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Sensitivity of ADOM Dry Deposition Velocities to Input Parameters: A Comparison With Measurements for SO_2 and NO_2 Over Three Land Use Types

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ABSTRACT *Dry deposition velocity measurements of SO_2 and NO_2 over a deciduous forest, a carrot field and a snow surface are compared with estimates obtained from the dry deposition module in the regional Eulerian Acid Deposition and Oxidant Model (ADOM). The comparison with measurements taken in the fall and winter shows large model overestimates, sometimes as large as a factor of 5. The NO_2 estimates are particularly poor and support existing evidence that models that employ the constant flux assumption for NO_2 are inadequate. The canopy and the snow surface resistances are the largest contributors to the total resistances for SO_2 and NO_2, except for situations in which some of the snow turns into liquid water, when the aerodynamic resistance becomes important.*

Increasing the magnitudes, taken from measurements, of the ADOM original values for the stomatal, cuticle, ground and snow resistances and decreasing the NO_2 mesophyll resistance and the Leaf Area Index (LAI) yield improved model results, particularly for SO_2, reducing the error by almost a factor of 5 at times. The new estimates compare favourably with those from a model that includes Wesely's canopy resistance parametrization. Over snow the NO_2 estimates are improved by as much as a factor of 6. Observed deposition velocities for SO_2 vary from 0 to 0.65 cm s^{-2} over a deciduous forest, 0 to 0.60 cm s^{-2} over a carrot field and are generally less than 0.05 cm s^{-2} over snow.

RÉSUMÉ *On compare les mesures de la vélocité des dépôts secs de SO_2 et de NO_2 sur une forêt d'arbres à feuilles caduques, un champ de carottes et une surface de neige, à des estimés du module de dépôts secs dans le modèle régional ADOM (Acid Deposition and Oxidant Model). La comparaison entres les mesures prises en automne et en hiver montre des grandes surestimations du modèle, parfois par un facteur de 5. Les estimés du*

NO_2 sont particulièrement pauvres et supportent la présumption actuelle que les modèles qui emploient l'hypothèse d'un flux constant pour le NO_2 sont inadéquats. Les résistances du couvert et de la surface de neige contribuent le plus aux résistances totales du SO_2 et du NO_2, sauf lorsqu'une partie de la neige se change en eau liquide, quand la résistance aérodynamique devient importante.

On peut améliorer le modèle en augmentant les intensités, provenant des mesures, des valeurs originales ADOM des résistances des pores, des cuticules, du sol et de la neige et en diminuant la résistance mésophyle et le rendement de l'indice LAI (Leaf Area Index), particulièrement pour le SO_2, réduisant l'erreur par près d'un facteur de 5. Les nouveaux estimés se comparent favorablement avec ceux d'un modèle qui inclu la paramétrisation de la résistance du couvert de Wesely. Sur la neige, les estimés du NO_2 sont améliorés par autant qu'un facteur de 6. Les vélocités de déposition observées pour le SO_2 varient de 0 à 0,65 cm s^{-2} au-dessus d'une forêt à feuillage caduc, de 0 à 0,60 cm s^{-2} au-dessus d'un champ de carottes, et généralement de moins de 0,5 cm s^{-2} au-dessus de la neige.

1 Introduction

The Acid Deposition and Oxidant Model (ADOM) was developed as a joint project by agencies in Canada, the United States and the Federal Republic of Germany. It is an Eulerian model, suitable for regional scales and is described in Venkatram et al. (1988) and Misra et al. (1988). In recent years two intensive field projects, one during the summer of 1988 and the other during the months of March and April 1990, were carried out to collect air quality and meteorological data that would be suitable for evaluating ADOM. As part of this endeavour, Padro et al. (1991) investigated the dry deposition module in ADOM for O_3 deposition velocities (V_d) over a deciduous forest in Ontario, Canada, using measurements from the first intensive (summer of 1988) Eulerian Model Evaluation Field Study (EMEFS), described in Hansen et al. (1991). Model deficiencies were identified and recommendations for improvement were made. This was an initial step in a continuing evaluation process to include the remaining 13 ADOM species that are being dry deposited over 9 distinct land surface types (including snow-covered ground).

Although the ADOM dry deposition module is structured to accept the input of grid cell-averaged meteorological data and to output grid-averaged (127 km × 127 km) deposition velocity (V_d), the V_d computations are done locally (employing grid-averaged input data) for each land use type and are then averaged arithmetically to yield grid-averaged V_d for each species. The grid-averaged data (consisting of surface temperature, ambient air temperature and anemometer-level wind) are not likely to represent correctly the meteorology over each land use type within the grid square. It is for these reasons that Padro et al. (1991) were justified in isolating the module from ADOM and testing it with local data that were collected over one specific site. The present study examines the dry deposition module in ADOM by comparing its output with measurements of SO_2 and NO_2 deposition velocities taken over a deciduous forest, a carrot field and a snow surface for fall and winter conditions. The module and the observations are also compared with estimates of V_d from Wesely's (1989) canopy resistance formulation. Although the purpose of our study is focused on model testing, the high quality of the present V_d data for

SO_2 and NO_2, obtained with a diode laser trace gas sensor, are a useful contribution on their own merit, particularly for NO_2, because of the sparseness of available data. The present V_d measurements are compared with other published SO_2 and NO_2 data. We shall see in a subsequent discussion that the NO_2 data show upward fluxes (due to chemical reactions or surface emissions) that are not consistent with the resistance analogue theory in ADOM (Padro et al., 1991; Wesely and Hicks, 1977; Hicks et al., 1989).

2 Data

Deposition velocities for SO_2 and NO_2 and supporting micrometeorogical data were collected during a series of short-duration intensive studies carried out in the fall and winter seasons of 1985/86 and 1986/87, respectively. The measurements were made over a deciduous forest, a carrot field and snow and are described in Edwards et al. (1988).

Deposition velocities, and sensible heat, latent heat and momentum fluxes were measured using the eddy correlation technique. An omni-directional sonic anemometer (Kaijo-Denki) coupled with a diode laser trace gas sensor and a Lyman-alpha hygrometer (AIR Inc.) were used for these measurements. All measurements were made on a tower. The data for carrots and part of the data for snow were collected at a site located near Holland Landing, Ontario (44°08′N, 79°37′W). The remainder of the snow data were obtained at a site located near Alliston, Ontario (44°06′N, 79°43′W). The mean height of measurement above the carrot and snow surfaces was 4 m. The deciduous forest measurements were made at a forest research site located near Canadian Forces Base Borden (44°19′N, 80°56′W), at a height of 15.4 m above the mean forest canopy height of 18 m. The forest canopy is described in Neumann et al. (1989).

