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Emission to the Atmosphere of Fossil-Fuel Pollutants

and their Effects.

by

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1. Introduction

Burning fossil fuels for energy liberates several important pollutants into the atmosphere, principally carbon dioxide CO_2, sulphur dioxide SO_2, nitrogen oxides NO and NO_2, and ammonia NH_3. This brief paper states, with a minimum of supporting evidence, what the approximate magnitudes of the emissions are , how the pollutants are then dispersed through the atmosphere, what the resulting ground-level concentrations are, how rapidly they are absorbed or deposited at the surface, and finally the current thinking on how these pollutants are affecting our environment or may affect it in the future.

2. Emissions

(i) Carbon dioxide

World emissions are not accurately known but are believed to be about 1.8×10^{10} tonnes CO_2 yr^{-1}. Roughly 60% of this comes from burning fossil fuels, 30% from burning forests, principally in the tropics, and the remaining 10% from other sources.

The United Kingdom contribution to this total is approximately 7.3×10^8 tonnes CO_2 yr^{-1}.

(ii) Sulphur dioxide

World emission figures are very uncertain due to the uncertain magnitude of <u>natural</u> emissions which are estimated to lie between 3.5×10^7 and 10×10^7 tonnes S yr^{-1}. Note these figures have been expressed in terms of S, not SO_2, since natural emissions are often in the form of H_2S which is rapidly oxidised to SO_2 in the atmosphere.

World emissions due to <u>man's activities</u> are estimated at 6.5×10^7 tonnes S yr^{-1}.

In highly industrialised areas like NW Europe the anthropogenic emissions dominate over the natural emissions by at least 4 : 1.

In the United Kingdom anthropogenic emissions are now about 5×10^6 tonnes SO_2 yr^{-1} (or 2.5×10^6 tonnes S yr^{-1}) having shown a decline since the decade ending in 1973 when the emissions were about

5.8×10^6 tonnes SO_2 yr^{-1}.

Power Station emissions have shown the following trend :

Year	Total Power Station Emissions	Coal-fired Power Station Emissions
1960	2×10^6 t yr^{-1}	
1965	2.4×10^6	
1970	2.76×10^6	2.13×10^6
1976	2.77×10^6	2.10×10^6

Table 1   United Kingdom Power Station Emissions of SO_2 .

There has also been a trend in the height at which U.K. emissions have been released. From 1969 to 1974 emissions from high-level sources (above about 60m) have increased from 47% to 58% of all emissions whereas medium-level sources have decreased from 35% to 29%. This has an important bearing on the amount of SO_2 deposited within the U.K. and the amount being advected away to be deposited elsewhere.

Figures 1 and 2 show the geographical distribution of SO_2 emissions within the U.K. (for 1970) and within Europe (estimated, 1972).

(iii) Nitrogen Oxides

U.K. emissions have been fairly steady over the period 1970 - 1976 at about 1.75×10^6 tonnes NO_2 yr^{-1}, of which power stations contribute roughly 0.78×10^6 tonnes NO_2 yr^{-1} (although mainly in the form NO). Transport and industry each emit a further 0.48×10^6 tonnes.

(iv) Ammonia

The greatest source of ammonia is from animal (and human) urea. Emissions are therefore rather uncertain as can be seen in Table 2.

Source	World Emissions ($\times 10^6$ tonnes N yr^{-1})	U.K. Emissions ($\times 10^4$ tonnes N yr^{-1})
Wild animals	2 - 6	< 0.8
Domestic animals & humans	20 - 35	≈ 6.6
Coal combustion	4 - 12	< 1.6
Total	26 - 53	< 9

Table 2.   Emissions of NH_3. Note the different units in the two columns.

3. Atmospheric Transport

Once the various pollutants are in the atmosphere they undergo:

(i) advection over hundreds or thousands of kilometres by the wind which varies in both space and time in response to changing synoptic pressure patterns and atmospheric stability.

(ii) diffusion by turbulent eddies on a very wide range of scales.

(iii) "dry" deposition by absorption or impaction on the underlying surface.

(iv) in some cases chemical change (often oxidation), the rate of which depends on various factors such as sunlight, relative humidity and the presence of other catalytic pollutants.

