

PARAMETERIZATION OF SURFACE RESISTANCES TO GASEOUS DRY DEPOSITION IN REGIONAL-SCALE NUMERICAL MODELS*

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Abstract—Methods for estimating the dry deposition velocities of atmospheric gases in the U.S. and surrounding areas have been improved and incorporated into a revised computer code module for use in numerical models of atmospheric transport and deposition of pollutants over regional scales. The key improvement is the computation of bulk surface resistances along three distinct pathways of mass transfer to sites of deposition at the upper portions of vegetative canopies or structures, the lower portions, and the ground (or water surface). This approach replaces the previous technique of providing simple look-up tables of bulk surface resistances. With the surface resistances divided explicitly into distinct pathways, the bulk surface resistances for a large number of gases in addition to those usually addressed in acid deposition models (SO_2 , O_3 , NO_x and HNO_3) can be computed, if estimates of the effective Henry's Law constants and appropriate measures of the chemical reactivity of the various substances are known. This has been accomplished successfully for H_2O_2 , HCHO , CH_3CHO (to represent other aldehydes), $\text{CH}_3\text{O}_2\text{H}$ (to represent organic peroxides), $\text{CH}_3\text{C(O)O}_2\text{H}$, HCOOH (to represent organic acids), NH_3 , $\text{CH}_3\text{C(O)O}_2\text{NO}_2$ and HNO_2 . Other factors considered include surface temperature, stomatal response to environmental parameters, the wetting of surfaces by dew and rain, and the covering of surfaces by snow. Surface emission of gases and variations of uptake characteristics by individual plant species within the landuse types are not considered explicitly.

Key word index: Dry deposition, surface resistance, SO_2 , acid deposition, numerical modeling.

INTRODUCTION

The removal of gases from the atmosphere by turbulent transfer and uptake at the surface provides a primary means of cleansing the atmosphere and delivering chemical doses to surface components. This process of dry deposition is important in a number of environmental issues, particularly 'acid rain', which deals with transport, chemical transformations, and deposition over regional or continental scales. Numerical simulations of such phenomena are often necessary to evaluate the effects of emissions in one area on deposition in another. The concern here is with dry deposition parameterizations suitable for use in numerical simulations.

The dry deposition module previously used with the Regional Acid Deposition Model (RADM) computed the dry deposition velocities for SO_2 , O_3 , NO_x (defined here as the sum of NO and NO_2), sulfate in sub- μm particles, and HNO_3 vapor in the U.S. and southern Canada (Sheih *et al.*, 1986; Walcek *et al.*,

1986; Chang *et al.*, 1987). The module is based on micrometeorological formulas and tables that list bulk surface resistances to uptake for the gases. The main objectives of this paper are to put these look-up tables on a more solid scientific footing and to derive methods for estimating the surface resistances of additional gaseous substances. For RADM, the additional substances of interest include H_2O_2 , HCHO and other aldehydes, organic peroxides, peroxyacetic acid, organic acids, NH_3 , peroxyacetyl nitrate (PAN) and HNO_2 . Another improvement addressed here is a more explicit method to evaluate changes in surface resistances resulting from surface wetness associated with dew and rain. This paper summarizes the changes made in the RADM dry deposition module, which are described in greater detail elsewhere (Wesely, 1988).

FRAMEWORK OF SURFACE RESISTANCE FORMULATIONS FOR SO_2 AND O_3

The familiar framework used in past dry deposition modules relies on the simple formulation for gas deposition velocity as follows:

$$v_d \equiv -F_z/C_z, \quad (1a)$$

where F_z is the flux density and C_z is the concentration at height z . The magnitude of the deposition velocity

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can be found as

$$|v_d| = (r_a + r_b + r_c)^{-1}, \quad (1b)$$

where r_a is the aerodynamic resistance (common to all gases) between a specified height and the surface, r_b is the quasilaminar sublayer resistance (whose only dependence on the properties of the gas of interest is its molecular diffusivity in air), and r_c is the bulk surface resistance (e.g. Wesely and Hicks, 1977; Garland, 1977; Baldocchi *et al.*, 1987). We assume that r_a and r_b will be evaluated with existing techniques but will suggest new methods to estimate r_c for the five seasonal categories and 11 landuse types employed with the

module (Sheih *et al.*, 1986; Walcek *et al.*, 1986). The landuse types are listed under Table 1, and the seasonal categories are (1) midsummer with lush vegetation, (2) autumn with unharvested cropland, (3) late autumn after frost but with no snow, (4) winter with snow on the ground, and (5) transitional spring with partial green coverage. Although Equation (2) is traditionally used primarily to address vegetated surfaces, r_c in the present paper addresses a much wider range of surface conditions.

The tables of r_c for SO_2 and O_3 used as primary module inputs in the past will be replaced with more detailed information. The approach taken here is to

Table 1. Input resistances (s m^{-1}) to the module for computations of surface resistances (r_c). Entries of 9999 indicate that there is no air-surface exchange via that resistance pathway