Theoretical constraints for siting, such as a sufficiently long homogeneous upstream surface, and methods of measurement imposed by the eddy correlation technique (Hicks et al., 1989), were closely followed. Data reduction techniques as employed by Webb et al. (1980), Businger (1986) and Hicks et al. (1989) were used. The resulting data set, although substantially reduced, was employed to investigate the ADOM dry deposition module. Such drastic data reductions are common in the literature (Hicks et al., 1989). The rms noise level of the TDL instrument was approximately 0.3 ppbv for NO_2 and 2 ppbv for SO_2. Data with signal-to-noise ratios less than 1 were rejected. The use of the eddy correlation technique and these sensor detection limits facilitate the measurement of deposition velocities on the order of 0.005 cm s^{-1} for NO_2 and 0.03 cm s^{-1} for SO_2 based on a 30-min sampling period and typical meteorological conditions experienced during the field studies. We shall see that these errors are much smaller than those of the model.

Supporting measurements included snow surface temperature (IR thermometer), net radiation, solar radiation, forest Leaf Area Index (LAI), and screen temperature. The forest LAI was deduced from the results of Neumann et al. (1989) who employed a leaf-litter collection technique. Unfortunately, measurements of surface temperature for the forest and carrot canopies were not available for the present study. Instead, the effective leaf surface temperature T_s at the zero-plane displacement height was calculated using the formulation described in Wesely et al. (1978),

$$T_s - T_a = T_* \kappa^{-1} [\ln (Z/Z_0) + 2 - \psi_H] \quad (1)$$

where T_s is the ambient air temperature at height Z, Z_0 is the momentum roughness length, $T_* = \overline{w'T'}/u_*$ is a temperature scaling parameter, u_* is the friction velocity, $\overline{w'T'}$ is the temperature flux, ψ_H (Dyer and Hicks, 1970) is an integral function accounting for deviations from neutral stability, and κ is the von Karman constant taken as 0.4.

3 Theory

a *The ADOM Model and Suggested Modifications*

A review of the ADOM dry deposition module for gaseous species has been described in Padro et al. (1991). Here, we shall present briefly the features of the module that are relevant to the present study. The basic concepts of dry deposition velocity are widely discussed in the literature (Wesely and Hicks, 1977; Wesely et al., 1978). The theory includes the assumption that the vertical flux in the surface layer is nearly constant. This may not always be valid for NO_2, which can rapidly change its concentrations because of chemical reactions or emissions from the soil.

The deposition velocity V_d is obtained from the sum of three resistances in series as follows:

$$V_d = (R_a + R_b + R_c)^{-1} \quad (2)$$

where R_a is the aerodynamic resistance to transfer of a species, as a result of atmospheric turbulence in the surface layer between a height Z and the surface, characterized by Z_0. It is computed from the following equation:

$$R_a(Z) = [0.74 \ln (Z/Z_0) - \psi_H(Z/L)]/\kappa u_* \quad (3)$$

Unlike (1), the functional form of ψ_H in (3) is taken from Businger (1973) to be consistent with the factor 0.74. L is a stability parameter (Monin-Obukhov length) and can be computed jointly with u_* from the basic surface layer equations, requiring only the temperatures at two different heights and the wind at one height, as computed in Padro (1983).

R_b is the quasi-laminar sublayer resistance caused to a large extent by molecular motion in a thin layer close to a boundary surface. It is computed from (Wesely and Hicks, 1977):

$$R_b = \frac{2}{\kappa u_*} (\nu/D_j)^{2/3} \quad (4)$$

where ν is the kinematic viscosity of air and D_j is the molecular diffusivity of a species j in air.

R_c is the canopy resistance, which is obtained from a sum of the following resistances in parallel:

$$\frac{1}{R_c} = \frac{1}{R_p} + \frac{1}{R_{cut}} + \frac{1 - F_{sn}}{R_g} + \frac{F_{sn}}{R_{sn}} \quad (5)$$

where

$$\frac{1}{R_p} = \frac{\text{LAI}}{r_{st} + r_{mj}}, \quad \frac{1}{R_{cut}} = \frac{\text{LAI}}{r_{cutj}} \tag{6}$$

The lower case symbols r_{st}, r_{mj} and r_{cutj} denote local leaf stomatal, mesophyll and cuticle resistances to the transfer of species j. They are converted to bulk R_p and cuticle (R_{cut}) resistances via the widely employed LAI approximation, explained in the literature and in Padro et al. (1991). R_g and R_{sn} denote ground and snow resistances, respectively. The contribution to the bulk canopy conductance ($1/R_c$) from snow depends upon the fraction (F_{sn}) of the ground that is covered with snow, as expressed in (5). In the present study $F_{sn} = 0$ for the forest and carrot field studies and $F_{sn} = 1$ for the snow-covered surface. For each canopy type, ADOM makes an abrupt and large change to the LAI when the season changes, in disagreement with the gradual LAI changes that occur in the real world during seasonal transitions. This causes, as we shall see, large errors in V_d. The resistances r_{cut} and r_{mj} are selected from estimates that are available in the literature. In ADOM, the r_m for SO_2 and NO_2 are 0 and 5 s cm^{-1}, respectively. The latter is considered to be too large by Wesely et al. (1982), who suggest 0.5 s cm^{-1}, and by Wesely (1989), who suggests about 0.0 s cm^{-1}. The resistance r_{st} is computed from

$$r_{st} = P/BD_j \tag{7}$$

$$B = B_{max} \sin[(t - t_d)\pi/12] + B_{min} \tag{8}$$

where P is a stomatal constant given the value 2.3×10^{-8} m^2, and B is the stomatal slit width, computed from a simple parametrization of the diurnal variation of radiation. B_{max} and B_{min} denote maximum (at midday sun) and minimum (at night) values of B. Sunrise time is denoted by t_d and other times of day by t. Shortcomings of this equation are discussed in Padro et al. (1991). At night and for values of soil moisture content and surface temperature (T_s) that are below assigned threshold values, B is set equal to B_{min}. In particular the threshold value for T_s is set at 283 K in ADOM.

