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# The Dispersion of Sulphur Pollutants over Western Europe [and Discussion]

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# The dispersion of sulphur pollutants over western Europe

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The various problems associated with the dispersion, advection and deposition of sulphur pollutants emitted into the atmosphere are reviewed in the light of experience gained during several long-range transport projects, in particular the O.E.C.D. project recently completed over western Europe.

Modelling and budgeting the exchange of pollution between countries is briefly discussed and it is noted that although 'statistical' modelling may be satisfactory when considering long-term effects, the episodic nature of deposition and the complex meteorological flows often associated with these abnormally high depositions suggests that smaller-scale and detailed modelling is required if these situations are to be properly understood and forecast.

## Introduction

Sulphur is emitted from all fossil-fuel burning plants into the atmosphere, mainly as sulphur dioxide although small concentrations of sulphate may also be present. Although some of this sulphur is deposited locally much of it is diffused into the atmosphere and carried by the winds over considerable distances. Eventually the sulphur is either dry-deposited or is removed by precipitation to the ground. Typically over Europe between 0.1 and 10 g S/m$^2$ are deposited each year by dry deposition, the larger values occurring near the major source regions, and between 0.2 and 2 g S/m$^2$ by wet deposition. While the larger wet depositions also occur near the major source regions they also tend to occur in areas of high rainfall induced by mountain ranges, as in southern Norway. It is often in these very wet areas that the soil is thin and acidic, and the sulphate coming down in the rain is not readily neutralized and flows into the streams and lakes when fish kill can result. The extent and nature of the damage as it is appreciated at the present time has been summarized in a report edited by Braekke (1976).

A major international study of the long-range transport of sulphur pollutants on a scale of 1000 km and more was initiated in 1971 by the Organisation for Economic Cooperation and Development (O.E.C.D.) and the final report is now available (O.E.C.D. 1977). The study initiated extensive measurements of air concentrations and concentrations-in-precipitation of various pollutants, principally sulphur dioxide and sulphates. Ground-level stations made 24 h average measurements; aircraft made occasional and shorter-period measurements. Mathematical–physical models were developed to simulate the source–dispersion–sink processes taking place in the atmosphere. These models attempted to provide information on the amount of pollution reaching each part of the chosen area and how this could be partitioned between local sources and more distance sources in each of the other countries of Europe. Essential to the study was the determination of an acceptable emission inventory for the study area and a means of calculating back-trajectories of the air carrying the pollution.

This paper relates the various factors influencing the transport of sulphur more or less in sequence from its emission, initial dispersion through the mixing layer, advection by the wind, dry deposition, chemical change and wet deposition in precipitation. Finally the modelling is briefly discussed followed by some of the budgeting results and a look at the potential importance of very heavy episodic depositions.

As far as possible, duplication of detailed results described in the O.E.C.D. report has been avoided. Nevertheless a fairly complete summary of the meteorological problems involved has been attempted, and, when relevant, specific contributions arising from the Meteorological Office's own work in the O.E.C.D. study have been included.

In general it may be concluded that relatively simple models such as those used in the O.E.C.D. study are capable of giving reasonable estimates of one country's annual contribution to another's total sulphur deposition, but that on a day-to-day basis, and particularly in complex episodic situations, more sophisticated modelling would be essential if, for example, sporadic emission control were ever to be considered feasible.

## EMISSIONS OF SULPHUR DIOXIDE

Most fossil fuels contain sulphur, a large proportion of which will escape in the waste gases to the atmosphere.

Typical sulphur contents as quoted by Weatherley (1977) from N.C.B., C.E.G.B. and *Petroleum Review*, April 1975, are roughly:

| | |
|---|---|
| coal | 1.2–1.5 % S; |
| fuel oil | 2.5–3 % S; |
| other petroleum fuels | 0.04–0.7 % S. |

The number of sources are of course extremely numerous; they vary with time in location and strength and so it is virtually impossible to give precise emission figures over a short period. Annual figures over grid squares with sides of the order of 100 km can be estimated rather more accurately, especially in the United Kingdom where statistical records of fuel consumption are maintained. Nevertheless, uncertainties do remain and the annual emission for the whole of the U.K. is probably only accurate to within less than 10% and for some other European countries to within only about 30%.

It must follow that in studying air concentrations of sulphur affecting a region at a given time, one of the biggest uncertainties must be the distribution of upwind emissions.

One of the first priorities at the beginning of the O.E.C.D. study was to establish the best emission fields that could be obtained. The Meteorological Office made an analysis of the emissions within the U.K. (Smith & Jeffrey 1975) with the use of a considerable number of data for 1970. Figure 1, taken from their paper, shows emissions of sulphur dioxide in thousands of tonnes for the year within 20 × 20 km Ordnance Survey squares covering the U.K.

Weatherley (1977) has shown that emission values have tended to decrease since 1970, although not entirely monotonically, and in 1974 were some 12 % less at about 5.4 Mt for the whole of the U.K. This decrease reflects the growing use of natural gas from the North Sea. Emission maps therefore have this unfortunate tendency to get rather out of date.

The Central Coordinating Unit of the O.E.C.D. study, the Norwegian Institute of Air Research (N.I.L.U.), compiled such emission data as was available to provide a similar emission map for Europe but on a 127 × 127 km square grid. In areas where no emission values were available a necessarily subjective assessment had to be made based on population figures and a rough idea of industrialization.

In western European countries, excluding Norway and Switzerland where fossil fuels are largely replaced by water power in the generation of electricity, emissions are roughly proportional to population at the rate of approximately 100 kg $SO_2$ released into the atmosphere per year for each person.

Thus the U.K. emissions worked out on this basis are $54 \times 10^6 \times 100$ kg $SO_2$, i.e. 5.4 Mt, in rather fortuitous agreement with the 1974 direct estimate. France, F.R.G. and Holland claim to have a lower rate, nearer 60 kg $SO_2\,a^{-1}$ per head, although this could either be simply a reflexion of rather less exact data or the use of substantially more natural gas or low-sulphur fuel oil.

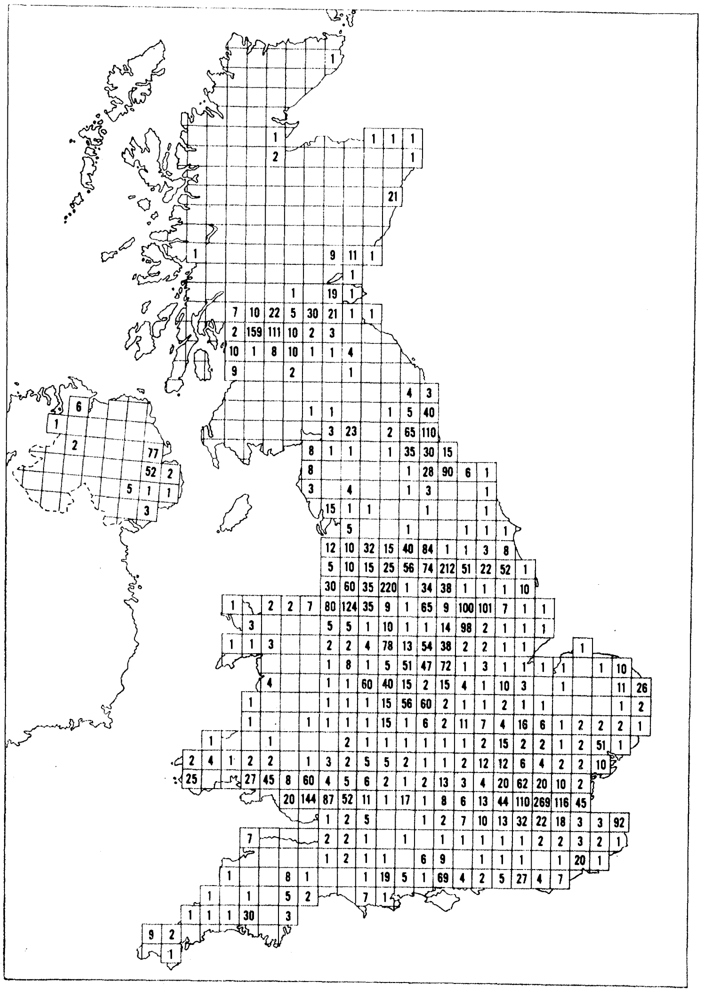

FIGURE 1. United Kingdom sulphur dioxide emissions for 1970 in thousands of tonnes per year. Each square represents an Ordnance Survey 20 × 20 km region.