Resistance component	Landuse type*										
	1	2	3	4	5	6	7	8	9	10	11
Seasonal category 1: midsummer with lush vegetation											
r_i	9999	60	120	70	130	100	9999	9999	80	100	150
r_{lu}	9999	2000	2000	2000	2000	2000	9999	9999	2500	2000	4000
r_{ac}	100	200	100	2000	2000	2000	0	0	300	150	200
r_{gsS}	400	150	350	500	500	100	0	1000	0	220	400
r_{gsO}	300	150	200	200	200	300	2000	400	1000	180	200
r_{cis}	9999	2000	2000	2000	2000	2000	9999	9999	2500	2000	4000
r_{cio}	9999	1000	1000	1000	1000	1000	9999	9999	1000	1000	1000
Seasonal category 2: autumn with unharvested cropland											
r_i	9999	9999	9999	9999	250	500	9999	9999	9999	9999	9999
r_{lu}	9999	9000	9000	9000	4000	8000	9999	9999	9000	9000	9000
r_{ac}	100	150	100	1500	2000	1700	0	0	200	120	140
r_{gsS}	400	200	350	500	500	100	0	1000	0	300	400
r_{gsO}	300	150	200	200	200	300	2000	400	800	180	200
r_{cis}	9999	9000	9000	9000	2000	4000	9999	9999	9000	9000	9000
r_{cio}	9999	400	400	400	1000	600	9999	9999	400	400	400
Seasonal category 3: late autumn after frost, no snow											
r_i	9999	9999	9999	9999	250	500	9999	9999	9999	9999	9999
r_{lu}	9999	9999	9000	9000	4000	8000	9999	9999	9000	9000	9000
r_{ac}	100	10	100	1000	2000	1500	0	0	100	50	120
r_{gsS}	400	150	350	500	500	200	0	1000	0	200	400
r_{gsO}	300	150	200	200	200	300	2000	400	1000	180	200
r_{cis}	9999	9999	9000	9000	3000	6000	9999	9999	9000	9000	9000
r_{cio}	9999	1000	400	400	1000	600	9999	9999	800	600	600
Seasonal category 4: winter, snow on ground and subfreezing											
r_i	9999	9999	9999	9999	400	800	9999	9999	9999	9999	9999
r_{lu}	9999	9999	9999	9999	6000	9000	9999	9999	9000	9000	9000
r_{ac}	100	10	10	1000	2000	1500	0	0	50	10	50
r_{gsS}	100	100	100	100	100	100	0	1000	100	100	50
r_{gsO}	600	3500	3500	3500	3500	3500	2000	400	3500	3500	3500
r_{cis}	9999	9999	9999	9000	200	400	9999	9999	9000	9999	9000
r_{cio}	9999	1000	1000	400	1500	600	9999	9999	800	1000	800
Seasonal category 5: transitional spring with partially green short annuals											
r_i	9999	120	240	140	250	190	9999	9999	160	200	300
r_{lu}	9999	4000	4000	4000	2000	3000	9999	9999	4000	4000	8000
r_{ac}	100	50	80	1200	2000	1500	0	0	200	60	120
r_{gsS}	500	150	350	500	500	200	0	1000	0	250	400
r_{gsO}	300	150	200	200	200	300	2000	400	1000	180	200
r_{cis}	9999	4000	4000	4000	2000	3000	9999	9999	4000	4000	8000
r_{cio}	9999	1000	500	500	1500	700	9999	9999	600	800	800

* (1) Urban land, (2) agricultural land, (3) range land, (4) deciduous forest, (5) coniferous forest, (6) mixed forest including wetland, (7) water, both salt and fresh, (8) barren land, mostly desert, (9) nonforested wetland, (10) mixed agricultural and range land, and (11) rocky open areas with low-growing shrubs.

divide the resistance r_c into several components, as is commonly done in resistance models in which series and parallel resistances are identified for various parts of the canopy (e.g. see reviews by Unsworth, 1980; Hosker and Lindberg, 1982; Baldocchi *et al.*, 1987). These components are illustrated in Fig. 1, beneath the resistances r_a and r_b . Analogously to Ohm's law in electrical circuits, r_c can be found as

$$r_c = [1/(r_s + r_m) + 1/r_{lu} + 1/(r_{dc} + r_{cl}) + 1/(r_{ac} + r_{gs})]^{-1}. \quad (2)$$

This formulation assumes that the concentrations representative of the plant mesophyll (C_m), substrates in the upper canopy (C_{lu}), substrates in the lower canopy (C_{cl}) and substrates at the ground surface (C_g) are in equilibrium with a single concentration (C_c) in air (e.g. by equilibrium partition coefficients). In this work, all four substrate concentrations will be assumed to be zero. While it may be useful, as will be discussed later, to use nonzero values for gases such as NO, NO₂ and NH₃ that are emitted from the surface, the distinctions among the substrate concentrations identified in Fig. 1 are not addressed in this paper because the distinctions are not used in this model.

The resistances contributing to r_c as depicted in Fig. 1 require some general explanation. First, they represent bulk properties and are not usually simply related to a single measurable quantity in the field.

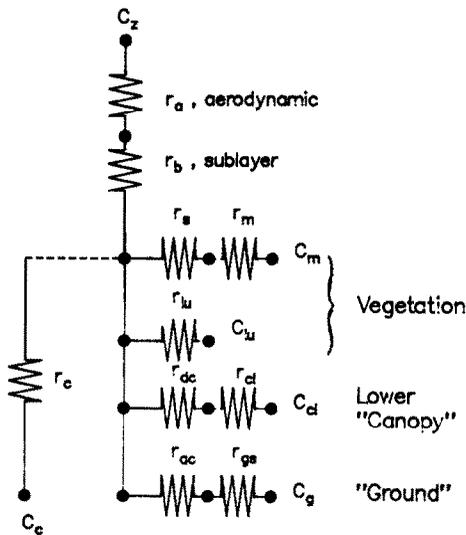


Fig. 1. Schematic diagram of pathway resistances used in the module, where r_c is derived via Equation (2). The term r_s represents the surface bulk resistance component for leaf stomata, r_m for leaf mesophyll resistance, r_{lu} for leaf cuticles in healthy vegetation and otherwise the outer surfaces in the upper canopy, r_{dc} for a gas-phase transfer affected by buoyant convection in canopies, r_{cl} for leaves, twig, bark or other exposed surfaces in the lower canopy, r_{ac} for transfer that depends only on canopy height and density and r_{gs} for the soil, leaf litter, etc., at the ground surface.