In the present study (5) is applied to three land surface types for the fall and winter. Without justification, ADOM retains the canopy conductances $1/R_p$ and $1/R_{cut}$ over snow, but it scales them with a small LAI value of 0.5. Since they are redundant over snow, we omit them altogether. The present study does not consider canopy wetness and melting of snow because the relevant data were not available. ADOM provides formulations of conductances for open water and a wet canopy but not for melting snow in which the liquid-water-to-air ratio is important. When such situations occur it is expected that ADOM estimates of V_d would be in error.

b *Application of Wesely's Canopy Resistance Model*

Wesely (1989) formulated a revised parametrization of the surface resistance (R_c) for the Regional Acid Deposition Model (RADM), discussed in Sheih et al. (1986) and Walcek et al. (1986). Including only terms that are relevant to the present study,

TABLE 1. Input resistances (s cm^{-1}) to compute canopy resistance R_c. An entry of 99 indicates no pathway via that resistance.

Species	R_{lu}	R_{ac}	R_g	R_{cl}	Seasonal and Surface Categories
SO_2	90	15	5	90	Deciduous forest in autumn
O_3	90	15	2	4	(No. 2 in Wesely)
SO_2	99	0	10	99	Snow in subfreezing winter
O_3	99	0	4	99	(No. 4 in Wesely)

Wesely's equation is given as

$$\frac{1}{R_c} = \frac{1}{R_{lu}} + \frac{1}{(R_{dc} + R_{cl})} + \frac{1}{(R_{ac} + R_g)} \tag{9}$$

where R_{lu} and R_{cl} represent bulk resistances for the exposed surfaces in the upper and lower canopy, respectively, and R_g is the ground resistance. These are listed in Table 1 and are adjusted owing to a temperature effect, given by 10 $\exp(-T_s - 4)$. Table 1 lists resistances for land use category 4 and season 2, taken from Wesely's (1989) classification for a deciduous forest in autumn, and land use category 8 and season 4 for a desert covered with snow in subfreezing winter conditions. The categories were selected in the present study on the basis of either calendar dates or (for snow) the occurrence of a uniform snow cover on the ground. R_{ac} is a resistance that depends on canopy height and R_{dc} is one that is due to buoyant convection, given by

$$R_{dc} = [1 + 1000(G + 10)^{-1}] \tag{10}$$

where G denotes solar radiation (W m^{-2}). Over snow R_{dc} is neglected. Stomatal and mesophyll resistances are also neglected in (9) in accordance with Wesley's autumn category. For NO_2, it can be computed from Wesely (1989) that $R_{lu}(NO_2) = 10\ R_{lu}$, $R_{cl} = 10\ R_{cl}(O_3)$ and $R_g = 10\ R_g(O_3)$, where the O_3 values are listed in Table 1. An entry 99 in Table 1 indicates that the resistance component has been neglected in (9).

Wesely's R_c is added in series to R_a and R_b as in (2) to yield estimates of V_d. These are compared with ADOM values and observations. It may be noted that no data on wetness were available so that no references are included here to Wesely's formulae for rain and dew. In all of the model tests no allowance was made for the possibility of melting snow.

4 Results and discussions

In the following sections we discuss model estimates of dry deposition velocities and compare them with observations. We identify model deficiencies from the analysis of individual resistances and conductances and suggest changes to the magnitudes of model parameters, in order to improve model estimates of V_d. The results are displayed following the format of Hicks and Matt (1988) and Hicks et al. (1989). We shall refer to estimates from ADOM as "ADOM", and from changes in ADOM as "modified ADOM" and compare them with Wesely's model values.

a *SO_2 and NO_2 Over a Deciduous Forest*

Figure 1 illustrates variations with time of the SO_2 dry deposition velocity obtained from measurements, from the ADOM model and from the modified ADOM model, for the deciduous forest for the four days in October 1986 listed in Table 2. The observed V_d varies from near zero to 0.65 cm s^{-1}, and the largest values appear in Fig. 1b. Baldocchi (1988) reported observed values of V_d for SO_2 in the range 0.3–1.3 cm s^{-1} over a fully leafed deciduous oak forest with corresponding model estimates in the range 0.4–0.7 cm s^{-1}. Whelpdale and Shaw (1974), Fowler (1978) and Matt et al. (1987) reported comparable V_d values for SO_2 over vegetated surfaces. The model, with two minor exceptions in Fig. 1d, overestimates the observed V_d, sometimes yielding values as large as 2.8 cm s^{-1}, noted in Fig. 1b. An analysis of the individual model resistances, illustrated in Fig. 2, reveals that the canopy is the dominant resistance component and is responsible for the overestimated V_d values. The large model V_d in Fig. 1b is due to the small model canopy resistance (R_c) and more specifically to the relatively large stomatal conductance ($1/R_p$) compared with the cuticle ($1/R_{cut}$) and ground ($1/R_g$) conductances, shown in Fig. 2b. Such large V_d values are expected from the model during the day, provided that the surface temperature (T_s) is $> 283°$ K (a threshold temperature explained in Section 3). The lower model V_d values in Fig. 1a are associated with lower temperatures, especially those below the threshold value of 283 K. The model V_d values in Figs 1c and 1d for 20 and 21 October, respectively, are, however, smaller than those in Fig. 1b in spite of the relatively high daytime temperatures. The reason for this is the abrupt decrease in the model LAI from 6.0 to 0.5 between 7 and 8 October (Figs 1a and 1b) and 20 and 21 October (Figs 1c and 1d) corresponding to the model's change of season. Included in Figs 1a–1d are V_d estimates from Wesley's (1989) model. In general, with the exception of Fig. 1b, Wesely's model is superior to the modified ADOM for SO_2, but at times it yields large errors, which may be partially due to the incomplete input data and the limited selection of seasonal categories.

It follows from the above analysis that in order to improve the model, modifications to the model canopy parameters are necessary, which was also discovered in Padro et al. (1991) for a fully leafed forest. Thus, the modified model includes a reduction of LAI from 6 to 1.5 for Figs 1a and 1b and an increase from 0.5 to 1.2 for Figs 1c and 1d, in agreement with estimated values (Edwards et al., 1988). The model's drastic seasonal change of LAI was not in agreement with the forest architecture of October 1986. Other suggested modifications are listed in Table 3, and apply to R_{cut}, R_g and B_{max}. The decrease in V_d due to these modifications is illustrated in Fig. 1 (as modified V_d), showing better agreement with observations. More fundamental sources of error in the model are due to simplified parametrizations and the basic assumptions in the model formulation (Padro et al., 1991). These include the omission of physical and physiological parameters in computing the stomatal resistance and the LAI approximation.

