A mathematical description of the multicomponent transport of gaseous components into needles of conifer trees is presented. Detailed physiology of the stomatal zone is taken into account, and diffusion through the atmospheric boundary layer, wax-filled anthercath, stomata, and substomatal cavity are described starting from the fundamental equations for multicomponent gas diffusion. The model was used to analyze the results from two sets of exposure experiments in which red spruce saplings were exposed to gas-phase H2O2 or to a combination of H2O2, SO2, and O3. Model calculations indicate that the wax-filled anthercath may provide a porous zone in which water can condense, thus protecting the sensitive inner tissues below the stomata from exposure to water-soluble, toxic, trace gases (such as SO2 and H2O2). The model was found to be sensitive to the accuracy of measurements of leaf temperature, dewpoint temperature of the chamber inlet and exit air, and gas flow rate and may provide some insight into the role of atmospheric pollutants in forest decline.

I. Introduction

Understanding the gas exchange between the atmosphere and plants is important to both atmospheric and plant scientists. Annual crop loss due to O3 damage, for example, has been estimated to be on the order of 2-5 billion dollars in the United States alone (1). Circumstantial evidence also links O3 exposure to high elevation spruce/fir forest decline in the United States and in Central Europe (2). Vegetation also plays an important role in the chemistry of the atmosphere. Many plant species have been found to be a source of highly reactive alkenes (e.g., ref 3), trace gases which are important O3 precursors. Vegetation also acts as a sink for many air pollutants (e.g., ref 4). For some species such as H2O2, losses to vegetative surfaces may be one of the most important loss processes (5). Therefore, the development of a fundamental model which describes the exchange of gases between plants and the environment would benefit both the plant science and atmospheric science communities.

Traditionally, the exposure of a plant to an atmospheric trace gas is characterized by the deposition velocity model (4), which inherently assumes that the leaf’s internal concentration of the pollutant, Cint, is zero (6, 7), so that

\[
Q = V_d (C_{amb} - C_{int}) = V_d C_{amb}
\]

where Q is the gas flux to the leaf, V_d is the deposition velocity, and C_{amb} is the ambient concentration. The deposition velocity (or resistance) model does not address the effects of the trace gas solubility or chemical reactions occurring in plant tissue. It also ignores the net convective flux of gases out of the leaf which develops when the plant is transpiring (8). The modified resistance model of Von Caemmerer and Farquhar (9), which takes into account the net flow of water vapor out of the leaf for calculating the intercellular CO2 concentration, applies only to the system of H2O, CO2, and air.

The Stefan–Maxwell equation, upon which the modified resistance model is based (9), assumes that the primary diffusion mechanism is molecular. In small volumes, however, molecule-wall collisions (Knudsen diffusion) may also contribute to diffusion. The Stefan–Maxwell equation can be modified to include the effects of the wall, so that the resulting equation includes Knudsen as well as molecular diffusion (10, 11):

\[
\frac{1}{RT} \frac{\partial P_i}{\partial z} = N_i^D + \sum_{j \neq i} x_i N_j^D - x_j N_i^D \frac{D_{ij}}{D_i}
\]

where \(N_i^D\) is the diffusive molar flux of species \(i\); \(D_{ij}\) is the molecular diffusion coefficient of species \(i\) with respect to \(j\); \(D_i^K\) is the Knudsen diffusivity of \(i\); \(x_i\) and \(P_i\) are the mole fraction and partial pressure of species \(i\), respectively; \(T\) is the absolute temperature; and \(R\) is the universal gas constant. This form of the Stefan–Maxwell equation was applied to the problem of diffusion in the stomatal region, where the stomatal pore diameter may approach the molecular mean free path so that Knudsen diffusion can become important (12). In ref 12, gas diffusion through the stomatal pore was treated as one-dimensional, multicompontent diffusion through a small capillary. By making some simplifying assumptions, ignoring chemical reactions in the leaf, and expressing gradients in finite-difference form, the resulting model presented in ref 12 is valid for no more than three gases.

In estimating the mass-transfer resistance due to the laminar boundary layer next to the leaf, unusual leaf geometries (aside from flat plate geometry) have been neglected in most of the modeling efforts reported to date. Other stomatal configurations (e.g., stomata not located at the leaf surface) are also typically neglected. For many conifers, however, the leaf is not flat but is approximately needle-shaped and is covered with a waxy surface into which the stomata are sunken.

In this work, we use gas transport theory to examine the transport of gases into conifer needles, taking into account the geometry of the spruce needle and the physiology of its stomatal zone. The assumption of a flat plate geometry is relaxed for the calculation of the boundary layer resistance. Reactive trace gases are considered by taking...
II. Spruce Needle Physiology

Red spruce (Picea rubens Sarg.) needles are spirally set on the tree's branches (15). The needles are 10-15 mm in length and four-sided. The cross-section is roughly diamond-shaped (16, 17). The sides of the needles are 0.5-1.0 mm in width. Stomata are located in rows, two to four rows on a side, on all four sides of the needles (18). On Sitka spruce, the rows are spaced about 70 μm apart (19). Within stomatal rows, the distance between stomatal centers is reportedly 100 μm for Sitka spruce (19) and for leaves in general (20).

Figure 1 illustrates our idealization of the stomatal zone and includes our best estimates of appropriate dimensions, based on information found in the literature on a variety of spruce. The needles are covered with a relatively thick layer of wax so that the stomata appear to be sunken (16). The stomata are located below the V-shaped stomatal antechamber. The distance from the top of the antechamber to the mouth of the stomatal pore is roughly 18 μm (19). On Sitka spruce (19) and red spruce (21), this antechamber is filled with a wax plug, from the top of the guard cells nearly to the epidermal surface. On Sitka spruce, the depth of the plug is 15-18 μm (19). The wax is in the form of finely divided tubes 1 μm in length by 150 nm in diameter, and voids between the wax tubes are roughly 1-2 μm across (19). The wax is comprised of cutin, a polymeric material consisting mainly of the esters of 16- and 18-carbon carboxylic acids and containing two or three hydroxyl groups (20). The stomatal pore depth of Sitka spruce is approximately 6 μm (19). In general, the stomatal pore is elliptical in shape, and the distance across is usually 5-10 μm (20).

In the internal regions of the needle, the cell is surrounded by the cell wall which is comprised primarily of water (up to 90%) (22). Also found in the cell wall are enzymes such as peroxidase (23, 24), and other chemical species such as ascorbic acid (25), an antioxidant that may play an important role as an atmospheric photochemical oxidant scavenger (26). The cell wall is approximately 1 μm in thickness (22).

III. Mathematical Formulation

Figure 2 illustrates a simplified schematic diagram of the stomatal zone, depicting four regions. Region I is the substomatal chamber. Diffusion of species involved in metabolic processes and chemical reactions of reactive gases (such as the reaction of O₃ with ascorbic acid dissolved in the cell wall water) are assumed to occur only at these walls, which are assumed to be comprised mainly of water. The reactions of ozone with several hydrocarbon constituents present in cell material have been discussed by Tingey and Taylor (27) and by Chameides (26), who examined the relative loss rates of ozone through reaction with ascorbic acid and certain hydrocarbons and found that the rate of loss due to reaction with ascorbic acid was...
the fastest. For lack of other available information, we therefore consider reaction with ascorbic acid for describing the ozone chemistry inside the needle. Transport through region II, the stomatal pore, is similar to flow through a small capillary. The pore radius is variable, depending primarily on light availability. The stomatal antechamber, region III, behaves as a porous medium packed with cylinders, through which diffusion is hindered by the tortuosity and porosity of the media. The uppermost region (region IV) is the laminar boundary layer over the needle surface. The thickness of this region, \( b_o \), is a function of the velocity and turbulence of the bulk air above the leaf.

