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"Dew" as a sink for sulphur dioxide

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ABSTRACT

Calculations suggest that transfer of SO_2 into leaf wetness ("dew") is relatively rapid and it should remain in equilibrium with the atmosphere. The volume of leaf wetness appears to be insufficient to absorb more than 0.3% of the SO_2 emitted in the U.K. each year unless it is neutralized by alkaline materials such as ammonia. Analysis of leaf wetness in winter at a semi-rural site gave SO_4^{2-} as $1.06 \pm 0.56 \times 10^{-4}$ mol l^{-1} which places the maximum deposition into "dew" over the U.K. at 0.12 Mtonne yr^{-1} (2.3% of emissions).

1. Sulphur dioxide deposition

A link between dew and the removal of air pollutants was suggested as early as 1661 by John Evelyn. The evidence of increased rates of deposition on to wet vegetation in more recent studies appears to support this early observation (e.g. Fowler and Unsworth, 1974). However, a simple calculation seems sufficient to dismiss dew as a significant sink. The annual dew fall in the British Isles amounts to no more than half a centimetre a year (Monteith, 1957). This is a volume of about 8.5×10^{11} litres per year. At a mean atmospheric sulphur dioxide concentration of 28 μg m^{-3} (0.01 p.p.m.), the equilibrium level of sulphur(IV) in the dew at 5 °C would be 2×10^{-5} mol l^{-1}, thus accounting for no more than 1100 tonne of sulphur dioxide per annum. This paper examines the mechanisms through which dew and other forms of intercepted precipitation may act as sinks for atmospheric sulphur dioxide.

The importance of turbulent transfer of sulphur dioxide to the ground was emphasized by Meetham (1951). This work seemed to indicate that the absorption by vegetation and other surfaces was important as a mechanism for removal of sulphur dioxide from the atmosphere. Chamberlain (1960) showed that for vegetation to absorb the required amount of sulphur dioxide to account for the losses noted by Meetham in his observational data, it would need to be a very efficient sink. Spedding (1969) found that the rate of deposition of sulphur dioxide was considerably enhanced at high humidities. More recently Fowler and Unsworth (1974) showed that the flux rate of sulphur dioxide on to wheat increased under conditions where dew had fallen, implicating water in a more direct way. Their field trials suggested that dew had a limited capacity to absorb sulphur dioxide. After some hours the rate of uptake by dew-covered vegetation decreases, a phenomenon which they attributed to a decrease in the pH of the dew, although they were not able to give pH measurements for the dewfall. The available measurements of deposition velocity (V_g) of sulphur dioxide over continental surfaces are summarized in Table 1. It is important to note that some results are capable of accounting for the removal of a large amount of the sulphur dioxide released in the British Isles each year, e.g. Garland et al. (1973) suggest as much as 40% is removed by vegetation.

2. Leaf wetness

Serious observations of dew probably began with Well's classic essay (1814). Monteith (1963) has suggested that much of the work since then has been nearer the realms of poetry than of science. Visual observations suggest that dew may be found some hundred mornings a year in south-east England (Drummond, 1945). Monteith (1963) has

Table 1. *Deposition rates of sulphur dioxide on to continental surfaces*

Authors	Year	Surface	V_g/m s^{-1} × 10^3
Always et al.	1937	Soil	1.5
Chamberlain	1960	Calculated for U.K.	18
Spedding	1969	Barley (lab.)	10
Garland et al.	1973	Grass (field)	8.5
Garland et al.	1974	Grass (field)	5.5
Fowler and Unsworth	1974	Wheat (field)	3.6
Hill and Chamberlain	1974	Alfalfa	28.3
Owers and Powell	1974	Grass	8
Whelpdale and Shaw	1974	Grass	24 (lapse) 26 (neutral) 5 (stable)
Shepherd	1974	Grass	8

Table 2. *Parameters of dew and guttation for a 0.5 mm "fall"*

	Dew	Guttation	Units
Droplet radius, r	0.3	1.0	m × 10^3
Droplet area, A	1.13	12.57	m^2 × 10^6
Droplet volume, V	1.13	41.9	m^3 × 10^{10}
Number of droplets per square metre	4.4	0.12	m^{-2} × 10^{-6}
Area of droplets per square metre	5.0	1.5	dimensionless
Half times for SO_2 transfer within the drop	2.8	30	s

shown that the maximum rate of dewfall is 0.067 mm hr^{-1} over a wide temperature range, although the actual rate of dewfall depends on both the humidity and wind speed, and will always be less than this maximum. Dew may also form by the transfer of water vapour from the soil to the leaf surface through the sub-foliar air in a process termed "distillation" (Monteith, 1957).

