4.3 A SIMPLE MODEL FOR VERTICAL TRANSPORT OF REACTIVE SPECIES IN THE CONVECTIVE ATMOSPHERIC BOUNDARY LAYER

Leif Kristensen[1]*, Donald H. Lenschow[2], David Gurarie[3], and Niels Otto Jensen[1]

[1]Risø DTU National Laboratory for Sustainable Energy, Roskilde, Denmark
[2]National Center for Atmospheric Research, Boulder, CO
[3]Department of Mathematics, Case Western Reserve University, Cleveland, OH

1. INTRODUCTION

The convective planetary boundary layer (CBL) is a melting pot of chemical species—some are emitted by surface sources, others are entrained from the overlying free atmosphere, and still others are created by reactions with other species or through photochemistry. This rich soup of reactive species is stirred by turbulence; the degree of commingling determined by the ratio of the time scale of the turbulence mixing to the time scale of chemical reaction, which is known as the Damköhler number. The turbulence mixing time scale, in turn, is controlled by the dominant eddy size and the turbulence intensity, which are functions of normalized CBL depth and the surface buoyancy flux. All in all, this makes for a complicated set of interactions that need to be dealt with to determine the vertical structure of mean concentrations and turbulence statistics.

In order to deal with this complexity, and identify the individual roles that turbulence and chemical reactivity play, it is useful to simplify and parameterize the processes so that models can be constructed that can be easily modified so that the parameter space can be easily explored. With this in mind, we have developed a simple one-dimensional model, patterned after the surface-layer models developed by Kristensen et al. (1997) for one first-order destruction process and Kristensen and Kirkegaard (2006) for one second-order destruction process, and extended it to the entire CBL, parameterizing the transport process throughout the CBL. We have applied it to a set of fast chemical reactants in the CBL that involves the odd nitrogen species NO and NO_2 (=NO_x), as well as O_3. As we shall see this involves one first-order process and one second-order process.

Our model is similar to that of Verver et al. (1997) and Verver et al. (2000) who carried out similar studies using a second-order closure model to calculate profiles of mean and turbulence statistics. However, instead of solving the set of nine or more differential equations by finite difference techniques at a specified set of levels throughout the CBL as they did, we first reduce the set of equations to two equations for NO_2 flux and concentration by using mass conservation of the radicals involved in the NO–NO_2–O_3 triad. We then obtain a numerical solution of these differential equations, and subsequently the entire set of concentration and flux profiles are easily obtained by substituting this solution into the equations for NO and O_3 fluxes and concentrations. The advantages of this approach are: 1) we can easily specify whatever vertical resolution we wish over any interval of the CBL, including using very fine resolution to resolve detailed structure in the surface layer; 2) solving the equations requires little computer time and capacity; and 3) it is easy to make changes in the transport and chemical parameterizations, and to quickly evaluate their impact on the resulting concentration and flux profiles.

The eventual goal is to extend the model to include volatile organic compounds (VOCs)—particularly those emitted by vegetation (e.g. isoprene)—that react on time scales comparable to CBL turbulent mixing times, to provide a simple tool for rapid estimation of surface emission rates, and possibly reaction rates, given measurements of VOC fluxes or profiles (or both) at one or more levels in the CBL. This approach again was anticipated by Verver et al. (2000), who also used their modeling technique to study the flux–gradient relationship for isoprene in the planetary boundary layer.

In the following we first derive the equations for the mean concentration and flux of a conserved species. In this way we obtain a fundamental scheme to be applied when the chemistry is included. At this stage the equations can be simplified by making them dimensionless (section 3). A number of turbulence statistics profiles, such as variances and heat flux, are prescribed and discussed in section 4. In section 5, the NO_x– O_3 triad is discussed as a simple example of the interaction between non-conserved species. With the tools to solve for concentrations and fluxes now in place, we outline in section 6 the procedure we have chosen for solving the equa-

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*Corresponding address: Leif Kristensen, Risø DTU National Laboratory for Sustainable Energy, Roskilde, Denmark. E-mail: leif.kristensen@tele2.dk

tions. Finally, a sample case is presented in section 7.

2. CONSERVED SPECIES

We consider a horizontally homogeneous and stationary flow, and a Cartesian coordinate system where the unit vector $\mathbf{i}$ is aligned with the mean wind, $\mathbf{k}$ vertical, and $\mathbf{j} = \mathbf{k} \times \mathbf{i}$. The position is characterized by

$$\mathbf{x} = x\,\mathbf{i} + y\,\mathbf{j} + z\,\mathbf{k} \tag{1}$$

and the instantaneous velocity vector by

$$\widetilde{\mathbf{u}}(\mathbf{x},t) = \widetilde{u}(\mathbf{x},t)\,\mathbf{i} + \widetilde{v}(\mathbf{x},t)\,\mathbf{j} + \widetilde{w}(\mathbf{x},t)\,\mathbf{k}. \tag{2}$$

In the CBL, the mean wind is assumed constant in magnitude and direction, and the velocity field is decomposed into a mean and fluctuation:

$$\widetilde{\mathbf{u}}(\mathbf{x},t) = U\,\mathbf{i} + u(\mathbf{x},t)\,\mathbf{i} + v(\mathbf{x},t)\,\mathbf{j} + w(\mathbf{x},t)\,\mathbf{k}, \tag{3}$$

where

$$U = |\,\langle \widetilde{\mathbf{u}}(\mathbf{x},t) \rangle\,| \tag{4}$$

is the space- and time-independent mean wind speed.

The potential temperature $\widetilde{\Theta}$[*] and the conserved scalar concentration $\widetilde{s}$ are similarly decomposed into means and fluctuations

$$\widetilde{\Theta} = \Theta(z,t) + \vartheta(\mathbf{x},t), \tag{5}$$

where we allow for a temporal change of the mean potential temperature due to the temperature flux divergence resulting from the difference between the surface heat flux and entrainment of heat from the free troposphere into the CBL, and

$$\widetilde{s} = S(z) + s(\mathbf{x},t), \tag{6}$$

where we neglect time change of the mean concentration S since we are seeking steady-state solutions for mean concentration and flux.