One factor concerning emissions relevant to the long-range transport problem is the height at which the sulphur is emitted. As will be shown in the next section, this has a small but significant effect on the fraction of sulphur dioxide deposited on the ground before the plume is thoroughly mixed through the boundary layer.

In the U.K. over the 5-year period 1969–74 the percentage of the total emission attributed to high-level sources (power stations and oil refineries) has risen steadily from 47 to 58 %, whereas the percentage from medium-level sources (other industries) has fallen from 35 to 29 %, and from low-level sources (domestic, transport, etc.) from 18 to 13 % (see Weatherley 1977). Overall these trends must increase the amount being advected to distant regions, thereby slightly increasing the depositions and resulting effects, if any, but at the same time decreasing relatively much more the close-to-source air concentrations and depositions resulting in very noticeable improvements in the health of local inhabitants and reductions in damage to buildings and plant life.

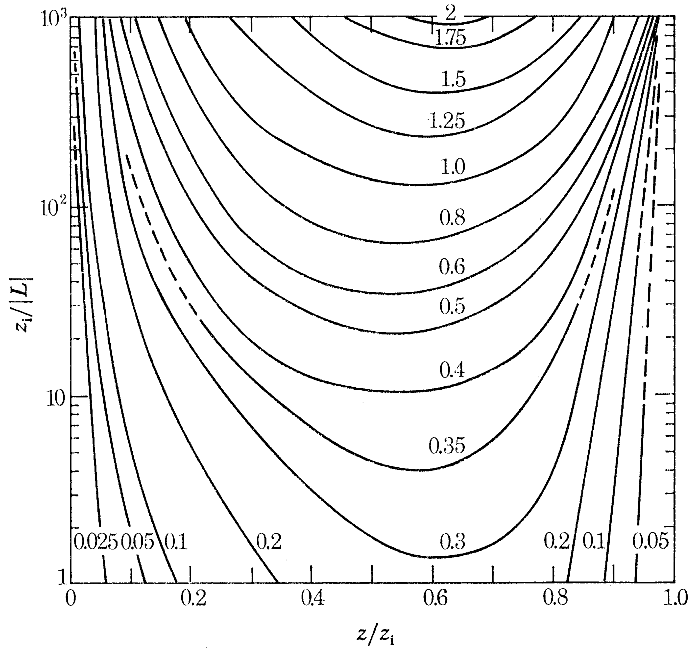

FIGURE 2. Contours of $K(z)/u_* z_i$ as a function of normalized height, $z/z_i$, and stability, $z_i/|L|$, where $z_i$ is the mixing depth, $u_*$ the friction velocity, $L$ the Monin–Obukhov length scale, based on data from the Minnesota field experiment (Izumi & Caughey 1976).

## DISPERSION

Once sulphur dioxide is released into the atmosphere it is subject to motions arising from the initial momentum and buoyancy of the plume, the mean wind, the wake of the chimney and the whole spectrum of turbulence in the ambient airflow. Many formulae have been presented to predict plume rise due to initial momentum and buoyancy. Those due to Briggs (1969) and Moore (1974) are best known and are based on considerable sets of data. In general the result is to replace the real chimney height by a higher effective source height. Sometimes the plume may penetrate through the top of the mixing layer into the relatively non-turbulent air above, when the sulphur can be transported over considerable distances effectively insulated from the sink at the ground, until ultimately by one process or another the plume is reincorporated into the mixing layer or the sulphur is washed out in precipitation.

For most low-level and medium-level sources, however, the plume rise is fairly small and in day-time at least the plume diffuses to the ground well before it diffuses to the top of the mixing layer. In these situations the concentration at ground level rises well above that predicted by the so-called box model, where the pollution is assumed to be uniformly mixed through the whole of the mixing layer. Dry deposition to the ground will be correspondingly high until the concentration falls to the box model value in a time or distance which depends very much on the stability and depth of the layer, $z_i$. The stability, $\mu_i$, may be represented by a ratio of two lengths: $z_i$ itself and the Monin–Obukhov length-scale, $L$, i.e.:

$$\mu_i = z_i/|L|.$$

According to an analysis by Smith (1977) of basic boundary-layer data taken from the Wangara experiment (Clarke *et al.* 1971) and from the Minnesota field experiment (Izumi & Caughey 1976) the diffusivity $K(z)$ can be expressed in similarity terms as shown in figure 2. The implication of this result is that the surface concentration will reach within 4 % of its box model value after a distance of travel $x$ given in day-time 'unstable' conditions by table 1, provided the surface Rossby number $G/fz_0$ is close to its normal land value of $10^6$. Thus if the geostrophic wind $G$ is $10\,\mathrm{m\,s^{-1}}$ the coriolis parameter $f$ is $10^{-4}\,\mathrm{s^{-1}}$, the surface roughness $z_0 = 0.1\,\mathrm{m}$, the upward surface sensible heat flux $H$ is $200\,\mathrm{W\,m^{-2}}$ and $z_i$ is 1200 m, then $\mu_i = 40$ and $x \approx 10\,\mathrm{km}$.

Table 1

| $\mu_i$ | 1 | 4 | 10 | 40 | 100 | 400 | 1000 |
|---|---|---|---|---|---|---|---|
| $x/z_i$ | 25 | 18 | 13.5 | 8.5 | 4.8 | 2.5 | 1 |

If, however, the geostrophic wind fell to $1\,\mathrm{m\,s^{-1}}$ the value of $z_i$ would not change appreciably but $G/fz_0$ would decrease to $10^{-5}$, $\mu_i$ would increase to about 1000 and $x$ decrease to about 1 km. In terms of time and also in terms of the fraction of $SO_2$ deposited, very little change would be observed. The deposition in the first case, however, would be spread over roughly ten times the area of that in the second.

Most low- and medium-level sources are situated in urban areas where two factors affect the vertical dispersion and related deposition. First, an urban area is a limited region of increased surface roughness. Secondly, it is an area where the upward surface sensible heat flux is significantly greater than in the surrounding countryside (frequently by as much as $70\,\mathrm{W\,m^{-2}}$) because of man-made heat sources and because less of the incoming natural radiation is used in evaporating surface moisture: a city is a relatively well drained and arid area. Both these effects tend to increase vertical dispersion and tend to militate against the formation of stable layers which would trap low-level emissions and give greatly enhanced depositions. Limited convergence of air in the area at low levels may also be induced, although these should not greatly affect the depositions.

Altogether then, accurate determination of the enhanced deposition close to the source over and above that given by the box model is fraught with difficulty but fairly simple calculations based on, for example, the Hanna–Gifford (1973) model of urban diffusion suggests that roughly an extra 10–20 % of the emitted $SO_2$ is likely to be deposited (Smith & Hunt 1977) within the first 50 km or so.

At night the air over the urban area may be nearly neutrally stratified whereas elsewhere it is stable. The urban plume may then be advected over the stable and slow-moving surface air in the countryside as it moves away and will be protected from further deposition until fumigation occurs in the following morning. In less-concentrated urban areas the air may be everywhere stable on most nights, the low-level plumes may be retained close to the ground and virtually all the sulphur dioxide will be lost by surface absorption.

Plumes disperse in the horizontal as well as the vertical. Unlike vertical turbulence where the range of eddy scales is limited by the depth of the mixing layer, with horizontal turbulence a fairly continuous spectrum exists from the very smallest eddies, through meso-scale eddies (range

1–100 km) up to synoptic-scale eddies of the size of anticyclones and depressions. The across-wind width of the plume is therefore very dependent on the time over which it is sampled: the longer the time, the broader the plume. Since on the one hand episodic deposition levels usually persist for several hours, and on the other, ground-level measurements are effective averages over 12 or 24 h, the width of the plume (or conversely the upwind source band affecting the receptor point) is governed principally by eddies in the synoptic range, and eddies in the micro scale and perhaps also the meso-scale are virtually unimportant. Fortunately variations in the synoptic pattern can be traced reasonably successfully from the network of meteorological measuring stations, and with somewhat less success into the immediate future using numerical weather forecasting models.

