Transfer to Terrestrial Surfaces [and Discussion]

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Transfer to terrestrial surfaces

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The processes by which atmospheric pollutants are transferred to the ground may be placed into two categories. Wet deposition, which includes all pollution reaching the surface in precipitation, and dry deposition which includes the sorption of gases and capture of particulate pollutants by terrestrial surfaces.

The properties of each of the removal mechanisms are described for the gases SO_2, NO_2, HNO_3 and the atmospheric aerosols containing sulphate and nitrate. Following a description of the processes, rates of deposition appropriate for a range of vegetation and atmospheric conditions are provided. The influence of changes in the properties of absorbing surfaces due to the presence of water or for vegetation to changes in stomatal conductance is discussed.

The use of transfer resistances to describe the mechanism of deposition is then extended to provide estimates of dry deposition of SO_2 on to Great Britain which are contrasted with wet deposition. The resulting maps show that over most of England, including central, eastern and southern areas, dry deposition exceeds wet deposition. For north west England, Wales and northern Scotland, particularly the large rainfall districts of the west, wet deposition exceeds dry deposition.

Introduction

Atmospheric sulphur and nitrogen compounds transferred to the ground are present in the atmosphere as gases (SO_2, NO, NO_2, HNO_3, NH_3), and as particles. The particles contain $(NH_4)_2SO_4$, NH_4HSO_4, H_2SO_4 and NH_4NO_3; at the humidities and temperatures that prevail over north western Europe such deliquescent particles are often present as droplets (Garland 1969).

The gas or particle may be deposited *directly* on to vegetation, soil or water: a process known as dry deposition; or it may be incorporated into a hydrometeor (cloud or rain drops, or snowflakes) and transferred by gravitational settling *indirectly* to the ground as wet deposition. In addition, cloud droplets may be transferred to vegetation by turbulent transfer and captured by impaction, this form of deposition being known as occult precipitation (Rutter 1975; Dollard & Unsworth 1983).

Ecological effects of sulphur- and nitrogen-containing air pollutants have generally been the subjects of two different lines of research, the first being effects of large concentrations (more than $20/10^9$ by volume) of the gases SO_2 and NO_2, and the second being the effects of long range transport of sulphur and nitrogen oxides. Each field has been reviewed at recent international conferences (see, for example, Unsworth & Ormrod 1982; S.N.S.F. 1980 respectively), and the experimental approaches in each field have generally been different.

The emphasis in studies of effects of large pollutant gas concentrations on vegetation has been to establish relations between gas concentrations and plant responses, the transfer being primarily by dry deposition. Such effects are generally limited to areas within 100 km of major sources of air pollutants. For effects of the above air pollutants at large distances from source

areas (more than 500 km) most studies until recently have been concerned with acidification of freshwater systems and effects on fish. For these areas wet deposition has generally contributed the bulk of the deposit. The relative importance of wet and dry deposition to total inputs for areas close to and at large distances from sources differ but the same physical processes of transfer of gases and particles to the ground apply at all distances from sources.

Knowledge of wet and dry deposition is based on very different approaches. Measurements of the chemical content of precipitation have been made since the mid-19th century (Laws *et al.* 1861; Smith 1872), though few long data sets are available. In the last two decades networks of precipitation sampling sites throughout Europe and North America have been established to determine the geographical distribution of wet deposition for the major ions in rain over large areas (Granat 1978; Wilson *et al.* 1982). Our knowledge of the composition of wet deposition is therefore based on very extensive data sets. By contrast, studies of dry deposition are more recent (Garland 1977; Fowler & Unsworth 1979; Wesley *et al.* 1982; Hicks *et al.* 1983). Dry deposition to natural surfaces is not monitored routinely anywhere, and our knowledge of the process is based on a few hundreds of hours of measurements over vegetation dominated by only five different plant species, (*Lolium perenne, Triticum aestivum, Zea mays, Glycine max,* and *Pinus sylvestris*).

In spite of these limitations it will be argued here that with an appropriate understanding of transfer processes it is possible to estimate regional inputs of sulphur and nitrogen compounds by dry deposition.

Wet deposition

The incorporation of sulphur and nitrogen compounds into cloud or raindrops operates on very variable time scales. As examples of extremes, an aerosol particle containing S or N may form the cloud condensation nucleus (c.c.n.) from which a raindrop is produced, or an SO_2 molecule may enter a raindrop just before the drop meets the ground. In order to describe the properties of wet deposition the different ways in which gases and particles may be captured must be considered. Particles and gases enter precipitation in different ways and are treated separately.

Particles

There are several processes by which particles may be captured by cloud or raindrops, most of which depend on particle size.

Diffusiophoresis

In this process particles are transported (swept) in the direction of a mean flux of vapour molecules in air, for example particles are moved by the diffusion current of water vapour towards a condensing droplet. From the work of Goldsmith *et al.* (1963), Garland (1978) showed that this mechanism could only account for a small proportion (less than 1 %) of the observed SO_4^{2-} in rain.

Thermophoresis

A related particle transfer process, results from temperature gradients close to cloud droplets or ice crystals and operates concurrently with and may reduce the efficiency of diffusiophoresis (Slinn & Hales 1971).

Diffusion

Rates of Brownian diffusion of aerosol particles arising from collision with air molecules vary inversely with particle size. The process may only be regarded as efficient for transport of particles smaller than 0.1 µm (Pruppacher & Klett 1978). From the work of Goldsmith *et al.* (1963), Fowler (1980) estimated the contribution of Brownian diffusion to the SO_4^{2-} and NO_3^- in rain to be *ca.* 3%. Similar conclusions were reached by Garland (1978) from the work of Mason (1971).
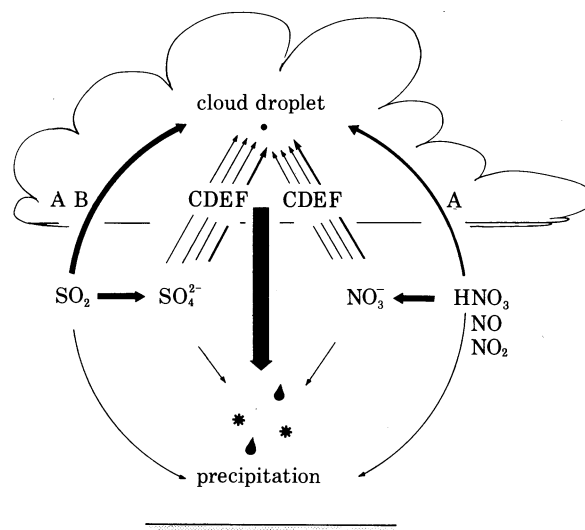

FIGURE 1. Pathways and mechanisms for the transfer of sulphur and nitrogen containing compounds to the ground in precipitation. A: dissolution; B: oxidation; C: diffusiophoresis; D: Brownian diffusion; E: impaction; F: cloud condensation nuclei pathway. Bold arrows indicate the major routes for wet removal of S- and N-containing compounds from the atmosphere.