These two quantities follow the equations

$$\frac{D\widetilde{\Theta}}{Dt} = \nu_\vartheta \nabla^2 \widetilde{\Theta} \tag{7}$$

and

$$\frac{D\widetilde{s}}{Dt} = \nu_s \nabla^2 \widetilde{s}, \tag{8}$$

where ν_ϑ and ν_s are the molecular diffusivities, and

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \widetilde{\mathbf{u}} \cdot \nabla = \frac{\partial}{\partial t} + U\,\frac{\partial}{\partial x} + \mathbf{u} \cdot \nabla \tag{9}$$

is the Lagrangian time derivative. Now (7) and (8) become

$$\left\{ \frac{\partial}{\partial t} + U\,\frac{\partial}{\partial x} \right\} \vartheta + w\frac{\partial \Theta}{\partial z} + \nabla \cdot (\mathbf{u}\vartheta) + \frac{\partial \Theta}{\partial t} = \nu_\vartheta \frac{\partial^2 \Theta}{\partial z^2} + \nu_\vartheta \nabla^2 \vartheta \tag{10}$$

and

$$\left\{ \frac{\partial}{\partial t} + U\,\frac{\partial}{\partial x} \right\} s + w\frac{\partial S}{\partial z} + \nabla \cdot (\mathbf{u}s) = \nu_s \frac{\partial^2 S}{\partial z^2} + \nu_s \nabla^2 s. \tag{11}$$

Taking the average of each of (10) and of (11), we get

$$\frac{\partial \langle w\vartheta \rangle}{\partial z} = -\frac{\partial \Theta}{\partial t} + \nu_\vartheta \frac{\partial^2 \Theta}{\partial z^2} \tag{12}$$

and

$$\frac{\partial \langle ws \rangle}{\partial z} = \nu_s \frac{\partial^2 S}{\partial z^2}. \tag{13}$$

Integrating (12) and (13) leads to

$$\langle w\vartheta \rangle = \langle w\vartheta \rangle_\circ - \int_0^z \frac{\partial \Theta(z',t)}{\partial t}\,\mathrm{d}z' + \underbrace{\nu_\vartheta \frac{\partial \Theta}{\partial z}\bigg|_z}_{\simeq 0} \tag{14}$$

and

$$\langle ws \rangle = \langle ws \rangle_\circ + \underbrace{\nu_s \frac{\partial S}{\partial z}\bigg|_z}_{\simeq 0}, \tag{15}$$

where the molecular diffusion terms can be neglected. In the well-mixed CBL the variation of the potential temperature with height can be ignored, i.e.,

$$\frac{\partial \Theta}{\partial z} = 0. \tag{16}$$

Since Θ in the CBL is an increasing function of time, the heat flux is, according to (14), a decreasing, linear function of height. As (15) shows, the flux $\langle ws \rangle$ is constant with height.

By subtracting these mean equations from the corresponding full equations (10) and (11) we obtain equations for the fluctuating quantities ϑ and s,

$$\left\{ \frac{\partial}{\partial t} + U\,\frac{\partial}{\partial x} \right\} \vartheta + \nabla \cdot (\mathbf{u}\vartheta) - \frac{\partial}{\partial z}\langle w\vartheta \rangle = \nu_\vartheta \nabla^2 \vartheta \tag{17}$$

and

$$\left\{ \frac{\partial}{\partial t} + U\,\frac{\partial}{\partial x} \right\} s + w\frac{\partial S}{\partial z} + \nabla \cdot (\mathbf{u}s) - \frac{\partial}{\partial z}\langle ws \rangle = \nu_s \nabla^2 s. \tag{18}$$

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[*] We use the term potential temperature, but in the convective boundary layer we really mean the virtual potential temperature, where the effect of humidity on air density has been included.

We also need the equation for the fluctuating vertical velocity w. This can be obtained from the conservation equation for momentum—the Navier-Stokes equation. In a similar way as how we used (10) and (11) to obtain (17) and (18), we get (e.g. Busch (1973)):

$$\left\{\frac{\partial}{\partial t}+U\frac{\partial}{\partial x}\right\} w+\nabla\cdot(\mathbf{u}w)-\frac{\partial\langle w^2\rangle}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial z}+\frac{g}{T}\vartheta+\nu\nabla^2 w, \qquad (19)$$

where ρ is the air density, p the fluctuating part of the static pressure, g the acceleration of gravity, T the average temperature of the boundary layer, and ν the kinematic viscosity.

Combining (18) and (19) we obtain by averaging

$$\langle w^2\rangle\frac{\partial S}{\partial z}+\frac{\partial}{\partial z}\langle w^2 s\rangle = -\frac{1}{\rho}\left\langle s\frac{\partial p}{\partial z}\right\rangle+\frac{g}{T}\langle\vartheta s\rangle+\nu_s\langle w\nabla^2 s\rangle+\nu\langle s\nabla^2 w\rangle. \qquad (20)$$

Following André et al. (1976), Moeng and Wyngaard (1989), and Verver et al. (1997) we use the parameterization

$$\frac{1}{\rho}\left\langle s\frac{\partial p}{\partial z}\right\rangle = \frac{\langle ws\rangle}{\tau_1}+b_1\frac{g}{T}\langle\vartheta s\rangle, \qquad (21)$$

where $b_1 \simeq 0.4$ is a dimensionless constant and $\tau_1 = \tau_1(z)$ “the return to isotropy” time scale.