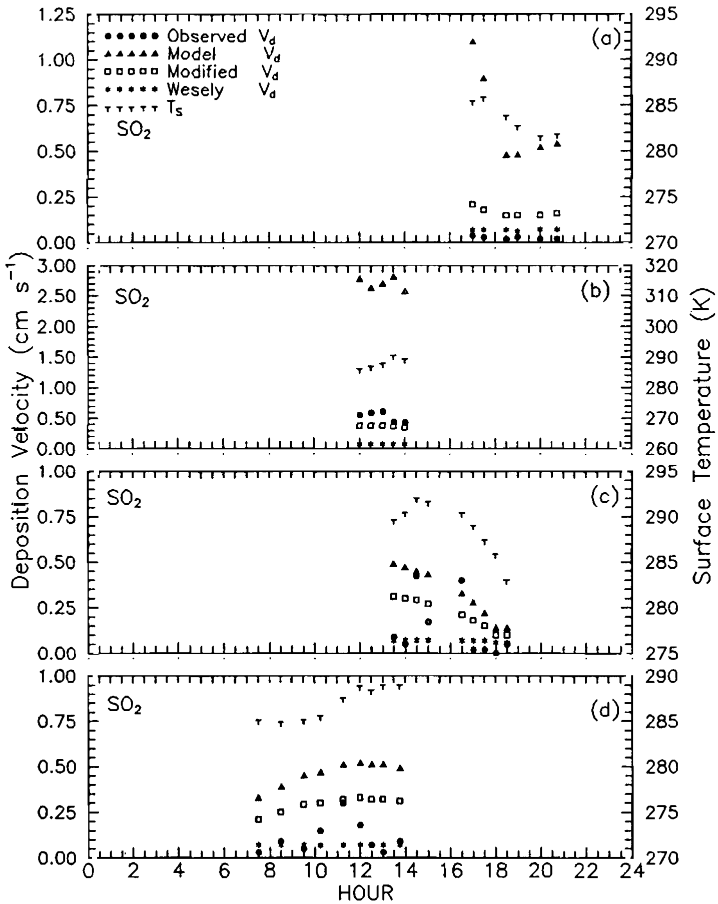

Fig. 1 Modelled and observed dry deposition velocities V_d and observed surface temperature T_s for SO_2 at the Borden Forest for 1986 on (a) 7 October, (b) 8 October, (c) 20 October and (d) 21 October.

TABLE 2. Parameters in the ADOM model and the modified model

Dates	Land Use	Species	Model		Modified Model	
			Z_0(m)	LAI	Z_0(m)	LAI
October 7, 8, 1986	Forest	SO_2	1.000	6.0	1.000	1.5
20, 21, 1986				0.5		1.2
7, 10, 1986	Forest	NO_2	1.000	6.0	1.000	1.5
22, 28, 1986				0.5		1.0
September 23, 30, 1985	Carrot	SO_2	0.200	3.0	0.2000	3.0
16, 19, 1985	Carrot	NO_2	0.200	3.0	0.2000	3.0
March 10, 1986	Snow	SO_2				
January 27, 1987			0.001	0.5	0.0005	0.0
February 5, 6, 22, 1987			0.001	0.5	0.0005	0.0
March 2, 1986	Snow	NO_2	0.001	0.5	0.0005	0.0
February 6, 1987						

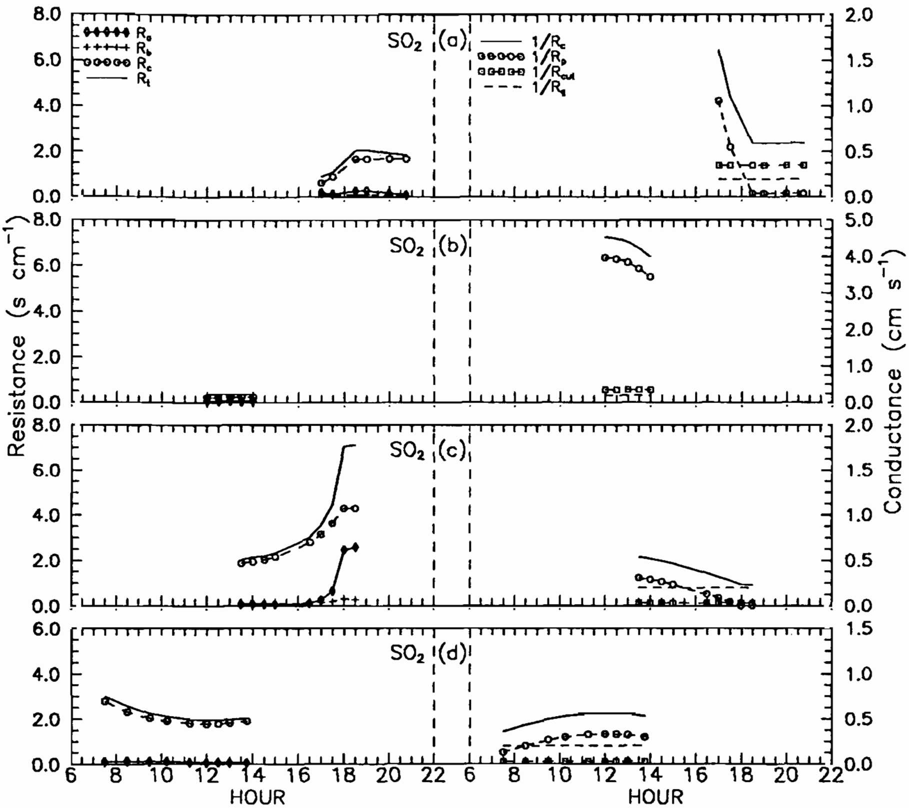

Fig. 2 As Fig. 1, except for modelled resistances and conductances.