Impaction

The process of inertial attachment of particles to cloud or raindrops arises through collisions when particles fail to follow the streamlines of airflow around droplets. The process depends strongly on particle size, becoming an efficient scavenging mechanism for particles larger than 5 µm (Hales 1983).

The above processes provide for efficient scavenging of particles smaller than 0.1 µm and larger than 5 µm, but most of the SO_4^{2-} and NO_3^- particles are in the intermediate size range 0.1–1.0 µm (Whitby 1978) for which the above processes may make only a minor contribution to the SO_4^{2-} and NO_3^- in rain. The deliquescent nature of aerosols containing S and N makes them efficient as cloud condensation nuclei (c.c.n.) and this represents an additional removal pathway. Garland (1978) argued that the c.c.n. removal route for aerosols containing SO_4^{2-} and NO_3^- is responsible for most of the observed SO_4^{2-} and NO_3^- in precipitation. Figure 1 illustrates the different wet removal mechanisms for particles and gases and table 1 provides an indication of the average importance of each pathway from arguments published elsewhere.

TABLE 1. THE RELATIVE IMPORTANCE OF DIFFERENT PROCESSES THAT CONTRIBUTE TO THE
SULPHUR AND NITROGEN IN RAIN

	contribution to wet deposited sulphur (%)	contribution to wet deposited nitrate nitrogen (%)	source
diffusiophoresis	2.5	2.5	Fowler (1980)
Brownian diffusion	2.5	2.5	from the work of Goldsmith et al. (1963)
impaction	10	10	Garland (1978)
solution and oxidation by cloud and rain drops	≈ 30	(1)	Garland (1978)
cloud condensation nuclei pathway	55	up to 85[1]	Garland (1978)

[1] HNO_3 gas uptake by cloud and rain droplets may make a substantial contribution but no published values were found; this would reduce the value for the c.c.n. pathway.

Gases

Uptake of SO_2 by falling rain leads to an equilibrium concentration of S^{IV} species in precipitation at the ground. This may be of considerable importance in determining effects on plants as such species have been shown to be more phytotoxic than SO_4^{2-} (Garsed 1981; Ferguson et al. 1978; Hocking & Hocking 1977). Cape (1983a, b) has shown that SO_2 (aq) is the most phytotoxic species. The S^{IV} species may contribute between 10% and 30% of wet deposited S, the larger values being found at urban sites (Gravenhorst et al. 1980; Davies 1979), where raindrops may be falling through a pronounced vertical gradient in SO_2 concentration. This aspect of wet deposition may therefore be of greater importance for effects on plants than it is as a removal mechanism.

Solution and oxidation of SO_2 within clouds is an important removal process (Gillani & Wilson 1983). The oxidation may proceed via many different reactions (Cox & Penkett 1983) with recent interest favouring reactions with H_2O_2. The average contribution of solution and oxidation to the SO_4^{2-} in precipitation remains uncertain, but is regarded (Gillani & Wilson 1983; McNaughton & Scott 1980), as a major component. Garland (1978) estimated that the solution and oxidation of SO_2 within clouds may contribute ca. 30% of the average SO_4^{2-} in precipitation. Chemical limitations in the uptake and oxidation of NO and NO_2 by cloud and raindrops (Lee & Schwartz 1981) make this process only a minor contributor to the NO_3^- in rain. HNO_3 gas uptake by cloud and rain may be much more important (Marsh 1983).

Uncertainties

To define regional wet deposition, networks of precipitation collectors are used. Much of the data have been obtained by using continuously open collectors which may receive a significant proportion of the measured SO_4^{2-} and NO_3^- through dry deposition onto the collector. The rate of SO_2 deposition onto a pyrex glass collector varies with time as the collector surface approaches saturation (Fowler & Cape 1984), whereas particle deposition seems to continue at a constant rate. For rural sites in Britain dry deposition of SO_2 gas and S-containing particles may contribute between 15 and 40% of the SO_4^{2-} in the bulk collectors used. Similar problems may lead to errors in NO_3^- and NH_4^+ wet deposition measurement.

In defining regional patterns of wet deposition some interpolation is necessary to obtain wet

deposition for areas between monitoring stations. In general this is unlikely to introduce significant errors with well designed networks of collectors, but an important exception occurs in mountainous regions where there may be substantial gradients in rainfall amount and composition with altitude. At present, rainfall composition measurements in the U.K. do not include sites on mountain tops. The combination of the well established large rainfall amounts at mountain sites with extrapolated values of rainfall composition suggests that wet deposition at such sites are large (Fowler *et al.* 1982).

Evidence to date shows that non-marine sulphate concentration in rain is only weakly dependent on rainfall amount (Granat 1978) and this leads to a strong dependence of the quantity of wet deposit on rainfall amount (Hicks & Shannon 1979). However the degree to which orographic enhancement of rainfall quantity may influence the concentrations of major ions in rain is less clear, and there are important but poorly quantified mechanisms by which mountain tops could receive both larger concentrations and larger rainfall amounts (Carruthers & Choularton 1983).

Vegetation and wet deposition

A description of the wet deposited SO_4^{2-}, NO_3^-, H^+ and other ions as measured by using standard precipitation collectors may not define the amount of a substance deposited on to vegetation because the capture of fine rain and cloud droplets by vegetation may lead to larger inputs to the ground than to a precipitation collector (Miller & Miller 1980). The mechanism of deposition of cloud droplets and fine rain is described in the section on occult deposition, and may be responsible for a substantial proportion of deposited S- and N-compounds at high altitude sites (Dollard *et al.* 1983).

DRY DEPOSITION

Direct transfer of gases and particles from the atmosphere to the ground comprises three stages: first, the materials must be transported through the free atmosphere to within a few millimetres of the surface; second, there is transport through a viscous sublayer of air close to the surface; last, the gas or particle must be captured by the surface. Figure 2 illustrates the three stages in the process, indicating the dominant transfer mechanism in each. Particles that are large enough to sediment out of the atmosphere under the influence of gravity make up a very small fraction of the aerosol mass in the atmosphere (Whitby 1978). Subsequent discussion is therefore restricted to the particle size range in which most of the SO_4^{2-} and NO_3^- is found (0.1–1.0 μm).