Rather, they correspond to properties or behaviors inferred from measurements of net vertical fluxes above the bulk surface. For example, r_s is the bulk canopy stomatal resistance and itself consists of series and parallel pathways of mass transfer due to the diffusion through leaf stomatal apertures that may exist on one or both sides of the leaves. Further, the leaves are distributed throughout the canopy and do not have uniform stomatal resistances because of varying solar irradiation, temperature, ventilation, etc. The mesophyll resistance (bulk: r_m) and the resistance of the outer surfaces in the upper canopy (bulk: r_{lu}), which corresponds to leaf cuticular resistance in healthy vegetation, would also vary according to position in the canopy. Another important point is that the landuse types represent very broad categories. For example, one type represents all agricultural crops, regardless of their heights and physiological characteristics. This lack of detail may result in a poor estimate of surface resistance for any particular surface cover, at a specific location and time.

The values assumed for baseline resistances are listed in Table 1. They form the basis for estimating the resistances for all the gases to be considered here. The values for r_i represent the minimum bulk canopy stomatal resistances for water vapor. It is well known that stomatal resistance varies with solar radiation and temperature. In the previous dry deposition module, solar radiation categories were used to form tables of resistance, and temperature was not explicitly included (Sheih *et al.*, 1986; Walcek *et al.*, 1986). Here we use the following generalized function to estimate the bulk canopy stomatal resistance:

$$r_s = r_i \{1 + [200(G + 0.1)^{-1}]^2\} \{400[T_s(40 - T_s)]^{-1}\}, \quad (3)$$

where G is the solar irradiation in W m^{-2} and T_s is the surface air temperature ($^{\circ}\text{C}$) between 0 and 40°C . Outside this range, we set r_s to a very large value, to implement the assumption that the transfer through stomata is stopped. Equation (3) is derived from a number of studies that formulated similar relationships specific to certain plant species (Baldocchi *et al.*, 1987). While our landuse map does not provide the detailed information necessary to make species-specific estimates of stomatal resistance, Equation (3) should provide representative values.

The combined minimum stomatal and mesophyll resistance for substance x can be found as

$$r_{smx} = r_s D_{\text{H}_2\text{O}}/D_x + r_{mx}, \quad (4)$$

where D_x is the molecular diffusivity of gas x in air, $D_{\text{H}_2\text{O}}$ is the molecular diffusivity for water vapor, and r_{mx} is the mesophyll resistance for the gas of interest. The scaling of stomatal resistance by the ratio of molecular diffusivities as indicated by the first term on the right-hand side of Equation (4) is a well known technique, though not without limitations (e.g. Ball, 1987). In addition, the description of mesophyll resistance in this manner, though common, can lead to

systematic errors because source-sink distributions in the substomatal cavity are different for different substances and can also depend on stomatal aperture size (e.g. Taylor *et al.*, 1983). Unfortunately, the generalized quantitative relationships necessary to compensate for these limitations in this modeling effort are not available for most of the substances and types of vegetation addressed here. Because numerous field studies have shown that bulk canopy mesophyll resistances for O_3 and SO_2 are small, we assume that the two resistances are zero, which is a reasonable approximation commensurate with the accuracies of Equations (3) and (4). Suggestions will be made later for methods to estimate r_{mx} for other substances.

The lower canopy resistance r_{cl} is meant to account for uptake pathways at the leaves, twig, bark, etc., while the ground surface resistance r_{gs} signifies uptake at the 'ground' by soil, leaf litter, snow, water, etc. In Table 1, separate values for SO_2 and O_3 are indicated by the additional subscripts 'S' and 'O', respectively. We expect that all surfaces represented by r_{lc} and r_{gs} have a reduced capacity for uptake when cold. For example, surface resistances for uptake of HNO_3 , SO_2 and NO_2 by snow increase markedly when its temperature decreases below $-2^\circ C$ (Johansson and Granat, 1986; Valdez, 1987). Accordingly, we approximate such an effect for all surfaces by adding the value, in sm^{-1} , of $1000 \exp[-T_s - 4]$ to r_{lc} , r_{lc} and r_{gs} for all substances. It is unknown whether this procedure is correct for every substance, and there may be notable exceptions. For example, recent work has shown that the rate of uptake of H_2O_2 by ice is not reduced when the temperature drops below freezing (Lee Y.-N., Brookhaven National Laboratory, private communication).

The approach of placing r_{ac} and r_{dc} along parallel resistance pathways (Fig. 1) can lead to difficulties if the fact is ignored that such resistances are actually partially in series, especially in tall vegetative canopies and other deep structures. The primary justification for the present procedure is that it allows empirical manipulation of the values of r_{dc} and r_{ac} to match experimental findings for diverse types of surfaces. As shown by Wesely (1983), for example, the value of r_{ac} for O_3 increases with representative heights and densities of 'canopies'. The values of r_{ac} are thus estimated mostly on the basis of the depth of the structure, and are assigned solely by landuse and season. The data of Wesely (1983) do not show a strong dependency of r_{dc} and r_{ac} on wind speed, although some dependency should exist. In effect, r_{ac} represents the situation in which there is a minimal level of ventilation at the ground beneath the canopy for the landuse type addressed. We neglect the effects of buoyancy-induced mixing on r_{ac} , which might be somewhat unrealistic but follows from a uncomplicated interpretation of the available field data.

The resistance r_{dc} is determined by the effects of mixing forced by buoyant convection when sunlight heats the ground or lower canopy and by penetration

of wind into canopies on the sides of hills. The following simplistic formula is used:

$$r_{dc} = 100[1 + 1000(G + 10)^{-1}](1 + 1000\theta)^{-1}, \quad (5)$$

where θ is the slope in radians of the local terrain, and r_{dc} is expressed in sm^{-1} . The value of 1000 for the coefficient of G is a rough estimate based on observations (Wesely, 1983; Wesely *et al.*, 1983); the coefficient of 1000 for θ is a first approximation for which no relevant data are at hand.

