# Atmospheric Transport and Transformation [and Discussion]

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# Atmospheric transport and transformation

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The meteorological factors determining the dispersion and deposition of pollutants are described. The results and limitations of attempts to model the deposition of anthropogenic sulphur over western Europe are given and compared with the measured deposition fields. The difficulty of monitoring the deposition on this scale is also emphasized as is the episodic nature of much of the deposition. Finally the atmospheric chemistry involved in the oxidation of sulphur dioxide and nitrogen oxide is described and evidence presented to illustrate the complexity of the factors determining the acidity of rain.

## 1. Introduction

In this paper an attempt is made to summarize the atmospheric processes important in understanding the details of the factors controlling transport and deposition of anthropogenic sulphur and nitrogen compounds at locations distant from the source areas.

In the first part of this paper, the purely meteorological problem of modelling the dispersion and deposition of pollutants is described. The latest assessment of the annual deposition of sulphur throughout Europe as derived by the European Monitoring and Evaluation Programme is summarized and some of the limitations of that work outlined. The episodic nature of the deposition of pollutants is emphasized.

In the second part of the paper, the difficulties of monitoring the deposition of sulphur and nitrogen compounds is illustrated by referring to experience in the U.K. with sampling systems operated side-by-side.

The results of analyses of data from the European Air Chemistry Network from 1955–1975 are briefly described. It is difficult to know to what degree such analyses can be of use other than to reflect the inadequacies of the methods involved. If it is true that for most of Europe the total deposition is not reflecting the increase in the emission of sulphur compounds, then we must conclude that the remainder is being transferred from the boundary layer to the rest of the troposphere thereby increasing the background global deposition and so to some degree diluting the regional problem.

In the third part of the paper atmospheric chemistry of the sulphur and nitrogen compounds is considered. In the models described in the first part of the paper such chemical processes are parametrized simply by assuming a conversion rate of sulphur dioxide to sulphate of $x$% per hour. It will be shown that such an assumption is very over-simplistic if applied on a single event basis. This will be illustrated by consideration of some recent results involving aircraft measurements near the U.K.

## 2. METEOROLOGY

### (*a*) *The atmospheric boundary layer*

Boundary layers are generated whenever a fluid flows over a solid surface. The situation is no different in the atmosphere. The presence of the ground changes the air's velocity, temperature, turbulence structure, and so on in its vicinity. One factor that is not generally present in other flows characterizes the atmosphere; the air and the surface are often at different temperature and moisture levels, and this causes heat and moisture to flow from one to the other. Usually (but not always) the flow of heat is into the atmosphere during the day over land, and in the reverse direction at night. On occasions this can cause big changes in the intensity of turbulence and in the depth of the boundary layer from day to night.

During the day, over land, the boundary layer is a region of rather rapid mixing and may be some 400–2000 m deep (depending on wind speed and the heat input from the ground). At night because of the stabilizing effect of having a cooled surface, the layer may be only some tens of metres deep and the intensity of vertical turbulence and subsequent mixing much less, or even non-existent. Above the boundary layer, the airflow is undisturbed by the ground, and vertical mixing is usually slow by comparison.

Over the sea, the boundary layer shows very little diurnal variation since incoming solar radiation penetrates through a deeper layer of the sea and changes the sea surface temperature only slowly. The stability of the air and the depth of the boundary layer evolve gradually in response to air–sea temperature differences, to the flux of water vapour and to changes in pressure gradient controlling the wind.

Pollutants emitted into the boundary layer are affected by its properties in at least four important ways.

(i) The associated turbulence will diffuse the pollutants throughout the layer with the result that some will be absorbed and deposited at the surface.

(ii) The same mixing will drive and maintain chemical reactions between various chemical species occurring naturally or injected as pollutants into the air.

(iii) The wind varies in a rather complex way within the boundary layer depending on its depth, stability, past history and the roughness of the underlying ground and its spatial variability. Precise determination of the travel of injected pollution is consequently rather difficult and at times this can be a source of significant error.

(iv) Cloud and rain have as their precursors the flow of heat and moisture from the surface through the boundary layer. Rain is particularly effective in removing certain pollutants from the air to the underlying surface.

### (*b*) *Modelling the fate of pollution in the atmosphere*

Figure 1 illustrates the processes that have to be modelled. Most of the processes have been very briefly referred to already, the rest are easily understood in broad terms. The basic difficulty is of course that there are never enough data available (and in several cases not enough proper understanding) to model what is going on adequately. As an example our understanding of how the windfield responds to realistically complex changes in orography (hills, valleys, coastlines etc.) is still very limited from both a theoretical and an observational standpoint in spite of important advances in our theoretical and experimental studies associated with rather idealized situations. Consequently all models describing the dispersion and deposition of pollutants emitted into the atmosphere, no matter how simple or sophisticated they attempt to be, ultimately rely heavily on empiricism and parametrization. Many models have been developed (see Pasquill & Smith 1983) that include in this sense the emission, advection, diffusion, chemical change, loss from the boundary layer and deposition processes. Which model is best for a potential user will depend very much on its intended use and an assessment of the model's validity in that context. It also depends on the availability (or otherwise) of required meteorological and emission data, and on the nature of the computer facilities to be used.

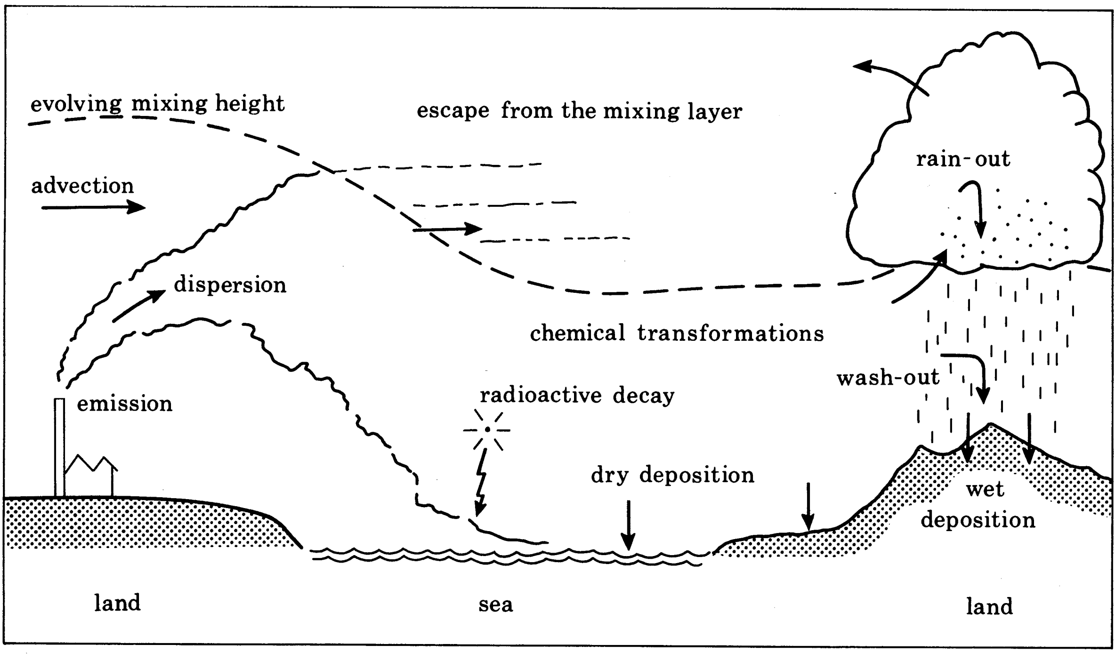


FIGURE 1. Processes involved in the transport and deposition of atmospheric pollutants.

Models can be subdivided in a variety of ways which can only be touched on very briefly here. Three of them are as follows:

(i) Models that use statistics of wind, boundary-layer depths and precipitation. Resulting deposition fields may have validity but only over long times (more than 1 year). The models are simple and very economical to run. Deposition fields for man-made sulphur oxides have been shown to be in surprisingly good agreement with 'observed' fields for Europe.

(ii) Models that use real hour-by-hour meteorological data, but because of the limitations of these data and the rather sparse observing network, still require the use of much parametrization and have validity over rather long times (more than several months). Of this type are the models used in the current European Monitoring and Evaluation Programme (E.M.E.P.) for studying the atmospheric transport of air pollution across Europe, mounted jointly under the auspices of the Economic Commission for Europe, the United Nations Environment Programme and the World Meteorological Organization, and involving the co-operation of most of the countries of Europe.

(iii) Complex models are being developed that are essentially extended mesoscale models and take account of topography and the three-dimensional equations of motion. They will require considerable non-standard meteorological data and a highly sophisticated computer facility and are therefore unlikely to be used except for discrete events of exceptional scientific interest or public concern.

In summary, all current models have the capability of giving rather long-term deposition fields. No model has yet been shown to be capable of giving reasonable estimates of deposition in the short term (i.e. over one or a few days). Fortunately from this point of view many of the ecological effects of air pollution are believed to be associated with rather long term depositions, although it is not unreasonable to assume that some effects may result from large episodic depositions occurring in a single rain event.

