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LONG TERM MEASUREMENTS OF SO_2 DRY DEPOSITION OVER VEGETATION AND SOIL AND COMPARISONS WITH MODELS

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Abstract

A semi-continuous series of measurements of SO_2 fluxes above soil, wheat and sugar beet has been used to quantify the major components of canopy and surface resistance in a wide range of conditions. The data show that over dry cereal canopy, the marked diurnal cycle in canopy resistance is regulated primarily by changes in stomatal resistance. Good agreement between a process based model of SO_2 deposition and the field data in dry conditions has been obtained. For a dew and rain wetted crop, the canopy resistance is decreased from 80 s m^{-1} to 55 s m^{-1}. Long-term (4 month) median deposition velocity (V_d) was 7.2 mm s^{-1} for wheat. For sugar beet, similar results are obtained with median V_d of 5.7 mm s^{-1}. There is also a clear dependence of r_c on SO_2 concentration with r_c decreasing from ~ 100 s m^{-1} at 4 μg m^{-3} SO_2 to 40 s m^{-1} at 20 μg m^{-3} for both crops. For bare soil, canopy r_c is small with a median value of 15 s m^{-1} for dry soil and 5 s m^{-1} for wet soil.

The widespread assumption of very small r_c for wet surfaces is clearly an over-simplification in current models. The influence of these new findings for annual dry deposition estimates will be discussed.

For both crop surfaces v_d increased in the presence of surface water for dew precipitation by typically 30%. The increased affinity of wet leaf surfaces for SO_2 uptake was equivalent to a 40% decrease in the canopy resistance r_c.

INTRODUCTION

The turbulent deposition of SO_2 to terrestrial surfaces represents the major removal process for boundary layer SO_2 over large areas of Europe. Even in the high rainfall regions dry deposition may contribute 20-30% of deposited sulphur. While wet deposition is routinely monitored throughout Europe and North America to provide estimates of wet deposition, the majority of countries rely on simple parameterization of dry deposition using monitored SO_2 concentrations and deposition velocities from the literature. In North America, the dry deposition monitoring network is in fact a series of monitoring stations for meteorological variables and SO_2 concentration for which deposition rates are inferred, the measurements do not provide flux to the surface directly.

Our understanding of dry deposition process in the field was provided by micrometeorological studies of fluxes of SO_2 to natural surfaces. The early work in the 1970's by Garland (1977) and Fowler and Unsworth (1979) amongst others, quantified the relative importance of surface and atmospheric processes in regulating deposition rates for a range of natural surfaces and atmospheric conditions. These analyses have been extended to provide annual dry deposition estimates on the basis of multiple resistance models Hicks *et al.* (1987), and similar approaches have been widely applied to estimate annual SO_2 inputs to catchments, regions or countries (Fowler, 1980; RGAR, 1990).

Although it was widely considered that rates of dry deposition could not be continuously monitored the recent work by Erisman *et al.* (1993) shows that instrumentation has developed to a point where simple flux-gradient approaches may be used to estimate dry deposition continuously at sites suitable for application of micrometeorological methods. The measurements by Erisman *et al.* demonstrated the importance of surface water on foliage on rates of SO_2 deposition and provide an excellent basis for the temporal extrapolation of fluxes from measured SO_2 concentration fields with appropriate meteorological and land use information.

This paper describes an SO_2 flux measurement station for continuous operation and reports results of a year of measurements of fluxes at an agricultural site in the English Midlands. The results are used to demonstrate the relative importance of different sinks at the terrestrial surfaces in a range of conditions, and the results of measurements are compared with model estimates.

THEORY AND METHODS

The measurements were made at a field site in arable agricultural land close to Sutton Bonington, a University of Nottingham field station. The equipment was placed close to a field boundary and provided a fetch of between 200 and 300 m in most wind directions, excepting the 45° sector centred on 180° within which an instrumentation cabin was placed to house the monitoring and logging equipment. The site provided winter wheat, bare soil and sugar beet according to sector and time of the year during the measurement period of April 1993 until June 1994.