Two other processes commonly wet vegetation: interception of precipitation and guttation. The result is not dew, but may act in a similar fashion with respect to the absorption of sulphur dioxide. The quantity of water intercepted by grasses which might represent typical ground cover is about 0.5 × 10^{-3} m (Clarke, 1940; Merriam, 1961). Guttation is an exudate of plants found under conditions of high humidity. It is frequently mistaken for dew and pointers for its recognition are given by Long (1958), e.g. the size difference (see Table 2). The overall effect of all these phenomena is to wet the plant surfaces and as all the forms of *leaf wetness* are likely to be of importance when considering plant deposition of sulphur dioxide on to vegetation this term will be used rather than the more specific term *dew*. Two extreme geometric forms of leaf wetness can be imagined:

(i) Leaves completely wetted by the water being spread in a thin film over the vegetation. Here 0.5 × 10^{-3} m of precipitation would be spread to a thickness of 6.25 × 10^{-5} m assuming the vegetation area eight times that of the ground (Spedding, 1969).

(ii) Liquid present as spherical droplets on non-wettable cuticle (Martin and Juniper, 1970).

3. Transfer of SO_2 into leaf wetness

The rate of transfer of sulphur dioxide into aqueous solution has been examined theoretically

Table 3. *Comparison between experimental and predicted results, assuming a 0.5 × 10^{-3} m dew-fall, and a sulphur dioxide level of 31 μg m^{-3}*

	Experimental values from Fowler et al. 1974	Predicted values into 0.5 mm leaf wetness
Amount of sulphur dioxide deposited	6800 μg m^{-2}	720 μg m^{-2}
pH resulting from this amount of dissolved sulphur dioxide	3.67	4.71
pH on oxidation to sulphur(IV)	3.37	4.41
Time to reach 50% of the total deposition	6 hours	50 minutes

Table 4. *Constants used in the calculations*

Constant	Symbol	25°	5°	Units	Source
$H_2O \cdot SO_2$ Dissociation const.	K'	0.0129	0.02	mol l^{-1}	Johnstone and Leppla (1934)
Henry's Law const. for SO_2	K_H	1.24	2.0	mol l^{-1} atm^{-1}	McKay (1971) Linke (1965)
Aqueous diffusion const.	D	1.8	0.99	m^2 s^{-1} × 10^9	Brocker and Peng (1974)

by Liss (1971) and is in good agreement with experimental observations (Brimblecombe and Spedding, 1972). In alkaline solution the rate of dissolution of the gas is controlled by turbulent transfer to the interface, while in acidic solution it is controlled by the slower transfer across the liquid boundary layer. At intermediate pH values it is possible to observe dissolution controlled by processes in both the gas and liquid boundary layer. The alkaline nature of ocean water has allowed an assumption of gas phase control of sulphur dioxide dissolution to be made when considering the importance of the oceans as a sink for this gas. The same simplification cannot necessarily be made for the dissolution of the gas in leaf water which is likely to be more acidic. The leaf water will be almost non-turbulent in contrast to the ocean surface and any "boundary layer" will be comparable with the size of the droplet. The droplets are of such low volume (1–4 μl) that dissolving sulphur dioxide will cause the liquid to become saturated quite quickly. The temperature will be different from those normally encountered and is likely to be quite low particularly for dew. In this paper the calculations have all been done for a temperature of 5°, the equilibrium constants used at this low temperature are compared with the higher temperature values in Table 4.

In many gas–liquid transfer problems the liquid phase transfer is the rate-determining step, because of the slower diffusion rates found in liquids. This is not the case for gases of high solubility, i.e. sulphur dioxide in alkaline solution, where rapid hydration causes steep concentration gradients which enhance the transport of sulphur(IV) species. In acidic solution the transport does become limited by the slow liquid diffusion coefficients, although if the distances through which the species must be transported are small then even under acidic conditions the liquid phase transport may not necessarily be the limiting step.

The approximately spherical droplets (radius, r) on leaf surfaces will approach saturation according to the equation (Crank, 1975)

$$\alpha = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2 t/r^2) \qquad (1)$$

where α is the ratio of sulphur(IV) concentration in the solution at time t, to the amount of sulphur(IV) in a saturated solution. This assumes that the

surface of the droplet remains saturated at all times by the rapid transfer of material to the droplet surface and that the rate of hydration within the droplet is rapid. The diffusion coefficient (D) is taken as being the same for all the sulphur(IV) species in solution (see Table 4). The series was summed on a computer and the times required for droplets of various radii to reach 50% saturation are given in the bottom row of Table 2. Even for the largest droplet (1 mm) the transport within the droplet is quite rapid, but the time scales are very slow compared with the hydration rates (microseconds, Liss (1971)) justifying the assumption that hydration was fast. The case of the leaf wetness being spread as a thin film can be approximated by semi-infinite diffusion and represented by (Crank, 1975)

$$M_t = 2S(IV)_{sat.}(Dt/\pi)^{1/2} \quad (2)$$

where M_t is the mass transferred to the film after time t. For a film 6.25×10^{-5} m thick 0.77 s would be required to achieve 50% saturation, not greatly different from the times required to reach the same degree of saturation in spherical droplets.

