

The deposition of sulphur dioxide to pine forest assessed by a radioactive tracer method

By J. A. GARLAND and J. R. BRANSON, *Environmental and Medical Sciences Division, A.E.R.E., Harwell, Oxfordshire OX11 0RA, England*

(Manuscript received October 14, 1976; in final form February 21, 1977)

ABSTRACT

Pine shoots, twigs and bark were exposed to $^{35}\text{SO}_2$ in the field using a small exposure chamber. The rate of uptake by pine needles was found to be proportional to their conductivity for water vapour, indicating stomatal control of SO_2 exchange. Other live surfaces absorbed negligible amounts but considerable uptake occurred on dead twigs bearing lichen and algae.

The results were used to predict that the deposition velocity for SO_2 to a pine forest canopy varies from about 0.1 cm s^{-1} at night to a daytime maximum value of 0.6 cm s^{-1} . The rate of uptake may be an order of magnitude faster when the canopy is wet. Dry deposition of SO_2 is probably the major mechanism for sulphur input to forests in Europe.

1. Introduction

Outside the major industrial areas, European forests are exposed to SO_2 concentrations well below the levels which are thought to reduce growth rates directly. However it has been alleged (Swedish Ministries for Foreign Affairs and for Agriculture, 1971) that anthropogenic sulphur transported in the atmosphere reduces forest productivity indirectly. The mechanisms proposed include deterioration of the acid-base status of the soil with leaching of nutrients, and retardation of the decomposition and release of nutrients from litter on the forest floor. It is also claimed that acidification of surface waters by deposited sulphur compounds results in serious reductions in fish populations.

These effects probably depend on the total rate of deposition of sulphur, regardless of the initial site and mode of deposition, since almost all the sulphur must eventually reach the forest floor as sulphate. The rate of deposition in precipitation has frequently been measured (e.g. Stevenson, 1968; Junge & Werby, 1958; de Barry & Junge, 1963) but there is little information regarding the rate of dry deposition, that is the direct absorption of airborne particles and gases. Thus the total deposition rate is uncertain if dry deposition is significant.

Comparable concentrations of SO_2 and sulphate particles are found in the atmosphere, the particles predominantly in the submicron size range. Chamberlain (1966, 1968) studied the deposition of gases and particles. His results show that reactive gases may deposit much more rapidly than submicron particles. Thus dry deposition of SO_2 may make an important contribution to the sulphur budget of land and sea surfaces, though the sulphate aerosol is probably not deposited at a significant rate except in rain.

Garland (1974), Shepherd (1974), Fowler & Unsworth (1974) and other authors have measured SO_2 deposition rates in field experiments for several surfaces, but there have been few measurements over forest. The concentration gradient method, employed successfully over smoother surfaces, proved unsuccessful in a series of measurements over forest (Garland, 1974), although Petit et al. (1976) report a single measurement over a mixed forest. Martin & Barber (1975) measured several concentration profiles at a pine forest. The concentration gradient above the canopy was small and difficult to measure, although the concentration decreased substantially within the canopy. Unfortunately the interpretation of the gradient within the canopy is not straightforward but deposition velocities of about 2 cm s^{-1} appear to be indicated by the data. Belot et al. (1974)

measured uptake of SO_2 by pine and oak shoots exposed to high concentrations of SO_2 enriched in ^{34}S , and Belot estimated the deposition velocity to a forest canopy to be about 1 cm s^{-1} using the results.

In this paper a technique for exposing pine shoots to SO_2 labelled with radioactive ^{35}S is described. The technique allows rapid measurement of the rate of uptake by shoots several centimetres long, at SO_2 concentrations in the range found in polluted air in rural Britain. The results are used to estimate the rate of deposition to an entire pine canopy by analogy with water vapour transfer.

2. Method

Pine shoots were exposed to SO_2 in a cylindrical perspex chamber 6 cm long and 7.5 cm in diameter, divided along an axial plane. Soft silicone rubber gaskets were fitted to the meeting edges. The air was mixed and circulated within the chamber by a miniature fan in a duct at one end, and air containing $^{35}\text{SO}_2$ could be passed through the chamber using two ports entering this duct. The two half cylinders were mounted on a spring clamp arrangement which facilitated enclosure of a pine shoot.

For each measurement a shoot was prepared by cutting the needles from 1 or 2 cm of the stem, 4 or 5 cm from the end of the shoot. The soft gaskets on the exposure chamber could then make a close seal around the bare stem while enclosing the end of the shoot, complete with its remaining needles. As soon as the chamber was closed a flow of 1 l min^{-1} of compressed air containing up to $300 \mu\text{g m}^{-3}$ of SO_2 labelled with ^{35}S was passed through the chamber. The flow was maintained for 1 min, at the end of which the flow was stopped and the chamber was immediately removed from the shoot. Without delay the shoot was cut from the tree and stored in a plastic bag for later analysis.