## ADVECTION

Although trajectory analysis has been carried out by meteorologists for a very long time to track air masses, important in forecasting future weather, the precision with which this can be done is not particularly high. The main reason for this (and this applies particularly to pollution released in the lower part of the atmosphere) is that wind varies in strength and direction with height. In ideal circumstances, when the pressure gradient is virtually constant in time and space and the underlying surface does not change character on scales of 100 km or more, boundary-layer theory predicts how wind speed will decrease as the ground surface is approached, and how wind direction will back away from the geostrophic direction until close to the ground the wind will have a component down the pressure gradient towards low pressure with magnitude depending on surface roughness, the geostrophic wind, latitude and air stability. Typically the surface wind will be backed some 10° over the sea, 20° over land during the day and 30° or more at night.

In more realistic situations, air parcels are normally undergoing acceleration or retardation which affects the balance of forces and the resulting flow vector. For example, boundary-layer air diverging slowly out of a slack anticyclonic region into a tighter low pressure system will be accelerating and will gain some of the required energy by increasing the angle of backing beyond the equilibrium values quoted above.

Mountains, sea breezes, marked temperature gradients, baroclinic effects and so on, can all cause variations of wind with height that are significantly different from the 'ideal'.

However, pollution in a well-mixed layer by definition is not advected by winds at one level alone but by all the winds in the layer as each element diffuses up and down by vertical turbulence. The stronger the vertical mixing, the more rapid is this sampling process and the more each and every element moves with the *average* velocity. Momentum is also efficiently exchanged in these circumstances and the layer cannot support large velocity shears anyway except very close to the ground. If the vertical mixing is relatively slight, the boundary layer (or mixing layer) is likely to be correspondingly shallow and again shears are not likely to be too important. Wind shear is in fact only likely to be important if either the boundary layer has shrunk leaving some of the pollution at levels now stably stratified where shear can play its full rôle, or if the boundary layer is still fairly deep but in a state of decreasing turbulent energy as in the latter part of the day.

Actual measurements of plumes over distance scales of the order of hundreds or even thousands of kilometres within the boundary layer are few and far between. What evidence exists suggests that trajectories in maritime conditions are usually easier to predict than, say, in winter–large continental conditions where strong stable stability results in very marked wind shears with height. Smith has analysed records of identifiable plumes originating in the U.K. and passing over Finland and has shown that in these westerly flows the average backing from geostrophic is 7° with an extremely small standard deviation of less than 4°. Measurements made by the Meteorological Research Flight aircraft during sulphur sampling flights in the boundary layer off the east coast of England confirm that in westerly flows the average backing is 10° in neutral or slightly unstable conditions with no significant reduction of speed below the geostrophic wind, whereas in slightly stable conditions the backing is nearer 20° with a 10 % reduction in speed (Smith & Jeffrey 1975). Proposed aircraft tracking of plumes carrying implanted tracers by the Central Electricity Research Laboratory and the Meteorological Office promise new and potentially very valuable data in the next few years on this topic.

Analysis of the behaviour of tetroons flying at a *constant* level in the boundary layer and being tracked by radar or by being returned to the launchers with details of their ultimate recovery point by members of the public, provides very useful information on the behaviour of low level winds. Pack (1977) has summarized many of these experiments mainly carried out in the U.S.A. by Angell, Peterson and others. Remembering that these are indicative of winds at just one level (about 100 m) and do not fully represent the behaviour of 'free' pollution plumes, the following are two of Pack's general conclusions:

(i) the backing in southerly flows is on average 20° from the surface geostrophic direction and about 40° for northerly flows;

(ii) the best trajectories were obtained using twice the 10 m wind speed veered by 10°, although even here the standard errors were not insignificant.

Pack also quotes radar-tracked tetroon experiments carried out by the Air Resources Laboratory at Las Vegas (Allen *et al.* 1967) in mountainous terrain. Using rather sparse wind data, Allen attempted to interpolate to estimate the winds affecting the tetroons. The effects of the terrain, etc., were however so great that the reconstructed trajectories were on average to the left of the real flight paths by roughly 20 % of the distance of travel, and the standard deviation was as much as 60 %.

Returning to pollution plumes, the best trajectories should be attained by using interpolated real measured winds, and the Heffter N.O.A.A. model (1975) provides an excellent basis for doing this. In many areas and especially over sea areas, real winds are not available in high enough spatial density or with great precision by current operational sondes. The use of the surface geostrophic wind is a very attractive alternative since it is based on relatively plentiful surface pressure observations made at 1 h or 3 h intervals. Sykes & Hatton (1976) has provided a sophisticated numerical interpolation scheme which uses these to predict trajectories. Such trajectories are of course subject to all the errors and uncertainties outlined earlier, even when mean backing and speed reductions are applied.

The Norwegian team at N.I.L.U. preferred to use 850 mbar† observed radiosonde winds to calculate their trajectories. Although these apply to a rather high level (typically 1500 m) which may often be above the boundary layer they have the advantage of being actual observed winds. Comparison of trajectories worked out by N.I.L.U. and by ourselves at the Meteorological Office with the use of modified surface geostrophic winds shows generally good agreement. The largest discrepancies occur in southerly winds when surface geostrophic winds permit substantial south to north advection, whereas the higher 850 mbar winds tend to curve the back-trajectories to

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† 1 mbar = $10^2$ Pa.

come in from the west. Looking at Norway as a receptor area this tends to decrease the contributions from source areas to the south and southeast in the N.I.L.U. results, to increase the contributions from countries to the southwest, principally the U.K. compared with the Meteorological Office model.

In summary, use of modified surface geostrophic winds, interpolated actual 850 mbar winds or interpolated mean boundary layer winds all have their particular advantages and disadvantages. More tracer studies are required to help decide which winds should be used taking into account availability, accuracy and frequency. Differences will almost certainly be apparent in single situations but it appears from the results of the various models that when averaged over a year or more, budgets of pollution transmission between countries are not very seriously affected by the choice.

TABLE 2

| surface (moist climates) | $v_g$ (mean values) |
|---|---|
| short grass | 0.5 |
| medium crops | 0.7 |
| forests | ?1.0 |
| calcareous soil | 0.8 |
| acid/peaty soil | 0.5 |
| typical mixed countryside | 0.8 |
| snow | 0.1 |
| water | 0.7 |
| cities | ?0.7 |

## DRY DEPOSITION

The gas, sulphur dioxide, is fairly readily absorbed by vegetation, soil and water. The rate of absorption is usually expressed as a velocity of deposition, $v_g$, which is defined as the ratio of the vertical downward flux to the surface to the air concentration. Since the latter is an increasing function with height, the velocity of deposition unfortunately has the property of being a function of height, and strictly also a function of stability. Some of the variability in quoted values of $v_g$ no doubt arises from the failure to standardize to a given low height and a specified stability. In this respect the use of a surface resistance as proposed by Chamberlain (1966) has many advantages. However, $v_g$ is still used, mainly because it has a simpler physical concept and because it is more readily incorporated into the basic conservation equations.

At the recent International Symposium on Sulphur in the Atmosphere (I.S.S.A.) held at Dubrovnik (1977) a very useful workshop summary on deposition was prepared, and several details in this section are quoted directly from it.

Table 2 summarizes some of the estimates of $v_g$ in centimetres per second for sulphur dioxide. As mentioned in the next section, sulphur dioxide in the atmosphere undergoes gradual oxidation to sulphate if it is not dry-deposited first. The sulphate is usually in the form of a fine aerosol (0.1–1.0 μm) which also has a deposition rate to the surface. Most theories and measurements imply that $v_g$ for sulphate is considerably less than that for sulphur dioxide and does not exceed 0.1 cm s$^{-1}$.

It has already been estimated that between 10 and 20 % of the emitted sulphur dioxide is deposited on average within the first few tens of kilometres while the plume is relatively concentrated near the ground. Thereafter the box model is reasonably applicable and the time-scale, $\tau$, for the concentration to fall to $1/e$ of its original value is $z_i/v_g$ when $z_i$ is the mixing depth. If

$z_i = 1000\,\mathrm{m}$ and $v_g \approx 0.01\,\mathrm{m\,s^{-1}}$, then $\tau \approx 10^5\,\mathrm{s}$ or roughly 1 day. In reality, during one day, stabilization of the lower layers will occur insulating most of the sulphur dioxide from deposition to the ground. Consequently the actual time-scale is rather larger and lies generally between 1 and 2 days. As the I.S.S.A. summary aptly points out, this deposition is very important to general global concentrations; without it and without removal in precipitation the concentration would rise by some $70\,\mathrm{\mu g\,m^{-3}}$ per year.