### (*c*) *Long-term depositions over Europe*

The Lagrangian trajectory model used at the so-called Meteorological Synthesising Centre-West (at the Institute of Meteorology in Oslo), in the E.M.E.P. is capable of estimating the contribution each European country makes, through its emission, to the average depositions in any other European country. The model works specifically for sulphur dioxide and its derivatives, but could be equally applied to other pollutants in which the emission fields and the conversion and loss parameters are known. Figure 2 shows the results of the model based

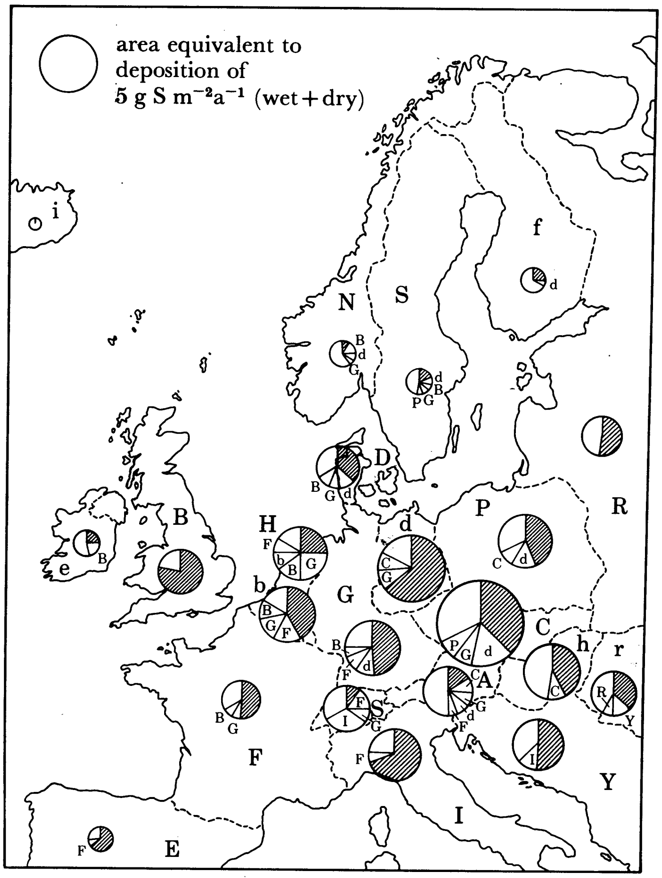


FIGURE 2. Total sulphur depositions within European countries as implied by the results of the E.M.E.P. MSC-W Lagrangian trajectory model. Depositions are represented in grams per square metre per year. The shaded areas denote the contribution from emissions within the same country. Other sectors are identified by letters corresponding to the country of origin. Contributions less than a 20° sector are lumped together with unidentified contributions in the unlabelled sector.

on data for 1978–1979. The size of the circle within each country is proportional to the average deposition of sulphur per square metre per year (see the key in the top left of the figure). The shaded part of the circle represents the deposition arising from emissions within the same country; other segments are labelled with the letter of the country of origin. The unlabelled segment includes contributions smaller than a 20° segment, or from natural sources, or from sources outside Europe. It is interesting to note that Czechoslovakia receives over 12 times as much sulphur deposition as Norway, and that although Britain contributes more than any other country to Norway's deposition, it really is a very small amount (*ca.* 0.15 g S $m^{-2}$ $a^{-1}$). Nevertheless Norway's depositions are not uniformly spread and are much higher in the south where, it is alleged, related fish-kill has been so prominent.

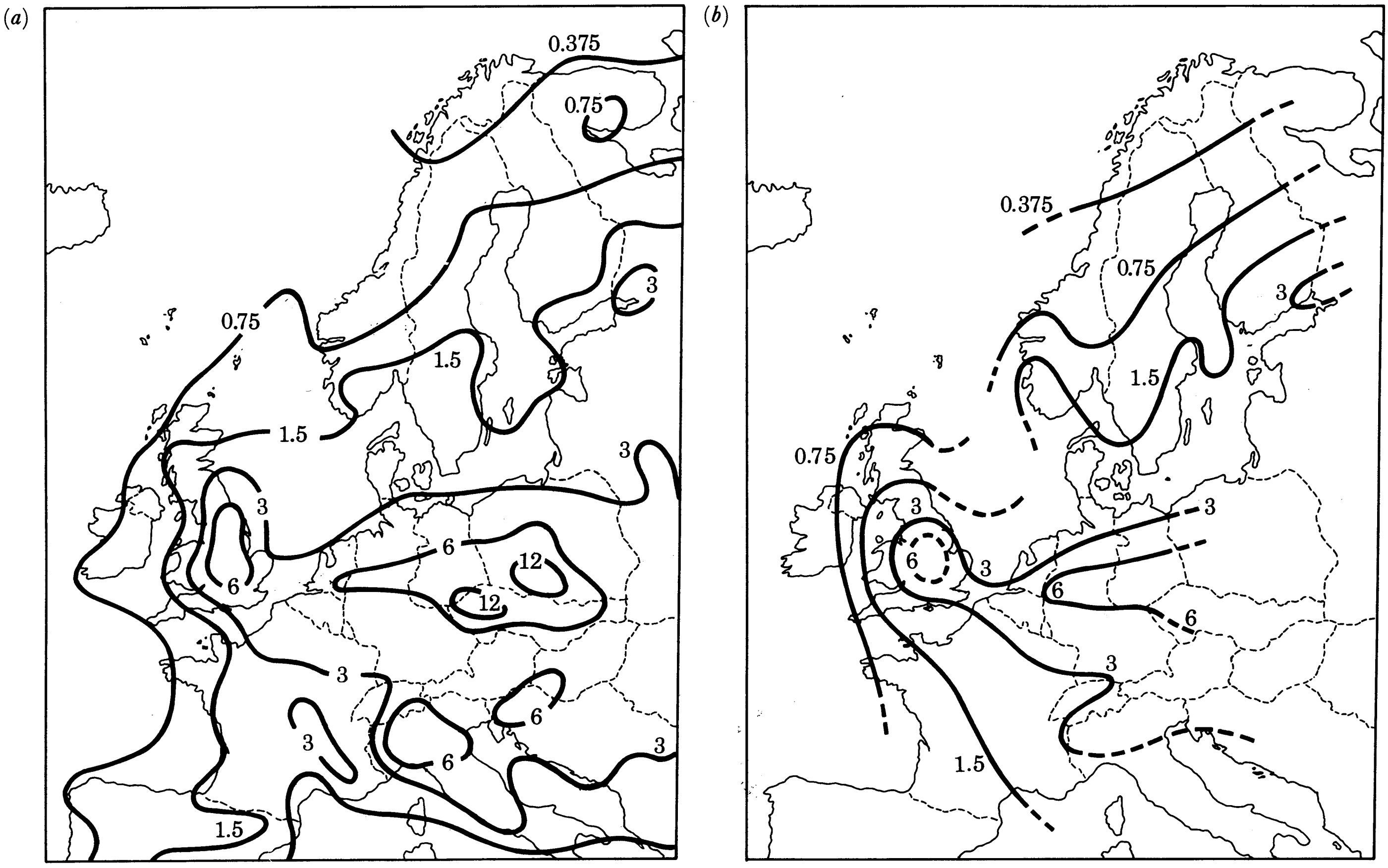
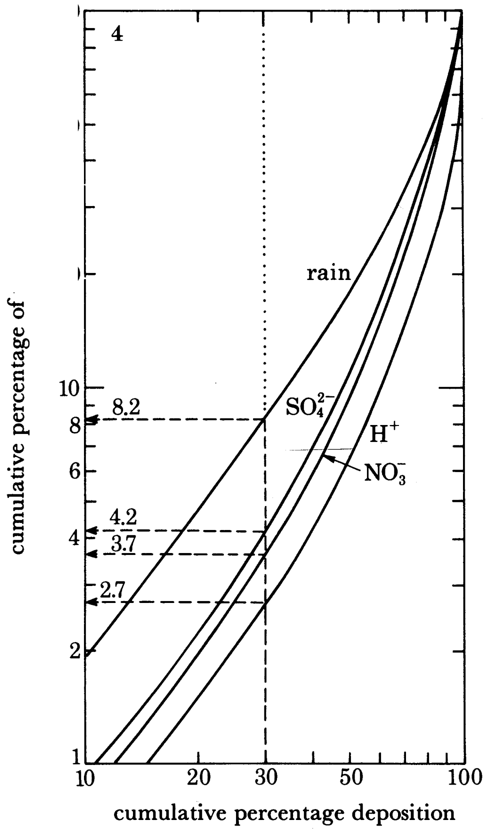


FIGURE 3. (*a*) Total sulphur depositions per unit area (g S $m^{-2}$ $a^{-1}$) from the E.M.E.P. model for a two-year period (1978 and 1979). (*b*) Total sulphur depositions (g S $m^{-2}$ $a^{-1}$) implied by interpolation between measurements made at the E.M.E.P. network of monitoring stations over the same two-year period.