The concentration, C , of $^{35}\text{SO}_2$ in the exposure chamber was determined several times during each series of measurements. For this purpose a known volume of air leaving the chamber was passed through a bubbler containing 10 ml of 1 volume hydrogen peroxide solution. Previous work has shown that this system is an efficient trap for SO_2 . The resulting solution was assessed by scintillation counting.

The $^{35}\text{SO}_2$ absorbed by each shoot was determined as follows. The needles were removed, counted and weighed. The total projected area, A , was determined from a previously established relationship between fresh needle weight and projected area. The needles were then oxidized by heating with nitric and perchloric acids until a few millilitres of a clear solution resulted. This was diluted to about 20 ml with distilled water and an aliquot taken for counting. In some cases the stem remaining after removal of the needles was treated similarly. Standard addition tests showed no significant quenching in the liquid scintillation counter.

The deposition velocity, v_N , for each shoot was calculated from the total activity in the needles, T :

$$v_N = \frac{T}{CA t}$$

where t was the duration of exposure.

Measurements on several shoots using exposure times from 1 to 6 min showed that v_N was independent of exposure time.

In some experiments the resistance for water vapour exchange was measured before the SO_2 exposure. This was achieved using a porometer chamber similar to the SO_2 exposure chamber, but made of cross-linked polystyrene and containing a sulphonated polystyrene humidity element. The shoot was enclosed in the chamber and the flow rate, V , of dry air required to maintain the relative humidity in the chamber at 50% was measured. Assuming the air and foliage to be at the same temperature, the conductance for water vapour transfer, v_w , was obtained from

$$v_w = \frac{V}{A}$$

This method was developed by Beardsall, Jarvis & Davidson (1972) and the chamber used with pine shoots was designed by Watts (1976).

3. Results

3.1. Variation of v_N for young needles with time of day and position in the canopy at Thetford Forest

Measurements were made at Thetford Forest, Norfolk, in a 45-year-old Scots pine stand, used in an extensive study of the micrometeorology of pine forest by the Institute of Hydrology. The trees are

about 20 m high and have a canopy 6 m deep. A tower within the stand gave access to the foliage of three trees. Measurements were made on 4 days in August 1975, taking material from three levels near the top, middle and bottom of the canopy. The weather was warm and bright on the mornings of

the 14th, 16th and 17th with cloud amounts increasing during each day. The 15th began wet, but brightened about midday and sampling was not started until the canopy had dried at mid-afternoon. Measurements were grouped into periods of about 1 h.

Table 1. Results of measurements of SO_2 deposition velocities v_N for needles of the current season on three trees

Date	Time	Level*	Tree A		Tree B		Tree C	
			Number of measurements	Mean v_N cm ⁻¹	Number of measurements	Mean v_N cm ⁻¹	Number of measurements	Mean v_N cm ⁻¹
14.8.75	1030	T	1	0.18	1	0.10	1	0.046
		M	1	0.13	1	0.13		
	1400	T	1	0.09	1	0.046	1	0.027
		M	1	0.044	1	0.029	1	0.034
	1630	T	1	0.06	1	0.038	1	0.018
15.8.75	1500	L	1	0.021	1	0.021		
		T	2		2	0.13		
		M			2	0.049		
	1730	L			2	0.045		
		T			3	0.053		
16.8.75	0830	M			3	0.017		
		L			2	0.011		
		T	1	0.10	2	0.10	1	0.08
	1130	M	2	0.051	2	0.10	1	0.046
		L			1	0.10	1	0.09
		T			2	0.07		
	1330	M			3	0.12		
		L			3	0.032		
		T			3	0.058		
	1630	M			3	0.044		
L				3	0.037			
T				2	0.045			
17.8.75	0900	M			3	0.033		
		L			3	0.018		
		T	1	0.11	2	0.08		
	1100	M	1	0.08	2	0.09		
		L			4	0.08		
		T			4	0.066		
	1300	M			4	0.062		
		L			2	0.045		
		T			3	0.049		
	1500	M			3	0.042		
		L			2	0.020		
		T			4	0.056		
	1800	M			3	0.021		
		L			2	0.029		
		T	1	0.041	2	0.053		
		M	1	0.048	3	0.026	1	0.024
		L			2	0.012		

* T signifies canopy top, M signifies mid-canopy, L signifies lower canopy.