The aircraft sampling flights over the North Sea described by Smith & Jeffrey (1975) were originated to compare total fluxes against upstream emissions and deduce losses to the intervening ground by dry deposition and the conversion rate of sulphur dioxide to sulphate. In 1971 the sampling system did not include sulphate and so nothing could be deduced directly about $v_g$. In 1973 this omission was rectified and the later results consistently pointed to a value of $0.8\,\mathrm{cm\,s^{-1}}$ over land and $0.7\,\mathrm{cm\,s^{-1}}$ over the sea, in full agreement with the values in table 2. The implication for the U.K. is that some 30 % of the emitted sulphur dioxide is dry deposited within our borders, that is roughly 1.7 Mt. It has been argued by F. Ross that part of this deposition is actually beneficial to agriculture in providing a source of sulphur essential for plant growth. In the main, agricultural areas of Britain the average air concentration is about $30\,\mathrm{\mu g\,m^{-3}}$ and the dry deposition rates range from some 50 to 200 kg S/ha each year.

Average rural concentrations, $\bar{C}$, in other countries can be roughly estimated from simple emission versus advection considerations, and provided the sulphur dioxide concentration largely originates within the country and not from neighbouring regions then the simple formula $\bar{C} = 90e/\sqrt{a}$, where $e$ is the emission in megatonnes per year and $a$ the area in thousands of square kilometres, gives an answer correct to within at least a factor of two. Dry depositions are then roughly $2\bar{C}$ in units of kilograms $S$ per hectare per year.

## CHEMICAL CHANGES

The oxidation of sulphur dioxide to sulphate is such a complex subject that it would be inappropriate here to give more than the briefest of outlines of our present knowledge and the experience we have gained in our own aircraft sampling flights.

In the O.E.C.D. project the main reason for studying the conversion to sulphate is that sulphate is the longer lasting species and is largely responsible for the long range transport. In many of the major American projects (M.I.S.T.T., S.U.R.E., M.A.P3.S.) the interest has centred round the possible health hazard associated with sulphate aerosol when in sufficiently high concentrations. In these projects large single plumes or dominant urban plumes have been tracked with aircraft and the conversion rates deduced by seeing how the sulphate concentration varies with downwind distance. The oxidation can take place by one or more of three general processes: by so-called homogeneous gas phase reactions depending on photooxidation, in aqueous droplets where the oxidation usually depends on metal catalysts (e.g. Fe, Mn) or ozone ($O_3$), or on surfaces. Ammonia plays a rather inadequately defined rôle in converting the sulphuric acid to ammonium sulphate.

The rate of conversion as implied by these plume studies varies considerably according to the internal chemistry of the plume, the relative humidity of the ambient air and the time of day (or incoming radiation). In the M.I.S.T.T. study Husar *et al.* (1977) found conversion rates as low as 0.1–0.5 % per hour at night and between 0.5 and 6 % during the day in the Labadie power plant plume.

In the Meteorological Office flights (Smith & Hunt 1977) the plumes were in general less intense and more diffuse. Nevertheless, at distances of 80–220 km downwind from the main upwind source areas, between 8 and 20 % of the original sulphur dioxide had been converted to sulphate. The interesting fact was that the conversion factor at these distances did not obviously correlate with either distance or time of travel but depended solely on relative humidity (see figure 3). The implication must be that the major part of the sulphate had been formed close to source where concentrations of sulphur dioxide and other relevant pollutants would be high, and that subsequent conversion once the plumes filled the mixing layer was sufficiently small to be masked by this initial conversion.

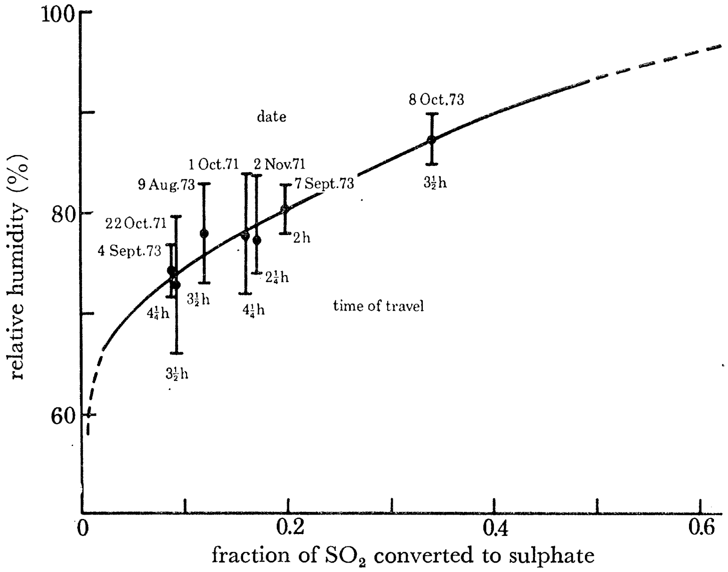

FIGURE 3. Implied fraction of the emitted $SO_2$ converted to sulphate as measured along the flight track off the East Coast of the U.K., as a function of relative humidity.

In order to try to determine the conversion rate once dispersion was complete through the mixing layer, five sampling flights were made during 1974–5 along the eastern North Sea either just off SW Norway or off west Denmark. Originally it has been intended to sample the same air late in the afternoon off the U.K. east coast and early the next morning on the other side of the North Sea, but this proved too difficult, especially without the use of tracers. As a result only on one flight, that of 22 August 1974, can an estimate of the conversion rate be made with any confidence. On this occasion there were two layers: a lower layer with an inversion extending up to about 260 m in which nearly all the sulphur dioxide had been deposited or converted to sulphate, and an upper layer in which the loss of sulphur dioxide was assumed to be due to conversion to sulphate only. Assuming that both layers had had identical sulphur dioxide and sulphate concentrations on leaving the U.K. east coast 18 h earlier, time constants for the exponential decay of sulphur dioxide by deposition and by conversion to sulphate were 7.3 and 99 h respectively. The latter is equivalent to a conversion rate of 1 % $h^{-1}$, which, while consistent with the American experience, confirms that with the present levels of precision in the aircraft system, variations of conversion with other parameters would be very difficult to detect with any certainty.

## WET DEPOSITION

The second major sink of sulphur in the atmosphere is removal through precipitation events. Typically in western European air, parcels will be advected into a rain (or snow) belt in a matter of a few days; the average time-scale is of the order of 3 days. Whenever significant precipitation is occurring, low-level convergence is almost always present to feed fresh water vapour into the cloud systems; otherwise the clouds would soon dry out. On the assumption that in a moderate rain situation the liquid water content of the cloud is not changing very significantly with time, the following simple sums show that subcloud layer convergence is sufficient to maintain the rainfall and to explain the observed wet deposition rates of sulphur in western Europe.

We suppose that the air in the subcloud layer has a relative humidity of 90 %, and at a temperature of 10 °C this corresponds to a mixing ratio of 10 g water per kilogram of air (that is roughly 1 $m^3$ of air). Although our arguments are not restricted to any particular rate of rainfall it is useful to digress and look at the case of moderate rain. Moderate rain is defined as a rate between 1 and 4 mm rain per hour. If this rain were to be balanced by an input of water vapour from the sub-cloud layer into the cloud, these rates would require vertical velocities between 3 and 12 cm $s^{-1}$, very reasonable values and similar to those actually measured. In general, however, if the concentration of sulphur (as $SO_2$ or sulphate) in the mixing layer is taken as approximately 10 μg S/$m^3$ (as typically observed in aircraft sampling flights), then on the assumption that all the sulphur is removed by one process or another into the rain, then 1 mm of rain, which corresponds to 100 $m^3$ of mixing layer air, must carry 100 × 10 μg S (i.e. 1 mg S). This sulphur burden is equivalent to a concentration of 3 mg $SO_4$/l, which is in very good agreement with measured values over a large part of NW Europe. Moreover, in southern Norway where the annual rainfall has an average of about 1 m, the implied wet deposition is 1 g S $a^{-1}$, again in very good agreement with direct measurements. Generalizing this analysis, the depletion of sulphur out of the mixing layer, along a trajectory, due to removal in precipitation can therefore to a good approximation be related to the rate of rainfall and to the observed mixing ratios.