Verification of such results is not simple. The E.M.E.P. programme includes air and precipitation-concentration measurements taken on a daily basis at a large number of sites across Europe which are reasonably remote from significant local sources. Dry depositions are inferred from air concentrations assuming a typical velocity of deposition of 0.8 cm $s^{-1}$ for sulphur dioxide. Wet depositions are directly inferred but questions of areal representativeness and bias are not always easily put aside. Figures 3*a* and *b* show the model's deposition field for most of Europe in grams per square metre per year and the inferred 'observed' deposition field obtained by smoothly interpolating between values at stations. In some areas the reliability of this process is quite low, especially over the sea, but even over areas like the U.K. where data from only two remote stations have been used. Bearing this strongly in mind, the two fields are broadly in good agreement. The correlation between calculated and 'observed' annual depositions, taking all the E.M.E.P. stations together, is about 0.8 from the E.M.E.P. Lagrangian model.

The data given in figures 2 and 3 refer to a two year period. The question must be posed: are these years representative and how much would the contributions to the depositions change if another period were selected? Some idea is obtained by comparing the contributions for three years 1974, 1975 and 1976 derived from the E.M.E.P. model. Taking the standard deviation of the contributions from one country to another, normalized by the mean, yields an estimated population value of 0.23 (i.e. an expected annual variation of 23 %). The corresponding value for the net deposition in a country is only 0.07 – i.e. a 7 % annual variation – although this may be an underestimate for the more peripheral countries in Europe and an overestimate for the more centralized countries.



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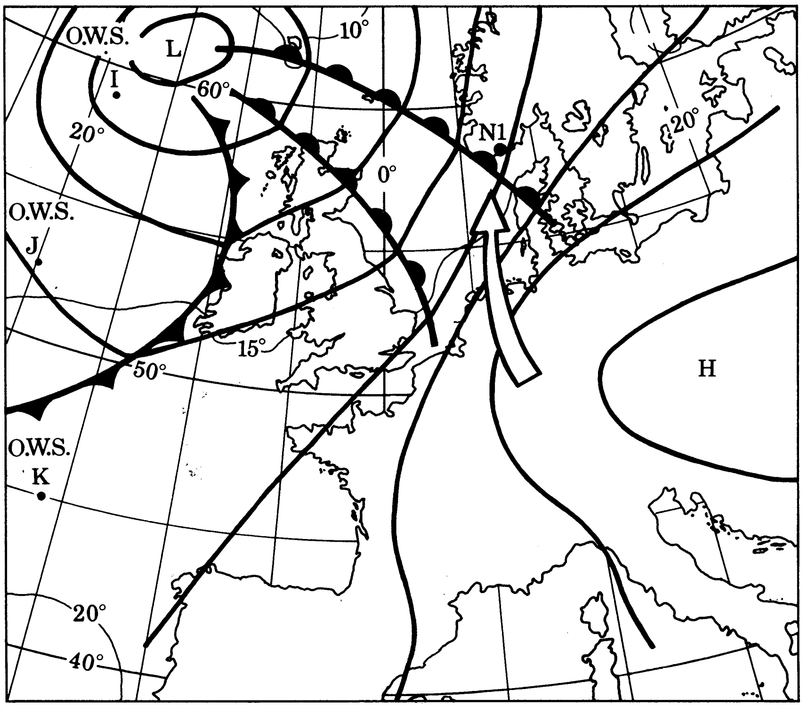

Figure 4. Daily measurements of the amount and composition of precipitation made at Goonhilly (50° 03′ N, 5° 10′ W) by Warren Spring Laboratory (Irwin & Keddie 1983). While rainfall is itself episodic, sulphate, nitrate and hydrogen ions are progressively more so.

Figure 5. A schematic diagram that shows the typical meteorological situation (a stagnant large high pressure region over central Europe and a mobile depression to the north of the U.K. with active fronts approaching Norway) which give rise to almost half the episodes in wet deposition concentration at Birkenes (N1) in southern Norway.

### (*d*) *Short term depositions over Europe*

As already noted, the development of models capable of dealing with single-event depositions, especially of episodic proportions, is a formidable problem. Two kinds of episodes, sometimes related, can be identified: episodes in terms of deposition and episodes in terms of concentration.

Considering the former first, episode-days are defined as those days with the highest wet depositions which, when summed, make up 30% of the annual wet deposition total. The number of episode-days, taken as a percentage of the total number of wet days, defines the 'episodicity'. A station is described as highly episodic if the episodicity is less than 5%, and unepisodic if greater than 10%. Figure 4 shows the episodic character of Goonhilly (50° 03′ N, 5° 10′ W) in 1980 (Irwin & Keddie 1983). In terms of rainfall, the episodicity is 8.2%: a fairly typical value for western Europe. For sulphate, nitrate and hydrogen ions, the station is highly episodic, especially for the latter. This implies that much of the deposition of these ions occurs on relatively few days per year (30% on only 4.2 cumulative-percent days for sulphate, 3.7 c.-p. days for nitrate and 2.7 c.-p. days for $H^+$). We will return to this point in the next section.

Episodes in concentration may be equally important in their ecological effect. Again the definition of an episode is largely arbitrary. If it is defined as a day when the concentration exceeds 3 times the long-term mean, the meteorological situations giving rise to episodes can be inspected to see if they have anything in common. It turns out that for many stations, a single synoptic situation is associated with half or more of such episodes. Typical is N1, an E.M.E.P. station in southern Norway, (see figure 5). Half the episodes there are associated with a depression crossing the Norwegian Sea with fronts passing N1, drawing into the associated rain areas heavily polluted air from a large anticyclonic slack-wind area over the industrialized areas of central Europe.

## 3. MONITORING OF DEPOSITIONS IN EUROPE

### (*a*) *European air chemistry network* (*E.A.C.N.*)

The E.A.C.N. was set up in 1955 (Egnér *et al.* 1955; Eriksson 1959, 1960) to determine the chemical composition of air and precipitation at sites in western Europe. The number of stations had reached 120 by the end of the International Geophysical Year (1957–1958) but then declined to about 50 by 1977; some of the remaining stations have also formed part of the W.M.O. B.A.P.Mo.N. network since 1971 (W.M.O. 1978). The precipitation collector consisted of a permanently open plastic funnel through which rain was channelled into a glass bottle, the contents of which were analysed at monthly intervals. The data from this network form the longest available set of continuous measurements of precipitation composition. They have been examined in two ways: one was to treat the data statistically as a homogeneous set from the whole network, and the other was to conduct a detailed experimental investigation into the errors associated with a few of the sites. The first approach has been adopted for sulphate by Granat (1978) and for acidity by Kallend *et al.* (1983). The second approach has been used by the Meteorological Office; the results are reported in §3 (*b*). The E.A.C.N. techniques for the determination of the chemical composition of aerosol particles have been critically examined by Brownscombe *et al.* (1973) and will not be considered further here.

### (*b*) *Measurements in the United Kingdom at Meterological Office sites*

Three sites have been operated by the Meteorological Office as part of the E.A.C.N.: Bracknell (51° 23′ N, 0° 47′ W, 70 m a.m.s.l., 1965–), Eskdalemuir (55° 19′ N, 3° 12′ W, 242 m a.m.s.l., 1958–) and Lerwick (60° 08′ N, 1° 11′ W, 91 m a.m.s.l., 1958–). At each site a permanently open precipitation collector has been operated on a monthly basis for the whole period. Since varying dates from 1973 onwards, each site has also had an automatic collector, open only during periods of precipitation. There has been a standard meterological raingauge at each site for at least the whole period of record.