(v) "wet" deposition: a washing-out of pollution during precipitation.

A major international study of the long-range transport of sulphur pollutants on a scale of 1000km was initiated in 1971 by the Organisation for Economic Cooperation and Development (OECD). Many ground-level stations made measurements over several years of 24 hour-averaged air concentrations, and concentrations in precipitation. Occasional aircraft flights sampled concentrations within and above the atmospheric boundary layer. These data were also compared with the predictions of mathematical-physical models developed to simulate the source-advection-dispersion-chemical change-sink processes taking place in the atmosphere. The results have been reported (OECD, 1977).

This work is now being carried further by a new ECE-WMO project initiated in 1978.

The OECD Project confirmed that sulphur is typically transported over large distances (at least 1000km) and surface depositions at these distances can be significant. Other conclusions were:

(i) Typically some 15% of the SO_2 is dry deposited within the first 50km provided the sources are not at high level.

(ii) Vertical dispersion is often restricted to the atmospheric boundary layer which is of variable depth, but rarely exceeds 2km.

(iii) When considering 24-hour average concentrations, lateral spread of plumes is dominated by so-called "Synoptic-swinging", that is changes in wind direction (and hence trajectories) resulting from changes in the mobile large-scale synoptic pressure field.

(iv) dry deposition velocity of SO_2 may depend to some degree on surface conditions but is about 0.8 cm s^{-1} over typical English countryside and over the sea. Sulphur dioxide, therefore, has an atmospheric life-time of between 1 and 2 days. Sulphate aerosol on the otherhand has

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.a. deposition velocity about an order of magnitude smaller, and its loss by this mechanism can often be ignored.

(v) conversion of SO_2 to sulphate is most rapid near the source where the concentrations are high and appears to depend most critically on the relative humidity of the air. Thereafter once the plume is well dispersed the conversion rate falls to about 0.5% per hour to 3% per hour (averaging perhaps about 1% hr^{-1}).

(vi) mountainous areas in Western Europe tend to have as much as four times the annual rainfall of nearby lowland areas. Since wet deposition of sulphate is rapid in rain, this means it tends to dominate over dry deposition in mountainous areas like Norway.

(vii) wet deposition also tends to be episodic in nature; that is, as much as 30% of the annual wet deposition of sulphate occurs in typically only 5% of all the wet days (or roughly 10 days in the year in Norway). Thus rather crude trajectory modelling is therefore rather suspect for wet deposition budgeting in which one attempts to apportion deposition to emissions in other countries. This is in contrast to dry deposition budgeting which is more uniform in time and permits some cancellation of errors in the trajectory methods.

(viii) in spite of all the uncertainties in the current models (for example for selecting the optimum advecting winds); their results averaged over one or more years, expressed in terms of deposition patterns in the "Sulphur contribution" one country gives to another, are in broad agreement with each other and actual measurements (where these are available), at least to the extent that they form a fair basis for making sensible decisions about the magnitude of the transport problem.

(ix) Table 4 gives the estimated deposition rates for southern Norway using one such model, that of Smith and Johnson (1978). The rates are given for 1972, 1973 and 1974. Year to year variations are evident.

(x) Table 5 gives percentage contributions to the total sulphur deposition in Norway coming from other countries according to two different models. The Smith and Johnson model applies to southern Norway whilst the OECD model applies to the average depositions over the whole of Norway. The OECD model estimated wet deposition by indirect methods which gave rise to a rather large 40% deposition of undecided origin in the Table.

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4. Surface Concentrations and Deposition Rates

Carbon Dioxide

Carbon dioxide is a naturally occuring constituent of the atmosphere amounting to about 0.03% by volume. Before about 1860 rural concentrations were probably very close to this natural level. Since then, and particularly in the last few decades, the levels have been rising rather quickly.

CO$_2$ Conc.

1860	293 ppm
1958	315 ppm
1977	334 ppm (or about 0.66g m^{-3})

The rate of rise now is about $\frac{1}{3}$% per annum and if the present acceleration of emissions of about 4% per year is maintained concentrations could double by 2040A.D. This would lead to emissions unrealistically increasing ten-fold. However any trend in emissions inevitably leads to an increase in CO$_2$ concentration and if a reasonable fraction of the world's fossil fuel deposits are ultimately burnt, at some stage in the future it is hard not to visualise a doubling of the residual atmospheric concentration.