The transfer of trace gases to vegetation surfaces can be seen slower than this. At times when leaf wetness is present for significant periods the wind velocity is likely to be comparatively low, so the aerodynamic resistance will be fairly high. For instance when the vegetation was wet Fowler and Unsworth (1974) found a mean resistance of 140 s m^{-1}. Assuming that the surface resistance (r_c) remains small (i.e. conditions that ensure the maximum possible rate of deposition), then the resistance and amount of material deposited are related by the equation (Chamberlain, 1960)

$$v_g = 1/r_a = W/Ct \quad (\text{assume } r_a \sim 200 \text{ s m}^{-1})$$

where V_g is the deposition velocity,

W the amount of SO_2 deposited in time t,

C the atmospheric SO_2 concentration.

As leaf wetness amounts to 0.5×10^{-3} m, an initial pH of 5.5 and an atmospheric concentration (C) of 28 μg m^{-3} requires 600 μg of sulphur dioxide to saturate the wetness on a square metre of the ground. From the above equation the time required to reach 50% saturation in the absence of surface resistance would be 2100 s (less than 40 min). This process is evidently slower than the transfer processes within the leaf wetness, so in a qualitative sense the calculations agree with the observations of Fowler and Unsworth (1974); the surface resistance is very small when vegetation is wet, sulphur dioxide transfer being controlled by turbulent transfer of the gas to the vegetation.

4. Capacity of leaf wetness for SO_2 absorption

The diffusive process within the droplet are so fast over the small distances involved that it must have an almost constant concentration throughout. Initially the transfer of sulphur dioxide into leaf wetness will be determined by the aerodynamic resistance of the air above the plant cover. As has already been shown, even here the transfer rates are relatively fast and that the droplets should approach saturation quite quickly (40 min). In terms of the field experiments, this means that there should be a rise in the surface resistance (r_c). If there is no oxidation then the flux of sulphur dioxide into the droplet will decrease in a first-order manner as it becomes saturated with sulphur(IV) species. The flux of sulphur dioxide into the leaf wetness while beginning at a high rate as determined in the previous section will decrease exponentially with a half life of 3000 s (50 min). Rapid saturation of the leaf water should mean that an almost negligible surface resistance (r_c) should persist for only a short time. However, this is in strong contrast to the results of Fowler and Unsworth (1974) under conditions where the vegetation was wet (see Table 3).

The surface resistance remains low for a period of some 9 h. In their results 6800 μg of sulphur dioxide is deposited on the crops over the night (1500 hours to 0900 hours the following day) which would make 0.5×10^{-3} m of leaf wetness 2.1×10^{-4} M in sulphur(IV), when saturation at the 31 μg m^{-3} sulphur dioxide concentration measured, would be about 1.95×10^{-5} M in sulphur(IV). Under equilibrium conditions about 5×10^{-3} m of leaf wetness would be required, which represents an excessively heavy dew fall.

An increase in capacity of the leaf wetness must be postulated if such experimental data are to be accepted. The increase in absorption capacity for sulphur dioxide could be accomplished by simply increasing the volume of water available on the leaves or by introducing some alkaline or buffering

material. The first explanation would meet objections from the point of view of the energy balance calculations, Monteith (1973), which show the rate of dew formation must be slow.

The introduction of alkaline materials on to the leaf surfaces would be a satisfactory method of increasing the capacity, but there is very little information available in the literature to suggest how much alkali might be expected. There are three fairly obvious sources of such material: (i) Alkaline particulate material on the leaf, such as soluble oxides, hydroxides or carbonates, which might arise from the air or short-range transport of soil particles (Brimblecombe and Todd, 1977). (ii) Ammonia has frequently been invoked as a neutralizing agent to increase the capacity of aqueous aerosols to absorb sulphur dioxide (e.g. Scott and Hobbs, 1967). The ammonia concentrations could be quite high so close to the soil where decaying organic material is a potential source of ammonia. Velbel (1903) found high ammonium concentrations in dew (3×10^{-4} mol l^{-1}) compared with the concentrations found in precipitation (0.6×10^{-4} mol l^{-1}). If all this ammonia were assumed to originate as a gas in the sub-foliar air, then it would have sufficient alkalinity to maintain a high rate of sulphur dioxide transfer to the leaf wetness for a long period of time. (iii) Finally there is the possibility that alkaline or buffering materials originate from the plant itself. Leaves are known to respond to acidic conditions by losing calcium (Fairfax and Lepp, 1975) which would effectively remove hydrogen ions from the leaf wetness. The plant would then have to replace this calcium by active transport from the soil. Alternatively the leaf may absorb sulphur dioxide from the leaf wetness. Although these mechanisms are feasible, little is known of the quantities or rates of transport involved, which allows only crude calculations to be made of the possible effects of alkaline material.