In the following analysis, cylindrical coordinates are assumed, and seven gaseous species are included. During photosynthesis, the plant takes up CO\(_2\) and gives off O\(_2\). Because the inner plant tissues are largely made up of water, the inner air spaces have a high relative humidity (RH), and the plant gives off H\(_2\)O. Since there are concentration gradients for these species, there will be a concentration gradient in N\(_2\) as well; therefore, this species is also considered, although we assume that there is no net flux of N\(_2\). The reactive trace gases under study are O\(_3\), SO\(_2\), and H\(_2\)O.

**Point Equations.** Inside the substomatal chamber, the stomatal pore, and the antechamber (regions I–III), the governing equations for gas transport are the point continuity equations for each gaseous species \( i \). Concentration gradients in the angular direction have been neglected. Quasi-steady-state conditions are assumed. All chemical reactions are assumed to be heterogeneous and to occur at the substomatal chamber wall only. With these assumptions, the continuity equation in cylindrical coordinates becomes

\[
\frac{1}{\rho} \frac{\partial}{\partial r} (\rho N_i \gamma) + \frac{\partial N_i}{\partial z} = 0
\]

(3)

where \( N_i \) is the total molar flux of \( i \) relative to stationary coordinates. This flux results from both diffusive mechanisms and from bulk movement of gases

\[
N_i = N_i^D + N_i^V
\]

(4)

where the superscripts \( D \) and \( V \) denote “diffusive” and “viscous” (convective) contributions, respectively (10,11), and boldface parameters denote vector quantities. The convective flux arises from a pressure gradient and corresponds to gas transport due to bulk movement of material

\[
N_i^V = \gamma_i N_i^V
\]

(5)

where \( N_i^V \) is the total molar convective flux. Multicomponent diffusion for a mixture of \( n \) gases is described by the generalized form of the Stefan–Maxwell eq (28) for ideal solutions. We assume the gas mixture is isothermal and neglect the forced diffusion terms and the pressure diffusion term since the pressure gradient is expected to be small. The modified form of the Stefan–Maxwell equation which includes Knudsen diffusion is used, extended to include vector quantities (10–12, 29)

\[
\frac{1}{RT} \nabla \Pi_i = \frac{N_i^D}{D_{ii}^K} + \sum_{j=1}^{n} \left( \frac{\gamma_i N_i^D}{D_{ij}} - \frac{x_i N_j^D}{D_{ij}} \right)
\]

(6)

where \( n \) is the number of species, \( \nabla \Pi_i \) the gradient of the partial pressure of \( i \), is an expression of the concentration gradient of species \( i \), \( R \) is the gas constant, \( T \) is the absolute temperature, \( D_{ii}^K \) is the Knudsen diffusivity of \( i \), and the \( D_{ij} \)’s are the binary diffusion coefficients that are assumed to approximate the concentration-dependent multicomponent diffusivities at the low gas densities encountered in this problem (30).

**Spatially Averaged Equations.** In order to solve these equations, the technique of spatial averaging is applied. This allows us to treat the model as if it is one-dimensional, in that the concentrations and fluxes vary in the axial direction. We recognize, however, that stomatal transport is three-dimensional. By spatial averaging, we can take into account area changes in the direction of the flow that are due, for example, to fluxes at the wall.

**Region I.** The transport equations for region I are area-averaged in the radial direction. For this approximation to be valid, the concentration gradient in the radial direction should be much less than that in the axial direction. This criterion is met if the condition

\[
\left( \frac{r_o}{L_o} \right)^2 \ll 1
\]

(7)

is satisfied, where \( r_o \) and \( L_o \) represent the radius and length of a given transport zone. In region I, this ratio has a value of 0.25, which is sufficiently small to justify this approach (31). The area-averaged form (28) of eq 3 for region I becomes

\[
\frac{2}{R_i} \frac{d}{dz} \langle N_i \rangle = 0
\]

(8)

where \( \langle N_i \rangle \) represents the area-averaged flux of species \( i \) in the \( z \) direction. \( N_i \rangle \) is the flux at the wall, and \( r_1 \) is the radius of the substomatal region.

The Stefan–Maxwell equation must also be area-averaged, which results in dispersion terms that depend on second derivatives of the concentration gradient (Table 1). These dispersion terms are neglected; therefore, the area-averaged Stefan–Maxwell equation takes the form

\[
\frac{1}{RT} \frac{d}{dz} \langle \Pi \rangle = \sum_{i=1}^{n} \langle x_i \rangle \left( \frac{D_{ii}^K}{D_i} - \langle x_i \rangle \right) \langle N_i \rangle
\]

(9)

The binary diffusivities for each gas are calculated from a Gilliland-type correlation (32). The Knudsen diffusivity for diffusion in a cylindrical tube of diameter \( d \) is calculated by (12, 32)

\[
D_{ii}^K = \frac{d}{3} \left( \frac{8RT}{\pi M_i} \right)^{1/2}
\]

(10)

where \( M_i \) is the molecular weight of species \( i \). In pores or in porous media, Knudsen diffusion is expected to be insignificant when the pore size, \( d \), is much larger than the molecular mean free path, \( \lambda \), or when the Knudsen number, defined by (11)

\[
K_n = \frac{\lambda}{d}
\]

(11)

is much less than 1. The molecular mean free path is a function of temperature, pressure, and the molecular size (11)

\[
\lambda = \frac{kT}{\sqrt{2\pi\sigma^2P}}
\]

(12)
Table I. Summary of Equations and Boundary Conditions Used in Model for Substomatal Chamber

<table>
<thead>
<tr>
<th>region I</th>
<th>equation</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stefan–Maxwell</td>
<td>( \frac{d(x_i)}{dx} = \sum_{j=m}^n \left( \langle x_i \rangle \langle N_{ij} \rangle - \langle x_j \rangle \langle N_{ji} \rangle \right) cD_{ij} )</td>
<td>((n-1)) equations</td>
</tr>
<tr>
<td>momentum eq</td>
<td>( \frac{d(P)}{dx} = 0 )</td>
<td>(n)th equation</td>
</tr>
<tr>
<td>continuity eq</td>
<td>( \frac{d(N_{ij})}{dx} = -2 \frac{N_{ij}}{R_i^2} )</td>
<td>(n) equations</td>
</tr>
<tr>
<td>fluxes boundary conditions</td>
<td>( \langle N_{ij} \rangle = \langle N_{ij} \rangle_{H_2O} )</td>
<td>mass conservation across interface</td>
</tr>
<tr>
<td>miscellaneous parameters</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where \( \delta \) is the Boltzmann constant and \( \sigma \) is the molecular radius. For \( N_2 \) at 20 °C and 10^5 Pa, \( \lambda \approx 0.07 \mu m \) (12). The Knudsen number for \( N_2 \) in the substomatal region, then, is on the order of \( K_n \approx 0.07/100 \) so that in region I Knudsen diffusion may be neglected. Because the chamber is relatively large and open, no pressure gradients are expected in this region. The air inside the substomatal chamber is also assumed to be isothermal. The multi-component diffusion of the gas mixture at low density in region I can then be described by the Stefan–Maxwell equations (neglecting the Knudsen diffusion)

\[
\frac{d\langle x_i \rangle}{dx} = \sum_{j=m}^n \left( \langle x_i \rangle \langle N_{ij} \rangle - \langle x_j \rangle \langle N_{ji} \rangle \right) \]