If $Q$ is the sulphur still carried in the atmosphere arising from emissions over unit time from upwind sources, $t$ is time in hours, $h$ is the mixing depth in kilometres, $m$ is the mixing ratio in grams per kilogram and $r$ is the rainfall rate in millimetres per hour then $\mathrm{d}Q/\mathrm{d}t = -rQ/mh$, and the time-scale in hours of this process is given by $\tau_s = mh/r$.

At warm fronts the input of sulphur is mainly from the warm sector air during the general upsliding process within the sloping frontal zone. However, some boundary layer air may be drawn up from the colder air ahead of the front, although experience in trying to seed warm fronts with silver iodide released at ground level in order to monitor rainfall modification suggests that usually little air penetrates the frontal inversion into the main rain-producing cloud.

Some sulphur still in the boundary layer may get removed in rain by direct sulphur dioxide and sulphate scavenging as the rain drops fall through the polluted air. This is a complex process and is discussed in the workshop summaries of the I.S.S.A. conference (Husar (ed.) 1977). There are unproven suggestions that these processes are not normally dominant in wet deposition of sulphur.

Returning to the low level convergence process into rain areas, the modelling of these convergences is particularly difficult on a fairly course grid as used in all current numerical trajectory models. This is particularly true in large thunderstorm situations where considerable volumes of boundary layer air can be swept into these dynamic clouds and cleansed by washout. Upward velocities over regions below cloud 1–2 km across can be as large as 1–10 m $s^{-1}$, implying normal local horizontal convergence rates of $10^{-3}$ to $10^{-2}$ $s^{-1}$. Such situations can lead to depositions of episodic proportions.

Another major problem in recording wet deposition and the associated loss from the trajectory is the general lack of a good areal coverage of rainfall. This is especially so in mountainous areas, where rainfall is strongly influenced by the topography and is spatially very variable, and also over sea areas like the North Sea where few or no data are available. Perhaps the biggest hope for the future in this problem is in the deployment of suitable weather radar. The successful use of radar in quantifying rainfall over areas 80 km in diameter has been described by Browning (1977) and Hill *et al.* (1977). In the next decade most of England and Wales will be covered in this way.

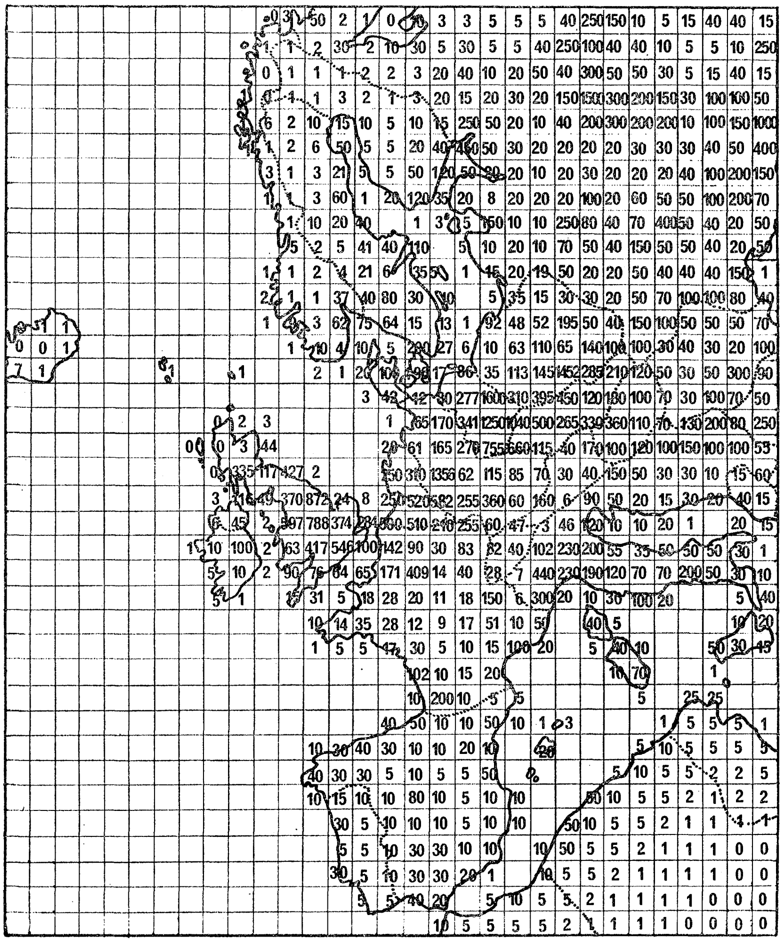

Figure 4. Sulphur dioxide emissions for 1972 in thousands of tonnes per year. The grid length is 127 km at 60° N.

## Modelling

Many attempts have been made at modelling some of the various processes outlined in the previous sections (see, for example, O.E.C.D. 1977; Scriven & Fisher 1975), both in order to produce sulphur deposition fields which agree satisfactorily with those produced from observations and, more particularly, to determine the fluxes of sulphur across national boundaries within

Europe. In the British Meteorological Office, a trajectory model has been developed (Smith & Johnson 1975) to calculate the relative contributions of different countries or regions in Europe to the total sulphur deposition in southern Norway. Back-trajectories were produced from a chosen point in Norway every twelve hours for the three year period 1972–4. The trajectories were based on surface geostrophic winds, modified in a simple fashion to make them more representative of winds in the boundary layer, and were taken back in time for at least 72 h or until precipitation was encountered. Each trajectory so produced was then related to a 127 km × 127 km emission grid for Europe (figure 4) and every grid square crossed by the trajectory was noted together with an indication of whether precipitation was occurring or not at the destination area in order to distinguish dry deposition from wet deposition occasions.

By assuming a constant mixing depth of 1 km and with the use of values of $SO_2$ deposition velocity and $SO_2$ to $SO_4$ transformation rate deduced from experiments discussed earlier, the amount of sulphur remaining in the air at the destination due to the emission in each crossed grid square could be determined and values for dry or wet deposition of sulphur were obtained. Although the model was essentially very simple, diurnal variations in emission and also diurnally varying amounts of local deposition and transformation at the source area were introduced. Some attempt was also made to include the effect on deposition of night-time stabilization. The contributions from all of the trajectories were then added to produce the results described in the next section.

Clearly this model, while producing useful results which agreed quite well with other models and tolerably well with observations, needs to be refined considerably to take into account many factors which are known to be of importance. Variations in mixing height and the corresponding wind shears encountered by the pollution should be introduced. Ways of estimating mixing height from readily available parameters have been developed (Smith 1975), but incorporating the effects of wind shear is difficult without introducing more than one level in the vertical. Introducing more detailed precipitation data is essential, with the use of any kind of measuring device available, especially over sea areas, while it will also be necessary to vary the dry deposition velocity according to the underlying surface.

One of the most important areas for improvement concerns the local depositions close to the sources. That not all of the sulphur emitted at a source is involved in long-range transmission has been discussed and allowances are made for this in the model. The term 'apparent emission' of a source can be used to describe that part of the total emission which is transported out of the source region. Exactly how much is deposited close to the source depends critically, as has been shown, on source height and on the mixing depth as well as on such mesoscale features as urban heat islands. Suitable ways of parameterizing the 'apparent emission' for each source at different times will be incorporated into future models.

## BUDGETS

Before outlining some of the results produced by the model described above, some idea of the uncertainties involved in the analyses should be given. As has already been stated, the accuracy of the national emission totals is thought to be between about 10 and 25 % for most of the countries which contributed to the O.E.C.D. experiment. For other countries the figures are probably less accurate while the individual grid square values are less accurate still. The accuracy of trajectories is hard to verify. The use of different advecting winds (such as the 850 mbar wind which has been used in some models (O.E.C.D. 1977)) can lead to startlingly different trajectories on certain occasions and individual cases might be quite inaccurate. Nevertheless, systematic errors over a three year period could be relatively unimportant.