TABLE 3. Values of model parameters

Land Use	Species	Model r_m (s cm^{-1})	Model r_{cut} (s cm^{-1})	Model R_g (s cm^{-1})	Model B_{max} (μm)	Modified Model r_m (s cm^{-1})	Modified Model r_{cut} (s cm^{-1})	Modified Model R_g (s cm^{-1})	Modified Model B_{max} (μm)
Forest	SO_2	0.0	17.0	5.0	10.0	0.0	30.0	10.0	2.5
Carrot	SO_2	0.0	17.0	5.0	10.0	0.0	30.0	10.0	2.5
Snow	SO_2			$R_{sn} = 3.0$				$R_{sn} = 10.0$	
Forest	NO_2	5.0	15.5	4.6	10.0	2.0	27.3	9.1	2.5
Carrot	NO_2	5.0	15.5	4.6	10.0	2.0	27.3	9.1	2.5
Snow	NO_2			$R_{sn} = 2.7$				$R_{sn} = 9.1$	

Figure 3 illustrates time variations of V_d for NO_2 over the deciduous forest for the four days in October 1986 that are listed in Table 2. With the exception of the fourth data point in Fig. 3a (for October 7), all the measured V_d values are zero or less, reaching a minimum of about -0.7 cm s^{-1} in Fig. 3c. These measurements were not corrected for sources and sinks between the surface and the measurement height (Andreae and Schimel, 1989). There is evidence in the literature that measurements

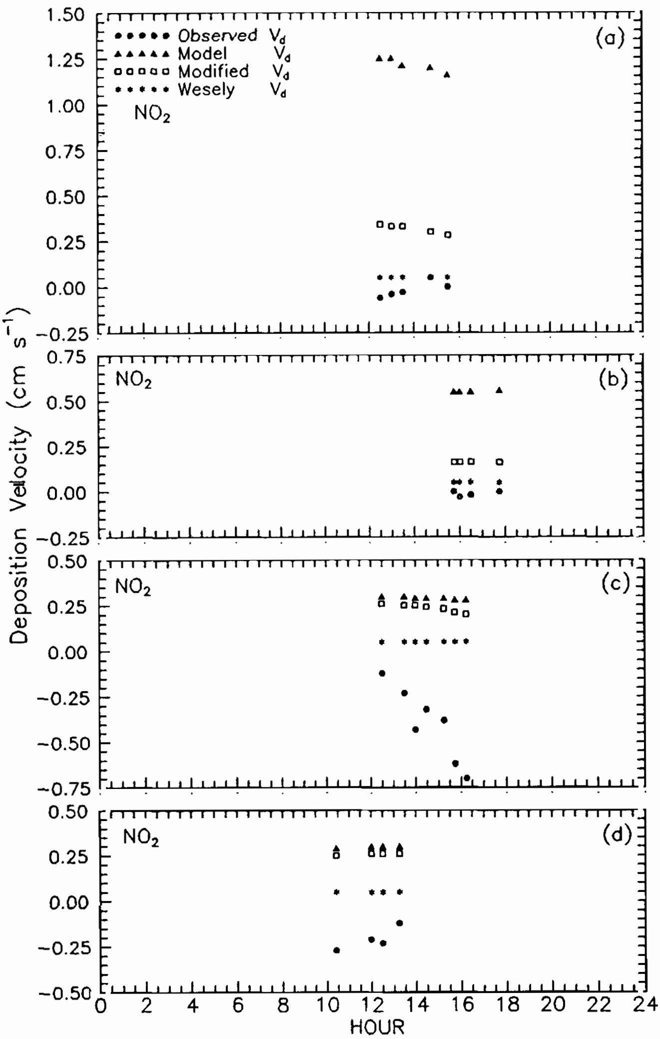

Fig. 3 As Fig. 1, except for modelled and observed dry deposition velocity V_d for NO_2.

of net fluxes for NO_2 and NO_x (NO + NO_2) include negative values (i.e. upward fluxes), especially in the afternoon when the surface temperature and solar radiation are expected to be large. For example, Delany et al. (1986) reported that net NO_x fluxes over grassland in the summer varied from −0.3 to +0.2 ppb m s^{-1}, the lower negative limit indicating net upward flux in the afternoon. The authors did not compute values of V_d, usually obtained from a linear relation between the flux and mean concentration, because of the occurrence of negative fluxes. Similarly, Slemr and Seiler (1984) reported large NO and NO_2 emissions from bare, vegetated and fertilized soil. They concluded that NO and NO_2 emissions correlated well with soil temperature and solar radiation, respectively, and both species depended upon soil moisture content. Earlier, Duyzer et al. (1983) suggested that the emissions may not necessarily come from the earth's surface but rather from chemical reactions in the air close to the earth's surface on a time-scale comparable with that of the turbulent fluxes. The production of NO_2 from local sources violates the constant flux assumption employed in formulating the theory for the dry deposition velocity. For this reason Duyzer et al. (1983) also did not compute V_d from the linear flux and concentration relation. A new formulation for V_d is required that includes changes in the local fluxes due to emissions and rapid chemical reactions. In contrast to Delany et al. (1986), Duyzer et al. (1983) reported that there was no influence on the fluxes of NO_x by rapid chemical reactions. Delany and Davies (1983), on the other hand, suggested that NO might be released from the ground and might affect, by chemical reaction, the measured NO_x deposition rates. Hicks and Matt (1988) reported another case of upward fluxes of NO_x (over a deciduous forest) and NO_2 (over an agricultural area) and their measurements showed a large scatter between NO_x, NO_2 fluxes and their respective concentrations, indicating the lack of a linear relation between flux and concentration. They concluded that NO_2 fluxes cannot always be represented by a resistance analogue model. One example when the resistance analogue was valid for NO_2 was reported by Wesely et al. (1982) for measurements when the chemical reactions were not significant and the number of negative fluxes of NO_2 were few. More generally, Fitzjarrald and Lenschow (1983) provided a theoretical justification for employing the resistance analogue to the sum of NO and NO_2 (NO_x) because of its conservative property. A brief summary of measured V_d values for NO, NO_2 and NO_x is presented in Table 2. There is a large variation in the magnitudes of V_d among the various studies and none of them reported negative V_d values. The wide range of V_d values may be attributed to their dependence upon the season, time of day, land use type, physiological and meteorological conditions and the methods of measurements.