Concentrations of SO_2 were monitored using a high sensitivity pulsed fluorescence monitor (TECO 43S) which sampled filtered air along heated sample lines at two heights in the surface layer and up to a height of 2.3 m. Wind speeds were measured at three heights and air temperature at two heights using sensitive cup-anemometers (Vector Instruments) and miniature thermocouples (Campbell Scientific) respectively. Precipitation, surface wetness, wind direction and total radiation were also monitored continuously at the site. All of the instrumentation was controlled and logged using a Campbell 21X micrologger. In addition to the long-term continuous measurements, 2 campaigns each of 2 weeks duration of measurement at the site were also made using a 5-point gradient system for SO_2, temperature and windspeed and a Campbell instruments Bowen ratio system.

The field data were analysed to provide fluxes of SO_2 (F_x) calculated from

$$F_\chi = -k^2 \frac{du}{d\ln(z-d)} \frac{d\chi}{d\ln(z-d)} (\phi_m \phi_h)^{-1}$$

where k is Von Karmans constant, u is windspeed, z height, χ is SO_2 concentration, d the zero place displacement and $(\phi_m\phi_h)^{-1}$ is a stability factor to correct fluxes for the effects of thermal stratification of the surface layers of the atmosphere. A detailed account of the standard micrometeorological theory is outside the scope of this short paper and may be found in Thom (1976) or Monteith & Unsworth (1990).

The sequential sampling system provided a measure of vertical gradients during periods with constant SO_2 concentration. However, non-stationarity in SO_2 concentration introduced an important source of uncertainty in the sequential sampling system, and contributed an average of 18% of the uncertainties in V_d. To overcome these effects the results were detrended and running median values were obtained for SO_2 concentration (χ), deposition velocity (V_d), the flux F_χ and r_c with a time constant of 3 hours.

For the continuous monitoring of fluxes there are a range of conditions which result in erroneous fluxes. It was necessary therefore to filter out data obtained when the wind direction was within the sector occupied by the instrument cabin, when atmospheric stability effects were too large to be corrected by standard approaches, and in this case data were rejected when Monin-Obukhov lengths were < 5m. For periods during which SO_2 concentration changed rapidly, non-stationarity effects were important, but these also provided important data for the investigation of processes and whenever possible, corrections to the data set to overcome sequential sampling errors were made and the data were accepted.

SO_2 concentrations at the site

The half-hour mean values of SO_2 concentrations for one year of monitoring are, as is usual, log normally distributed. The mean concentration is 12.8 μg m^{-3}, geometric mean 6.1 μg m^{-3} and geometric standard deviation is 3.5 as shown in Fig. 1. There is a clear diurnal cycle in SO_2 concentration at the site with a minimum at 0300 GMT and maximum at 1300 GMT. Similarly, windspeed shows a marked diurnal cycle with a minimum at 0500 GMT and a maximum at 1400

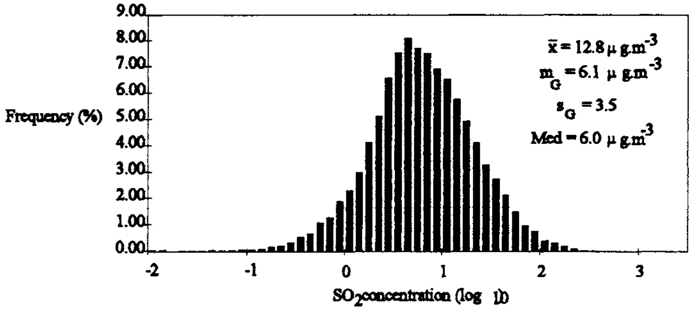

Figure 1. The log-normal distribution of SO_2 concentrations (April 1993 - April 1994).

GMT. The SO_2 data show a pronounced sector dependence with concentrations being largest (~ 15 $\mu g\ m^{-3}$) with northerly winds and smallest with southerly winds ~ 5 $\mu g\ m^{-3}$, as shown in Fig. 2.

The measurements of SO_2 deposition may be divided into three groups, according to the surfaces present during the year within the upwind fetch, as wheat, sugar beet and bare soil.