Particles

For particles smaller than 1.0 μm in diameter, transfer in the free atmosphere is effected by turbulent diffusion and depends on windspeed, surface roughness and temperature stratification of the lowest layers of the atmosphere. However, transfer through the viscous sublayer close to the surface presents a considerable restriction to the transfer of 0.1–1.0 μm particles. For much smaller particles Brownian diffusion effects the transfer and for particles much larger than 5 μm impaction provides the means of penetrating this viscous sublayer. The problem is similar whether particle transfer is to the ground or to cloud droplets. A consequence of the inefficient dry removal mechanism is a gradual increase in the particle concentration during calm dry
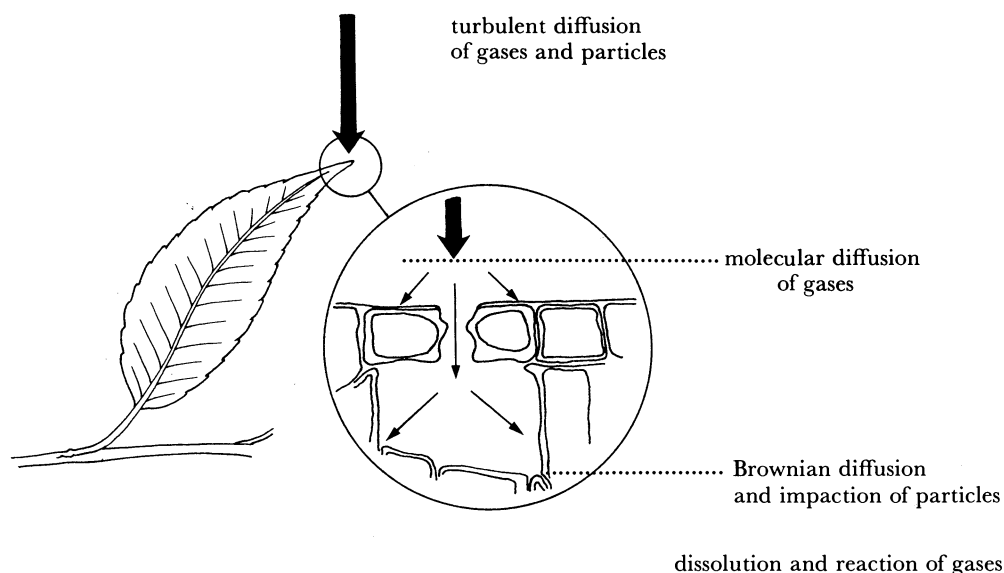
FIGURE 2. Processes contributing to the transfer of sulphur and nitrogen compounds from the atmosphere to vegetation by dry deposition.

anticyclonic weather and a reduction in visibility (Whelpdale 1978). Rates of deposition of particles in the size range 0.1–1.0 μm in laboratory studies to grass are small (deposition velocity $v_g < 0.1$ mm s^{-1}; Chamberlain 1975). Field measurements show more variable results for particles containing S and N. Garland (1978, 1983) reports consistently small values $v_g < 0.5$ mm s^{-1}; Hicks *et al.* (1983) and Wesely & Hicks (1979) report more variable and generally larger values, v_g of 1–8 mm s^{-1}. The possibility that a small concentration of large (over 5 μm) particles is present has been suggested (Garland 1978; Hicks *et al.* 1982), but has not been confirmed by measurements. Until agreement is reached on the deposition velocities for these particles, inputs by this mechanism must remain uncertain.

Gases

For the gases SO_2 and NO_2, although only a few hundred hours measurements of dry deposition rates on to vegetation are available, the main properties of the process have been established.

Nitric oxide, NO, is an important component of atmospheric NO_x but is not deposited on to natural surfaces at a significant rate (Grennfelt *et al.* 1983). On the contrary, it appears for some surfaces that there is a net flux of NO away from the ground (Gravenhorst & Böttger 1983). Ammonia is another gaseous N-compound in the atmosphere that plays an important part in atmospheric chemistry but again the transfer appears to be away from the ground (Denmead *et al.* 1974). The following discussion is restricted to the gases SO_2, NO_2 and HNO_3 whose net transfer is towards the surface.

In describing the mechanism and in quantifying the relative importance of atmospheric and surface processes in the transfer of SO_2, NO_2 and HNO_3 a resistance analogy has proved valuable. The flow of pollutant gas through the two atmospheric transfer steps in series and into the various surface sinks that exist in parallel (figure 3) is treated as analogous to the flux of electrical current through a simple network of resistances.

A detailed description of the resistance analogy applied to the exchange of momentum, heat and gases between vegetation and the atmosphere is given by Thom (1975).

The total transfer resistance between a defined height in the atmosphere and the absorbing surface r_t is identical to the reciprocal of deposition velocity v_g, the latter providing a measure of the conductivity of the atmosphere–surface combination for the gas and is widely used to parametrize gas uptake at the ground (Chamberlain 1960). The advantage of the resistance
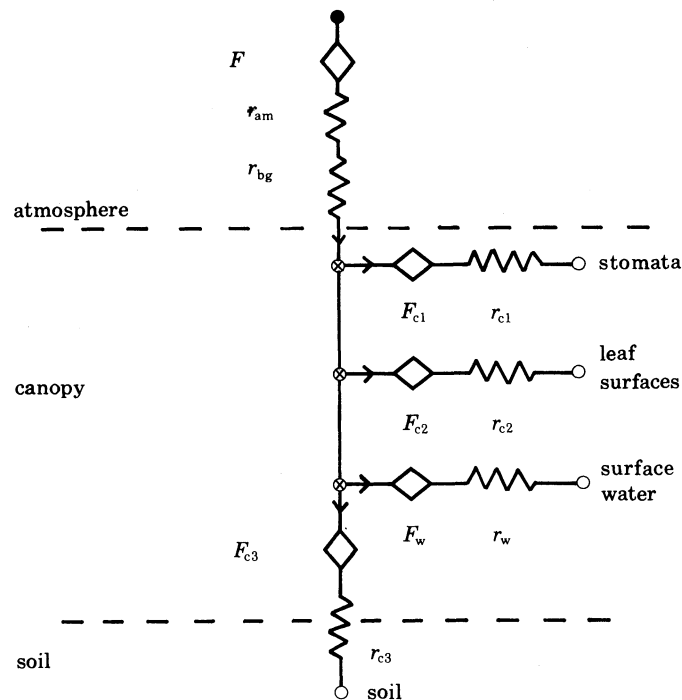

FIGURE 3. A resistance analogue for pollutant uptake by crop canopies. The total resistance r_t is the sum of atmospheric resistances $r_{am} + r_{bg}$ and canopy resistance r_c. Canopy resistance is determined by up to four parallel paths, stomata r_{c1}, external plant surfaces r_{c2}, surface water r_w, and soil r_{c3}; corresponding fluxes are denoted by the prefix F.

analogy is mainly the simple way in which atmospheric and surface resistances may be separated or combined to quantify the importance of individual steps or to produce an overall value of the deposition velocity for a given surface. The techniques available for measuring fluxes of these gases to vegetation or soil range from micrometeorological, in which exchange between a large area (10^5 m^2) of vegetation and the atmosphere is measured, to cuvette methods in which small areas (less than 1 m^2) of vegetation are enclosed. Atmospheric resistances ($r_{am} + r_{bg}$) may be subtracted from the total resistance r_t to give r_c the canopy resistance which is a measure of the affinity of the absorbing surface for uptake. Although measurements exist for several different plant canopies the results may be summarized in two classes, short vegetation (height < 2 m) and tall vegetation (forests), height H > 10 m.