The wet deposition figures are greatly influenced by the simple manner precipitation is included in the model and the combined wet and dry deposition totals are probably only accurate to within about 40–50 %. Also, comparing results from the model with observations from a

TABLE 3. AVERAGE CONTRIBUTIONS BY REGIONS 1972–1974

| region | distribution of wet deposition (%) | distribution of dry deposition (%) | distribution of total deposition (%) | total deposition mg $SO_2$ $m^{-2}$ $a^{-1}$: annual average | total deposition mg $SO_2$ $m^{-2}$ $a^{-1}$: per 100 kt emission |
|---|---|---|---|---|---|
| British Isles | 34.4 | 22.2 | 30.7 | 895 | 15.0 |
| Norway | 10.9 | 32.2 | 17.4 | 507 | 323 |
| G.D.R. | 11.0 | 9.9 | 10.7 | 312 | 6.3 |
| F.R.G. | 11.4 | 7.2 | 10.1 | 295 | 7.3 |
| Sweden | 4.4 | 6.9 | 5.2 | 152 | 14.8 |
| Holland | 4.3 | 2.9 | 3.9 | 114 | 9.5 |
| Poland | 3.4 | 3.9 | 3.5 | 102 | 2.7 |
| Denmark | 3.3 | 3.7 | 3.4 | 99 | 26.2 |
| France | 4.1 | 1.9 | 3.4 | 99 | 4.1 |
| Belg./Lux. | 3.9 | 2.3 | 3.4 | 99 | 8.1 |
| Czech. | 3.5 | 2.7 | 3.2 | 93 | 2.9 |
| U.S.S.R. | 2.3 | 2.4 | 2.4 | 70 | 0.7 |
| Italy | 1.1 | 0.5 | 0.9 | 26 | 0.9 |
| Finland | 0.5 | 0.5 | 0.5 | 14 | 3.0 |
| others | 1.5 | 0.8 | 1.3 | 38 | 1.0 |
| total | **100.0** | **100.0** | **100.0** | **2915** | |

annual average wet deposition 2022 mg $SO_2$ $m^{-2}$ $a^{-1}$
annual average dry deposition 893 mg $SO_2$ $m^{-2}$ $a^{-1}$

TABLE 4. DEPOSITION BY REGIONS FOR EACH YEAR 1972–1974
(PERCENTAGES OF GRAND TOTAL FOR EACH YEAR)

| | 1972 total: 3698 mg $m^{-2}$ | | 1973 total: 2231 mg $m^{-2}$ | | 1974 total: 2823 mg $m^{-2}$ | |
|---|---|---|---|---|---|---|
| region | dry deposition | deposition in rain | dry deposition | deposition in rain | dry deposition | deposition in rain |
| British Isles | 5.3 | 20.9 | 7.2 | 22.6 | 8.5 | 28.7 |
| Norway | 7.8 | 5.5 | 12.7 | 11.3 | 10.3 | 7.5 |
| G.D.R. | 3.9 | 11.3 | 2.5 | 5.1 | 2.3 | 4.9 |
| F.R.G. | 2.2 | 8.5 | 1.8 | 6.9 | 2.5 | 7.9 |
| Sweden | 1.9 | 3.1 | 2.1 | 3.5 | 2.4 | 2.7 |
| Holland | 0.9 | 3.4 | 1.0 | 3.2 | 0.9 | 2.4 |
| Poland | 1.1 | 2.9 | 0.8 | 2.0 | 1.6 | 1.8 |
| Denmark | 1.4 | 3.1 | 1.0 | 2.1 | 0.9 | 1.4 |
| France | 0.7 | 3.2 | 0.5 | 2.3 | 0.5 | 2.9 |
| Belg./Lux. | 0.7 | 2.9 | 0.8 | 2.6 | 0.6 | 2.4 |
| Czech. | 1.1 | 3.9 | 0.8 | 1.7 | 0.5 | 1.1 |
| U.S.S.R. | 0.5 | 1.0 | 0.5 | 3.3 | 1.2 | 1.1 |
| Italy | 0.2 | 1.0 | 0.1 | 0.0 | 0.1 | 1.0 |
| Finland | 0.1 | 0.1 | 0.1 | 0.3 | 0.3 | 0.6 |
| others | 0.2 | 1.2 | 0.2 | 1.0 | 0.3 | 0.7 |
| total | **28.0** | **72.0** | **32.1** | **67.9** | **32.9** | **67.1** |

number of measuring stations in southern Norway, it was apparent that the model tended to overestimate the amount of wet deposition and underestimate the dry deposition.

However, bearing the foregoing comments in mind, the results from the model are summarized in tables 3 and 4. These were obtained by calculating the number of trajectories crossing each grid square and the contribution that each square made per trajectory to the wet and dry deposition in southern Norway. From this, and by grouping the squares into countries or regions, the figures shown in the tables could be deduced. It can be seen from table 3 that there is a considerable annual variation in the total deposition, the source of which can be ascribed to the variations in annual rainfall which occur. Rainfall at Lista in southern Norway, for instance, was about 15 % below the average for the previous 20 years in 1973 and about 10 % above in 1974.

TABLE 5. ESTIMATED PERCENTAGE CONTRIBUTIONS TO TOTAL SULPHUR DEPOSITION IN NORWAY FOR 1974 GIVEN BY SMITH & JOHNSON (1975) AND O.E.C.D. (1977)

| | percentage contribution | |
|---|---|---|
| country | Smith & Johnson | O.E.C.D. |
| British Isles | 37.2 | 28.0 |
| Norway | 17.8 | 12.0 |
| G.D.R. | 7.2 | 4.0 |
| F.R.G. | 10.4 | 4.0 |
| Sweden | 5.1 | 3.6 |
| Holland | 3.3 | 1.6 |
| Poland | 3.4 | 2.0 |
| Denmark | 2.3 | 3.2 |
| France | 3.4 | 3.6 |
| Belgium | 3.0 | 1.6 |
| Czechoslovakia | 1.6 | 1.2 |
| U.S.S.R. | 2.3 | — |
| Italy | 1.1 | 0 |
| Finland | 0.9 | 0.4 |
| others | 1.0 | 1.6 |
| undecided | — | 40.0 |

Over longer periods it might be expected that the annual rainfall amounts will vary between about 50 % and 150 % of the long-term average at any particular site. Any trend in annual rainfall over a period of years will of course lead to a corresponding trend in sulphur deposition for the years in question. Table 3 shows that rainfall occurring with the prevailing southwesterly winds cause the British Isles to be responsible for the biggest single contribution to wet deposition although again there are considerable yearly variations.

A different picture emerges with regard to dry deposition. The Norwegians themselves provide the largest contribution, showing the importance of local sources, and the frequency of southwesterly winds are again shown up in the British Isles figures. Table 4 shows the mean percentage of the total deposition per year contributed by each country. With the use of this model, then, Britain is responsible for about 30 % of the total deposition in Norway during the three years studied.

Table 5 compares the results of the model with results given in O.E.C.D. (1977) for a single year 1974. The latter are claimed to be accurate to within about ± 50 % and are for the whole of Norway while the former refer only to the southern part of the country. The same pattern can be seen in both sets of results although in the O.E.C.D. column, a disturbingly large amount (40 %) of the deposition was from 'undecided' origins. This arises in part from the way N.I.L.U.

estimated rainfall from a comparison of model-calculated concentrations of total sulphur with observed concentrations of sulphate in precipitation which implies a non-zero wet deposition even when air sulphur concentrations fall to zero. The causes of this apparent anomaly are not fully understood but one possibility is that local sources are making an inadequate contribution in the N.I.L.U. model. In Norway much of the rain is associated with westerly flow from over the Atlantic without any upwind input of sulphur, and the N.I.L.U. technique gives an apparent sizeable wet deposition without any clear origins. The Meteorological Office model used actual rainfall observations to assess wet deposition and so avoided this problem of an 'undecided' source. When considering amounts of wet deposition it is interesting to note that the correlation between rainfall and sulphate wet deposition is not particularly high on a day-by-day basis. Indeed in some areas it has been found to be as low as 0.2 although more normally it is 0.6–0.7. This means that it is not advisable to look *only* at rainfall distribution in order to draw conclusions about the wet deposition pattern. The reason for this is in the position of each area relative to the main emission areas. Sites just to the west of major source areas in Europe, for instance, will only receive small concentrations of sulphate in most of their heavier rainfall, which will tend to occur when the winds are westerly in direction. However, easterly winds, although less common and producing relatively small rainfalls, will tend to be rather heavily polluted. This means that at such a site wet deposition tends to be uniform in magnitude and has a quite different magnitude–frequency distribution from the rainfall. The importance of this becomes apparent in the next section.