The values of r_{ac} , r_{gs} and r_{cl} in Table 1 have been adjusted to produce good estimates of the total surface resistance, r_c , rather than to give extremely realistic estimates of these three components. Obvious examples of necessary adjustments concern the values of r_{cl} , because r_{dc} calculated by Equation (5) is often small regardless of landuse type and seasonal category. One example is that r_{cl} has been set to large values for lakes and bare ground in order to cut off mass transport to the (nonexistent) plant canopy, regardless of the values of r_{dc} . In the cases of seasonal category 4 (wintertime with snow) and landuse type 2 (agricultural land) for O_3 , r_{cl} has been allowed to be as small as $1000 sm^{-1}$ in order to allow O_3 destruction at the surfaces of dry materials such as bushes that protrude above the snow.

The gas-phase sublayer resistance r_b is shown as being common to all lower branches of the pathways in Fig. 1, although it is normally only applicable to transfer at the upper portions of the overall surface. Ideally, suitable bulk sublayer resistances would be explicit parts of what is now shown as r_{ac} and r_{dc} . However, formulation of such sublayer resistances in the lower canopy and at the ground beneath the canopy is quite difficult, because these resistances depend on local rates of momentum transfer, for which simple parameterizations are not readily available. While the positioning of r_b in Fig. 1 is consistent with the methods by which the values of r_{ac} and r_{dc} have been inferred from experimental results, the present approach might be inadequate for situations in which the molecular diffusivity of the substance of interest is much different from those for SO_2 and O_3 , when exchange at surfaces below the upper canopy comprises a large portion of the net vertical flux above the canopy.

EXTENSION TO OTHER SUBSTANCES

Nitric oxide, NO_2 , and HNO_3 vapor were treated fairly explicitly by Sheih *et al.* (1986), but other compounds such as NH_3 , H_2O_2 , $HCHO$ and other aldehydes, organic acids, organic peroxides and peroxyacetic acid have been treated in a less thorough fashion (Chang *et al.*, 1987). As a result of their reactivity or solubility, all these substances and others such as PAN and HNO_2 may be deposited on the surface of the Earth at a significant rate. Past work has

shown many times that both reactivity and solubility are important factors in affecting the uptake rates by vegetation (e.g. Hill, 1971). As already discussed with regard to Equation (4), the ratio of the molecular diffusivities of trace gases in air to that of water vapor directly affects their stomatal resistances in vegetation. Table 2 lists the properties we will use to estimate the surface resistances for these gases.

The effective Henry's Law constants in Table 2 are used to scale the rates of uptake by moist and wet surfaces relative to rates for SO₂ uptake. We thus effectively assume that removal after dissolution is quite effective. Although this assumption appears to be valid for uptake of SO₂ by the extracellular water in the substomatal cavities of plant leaves, it might not apply to all substances and substrates considered in this paper. Also, the Henry's Law constants listed are not adjusted for the effects of ionic strength on the solubility of gases. To represent the ability of the gas to go into such aqueous solutions, this effective Henry's Law constant incorporates the effects of acid-base equilibria at a pH of 7. While this pH may be too high for some fresh water lakes, it is reasonable for ocean water and some large lakes such as the Great Lakes. Also, near-neutral conditions are typical of plant sap, whose pH presumably is not much different from that encountered in the substomatal cavities in the leaves of many plants (Canny, 1984). We assume that the hydration and formation of ions are rapid (to the

extent that they occur), as is the case for SO₂ (Martin, 1984).

The values listed in Table 2 for the negative log of electron activity for half redox reactions in neutral aqueous solutions [$pe^0(W)$] and the overall second-order reaction rates [$k^{(2)}$] with S(IV) provide a means to estimate a reactivity factor f_0 for oxidation of biological substances. Three categories are used: highly reactive ($f_0=1$), which implies that the gas is as reactive as O₃; slightly reactive ($f_0=0.1$); and non-reactive ($f_0=0$). The slightly reactive category is intended primarily to set plant leaf mesophyll resistances to very small values and to allow rapid uptake of gases through plant leaf stomata. As is evident in Table 2, the value of $f_0=0.1$ is assigned to substances that have a rather small value of $pe^0(W)$ but still have a significant second-order reaction with S(IV). This procedure is based on the hypothesis that if a substance can oxidize S(IV), it will be removed rapidly in the slightly reducing environment of the substomatal materials. Support for this hypothesis comes from the observations that NO₂ seems to have a small mesophyll resistance (Wesely *et al.*, 1982; Delaney and Davis, 1983). The use of reactivity with S(IV) as an indicator, nevertheless, is only an expedient that takes advantage of the large amount of information that has become available on this pseudo-first-order reaction rate (see references listed in Table 2). This is not meant to imply that the S(IV) components of SO₂(aq),

Table 2. Gases considered in the dry deposition module and their properties relevant to estimating resistances to dry deposition

Gaseous species	Symbol	D_{H_2O}/D_x^*	$H^{*\dagger,\ddagger}$ (Matm ⁻¹)	$pe^0(W)\ddagger,\S$	$k^{(2)\parallel}$ (M ⁻¹ s ⁻¹)	f_0
Sulfur dioxide	SO ₂	1.9	1×10^5	-5	-	0
Ozone	O ₃	1.6	0.01	28	6×10^8	1
Nitrogen dioxide	NO ₂	1.6	0.01	—	2×10^6	0.1
Nitric oxide	NO	1.3	2×10^{-3}	—	$< 1 \times 10^{-2}$	0
Nitric acid vapor	HNO ₃	1.9	1×10^{14}	7	$< 1 \times 10^{-2}$	0
Hydrogen peroxide	H ₂ O ₂	1.4	1×10^5	23	7	1
Acetaldehyde	(ALD) [¶]	1.6	15	<0	-	0
Formaldehyde	HCHO	1.3	6×10^3	-3	-	0
Methyl hydroperoxide	(OP) [¶]	1.6	240	—	2	0.1
Peroxyacetic acid	PAA	2.0	540	—	600	0.1
Formic acid	(ORA) [¶]	1.6	4×10^6	-8	-	0
Ammonia	NH ₃	1.0	2×10^4	-	-	0
Peroxyacetyl nitrate	PAN	2.6	3.6	—	$> 3 \times 10^3$	0.1
Nitrous acid	HNO ₂	1.6	1×10^5	6	4×10^{-4}	0.1

—: Not relevant.