Not all the emitted CO$_2$ remains in the atmosphere. About $\frac{1}{3}$ is absorbed in the oceans, which is an enormous reservoir of CO$_2$, about $\frac{1}{3}$ in the biomass (including forests), leaving about $\frac{1}{3}$ in the atmosphere.

Sulphur Dioxide

If e is the emission of SO$_2$ in 10^6 tonnes yr^{-1} in a country or region

a is the area in thousands of km^2 of the country or region

$\bar{C}$ is the average rural concentration in μg m^{-3} due to these internal sources.

then approximately:

$$\bar{C} = 90 \frac{e}{\sqrt{a}} \quad \mu g\ m^{-3}\ SO_2$$

and the corresponding average dry deposition is

$$\bar{D} = 18 \frac{e}{\sqrt{a}} \quad g\ m^{-2}\ yr^{-1}\ S$$

due to these internal emissions.

These simple approximate formulae agree well with measured values for the U.K. giving $\bar{C} \approx 32\,\mu g\ m^{-3}$ and $\bar{D} \approx 6.5\ g\ S\ m^{-2}\ yr^{-1}$.

Typical measured values of rural $\bar{C}$ are about 30μg m^{-3} and in urban areas $\bar{C} \approx 100 - 200\,\mu g\ m^{-3}$.

A simplified version of the Warren Spring Laboratory U.K. winter mean SO$_2$ map is given in Figure 3.

Some 30% of the U.K. emissions are dry deposited within our national boundaries and this amounts to roughly 6 g S m^{-2} yr^{-1} (i.e. 60 kg S ha^{-1} yr^{-1})

in agreement with the above formula.

The OECD model (see Figure 4) rather underestimates this deposition. Roughly 7 - 10% of the U.K. emissions are wet deposited within the U.K. since it rains according to location about this proportion of the time.

Thus just below 40% of all our SO_2 emissions are deposited within the U.K.. A further 10 - 20% is probably deposited over the surrounding sea areas, leaving some 40 - 50% to be deposited elsewhere.

Measured wet depositions of sulphate over western Europe in 1974 are shown in Figure 5 and display the importance of the two main factors: air concentrations and rainfall.

Nitrogen Oxides

NO_x values are usually highest in urban areas. Typical London values for NO surface concentrations are 4 pphm (average) peaking to 70 pphm, and for NO_2 3.5 pphm peaking to 20 pphm. NO_x can form nitrates and be washed out in rain.

Fertilisers are another important source of atmospheric nitrate. Nitrate in rain is now commonly about half that of sulphate on an equivalent basis.

The nitrate component has doubled in the U.K. over the period 1955 - 1970 but for all its potential importance has not been studied as well as the sulphate component.

Ammonia

Estimates of deposition rates over western Europe have been made for 1958. Dry deposition varied from 0.5 to 3 $g\ m^{-2}\ yr^{-1}$ whereas wet deposition varied from 0.1 to 0.4 $g\ m^{-2}\ yr^{-1}$.

5. Effects on the Environment

(i) General comments

Good data on effects is of relatively recent origin and the subject is therefore plagued by the lack of long records stretching over many decades from which the influences of short period variations of weather (and other important contributory factors) could be largely eliminated.

As far as acid rain is concerned, there is in fact a rather poor correlation between acidity (pH) and the concentrations of sulphate and nitrate in the rain. Over western Europe as a whole the supposed upward trend is acidity since 1950 is confused by the abnormally alkaline precipitation experienced in

1955. Indeed there is no significant change in acidity since 1965.

The partially neutralising NH_4 cation is of animal origin and in plumes crossing large areas of sea this effect is small compared with plumes travelling over land

(ii)   Effect of SO_2 and acid rain on crops and vegetation

    a. Abnormally high air concentrations of SO_2 have been shown to cause visible damage or even death to plants.
    b. More modest concentrations of SO_2 in the range 40 - 700μg m^{-3} have yielded rather contradictory reductions in crop yield which suggests that other factors are involved.
    c. There is as yet insufficient data to assess the damage, if any, due to SO_2 concentrations that are on average low but sometimes peak to relatively high concentrations.
    d. It has been postulated that, to some degree, relatively low concentrations of SO_2 in the air could be beneficial to plant growth.
    e. Rain containing acid at realistic concentrations has not been shown to result in any measureable effects on vegetation, including forests.