## EPISODES

In some parts of Europe a significant proportion of the total annual wet deposition occurs on only a few days of the year. We can describe this feature quantatively by defining 'episode-days' at a given point as those days with the highest wet depositions which, when summed, account for 30 % of the total annual wet deposition and then define the 'episodicity' at that place as the ratio of the number of episode-days to the total number of rainfall days (figure 5 gives an example of these definitions. The episodicity at Cottered in the east Midlands is 5.3 % from 1974 data). Using these definitions it can be shown that, for 1974 data, many parts of central and southern Norway, as well as parts of south Switzerland and Scotland, have episodicities of less than 5 %. These areas are distant from the main industrial regions and the air is normally unpolluted. Just occasionally, however, air arriving there will have crossed a source area some time before, and if this air is introduced into frontal rain or thunderstorms, high depositions can occur. In these 'highly episodic' areas the number of episode-days is typically less than 10 and can be as low as 4, i.e. 30 % of the total annual wet deposition falls on 4 days.

The importance of the effect of episodes on the environment is not entirely obvious at present, although it is possible that occasions of significant wet deposition of unusually low pH may result in marked fish kill in streams and small lakes. The relevance of episodes with regard to any possible control of emissions is however, clearer. If the mechanisms leading to episodes could be sufficiently understood to be included in models, it would be possible for budgeting during episode-days to be carried out. However, the very nature of episodes precludes the possibility of them being adequately dealt with by statistical models of the type described earlier. These isolated events will have to be treated individually and may lead to significantly different results. It has been observed that most episodes are associated either with slow-moving frontal systems where heavy and prolonged rainfall can be produced by convergence of moist air at low levels, often enhanced by mountains, or with a slow-moving anticyclone centred over a major source area. If, in this latter case, air from near the centre of the anticyclone, which is by then heavily polluted, becomes drawn into a frontal zone, only relatively small amounts of rain can lead to high depositions.

Figure 6 shows back-trajectories for the 4 episode-days in 1974 at a site in southern Norway. It can be seen that all trajectories pass over major emission areas to the south or east. One of these

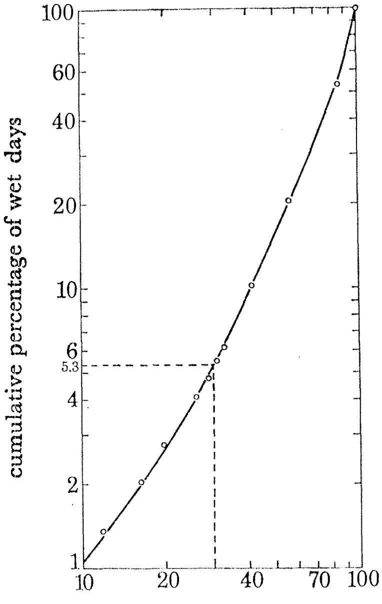

Figure 5. The cumulative percentage of deposition plotted against cumulative percentage of wet days, plotted on logarithmic scales, for Cottered in the east Midlands.

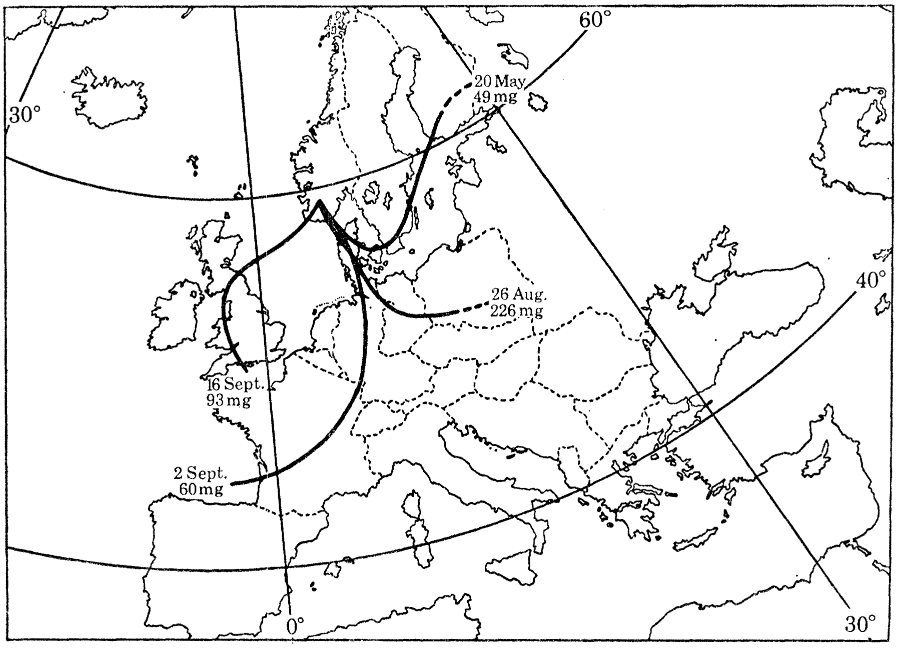

Figure 6. Back-trajectories for the 1974 episode-days at Vatnedalen in southern Norway.

trajectories, together with part of the emission grid and measured values of surface geostrophic wind, is shown in detail in figure 7. Some 48 h before the destination time, the trajectory was over a high emission area in the German Democratic Republic and Poland and close to a slowly moving anticylcone. As can be seen from the diagram, the surface geostrophic winds were only about 3–4 m s$^{-1}$ allowing high concentrations of sulphur to accumulate. The polluted air was then drawn towards southern Scandinavia where a frontal system was approaching from the west. The increasing wind along the trajectory meant that only a relatively small amount of dry deposition took place, this loss to the ground being inversely proportional to the wind speed. Finally the air, which still contained high concentrations of sulphur, was drawn into the frontal zone over the mountains where large amounts of rain occurred with associated thunderstorms and produced by far the largest wet deposition of the year there.

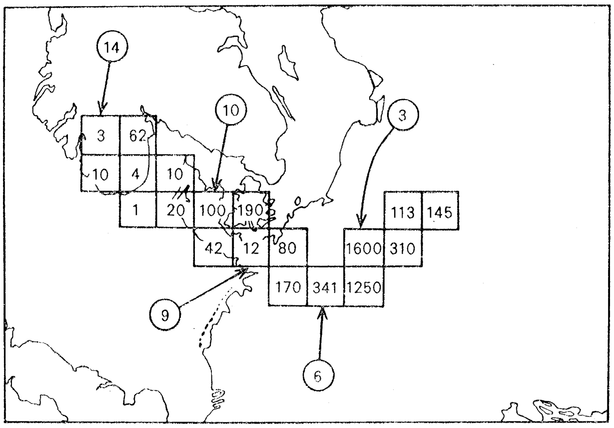

FIGURE 7. Back-trajectory for 0h 00 G.M.T., 27 August 1974, from Vatnedalen with relevant part of emission grid (figure 3). Number in circles refer to surface geostrophic winds (metres per second) along the route.

In fact, the rates of horizontal convergence which can be found near to thunderstorms can lead to wet depositions of about twice that which would be expected from calculations not including this feature. Especially in mountainous areas it would appear important to introduce convergence effects into any modelling attempts to assist with the correct handling of episodes.

## REFERENCES (Smith & Hunt)

Allen, P. W., Jessup, E. A. & White, R. E. 1967 *Proceedings of U.S.A.E.C. Symposium Meteorological Information Meeting*, Chalk River, Ontario, Canada. A.E.C. L.-2787 (ed. C. A. Mawson), pp. 176–190. Chalk River: Atomic Energy of Canada Ltd.

Braekke, F. H. (ed.) 1976 *Impact of acid precipitation on forest and freshwater ecosystems in Norway*. S.N.S.F. project, NISK, 1432- NLH, Norway.

Briggs, G. A. 1969 *Plume rise*. TID-25075, Clearing House for Fed. Sci. and Tech. Information, National Bureau of Standards, Springfield, Virginia.