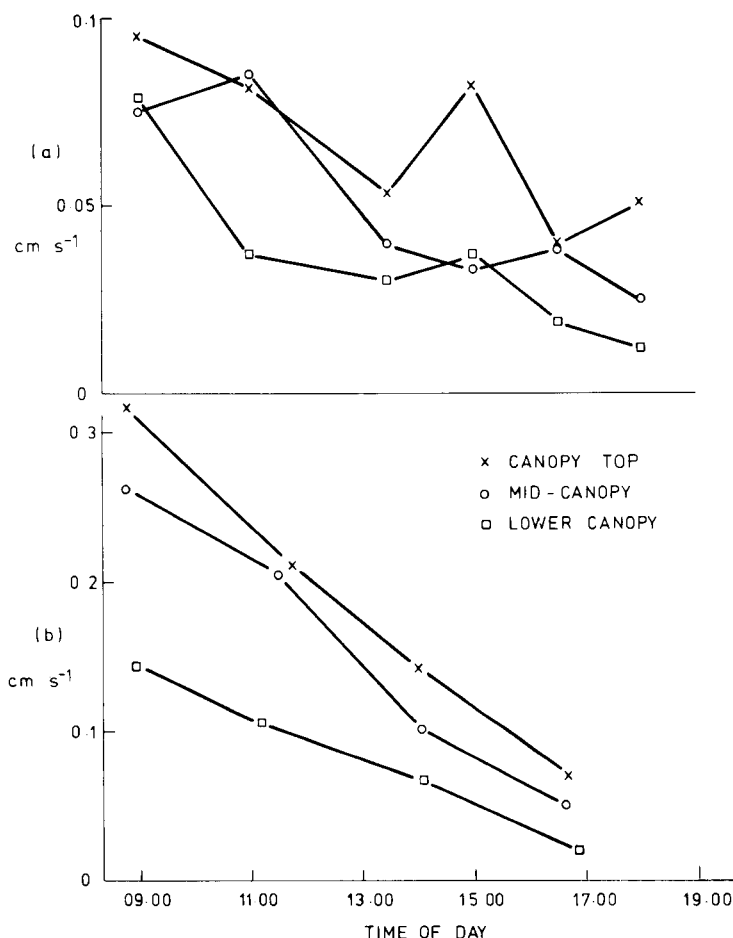


Fig. 1. The daily variation of pine needle conductance for (a) SO_2 and (b) water vapour at Thetford Forest.

Table 1 shows a summary of the results obtained with needles which had emerged during the spring of the same year. In Fig. 1, the values from each level are treated separately, values from all 4 days being grouped according to time of day and averaged to obtain a mean diurnal trend. The figure shows that v_N is generally higher at the top of the canopy than at the bottom. A similar variation of the conductance of shoots for water vapour with height and time was found by Watts (1976) in measurements made on August 16 and 17. The mean trend found in these measurements is also shown in Fig. 1. The similarity of the trend of water vapour and SO_2 conductances suggests that both are controlled by the same mechanism, viz. diffusion through the stomata.

3.2. Additional measurements at Thetford

Table 2 compares measurements of v_N for needles which had grown during the season when measurements were made, and those, located further down the shoot, from the previous season. In practically every case the older needles absorbed less SO_2 , on average by 38%.

Data from Table 1 can be used to compare v_N for young needles on three trees. Analysis of variance between readings obtained on seven occasions for the same level and period but on different trees shows that there is a significant difference between trees. The mean values of v_N for the three trees and for these occasions are in the ratio 1:0.77:0.48.

The trees at Thetford carry dead branches,

Table 2. Comparison of SO_2 deposition velocities, v_N , for needles of the current season (new) and the previous season (old)

Date	Time	Tree and level	New needles	Old needles		
			Number of measurements	Mean $v_N \text{ cm}^{-1}$	Number of measurements	Mean $v_N \text{ cm}^{-1}$
14.8.75	1030	A M	1	0.13	1	0.044
16.8.75	0830	A T	1	0.10	1	0.08
		B M	2	0.10	1	0.05
		B T	2	0.07	1	0.049
		B M	3	0.12	1	0.027
	1130	B L	3	0.032	1	0.023
		B L	3	0.037	1	0.030
		B T	2	0.045	2	0.036
		B M	3	0.033	1	0.022
	1330	B L	3	0.018	1	0.014
		BT	2	0.08	1	0.055
		B T	4	0.066	1	0.07
		B M	4	0.062	1	0.043
	1630	B T	3	0.049	1	0.048
		B M	3	0.042	1	0.024
		B L	2	0.020	1	0.013
		B M	3	0.021	1	0.017
17.8.75	0900	A M	1	0.048	1	0.028
	1800	A M	1			

located below the living canopy and supporting lichen and algae. A few such twigs were exposed to $^{35}\text{SO}_2$ to discover whether this material was a significant sink. Using the total surface area of stems, reckoned as cylinders about 0.5 cm diameter the value of v_N for this material was about 0.13 cm s^{-1} , comparable with the higher values for needles.