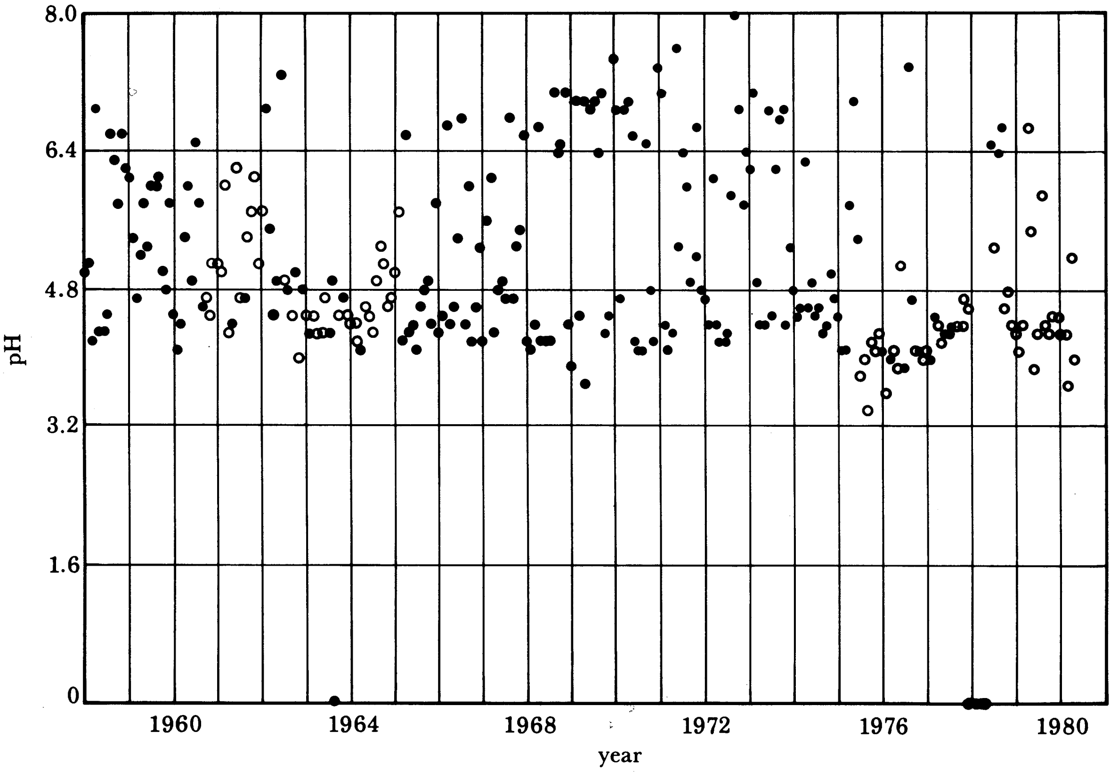

FIGURE 6. The monthly record of pH at Eskdalemuir, 1958–1980. The open circles passed the quality criteria described in the text, the solid circles did not. Zero pH means missing data or insufficient data for analysis.

### (i) *Chemical analysis errors*

In the most recent intercomparison exercise, nine U.K. laboratories were asked to analyse synthetic rainwater samples. Coefficients of variation for $H^+$ analysis ranged from 10–23%, and from 21–24% for $SO_4^{2-}$ (Irwin 1982).

### (ii) *Quality control of the data*

Examination of the records, analyses and procedures for the 3 sites indicated a need for careful quality control of the past data, particularly before 1973. The following criteria were applied:

(i) there should have been no visible organic contamination;

(ii) there should have been at least 10 mm rainfall collected during the month;

(iii) the Na/Cl mass ratio should be less than 1.8 times that of seawater;
and

(iv) the ionic balance should have been satisfactory to the analyst at the Laboratory for the Government Chemist.

The application of these measures to the data had the effects shown in figure 6, where the time series of pH is shown, with accepted and rejected data points distinguished. The largest single cause was sodium contamination from inadvertent use of soda glass wool filters at the base of the collection funnel; laboratory tests indicated that pH was affected as well. Virtually all the samples failing criterion (iv) also failed criterion (iii).

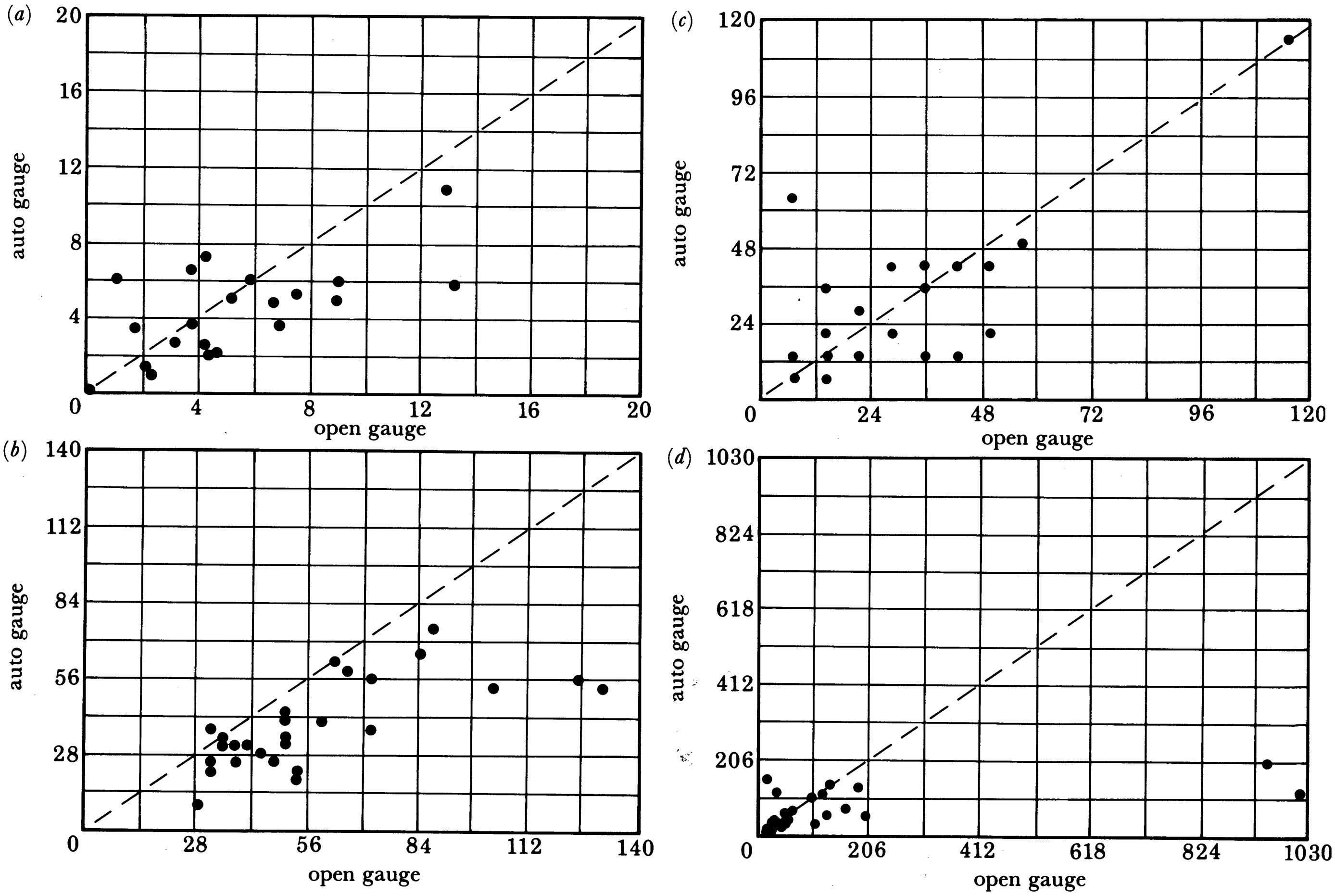

FIGURE 7. Comparison of the composition of the precipitation collected by an automatic gauge open only during precipitation (ordinate) with that collected by a permanently open device (abscissa). Units are micromoles per litre. (*a*) $H^+$; (*b*) $SO_4^{2-}$; (*c*) $NO_3^-$; (*d*) $NH_4^+$.

### (iii) *Operation of pairs of adjacent open collectors*

Some long term testing of reproducibility at Lerwick and Bracknell was conducted. Identical, proximate open collectors were operated for several years, 8 m apart at Bracknell and 300 m apart at Lerwick. Time series analysis of species concentrations, after application of the quality control criteria, showed generally good correlation between the two collectors at a site; this correlation was better at Bracknell than at Lerwick. The variability of a species between the Bracknell gauges was typically 20%. Statistical analysis, however, showed that for some serially well correlated species, the data were not from the same populations. The data for conductivity, $SO_4^{2-}$, $Cl^-$, $Na^+$, $K^+$ and $Mg^{2+}$ were not from the same population at Bracknell, but pH, $NO_3^-$, $NH_4^+$, $Ca^{2+}$ and $H^+/HCO_3^-$ were. At Lerwick the same conclusions applied except for conductivity, $Cl^-$ and $K^+$. There is therefore some evidence of systematic differences between adjacent open collectors operated on a monthly basis according to E.A.C.N. protocols. The implications for the rest of the network are not clear, but it should be pointed out that these results are from a long term test of the overall protocol of a routine monitoring operation, and are therefore different from shorter term tests of spatial variability conducted by Slanina *et al.* (1979) and Granat (1977).

### (iv) *Comparison of adjacent open and wet-only collectors*

There are data records of useful length from the wet-only collectors at Lerwick and Eskdalemuir. The funnels are stainless steel and thermostatted so as to melt collected ice or snow; the height of exposure, monthly collection and analytical procedures are otherwise identical to those of the open collectors. At Lerwick a prototype wet-only collector with a plastic funnel was operated 1973–1977, superseded by a permanent one with a stainless steel funnel. The Lerwick data show that the open collector caught more $SO_4^{2-}$, $NO_3^-$, $Cl^-$ and $NH_4^+$ in most months. The rate of dry deposition of these ions on the funnel material may be calculated by differencing the depositions in the two collectors: the results indicate a possible maximum in winter months. This apparent dry deposition varied, as a percentage of the total, for different species and was highly variable from month to month.

The comparison between the adjacent bulk and wet-only collections at Eskdalemuir, made over a 4-year period, is complicated by the differing funnel materials. However, the open collector consistently showed more $SO_4^{2-}$, $NO_3^-$ and $NH_4^+$ as may be seen from figure 7; on occasions when the wet-only gauge collected more, the differences were generally within the limits of analytical error and the variability in adjacent open collectors. The hydrogen ion concentrations were more scattered about the line with a slope of unity on a scatterplot (figure 7*a*), but did show a tendency for more acid values in the open collector. The reverse was true at Lerwick.