(13)

where \( c \) is the total molar concentration or \( (P)/R_T \). In this form, the Stefan–Maxwell equations result in \((n-1)\) independent equations. The \( n \)th equation is obtained from the momentum balance (10). Based on the assumption that the substomatal chamber is relatively isobaric compared to the stomatal pore, the \( n \)th equation becomes

\[
\frac{d(P)}{dx} = 0 \]

(14)

The surfaces of the guard cells are assumed to be inert. All other walls of the substomatal chamber are assumed to be composed mainly of water and are, therefore, treated as a liquid film of thickness \( \delta \); therefore, the only source or sink of any gaseous species is through this film. Since the surfaces are primarily interested in the reactive air pollutants, for the unreactive gases (i.e., \( O_2, CO_2, \) and \( H_2O \)), the flux at the wall is assumed to be uniform for all surfaces. For a more detailed model of \( CO_2 \) assimilation, the kinetics of photosynthesis could also be included (e.g., ref 34). By material balance, the flux at this wall is related to the flux on a leaf area basis through the ratio of total leaf area to total internal surface area

\[
N_{ij}\delta \approx R \delta = \frac{Q(A_L)}{n_{st}A_{int}} \]

(15)

where \( Q \) is the experimentally determined molar flux to the leaves, \( A_L \) is the experimentally measured total leaf area, \( n_{st} \) is the number of stomata per unit leaf area, and \( A_{int} \) is the reactive portion of the substomatal chamber wall surface area (i.e., the area of the liquid film) for a single substomatal cavity.

By mass balance, the flux of any reactive species at the cell wall can be related to the homogeneous reaction rate of consumption \( (R) \) in the liquid film on the surface of the cell wall

\[
N_{ij}\delta = R \delta \]

(16)

where \( \delta \) is the liquid film thickness. For \( O_3 \), which is assumed to react with ascorbic acid in the cell wall (second-order-reaction rate constant is \( k \)), the water solubility is low (Henry’s law constant \( = 10^{-2} \) mol L\(^{-1}\) atm\(^{-1}\), 26). The concentration of ascorbic acid in the cell wall water ([AA]) is therefore not expected to change significantly, and the reaction expression is treated as a pseudo-first-order reaction

\[
R_{O_3} = -k_{O_3} H_2O \langle P_{O_3} \rangle \]

(17)

where \( k_{O_3} \) equals \( k\langle AA \rangle \) and is estimated to be on the order of \( 3000–60 000 \) s\(^{-1}\) (26). In this rate equation \( R_{O_3} \) is the rate of disappearance of \( O_3 \) in the cell wall by reaction, \( \langle P_{O_3} \rangle \) is the partial pressure of \( O_3 \) in the substomatal chamber, and \( H_2O \) is the Henry’s law constant for \( O_3 \) (mol L\(^{-1}\) atm\(^{-1}\)). For \( H_2O_2 \) and \( SO_2 \) the Henry’s law constants are on the order of \( 10^5 \) mol L\(^{-1}\) atm\(^{-1}\) (35) and \( 10^9 \) mol L\(^{-1}\) atm\(^{-1}\) (ref 36, and references cited therein), respectively. The pseudo-first-order rate constants for the reactions of \( H_2O_2 \) and of \( SO_2 \) in the cell wall water are assumed to be similar to that given above for \( O_3 \).

**Region II.** In the stomatal pore (region II), the pore radius to length ratio ranges from 0.05:10 or less to 5:10, depending on whether the stomata are closed or open. Therefore, according to the criterion of eq 7, it is adequate to area-average the governing equations for this region as well. The area-averaged form of the continuity equation (eq 8) and the area-averaged form of the Stefan–Maxwell equation (eq 9) are applied to gas transport in this region. Because of the small dimensions of the stomatal pore, the Knudsen number ranges from 0.01 to 0.1 in the stomata. Both Knudsen and molecular diffusion could therefore contribute to the gas transport in region II. The Knudsen...
Table II. Summary of Equations and Boundary Conditions Used in Model for Stomatal Pore

<table>
<thead>
<tr>
<th>Region II</th>
<th>Equation</th>
<th>Comments</th>
</tr>
</thead>
</table>
| Stefan–Maxwell | \[-\frac{1}{RT} \frac{d(P_i)}{dx} = \frac{\langle N_{ij}^D \rangle}{D_{ij}^K} + \sum_{j=1}^{n} \frac{\langle x_j \rangle \langle N_{ij}^D \rangle}{D_{ij}^K} - \frac{\langle x_i \rangle \langle N_{ij}^D \rangle}{D_{ij}^K} \]
| | | (n – 1) equations |
| Convective flux | \[-\frac{1}{RT} \frac{d(P_i)}{dx} = \sum_{j=1}^{n} \frac{\langle N_{ij}^D \rangle}{D_{ij}^K} \]
| | | nth equation |
| Continuity | \[-\frac{d}{dx} \langle N_{ij} \rangle = \frac{2\mu}{RT} \frac{d(P_i)}{dx} \]
| | | n equations |
| Boundary conditions | \[\langle (N_{ij})A \rangle_{II} = \langle (N_{ij})A \rangle_{III} \]
| | | conservation of mass across interface |

Diffusion term is therefore retained in the Stefan–Maxwell equation for region II (Table II).

In region II, both diffusive and convective fluxes contribute to the total flux. The convective flux in the stoma is assumed to behave similarly to that in a capillary tube, and the Hagen–Poiseuille equation for laminar flow of gases in capillaries \((11, 30)\) can be assumed to be valid

\[
\langle N_i^V \rangle = \frac{(2R\mu)^2}{32\mu} \frac{\langle P_i \rangle}{RT} \frac{d\langle P_i \rangle}{dx} \quad (18)
\]

where \(\mu\) is the gas viscosity, and \(R_I\) is the stomatal radius.