The sum of the last two terms in (20) can be combined as

$$\nu_s\langle w\nabla^2 s\rangle+\nu\langle s\nabla^2 w\rangle = -(\nu_s+\nu)\langle\nabla w\cdot\nabla s\rangle. \qquad (22)$$

For small-scale, isotropic turbulence this sum is zero, as pointed out by Wyngaard (1982) (p. 82). Neglecting third-order terms, (20) can be written as

$$\langle w^2\rangle\left\{\frac{\partial S}{\partial z}+\frac{\langle ws\rangle}{\langle w^2\rangle\tau_1}\right\} = (1-b_1)\frac{g}{T}\langle\vartheta s\rangle. \qquad (23)$$

To close the problem we derive an equation for the covariance $\langle\vartheta s\rangle$ by combining (17) and (18):

$$\langle w\vartheta\rangle\frac{\partial S}{\partial z}+\frac{\partial}{\partial z}\langle w\vartheta s\rangle = -(\nu_\vartheta+\nu_s)\langle\nabla\vartheta\cdot\nabla s\rangle. \qquad (24)$$

Following Verver et al. (1997) the right-hand side of (24) can be expressed in terms of a height dependent dissipation time scale $\tau_4 = \tau_4(z)$:

$$(\nu_\vartheta+\nu_s)\langle\nabla\vartheta\cdot\nabla s\rangle = \frac{\langle\vartheta s\rangle}{\tau_4}. \qquad (25)$$

Finally, (24) can be written

$$\langle w\vartheta\rangle\frac{\partial S}{\partial z}+\frac{\langle\vartheta s\rangle}{\tau_4(z)} = 0, \qquad (26)$$

where third-order terms have been neglected. With the prescribed parameter functions $\langle w^2\rangle$, $\langle w\vartheta\rangle$, $\tau_4(z)$, $\tau_1(z)$, and the constant $(1-b_1)\,g/T$, (15), (23) and (26) can be solved for the gradient $\partial S/\partial z$ and the covariance $\langle\vartheta s\rangle$. As (15) shows, we have already one integral constraint, namely the constant flux

$$\langle ws\rangle = \langle ws\rangle_\circ. \qquad (27)$$

The two equations to be solved, therefore, are

$$\langle w^2\rangle\left\{\frac{\partial S}{\partial z}+\frac{\langle ws\rangle_\circ}{\langle w^2\rangle\tau_1}\right\} = (1-b_1)\frac{g}{T}\langle\vartheta s\rangle. \qquad (28)$$

and (26).

3. DIMENSIONLESS FORMULATION

For computational purposes it is advantageous to recast the equations in a dimensionless form. We have three quantities which characterize the equations: the height of the CBL h, the surface temperature flux $\langle w\vartheta\rangle_\circ$, and the buoyancy parameter g/T. They are all considered constant in space and quasi-constant in time. The buoyancy parameter can safely be considered constant in time, but the quantities $\langle w\vartheta\rangle_\circ$ and h are of course varying with time in the convective boundary layer. However, their rate of change is considered so small that here we may take them as constants. We define the convective velocity scale[†] by

$$w_* = \left((1-b_1)\frac{g}{T}\langle w\vartheta\rangle_\circ h\right)^{1/3}, \qquad (29)$$

the dimensionless quantities by

$$\left\{\begin{array}{c}\zeta\\ f\\ \gamma\end{array}\right\} = \left\{\begin{array}{r}z/h\\ \langle ws\rangle/w_*\\ \langle\vartheta s\rangle/T_*\end{array}\right\}, \qquad (30)$$

and the parameters to be specified by

$$\left\{\begin{array}{c}\theta_1\\ \theta_4\\ \omega^2\\ \varphi_T\end{array}\right\} = \left\{\begin{array}{r}w_*\tau_1(z)/h\\ w_*\tau_4(z)/h\\ \langle w^2\rangle/w_*^2\\ \langle w\vartheta\rangle/(w_*T_*)\end{array}\right\}, \qquad (31)$$

where

$$T_* = \frac{\langle w\vartheta\rangle_\circ}{w_*}. \qquad (32)$$

The three equations (27), (28), and (26) now take the form

$$f = f_\circ, \qquad (33)$$

$$\omega^2\frac{\partial S}{\partial\zeta}-\gamma = -\frac{f_\circ}{\theta_1}, \qquad (34)$$

[†] For convenience we have included the factor $(1-b_1) \simeq 0.6$ in the definition in the convective velocity scale.

and

$$\varphi_T \frac{\partial S}{\partial \zeta} + \frac{\gamma}{\theta_4} = 0. \tag{35}$$

Specifying $f_\circ$, we may solve (34) and (35) for $\partial S/\partial\zeta$ and γ to obtain

$$\frac{\frac{\partial S}{\partial \zeta}}{f_\circ} = -\frac{1}{\theta_1\left(\omega^2 + \theta_4\varphi_T\right)} \tag{36}$$

and

$$\frac{\gamma}{f_\circ} = \frac{\theta_4\varphi_T}{\theta_1\left(\omega^2 + \theta_4\varphi_T\right)}. \tag{37}$$

The right-hand sides of these two equations are considered known and we see that (36) is a (dimensionless) relation between the flux and the gradient of the corresponding scalar; that is, it defines the dimensionless turbulent diffusivity

$$\chi(\zeta) \equiv \frac{K}{w_* h} = \theta_1\left(\omega^2 + \theta_4\varphi_T\right), \tag{38}$$

where $K(z)$ is the turbulent diffusivity for passive scalars.

4. PARAMETERIZING THE STRUCTURE OF THE CONVECTIVE BOUNDARY LAYER

The equations require profiles of the variances of the vertical velocity $\langle w^2\rangle$ and the potential temperature $\langle\vartheta^2\rangle$, and of the temperature flux $\langle w\vartheta\rangle$, in addition to the time constants τ_1 and τ_4.

We use the formulation by Lenschow et al. (1980) for $\langle w^2\rangle$

$$\omega^2 = \frac{\langle w^2\rangle}{w_*^2} = 1.8\left(\frac{z}{h}\right)^{2/3}\left(1 - 0.8\frac{z}{h}\right)^2. \tag{39}$$

The variance profile used here converges to the free convection limit in the surface layer; that is, for simplicity we have neglected the contribution of shear production. This means that for small z/h, $\langle w^2\rangle/w_*^2 \propto (z/h)^{2/3}$.