—: Information not found.

* Computed as the square root of ratio m_x/m_{H_2O} of molecular weights.

† Effective values for water with near-neutral pH.

‡ Drawn primarily from summaries by Schwartz (1984); Gaffney *et al.* (1987); Lind and Kok, 1986 (methyl hydroperoxide and PAA); Jacob, 1986 (formic acid).

§ Obtained primarily from Stumm and Morgan (1981) and Morel (1983).

¶ Pseudo-first-order rate constants for oxidation of S(IV) in water with near-neutral pH, derived for O₃ (Hoffman, 1986); NO₂ (Lee and Schwartz, 1983); NO and HNO₃ (Martin *et al.*, 1981); H₂O₂ (articles reviewed by Seinfeld, 1986); methyl hydroperoxide and PAA (Lind *et al.*, 1987); PAN (Lee, 1984; Calvert *et al.*, 1985); HNO₂ (Oblath *et al.*, 1981).

¶ Class of substances (aldehydes, organic peroxides, and organic acids) represented by the species shown.

HSO_3^- , and SO_3^{2-} in extracellular water are unaffected by other reactions [e.g. see Mudd (1975a) for a discussion of the fate of SO_2]. The reality may be that the pathways to uptake of substances such as NO_2 are strongly influenced by enzymatic processes (e.g. Law and Mansfield, 1982). Further, these pathways may be cut off when the gas-phase concentrations reach a fairly low value corresponding to a compensation point for the biota (Johansson, 1987).

The mesophyll resistance in Equation (4) is computed for any substance x on the basis of the key parameters H^* and f_0 :

$$r_{\text{mx}} = (H^*/3000 + 100f_0)^{-1}. \quad (6)$$

This relationship assumes that two parallel pathways exist to the extracellular water inside plant leaf stomata, which is concomitant with the fact that O_3 , which is poorly soluble in water, and SO_2 , which has a low oxidation potential, both have a mesophyll resistance near zero. The pathway based on f_0 produces very small values of r_{mx} when f_0 is 1 or 0.1. The other pathway is via dissolution in the aqueous solution, and the factor 3000 M atm^{-1} is derived in part from the consideration that if H^* is sufficiently large, the concentration that can be achieved in the aqueous phase represents a large sink for the substance. As Equation (6) indicates, values of H^* greater than about ten will result in fairly rapid uptake. The value of 3000 is derived from considerations of CO_2 uptake by vegetation. For example, it is well known that uptake rates of $1 \text{ mg m}^{-2} \text{ s}^{-1}$ are approached with lush vegetation in optimum ambient conditions (e.g. Monteith, 1973). This rate corresponds to a (bulk canopy) mesophyll resistance of approximately 600 s m^{-1} . At a pH of seven, H^* for CO_2 is near 4.4, and the value of 3000 as a rounded-off equivalent to $(4.4)(600)$ is used in Equation (6). Although the hydration rate of CO_2 is normally slow (Quinn and Otto, 1971), we have assumed that it is accelerated by enzymatic reactions in the leaf, which would allow rapid equilibrium to be established.

The resistance of the outer surfaces in the upper canopy (leaf cuticular resistance in healthy vegetation) is computed as

$$r_{\text{lux}} = r_{\text{lu}}(10^{-5}H^* + f_0)^{-1}. \quad (7)$$

This allows for two parallel routes to the substrate, one analogous to SO_2 pathways and one to O_3 pathways. Substances such as HNO_3 that have a very high solubility in aqueous solution will be removed rapidly at the surface, as is indicated by the first term on the right-hand side. The second term allows highly reactive substances to behave as O_3 and is effective in reducing uptake for substances classified as slightly reactive ($f_0 = 0.1$).

For uptake of a gas that has a nonzero value of f_0 and does not have an extremely large value of H^* , Equation (7) implies that the gas will diffuse through the outer surfaces and cuticles of leaves in the same way as do SO_2 and O_3 . No adjustments are made for

molecular size and varying diffusivities in air, just as no differentiation between SO_2 and O_3 is made in the values of r_{lu} . We could, for example, hypothesize that uptake at outer surfaces is limited by molecular diffusion in air and then modify the terms on the right-hand side accordingly. This hypothesis would envision the outer surfaces as being impervious except for tiny air-filled gaps, smaller than stomatal openings. However, such scaling with diffusivities is questionable even for CO_2 , which is one of the few substances other than water vapor that has been studied with regard to leaf cuticular resistances (e.g. Holmgren *et al.*, 1965). In addition, Equation (7) does not account for the possibility that nonpolar substances might dissolve readily in the waxy covering of the cuticle. For example, it has been found that vapor-phase PCBs accumulate to a significant extent in plant leaves (Buckley, 1982), and that the octanol-water partition coefficient appears to be a key parameter for describing the foliar uptake of organic compounds (Travis and Hattemer-Frey, 1988).

The resistance of the exposed surfaces in the lower portions of structures (canopies, buildings) above the ground is computed as the parallel sum of resistances corresponding to those for SO_2 and O_3 :

$$r_{\text{clx}} = [H^*/(10^5 r_{\text{cis}}) + f_0/r_{\text{cio}}]^{-1}. \quad (8)$$

The two terms on the right-hand side have the same function as the terms on the right-hand side of Equation (7), but here the individual resistances, r_{cis} and r_{cio} , have been incorporated.