The \(n\)th equation is, again, an expression of the momentum balance and can be obtained by writing the modified Stefan–Maxwell equation for the total pressure, making use of the relationship \(P = \sum_{i=1}^{n} P_i\). Because of the constraint on the diffusive fluxes that they sum to zero, the resulting expression for the \(n\)th equation becomes

\[
\frac{1}{RT} \frac{\partial \langle \rho \rangle}{\partial z} = \sum_{j=1}^{n} \frac{\langle N_{ij}^D \rangle}{D_{ij}^K} \quad (19)
\]

The walls of the stomatal pore are assumed to be impermeable and nonreactive; therefore, in region II the wall boundary condition is zero for all species

\[N_{ij}=0 = \langle N_{ij} \rangle \quad (20)\]

Region III. The antechamber (region III) is filled with finely divided wax tubes and behaves as a porous medium. In this region, the equations are volume-averaged, using the spatial averaging theorem \((28)\). Ignoring dispersion terms and any potential losses due to absorption on surfaces in this region, the volume-averaged form of the continuity equations becomes

\[
\frac{d}{dx} \langle N_{ij} \rangle = 0 \quad (21)
\]

for gaseous species \(i\) which do not react with the surfaces in this region. This region is thought to be relatively inert to \(\text{SO}_2\) and \(\text{O}_3\) and reactive to \(\text{H}_2\text{O}_2\). Although it is recognized that reactive gases may be lost due to heterogeneous reaction in this region, for the remainder of these calculations the reaction rates for \(\text{O}_3, \text{H}_2\text{O}_2\), and \(\text{SO}_2\) are assumed to be zero so that the concentration profiles calculated represent upper limits.

Similarly, the Stefan–Maxwell equation must be volume-averaged. Applying volume-averaging and again neglecting dispersion terms, the \(z\)-component of the Stefan–Maxwell equation becomes

\[
-\frac{1}{RT} \frac{\partial \langle P_i \rangle}{\partial z} = \frac{\langle N_{ij}^D \rangle}{D_{ij}^K} + \sum_{j=1}^{n} \frac{\langle x_j \rangle \langle N_{ij}^D \rangle}{D_{ij}^K} - \frac{\langle x_i \rangle \langle N_{ij}^D \rangle}{D_{ij}^K} \quad (22)
\]

where \(\phi\) is the component of the tortuosity tensor along the \(z\)-direction \((37)\).

The effective diffusivities can then be written in terms of the diffusion coefficients and the correction factor \(1 + \phi\) that is related to the volume fraction \(\varepsilon\) (the porosity, or the ratio of pore volume to total volume) and the tortuosity \(\tau\) of the porous medium

\[
D_{ij,\text{eff}} = D_{ij}(1 + \phi) = \frac{\varepsilon \tau}{D_{ij}} \quad (23)
\]

and the volume-averaged Stefan–Maxwell equation in the \(z\)-direction becomes (Table III)

\[
-\frac{1}{RT} \frac{\partial \langle P_i \rangle}{\partial z} = \frac{\langle N_{ij}^D \rangle}{D_{ij,\text{eff}}} + \sum_{j=1}^{n} \frac{\langle x_j \rangle \langle N_{ij}^D \rangle}{D_{ij,\text{eff}}} - \frac{\langle x_i \rangle \langle N_{ij}^D \rangle}{D_{ij,\text{eff}}} \quad (24)
\]

In region III, the void spaces in the porous media are very small so that both molecular and Knudsen diffusion are considered to be important. The Knudsen number in this region is on the order of 0.1–1.0. The total flux includes both diffusive and convective contributions. The convective flux is described by Darcy’s law for flow through a porous medium \((11, 28, 30)\)

\[
\langle N_i^V \rangle = -\frac{k_p}{\mu} \frac{\partial \langle P_i \rangle}{\partial x} \quad (25)
\]

where \(c\) is the total concentration of gases. The permeability, \(k_p\), can be estimated by the laminar contribution to the Ergun equation \((30)\)

\[
k_p = \frac{d_p^2 c^3}{150(1 - \varepsilon)^2} \quad (26)
\]

where \(d_p\) is the characteristic particle length.

Region IV. The total flux of species \(i\) in the \(z\)-direction through the boundary layer is assumed to include contributions from both the diffusive flux and the bulk convective flow \((12, 30)\). The diffusive component is proportional to the concentration gradient

\[
N_{ij}^D = -k_{ij} \Delta x_{ib} \quad (27)
\]

where \(k_{ij}\) is the boundary layer mass-transfer coefficient.
Table III. Summary of Equations Used in Model for Porous Antechamber

region III equation comments

Stefan–Maxwell

\[ \frac{1}{RT} \frac{d(P)}{dz} = \sum \left\{ \frac{(V^0)}{D_{i,}\text{eff}} - \frac{(x_i)}{(N^{0})} \right\} \]

\((n-1)\) equations

continuity

\[ \frac{d(N^0)}{dP} = 0 \]

\(n\) equations

fluxes

\[ (N^0) = (N^0) - (x_i)(N^{0}) \]

\[ N^0 = -k_x \frac{d(P)}{dz} \]

\[ k_x = \frac{150(1-\epsilon)}{D_{i,\text{eff}}} \]

\[ D_{i,\text{eff}} = D_i + \frac{D_j}{\rho_j} \]

boundary conditions

\[ ((N^0) (A))_{III} = ((N^0) (A))_{IV} \]

conservation of mass across interface

Table IV. Summary of Equations and Boundary Conditions Used in Model for Boundary Layer

region IV equation comments

fluxes

\[ x_m = \frac{-N_{i, \text{a}} + x_{i,a}(k_{i,m} + \frac{1}{2}N_{i,a})}{k_{i,m} - \frac{1}{2}N_{i,a}} \]

\(n\) equations

\[ N_i = \sum \frac{N_{j,t}}{k_{j,m} - \frac{1}{2}N_{i,a}} \]

\[ k_{i,m} = \frac{D_j(Sc_i)^{2/3}}{0.600(Re)^{0.487}} \]

\[ Sc_i = \frac{D_i}{\mu} \]

\[ Re = \frac{vD_i}{\mu} \]

boundary conditions

\[ (N_{i, IV})_{IV} = Q_i \]

initial conditions

\[ Q_i \]

molar flux of i per unit leaf area measured experimentally

\[ v \]

air velocity near needles measured experimentally

number is 0.78. The dimensionless parameter, \(J_D\), is empirically correlated for a number of geometries. For gaseous flow past single cylinders, \(J_D\) is correlated to the Reynolds number, \(Re\) (38)

\[ J_D = 0.600(Re)^{0.487} \]

(31)

This correlation applies for cylinders for which mass transfer to the ends is not considered, for Schmidt numbers ranging from 0.6 to 2.6 for gases, and for Reynolds numbers of 50–50 000. The characteristic length used in the calculation of \(Re\) is the cylinder diameter. For a wind speed of 30 cm s\(^{-1}\), needle diameter of 1 mm, and air at 25 °C and 1 atm, the Reynolds number is 20.

Boundary Conditions and Computational Methods.

Summaries of all equations for each region are given in Tables I–IV. To formulate this problem, for each region a set of nonlinear, ordinary differential equations is solved. The boundary conditions for each region include the flux at the wall and the flux in the axial direction at the top of each section. Since we only know the fluxes and concentrations at the outer surface of the leaf, we start at the boundary layer and work inward. The fluxes and concentrations calculated at the end of one region are used then as the initial boundary conditions for the next region.