(iii)   Effect of acid rain on soils

    a. Microbiological activity in unfertilised soil causes a loss of soil lime which for example at Rothamstead amounts to about 650 mE $CaCO_3$ m^{-2} yr^{-1}. This can be compared to the effect of acid rain which is only about 13 mE $CaCO_3$ m^{-2} yr^{-1}.

        On cultivated land (including forests) this loss may or may not be balanced depending on local land management procedures.
    b. Forests are usually on acid soils. Unfortunately forests increase soil acidification partially due to the export of timber reducing soil cation content. Humic acids are generated in coniferous forest canopies and in their leaf mould, swamping effects of mineral acid rain.
    c. There is a rather poor relation between acidity of rain input and the acidity of stream output. This is because soils act as massive ion-exchange beds.
        In very wet weather or on recently cleared forest land, water tends to run off the surface and not sink through any depth of soil. Water becomes very acid from the effects of the humus top layer.

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(iv) <u>Effect of acidity on fish</u>

     a.   Fish live in water with significantly different ionic content to that of incident rain water since most of it has passed through the surrounding soil.

     b.   Parts of S. Norway and S. Sweden have experienced a significant decline in fish population (mainly salmon, perch and brown trout) over the last 80 years or more. This correlates with increasing consumption of fossil fuels, but far from perfectly, e.g. a large drop just prior to 1916 does not apparently relate to a corresponding increase in SO_2 output.

Data on fish stocks are not good prior to about 1960.

Interpretation is difficult without adequate information on changes in

          amount of fishing

          fishing management

          disease (a protozoan parasite is common)

          pollution

          loss or spoiling of spawning sites (e.g. near forests being harvested, near hydroelectric power stations).

     c.   Dramatic fish kills have been experienced many times over the last 100 years and have often been attributed to natural acids from bogs flushed by heavy rain. Acidic pulses during the early stages of the spring snow melt may cause similar effects, although it has not been conclusively demonstrated that the acid is of anthropogenic origin (i.e. SO_4 and NO_2.)

     d.   The total salmon catch in Norway as a whole has actually increased dramatically over the last few decades.

     e.   Considerable quantities of weak acids (including humic acids derived from vegetation decay) are known to exist in S. Norwegian rivers. What effect this has on the fish is not known.

(v)   <u>Climatic effects of increasing CO_2</u>

     To paraphrase Mason (1978) :

"The concentration of carbon dioxide in the atmosphere has increased by about 15% during this century and is currently rising at about $\frac{1}{3}$% per annum due largely to the burning of fossil fuels. Since it strongly absorbs the long wave radiation emitted by the Earth's surface, higher concentrations of CO_2 should produce higher temperatures in the troposphere by the so-called "greenhouse effect" but, because the CO_2 in the stratosphere emits more infrared

radiation to space than it absorbs there should be a corresponding cooling of the stratosphere. The overall effect could be to raise surface air temperatures by 2K with considerable regional and local variations and rises of perhaps 5K in polar regions (with an uncertainty factor of two either way) resulting in some significant retreat poleward of the ice and snow cover. Average relative humidities might rise some 2%. An increase in cloud cover is likely to result and this is an important feed-back mechanism in reducing the temperature rises, which is not/included in the estimates. An increase in rainfall up to some 7% has been postulated although this is likely to be particularly variable".

Global sea-level might rise as the polar region warmed up sufficient to flood some coastal areas, although this is highly conjectural at this stage in our modelling.

Since the energy reflected or emitted to space by clouds amounts to nearly one half of the incoming solar radiation, a change of 1% in the total cloud cover could mask the effect of a 25% increase in carbon dioxide .

Obviously even more realistic models need to be developed . At the present time it is hard to become alarmed at the above prophecies since world temperatures show no obvious signs of increasing . If anything a small drop in temperature may have occured over the last decade .