The heat flux $\langle w\vartheta\rangle$ decreases linearly from a positive value $\langle w\vartheta\rangle_\circ$ at the ground to a negative value at the top $z = h$ of the boundary layer due to entrainment from aloft. We apply the simple analysis by Tennekes (1973) and assume the expression[‡]

$$\varphi_T = \frac{\langle w\vartheta\rangle}{\langle w\vartheta\rangle_\circ} = \frac{\langle w\vartheta\rangle}{w_* T_*} = 1 - 1.2\,\frac{z}{h}. \tag{40}$$

The time constants entering (21) and (25) are set to (Verver et al., 1997)

$$\tau_i = \frac{10}{a_i}\,\frac{\kappa z\,(1 - z/h)}{\langle w^2\rangle^{1/2}}, \quad i = 1, 4, \tag{41}$$

where a_i are dimensionless constants and $\kappa = 0.4$ the von Kármán constant. Inserting (39) we get

$$\theta_i = \frac{h\tau_i}{w_*} = \frac{3}{a_i}\,\frac{\left(\frac{z}{h}\right)^{2/3}\left(1 - \frac{z}{h}\right)}{1 - 0.8\frac{z}{h}}, \quad i = 1, 4. \tag{42}$$

Inserting (39), (40), and (42) into (37) and (38) we have determined the dimensionless temperature-scalar covariance γ and the dimensionless turbulent diffusivity χ, except for the two dimensionless constants a_1 and a_4. However, we have one constraint in a relation between these two constants, namely the functional form of $\chi(\zeta)$ at the bottom of the boundary layer. We assume in accordance with Wyngaard and Brost (1984), and Holtslag and Moeng (1991) that near the surface the diffusivity approaches

$$\chi(\zeta) = \zeta^{4/3}. \tag{43}$$

This is consistent with our expression for $\chi(\zeta)$ that includes the parameter functions (39), (40), and (42) if the identity

$$\frac{3}{a_1}\left(1.8 + \frac{3}{a_4}\right) = 1 \tag{44}$$

is true. Verver et al. (1997) use $(a_1, a_4) = (4.85, 2.5)$. These values do not fulfill (44). We find, with our choice of dimensionless parameters in (39), (40), and (42), that for (44) to be true, the only two possibilities are $(a_1, a_4) = (9, 2.5)$ and $(a_1, a_4) = (4.85, -16.4)$. Since the second possibility is unphysical we use the first possibility in the following. The profiles of the dimensionless diffusivity and the dimensionless temperature-scalar covariance are shown in Figs. 1 and 2.

5. NON-CONSERVED SPECIES

When we have gases which interact, the rate equation (8) must be generalized to account for the extra sources and sinks inside the boundary layer. Instead of (8) we write for N mutually interacting species

$$\frac{D\tilde{s}_i}{Dt} = \tilde{\mathcal{R}}_i + \nu_s\nabla^2\tilde{s}_i, \qquad i = 1, 2, \ldots, N \tag{45}$$

where $\tilde{\mathcal{R}}_i$ represents the rate of concentration increase due to the interaction with all the other species and where the kinematic diffusivity ν_s is assumed the same for all the species. As in the case of conserved species, we decompose $\tilde{s}_i$ into a mean and fluctuations:

$$\tilde{s}_i(x, y, z, t) = S_i(z, t) + s_i(x, y, z, t), \quad i = 1, 2, \ldots, N. \tag{46}$$

[‡] The factor 1.2 implies that the entrainment heat flux at the CBL top is 20% (downwards) of the surface heat flux (upwards). It is not a fixed fraction, but only a typical value; it varies with the turbulence intensity in terms of e.g. w_*, the wind shear, and the temperature stratification in the overlying free troposphere.

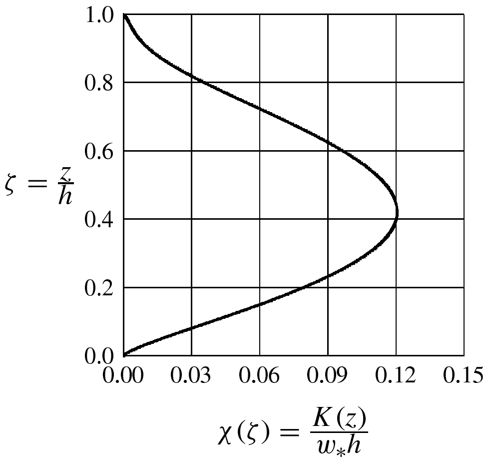

Figure 1: The dimensionless diffusivity profile $K/(w_* h)$.

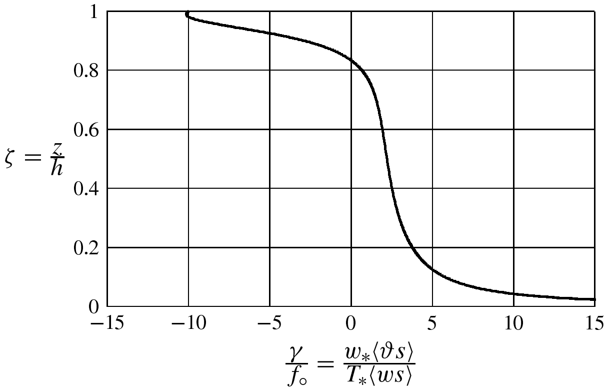

Figure 2: Profile of the dimensionless ratio of the temperature-scalar covariance and the constant scalar flux (37).

In a similar way we decompose

$$\widetilde{\mathcal{R}_i}(x,y,z,t) = \mathcal{R}_i(z,t) + r_i(x,y,z,t), \quad i = 1,2,\ldots,N, \tag{47}$$

where

$$\mathcal{R}_i = \left\langle \widetilde{\mathcal{R}_i} \right\rangle . \tag{48}$$

The equations for the mean S_i and fluctuations $\widetilde{s_i}$ in (45) become the following generalizations of (13) and (18)

$$\frac{\partial S_i}{\partial t} + \frac{\partial \langle ws \rangle}{\partial z} = \mathcal{R}_i + \nu_s \frac{\partial^2 S}{\partial z^2}, \tag{49}$$

where we have kept the prognostic term, and

$$\left\{ \frac{\partial}{\partial t} + U \frac{\partial}{\partial x} \right\} s_i + w \frac{\partial S_i}{\partial z} + \nabla \cdot (\mathbf{u} s_i) - \frac{\partial}{\partial z} \langle w s_i \rangle = r_i + \nu_s \nabla^2 s_i. \tag{50}$$