It is not possible from these comparisons of adjacent open and wet-only collectors to draw conclusions about dry deposition rates to natural surfaces more representative of those over any significant area of the Earth.

## (*c*) *Trends in E.A.C.N. data*

### (i) *Trends in the U.K.*

Figures 8*a*, *b* and *c* show time series of quality controlled data at the three Meteorological Office sites for sulphate, nitrate and hydrogen ion. Because monthly data attenuate the frequency distribution of acidity at both low and high values, the regression of pairs of ions is inaccurate. It is not possible to interpret the changes in $H^+$ over the period of record in terms of excess $SO_4^{2-}$and $NO_3^-$; the results of an attempt to interpret the data in these terms, by obtaining values $x$ and $y$ for $H_xSO_4$ and $H_yNO_3$ statistically are shown in table 1. The change in ion concentrations from (1958–1967) to (1975–1979) is shown in table 2.

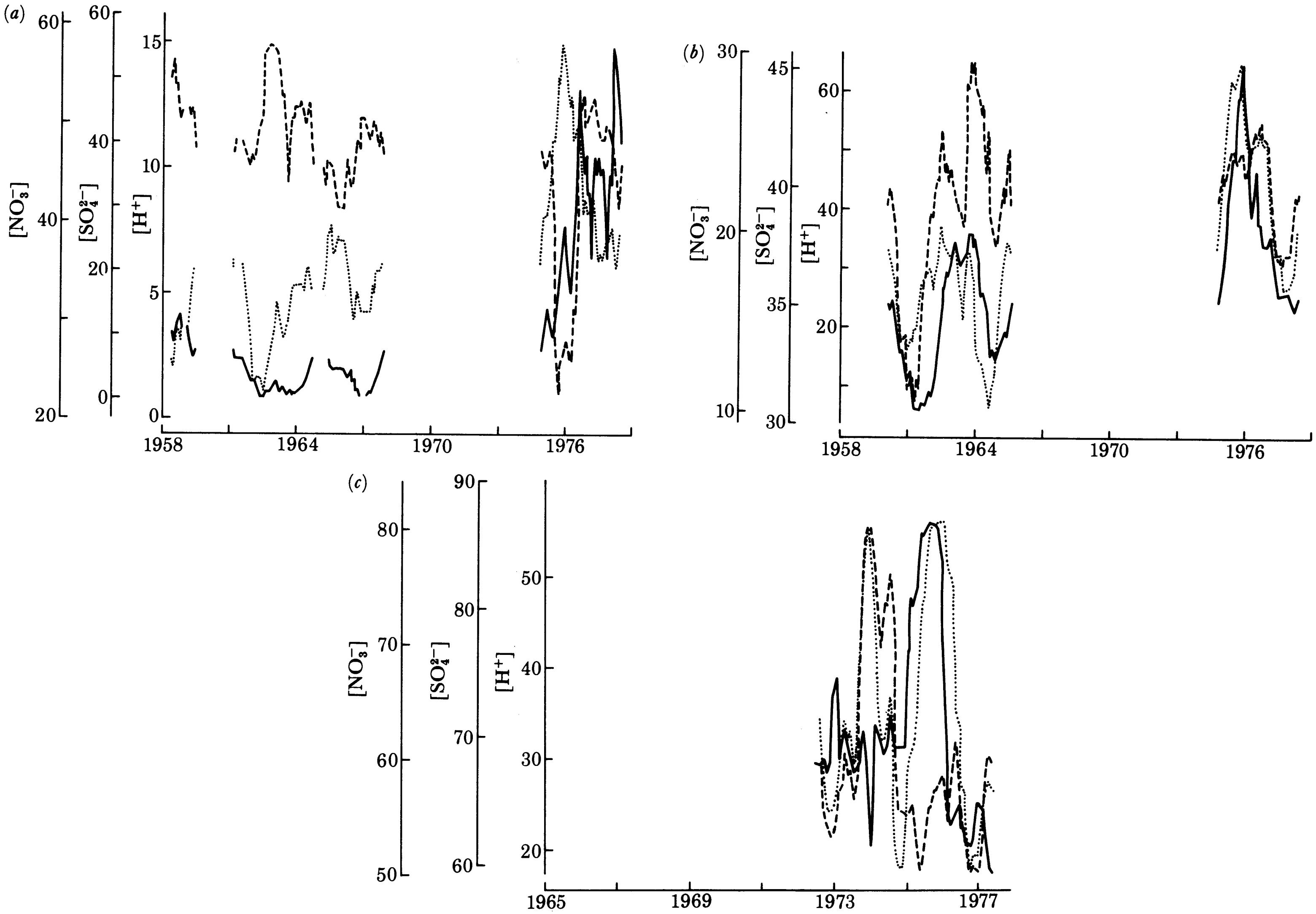

FIGURE 8. Twelve month running means of H$^+$ (solid line), non-marine SO$_4^{2-}$ (dashed line) and NO$_3^-$ (dotted line). Units are micromoles per litre. (*a*) Lerwick; (*b*) Eskdalemuir; (*c*) Bracknell.

### (ii) *Trends in western Europe*

An alternative approach to trends in acidity has been taken by Kallend *et al.* (1983), who performed a statistical evaluation of the E.A.C.N. data as a whole. They used 120 sites with 5 or more years of record during the period 1956–1975. A statistically significant trend ($P < 0.05$) of increasing annual average acidity was found at 29 stations, with a negative trend at a further 5 sites. The analyses showed that the increased annual average values of $[H^+]$ arose from an increase in the number of intermittent high monthly values after about 1964; some months continued to show values as low as those before 1964. This behaviour is reflected in the time series of annual average precipitation acidity at several sites, which show an apparent step increase about 1964. Comparison of data from a cluster of four Swedish sites (within 25 km of each other) showed poor correlations, suggesting that much of the variance was caused by local rather than synoptic scale influences. Similar analysis of the nitrate data showed significant increases in 55 stations, with no station showing a decrease. Non-marine sulphate showed a significant increase at 23 sites, with one exhibiting a decrease.

TABLE 1. STATISTICAL REGRESSION TO $H_xSO_4$ AND $H_yNO_3$

| station | $x$ | $y$ | [excess $SO_4^{2-}$]/(μmol l$^{-1}$) (not associated with $H^+$) | [$NO_3^-$]/(μmol l$^{-1}$) (not associated with $H^+$) |
|---|---|---|---|---|
| Lerwick | −2.9 | 9.5 | 40.3 | 5.9 |
| Eskdalemuir | 4.7 | 17.2 | 28.4 | 1.7 |
| Bracknell | 2.5 | 9.6 | 44.4 | 7.8 |

TABLE 2. CHANGES IN AVERAGE IONIC CONCENTRATIONS (MICROMOLES PER LITRE) BETWEEN 1958–1967 AND 1975–1979

| station | $\Delta[H^+]$ | $\Delta$[excess $SO_4^{2-}$] | $\Delta[NO_3^-]$ |
|---|---|---|---|
| Lerwick | +16.4 | −6.2 | +3.1 |
| Eskdalemuir | +18.0 | +0.3 | +1.5 |

Granat (1978) analysed the E.A.C.N. data for the years 1955–1975 for the behaviour of non-marine sulphate in precipitation. An important conclusion was that the concentrations of $SO_4^{2-}$, and its deposition rate, showed long term fluctuations which varied markedly between different areas. It was also apparent that only for a small fraction of the area was there an increase in sulphate deposition corresponding to the approximately 35% increase in sulphur emissions during the period 1965–1975; over most of the area the deposition remained constant or declined. In these considerations it is worthy of note that changes in trajectory climatology over the period may have affected the depositions to some extent.

## 4. ATMOSPHERIC CHEMISTRY

### (*a*) *Basic considerations*

Two gases are produced during fossil fuel burning which may be transformed in atmospheric conditions to produce strong acids in rain. They are nitric oxide, NO, and sulphur dioxide, $SO_2$, which can be the precursors of nitric and sulphuric acids respectively. Coal burning produces hydrogen chloride, HCl, which can in addition form a third strong acid, hydrochloric, by direct dissociation in the aqueous phase. It may well be that more attention should be paid to the role of HCl in determining the acidity of rainfall but it falls outside the scope of this symposium. For $SO_2$ and NO, however, the possible transformations by chemical reaction must be considered.

$SO_2$ dissolves physically in water; from this state, the anions derived from sulphite, $HSO_3^-$ and $SO_3^{2-}$ may be formed. In the presence of other species, the $SO_3^{2-}$ may undergo oxidation to sulphate $SO_4^{2-}$. The rate at which this occurs depends upon the concentrations of $O_3$, $H_2O_2$, $NH_3$ and $H^+$ among others. Another way in which sulphate may enter precipitation is if some previous physico-chemical processes have produced an aerosol, whose particles contain the anion, and which have then acted as condensation nuclei for water droplet growth or been captured by the cloud or by some other physical process such as Brownian capture or impaction. Such sulphate aerosol may have been formed in two ways, from evaporation of a precursor cloud droplet, or via gas-to-particle conversion by means of homogeneous gas phase photochemistry.