6. Acknowledgements

I wish to express my gratitude for the considerable amount of useful information provided by the following:

On soils and fish: Dr. G.Howells, CERL, Leatherhead.

On plants   : Dr. L.Fowden & his colleagues at the Rothamsted Experimental Station.

On emissions & } : Dr. M.Williams of Warren Spring Laboratory, Stevenage.
concentrations }

I regret if through ignorance I have misrepresented any of their information in my text. Clearly in such a brief report I could not attempt to give adequate justification for most of the statements made or proper reference to the origins of much of the data. To all concerned I apologise for these omissions.

7. References

Mason, B.J.,1978,Proc. R. Soc. Lond. A. 363 297 - 333,. Recent advances in the numerical prediction of weather and climate.

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

Smith, F.B. & 1975,Sulphur transport in western Europe during 1972 - 1974 from Johnson, D.A.   trajectory analysis and experimental measurements. Internal Meteorological Office Paper.
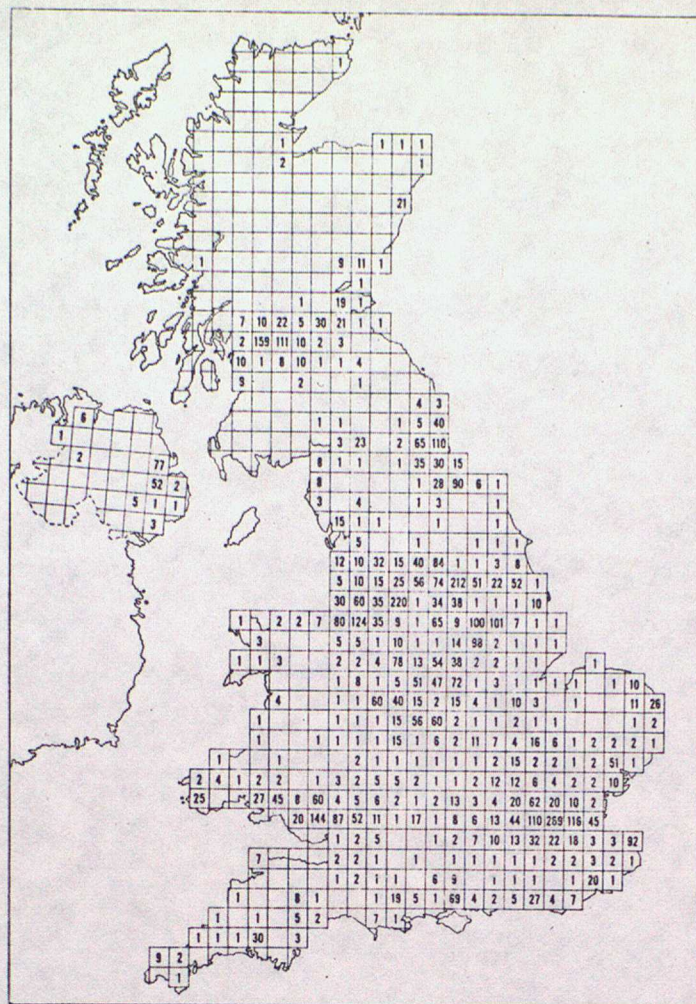
FIGURE 1. United Kingdom sulphur dioxide emissions for 1970 in thousands of tonnes per year. Each square represents an Ordnance Survey 20 × 20 km region.
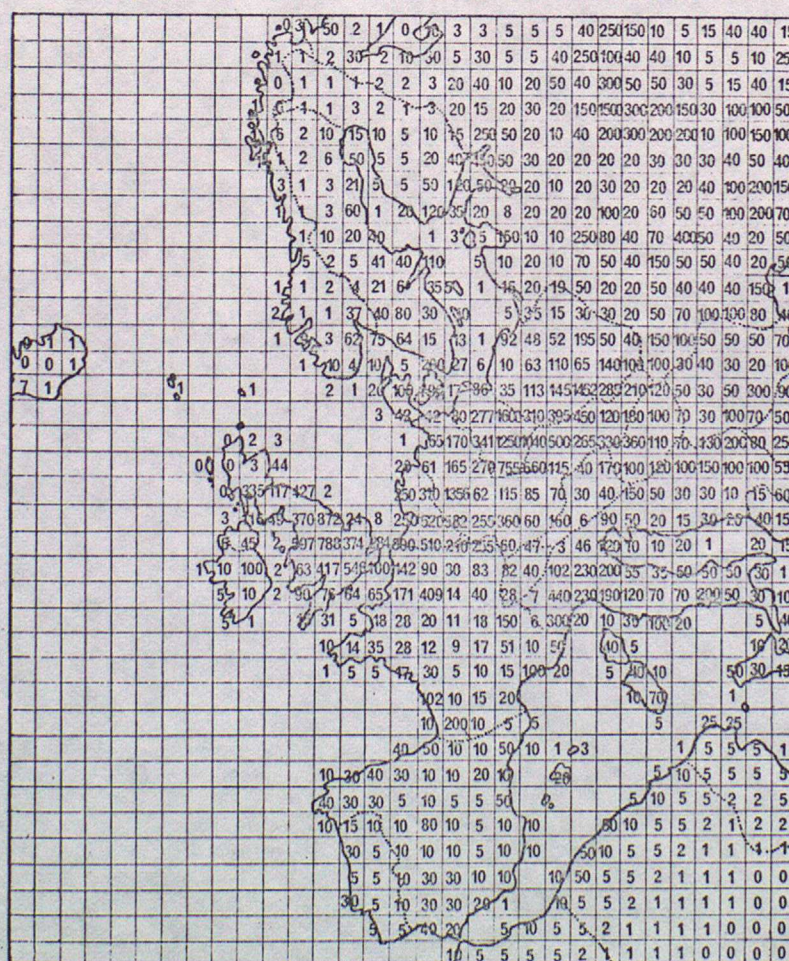