(i) *Short vegetation*

Most measurements are for grassland or agricultural crops. Atmospheric resistances ($r_{am} + r_{bg}$) decrease with vegetation height and windspeed from typically 200 s m^{-1} at low windspeeds (less than 1 m s^{-1}) over vegetation 10 cm tall to 20 s m^{-1} at a windspeed of 4 m s^{-1}

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over 1 m vegetation (table 2). These values provide upper limits to the deposition rate (i.e. for the case where $r_c = 0$, $v_g = (r_{am} + r_{bg})^{-1}$), the deposition velocity in these conditions in a maize crop for a windspeed of 4 m s^{-1} would exceed 80 mm s^{-1}, but such values are unlikely.

TABLE 2. ATMOSPHERIC RESISTANCE $(r_{am} + r_{bg})$ FOR TRANSFER OF POLLUTANT GASES
ON TO VEGETATION

vegetation	crop height/m	atmospheric resistance $(r_{am} + r_{bg})/$s m^{-1} windspeed	
		1 m s^{-1}	4 m s^{-1}
grass	0.4	130	30
cereals	1.0	70	20
maize	2.0	50	12
forest	10.0	25	10

The conditions of small windspeeds and large atmospheric resistance tend to occur on calm nights, an effect of the stable stratification of the air near the ground on such occasions. With these conditions the rate of removal at the ground may exceed the rate of transfer of pollutant gas to atmospheric layers near the ground from greater heights resulting in reduced gas concentrations in the air close to the surface. The effect is shown in figure 4 for three days with calm clear nights, and is discussed by Garland & Derwent (1979).
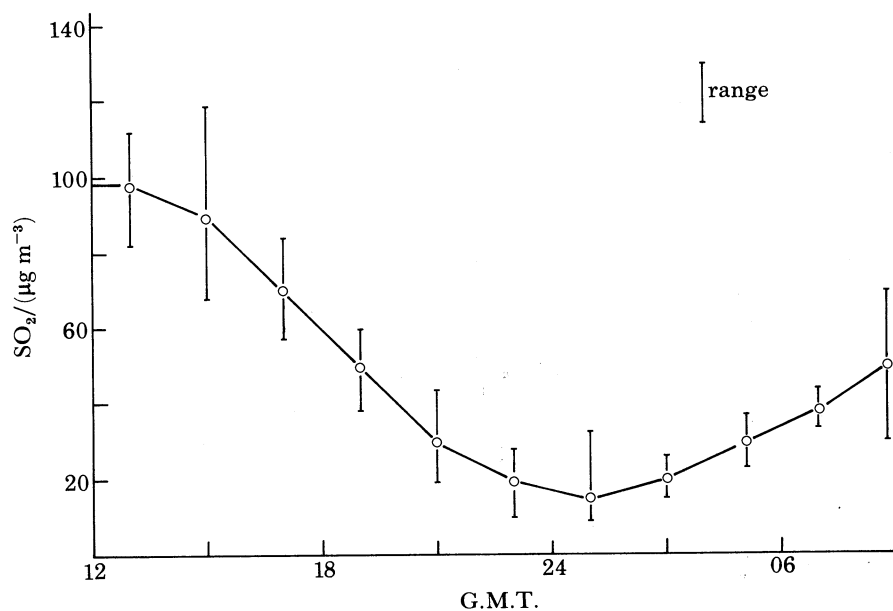

FIGURE 4. The average change in SO_2 concentration 1 m above a cereal crop over three days showing nocturnal depletion of SO_2 in the air close to the surface.

Atmospheric resistances do not generally represent the largest restriction in the deposition process and consequently deposition rates are seldom influenced strongly by atmospheric factors such as windspeed. For most short vegetation, canopy resistance r_c represents over 70% of r_t and variations in deposition rates are due mainly to variations in r_c (Fowler & Unsworth 1979). While the vegetation is growing, day time maxima in deposition velocity for SO_2 of 8–10 mm s^{-1} and nocturnal minima of 2–4 mm s^{-1} are common. Figure $5a$ shows an occasion when the

[30]

majority of the variation in v_g was the consequence of changes in r_c. Deposition rates of NO_2 show a similar diurnal cycle (Wesley *et al.* 1982) from a day-time maximum v_g of 6 mm s^{-1} to a nocturnal minimum of 1 mm s^{-1}. The diurnal cycle in r_c (and consequently v_g) for a dry crop is due mainly to stomatal movements. Stomata have been shown to be the major sink for SO_2 and NO_2 in short field crops (SO_2: Fowler & Unsworth 1979; NO_2: Wesley *et al.* 1982), confirmed by laboratory studies of Black & Unsworth (1979) and Hällgren *et al.* (1982). For day-time conditions, 70–80% of the SO_2 flux is absorbed by stomata, the remaining flux representing sorption on to the external surfaces of plants. For NO_2, negligible uptake on external plant surfaces seems to occur.
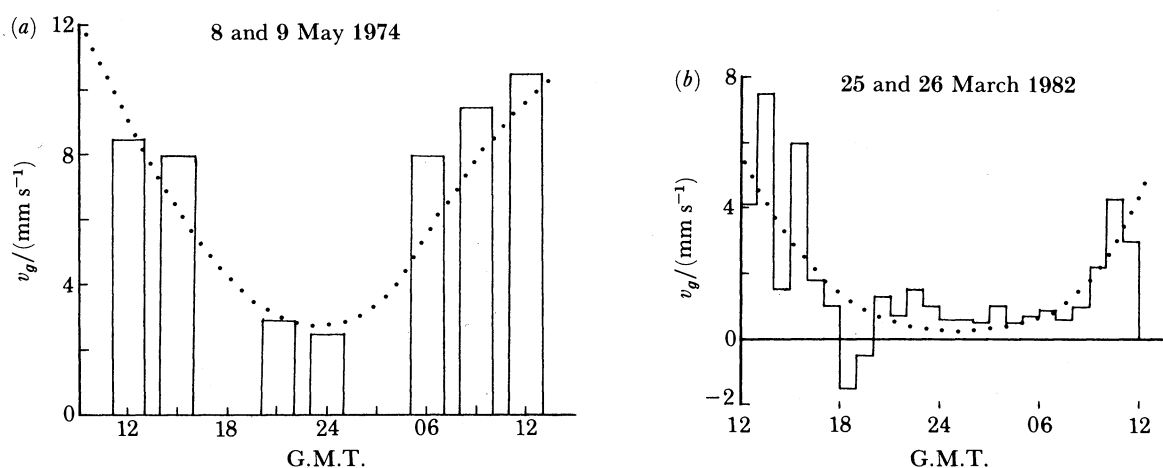

FIGURE 5. (*a*) A daily cycle in deposition velocity (v_g) for SO_2 from measurements above a wheat (*Triticum aestirum*) canopy. (*b*) A daily cycle is deposition velocity for SO_2 from measurements above a Scots pine (*Pinus sylvestris*) canopy.