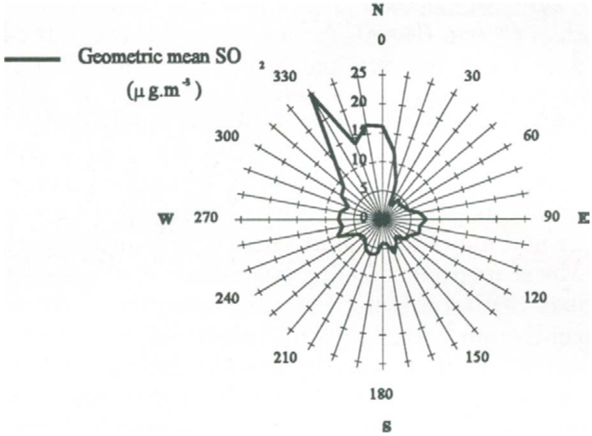

Figure 2. Wind sector dependence of sulphur dioxide air concentrations at Sutton Bonington (April 1993 - April 1994).

Dry deposition on to wheat

The measurements over winter wheat were made during the period April-July 1993 during which the canopy height and leaf area index increased from 30cm to ~100cm and 1.5 to 4.5 respectively.

Considering the whole data set for the period, the median of the population of hourly average data for deposition velocity was 7.2 mm s^{-1} whereas that of the maximum rates of deposition (V_{max}) possible was 17.1 mm s^{-1} showing that canopy resistance exerted a major control

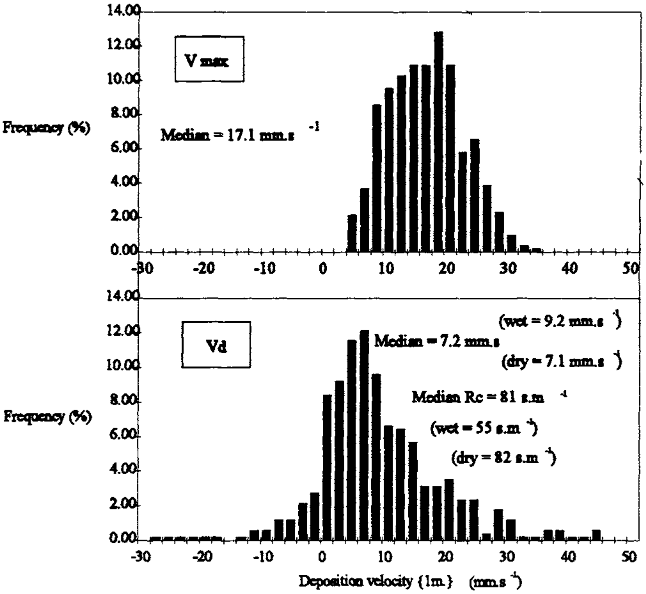

Figure 3. Frequency distribution of V_{max} and V_d 1m. above a wheat canopy (April - July 1993). Negative values denote SO_2 emission - or more likely release to the atmosphere of pre-deposited SO_2.

over rates of deposition under moist conditions (Fig. 3). The median canopy resistance r_c was 81 s m^{-1} for the whole data set. The leaf wetness sensor data were used to show the average influence of leaf wetness on canopy resistance and deposition velocity as shown in Fig. 3. These data show, as expected, that r_c is significantly smaller in wet conditions averaging 55 s m^{-1} than in dry conditions (83 s m^{-1}) but the wet surfaces were **not** generally a perfect sink for the SO_2.

The generalized data from Fig. 3 conceal large diurnal variations in deposition velocity which result from both changes in both r_a, r_b and r_c. Typical diurnal variations in V_d for the vegetative phase of the crop growth are shown in Fig. 4 with afternoon maxima in V_d of 10 to 15 mm s^{-1} and nocturnal minima of 2 to 5 mm s^{-1}. It is important to recognise that a significant fraction of the diurnal variation in V_d results from the decrease in windspeed and the increase in atmospheric stability during the night which lead to a marked diurnal cycle in r_a and r_b. The effect is clear even averaged over the April-July data set as shown for the wheat crop in Fig. 5. The small effects of liquid water on leaf surfaces on r_c relative to those reported by Erisman *et al.* (1993) may result from solution and oxidation processes in the liquid film not being sufficiently rapid to maintain or oxidise the S^{IV} in solution as the water evaporates. An example of this