FIGURE 2. Sulphur dioxide emissions for 1972 in thousands of tonnes per year. The grid length is 127 km at 60° N.

FIGURE 3.

WINTER MEAN
CONCENTRATIONS
OF SO$_2$
1975–76

(based on a more detailed map
by Warren Spring
Laboratory)

$\bar{C}$ > 50µg m^{-3}

$\bar{C}$ > 100µg m^{-3}

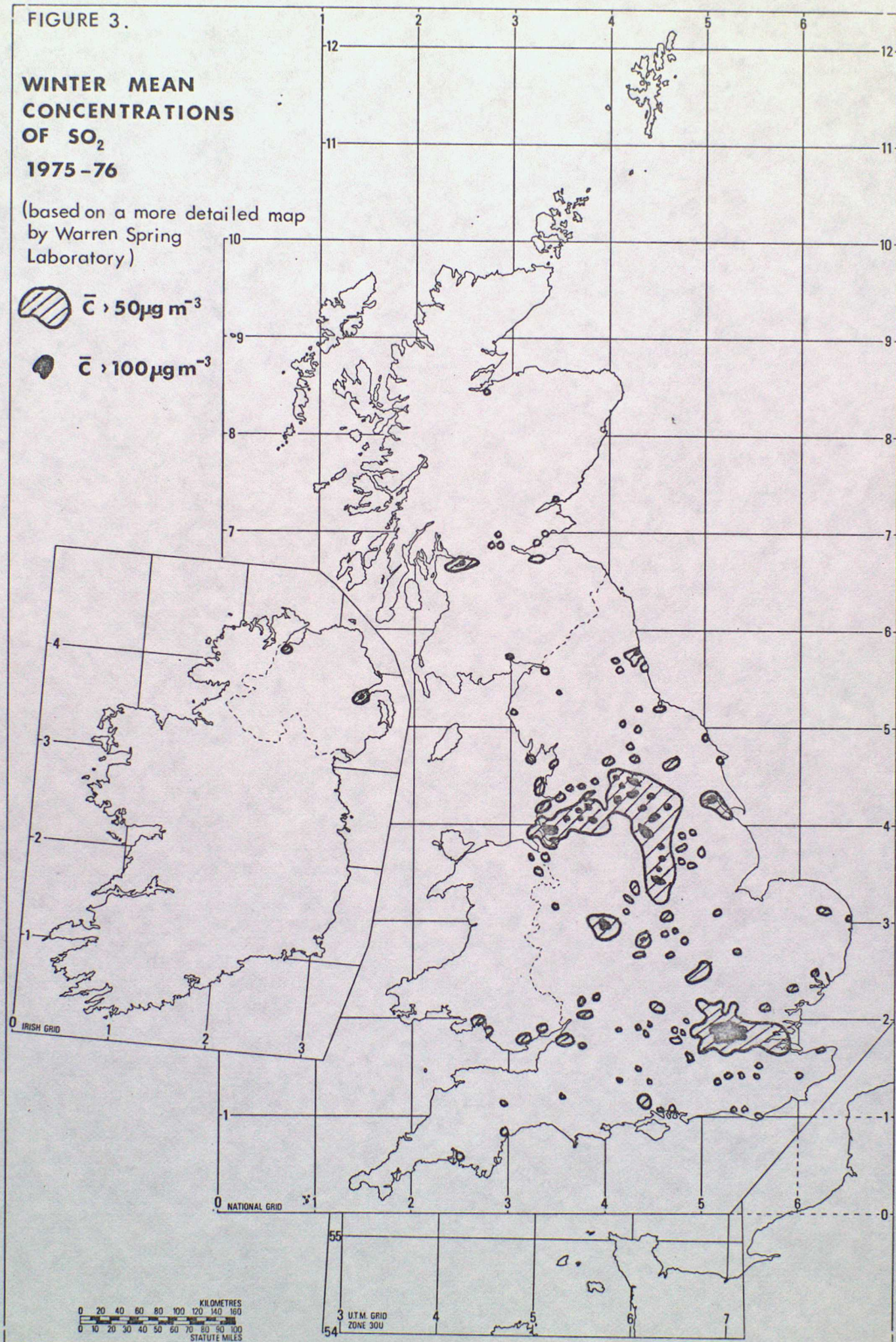| region	1972 total: 3698 mg m^{-2}		1973 total: 2231 mg m^{-2}		1974 total: 2823 mg m^{-2}	
	dry deposition	deposition in rain	dry deposition	deposition in rain	dry deposition	deposition in rain
British Isles	5.3	20.9	7.2	22.6	8.5	28.7
Norway	7.8	5.5	12.7	11.3	10.3	7.5
G.D.R.	3.9	11.3	2.5	5.1	2.3	4.9
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