3.3. Measurements made at A.E.R.E., Harwell

In order to confirm the relationship between the exchange of SO_2 and water vapour, measurements were made in a small plantation of 10-year-old Scots pine at A.E.R.E. The water vapour conductance of each shoot was measured, using the technique described above, 1 or 2 min before exposure to $^{35}\text{SO}_2$. Needles of the current year's growth were used, and a wide range of conductance was observed by working at various times of the day and night.

The results (Fig. 2) show considerable scatter but the conductances for SO_2 and water vapour appear to be proportional. The mean ratio 1.98 is close to the ratio of diffusivities (2.1) indicating that the SO_2 uptake is indeed controlled by stomata. A similar conclusion was reached by Belot et al. (1974) for pine, and Spedding (1969) for barley.

Adsorption by the cuticle, or by traces of soil or other materials on the outer surface of the leaves can have played little part in SO_2 uptake, for linear regression analysis shows no significant intercept on the SO_2 conductance axis.

In a further experiment shoots were shaken for 1 min in distilled water after exposure to $^{35}\text{SO}_2$. The summary in Table 3 indicates that a large proportion of the absorbed sulphur can be removed if the washing is performed soon after exposure, but that little sulphur is accessible after a delay of some tens of minutes. Two explanations appear to be possible. The sulphur removed may be leached from epidermal cells, perhaps the guard cells, and may be converted to a less soluble form after exposure, or translocated to less accessible sites within the leaf. Alternatively, SO_2 may be reversibly adsorbed by the cuticle, and evaporate soon after the exposure. Such material would not have contributed to the permanently sorbed sulphur of Fig. 2, nor to the uptake of SO_2 by the forest.

Further experiments were performed to discover whether ^{35}S could be recovered from the stems of shoots exposed to $^{35}\text{SO}_2$. Such sulphur might have resulted from translocation from the leaves or from direct uptake by the surface of the stem. Nine

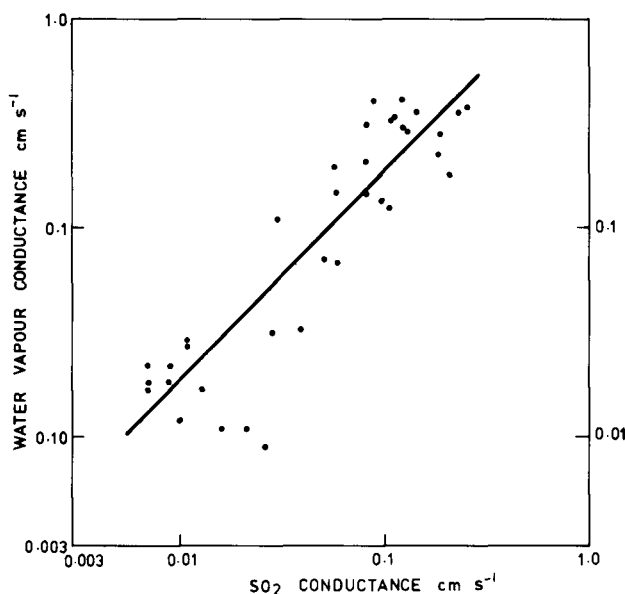


Fig. 2. The conductances for water vapour and for SO_2 measured on Scots pine shoots.

Table 3. *Effect of washing shoots after exposure to $^{35}\text{SO}_2$*

Number of shoots	Exposure conditions	v_N cm s^{-1}	Delay before washing (min)	Percentage ^{35}S removed
5	Daytime, RH = 81% overcast sky	0.02–0.03	20 to 280	4 to 9
3	Daytime, detached shoots with stems in water	0.07–0.23	0.05	70
11	Night, RH = 80%	0.016–0.03	2	20 to 50

shoots were exposed for times from 1 to 9 min. The shoots were culled and the needles removed from the stems promptly after exposure. The amount of activity associated with the stem was found to vary from 1% to 8% of that in the needles. The proportion did not increase with exposure time, as might have been expected had the activity reached the stem by translocation.

Finally, measurements were made of the rate of uptake by the bark of living branches and trunks. The results indicated deposition velocities of the order of $10^{-3} \text{ cm s}^{-1}$.