In the case of nitric oxide, conversion to a soluble form (nitric acid vapour, $HNO_3$, or dinitrogen pentoxide, $N_2O_5$) must occur, probably in the gas phase, before incorporation into aqueous droplets can take place.

The influence of chemical kinetics is felt via the sequences of elementary collisional steps in which the primary emitted species, $SO_2$ or NO, are oxidized to the strong acid anion. Considering first $SO_2$, it is believed that the homogeneous gas phase oxidation proceeds via reaction with OH radicals generated photochemically in the presence of ozone and water vapour. If a very simple mechanism is formulated:

$$O_3 + h\nu \rightarrow O(^1D) + O_2, \tag{1}$$

$$O(^1D) + H_2O \rightarrow OH + OH, \tag{2}$$

$$OH + SO_2 + M \rightarrow HSO_3 + M, \tag{3}$$

$$OH + C \rightarrow \text{products}, \tag{4}$$

where C can be any other molecule (CO, $CH_4$, $NO_2$ etc.) that consumes OH, a simple rate equation for the loss of $SO_2$ can be derived by using the steady state assumption for $O(^1D)$ and OH. It is

$$\frac{d[SO_2]}{dt} = -k_3[SO_2]\,[M]\left(\frac{2J_1[O_3]}{k_3[SO_2]\,[M]+k_4[C]}\right).$$

Presently accepted rate coefficient data generally indicate that in conditions where plumes have been diluted, $k_4[C] \gg k_3[SO_2]\,[M]$ and the rate of $SO_2$ loss is proportional to the product of $SO_2$ and $O_3$. Since ozone is not directly consumed by $SO_2$, any change in $SO_2$ concentration will cause a proportional change in its rate of transformation. If however rate coefficient data were revised, so that transformation $k_3[SO_2]\,[M] \approx k_4[C]$, this conclusion would no longer apply, because reaction with $SO_2$ would be a significant sink for OH radicals. The oxidation of NO is a different matter. Here the principal reaction is

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{5}$$

and because this reaction is a major loss mechanism for tropospheric ozone, the rate of transformation of NO is not necessarily proportional to changes in NO concentration.

A further complication is that to some extent NO and $SO_2$ are correlated in the atmosphere by virtue of being produced by fossil fuel combustion, and that this may cause nonproportionalities as reaction (5) consumes oxidant ($O_3$) otherwise destined to participate via reaction (1).

It should be noted that in the acid rain problem we are not generally dealing with the highly nonlinear, long length, catalytic chain reactions that are characteristic of the stratosphere. Further simple points are that the driving force for the photochemistry is sunlight and that chemical reactions are temperature dependent, so that diurnal and seasonal variations in oxidation rates may be expected.

It is not within the scope of this paper to consider the whole range of atmospheric chemical processes that contribute to the composition of precipitation. The approach will be to consider what recent aircraft-based work has done to advance understanding in the context of the U.K. and western Europe.

An important question which has been raised recently is whether or not the depositions are proportional to emissions, over space and time scales of importance. The definition of characteristic space and time scales for effects is a matter for soil scientists, biologists and ecologists, and is a matter of some importance in the proportionality argument: if episodicity is important, and if brief exposures over sub-synoptic scale areas matter, then the problem is far more complicated, and proportionality will not be easy to demonstrate.

### (*b*) *C.E.R.L.–Meteorological Office aircraft flights over the North Sea*

Recent flights by the Meteorological Office's C130 Hercules aircraft, which has been equipped with additional instruments built by the Central Electricity Generating Board Research Laboratories (C.E.R.L.) at Leatherhead, have produced two findings relevant to the proportionality arguments (Cocks *et al.* 1983). On flights over the North Sea on 28 and 29 January 1981 this aircraft was used to measure continuously and in real time $O_3$, $NO_x$ and $SO_2$, together with sulphur hexafluoride which had been injected as an inert tracer into the emission stack of Eggborough Power Station (53° 42′ N, 1° 6′ W). During the flights, the boundary layer was about 400 m deep, and contained stratiform cloud with a liquid water content of 0.2–0.6 $g^{-3}$ and a mean droplet diameter of about 6 μm. The insolation, integrated over the solar spectrum, was about 15% of the clear air maximum expected for the time and place.

Ground based measurements indicated that the Eggborough plume was mixed vertically in the boundary layer within about 20 km of the source. The labelled plume was detected at 105 km from source on 28 January, and 650 km from source, near the Danish coast, on 29 January. These positions corresponded to plume travel times of about 5 h from 0900 GMT and 24 h from 1200 GMT on 28 January, respectively, and were the result of southwesterly winds with mean speeds of 5–10 m $s^{-1}$.

Measurements of $[NO_2]/[NO]$ and $[O_3]$ and the $SF_6$ tracer along the cross-plume traverses at 105 km and 650 km are shown in figures 9*a* and *b*. The tracer identifies the centre of the plume; in that region, the ozone is depleted as a consequence of

$$NO + O_3 \rightarrow NO_2 + O_2.$$

However, the central $[NO_2]/[NO]$ ratio is not accordingly elevated. The measurements show that less than half of the primary NO has been oxidised in much of the plume, and less than one third at the plume centre after 24 h of travel, 650 km from source. Ozone is depleted in the plume by the above reaction, and it is clear that mixing of the plume with ambient air, which could replenish the ozone to about the $20 \times 10^{-9}$ by volume level, is in fact rate limiting. This and the arguments in §4 (*a*) suggest that, for this plume, reductions in NO emission will not cause proportional reductions in the formation of nitrate at these distances. It is important to emphasize that the supply of oxidant is ozone or OH free radicals derived from ozone reacting photochemically with water vapour, and that the ozone and water vapour come from the ambient natural troposphere which has received much of its ozone as a result of exchange of air between the troposphere and the ozone-rich stratosphere.

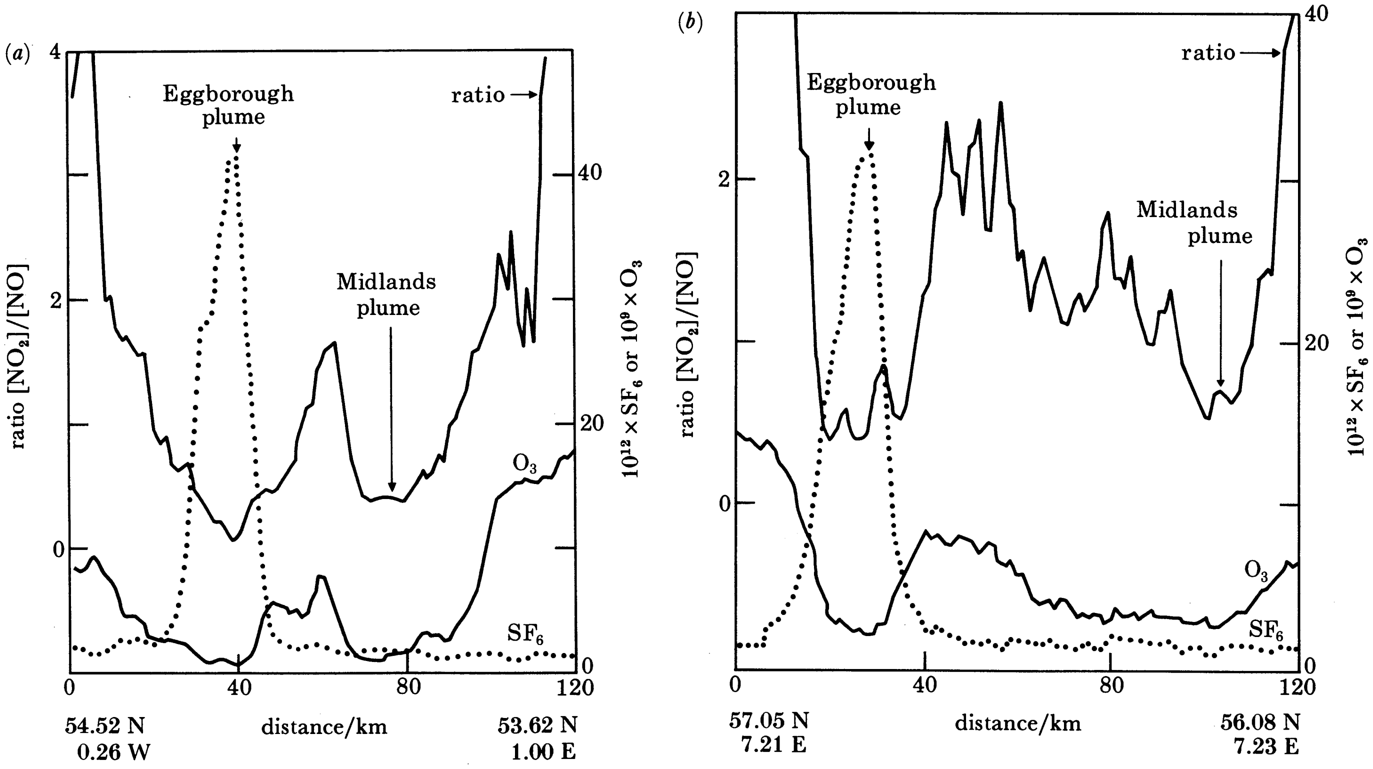

FIGURE 9. Cross-plume profiles at a height of 150 m. Latitude and longitude are in decimal degrees. (*a*) 28 January 1981, 105 km from Eggborough power station; (*b*) 29 January 1981, 650 km from Eggborough power station.