Combining this equation with (17) and (19) we obtain the three prognostic equations

$$\begin{aligned} \frac{\partial}{\partial t} \langle w s_i \rangle + \langle w^2 \rangle \frac{\partial S_i}{\partial z} + \frac{\partial}{\partial z} \langle w^2 s_i \rangle = \\ -\frac{1}{\rho} \left\langle s_i \frac{\partial p}{\partial z} \right\rangle + \frac{g}{T} \langle \vartheta s_i \rangle + \langle w r_i \rangle \\ - \underbrace{(\nu + \nu_s) \langle \nabla w \cdot \nabla s_i \rangle}_{\simeq 0 \, \text{Wyngaard (1982)}}, \end{aligned} \tag{51}$$

$$\begin{aligned} \frac{\partial}{\partial t} \langle \vartheta s_i \rangle + \langle w \vartheta \rangle \frac{\partial S_i}{\partial z} + \frac{\partial}{\partial z} \langle w \vartheta s_i \rangle = \\ \langle \vartheta s_i \rangle + \langle r_i \vartheta \rangle - (\nu_\vartheta + \nu_s) \langle \nabla \vartheta \cdot \nabla s_i \rangle, \end{aligned} \tag{52}$$

and

$$\begin{aligned} \frac{\partial}{\partial t} \langle s_i s_j \rangle + \langle w s_i \rangle \frac{\partial S_j}{\partial z} + \langle w s_j \rangle \frac{\partial S_i}{\partial z} + \frac{\partial}{\partial z} \langle w s_i s_j \rangle = \\ \langle r_i r_j \rangle - 2 \nu_s \langle \nabla s_i \cdot \nabla s_j \rangle . \end{aligned} \tag{53}$$

These three equations (51), (52), and (53), together with (49) constitute our general set of equations for N interactive gas species in the CBL. To proceed we must specify their interactions in terms of $\widetilde{\mathcal{R}_i}$ for $i = 1,2,\cdots,N$. Below this is illustrated by the simple case with $N = 3$.

The NO_x–O_3 triad reactions (Leighton, 1961) in a sunlit CBL are

$$O(^3P) + O_2 \rightarrow O_3 \tag{54}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{55}$$

$$NO_2 + h\nu \rightarrow NO + O(^3P). \tag{56}$$

Here $h\nu$ represents one quantum of ultraviolet light while ^3P indicates that the atomic oxygen is in its ground state.

If there is a large supply of O_3, as is often the case in an urban environment, the process (55) will be the main mechanism of NO removal. In rural and remote areas NO will often be destroyed by other peroxy radicals (Ridley et al., 1992). However, following Lenschow and Delany (1987), we assume that a first simple approach to a calculation of the mean concentrations and fluxes of O, O_3, NO, and NO_2 can be based on the reactions (54), (55), and (56). The corresponding dynamic equations governing these transformations, as well as the molecular diffusion and turbulent transport of the four species O, O_3, NO, and NO_2 are

$$
\begin{aligned}
\frac{D[\mathrm{O}]}{Dt} &= -\frac{[\mathrm{O}]}{\tau_{\mathrm{O}}} + \frac{[\mathrm{NO_2}]}{\tau_{\mathrm{NO_2}}} + \nu_{\mathrm{O}} \frac{\partial^2 [\mathrm{O}]}{\partial x_i \partial x_i}, && (57)\\
\frac{D[\mathrm{O_3}]}{Dt} &= -k[\mathrm{O_3}][\mathrm{NO}] + \frac{[\mathrm{O}]}{\tau_{\mathrm{O}}} + \nu_{\mathrm{O_3}} \frac{\partial^2 [\mathrm{O_3}]}{\partial x_i \partial x_i}, && (58)\\
\frac{D[\mathrm{NO}]}{Dt} &= -k[\mathrm{O_3}][\mathrm{NO}] + \frac{[\mathrm{NO_2}]}{\tau_{\mathrm{NO_2}}} \\
&\quad + \nu_{\mathrm{NO}} \frac{\partial^2 [\mathrm{NO}]}{\partial x_i \partial x_i}, && (59)\\
\frac{D[\mathrm{NO_2}]}{Dt} &= -\frac{[\mathrm{NO_2}]}{\tau_{\mathrm{NO_2}}} + k[\mathrm{O_3}][\mathrm{NO}] \\
&\quad + \nu_{\mathrm{NO_2}} \frac{\partial^2 [\mathrm{NO_2}]}{\partial x_i \partial x_i}. && (60)
\end{aligned}
$$

The quantities τ_{O} and $\tau_{\mathrm{NO_2}}$ are the mean life-times for the first-order processes, k the reaction constant for the second-order process and ν_{O}, $\nu_{\mathrm{O_3}}$, ν_{NO}, and $\nu_{\mathrm{NO_2}}$ the molecular diffusivities.

In (57) the first two terms are large compared to the other terms so there is an effective balance between destruction of $O(^3P)$ and creation of NO_2. For this reason $O(^3P)$ need not be further considered here, and we consider only the one first-order time constant $\tau = \tau_{\mathrm{NO_2}}$.

For convenience we introduce the dimensionless concentrations

$$
\left\{ \begin{array}{c} \tilde{s}_1 \\ \\ \tilde{s}_2 \\ \\ \tilde{s}_3 \end{array} \right\} = k\tau \times \left\{ \begin{array}{c} [\mathrm{O_3}] \\ \\ [\mathrm{NO}] \\ \\ [\mathrm{NO_2}] \end{array} \right\}, \qquad (61)
$$

where all three quantities are functions of Cartesian position (x,y,z) and time t. The equation (8) for conserved species must now be replaced by

$$
\frac{D\tilde{s}_i}{Dt} = (i^2 - 3i + 1)\,\widetilde{\mathcal{R}} + \nu_s \nabla^2 \tilde{s}_i, \quad i = 1,2,3, \qquad (62)
$$

where the molecular diffusivity is assumed the same ν_s for all the scalars, and where

$$
\widetilde{\mathcal{R}} = \frac{1}{\tau}\,(\tilde{s}_1 \tilde{s}_2 - \tilde{s}_3) \qquad (63)
$$

describes the reaction rates. Defining the sum concentrations as

$$
\tilde{c}_i = \tilde{s}_i + \tilde{s}_3, \quad i = 1,2 \qquad (64)
$$

and neglecting molecular diffusion in (53), we get the two conservation equations

$$
\frac{D\tilde{c}_i}{Dt} = 0, \quad i = 1,2 \qquad (65)
$$

of the two sum-concentrations. These behave, in other words, like conserved species.