4. Deposition of SO_2 to a forest canopy

4.1. Deposition to a dry pine canopy

The deposition velocity to the complete forest canopy can be estimated using the measurements

of exchange rates for water vapour and the relationship established above between water vapour and SO_2 conductance. Stewart & Thom (1973) and Gash & Stewart (1975) discussed evaporation from the Thetford Forest canopy. They described the transfer process in terms of resistances to transport, being reciprocals of conductance. The resistances for processes acting in series are additive. For water vapour they distinguished resistances relating to

4.1.1. turbulent transfer from the chosen reference height z_R (20.5 m) to the effective height of the momentum sink,

$$r_A = \frac{u(z_R) \phi_V}{u_*^2 \phi_M}$$

where $u(z_R)$ is the windspeed at the reference height, u_* the friction velocity and ϕ_V and ϕ_M functions of the Richardson Number

reflecting the influence of temperature gradients on the transfer of vapour and momentum;

- 4.1.2. turbulent transfer between the heights of the effective sink for momentum, d , and the effective source for water vapour, c

$$r_H = \frac{d - c}{k u_* (h - d)} = - \frac{0.33}{u_*}$$

where k , ~ 0.4 , is von Karman's constant;

- 4.1.3. the "bluff body" effect introduced by Chamberlain (1966) and evaluated for forest by reference to Thom (1972):

$$r_B = 1.45 u_*^{-6/7} (3.0 u_*^{2/7} - 1)$$

- 4.1.4. the bulk physiological resistance, representing diffusion through stomata, r_s .

Thus the exchange velocity or canopy conductance

$$v(z) = \frac{E}{\chi(z) - \chi(0)} = r^{-1} = (r_A + r_H + r_B + r_s)^{-1}$$

where E is the flux to the forest per unit land area, $\chi(z_R)$ and $\chi(0)$ concentrations per unit volume of air of the diffusing material at height z_R and in equilibrium with the surface respectively. For water vapour $\chi(z_R)$ and $\chi(0)$ are identified with the absolute humidity at height z and the saturation absolute humidity at the effective mean leaf temperature. For SO_2 , $\chi(0)$ is taken to be zero, since the equivalence of water vapour and SO_2 transfer for pine shoots implies that the concentration of the gas within the substomatal cavities is zero.

The magnitudes of the resistances r_A to r_s for SO_2 will be estimated by reference to the values of Stewart & Thom (1973) and Gash & Stewart

(1975) for water vapour, based on measurements at Thetford Forest. The bulk physiological resistance is typically an order of magnitude larger than each of the other terms. Thus considerable variations in the magnitudes of the other terms are unimportant when estimates of the total resistance are required.

The turbulent exchange terms, r_A and r_H are expected to be equal for SO_2 and water vapour, subject to the assumption that the sinks of SO_2 and sources of water vapour are similarly distributed in the canopy. The evidence presented above, that SO_2 transport to leaves, like evaporation, is controlled by the stomata supports this assumption. SO_2 uptake by bark may reduce the effective height of the SO_2 sink, but the resulting change in r_H probably has a negligible effect on the total resistance. The bluff body and stomatal terms both depend on the molecular diffusion coefficient, and will be larger for SO_2 . The effect on the bluff body term has been calculated by reference to Thom (1972, eq. 15), while the bulk physiological resistance is expected to be inversely proportional to the diffusion coefficient as were the resistances for individual shoots (Fig. 2).

Table 4 shows typical values of the resistances for water transfer drawn from Stewart & Thom (1973) and Gash & Stewart (1975), and also the values deduced for SO_2 . No allowance has as yet been made for uptake on surfaces other than the pine needles.

The measurements reported above suggest that dead wood is a significant sink but that the surfaces of living branches and trunks are not. The contribution of dead wood in the canopy is not reflected in r_s since the surface does not contribute to transpiration, but may be represented by a

Table 4. *Typical daytime values of resistances to water vapour transport at Thetford forest, and corresponding values deduced for SO_2*

Term	Value for water vapour	Expected value for SO_2
$r_A \text{ s cm}^{-1}$	0.024 to 0.047	0.024 to 0.047
$r_H \text{ s cm}^{-1}$	-0.0027 to -0.0077	-0.0027 to -0.0077
$r_B \text{ s cm}^{-1}$	0.027 to 0.04	0.051 to 0.085
$r_s \text{ s cm}^{-1}$	0.7 to 2.4	1.5 to 5.0
$\Sigma r \text{ s cm}^{-1}$		1.6 to 5.1
$v_g = 1/r \text{ cm s}^{-1}$		0.6 to 0.2