Since this problem is set up as an initial value problem, and since the formulation includes a series of nonlinear, ordinary differential equations, the Runge–Kutta method is used to solve the problem in a stepwise fashion through the leaf, starting at the ambient air interface. Conservation of mass and continuity of pressure are assumed at each interface. Given a constant mass rate across the boundary between regions, the concentration is calculated across the interface and at each step. If, at any point during the calculation, the concentration of a given species is calculated to be less than zero, it is set equal to zero, and the entire set of equations is reduced by also setting the flux of that species and the derivatives of both the concentration and the flux of that species to zero.

The fluxes of CO\(_2\), H\(_2\)O, O\(_2\), SO\(_2\), and H\(_2\)O\(_2\) as determined from controlled environment chamber tests and the atmospheric concentrations of all species provide initial conditions. We assume that the net flux of N\(_2\) is zero. To estimate the O\(_2\) flux, we consider relevant plant processes. During photosynthesis, CO\(_2\) and H\(_2\)O are metabolized to
synthesize carbohydrates (39)

\[
\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O}) + \text{O}_2 + \text{H}_2\text{O}
\]  

During respiration (which occurs during both day and night), glucose and other carbohydrates are oxidized to produce \text{CO}_2 and water (39)

\[
\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}
\]

Based on these chemical processes then, we assume that the net flux of \text{O}_2 is equal in magnitude but opposite in direction to the net flux of \text{CO}_2 for both daytime and nighttime cases. Water vapor evolved as a product of photosynthesis and respiration is neglected in the following analysis because its contribution to the total transpiration rate is very small. The relative humidity in the intercellular spaces is generally thought to be between 96 and 99% (40); the relative humidity in the substomatal chamber is therefore assumed to be 98.5% in the following analysis. Since the substomatal \text{H}_2\text{O} concentration is calculated in this procedure, the resulting relative humidity is compared to 98.5%; the stomatal radius is adjusted, and the entire calculation is repeated until this criterion is satisfied.

IV. Results and Discussion

Two sets of experiments were analyzed using this model. The first set investigated the simultaneous exposure of isolated branches of red spruce to a combination of \text{O}_3, \text{SO}_2, and \text{H}_2\text{O}_2 (13). The second set of experiments, presented in a companion paper (4), measured the uptake rate of gaseous \text{H}_2\text{O}_2 by red spruce saplings in a whole-tree, continuous mixed-flow exposure chamber (MFC).

Simultaneous Exposure of \text{SO}_2, \text{O}_3, and \text{H}_2\text{O}_2. Base Case: Ennis et al. (13) Daytime Conditions. A summary of the operating parameters used to establish a base case (from ref 13) is given in Table V. The stomatal radius is assumed to be 2.5 \mu m for daytime conditions. The stomatal density (per cm\(^2\)) was adjusted until the desired relative humidity in the substomatal chamber (region I) was 98.5%. For the base case, we estimated 2850 stomata per cm\(^2\) of leaf area. Jeffree et al. (14) have suggested a stomatal density as high as 6000 per cm\(^2\) for greenhouse-grown spruce.

Concentration profiles for \text{CO}_2, \text{H}_2\text{O}, and \text{O}_3, \text{SO}_2, and \text{H}_2\text{O}_2 are shown in Figures 3–5. The base case substomatal \text{CO}_2 concentration calculated by the model is approximately 148 ppm. This value is comparable to or lower than values reported elsewhere that were estimated for spruce using a multiple resistance method. Estimates have ranged from approximately 170 to 200 ppm for Sitka spruce (41) and from 50 to 270 ppm for several coniferous species for a range of water and ambient \text{CO}_2 conditions (42).

From Figures 3–5 and Table VI we see that, during the daytime, the stomatal antechamber (region III) provides an important resistance to gas transport. It also appears that there is a significant sink in this region for \text{H}_2\text{O}_2 and \text{SO}_2, which disappear shortly after entering this porous zone. The \text{O}_3 concentration appears to approach zero in or near the stomatal pore, which is consistent with both experimental and mathematical results reported by other researchers. Laisk et al. (43) concluded that the \text{O}_3 concentration in the leaf intercellular air space is nearly zero based on chamber uptake experiments on sunflowers. Chameides (26) calculated that, for cell wall thickness of

<table>
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<tr>
<th>Parameter</th>
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<tr>
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<td>\text{H}_2\text{O}_2, ppth</td>
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<td>\text{H}_2\text{O}, ppm</td>
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<table>
<thead>
<tr>
<th>Fluxes, mol m(^{-2}) s(^{-1})</th>
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<tr>
<td>\text{CO}_2</td>
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<td>\text{H}_2\text{O}_2</td>
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<td>\text{SO}_2</td>
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<table>
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<th>Chamber Conditions</th>
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<td>T, °C</td>
</tr>
<tr>
<td>P, atm</td>
</tr>
<tr>
<td>RH, %</td>
</tr>
<tr>
<td>v, cm s(^{-1})</td>
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</table>

<table>
<thead>
<tr>
<th>Assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPD, ppth</td>
</tr>
<tr>
<td>(n_{\text{sa}}), cm(^{-1})</td>
</tr>
<tr>
<td>(\epsilon/\tau)</td>
</tr>
</tbody>
</table>

* Base case conditions taken from ref 13. Concentrations are those measured at the outlet of the enclosed branch chamber. Fluxes are per unit area of leaf area as measured by a glass bead technique. \(v\) is the air velocity next to the needle. To run the simulation, the leaf temperature was assumed to be that of the chamber and the inner water vapor content was determined by assuming 98.5% relative humidity in the substomatal cavity. VPD is the vapor pressure deficit across the stomata (ppth), or the difference between the water vapor content of the air next to the needle and the water vapor content in the substomatal cavity (i.e., the intercellular water vapor content).

The stomatal number density is assumed to be 2850 per cm\(^2\) of needle surface area. The ratio \(\epsilon/\tau\) is the obstruction factor assumed for the stomatal antechamber.

![Figure 3. Concentration profiles for \text{CO}_2, water vapor, in stomatal zone. These profiles are for idealized stomatal zone in red spruce needle and are the results of the simulation of the base case taken from ref 13. Daytime and nighttime \text{CO}_2 profiles are indicated by open and filled circles, respectively. Daytime and nighttime \text{H}_2\text{O}_2 profiles are indicated by dashed and solid lines, respectively. Intercellular \text{CO}_2 concentration is approximately 150 ppm for the daytime case and approximately 500 ppm for the nighttime case. This figure illustrates that the porous antechamber \((z = 0 \text{ to } z = 18 \mu m)\) provides a significant resistance to gas transport, particularly during the daytime, while at night the stomata \((z = 18 \text{ to } z = 28)\) contributes a larger resistance.](image-url)
which occurs as light available for photosynthesis is reduced (44, 45). Therefore, to simulate case II (nighttime), the stomatal pore radius was reduced from 2.5 to 0.92 μm in order to maintain the relative humidity in the substomatal zone, which is assumed to remain roughly constant inside the plant needle, again at approximately 98.5%. Due primarily to this reduction in stomatal aperture, we find that now the stomatal pore itself provides a very significant resistance to gas exchange (Figures 3–5; Table VI). Similar to the daytime case, the trace species disappear before reaching the substomatal region.