Similarly, we get for the sum-concentrations[§]

$$
\tilde{c}_i = C_i(z) + c_i(x,y,z,t), \qquad i = 1,2. \qquad (66)
$$

The rate equations (53) take the form

$$
\begin{aligned}
&\left\{ \frac{\partial}{\partial t} + U \frac{\partial}{\partial x} \right\} (S_i + s_i) + w \frac{\partial S_i}{\partial z} + \nabla \cdot (\mathbf{u} s_i) = \\
&(i^2 - 3i + 1)\,\widetilde{\mathcal{R}} + \nu_s \nabla^2 (S_i + s_i), \quad i = 1,2,3. \qquad (67)
\end{aligned}
$$

Taking the mean of this equation, we get

$$
\frac{\partial S_i}{\partial t} + \frac{\partial}{\partial z} \langle w s_i \rangle = (i^2 - 3i + 1) \left\langle \widetilde{\mathcal{R}} \right\rangle + \underbrace{\nu_s \frac{\partial^2 S_i}{\partial z^2}}_{\simeq 0}. \qquad (68)
$$

The equation for the fluctuating part s_i is obtained from (67) and (68):

$$
\begin{aligned}
&\left\{ \frac{\partial}{\partial t} + U \frac{\partial}{\partial x} \right\} s_i + w \frac{\partial S_i}{\partial z} + \nabla \cdot (\mathbf{u} s_i) - \frac{\partial}{\partial z} \langle w s_i \rangle = \\
&(i^2 - 3i + 1)\, \frac{S_1 s_2 + S_2 s_1 - s_3}{\tau} + \nu_i \nabla^2 s_i. \qquad (69)
\end{aligned}
$$

The conservation rule (65) then translates to

$$
\frac{\partial}{\partial z} \langle w c_i \rangle = 0, \quad i = 1,2. \qquad (70)
$$

where

$$
\langle w c_i \rangle = \langle w s_i \rangle + \langle w s_3 \rangle, \quad i = 1,2. \qquad (71)
$$

The average of $\widetilde{\mathcal{R}}$ is determined from (54):

$$
\left\langle \widetilde{\mathcal{R}} \right\rangle = \frac{1}{\tau} \left\{ S_1 S_2 - S_3 + \langle s_1 s_2 \rangle \right\}. \qquad (72)
$$

We neglect the third-order terms and, closely following the procedure outlined in section 2, we obtain the nine equations

$$
\begin{aligned}
\frac{\partial S_i}{\partial t} + \frac{\partial}{\partial z} \langle w s_i \rangle &= (i^2 - 3i + 1)\, \frac{S_1 S_2 - S_3 + \langle s_1 s_2 \rangle}{\tau}, \\
&\qquad i = 1,2,3, \qquad (73)
\end{aligned}
$$

$$
\begin{aligned}
&\frac{\partial}{\partial t} \langle w s_i \rangle + \langle w^2 \rangle \left\{ \frac{\partial S_i}{\partial z} + \frac{\langle w s_i \rangle}{\langle w^2 \rangle \tau_1} \right\} = \\
&\quad (i^2 - 3i + 1)\, \frac{S_2 \langle w s_1 \rangle + S_1 \langle w s_2 \rangle - \langle w s_3 \rangle}{\tau} \\
&\quad + (1 - b_1)\, \frac{g}{T} \langle \vartheta s_i \rangle, \quad i = 1,2,3, \qquad (74)
\end{aligned}
$$

[§] We are seeking steady-state solutions and let S_i be time dependent for computational reasons. However, the sum concentrations C_i are assumed constant in time.

and

$$\begin{aligned}&\frac{\partial\langle\vartheta s_i\rangle}{\partial t}+\langle w\vartheta\rangle\frac{\partial S_i}{\partial z}+\frac{\langle\vartheta s_i\rangle}{\tau_4(z)}\\&\qquad=(i^2-3i+1)\frac{S_2\langle\vartheta s_1\rangle+S_1\langle\vartheta s_2\rangle-\langle\vartheta s_3\rangle}{\tau},\\&\qquad i=1,2,3,\end{aligned}\tag{75}$$

where, for computational purposes, the prognostic terms are included.

The nine equations (73), (74) and (75) do not quite constitute a closed system since (73) contains the scalar covariance $\langle s_1 s_2\rangle$. However, we consider this quantity a small perturbation which can be determined and included later if we initially ignore it. Once we have determined S_i in this way, we may derive all second-order scalar-scalar covariances by means of (69). This will be shown in the last part of this section.

Combining the three equations (74) we get, in view of (66) and (71), the two equations

$$\langle w^2\rangle\left\{\frac{\partial C_i}{\partial z}+\frac{\langle wc_i\rangle_\circ}{\langle w^2\rangle\tau_1}\right\}=(1-b_1)\frac{g}{T}\langle\vartheta c_i\rangle,\quad i=1,2.\tag{76}$$

Similarly we obtain from (75)

$$\langle w\vartheta\rangle\frac{\partial C_i}{\partial z}+\frac{\langle\vartheta c_i\rangle}{\tau_4(z)}=0,\quad i=1,2.\tag{77}$$

We have here left out the prognostic terms and used the fact that $\langle wc_i\rangle=\langle wc_i\rangle_\circ$ are constant with height. It is of course no surprise that the last two equations have exactly the same form as the equations (28) and (26) pertaining to conserved scalars.