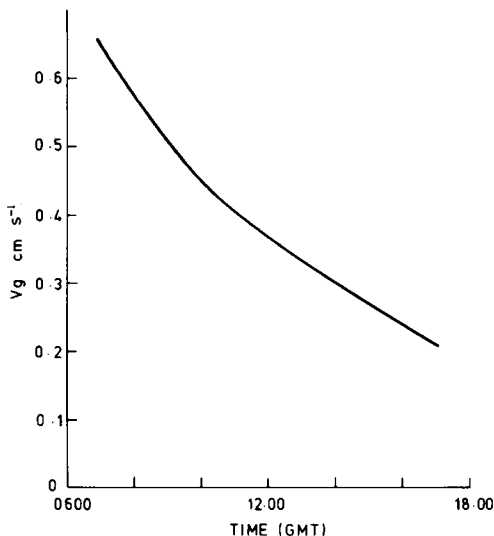


Fig. 3. The deposition velocity for SO_2 to a dry pine forest canopy predicted from typical water vapour transfer resistances due to Gash & Stewart (1975).

resistance r_p acting in parallel with r_s . The relative areas, uptake rates, and the depressed SO_2 concentration near the bottom of the canopy (Martin & Barber, 1975) suggest that r_p should be about $10r_s$ so that uptake by the dead wood should be of little consequence in daytime. Gash and Stewart show that there is a marked diurnal variation of r_s , but that values are not very sensitive to time of year. Thus the predicted diurnal variation of SO_2 deposition velocity for a dry pine canopy (Fig. 3) is expected to be typical of conditions in spring, summer or autumn.

The deposition velocity expected at night may be estimated using the observation that the nocturnal conductances for SO_2 measured at Harwell were about fifteen times smaller than the highest daytime values. Thus r_s at night is expected to rise to about 20 s cm^{-1} and limit the deposition velocity to 0.05 cm s^{-1} . If dead wood absorbs at night the total deposition velocity might be twice this value.

The deposition velocities for pine forest deduced above are smaller than the mean values for grass, soil and other surfaces (Garland, 1974), because of the large value of r_s . They are also smaller than the values suggested by the profile measurements of Martin & Barber (1975).

4.2. SO_2 deposition when the canopy is wet

The above experiments provide no information on the behaviour of SO_2 when the canopy is wetted

by rain or dew, and the following discussion is necessarily very speculative. The purpose is simply to indicate that uptake by intercepted water may have an important influence on deposition.

Stewart and Thom expect that for evaporation from a wet canopy r_s falls to zero, and give a value of $7.5/u$ for the remaining resistances. Values of u from 0.1 to 2.0 m s^{-1} must occur, so that deposition velocities in the range 1.27 to 27 cm s^{-1} should be expected on the assumption that the equivalence between SO_2 and water vapour exchange is maintained. However, deposition of SO_2 into the limited quantity of water supported by the canopy must soon result in equilibrium between the water and gas phases. (Rain water may already be in equilibrium when it reaches the canopy.) Thereafter the rate of uptake will be limited by the rate of oxidation of the resulting dissolved tetravalent sulphur species to sulphate. The oxidation process is known to be influenced by the presence of catalysts such as iron and manganese ions, and may be accelerated by the presence of ozone, but ultimately the oxidation reactions practically cease when the pH falls to the neighbourhood of 3.0. In consequence the final sulphate concentration in the water phase is 50 mg l^{-1} . However the concentrations may be increased somewhat if neutralizing cations can be leached from the foliage or supplied as ammonia by the atmosphere.

Pine canopies can intercept 1 mm or more of rainfall (e.g. Rutter, 1965) but the amount retained decreases during the drying period as a result of evaporation and drainage. In the absence of detailed knowledge of the chemical composition of the intercepted water the extent of absorption of SO_2 can be estimated only approximately, and for this purpose it is assumed that the mean quantity of intercepted water retained during the drying period is 1 mm. The uptake limit then amounts to 50 mg m^{-2} of sulphate following each episode of rain.

Such a limitation to the uptake of sulphur dioxide was found by Fowler & Unsworth (1974) when studying SO_2 uptake by a wheat crop bearing dew. Their results suggest that the surface resistance remained below 0.1 s cm^{-1} until the deposition was near its limit. A similar value of surface resistance would limit deposition velocity for the forest to 1 to 8 cm s^{-1} , depending on wind speed, and SO_2 concentrations of 17 to $130 \text{ } \mu\text{g m}^{-3}$ would be required to deposit the probable limit of 50 mg m^{-2} as sulphate if the canopy remained wet for 6 h. Such concentrations might exist over

forests in industrialized zones but are unlikely in the more remote areas of Europe. In lowland Britain rainfall exceeding 2.5 mm occurs typically on 100 days per year. A pine canopy retains approximately 1.5 mm and evaporation proceeds at roughly 0.1 mm h⁻¹ in winter or 0.3 mm h⁻¹ in summer (Rutter, 1966). Consequently intercepted water is present for 13% of the time in addition to the 7% for which rain is falling. Further, if dew occurs on half the nights without rain, the canopy may be wetted another 130 occasions per year amounting to some 10% of the time, making totals of 230 occasions per year, and 30%.