**H₂O₂ Uptake Experiments.** The H₂O₂ uptake experiments conducted by Claiborn and Aneja (14) employed a whole-tree MFC containing 2–4 red spruce saplings. A series of experiments were conducted for varying dewpoint temperature and inlet H₂O₂ concentration. The CO₂ and H₂O fluxes were periodically calculated. The CO₂ concentration was 480 ± 50 ppm during the day and 390 ± 30 ppm at night. The average CO₂ flux was (2.31 ± 0.71) × 10⁻⁵ mol cm⁻² s⁻¹ during the day and (1.54 ± 0.83) × 10⁻⁶ mol cm⁻² s⁻¹ at night. It should be pointed out that the levels of CO₂ exchange measured in the experiments of Claiborn and Aneja (14) are higher than those measured for red spruce by other investigators. Ennis et al. (13) measured daytime exchange rates on the order of 10⁻¹⁰ mol cm⁻² s⁻¹ for a red spruce sapling in their branch chamber experiments. Hanson and McLaughlin (46) reported similar rates for red spruce seedlings. Pier et al. (47) and McLaughlin et al. (48) reported rates of approximately 0.05 and 0.055 μmol s⁻¹ per g of dry weight for red spruce seedlings in field exclusion chambers and red spruce saplings in their natural environment, respectively. Using a ratio of 1.5 g of dry weight per 200 cm² leaf area (13), these rates correspond to 4 × 10⁻¹⁰ mol cm⁻² s⁻¹, which is somewhat higher than those rates measured by Ennis et al. (13) and Hanson and McLaughlin (46), but not as high as those measured by Claiborn and Aneja (14). These apparent discrepancies may be due to the elevated CO₂ condition of the latter experiments or to differences in leaf area measurement techniques. For simulating these experiments, the CO₂ concentration was assumed to be 400 ppm, and the flux was set at average values.

The H₂O flux for each experiment was correlated to the exposure chamber outlet water vapor pressure difference across the leaf (VPD) (Figure 6). In order to compute the vapor pressure difference, the leaf temperature was assumed to be equal to the chamber air temperature. During periods for which the light was on (days), the temperature was 25.0 ± 1.0 °C. As before, the inner (substomatal) relative humidity was assumed to be 98.5%. We calculated an error of approximately 35% associated with this method of estimating the water vapor flux.

The operating conditions for these experiments are summarized in Table VII. To model these experiments, the stomatal density calculated from the base case was retained, and the stomatal radius required to obtain 98.5% relative humidity was recalculated. With the exception of the first daytime run, the H₂O₂ disappears in approximately the same place for this set of experiments, or at approximately z = 4–6 μm for daytime runs (Table VIII). The previous simulations of the base case and case II indicated that the H₂O₂ disappeared earlier (at z = 2 μm). The results of the current simulations of the nighttime experiments were more variable than those for the daytime experiments for prediction of the location at which the H₂O₂ concentration goes to zero (at z between 2 and 10 μm). The reason for this variability is not known.

The stomatal radius calculated based on 2850 stomata per cm² was considerably lower than that assumed for the base case (0.9–1.5 μm compared to 2.5 μm). It is interesting to note that for the nighttime case the radii calculated were much more similar to that calculated in case II (0.9–1.2 μm compared to 0.9 μm). The stomatal radius responds to a number of factors including CO₂ concentration of the air. For example, when the CO₂ concentration in the air is increased, the stomata tend to close (44). This factor may have contributed to the difference in calculated radii, since the experiments by Claiborn and Aneja (14) were conducted at higher CO₂ concentration (400–600 ppm compared to 354 ppm). The CO₂ concentration would have less of an effect at night, so that the calculations for the nighttime conditions are consistent with this hypothesis. The stomatal pore size is also related to the VPD; many plants close their stomata as the relative humidity decreases (and the VPD increases) (44). For the series of experiments by Claiborn and Aneja, the relative humidity varied from 34 to 65% during the day and from 37 to 68%.
The leaf temperature was varied in the base case from 26 to 29 °C (Table IX), the calculated substomatal CO₂ concentration changed from 148 to 48 ppm. The water vapor concentration, at constant 98.5% RH in the substomatal chamber, changed from 40 to 48 ppm (parts per thousand). The stomatal radius required to give 98.5% concentration from 2.5 to 1.6 μm. The leaf temperature was found to be 21.99 °C during the night (Table VII). The largest radius calculated for these experiments was 1.5 μm for 65% RH (run 6a). The experiments by Ennis et al. (13) were operated at a lower relative humidity (57%) during the day and (73%) at night.

Sensitivity Analysis. Leaf Temperature. In order to estimate the internal water vapor content, the leaf temperature was assumed to be equal to the ambient temperature. In reality, however, there may be a difference of several degrees between these temperatures. When the leaf temperature was varied in the base case from 26 to 29 °C (Table IX), the calculated substomatal CO₂ concentration changed from 148 to 48 ppm. The water vapor concentration, at constant 98.5% RH in the substomatal chamber, changed from 40 to 48 ppth (parts per thousand). The stomatal radius required to give 98.5% RH changed from 2.5 to 1.6 μm. The leaf temperature was found to be important when determining the intercellular CO₂ concentration and the stomatal radius; however, since the trace gases all disappeared before reaching the substomatal cavity, the leaf temperature had little effect on their concentration profiles.
We found that the characteristics of the waxy plug had little effect on the calculated intercellular concentration profiles. For example, reducing the total airflow rate and gaseous fluxes changed the location at which the concentration disappears from the leaf surface. While the concentration was not changed significantly as a result of these changes, the profiles of the traces gases as a result of these changes, the profiles of the traces gases

Table VIII. Results of Simulations of Experiments of Claiborn and Aneja (14)

<table>
<thead>
<tr>
<th>run no.</th>
<th>stomatal density</th>
<th>radius of stomata, µm</th>
<th>(CO₂) ppm</th>
<th>(H₂O) ppm</th>
<th>VPD ppth</th>
<th>RH %</th>
<th>z₁, H₂O = 0 µm</th>
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</thead>
<tbody>
<tr>
<td>3a</td>
<td>2850</td>
<td>0.89</td>
<td>200.6</td>
<td>30.8</td>
<td>20.3</td>
<td>34.1</td>
<td>17</td>
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<td>3b</td>
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<td>0.92</td>
<td>214.7</td>
<td>30.6</td>
<td>19.8</td>
<td>38.9</td>
<td>1</td>
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<tr>
<td>3c</td>
<td>2850</td>
<td>1.08</td>
<td>207.2</td>
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<td>16.0</td>
<td>61.1</td>
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</tr>
<tr>
<td>3d</td>
<td>2850</td>
<td>1.05</td>
<td>209.5</td>
<td>30.8</td>
<td>15.7</td>
<td>49.0</td>
<td>6</td>
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<tr>
<td>4</td>
<td>2850</td>
<td>1.00</td>
<td>244.9</td>
<td>30.5</td>
<td>16.7</td>
<td>45.2</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>2850</td>
<td>1.07</td>
<td>264.8</td>
<td>30.4</td>
<td>15.2</td>
<td>50.0</td>
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</tr>
<tr>
<td>6a</td>
<td>2850</td>
<td>1.50</td>
<td>324.2</td>
<td>30.8</td>
<td>10.7</td>
<td>65.3</td>
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<td>298.6</td>
<td>30.7</td>
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<td>59.0</td>
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<tr>
<td>7</td>
<td>2850</td>
<td>1.29</td>
<td>304.1</td>
<td>30.8</td>
<td>15.2</td>
<td>50.6</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>2850</td>
<td>1.29</td>
<td>304.7</td>
<td>30.8</td>
<td>12.2</td>
<td>60.4</td>
<td>6</td>
</tr>
<tr>
<td>9</td>
<td>2850</td>
<td>0.90</td>
<td>259.3</td>
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<td>20.3</td>
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<td>6a</td>
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<td>445.0</td>
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<tr>
<td>Ennis et al.</td>
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<td>136.6</td>
<td>39.8</td>
<td>17.2</td>
<td>56.8</td>
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</table>