The depletion of ozone in the plume centre by NO also has implications for the oxidation of $SO_2$, the rate determining step of which in the gas phase is believed to be reaction with OH. The oxidizing hydroxyl radicals are produced through photochemistry initiated by ozone, and hence any change in the $[SO_2]/[NO]$ ratio in emissions may lead to non-proportionality in the gas phase oxidation of $SO_2$. If, as seems likely, the oxidizing species in the aqueous phase is either ozone or hydrogen peroxide, the aqueous phase oxidation of $SO_2$ to $SO_4^{2-}$ will also be slowed, because $H_2O_2$ originates in the gas phase via $O_3$-induced photochemistry, and as indicated, $O_3$ is depleted.

Thus, if the conditions in which plumes mix slowly with ambient air are common occurrences, the oxidation rates will be slow because of a shortage of oxidant. This condition should not be expected to apply necessarily to oxidation in the aqueous phase in more vigorous precipitating clouds where the mixing processes are more rapid.

### (*c*) *C.E.R.L.–Meteorological Office flight round Britain*

Measurements during a flight by the Hercules aircraft round mainland Britain at 150 m altitude in anticyclonic easterly flow on 21 July 1982 showed a very low background influx of $SO_2$ coming from over the North Sea. However, 4 plumes were resolved off the Welsh coast (figure 10) and the $SO_2$, $SO_4^{2-}$ and $O_3$ content measured. At the same time, an instrumented Jetstream aircraft was used to measure $SO_2$, $SO_4^{2-}$, $O_3$, NO and $NO_2$ upwind (eastward) of Wales. The integrated upwind source was estimated to be 236 t $SO_2$ $h^{-1}$, distributed as shown in figure 11. The flux at the Jetstream flight track was estimated to be 167 t $SO_2$ $h^{-1}$, with 8 t $SO_4^{2-}$ $h^{-1}$.

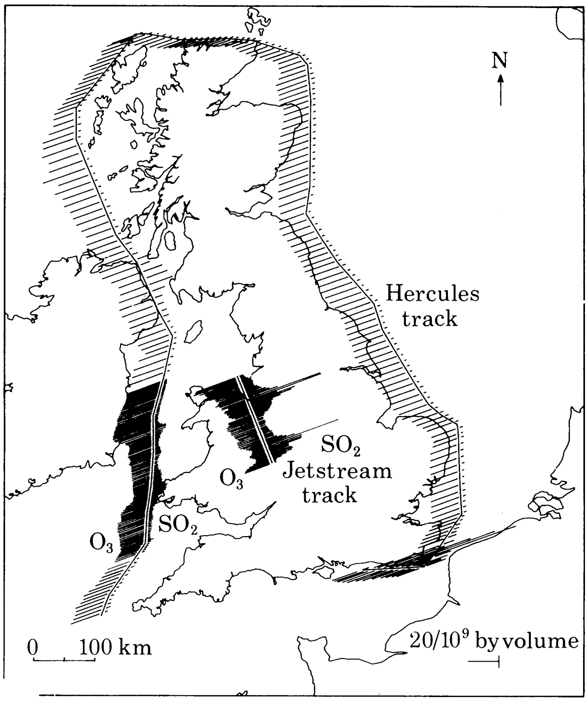

FIGURE 10. Aircraft flights, 21 July 1982. The Hercules circumnavigated mainland U.K. in a counterclockwise direction at an altitude of 150 m, while the Jetstream leg shown from the West Midlands to the Mersey estuary was at 400 m. In this region, the amounts of $SO_2$ and $O_3$ are shown on an identical scale by the lines at an angle to the aircraft tracks. The angle corresponds to the wind direction (roughly 070°) in the region of the main plumes; the $SO_2$ values are the lines on the east side of the tracks, the $O_3$ are those to the west.

At the Hercules flight track the estimated fluxes were 48 t $SO_2$ $h^{-1}$ and 40 t $SO_4^{2-}$ $h^{-1}$. There was a high loss rate (27 % $h^{-1}$) during the $4\frac{2}{3}$ h long passage over Wales, 7 % $h^{-1}$ of which was oxidation. The remaining 20 % $h^{-1}$ loss rate would be equivalent to an unrealistically high dry deposition velocity of 6–7 cm $s^{-1}$. Satellite pictures of the day in question showed a near stationary stratocumulus deck over Wales, not advected with the 9 m $s^{-1}$ mean wind in the boundary layer, which was capped with a strong inversion at an average height of 1200 m. Thus in the clear air boundary layer between the sources and the Jetstream track, the oxidation rate was 1 % $h^{-1}$ and the dry deposition velocity 2 cm $s^{-1}$. In the boundary layer with stratiform, wave-like cloud over Wales, the oxidation rate was 7 % $h^{-1}$ and the equivalent deposition velocity 6–7 cm $s^{-1}$. The stratiform cloud thus has a high oxidation rate associated with it; the high apparent dry deposition velocity may speculatively be associated with the impaction of droplets on the Welsh topography and is consistent with the terminal velocity of drizzle sized drops. Rainfall was reported for 21 July of 1.1, 0.4 and 0.2 mm at only 3 sites in central and south Wales, the remainder (about 500) giving zero returns. However few of these raingauges are near the hill tops.

It thus seems clear that on this occasion, a near stationary layer of stratiform cloud over Wales, with wave-like characteristics, gave an oxidation rate of $SO_2$ to $SO_4^{2-}$ of 7% $h^{-1}$, and was associated with an additional loss rate of $SO_2$ of 20% $h^{-1}$. A more complete interpretation of these results will be published by Bamber *et al.* (1984).

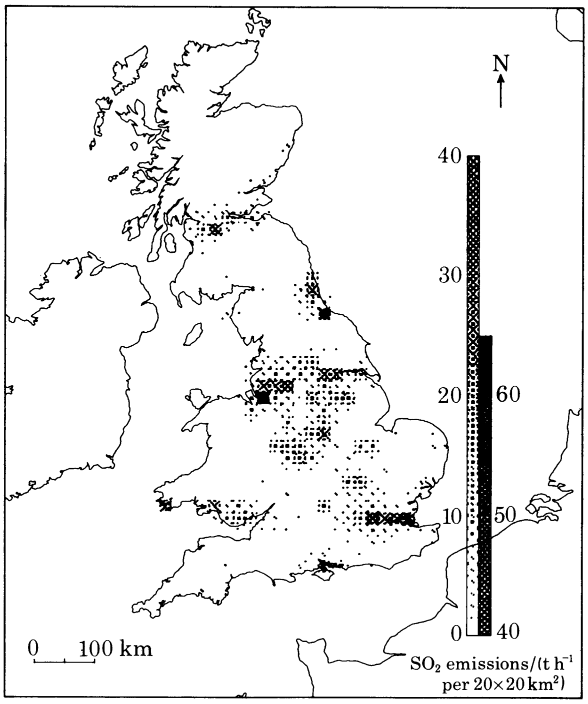

FIGURE 11. Mainland U.K. $SO_2$ emissions for 21 July 1982. The power station data are based on actual loads for the day, while other sources are an interpolation of monthly data. Units are tonnes per hour of $SO_2$ per $20 \times 20$ $km^2$.

These two aircraft investigations point out the great variety of fates which may befall plumes of $SO_2$ and NO. On one hand, in the winter flight there was little plume spread, and little oxidation because of low insolation and a diffusion-limited supply of oxidant. On the other hand, in the summer flight, there was a high oxidation rate associated with a layer of stratiform cloud.

## 5. CONCLUSIONS

There is no doubt that even using the over simplified meteorological models presently available to us it is possible to account for the main features of the annually averaged patterns of deposited anthropogenic sulphur over large areas in Europe as given by the daily sampling of the E.M.E.P. network. The simple techniques whereby the deposition has been monitored on the European scale over the past two decades by the E.A.C.N. have severe limitations mainly because of local short scale variability and the inadequacies of monthly sampling. It would appear that for most of Europe the total deposition is not reflecting the increase in emission of sulphur compounds thus, especially if such a conclusion also applies to other industrial regions, one would expect the global background to be increasing. To some degree this dilutes the regional problem.

Potentially harmful depositions may be prevented in the future by a variety of strategies. The most obvious is by emission control which uses desulphurisation methods: a costly procedure. However, such a strategy could only be justified on the assumption that the deposition in the area at risk was at least directly proportional to the emission. We have presented enough evidence in this paper to suggest that the conversion of $SO_2$ and NO to $SO_4^{2-}$ and $NO_3^-$ is not necessarily a proportional process. This could imply more research on the detailed atmospheric chemical processes is required before such a strategy is scientifically justified.