In such a regime the more rapid deposition to the wet canopy might result in deposition of 115 kg ha⁻¹ y⁻¹ as SO₂ where SO₂ concentrations are sufficient to reach the deposition limit on each occasion (say 50 µg m⁻³). Deposition during dry periods with mean deposition velocities of 0.3 cm s⁻¹ by day and 0.1 cm s⁻¹ by night would contribute 22 kg ha⁻¹ y⁻¹. Corresponding figures for a more remote area with a mean concentration ten times smaller might be 14 kg ha⁻¹ y⁻¹ in wet periods and 2.2 kg ha⁻¹ y⁻¹ in dry. The larger relative contribution in the second case arises because the limiting pH is not reached before the water evaporates. For comparison, rain deposits about 15 kg SO₂ ha⁻¹ y⁻¹ over southern England.

These values indicate the relative importance of dry deposition of SO₂ to the sulphur budget of forest, and the possible importance of deposition during periods when the canopy is wet. Further work by a method capable of use over a wet canopy is clearly desirable.

4.3. *Leaching from forest canopies*

It has been observed (Bjor et al., 1974; Bache, 1976) that increased quantities of sulphate reach the ground in the throughfall and stemflow below forest canopies, as compared with incident precipitation. Several workers have suggested that the additional sulphur represents dry deposited material mobilized by solution in rain water. Experiments reported above show that the sulphur taken up by needles in dry conditions rapidly becomes inaccessible, and that negligible amounts are absorbed by bark. Dead wood, however, may retain measurable amounts of sulphur, and Ulrich and co-workers (see Malmer, 1974, p. 70) have suggested that the increased acidity in throughfall can be attributed to this material. However, consideration of the magnitudes involved shows

that this mechanism can explain only a few per cent of the observed sulphur enrichment. Two possibilities remain, leaching from within the needles, or solution of sulphur previously accumulated on surfaces wetted by rain, fog or dew. The data of Bjor et al. indicate an additional 9 kg ha⁻¹ of sulphur as SO₂ in precipitation penetrating spruce and pine canopies during a period of 127 days, in an area (Birkenes, Norway) where the mean SO₂ concentration is about 5 µg m⁻³. Uptake on wet surfaces at such a concentration was estimated above at 14 kg ha⁻¹ y⁻¹. Similarly, the results of Bache show enrichment of 27 kg ha⁻¹ as SO₂ in 153 days where the mean concentration was 73 µg m⁻³. It is appropriate to compare this result with the prediction of 115 kg ha⁻¹ y⁻¹ derived above.

The differences between observation and prediction may arise from the uncertainties mentioned in Section 4.2 or from climatic variation and its influence on the frequency and duration of periods with water on the canopy. Thus it may be possible to account for the enrichment in terms of uptake of SO₂ on wet surfaces, but exchange with sulphur within the needles cannot be ruled out.

5. Conclusions

Measurements show that the uptake rate of SO₂ by pine needles at Thetford Forest varies in a similar manner to the water vapour conductance. The relationship between exchange of SO₂ and water vapour was confirmed by additional measurements at A.E.R.E., Harwell, which also showed that the conductances are in the ratio of the molecular diffusivities. The deposition velocity to a dry pine canopy deduced by analogy with transpiration, varies from 0.2 to 0.6 cm s⁻¹ during daytime. In the presence of intercepted water the deposition velocity may be an order of magnitude higher. The contribution of dry deposition to the rate of input of atmospheric sulphur to forest is probably comparable to or larger than deposition in precipitation, and the uncertain deposition rate to the wet canopy may be of great importance.

6. Acknowledgements

The authors wish to thank Professor P. Jarvis, Dr W. R. Watts and Dr I. Neilson for the design and supply of the exposure chamber and poro-

meter, and access to unpublished data. Thanks are also due to the Institute of Hydrology for access to the field site and for the use of field measurements,

and to Dr P. Robins for information on forest climatology. This work was funded by the Department of the Environment.