* The stomatal density is that assumed, per cm² of leaf area, for each run simulation. The stomatal radius is that necessary to give 98.5% RH in the substomatal chamber (mpm). Calculations for experiments 3a and 6a were also repeated using a stomatal radius of 2.5 µm, and the stomatal density was adjusted to achieve 98.5% RH in the substomatal chamber (mpm). The flux in the last three rows refers to H₂O and represents the fraction of the total flux to the vegetative surfaces to reach the stomatal zone, varied from 100% (base case) to 75%, 50%, and 25%.

Table IX. Sensitivity Studies

<table>
<thead>
<tr>
<th>case</th>
<th>(CO₂)base ppm</th>
<th>(H₂O)base ppm</th>
<th>rₑ, µm</th>
<th>z₁, µm, for (H₂O) = 0</th>
<th>z₁, µm, for (SO₂) = 0</th>
<th>z₁, µm, for (H₂O) = 0</th>
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<tbody>
<tr>
<td>base case, day</td>
<td>147.9</td>
<td>39.8</td>
<td>2.5</td>
<td>2</td>
<td>3</td>
<td>14</td>
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<tr>
<td>night</td>
<td>499.1</td>
<td>28.5</td>
<td>0.92</td>
<td>2</td>
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<td>40.1</td>
<td>1.89</td>
<td>3</td>
<td>5</td>
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<tr>
<td>r = 5.0</td>
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<td>7.0</td>
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<td>3</td>
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<td>Q₁ + 10%</td>
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<td>3</td>
<td>13</td>
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<td>Q₁ = 10%</td>
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<td>39.8</td>
<td>2.17</td>
<td>2</td>
<td>3</td>
<td>16</td>
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<td>39.8</td>
<td>1.65</td>
<td>3</td>
<td>5</td>
<td>21</td>
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<tr>
<td>nₑₑ − 20% (2300)</td>
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<td>39.8</td>
<td>4.50</td>
<td>2</td>
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<td>12</td>
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<tr>
<td>z₁ = 15 and z₂ = 5 µm</td>
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<td>39.8</td>
<td>1.64</td>
<td>2</td>
<td>3</td>
<td>14</td>
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<tr>
<td>dₑₑ = 1.5 µm</td>
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<td>39.8</td>
<td>1.99</td>
<td>3</td>
<td>4</td>
<td>20</td>
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<tr>
<td>dₑₑ = 0.75 µm</td>
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<td>39.8</td>
<td>4.7</td>
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<tr>
<td>0.75 flux</td>
<td>147.9</td>
<td>39.8</td>
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<td>4</td>
<td>3</td>
<td>14</td>
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<tr>
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<td>39.8</td>
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<td>8</td>
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<td>0.26 flux</td>
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<td>39.8</td>
<td>2.5</td>
<td>17</td>
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<td>14</td>
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</table>

* Base case conditions taken from average daytime (light-on) conditions given by ref 13. Nighttime case denotes light-off. Leaf temperature (Tₑₑ) in base case is assumed to equal to chamber air temperature. r is the estimated stomatal antechamber tortuosity (=3.0 in base case). Qₑₑ denotes the chamber airflow rate, slpm. rₑₑ denotes the stomatal antechamber density (cm⁻¹). Calculations for experiments 3a and 6a were also repeated using a stomatal radius of 2.5 µm, and the stomatal density was adjusted to achieve 98.5% RH in the substomatal chamber (mpm). The flux in the last three rows refers to H₂O and represents the fraction of the total flux to the vegetative surfaces to reach the stomatal zone, varied from 100% (base case) to 75%, 50%, and 25%.

**Porous Plug Parameters.** The effect of the ratio of bed porosity to tortuosity was examined since this value was assumed to be equal to average values for porous media. We found that the characteristics of the waxy plug had little effect on the calculated intercellular CO₂ concentration. This parameter was, however, important to the concentration profiles of the trace species in the wax plug (Table IX).

**Gas Fluxes.** The fluxes of all gases were determined from the total chamber airflow rate, the concentration difference across the reactor, and the leaf area. Therefore, errors in any of these measurements will affect the gas flux calculations. We varied the fluxes of all species by ±10% and found that there was little impact on the CO₂ concentration profile and a small effect on the trace gas concentration profiles. For example, reducing the total airflow rate and gaseous fluxes changed the location at which the O₃ concentration disappears from 14 to 16 µm from the leaf surface.

**Stomatal Density.** In order to examine the sensitivity of this model to estimated stomatal number density, the stomatal density was decreased by 20%. In order to keep 98.5% RH inside the needle for this density, it was necessary to increase the stomatal pore radius to 4.5 µm. While the CO₂ concentration was not changed significantly as a result of these changes, the profiles of the traces gases
did respond to this parameter. The effect on the O₃ profile, in particular, was that the concentration approached zero at an earlier location in the stomata.

**Stomatal Dimensions.** Dimensions of the stomatal region were also adjusted to examine the effects on the model calculations. The wax plug depth (z₁) was adjusted from 18 to 15 µm, and the stomatal depth (z₂) was reduced from 10 to 5 µm, so that the top of the substomatal chamber was then located at \( z = 20 \) µm rather than at \( z = 28 \) µm in the base case. The resulting profiles indicate that the internal concentrations of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) do not change substantially; however, the point at which the \( \text{O}_3 \) concentration goes to zero is much closer to the top of the substomatal chamber.

The ozone concentration in the substomatal chamber appears to be zero for all the cases that were considered in this study. This is probably due to fast reaction rates either with cuticular surfaces or with mesophyll surfaces compared to molecular diffusion rates and should not be interpreted to suggest that red spruce would be tolerant to ozone at the levels examined in this work. A better understanding of the stomatal dimensions would clarify where the ozone disappears and give an indication as to which chemistry is more important (cuticular vs mesophyll). These calculations therefore suggest that, in order to obtain a reasonable estimate of the fate of reactive pollutants in the stomata, good estimates of the stomatal density and the stomatal dimensions should be obtained.