Computation of resistance to uptake at the 'ground' surface takes an approach equally simple as that in Equations (7) and (8). For the varied situations that include bodies of water, bare soil, and litter beneath forest canopies, the resistance is computed as

$$r_{\text{gsx}} = [H^*/(10^5 r_{\text{gss}}) + f_0/r_{\text{gso}}]^{-1}. \quad (9)$$

For surfaces with a pH significantly < 7 , it would be desirable to use appropriately adjusted values of H^* , even for SO_2 .

EFFECTS OF DEW AND RAIN

One effect of dew and rain at the surface is the covering of leaf stomata, which cuts off direct gas exchange when the stomata are open. Field observations in recent unpublished experiments at Argonne National Laboratory indicate that about two-thirds of the leaves in a canopy are typically covered, although the amounts can vary widely. Accordingly, the value of r_s in equation (4) should be increased by a factor of 3. The only other adjustment we make is in the value of r_{lu} , for the leaves in the upper canopy. Since we thus assume that altered resistances in other portions of the canopy are relatively insignificant, care must be taken to make arithmetic adjustments that allow some effects of dew when the 'canopy' is not vegetative, such as in urban areas. For dew, the results

of the experiments at Argonne National Laboratory indicate that the resistance to SO₂ uptake by vegetation is probably decreased (found earlier by Fowler and Unsworth, 1979), but the uptake of O₃ is retarded. A reasonable approximation for the resistance to SO₂ uptake by a dew-covered surface is

$$r_{1uS} = 100 \text{ s m}^{-1}, \quad (10)$$

which results in a very small value of r_c . For O₃, the dew acts as a barrier to surface removal:

$$r_{1uO} = [1/3000 + 1/(3r_{1u})]^{-1}, \quad (11)$$

where the second term on the right-hand side takes into account the reduction of dry areas available for removal. The value of 3000 s m⁻¹ in the first term is only a rough approximation.

Wetting of surfaces by rainfall probably has quite different effects. Unpublished measurements by Argonne National Laboratory indicate that rainfall results in an increase of resistance to SO₂ uptake and may actually decrease the resistance to O₃. This is reasonable because the rainfall may be sufficiently saturated with S(IV) to prevent further uptake of SO₂ and allow limited chemical reaction with O₃. The extent of such behavior would depend on the chemical properties of the ambient atmosphere and of the substrates, as well as those of the rainfall. As a first approximation, we estimate the resistance to SO₂ uptake by a surface wetted by rainfall to be

$$r_{1uS} = [1/5000 + 1/(3r_{1u})]^{-1}, \quad (12)$$

which has a structure similar to Equation (11). For O₃, rainfall might have a weaker effect on surface removal, if the rain is not too acidic:

$$r_{1uO} = [1/1000 + 1/(3r_{1u})]^{-1}. \quad (13)$$

A special exception should be made for SO₂ uptake in urban areas, which here refers to areas with very little vegetation. Preliminary results indicate that fairly porous materials such as limestone take up SO₂ rather rapidly when wet or when the relative humidity is high (Youngdahl A. C., Argonne National Laboratory, private communication). In an attempt to take this factor into account, we recommend that the value of r_{1uS} be adjusted for landuse type 1 when wet conditions prevail, so that Equations (10) and (12) are then replaced with the following:

$$r_{1uS} = 50 \text{ s m}^{-1}.$$

This will probably require modification as better information is obtained.

For substances other than SO₂ and O₃, the following formulation replaces Equation (7) if either dew or rain wets the surface:

$$r_{1ux} = [1/(3r_{1u}) + 10^{-7} H^* + f_0/r_{1uO}]^{-1}, \quad (14)$$

where reduction of dry area, solubility in water, and chemical reactivity are taken into account by the first, second, and third terms, respectively, on the right-

hand side. In this case, r_{1uO} is taken from Equation (11) for dew and from Equation (13) for rain.

In practical application of Equations (10)–(14), information on dewfall and rainfall events must be provided from sources external to the dry deposition module. A direct computation of the surface wetness would be most desirable, e.g. by estimating the amount of free surface water accumulated and then evaporated. Alternatively, surface relative humidity might be a useful index. After dewfall and rainfall events are completed, surface wetness often disappears as a result of evaporation after approximately 2 hours of good atmospheric mixing, the period of time recommended earlier (Sheih *et al.*, 1986) and found to be typical for dew during recent experiments at Argonne National Laboratory. An important subcategory of surface wetness is that caused by cloudwater impaction on surface elements. Resistance would probably then be altered in a similar fashion as they are for rainfall, since cloudwater concentrations of the chemically important ions are usually at least as large as they are in rain (e.g. Unsworth and Crossley, 1987; Weathers *et al.*, 1988).

RESULTS AND CONCLUSIONS

Examples of computed surface resistances are shown in Table 3 for one landuse type (deciduous forest), selected values of G , and one case each for dew and rain when G is zero. The surface temperatures assumed were 25, 10, 2, 0 and 10°C for seasonal categories 1–5, respectively. The values of r_c for SO₂, O₃ and HNO₃ estimated with these procedures are usually about the same as those found with the previous dry deposition module (Sheih *et al.*, 1986; Wesely, 1988). For the minor differences that exist, the present results are probably more realistic, partially because they are more rigorously derived. The uptakes of SO₂ and O₃ by healthy vegetation during the daytime are controlled by stomatal resistances. Ozone surface resistances tend to be smaller than those for SO₂, and the differences are accentuated for surfaces that are rather inactive biologically, such as senescent vegetation and surfaces typical of winter and autumn landscapes.

Values of surface resistances for HNO₃ and NO are not shown in Table 3 because they always signify extremes. Surface resistances for HNO₃ are practically negligible, in accordance with its very large value for Henry's Law constant. (A value of r_c near 10 s m⁻¹ should be assumed for HNO₃ and other substances whenever r_c is nearly zero, in order to avoid unrealistic estimates of extremely high deposition velocities over unusually rough surfaces.) At the other extreme, the surface resistances for NO are always very large, as determined by its low solubility and chemical reactivity.