REFERENCES

- Beardsell, M. F., Jarvis, P. G. & Davidson, B. 1972. A null-balance diffusion porometer suitable for use with leaves of many shapes. *J. Appl. Ecol.* 9, 677–690.
- Belot, Y., Baille, A. & Delmas, J.-L. 1976. Modèle numérique de dispersion des polluants atmosphériques en présence de couvert végétal. *Atmos. Environment* 10, 89–98.
- Belot, Y., Bourreau, J. C., Dubois, M. L. & Pauly, C. S. 1974. Mesure de la vitesse de captation du dioxyde de soufre sur les feuilles des plantes au moyen du soufre 34 FAO/IAEA Isotope ratios as pollutant source and behaviour indicators 18–22 Nov. Vienna, Austria (IAEA-SM-191-18).
- Bjor, K., Hornvedt, R. & Joranger, E. 1974. *Distribution and chemical composition of precipitation in a southern Norway forest stand* (July–December 1972). Norwegian Council for Scientific and Industrial Research, Report 1/74.
- Bache, D. H. 1976. *Sulphur dioxide uptake and the leaching of sulphates from a pine forest*. SSD/MID/R12/76, Central Electricity Generating Board.
- Chamberlain, A. C. 1966. Transport of gases to and from grass and grass-like surfaces. *Proc. Roy. Soc. A* 290, 236–265.
- Chamberlain, A. C. 1967. Transport of lycopodium spores and other small particles to rough surfaces. *Proc. Roy. Soc. A* 296, 45–70.
- deBarry, E. & Junge, C. E. 1963. Distribution of sulphur and chlorine over Europe. *Tellus* 15, 370–381.
- Fowler, D. & Unsworth, M. H. 1974. Dry deposition of sulphur dioxide on wheat. *Nature* 249, 389–390.
- Garland, J. A. 1974. Dry deposition of SO₂ and other gases. Atomosphere-surface exchange of particulate and gaseous pollutants. Richland, Washington, Sept. 4–6 CONF 74092.
- Gash, J. H. & Stewart, J. B. 1975. The average surface resistance of a pine forest derived from Bowen ratio measurements. *Boundary-Layer Meteorol.* 8, 453–464.
- Junge, C. E. & Werby, R. T. 1958. The concentration of chloride, sodium, potassium, calcium and sulphate in rain over the United States. *J. Meteorol.* 15, 417–425.
- Malmer, N. 1974. *On the effects on water, soil and vegetation of an increasing atmospheric sulphur supply*. SNV PM 452E. National Swedish Environment Protection Board.
- Martin, A. & Barber, F. R. 1975. Exploratory measurements of the deposition of sulphur dioxide to a pine forest. SSD/MID.R. 44/75. (CEGB, Midlands Region, Ratcliffe on Soar, Nottingham.)
- Petit, C., Trinite, M. & Valentin, P. 1974. Study of turbulent diffusion above and within a forest application in the case of SO₂. *Atmos. Environment* 10, 1057–1063.
- Rutter, A. J. 1966. *An analysis of evaporation from a stand of Scots pine. International symposium on forest hydrology*. Pergamon Press, Oxford and New York.
- Shepherd, J. C. 1974. Measurements of the direct deposition of sulphur dioxide onto grass and water by the profile method. *Atmos. Environment* 8, 69–74.
- Spedding, D. J. 1969. Uptake of sulphur dioxide by barley plants at low sulphur dioxide concentrations. *Nature* 224, 1229–1231.
- Stevenson, C. M. 1968. An analysis of rainwater and air over the British Isles and Eire for the years 1959–1964. *Q. J. Roy. Met. Soc.* 94, 56–70.
- Stewart, J. B. & Thom, A. S. 1973. Energy budgets in pine forest. *Q. J. Roy. Met. Soc.* 154–170.
- Swedish Ministries for Foreign Affairs and for Agriculture 1971. Air pollution across national boundaries. The impact on the environment of sulphur in air and precipitation.
- Watts, W. R. 1976. Private communication.

ОСАЖДЕНИЕ ДВУОКИСИ СЕРЫ НА СОСНОВЫЙ ЛЕС ПО ДАННЫМ МЕТОДА РАДИОАКТИВНЫХ ТРАССЕРОВ

В небольшую экспозиционную камеру, содержащую ³⁵SO₂, помещались побеги, ветки и кора сосны. Скорость поглощения сосновыми иглами была найдена пропорциональной их проводимости для водяного пара, что указывает на stomатический контроль обмена SO₂. Другие поверхности живых тканей поглощали пренебрежимые количества, однако, значительное поглощение происходило на сухих сучьях, покрытых

лишайником и водорослями. Результаты использовались для получения оценки скорости поглощения SO₂ в сосновом лесу, изменяющейся от 0,1 см/с ночью до 0,6 см/с — максимальной величины днём. Скорость поглощения может быть на порядок величины больше, когда лес влажный. Сухое осаждение SO₂, вероятно, является главным механизмом ввода серы в леса в Европе.