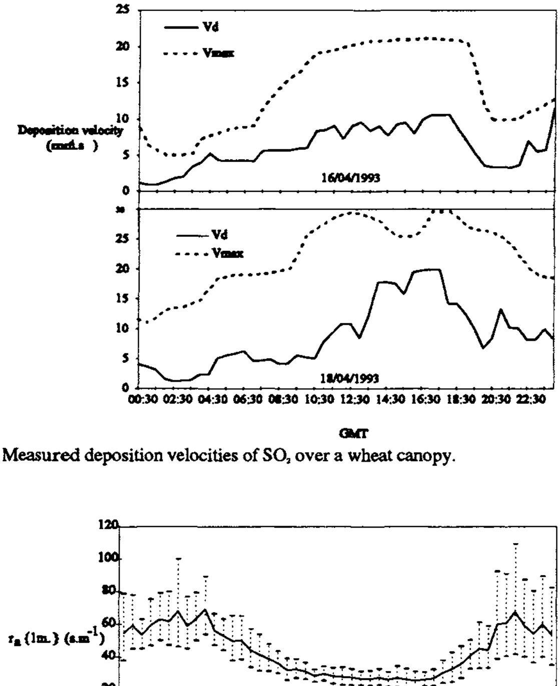

Figure 4. Measured deposition velocities of SO_2 over a wheat canopy.

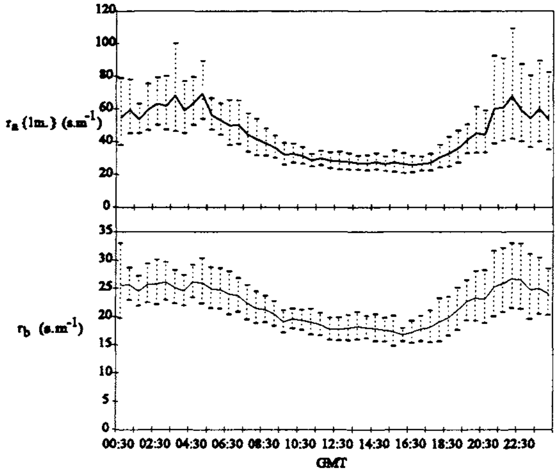

Figure 5. Mean diurnal cycle of atmospheric aerodynamic (r_a {1m.}) and viscous sub-layer (r_b) resistances to SO_2 transfer above a wheat canopy (April - July 1993). Values are geometric means and 95 % confidence intervals.

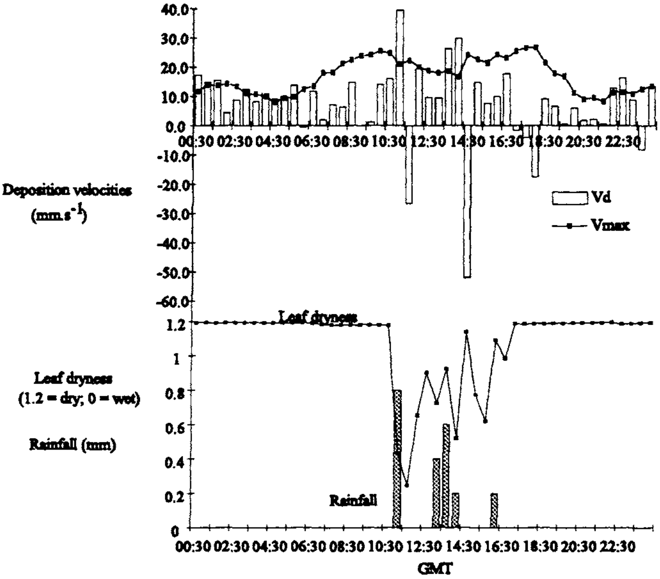

Figure 6. SO_2 exchange over a wheat canopy (23/07/1993): influence of precipitation and leaf wetness on the dry deposition velocity of SO_2. Precipitation events that occur at 11:00 and between 13:30 and 14:30 result in a wetted canopy and increased deposition velocity at 11:00-11:30 and 13:30-14:00; soon after, emission occurs (negative V_d) as the result of desorption of unoxidized SO_2 during evaporation.