The separation of stomatal and external uptake may be represented by subdividing r_c into a number of components that act in parallel (figure 3) such that

$$r_c^{-1} = r_{c1}^{-1} + r_{c2}^{-1} + r_{c3}^{-1};$$

(r_{c1} stomatal; r_{c2} leaf surface and r_{c3} soil).

Too few measured values for HNO_3 fluxes are available but from the measurements of Huebert (1983) the large deposition velocities suggest a small value for r_c, so that rates of deposition are determined mainly by atmospheric transfer ($v_g \approx (r_{am} + r_{bg})^{-1}$).

For crops generally, stomatal SO_2 or NO_2 uptake may be estimated from a knowledge of the canopy conductance to water vapour, making allowance for the different molecular diffusivities of H_2O, NO_2 and SO_2, provided that no significant internal resistance inside leaves is present. An internal resistance represents a chemical restriction to uptake within leaves and has been observed for NO_2 transfer to maize (Wesely *et al.* 1982) and SO_2 transfer to Scots pine (Hällgren *et al.* 1982). Transfer resistances for SO_2 and NO_2 transfer to short vegetation are summarized in table 3.

(ii) *Forests*

Atmospheric turbulence over forests is large (Jarvis *et al.* 1975) and permits very large potential rates of deposition of SO_2, NO_2 and HNO_3. Values of ($r_{am} + r_{bg}$, table 2) for a 10 m pine canopy are typically 10 s m^{-1} even at modest windspeeds, permitting potential deposition

[31]

velocities up to 100 mm s^{-1} if r_c is negligible. As for shorter crops, rates of atmospheric transfer are largest during the day and smallest at night but the size of the diurnal change for forests is smaller. Practical and theoretical difficulties with measurements have restricted the number of direct measurements of SO_2 and NO_2 transfer to forests. Recent measurements (Fowler & Cape 1983) for SO_2 in dry conditions again show a diurnal cycle in v_g but the daytime minimum in r_c was 200–300 s m^{-1} and nocturnal values of 500–1000 s m^{-1} were common. Canopy

TABLE 3. TYPICAL TRANSFER RESISTANCES FOR SO_2 AND NO_2 ON TO VEGETATION

| | | canopy resistances/s m^{-1} | | | | deposition velocity/mm s^{-1} | |
| | | r_{c1} | | r_{c2} | | v_g | |
time	season	SO_2	NO_2	SO_2	NO_2	SO_2	NO_2
		short vegetation 0.1–2.0 m					
day	April–Sept.	100	150	250	1000	8	6
night	April–Sept.	∞	∞	250	1000	3	1
day	Oct.–March	500	500	250	1000	4	3
night	Oct.–March	∞	∞	250	1000	3	1
		forests > 10 m					
day	April–Sept.	250	250	500	1000	6	5
night	April–Sept.	∞	∞	500	1000	2	1
day	Oct.–March	500	500	500	1000	4	2
night	Oct.–March	∞ ∞	∞	500	1000	2	1

Notes: (i) resistance notation as figure 3; (ii) $r_{am} + r_{bg}$ taken as 50 s m^{-1} for short crops, and 10 s m^{-1} for forests; (iii) NO_2 values from Wesely *et al.* (1982) for short crops and Grennfelt *et al.* (1983) for forests; SO_2 values from Fowler & Unsworth (1979) for short crops and Fowler & Cape (1983) for forests.

TABLE 4. SO_2 TRANSFER TO A SCOTS PINE CANOPY SHOWING THE PRESENCE OF AN INTERNAL RESISTANCE TO SO_2 UPTAKE WITHIN THE LEAVES

time (G.M.T.)	deposition velocity v_g/mm s^{-1}	bulk stomatal resistance for H_2O, r_{wv}/s m^{-1}	bulk stomatal resistance for SO_2, r_{c1}/s m^{-1}	'internal' resistance, r_{int}/s m^{-1}
1230–1330	6.9	78	151	0
1330–1430	3.2	56	356	253
1430–1530	4.7	52	232	128
1530–1630	1.8	100	714	514
1630–1730	1.5	170	909	569
1730–1830	0.4	∞	∞	—

Notes: (i) for notation see figure 3; (ii) $r_{am} + r_{bg}$ taken as 10 s m^{-1} (windspeed 3 m above tree tops *ca.* 3 m s^{-1}); (iii) r_{c2} the canopy resistance for a dry canopy with closed stomata (approx. leaf surface uptake), taken as 2500 s m^{-1} from the value of r_c at 1730–1830; (iv) internal resistance r_{int}, is the residual canopy resistance when the leaf surface r_{c2} and bulk stomatal resistance to water vapour loss have been removed.

resistance generally represented 90 % of the total resistance to transfer, so that deposition rates are almost exclusively under the control of surface processes. This limited v_g typically to 5 mm s^{-1} and 1 mm s^{-1} respectively. For NO_2 Grennfelt *et al.* (1983), also reported large values for r_c from cuvette measurements on Scots pine, and for a canopy a daytime v_g of 5 mm s^{-1} and night value of much less than 1 mm s^{-1} are consistent with their measurements. Deposition rates on to forests appear to be smaller than on to shorter crops and very much smaller than the maximum values permitted by atmospheric transfer.

Stomata are still the major sink for SO_2 and NO_2 in forests and are responsible for the diurnal cycle in deposition rate (figure 5 b). The modest rates of deposition reflect in part the quite large

canopy resistances of forests for water vapour loss (Jarvis *et al.* 1975), a measure that reduces evapo-transpiration and prevents excessive water potentials developing in the plant. However, the presence of an internal resistance has been detected. In the SO_2 flux measurements of Fowler & Cape (1983) an internal resistance represented 50 % of r_t during the day (table 4) whereas the NO_2 transfer was limited by an internal resistance only when the plants were under water stress conditions (Grennfelt *et al.* 1983).