The equations for the derivation of the scalar-scalar covariances are

$$\begin{aligned}&\frac{\partial}{\partial t}\langle s_i^2\rangle+2\langle ws_i\rangle\frac{\partial S_i}{\partial z}\\&\qquad=2(i^2-3i+1)\frac{S_1\langle s_i s_2\rangle+S_2\langle s_i s_1\rangle-\langle s_i s_3\rangle}{\tau}\\&\qquad\quad-2\nu_s\langle(\nabla s_i)^2\rangle,\qquad i=1,2,3,\end{aligned}\tag{78}$$

where third-order terms have been ignored. We follow Verver et al. (1997) and use the parameterization of the molecular term

$$2\nu_s\langle\nabla s_i\cdot\nabla s_j\rangle=\frac{\langle s_i s_j\rangle}{\tau_3(z)}.\tag{79}$$

We assume with Verver et al. (1997) that τ_3 is equal to τ_4. In an equilibrium state (70) then becomes

$$\begin{aligned}\langle ws_i\rangle\frac{\partial S_i}{\partial z}&=(i^2-3i+1)\frac{S_1\langle s_i s_2\rangle+S_2\langle s_i s_1\rangle-\langle s_i s_3\rangle}{\tau}\\&\qquad-\frac{\langle {s_i}^2\rangle}{2\tau_4(z)},\quad i=1,2,3.\end{aligned}\tag{80}$$

We obtain three more equations from the sum-concentrations $(C_i,c_i)=(S_i+S_3,s_i+s_3)$, $i=1,2$ which also follow (69) and (80), with the first term on the right-hand side set equal to zero, if we replace s_i by c_i:

$$\langle wc_i\rangle\frac{\partial C_i}{\partial z}=-\frac{\langle {c_i}^2\rangle}{2\tau_4(z)},\ i=1,2,\tag{81}$$

$$\langle wc_1\rangle\frac{\partial C_2}{\partial z}+\langle wc_2\rangle\frac{\partial C_1}{\partial z}=-\frac{\langle c_1 c_2\rangle}{\tau_4(z)}.\tag{82}$$

The six equations (80), (81), and (82) can, with patience, great care and with Mathematica (Wolfram, 1999) as a crutch, be solved for $\langle s_1 s_2\rangle$. First, however, we recast the basic equations (73), (74) and (75) in a dimensionless form as follows

$$\left\{\begin{array}{c}\theta\\ f_i\\ F_i\\ \gamma_i\\ \Gamma_i\end{array}\right\}=\left\{\begin{array}{r}w_*t/h\\ \langle ws_i\rangle/w_*\\ \langle wc_i\rangle_\circ/w_*\\ \langle\vartheta s_i\rangle/T_*\\ \langle\vartheta c_i\rangle/T_*\end{array}\right\}\tag{83}$$

and the dimensionless parameter, the Damköhler number,

$$\mathcal{D}=\frac{h}{w_*\tau}.\tag{84}$$

In dimensionless form (73), (74) and (75) become

$$\begin{aligned}&\frac{\partial S_i}{\partial\theta}+\frac{\partial f_i}{\partial\zeta}=\\&\qquad\mathcal{D}\times(i^2-3i+1)(S_1S_2-S_3+\langle s_1s_2\rangle),\end{aligned}\tag{85}$$

$$\begin{aligned}&\frac{\partial f_i}{\partial\theta}+\omega^2(\zeta)\left\{\frac{\partial S_i}{\partial\zeta}+\frac{f_i}{\omega^2\theta_1}\right\}=\\&\qquad\mathcal{D}\times(i^2-3i+1)\,(S_2f_1+S_1f_2-f_3)+\gamma_i\end{aligned}\tag{86}$$

and

$$\begin{aligned}&\frac{\partial\gamma_i}{\partial\theta}+\varphi_T(\zeta)\frac{\partial S_i}{\partial\zeta}+\frac{\gamma_i}{\theta_4}=\\&\qquad\mathcal{D}\times(i^2-3i+1)\,(S_2\gamma_1+S_1\gamma_2-\gamma_3)\,.\end{aligned}\tag{87}$$

The summed equations become

$$\frac{\partial F_i}{\partial\zeta}=0,\tag{88}$$

$$\omega^2\frac{\partial C_i}{\partial\zeta}-\Gamma_i=-\frac{F_i}{\theta_1},\quad i=1,2\tag{89}$$

and

$$\varphi_T\frac{\partial C_i}{\partial\zeta}+\frac{\Gamma_i}{\theta_4}=0,\quad i=1,2.\tag{90}$$

For $\mathcal{D}=0$, which corresponds to $\tau=\infty$ (i.e. no decay of NO_2) we obtain the same three equations as (88), (89), and (90) in their diagnostic form if we make the replacement $(C_i, F_i, \Gamma_i) \rightarrow (S_i, f_i, \gamma_i)$.

Since F_i is constant with height we can determine $\partial C_i/\partial\zeta$ and Γ_i as functions of ζ once F_i has been specified. From (89) and (90) we get

$$\frac{\frac{\partial C_i}{\partial \zeta}}{F_i} = -\frac{1}{\theta_1\left(\omega^2+\theta_4\varphi_T\right)}, \quad i=1,2 \tag{91}$$

and

$$\frac{\Gamma_i}{F_i} = \frac{\theta_4\varphi_T}{\theta_1\left(\omega^2+\theta_4\varphi_T\right)}, \quad i=1,2. \tag{92}$$

These two equations are equivalent to (36) and (37).