effect is shown in Fig. 6 in which the wetting of the wheat canopy by rain initially results in a large rate of deposition but as the canopy dries after a brief shower a peak in SO_2 emission is observed. Clearly, the emission is consistent with loss of dissolved S^{IV} back to the gas phase as water evaporates in warm sunny conditions, and the sequence of events is repeated following a further shower later in the day. These effects are not the general rule but do serve to illustrate the point that the assumed reduction in r_c to values close to zero require the chemical processing of the S^{IV} in solution to proceed to SO_4^{2-} and for the acidity generated in the aqueous film to be neutralized by soil derived base cations or by ammonia to prevent r_c increasing as the aqueous and gas phase SO_2 achieve an equilibrium.

The process is discussed in some detail by Brimblecome (1978) and by Chameides (1987) largely on theoretical grounds but in neither case are there field data for canopy exchange of water and SO_2 to confirm the details of the kinetics of the processes. Such field data are necessary for a range of conditions to provide a satisfactory basis for modelling the effects of surface water on the values of r_c and V_d and hence long term rates of exchange. Until then, the application of average r_c values obtained by experiment are the only alternative, and clear differences are shown in the data presented here and that by Erisman *et al.* (1993).

The mean diurnal changes in V_d for dry canopies are those driven mainly by changes in stomatal resistance with daytime minima for r_c entirely consistent with measured stomatal resistance (r_s). These findings are consistent with the data for grassland by Erisman *et al.* (1993), Garland (1977), and for wheat by Fowler and Unsworth (1979).

The collection of a substantial data set allows the variation in r_c with a range of variables to be examined. In particular it is important to show whether the deposition velocity is strictly independent of SO_2 concentration. By sorting the data by concentration the relationship between V_g, r_c and atmospheric resistances with SO_2 concentration has been investigated. The analysis shows in Fig. 7 that the atmospheric resistances are almost constant with SO_2 concentration in the range 1 to 20 μ g m^{-3}. However there is a clear reduction in r_c with increasing SO_2 concentration over the range 2 to 12 μ g SO_2 m^{-3} from 150 s m^{-1} at 2 μ g $_{SO2}$ m^{-3} to 50 s m^{-1} at 12 μg SO_2 m^{-3}.

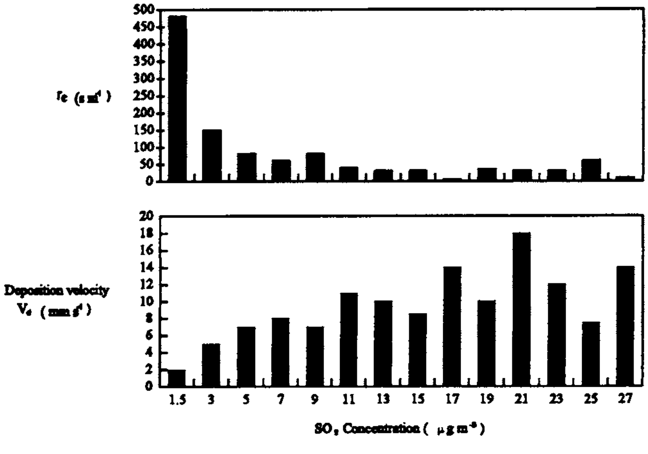

Figure 7. Dry deposition of SO_2 onto a wheat canopy (April-July 1993). Variations of canopy resistance and deposition velocity with SO_2 concentration. Reference height is 1m. above the zero-plane.