5. Conclusions

In the absence of alkaline materials (or rapid uptake of sulphur by the leaf) the controls on uptake by leaf wetness appear to be thermodynamic rather than kinetic, as the transfer times are short (about an hour) compared with the typical duration of leaf wetness (many hours). The water has enough time to come to equilibrium with the atmosphere which means that the deposition is controlled by the capacity of the solvent to absorb sulphur dioxide rather than the faster transfer processes. The fact that dew has a very low volume has already been noted, but other forms of leaf wetness make more significant contributions. If oxidation occurs, the fact that they largely re-evaporate will not be important. Any unoxidized sulphur dioxide within the leaf wetness will be released into the atmosphere on evaporation. If the sulphur dioxide were largely unoxidized and evaporation rapid (about $\frac{1}{2}$ hour) then the vertical gradient of sulphur dioxide set up by this flux would be of the same magnitude as those found during deposition, but in the opposite direction. If one assumes two hundred leaf wetting events per year and that each one contributed 0.5×10^{-3} m of precipitation at pH 5.5 one could expect this to absorb 0.12 g m^{-2} yr^{-1} in equilibrium with sulphur dioxide at 28 μg m^{-3}. That would amount to about 2×10^4 tonnes over the U.K. This represents an upper limit in the absence of alkaline materials as it does not allow for residual amounts of acid which would be left on the leaf after small showers. The presence of alkaline material at 3×10^{-4} eq. l^{-1} from any of the sources discussed would increase the absorption (as S(VI)) by an extra 1.0 g m^{-2} yr^{-1}. This would be about 0.18 Mtonne, a significant, but not large fraction of the 5 Mtonne releases that occur in the U.K. at present.

These theoretical calculations may be compared with some analyses of samples of leaf wetness collected in the late autumn and winter of 1976 at a relatively unpolluted semi-rural site on the outskirts of Norwich, England. Large samples (greater than 10 ml) were collected from the grass (mainly of genus *Poa*) and analysed for sulphate concentration on a Technicon Auto Analyser using Persson's method (1966). The mean sulphate concentration from 27 samples was found to be 1.06×10^{-4} mol l^{-1} (standard deviation 0.56×10^{-4} mol l^{-1}; range 0.44–2.77×10^{-4} mol l^{-1}; *median* value 0.88×10^{-4} mol l^{-1}). As dew contains a large proportion of plant-derived ions (Brimblecombe and Todd, 1977) and sulphate appears to be readily leached from leaves (Raybould et al., 1977) the value represents an upper limit to the amount of sulphate deposited in leaf wetness. If all the sulphate found in the samples had been deposited as sulphur dioxide this would

represent 0.12 Mtonne yr^{-1} over the U.K. assuming 200 leaf wetness events in the year.

While this quantity of sulphur dioxide may represent only 2.4% of the total emissions, precipitation and leaf wetness must be responsible for removing the large amount of sulphur that is deposited on plant surfaces by other mechanisms. Meetham (1951) suggested that 40% of the sulphur was transferred to the ground in the U.K. by dry deposition. A megatonne of sulphur deposited annually over England would mean some 10 g to every square metre per year. Assuming leaf area to be about eight times the ground area, the rate of sulphur deposition would represent some 50 μmol per year on a small grass blade. The amount of deposited sulphur(IV) would be the equivalent of almost a milligramme of calcium per leaf if it were required for neutralization. Despite the fact that surface wetness may not act as a significant sink for sulphur dioxide it is evident that both leaf wetness and alkaline materials on the plant surface are potentially very important in controlling the surface pH and hence the loss of cations from plant leaves in industrialized countries.

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"РОСА" КАК СТОК ДЛЯ ДВУОКИСИ СЕРЫ

Расчеты показывают, что перенос SO_2 во влагу листьев, "росу", сравнительно быстрый процесс и должен оставаться в равновесии с атмосферой. Представляется, что объем влаги на листьях недостаточен, чтобы поглощать более 0,3% SO_2, выпускаемого ежегодно в воздух в Соединенном королевстве (СК), если только он не нейтрализуется щелочными веществами, такими, как аммиак. Анализ влажности листьев зимой в полусельской местности дает концентрацию SO_4^{2-} в количестве $(1{,}06 \pm 0{,}56) \cdot 10^{-4}$ моль/литр, что дает максимальное осаждение SO_2 в росу в СК в размере 0,12 мегатонны в год (2,3% от эмиссии).