The quite small rates of SO_2 deposition at night show that uptake on to external surfaces is small, and for NO_2 negligible. This suggests that for dry conditions in winter when r_c is known to be large, rates of dry deposition for SO_2 and NO_2 on to forests are probably small, v_g 1–2 mm s^{-1}.

Table 3 summarizes the values of v_g and r_c for SO_2 and NO_2 transfer to conifer forests. For HNO_3 gas, the lack of field measurements leads to considerable uncertainty but if $r_c = 0$ deposition rates of HNO_3 are likely to be very large on to forests, with v_g in the range 10–100 mm s^{-1}.

Transfer to wet surfaces. For large particles a liquid film may help to absorb momentum from a depositing particle and reduce bounce off (Chamberlain 1975), but surface water is unlikely to significantly influence the capture by the surface of particles in the size range 0.1–1.0 μm. For gases, atmospheric resistances $(r_{am} + r_{bg})$ remain unchanged from those in dry conditions but the normal sites for uptake (leaf surfaces and stomata) are partly covered by a water film. The degree to which vegetation is wetted varies with plant species, leaf age, and may be influenced by the presence of air pollutants (Cape 1983). As SO_2 is a soluble gas it has been argued (Garland 1978) that rates of SO_2 transfer on to wet vegetation may be large and limited only by atmospheric transfer. For vegetation wetted by dew Fowler (1978) showed that this was the case, at least while dew was accumulating on leaf surfaces. However, during a period when fresh dew was unlikely to form, a canopy resistance associated with the existing dewfilm appeared and increased rapidly. This was considered to be the result of SO_2 uptake into a layer of 'pure' water which continued until equilibrium was achieved between gas phase and solution phase SO_2.

TABLE 5. SO_2 TRANSFER TO A SCOTS PINE CANOPY DURING RAIN

(Atmospheric resistance $r_{am} + r_{bg}$ taken as 30 s m^{-1}, windspeed 3 m above forest canopy *ca.* 2 m s^{-1}.)

time (B.S.T.)	concentration/μg SO_2 m^{-3}	SO_2 flux towards the surface/μg SO_2 m^{-2} s^{-1}	deposition velocity/mm s^{-1}	canopy resistance/s m^{-1}
2125	12.7	2.21×10^{-2}	1.75	540
2145	13.7	2.33×10^{-2}	1.72	550
2205	12.7	2.37×10^{-2}	1.87	510
2205	16.9	4.94×10^{-2}	2.93	310
2245	18.2	1.05×10^{-2}	0.58	1690
2305	17.5	1.60×10^{-2}	0.94	1030
2325	14.9	1.8×10^{-2}	1.23	780
2345	14.6	5.17×10^{-2}	3.54	260
0005	9.9	4.30×10^{-2}	4.36	200

In contrast to the efficient sink presented while fresh dew is forming, rain-wetted vegetation shows different properties. A series of measurements of SO_2 transfer to a rain wetted Scots pine canopy (Fowler & Cape 1983) shows only modest rates of deposition. Canopy resistance during the measurements were consistently *ca.* 300 s m^{-1} limiting v_g to 2–3 mm s^{-1}. Table 5 summarizes

the results of these measurements. It appears that in this case the S^{IV} in rain was close to equilibrium with respect to air concentrations of SO_2 before it reached the forest and that rates of deposition onto the wet canopy were controlled by chemical reactions in the liquid film where S^{IV} species were being removed from solution by oxidation to S^{VI}. More field measurements are necessary to confirm the above results, and such measurements must include analyses of the rain and surface water for the major ions present and their oxidation state. For NO_2, chemical limitations to uptake by water make likely deposition rates on to wet foliage very small (Lee & Schwartz 1981). HNO_3 deposition rates on to wet foliage would be expected to differ little from rates of HNO_3 deposition rates on to dry foliage, i.e. $r_c \approx 0$ but field measurements are required.

Occult deposition

Vegetation may intercept wind-blown cloud or fog droplets directly by impaction. Such droplets lie in the size range 10–50 μm and are efficiently captured by vegetation. The process described as occult precipitation (Rutter 1975) has been reviewed by Kerfoot (1968) and in areas where low cloud is common (coastal areas and high altitudes) it may represent a significant hydrological input. The process may also be important as a solute transfer process for the same areas because cloud water may show very large concentrations of the major ions (Tomlinson et al. 1980). For a site in the north of England, Dollard et al. (1983) showed that inputs by this mechanism may be of the order 10–20 % of wet deposition for SO_4^{2-}, NO_3^- and H^+. However, the very large concentrations reported for cloud water of 2500 μeq SO_4^{2-} l^{-1}, 2400 μeq NO_3^- l^{-1} and 400 μeq H^+ l^{-1} (Dollard et al. 1983) may make effects of this form of deposition proportionately greater than its contribution to total deposition.

The capture of fine rain by vegetation is similar to that of cloud capture and may lead to larger inputs of water to forests than to a rain gauge. Miller & Miller (1980) discussed the capture of fine rain by trees as a component of 'filtering' and showed that concentrations of most ions collected in a rain gauge with a wire grid above the funnel were greater than those in rain collected in a conventional gauge. The degree of enhancement of concentration varied with the ionic species but was of the order of a factor of 2 for S and total N.

The mechanism of transfer of cloud droplets to vegetation is limited only by atmospheric transfer (Dollard & Unsworth 1983) with deposition velocity typically 2–3 times the bulk sedimentation velocity. Over grassland overall deposition velocities between 30 and 60 mm s^{-1} were obtained, for forests values between 50 and 150 mm s^{-1} should be expected.