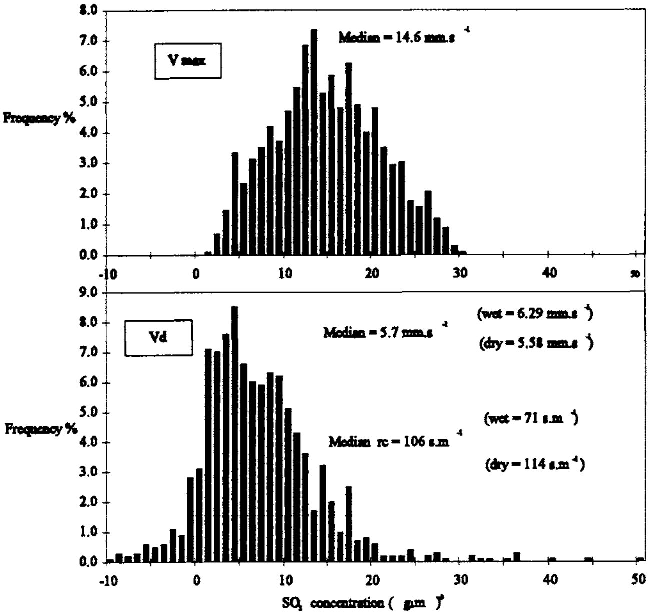

Figure 8. Frequency distribution of V_{max} and V_d 1m. above a sugar beet canopy (May-July 1994).

Dry deposition of SO_2 on to sugar beet

An extensive data set obtained for measurements of SO_2 fluxes over sugar beet were obtained during the period May to July 1994. The median deposition velocity was 5.7 mm s^{-1} whereas 1 hour of V_{max} was 14.6 mm s^{-1}. Median deposition velocities to dry and wet canopies of sugar beet were 5.6 and 6.3 mm s^{-1} respectively as shown in Fig. 8.

An example of the differences in behaviour of V_d and r_c in these measurements with those of Erisman may be seen in the data for two days over the sugar beet crop. The first day (8/6/1994) a warm

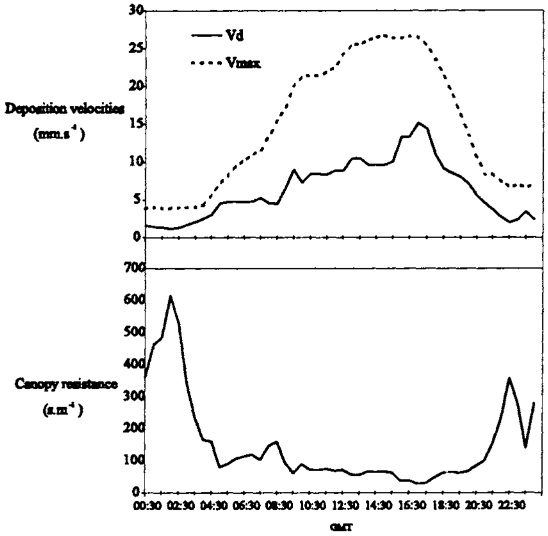

Figure 9. Diurnal variations in canopy resistance and deposition velocity of SO_2 over a dry sugar beet canopy (08/06/1994).

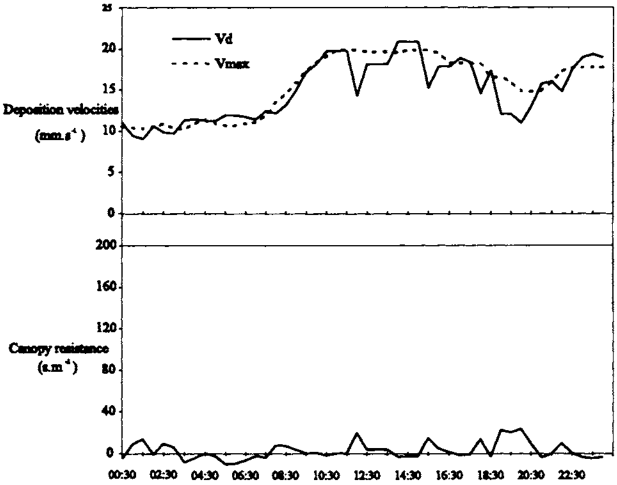

Figure 10.Dry deposition of SO_2 onto a wet sugar beet canopy. Surface wetness is assumed to reduce canopy resistance to near-zero values, allowing large rates of dry deposition even during night-time.