**Losses to Non-Stomatal Surfaces.** In \( \text{H}_2\text{O} \) chamber experiments, losses to nonplant surfaces in the exposure chamber are high, even if relatively inert surfaces, such as Teflon, are used (13,14). The fraction of the flux to needle surfaces which is attributed to decomposition on non-stomatal regions was estimated (14) to average 40 ± 26% for light-on conditions and 83 ± 6% for light-off conditions. The sensitivity of this model to the \( \text{H}_2\text{O}_2 \) flux was therefore also examined in this analysis. Reducing the \( \text{H}_2\text{O}_2 \) stomatal flux to 50% and to 10% of its base case value changed the location at which the \( \text{H}_2\text{O}_2 \) concentration goes to zero from 2 µm (base case) to 4 µm (i.e., still in the antechamber) (50%) to 17 µm (or nearing the top of the stomata) (10%). The sensitivity of this calculation to the \( \text{H}_2\text{O}_2 \) flux suggests that the decomposition of \( \text{H}_2\text{O}_2 \) on non-stomatal plant surfaces should be more closely examined.

**Capillary Condensation.** These simulations predicted that both \( \text{SO}_2 \) and \( \text{H}_2\text{O}_2 \) consistently disappeared in the porous wax plug (i.e., region III) without reaching the stomata. Furthermore, this result was found consistently during the sensitivity studies. This result is not unexpected for \( \text{H}_2\text{O}_2 \) since it is possible that \( \text{SO}_2 \) decomposes on the leaf surface and in the porous wax medium of region III. However, \( \text{SO}_2 \) has been observed to respond to stomatal activity (e.g., ref 49); therefore, \( \text{SO}_2 \) was expected to reach the stomata. Since the waxy material in the stomatal antechamber is typically assumed to be relatively inert, we examined the possibility that liquid water could equilibrate with water vapor in this region, thus providing a sink for \( \text{SO}_2 \) and \( \text{H}_2\text{O}_2 \). As the relative humidity of the surrounding air increases, adsorption of water vapor into porous media increases until the adsorbed water behaves like liquid water (refs 50 and 51, and references cited therein). The Kelvin equation was used to calculate the ratio of the equilibrium partial pressure of water vapor over a cylindrical meniscus of condensing water, \( P \), to the saturation vapor pressure over a flat surface, \( P_o \), given the meniscus radius \( r \) (cm) and the contact angle \( \phi \) (51):

\[
P/P_o = \exp\left(-\frac{\sigma V \cos(\phi)}{rR^2T}\right)
\]

where \( \sigma \) is the surface tension of water (at 20 °C, \( \sigma = 72.88 \) erg cm⁻²), \( V \) is the molar volume of liquid water (18 cm³ mol⁻¹), \( T \) is in K, and \( R \) is the ideal gas constant (8.314 × 10⁻⁵ erg mol⁻¹ K⁻¹). Figure 7 shows the ratio \( P/P_o \) as a function of the cylindrical meniscus radius for contact angles of 65° and 85°. Since the cutin is made up of the esters of carboxylic acids and contains 2–3 hydroxyl groups, this material is suspected of being slightly more hydrophilic than materials such as Teflon or polyethylene (52), for which contacts angle range from 94 to 117° (53).

For pore radii in the range of 0.1–1 µm (the range of dimensions in the antechamber) and contact angle in the range of 65°–85°, the critical relative humidity is estimated to range from 60 to 90%. This range is similar to the relative humidity calculated in the base case at the bottom of the waxy plug region, which approaches 85% and 75% in the daytime and nighttime cases, respectively.

We interpret this to suggest that it may be possible for water to condense in the stomatal antechamber, thus providing a sink for water-soluble gases. For other vegetative species, fluxes of \( \text{SO}_2 \) have been observed to respond to stomatal aperture (i.e., lower fluxes observed during dark periods, e.g., ref 49). We recognize that liquid water would provide only a temporary sink for \( \text{SO}_3 \) because partitioning of \( \text{SO}_3 \) between the gas and liquid phases would eventually reach an equilibrium, unless an aqueous phase sink exists such as the presence of gaseous \( \text{H}_2\text{O}_2 \) which oxidizes \( \text{SO}_2 \) in the aqueous phase (e.g., ref 54). We speculate that in the experiments of Ennis et al. (13) the presence of \( \text{H}_2\text{O}_2 \) may have affected the fate of \( \text{SO}_3 \) in the needle. A similar phenomenon was observed by Van Hove et al. (49) during simultaneous exposure of bean plants to \( \text{NF}_3 \) and \( \text{SO}_2 \) during which the deposition to external surfaces was found to increase with increasing relative humidity and simultaneous exposure enhanced the deposition of both species. It would be interesting to examine the uptake by conifers of \( \text{SO}_2 \) alone and then in simultaneous exposures to determine whether the uptake of
SO_{2} is affected by the presence of oxidative species with which it may react. An examination of the relationship between the ambient relative humidity and the location at which H_{2}O_{2} disappears for the data by Claiborn and Anega (14) found no statistically significant correlation between these parameters, as might be expected from the above discussion; however, their experiments did not include a wide range of relative humidities. It appears that the H_{2}O_{2} disappears relatively soon in the leaf, regardless of the relative humidity or the presence of other gases. The presence of light appears to enhance the loss process (Table VIII), since during the day the H_{2}O_{2} disappeared sooner than during the night. We speculate that H_{2}O_{2} decomposes on the surface of the spruce needle and that this decomposition is enhanced during the daytime conditions, either by the increased leaf temperature or by photolytic processes.

V. Summary and Conclusions

A mathematical model was developed to describe the transport of gases into conifer needles. The model was applied to the specific cases of O_{3}, SO_{2}, and H_{2}O_{2} transport into needles of red spruce and takes into account the effects of photosynthesis, transpiration and respiration during daytime and nighttime conditions. The model considers the multicomponent gas diffusion, heterogeneous chemical reactions inside the needle, and specific leaf geometry and stomatal features. The model was used to analyze two sets of experiments which studied the uptake of several reactive air pollutants by red spruce (13, 14). Although the model is not verifiable in its present formulation, its predictions of intercellular gaseous concentration profiles are reasonably enlightening.

Unlike the typical deposition velocity model, which has been applied to leaves with a flat plate geometry, this model specifically takes into account the detailed anatomy of the leaf. Model calculations suggest that the wax plug of the stomatal antechamber offers a significant resistance to gas transport into and out of the stomatal region. During the day, this plug may provide a larger resistance to transport than the stomata. If there is a sink for O_{3} other than in the substomatal zone, it is apparently not as efficient as that for H_{2}O_{2} or SO_{2}.

The results of our sensitivity studies indicate that, in order to accurately calculate the inner CO_{2} concentration, very accurate measurements of the leaf temperature, chamber inlet and outlet air dewpoint temperature, and total chamber gas flow rate are required. In order to understand the fate of reactive and/or water-soluble trace gases, a good chemical characterization of the waxy plug as well as good estimates of all stomatal zone dimensions are needed. The assumption that the waxy cuticular material is inert does not appear to apply to gaseous H_{2}O_{2} and may not apply to other gaseous species (such as SO_{2} and O_{3}). The reactivity of the cuticular wax with these atmospheric trace gases, when exposed singularly or in the presence of other trace gases, should be further investigated.

Although these calculations suggested that, for all cases considered, the ozone concentration in the substomatal chamber appears to be zero, we point out that this should not be interpreted to suggest that the red spruce would be tolerant to ozone for the conditions examined in this work. In order to use this model to examine the implications of exposure to air pollutants for forest decline, more detailed information is needed on the chemistry and biochemistry of the specific air pollutant in plant tissues.

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