Discussion

The use of transfer resistances made a valuable contribution in separating the different processes contributing to the transfer of pollutants to the ground. The results based on a few hundreds of hours measurements provide sufficient information to parametrize the dry removal process. Such information could be incorporated in long range transport models (Fisher 1978) or used to define inputs over large areas (Galloway & Whelpdale 1980). In this way particular surfaces or situations may be identified as areas for more measurements. As an example figure 6 shows estimates of the annual dry deposition of SO_2 on to Great Britain calculated by simplifying surfaces into 5 land classes and by assigning appropriate average deposition velocities to each from the literature for summer and winter (table 6). The assumptions in
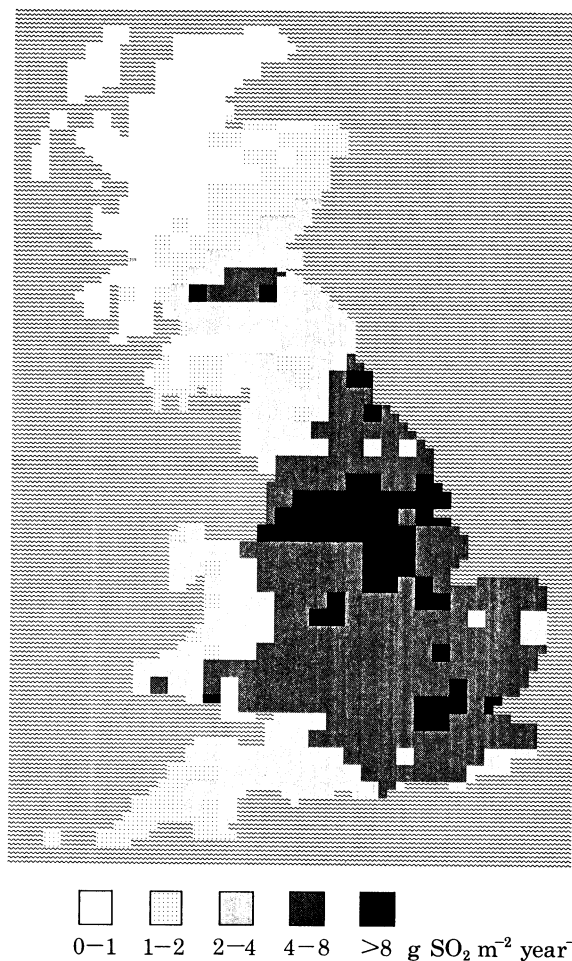
0—1   1—2   2—4   4—8   >8   g SO_2 m^{-2} year^{-1}

FIGURE 6. Annual dry deposition of SO_2 in Great Britain (data for 1979) from U.K. and continental sources.

TABLE 6. LAND USE CLASSES AND DEPOSITION VELOCITIES USED TO PRODUCE FIGURE 6

(Annual average SO_2 concentrations for 1979 for each 20×20 km grid square were obtained from the work of Fisher (personal communication). Summer and winter values were taken as 0.8 and 1.2 of the mean annual values.)

land use	land use areas expressed as percentage of the area of Great Britain	v_g summer/mm s^{-1}	v_g winter/mm s^{-1}
urban	2.6	17.0	17.0
forest	5.9	4.0	2.0
arable	31.8	6.7	5.0
permanent grass	37.6	5.9	3.7
hill land	22.2	5.0	4.0

table 6 for forest, arable cropland and grassland are well supported by the literature but no measurements are available to define an appropriate r_c for urban areas. Hill-land has also been the subject of few measurements. Inputs by dry deposition may be compared with measured wet deposition (figure 7) and total deposition (figure 8).

The measurements of wet deposition are taken from Barrett *et al.* (1983). Inputs of sulphur

FIGURE 7. Annual measured wet deposition of sulphur (expressed as SO_2) in Great Britain (data for 1979) from the work of the U.K. review group on acid rain Barrett *et al.* (1983).

by dry deposition exceed measured wet deposition inputs in most of central southern and eastern England by a factor not less than 2, whereas in the high rainfall areas of northern and western England and Scotland inputs by wet deposition are larger than dry deposition. For the large rainfall areas of the west central highlands of Scotland where SO_2 concentrations are small, wet deposition inputs exceed dry for sulphur by a factor of 4. Inputs by occult deposition are not known but for upland forest could be large, more field measurements are needed.

More information is also required for the surface resistance of urban areas for SO_2, and more measurements of SO_2 deposition on to hill vegetation and rain wetted vegetation are also necessary. For HNO_3 and NO_2 more measurements over both short and tall vegetation are required to confirm the few data currently available.

The transfer resistances may also be used to deduce the dose of a pollutant gas into leaves (stomatal uptake) providing a measure of Pollutant Absorbed Dose (Fowler & Cape 1982). The use of this concept may provide a better estimate of dose for studies of the dose–response relation in vegetation where the current measure of dose is either the product of air concentration and time, or simply mean air concentration.

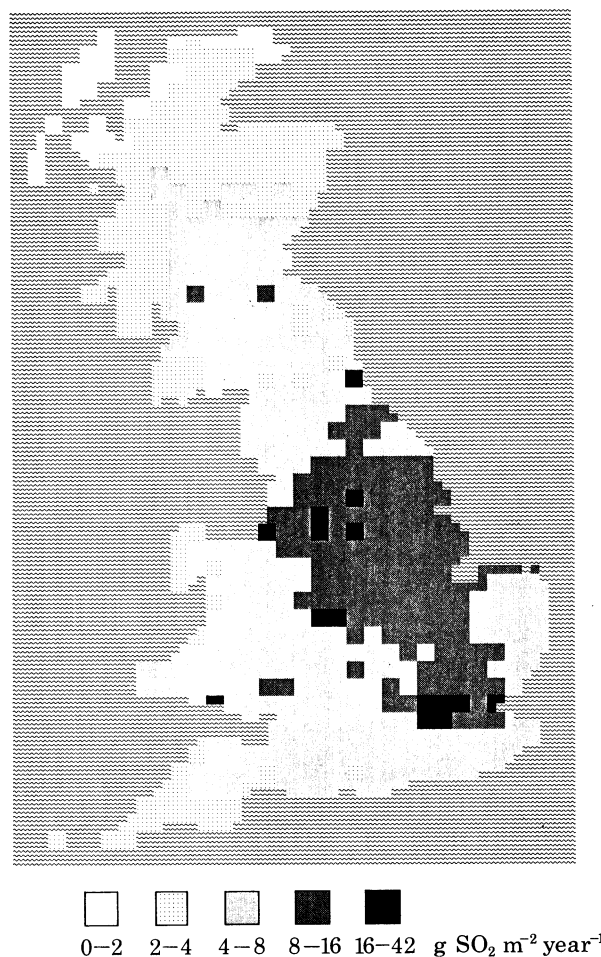0–2   2–4   4–8   8–16   16–42   g SO$_2$ m^{-2} year^{-1}

FIGURE 8. Annual total (wet and dry) deposition of sulphur in Great Britain from figures 6 and 7.

For wet deposition, the relation between altitude and rainfall composition is required. This may be confounded by properties of interception of fine rain and cloud (occult deposition) another important area for further field studies.

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Discussion

M. H. Unsworth (*Institute of Terrestrial Ecology, Bush Estate, Penicuik, Midlothian U.K.*). The existence or lack of proportionality between emissions from one area and total deposition in another must depend in a complex manner on the position and size of each area, atmospheric chemistry and physics, and the time of averaging. However, for dry deposition, which is the dominant input in southern Britain and industrialized Europe, I would expect proportionality between emissions and deposition, at least as an annual average? Such dry deposition, washed from vegetation by rain, could be an important contribution to acid episodes in soil and water.