sunny early summer day, shows the common diurnal cycle in V_d with mid-day maxima of 10 mm s^{-1} and small nocturnal minima of 2 mm s^{-1} in calm, strongly stable conditions (Fig. 9). By contrast, for a day during the preceding October (13/10/93) the deposition velocity shows V_d very close to V_{max} all day, for a canopy in cool wet conditions (Fig.10). On this day there was no evidence of r_c increasing with time in the presence of a wet canopy. The reason r_c does not increase, and that the surface remains a 'perfect sink' for SO_2 is a matter of speculation but must be closely linked to the chemical processing of the dissolved SO_2.

SOILS

Following the harvest of the winter wheat crop the field was cultivated and provided a long period of smooth bare soil over which SO_2 fluxes were measured.

The median V_d was 13 mm s^{-1} and was quite close to the median V_{max} of 15 mm s^{-1}. The underlying canopy resistance was therefore very small and averaged just 12 s m^{-1}. The surface was behaving almost as a perfect sink for SO_2 and while the presence of liquid water did reduce r_c as shown in Fig. 11 to 4.9 s m^{-1} the increase in deposition velocity was small (to 15 mm $s^{-1)}$ and was then almost equal to V_{max}.

The very large rates of deposition to base soil were larger than those reported by Garland)1977) and by Payrissat and Beilke (1975). A consequence of the small r_c

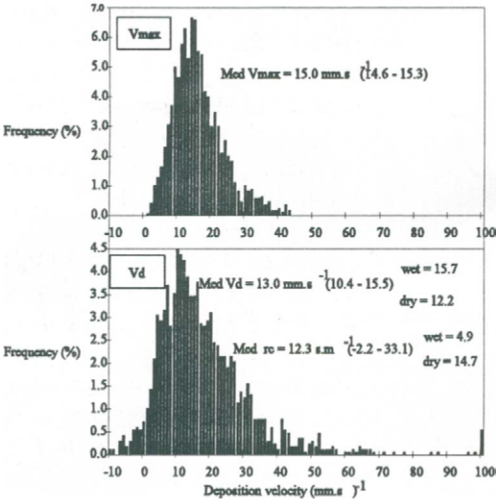

Figure 11. Frequency distribution histograms for measured deposition velocities (V_d) and maximum deposition velocities allowed by turbulence (V_{max}) over bare soil at Sutton Bonington (January-May 1994). Figures in brackets are 95 % confidence intervals.

is that V_d for the bare soil increased almost linearly with wind speed (Fig. 12). The r_c values widely applied in models of SO_2 dry deposition are generally much larger than those reported here and, if such values as those reported here are applicable generally, the uptake by arable land is winter will be much larger than has been assumed and landscape values for V_g in winter should be significantly larger.

Comparison of modelled and measured deposition velocities

The application of resistance models to estimate rural SO_2 dry deposition is now a standard technique by Hicks *et al.* (1987), Fowler (1980) and by Sandness (1993) and Erisman (1994). The application and methods in all cases differ although the underlying principles are common.

In the method applied for the UK (RGAR 1990) the landscape is subdivided at 5 categories (arable, forest, grassland, moorland and urban). The stomatal response to light and temperature for species representative of such land uses are used to calculate the canopy resistance for water vapour, which is corrected for diffusivity differences between SO_2 and H_2O to provide stomatal uptake for SO_2. The leaf surface resistance is assumed constant and quantified by experiment. Climatological, or measured meteorological data (radiation air temperature, wind velocity and canopy heights) are then used to calculate V_d which are combined with monitored SO_2 concentration to yield the flux.