Although considerable evidence exists that the resistance analogue is often incorrect for computing the NO_2 V_d over vegetated surfaces, we shall, nevertheless, apply it in its present form in ADOM for instructive purposes. Its application for a snow surface is considered valid. The ADOM model estimates of V_d for NO_2 over the forest yields, as expected, positive values ranging from 0.3 to 1.2 cm s^{-1}, illustrated in Fig. 3. These estimates are larger than and opposite in sign to the observed values. Again, the model V_d in Figs 3a and 3b are influenced by the large ADOM LAI of 6, shown in Table 2, and the relatively small resistances assigned to R_g and R_{cut} compared with their more commonly used values, as in Baldocchi (1988), shown in Table 3. The large V_d values occur, in spite of the large NO_2 mesophyll resistance (r_m) of 5 s cm^{-1}, which the ADOM module assigns to NO_2. The model V_d was even larger (not shown here) when the value of 0.5 s cm^{-1} suggested by Wesely et al. (1982) was employed. We, therefore, tested the sensitivity of ADOM with a mesophyll resistance value of 2 s cm^{-1} (Table 3), recognizing that this is considered high. In Figs 3c and 3d the model V_d values are smaller than those of Figs 3a and 3b because the model LAI was seasonally reduced to 0.5, as noted in the discussion of SO_2. Our suggested value for LAI in Table 2 is 1.0. The modified model estimates of V_d show a significant reduction in V_d from the original ADOM values in Figs 3a and 3b, but only a minor reduction in Figs 3c and 3d. The latter smaller influence of the modified model is due to the increase in LAI from the ADOM value of 0.5 to 1.0. Included in Figs 3a–3d are estimates from Wesely's model. In the light of the difficulties in modelling NO_2 using the resistance analogue, Wesely's model yields encouraging results with V_d values near zero.

b *SO_2 and NO_2 Over a Carrot Field*

Figures 4a and 4b illustrate measured daytime values of V_d for SO_2 over a carrot field for 23 and 30 September 1985 in comparison with the ADOM and the modified ADOM results. The values range from 0.05 to about 0.60 cm s^{-1}. The model, as for V_d over the forest, overestimates the deposition velocities, yielding values as large as 1.8 cm s^{-1}. Employing similar reasoning to that of the forest study, parameter modifications were made to ADOM (Table 2), yielding V_d values that are in better agreement with the observations. The afternoon behaviour of the model V_d in Fig. 4a is typical of a sunny day, showing a decrease in V_d with decreasing sunlight. The last three observed data points follow a pattern similar to the model's but the first three data points do not and they must be influenced by a mechanism other than the solar radiation that occurred during clear skies (sunny day), assumed by the model. Such details, if at all possible, may be simulated by the model only if more detailed meteorological and physiological input data become available. In particular, accurate measurements of canopy wetness, soil moisture and cloud amounts are essential to improve model estimates.

Figures 4c and 4d illustrate observed NO_2 V_d values over the carrot field, varying from −0.10 to 0.25 cm s^{-1} during the afternoon hours. These (except for the negative values) are comparable with other published observations shown in Table 4. Most of the observed V_d values in Fig. 4c are near zero so that the model and the modified model cannot provide good estimates, but in Fig. 4d, where most of the observed V_d are greater than zero, the pattern and magnitudes of the modified model show better results. This indicates, perhaps, that there may be situations when NO_2 fluxes bear a linear relationship to the concentrations. Such cases were reported by Wesely et al. (1982) when the amount of NO in the air was small compared with that of NO_2.

c *SO_2 and NO_2 Over Snow*

Figure 5 illustrates time variations of measured V_d for SO_2 over snow for 10 March 1986 and four days in the winter of 1987, shown in Table 2. The values range from 0 to about 0.3 cm s^{-1}, the majority of the observations being <0.05 cm s^{-1}, and only one having a magnitude of 0.3 cm s^{-1}. The V_d values are comparable with measurements reported in the literature, which range from 0.005 to 0.250 in Table 5 (excluding the large value of 1.6 cm s^{-1} reported by Whelpdale and Shaw, 1974). The range in V_d results from the influence of various meteorological conditions and snow surface temperatures. It can be deduced from the details in Table 5 and

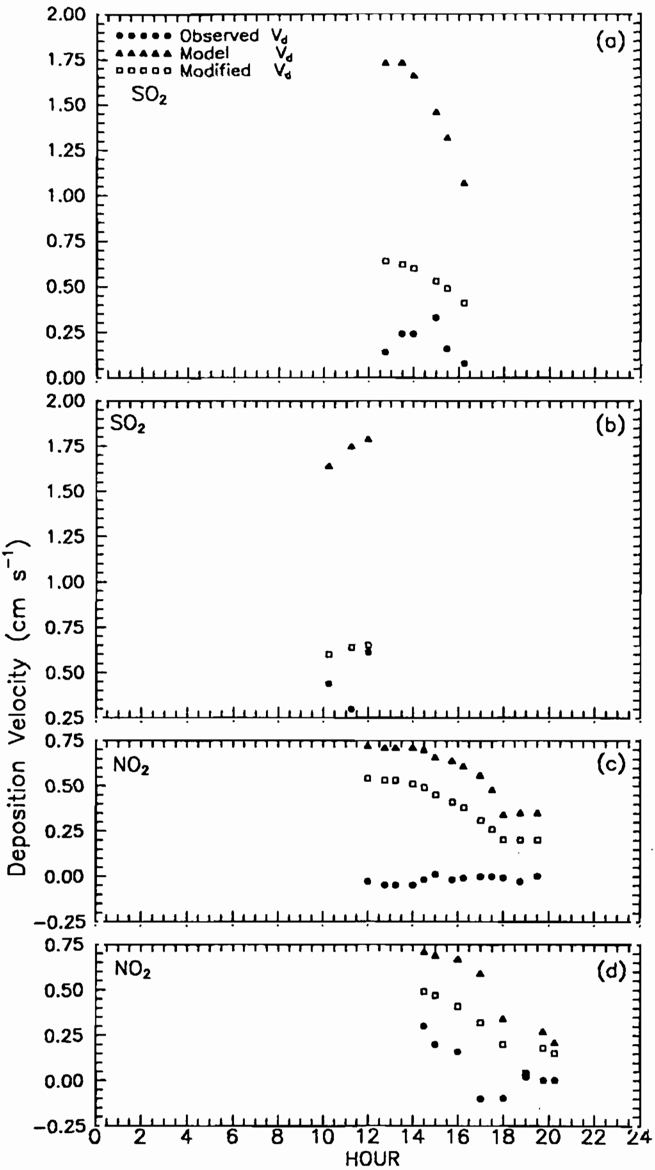

Fig. 4 Modelled and observed dry deposition velocities V_d over a carrot field for 1985 for SO_2 on (a) 23 September and (b) 30 September and for NO_2 on (c) 16 September and (d) 19 September.