$0-1$ $1-2$ $2-4$ $4-8$ >8 g SO_2 m^{-2} year^{-1}

FIGURE 6. Annual dry deposition of SO_2 in Great Britain (data for 1979) from U.K. and continental sources.
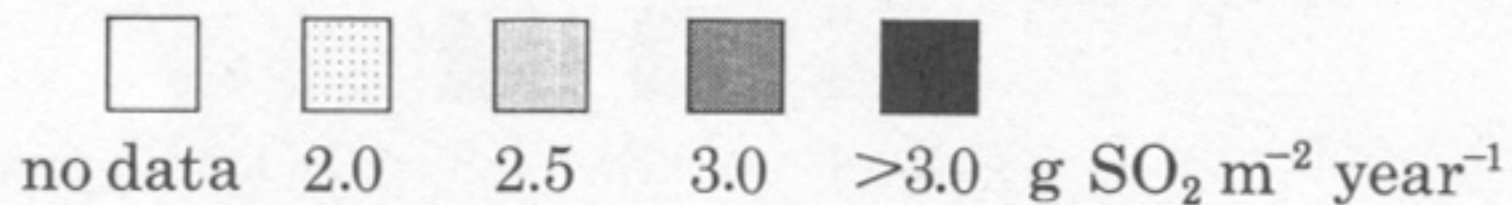
FIGURE 7. Annual measured wet deposition of sulphur (expressed as SO_2) in Great Britain (data for **1979**) from the work of the U.K. review group on acid rain Barrett *et al.* (1983).

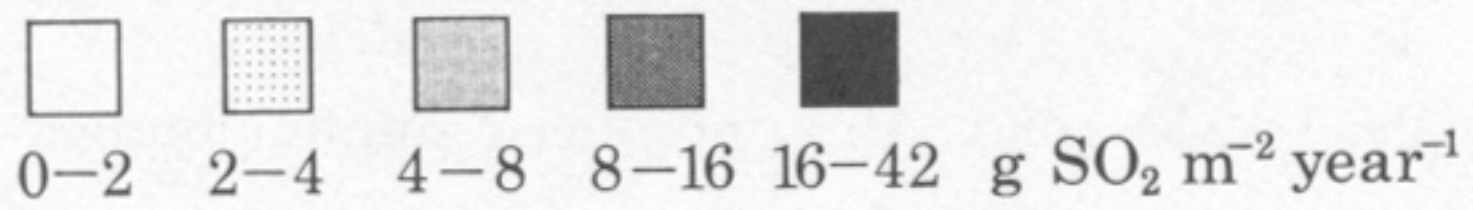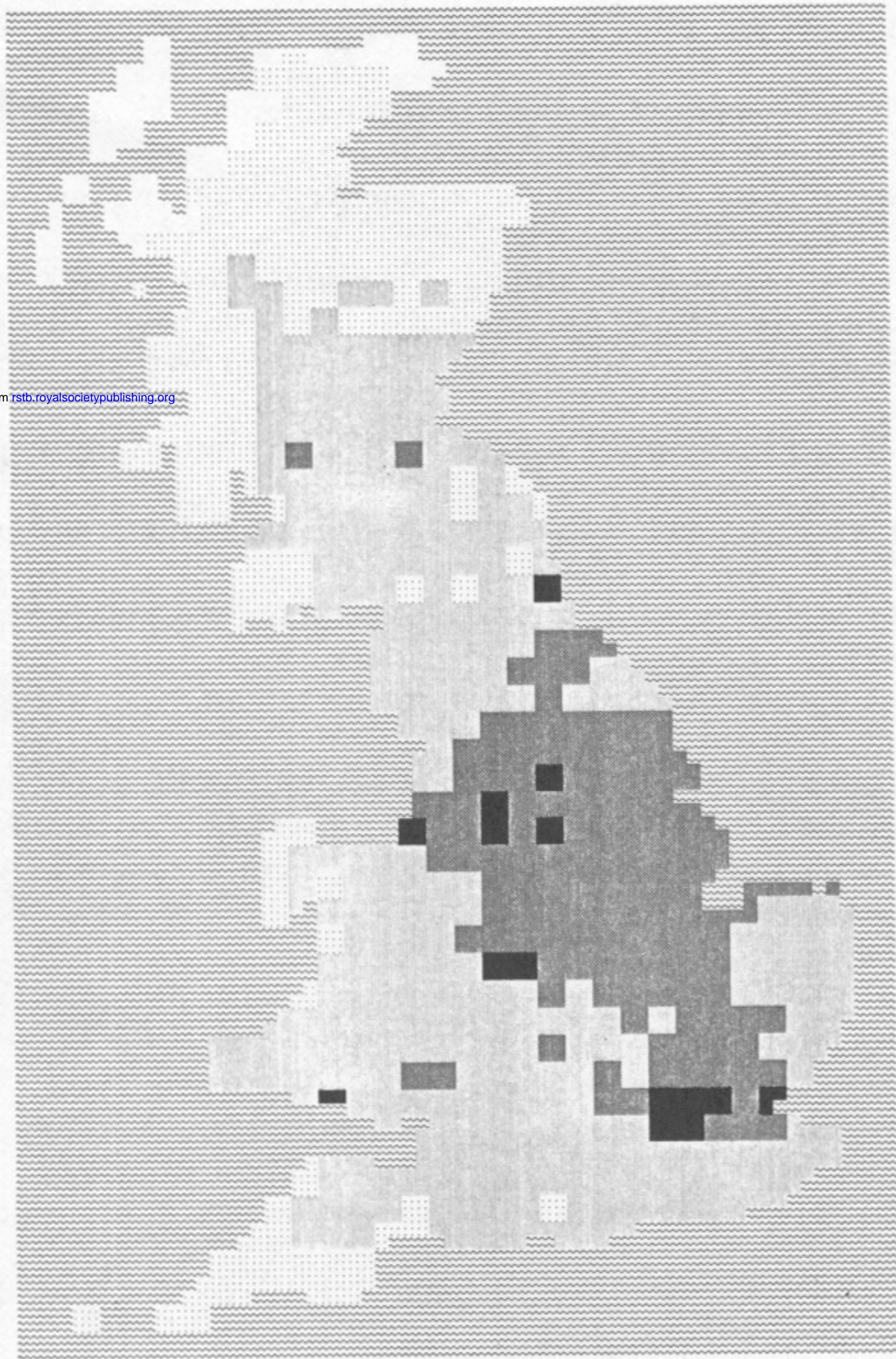0−2   2−4   4−8   8−16   16−42   g SO_2 m^{-2} $year^{-1}$

FIGURE 8. Annual total (wet and dry) deposition of sulphur in Great Britain from figures 6 and 7.