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

country	percentage contribution	
	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

Fig. 4 Estimated pattern for total dry deposition of sulphur (Trajectory model). Unit: g S m^2. Deposition velocity for sulphur dioxide: 0.8 cm s^{-1}. Deposition velocity for particulate sulphate: 0.2 cm s^{-1}. Additional local deposition of 15% also included (see text) (OECD.)
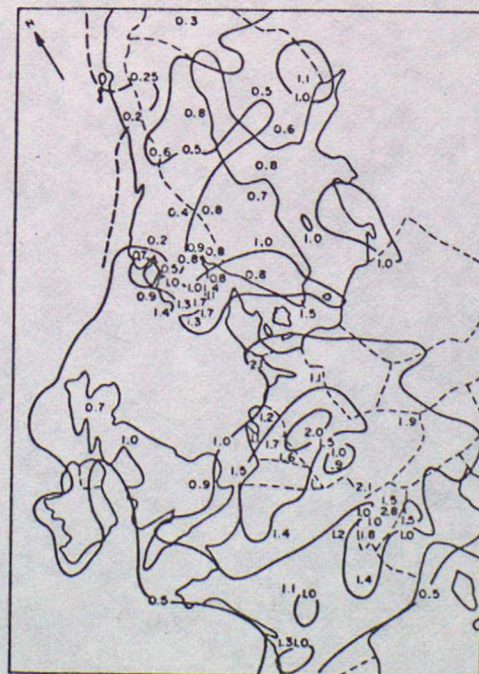

Fig. 5 Wet deposition of sulphate in 1974 (g S m^{-2}) obtained from measurements. An annual mean concentration field for sulphate in precipitation was constructed on basis of the measured values, and thereafter multiplied by the annual precipitation field (OECD.)