An alternative strategy might be to reduce the emission of other components, such as hydrocarbons, in the pollution mixture, which may reduce the oxidation processes in the air, and thereby reduce regional wet deposition rates more cheaply than desulphurisation. But the rationale behind such a strategy must be regarded as very speculative at the present time in view of inadequate knowledge of the atmospheric chemistry involved.

Another possibility, with appeal to the meteorologist, is based on our earlier discussion of the importance of episodes. If trajectories of plumes can be forecast with sufficient reliability to predict when deposition from a major emitter will travel to a particularly sensitive receptor area (and especially if forecasts of the probability of rain can be given that could lead to expectations of episodic depositions) then it could be argued that a very cost-effective way of reducing the depositions would be for major emitters to change over to low sulphur fuel when such 'alerts' were forecast. An early study in 1974 of the feasibility of doing this for sources in the U.K. Midlands and a receptor area in Southern Norway suggested that only about a 45% success rate could be achieved. However forecasting models have improved since then and it is our intention to repeat the study shortly using the improved 'fine-mesh' forecasting model currently being established on the Meteorological Office computer.

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## *Discussion*

J. Jacobson (*Boyce Thompson Institute, Cornell University, New York, U.S.A.*). The question of quantitative relations between deposition and emission of sulphur compounds is one that is being debated now in the U.S.A. Other components of the atmosphere may determine the rate of conversion of $SO_2$. However, the practical question for policy decisions may be what happens on a time- and space-averaged basis. For large regions over long time periods there probably is a proportional relation between deposition and emissions as indicated in the recent report from the U.S. National Academy of Sciences.

P. Goldsmith. What Dr Jacobson says about time and space averages must be true, since what goes up into the atmosphere by way of anthropogenic pollution must come down somewhere. Thus taken overall there must be a proportionality relation between deposition and emission.

However it must be remembered that the bulk of deposition occurs at places close to the source regions probably as a consequence of direct deposition to the surrounding surfaces. This is certainly so for $SO_2$ sources as is clearly seen in figure 2 of our paper. Thus in any averaging process the near field deposition will probably predominate. It does not follow, however, that deposition at specific target areas a long distance from the main sources will also experience average deposition proportional to the emissions. The deposition in these regions, unlike that in the near field area, is largely by precipitation and dry deposition of particulate matter. Therefore one is concerned with the chemical transformation of $SO_2$ and NO to sulphate and nitrate both within the gaseous and aqueous states. These processes on a day to day basis are not necessarily linear as demonstrated in the paper. Whether they are linear if averaged over a long period is a matter for debate but I would argue that it would very much depend upon the meteorological circumstances (radiation, temperature, humidity, wind variability, trajectory tracks, cloud cover, precipitation etc.), as well as the ozone and associated minor constituent concentrations over the averaging period. Meteorological variability could mean that an averaging period long enough to ensure proportionality is too long for the argument to be used in arriving at policy decisions involving long range transport and deposition of pollutants.

R. A. Barnes (*Esso Research Centre, Abingdon, Oxfordshire*). I was very pleased that Mr Goldsmith raised the issue of nonlinearity; essentially the possibility that a reduction in precursor emissions may not be reflected in a *pro-rata* reduction in deposition in the ecologically sensitive receptor areas, which I am sure we will be hearing about later, because of the vagaries of atmospheric chemistry and meteorology.

I should like to ask Mr Goldsmith if he feels that on the regional or sub-regional scale (not the north-American scale to which Dr Jacobson has just referred) the current demands to control $SO_x$ and $NO_x$ emissions represent a crude and hasty approach to reducing ecological damage in the sensitive areas which may not be effective at the levels proposed? Would he consider that it would be wiser to provide science – especially the disciplines of atmospheric chemistry and meteorology – with the time and resources to identify a more subtle and elegant solution to the present environmental problems?

P. Goldsmith. In my answer to Dr Jacobson, I have already pointed out that there is a considerable difference between near field deposition and that at significant distances from the main source regions. The former is the traditional pollution problem and experience has shown that it can be alleviated by actions aimed at reducing the concentration of pollutants close to the ground. The restriction of emissions is the most effective way of achieving this, but increasing the height of emissions can also make a contribution to lessening the local problem.

However, when it comes to deposition at some sensitive site a considerable distance from the emitting regions then it is clear from my paper that the proportionality argument does not necessarily hold.

Dr Barnes asks a number of leading questions. I can only say that in my opinion we have a great deal to learn of the chemical transformation, meteorological and scavenging processes involved in transport and deposition of potentially acidic pollutants before any control strategy can be accepted with the proper degree of confidence.

I. Th. Rosenqvist (*Oslo University, Box* 1097, *Blindern, Oslo*). In your paper you point to the fact that most of the acid deposition in precipitation takes place in episodes and not in amounts proportional to precipitation. I shall take this opportunity to mention another fact, i.e. that acid deposition in the acidified rivers does not depend on the episodic nature of the acid rain.

P. Goldsmith. Professor Rosenqvist (poster session) points out that there is little relation between pulses of acidity in lakes and rivers and pulses of acidity in the precipitation. This is not unexpected since the hydrological processes act as an integrating mechanism for the meteorological episodes, and produce their own episodes reflecting those hydrological processes of which snow melt is but one.

Dr Holdgate in his summary suggests that Rosenqvist's evidence is not consistent with the possibility of using a control strategy based on meteorological forecasting of high deposition periods for a specific target area. Such a conclusion is inconsistent. The purpose of a control strategy is to reduce the total deposition over the area in question. The fact that such deposition is subsequently subject to hydrological adjustment does not affect the basic concept.

N. A. Sorensen (*Norway Institute of Technology, Trondheim, Norway*). I agree with Mr Goldsmith in that what we put up comes down again; the question is when does it come down?

The deposition maps that were presented by Mr Goldsmith resembled those of the O.E.C.D. project LRTAP. These maps indicate that the sulphur deposition to Scandinavia should increase as the emissions of central and western Europe rise. These indications are in agreement with statements of, among others, Professor Frank Odén that the sulphate concentrations of the main Swedish rivers have increased about 2.5 times between 1910 and 1970.

As will be obvious from my poster which presents all the original Swedish sulphate determinations for Klaräbrin, this is due only to uncritical use of data. Treated correctly the data give no significant increase or decrease in sulphate concentrations between 1902 and 1980. The deposition model of LRTAP must be very from the truth.

P. Goldsmith. I cannot agree that the results of the O.E.C.D. modelling project can be used to tell us much about past trends in deposition between 1910 and 1970. The model was applied to a specific two year period and it cannot be assumed that this period was representative of the appropriate meteorology for the whole of the sixty year period.

I find Dr Sorensen's analyses of the past data on sulphate concentration in Swedish rivers very interesting and feel they rather parallel our experience described in our paper about the dangers of uncritical evaluation of past precipitation chemistry data. It is important to realize that analyses of past measurements of sulphate concentration in both precipitation and European surface waters must be treated with considerable caution.

B. A. **Thrush**, F.R.S. (*University of Cambridge, Department of Physical Chemistry, Cambridge*). The very low concentration of ozone in a sulphur dioxide plume shown in one of Mr Goldsmith's diagrams is of great importance, because it shows the rate of oxidation in a plume can be limited by the supply of oxidant. Not only does ozone oxidize nitrogen oxides, it is also the dominant precursor of the hydroxyl radical. These are generated as a result of the photolysis of ozone at wavelengths below 315 nm which yields an excited oxygen atom that reacts with a water molecule to give two hydroxyl radicals. The rate-limiting initial step in the gas-phase oxidation of sulphur dioxide is addition of a hydroxyl radical, and a similar process involving nitrogen dioxide is the main source of nitric acid.

P. F. **Chester** (*Central Electricity Research Laboratories, Kelvin Avenue, Leatherhead, Surrey, U.K.*). In relation to deposition at high altitudes, in southernmost Norway the concentration of excess sulphate in lake water decreases systematically by a factor of 4 for an increase in altitude of 1000 metres. Chloride decreases by a factor of 8. This does not seem explicable in terms of differences in annual rainfall with altitude, as recorded at E.A.C.N., O.E.C.D. and E.M.E.P. stations in the region.

P. **Goldsmith**. I do not think it reasonable to expect a simple relationship between altitude and precipitation amount or chemical deposition. For instance in many meteorological situations one expects an enhancement of the amount of frontal precipitation to be orographically induced over a coastal range of hills when the low level wind is blowing moist air from over the sea across the hills. Further inland, terrain at a similar altitude would not receive the same rainfall enhancement simply because the excess condensed water produced by the enforced lift would have already been washed out in the coastal regions. Shower precipitation is often influenced by quite different mechanisms in hilly regions. Such considerations as these are also applicable when considering the chemical concentration of precipitation expected in hilly regions under differing meteorological conditions.

I believe that the question of deposition as a function of altitude requires a full consideration of the synoptic meteorology and the nature of the terrain for its solution.