As is desired, the calculated surface resistances for NO₂ are usually quite large except for lush vegetation

Table 3. Computed surface resistances r_c ($s\ m^{-1}$) for landuse type 4, deciduous forest. Values of 9999 indicate very large resistances; otherwise the values have been truncated to give only two significant digits

Seasonal category	Solar irradiation ($W\ m^{-2}$)						
	800	500	300	100	0	0 Wetted Dew	0 surface Rain
Sulfur dioxide							
1	120	130	160	370	1000	90	1100
2	1300	1300	1300	1300	1400	90	1200
3	1100	1100	1100	1100	1100	90	1000
4	980	980	980	990	1000	1000	1000
5	260	280	330	620	1100	90	1000
Ozone							
1	100	110	130	320	950	950	580
2	430	460	520	700	1200	940	570
3	390	420	460	600	950	760	500
4	550	610	700	1000	3000	3000	3000
5	180	190	220	430	940	810	520
Nitrogen dioxide							
1	120	130	160	480	2800	2700	2300
2	1800	1800	1800	1900	2600	2400	2100
3	1700	1700	1700	1800	2300	2200	1900
4	3800	3800	3900	4300	9500	9500	9500
5	270	290	350	850	2400	2300	2000
Hydrogen peroxide							
1	80	90	110	250	640	80	80
2	400	430	480	640	1000	90	80
3	360	380	420	540	830	80	80
4	390	420	460	610	980	980	980
5	150	170	190	370	740	80	80
Acetaldehyde							
1	320	330	370	790	9999	9999	9999
2	9999	9999	9999	9999	9999	9999	9999
3	9999	9999	9999	9999	9999	9999	9999
4	9999	9999	9999	9999	9999	9999	9999
5	510	540	630	1600	9999	9999	9999
Formaldehyde							
1	100	110	130	450	6600	1300	1300
2	8100	8100	8100	8100	8100	1300	1300
3	7800	7800	7800	7800	7800	1300	1300
4	2800	2800	2800	2800	2800	2800	2800
5	250	270	330	1000	7500	1300	1300
Methyl hydroperoxide							
1	120	130	160	480	2800	2500	2100
2	1800	1800	1800	1900	2600	2300	2000
3	1700	1700	1700	1800	2300	2100	1800
4	3500	3600	3600	4000	8000	8000	8000
5	270	290	350	840	2400	2100	1900
Peroxyacetic acid							
1	140	160	190	570	2800	2300	2000
2	1800	1800	1800	1900	2600	2100	1800
3	1700	1700	1700	1800	2300	1900	1700
4	3300	3300	3400	3700	6800	6800	6800
5	320	350	420	950	2400	2000	1800
Formic acid							
1	30	30	30	40	40	0	0
2	130	140	150	160	190	0	0
3	130	130	140	160	180	0	0
4	270	300	330	450	660	660	660
5	50	60	60	80	90	0	0

Table 3. (Contd.)

Seasonal category	Solar irradiation (W m^{-2})						
	800	500	300	100	0	0 Wetted Dew	0 surface Rain
Ammonia							
1	70	80	100	310	2600	430	430
2	3200	3200	3200	3200	3300	430	430
3	2900	2900	2900	2900	2900	430	430
4	1500	1500	1500	1500	1500	1500	1500
5	180	190	230	670	2800	430	430
Peroxyacetyl nitrate							
1	190	200	250	700	2800	2700	2300
2	1800	1800	1800	1900	2600	2400	2100
3	1700	1700	1700	1800	2400	2200	1900
4	3800	3900	4000	4400	9700	9700	9700
5	400	430	510	1000	2400	2300	2000
Nitrous acid							
1	100	110	140	340	1000	90	90
2	1300	1300	1300	1300	1400	90	90
3	1100	1100	1100	1100	1100	90	90
4	980	980	980	990	1000	1000	1000
5	230	250	290	580	1100	90	90

exposed to solar radiation, when leaf stomata are open. This conforms to a number of experimental investigations involving atmospheric concentrations of at least a few ppbV of NO_2 over a variety of surfaces recognized in each study as not being sources of the gas (e.g. Wesely *et al.*, 1982; Delaney and Davis, 1983; Gravenhorst and Bottger, 1983). Use of the value $f_0 = 0.1$ in Equation (6) implies fairly efficient uptake through stomata. It has been suggested that the measurement methods used in some of the field work tended to cause underestimates of NO_2 surface resistances because of interference by HNO_3 in sensor response (Huebert, 1983), but subsequent unpublished reevaluations by several investigators have indicated that overestimates were more likely because the interference may have only increased the mean concentrations and not the eddy fluctuations measured. The recommendations of Sheih *et al.* (1986), which ignored the possible HNO_3 effect, are still plausible: the minimum computed values of r_c for NO_x should be about 1.75 times the corresponding O_3 resistances over lush vegetation during a summer midday. For these conditions, the value of the ratio of r_c for NO_2 to that for O_3 is 1.2 in Table 3 and averages to about 1.5 for all landuse types that indicate a surface covered with vegetation. This value of 1.5 would increase to near the target value of 1.75 if NO_x were considered instead of NO_2 because the NO component of NO_x has a concentration typically about 10% of NO_2 concentration in nonurban areas and has a very large surface resistance.