Browning, K. A. 1977 *The short period weather forecasting pilot project*. Internal Meteorological Office Paper.

Chamberlain, A. C. 1966 *Proc. R. Soc. Lond.* A **290**, 236.

Clarke, R. H., Dyer, A. J., Brook, R. R., Reid, D. G. & Troup, A. J. 1971 *The Wangara Experiment: boundary layer data*. Melbourne: C.S.I.R.O.

Hanna, S. R. & Gifford, F. 1973 *Atmos. Environ.* **7**, 131–136.

Heffter, J. L., Taylor, A. D. & Ferber, G. J. 1975 *A regional–continental scale transport, diffusion and deposition model*. N.O.A.A. tech. Memo E.R.L. ARL–50, 28 pages.

Hill, F. F., Whyte, K. W. & Browning, K. A. 1977 *Met. Mag.* **106**, 69–89.

Husar, R. B., Patterson, D. E., Husar, J. D., Gillani, N. V. & Wilson, J. E. 1977 In *Proceedings of the International Symposium on Sulphur in the Atmosphere. Atmos. Environ.* **12**, 549–568.

I.S.S.A. Husar, R. B. (ed.) 1977 *Proceedings of the International Symposium on Sulphur in the Atmosphere*, Dubrovnik. *Atmos. Environ.* **12** (1–3).

Izumi, Y. & Caughey, J. S. 1976 *Minnesota 1973 atmospheric boundary layer experiment data report.* Air Force Cambridge Research Laboratories Report Number AFCRL-TR-76-0038.

Moore, D. J. 1974 *Atmos. Environ.* **8**, 441–458.

O.E.C.D. 1977 *The O.E.C.D. programme on long range transport of air pollution.* Paris: O.E.C.D.

Pack, D. H., Ferber, G. J., Heffter, J. L., Telegadas, K., Angell, J. K., Hoecker, W. H. & Machta, L. 1977 In *Proceedings of the International Symposium on Sulphur in the Atmosphere. Atmos. Environ.* **12**, 425–444.

Scriven, R. A. & Fisher, B. E. A. 1975 *Atmos. Environ.* **9**, 49–68.

Smith, F. B. 1975 *Sci. Prog. Oxf.* **62**, 127–151.

Smith, F. B. 1977 *Application of data from field programmes to estimation of K-profiles and vertical dispersion.* Internal Meteorological Office paper.

Smith, F. B. & Hunt, R. D. 1977 In *Proceedings of the International Symposium on Sulphur in the Atmosphere. Atmos. Environ.* **12**, 461–478.

Smith, F. B. & Jeffrey, G. H. 1975 *Atmos. Environ.* **9**, 643–659.

Smith, F. B. & Johnson, D. A. 1975 *Sulphur transport in Western Europe during 1972–1974 from trajectory analysis and experimental measurements.* Internal Meteorological Office paper.

Sykes, R. I. & Hatton, L. 1976 *Atmos. Environ.* **10**, 925–934.

Weatherley, M.-L. P. M. 1977 *Fuel consumption, and smoke and sulphur dioxide emissions, in the United Kingdom, up to 1976.* Warren Spring Laboratory, Report LR 258 (AP).

## *Discussion*

M. H. Unsworth (*University of Nottingham School of Agriculture, Sutton Bonington, Loughborough, Leics. LE12 5RD, U.K.*). Although there are a number of published measurements of deposition velocities for sulphur dioxide to natural surfaces, there have been few studies in winter when surfaces are often wet with dew and rain. Observations by Fowler (Fowler & Unsworth 1974; Fowler 1976) showed that when a wheat crop was wet with dew it had a much lower resistance to $SO_2$ uptake than when the crop was dry; a few measurements during rainfall led to similar conclusions (Fowler 1976). These observations suggest that deposition velocities for $SO_2$ on wet vegetation may be larger than the generally accepted values for dry surfaces. Would Dr Smith like to comment on the likely consequences of such a result on his calculations of long-range transport?

### *References*

Fowler, D. & Unsworth, M. H. 1974 *Nature, Lond.* **249**, 389–390.

Fowler, D. 1976 Uptake of sulphur dioxide by crops and soil. Ph.D. thesis, University of Nottingham.

F. B. Smith. The consequences of a higher deposition velocity when the underlying vegetation is wet are not readily assessed. Two rather inadequate statements may, however, be made. Suppose the air behind a rain belt advects without actually catching it up and the sulphur dioxide it carries is affected by an enhanced deposition velocity along the whole of its track. As Professor R. S. Scorer once pointed out, the increased losses and subsequent lowering of air concentration tend to lead to a virtual independence of deposition rate on deposition velocity at ranges of about 1000 km from source. This distance corresponds well with the distance of the main European source regions from southern Norway. If, however, the air does gets advected into the rain belt, less sulphur will be there to be wet-deposited out, although this reduction will to some extent be minimized by the somewhat rapid oxidation of the sulphur dioxide to sulphate in the rather humid conditions along the tract and a consequent reduction in losses by dry deposition. Overall, then, some reduction in wet-deposition must be expected if Dr Unsworth's suppositions are correct.

R. A. Scriven (*Central Electricity Research Laboratories, Kelvin Avenue, Leatherhead, Surrey, U.K.*). As Dr Smith has described, it is now estimated that about 25 % of the sulphur deposited annually in Norway comes from the U.K. Although this is the largest contribution to this area from individual European countries, some further amplification of Dr Smith's figures is required to put the U.K. position properly into perspective.

In the O.E.C.D. study it was found that about 40 % of the deposition in Norway could not be allocated to any particular country because of the uncertainties associated with specifying wind trajectories accurately and because of the significant amount of sulphate in rain arriving on wind from the Atlantic sector where there were no industrial sources. In fact the average concentration of sulphate in rain from this sector was found to be one half of that from W–SW sector which contains the U.K. as the only major source. The corresponding sulphate in rain concentrations from the southerly and easterly sectors where the rain arrives in Norway on winds from the main continental source regions are three to four times that from the U.K. sector. The amount of rain coming from these sectors is about one-sixth of the total whereas the amount from the U.K. sector is about one-half. Hence, while the depositions from these various sectors are comparable the continental contribution consists of fewer occasion of higher concentrations as compared with the more frequent low concentration contribution from the U.K. sector. This distinction is likely to be important when discussing biological and geochemical effects.

The fact that a significant amount of sulphate arrives in Norway from winds in the Atlantic sector suggests that sulphur emitted from natural sources together with man-made emissions in North America (A. Nyberg 1977 *Q. Jl R. met. Soc.* **103**, 607–613) is travelling intercontinental distances as sulphate aerosol, the removal rate of which dry processes is known to be small.

P. F. Chester (*Central Electricity Research Laboratories, Kelvin Avenue, Leatherhead, Surrey, U.K.*). In introducing his paper, Dr Smith noted the assumption behind the O.E.C.D. survey that a major part of the acidity in Scandinavian rivers and lakes has its origins in rain borne sulphur compounds. In view of the extensive and detailed understanding of the transport and transformation of atmospheric sulphur exemplified by the last two papers, it is timely to contrast this body of knowledge with that on which the motivating assumption is based. Rosenqvist, in a recent (1976) report for the Norwegian Council of Scientific Research, discussed a number of biochemical and geochemical reactions having an important influence on Scandinavian inland waters. Until recently, the available chemical analysis have not included factors which would demonstrate the presence of absence of such mechanisms. However, in the spring of 1977, members of the Central Electricity Research Laboratories, working with scientists of the Norwegian S.N.S.F. Project, on the Tovdal River in Southern Norway, measured weak acid concentrations, which were presumably derived from interactions with the soil, up to 20 times those of the strong acids present. We estimate that the pH would have risen by only 0.2–0.3 if no strong acids had been present at all. It would appear that further work is necessary to elucidate the reaction paths leading to low pH in Scandinavian waters so as to identify more completely the responsible environmental factors. The results referred to will be reported in more detail elsewhere.

## *Reference*

Rosenqvist, I. T. 1976 *Contribution to an analysis of the buffer effect of geological materials in respect of strong acids in rain water with examples from Numedal.* Report submitted to N.A.V.S. (Norwegian Council for Scientific Research).