}. Dry and wet deposition processes are also of comparable overall importance, although dry deposition of SO_2 dominates near sources and wet deposition occurs only during precipitation. Typical overall removal rates are 2–4% h^{-1}.

Both transformation and deposition processes are currently incorporated in most long-range transport models by using first-order decay terms. The average decay rates so determined show reasonably good agreement with the laboratory and field data available.

- To advance the modelling of chemical transformation processes, further work is required on (i) the effects of other pollutants, catalysts, temperature and humidity; and (ii) the space and time variability of the processes.
- To improve the modelling of wet deposition, (i) routine measurements of the extent, duration, and intensity of precipitation events are required; and (ii) further research is necessary to obtain a better understanding of the physics and chemistry of the scavenging processes.
- To improve the modelling of dry deposition, a better understanding of the influence of variations in surface characteristics and atmospheric stability on the deposition processes is required.

The various models used to describe pollutant behaviour over the regional-to-continental scales can be classified as either event or climatological models. In perhaps the most up-to-date application of these models, i.e. in the OECD programme, computed annual mean concentration and deposition fields show good agreement with measured values on a large scale. In describing episodes, these models are capable of reproducing the main features of the fields.

- To improve model accuracy and applicability to episodes, more realistic incorporation of physical and chemical processes is necessary, particularly for chemical transformations and wet deposition.
- Systematic comparison of model results with observations (model validation) is essential to determine model accuracy and to develop confidence in model use.
- To gather adequate data for verification studies, a combination of data from regular monitoring and more intensive measurements is required.

Models of differing complexity are required for different applications: it is important to assess the minimum degree of complexity required in each process model in relation to its predictive needs.

Global and regional concentration data for sulphur oxides in air and sulphate in precipitation are rather sparse. A few records, notably precipitation chemistry data from the European Air Chemistry Network, extend back for more than 10 years. More and more air concentration data are becoming available from network operations in North America and Europe. Data from the Southern Hemisphere are extremely limited.

- There is continuing need for measurements of the various sulphur compounds in "clean global background" conditions and "clean regional background" conditions, both to assess natural concentration levels and to determine trends. Because of the very low concentrations encountered, continuing development of highly sensitive measurement techniques is required as are careful intercomparisons of various techniques.

Budget estimates over north-western Europe indicate that approximately two-thirds of man-made sulphur is deposited within distances of about 1000 kilometres from the main source areas. Dry deposition and wet deposition contribute roughly equal amounts. A similar situation is likely to prevail in eastern North America.

- The collection of appropriate data should commence, so that budgets can be made, in those regions of the world where intense industrialization may be expected in the coming decade or so (e.g. India, Brazil).

Large-scale studies in several countries have responded to concerns resulting from acid precipitation and long-range transport, while in the United States more emphasis has been placed on health effects. All studies confirm that sulphur compounds do travel long distances in the atmosphere, and that air quality and deposition in any one country are

measurably affected by emissions from neighbouring countries. Several important recommendations on large-scale projects, which are quite relevant to this review, emerged from the International Symposium on Sulfur in the Atmosphere. They were:

- To increase spatial coverage and better quantify transformation, transport, and removal of sulphur compounds, existing and newly planned large-scale studies must continue. Such studies could be designed with greater precision if the relationship between pollutant concentrations and ecological and health effects were more precisely understood. A close, iterative exchange is needed between those defining physico-chemical phenomena and those studying environmental effects.
- Networks established by different organizations or agencies should employ methods which can be intercalibrated, and frequent intercalibrations of both sampling techniques and analytical methods should be carried out. Continuous analysis of network data is necessary to ensure data reliability.
- Participants in large programmes should meet as needed to exchange results, to examine programme coverage, and to conduct intercalibration activities.

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