The resistances computed for NO_2 for surfaces other than sunlit vegetation appear to be quite large. This results from use of relatively small values of f_0 and H^* in Equations (7), (8) and (9). Sheih *et al.* (1986) suggested that these resistances indeed should be high, near 1000 s m^{-1} , and recommended that, in general, the sum of NO and NO_2 should be considered rather than NO_2 alone. This was suggested because rapid in-air chemical reactions can cause a significant change of NO and NO_2 vertical fluxes between the surface and the point at which deposition velocities are applied, but the sum of NO and NO_2 fluxes should be practically unchanged (Fitzjarrald and Lenschow, 1983). This summing is clearly a desirable procedure, especially in nonurban environments away from local anthropogenic emissions, where concentrations of NO_2 and NO are much smaller than O_3 concentrations.

This effort to evaluate surface resistances does not consider the fact that nitrogen compounds are often emitted from soils, particularly when atmospheric concentrations are lower than a few ppbV. Emissions have been reported for NH_3 , NO and NO_2 (e.g. Dabney and Bouldin, 1985; Galbally, 1985; Anderson and Levine, 1987; Williams *et al.*, 1987). A first approximation to account for these emissions and thus obtain more realistic estimates of air-surface exchange would involve adjusting r_c values found with Equation (2) for NH_3 , NO and NO_2 by multiplying each r_c by $|C_x/(C_x - C_c)|$, where C_c is equal to an assumed compensation point of perhaps 2 to 3 ppbV. If C_c is $> C_x$,

r_c should remain positive and v_d should be made negative.

The computed surface resistances for SO_2 , O_3 , HNO_3 , NO and NO_2 generally conform to expectations based on results from numerous experiments at specific sites, as reviewed by Sheih *et al.* (1986). However, experimental data to confirm the calculated resistances for the large areas meant to be addressed, e.g. with the Regional Acid Deposition Model (Walcek *et al.*, 1986; Chang *et al.*, 1987), are not available. Uncertainties are difficult to quantify. In a recent comparison of models, relative uncertainties for weekly estimates of deposition velocities computed for these substances for selected areas in the eastern U.S. are approximately $\pm 30\%$, if one ignores the possible effects of surface nonuniformities such as hills (Wesely and Lesht, 1988).

The resistances for many of the additional substances are predictions that in many cases have no supporting field or laboratory observations. Except where noted, the resistances for the additional substances are calculated with no substantiation by experimental data. Hydrogen peroxide has the unusual properties of being both moderately soluble in water, as is SO_2 near a pH of seven, and as strong an oxidizing agent as O_3 . Rapid removal takes place at wet surfaces, and moderately rapid deposition occurs over vegetation. Many surfaces that may seem somewhat inert, such as in unharvested agricultural areas, remove H_2O_2 fairly efficiently. Solubility alone is highlighted in the surface resistances calculated for formaldehyde (HCHO), formic acid (HCOOH, or ORA to represent organic acids), and acetaldehyde (CH_3CHO , or ALD to represent aldehydes other than HCHO). Formaldehyde is taken up rather rapidly at liquid water surfaces and by sunlit vegetation, but has much less interaction with soils and senescent vegetation. The rather large solubility of formic acid allows it to be taken up rapidly at many different types of surfaces. Variations on the same theme are seen for NH_3 and HNO_2 . Laboratory and field observations have shown that NH_3 can be taken up quickly through leaf stomata and by moist surfaces in an agricultural crop (Hutchinson *et al.*, 1972; Denmead *et al.*, 1978; Lemon and Van Houtte, 1980; van Hove *et al.*, 1987). The resistances to NH_3 uptake by green vegetation (seasonal categories 1 and 5) are smaller than the corresponding resistances for SO_2 because r_{smx} calculated with Equation (4) for NH_3 is reduced by almost a factor of 2 as a result of its larger molecular diffusivity.

The remaining three substances, methyl hydroperoxide ($\text{CH}_3\text{O}_2\text{H}$, or OP to represent several organic peroxides), peroxyacetic acid [$\text{CH}_3\text{C}(\text{O})\text{O}_2\text{H}$, or PAA], and peroxyacetyl nitrate [$\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$, or PAN], have slightly limited solubility and are moderately reactive as oxidants. PAN is the least soluble and thus has the largest surface resistance of the three substances for sunlit green vegetation. Interpretation of data of Mudd (1975b) leads to the conclusion that

PAN (as well as peroxypropionyl nitrate) can be taken up quite rapidly through leaf stomata; Hill (1971) and Garland and Penkett (1976) found that deposition velocities for PAN are typically 1/2 to 1/3 of those for O_3 . This is at least partially consistent with computed estimates of surface resistances, from which we infer that maximum deposition velocities near 0.005 m s^{-1} are possible, for the optimum conditions of a fully sunlit, lush vegetative canopy. By comparison with the computed surface resistances for acetaldehyde, it is apparent that the chemical reactivity of PAN is probably the major factor affecting its surface resistance, not its solubility in water.

The dry deposition module is more rigorous and versatile than previous versions, but still has a number of limitations. The surface resistances that can be computed are specific to 11 landuse types and thus might not be directly useful in numerical models that use different surface characterizations. Oversimplifications are often necessary in order to use only 11 landuse types and five seasonal categories. For open bodies of water, we have assumed an aqueous pH near 7, which is undoubtedly too large for many small bodies of water. For O_3 , we have assumed that the surface resistance suitable for seawater is relevant ($r_c = 2000 \text{ s m}^{-1}$), which is probably too small for fresh water. In general, the dry deposition module will probably not produce very accurate estimates of dry deposition for a short time period in a particular small area. Rather, the estimates are intended for long-term averages over at least several weeks and for rather large areas over which the individual variations of plant species composition and factors such as soil moisture content are smoothed. For vegetation, uptake resistances by individual plant species have not been identified, and the influence of varying leaf areas (green or senescent) has not been tied explicitly to a measurable quantity such as LAI (leaf area index). The height of vegetation is only considered indirectly via landuse type. Soil alkalinity or acidity is not explicitly taken into account even though SO_2 removal rates by dry or acidic soils are undoubtedly much slower than by wet or alkaline soils.

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