a suggestion by Valdez et al. (1987) that the uptake of SO_2 by snow depends primarily upon the liquid-water-to-air ratio in the snowpack. The results of Cadle et al. (1985) yielding a large V_d of 0.15 cm s^{-1} when the snow had appreciable exposure time above −3°C lend support to this suggestion. The large measured V_d values in Fig. 5a are associated with the occurrence of above freezing surface

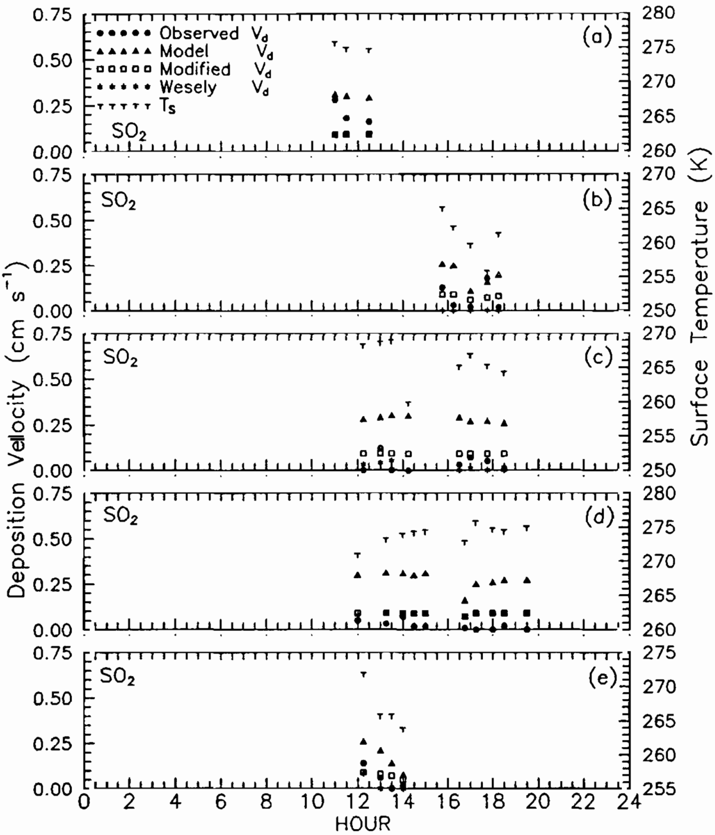

Fig. 5 Modelled and observed dry deposition velocities V_d and observed surface temperature T_s for SO_2 over a snow surface for 1986 on (a) 10 March and for 1987 on (b) 27 January, (c) 5 February, (d) 6 January and (e) 27 February.

TABLE 4. Cited dry deposition velocities for NO, NO_2 and NO_x measured over vegetated surfaces

Species	V_d (cm s^{-1})	Land use	Reference
NO_2	1.90	Alfalfa	Hill (1971)
NO	0.10	Alfalfa	Hill (1971)
NO	0.10–0.20	Freshly prepared surface	Judeikis and Wren (1978)
$NO_x(NO + NO_2)$	0.02–0.50	Grass/alfalfa	Sehmel (1980)
NO_x	0.67	Prairie land	Kasting (1980)
NO_x	0.05–0.56	Soybean field	Wesely et al. (1982)
NO_x	0.10–0.60	Grass (cut)	Delany and Davies (1983)
NO_x	0.00–1.50	Grass (pasture)	Duyzer et al. (1983)
NO, NO_2	0.09	Coniferous forest	Granat and Johansson (1983)

temperatures, which may be an indication that melting snow influenced the uptake of SO_2.

The ADOM module, again overestimates V_d in comparison to measurements. Analysis of model resistance components shows (Fig. 6) that the canopy resistance R_c (generally dominated by the snow surface resistance R_{sn}) is the largest term,

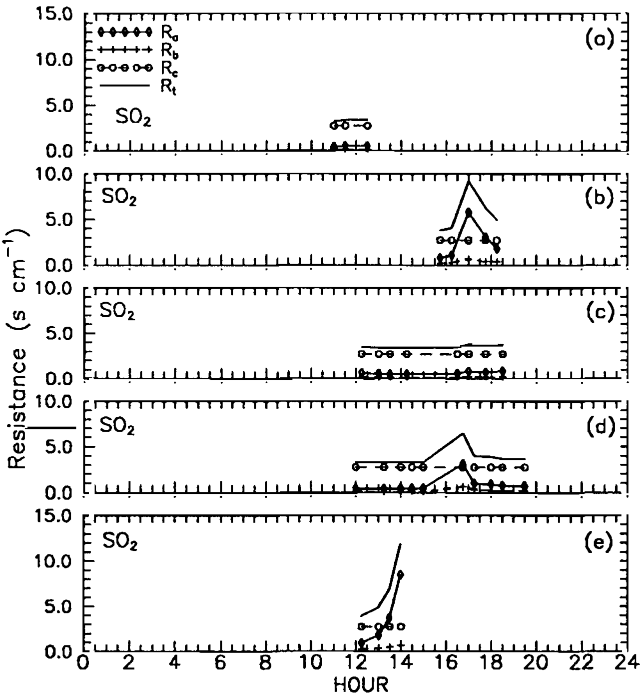

Fig. 6 As Fig. 5, except for modelled resistances.

TABLE 5. Cited dry deposition velocities of SO_2, NO and NO_2 measured over snow

Species	V_d (cm s^{-1})	Method and Atmospheric and Snow Conditions	Reference
SO_2	0.050–1.600	Concentration gradient in air; stable to unstable conditions	Whelpdale and Shaw (1974)
SO_2	0.100	Inferred from snow samples and air measurements; low wind and stable conditions	Dovland and Eliassen (1976)
SO_2	0.250	Snow samples	Barrie and Walmsley (1978)
SO_2	0.300–0.400	Measured fluxes and modelled concentrations	Barrie and Walmsley (1978)
SO_2	≤0.100	Laboratory experiment	Granat and Johansson (1983)
NO NO_2	≈0.000	Laboratory experiment	Granat and Johansson (1983)
SO_2	0.150	Field study over snow with appreciable exposure time above −3°C	Cadle et al. (1985)
SO_2	0.060	Field study over snow below −3°C	Cadle et al. (1985)
SO_2	0.140	Laboratory experiment when sunlight and melting allowed water to drain	Valdez et al. (1987)
SO_2	0.060	Snow held below 0°C	Valdez et al. (1987)
SO_2	0.070	Snow held below 0°C	Valdez et al. (1987)
SO_2	0.050	New snow	Valdez et al. (1987)
SO_2	0.040	Snow held below −2°C	Valdez et al. (1987)
NO_2	0.005	In darkness	Valdez et al. (1987)
NO_2	0.012	In sunlight	Valdez et al. (1987)