One of the most valuable products of the SO_2 deposition monitoring study is the large data set to check against model production. A comparison of the UK dry deposition model (Smith & Fowler, 1994) with the measurements reported here is presented in Fig. 13 for a dry wheat canopy in its vegetative phase. The agreement between measurements and the model

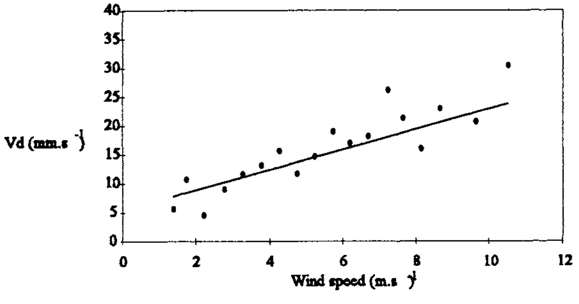

Figure 12. Mean variations with wind speed of deposition velocity for SO_2 over bare soil (January-May 1994). Reference height is 1m. above the zero-plane

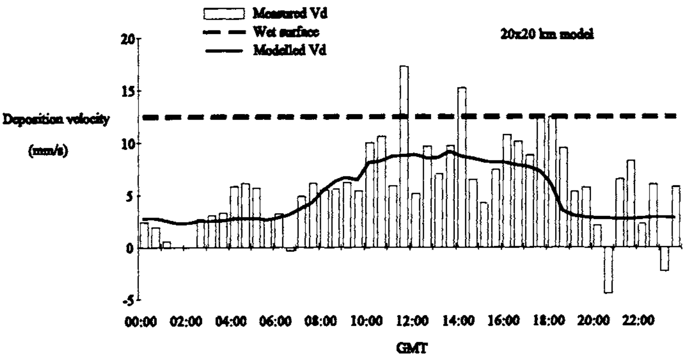

Figure 13. Dry deposition of SO_2 onto a wheat canopy (16/04/1993). Measurements are compared to model predictions using half-hourly meteorological data and mean deposition velocities computed for a 'wet surface' day. Reference height is 1 m. above the zero-plane.

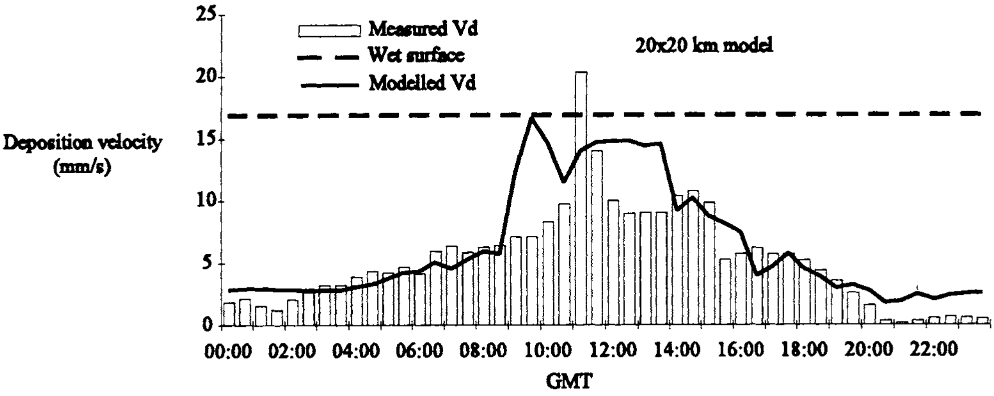

Figure 14. Dry deposition of SO_2 onto sugar beet (07/06/1994). Measurements are compared to model predictions using half-hourly meteorological data and mean deposition velocities computed for a 'wet surface' day. Reference height is 1 m. above the zero-plane.

is excellent on average although some of the 30 minute measurements differ significantly from the model, largely as a result of non-stationarity effects.

For wet surfaces, as shown earlier, the assumption of constant and small value for r_c provides a poor estimate of SO_2 deposition onto the sugar beet canopy to wet conditions (Fig. 14). The data show consistently smaller rates of deposition when the canopy was wet. This, as described earlier, is a consequence of oversimplistic assumptions about the chemical behaviour of the S^{IV} in the liquid film on the sugar beet canopy.

The overall results of the model and measurement comparisons for the two canopies vegetation show that

1. Diurnal and seasonal cycles in V_d are simulated very well by the model for dry canopies of either sugar beet or wheat.

2. Wet canopies are not perfect sinks and to model the r_c and V_d for those more knowledge of the processes in liquid films is necessary. A fix for the model can be provided by setting r_c for wet canopies at this site to 60 s m^{-1}.

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