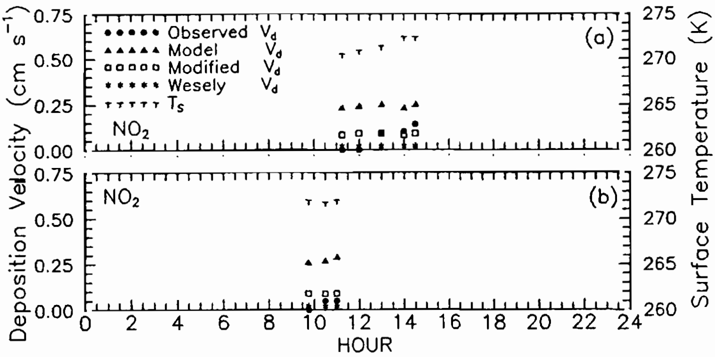

Fig. 7 Modelled and observed dry deposition velocities V_d and observed surface temperature T_s for NO_2 over a snow surface for (a) 2 March 1986 and (b) 6 February 1987.

with a few exceptions when R_a is equal to it or larger. Some R_a influence is noted in Figs 6b, 6d and 6e with a corresponding effect upon V_d, shown in Figs 5b and 5d, and to a larger extent in Fig. 5e. The variation of model V_d with time in Fig. 5e is quite similar to those of the observed data and T_s. It is tempting to deduce from this that the observed V_d bears some relationship to atmospheric stability, such as can be quantified by the Richardson number, but in view of the published measurements in Table 5, excepting those of Whelpdale and Shaw (1974), the more likely cause for the V_d pattern is the influence of the surface temperature. Under direct sunlight, surface temperatures may influence the uptake of SO_2 by two independent mechanisms: one is melting, and the other is the creation of neutral or unstable atmospheric conditions. It is more likely that the increase in surface conductance is due to melting rather than the decrease in the aerodynamic resistance, influenced by increased atmospheric instability. Unfortunately, Whelpdale and Shaw's (1974) classification of V_d with atmospheric stability did not include surface temperatures so that it is difficult to conclude whether their large V_d values were due to unstable conditions or to melting snow. The modified ADOM included an increase in R_{sn} to 10.0 s cm^{-1} from the model assigned value of 3.0 s cm^{-1}, more in agreement with measurements (Edwards et al., 1988). Results of the improved, modified V_d are illustrated in Fig. 5 along with results from Wesely's model. At times its agreement with the observations is better, but in general it is comparable to the modified ADOM, having, for example, exactly the same values in Fig. 5d.

Figure 7 illustrates eight data points of V_d for NO_2 over snow for two days listed in Table 2. Unlike the results for the deciduous forest and the carrot field, there are no negative values of V_d over snow. Values range from 0 to 0.15 cm s^{-1}. The literature reveals few studies with which these measurements can be compared. Only 3 reported values are listed in Table 5, viz. 0.0, 0.005 and 0.012 cm s^{-1}. In Fig 7a, the time variation of V_d follows a pattern similar to that of T_s, indicating perhaps a higher uptake due to surface temperature, although melting may not have begun, since T_s was slightly below freezing. The measurements were taken under sunny conditions. The model overestimates the observed V_d, yielding values

TABLE 6. Ranges of measured and modelled dry deposition velocities for SO_2 and NO_2

Species	Land Use	Measured V_d (cm s^{-1})	Model V_d (cm s^{-1})	Modified Model V_d (cm sa^{-1})
SO_2	Deciduous forest	0.00–0.65	0.15–2.80	0.10–0.40
NO_2	Deciduous forest	−0.70–0.00	0.30–1.20	0.15–0.35
SO_2	Carrot field	0.05–0.60	1.05–1.80	0.40–0.65
NO_2	Carrot field	−0.10–0.25	0.05–0.70	0.05–0.55
SO_2	Snow	0.00–0.15	0.08–0.30	0.05–0.10
NO_2	Snow	0.00–0.15	0.20–0.25	0.07–0.10

around 0.25 cm s^{-1}. Applying modifications similar to those for SO_2 (Table 3), the modified model yields values of V_d that are in better agreement with measurements. To simulate the pattern of V_d measurements for SO_2 and NO_2 over snow would require more detailed input of surface temperatures especially near the melting point and the employment of a theory that explains the uptake of gaseous species in wet snow. This also applies to Wesley's model, which generally shows underestimated values. Again, this may be partially due to our lack of proper input data.

5 Summary and conclusions

Dry deposition velocities from the ADOM dry deposition module for SO_2 and NO_2 have been compared with measurements over a deciduous forest, a carrot field and a snow surface. In all cases the model yielded larger values than those obtained from measurements. Increasing the cuticle, ground and snow surface resistances and decreasing the LAI and stomatal resistance (by reducing the average size of stomatal openings because of sunlight) yielded V_d values that were in better agreement with measurements and results published in the literature. Table 6 provides a summary of the measurements, model estimates and the modified model estimates of V_d. For NO_2, none of the models have been able to duplicate the negative V_d values that were obtained from measurements over the canopies. This result was expected because of the possibility of local NO_2 emissions and chemical reactions and the inadequacy of the theory of dry deposition velocity in such circumstances. The theory may be, however, valid for NO_x because its amount is approximately conserved. In contrast, no negative NO_2 V_d values were measured over snow, as expected, because of the lack of decayed material in the soil, which can emit NO and/or NO_2, which perhaps may change because of chemical reactions in the air.

It can be concluded that the dry deposition velocity is dominated by the bulk canopy resistances (in fall) and the snow surface (at 0°C or lower) resistances, which are quite large. It is recommended that the model-assigned values of LAI be made more compatible with the measured seasonal values. Similar ADOM overestimates for O_3 V_d obtained by Padro et al. (1991) over a fully leafed deciduous forest also showed improvement when canopy parameters were modified. It is also recommended that further tests be conducted using Wesely's model, which showed encouraging results.

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