The covariance $\langle s_1 s_2\rangle$ can now be determined from (80), (81), and (82) in their dimensionless forms:

$$\begin{aligned} \frac{f_i S_i'}{\mathcal{D}} \;=\; & (i^2-3i+1)\{S_1\langle s_i s_2\rangle + S_2\langle s_i s_1\rangle - \langle s_i s_3\rangle\} \\ & -q\langle s_i^2\rangle, \qquad\qquad i=1,2,3 \end{aligned} \tag{93}$$

$$\frac{F_i C_i'}{\mathcal{D}} = -q\langle c_i^2\rangle = -q\{\langle s_i^2\rangle + 2\langle s_i s_3\rangle + \langle s_3^2\rangle\}, \quad i=1,2, \tag{94}$$

and

$$\begin{aligned} \frac{F_1C_2'+F_2C_1'}{2\mathcal{D}} \;=\; & -q\langle c_i^2\rangle = -q\{\langle s_1s_2\rangle + \langle s_2s_3\rangle \\ & +\langle s_3s_1\rangle + \langle s_3^2\rangle\}, \end{aligned} \tag{95}$$

where

$$S_i' = \frac{\partial S_i}{\partial \zeta}, \tag{96}$$

$$C_i' = \frac{\partial C_i}{\partial \zeta}, \tag{97}$$

and

$$q = \frac{1}{2\mathcal{D}\theta_4}. \tag{98}$$

We can now construct a set of six linear equations with six unknowns, which are presented in Figure 3 We find that

$$\langle s_1s_2\rangle = -\frac{num}{q(1+q+S_1+S_2)(1+2q+S_1+S_2)}, \tag{99}$$

where

$$\begin{aligned} num \;=\; & A_{11}S_2(1+S_1) + A_{22}S_1(1+S_2) \\ & -A_{12}(1+S_1+S_2+2S_1S_2) \\ & +q\{(A_{11}+A_{22}-2A_{12})(1+S_1+S_2) - A_{12} \\ & -a_{11}(1+S_1) - a_{22}(1+S_2) + a_{33}\} \\ & +q^2\{A_{11}+A_{22}-2A_{12}-a_{11}-a_{22}\}. \end{aligned} \tag{100}$$

Here we have used the notation

$$a_{ii} = \frac{f_i S_i'}{\mathcal{D}}, \quad i=1,2,3, \tag{101}$$

$$A_{ii} = \frac{F_i C_i'}{\mathcal{D}}, \quad i=1,2, \tag{102}$$

and

$$A_{12} = \frac{F_1C_2'+F_2C_1'}{2\mathcal{D}}. \tag{103}$$

6. SOLVING THE EQUATIONS

Here we outline the procedure for solving for concentrations and fluxes, and demonstrate that we can reduce the problem to three equations in $S \equiv S_3$, $f \equiv f_3$, and $\gamma \equiv \gamma_3$ for the NO_2 concentration.[¶]

First we note that we can make the replacements $(f_1, f_2) = (F_1 - f_3, F_2 - f_3)$ and $(S_1, S_2) = (C_1 - S_3, C_2 - S_3)$, where

$$C_i(\zeta) = C_i^\circ + F_i \int_{\zeta}^{\zeta^\circ} \frac{d\zeta'}{\theta_1(\zeta')\,(\omega^2(\zeta')+\theta_4(\zeta')\varphi_T(\zeta'))}, \quad i=1,2, \tag{104}$$

is obtained by integrating (91). The quantities C_i° are the sum concentrations at the reference level ζ°, which is the top of our model domain. We use $\zeta^\circ = 1/1.2$, which is the level at which the buoyancy flux changes sign. This is also consistent with estimates of the thickness of the entrainment zone (Gryning and Batchvarova, 1994), which is about as far as one can take a parameterized model of this type.

Further, γ is eliminated by expressing it in terms of F_1, F_2 in the two relations (92) and f and S in the steady-state form of (87) for γ ($i=3$):

$$\gamma(\zeta) = \frac{\theta_4\varphi_T\left\{\mathcal{D}\left(F_2S_1+F_1S_2\right) - \theta_1\left(\omega^2+\theta_4\varphi_T\right)\frac{\partial S}{\partial \zeta}\right\}}{\theta_1\left\{1+\mathcal{D}(1+S_1+S_2)\theta_4\right\}\left\{\omega^2+\theta_4\varphi_T\right\}}. \tag{105}$$

We have now reduced the problem to solving the two equations (85) and (86) for $i=3$:

$$\frac{\partial S}{\partial \theta} + \frac{\partial f}{\partial \zeta} = \mathcal{D}(S_1S_2 - S + \langle s_1s_2\rangle), \tag{106}$$

$$\frac{\partial f}{\partial \theta} + \omega^2\left\{\frac{\partial S}{\partial \zeta} + \frac{f}{\omega^2\theta_1}\right\} = \mathcal{D}\left(S_2 f_1 + S_1 f_2 - f\right) + \gamma. \tag{107}$$

These two equations are solved for S and f by iteration under the assumption that the covariance $\langle s_1s_2\rangle$ can be considered a perturbation which is neglected in the first calculation and then, determined by (99), inserted in the second calculation.

We are seeking a steady-state solution for the concentrations and fluxes. This is obtained by solving (106)

[¶] We have omitted the subscript 3 for convenience.

$$\left\{\begin{array}{cccccc} -(S_2+q) & 0 & 0 & -S_1 & 0 & 1 \\ 0 & -(S_1+q) & 0 & -S_2 & 1 & 0 \\ 0 & 0 & -(1+q) & 0 & S_1 & S_2 \\ -q & 0 & -q & 0 & 0 & -2q \\ 0 & -q & -q & 0 & -2q & 0 \\ 0 & 0 & -q & -q & -q & -q \end{array}\right\} \times \left\{\begin{array}{c} \langle s_1^2\rangle \\ \langle s_2^2\rangle \\ \langle s_3^2\rangle \\ \langle s_1 s_2\rangle \\ \langle s_2 s_3\rangle \\ \langle s_3 s_1\rangle \end{array}\right\} = \left\{\begin{array}{c} \frac{f_1 S_1'}{\mathcal{D}} \\ \frac{f_2 S_2'}{\mathcal{D}} \\ \frac{f_3 S_3'}{\mathcal{D}} \\ \frac{F_1 C_1'}{\mathcal{D}} \\ \frac{F_2 C_2'}{\mathcal{D}} \\ \frac{F_1 C_2' + F_1 C_1'}{2\mathcal{D}} \end{array}\right\}$$

Figure 3: The matrix formulation of the six linear equations.

and (107) as partial differential equations with the time θ and the height ζ as independent variables, using a relaxation scheme in θ. The boundary conditions for these steady-state solutions are the surface fluxes f_1, f_2, and $f = f_3$ and three flux-concentration relations at the top of the boundary layer. The first three are applied to obtain F_1 and F_2 in (104). The next three are specifications of fluxes at the top of the boundary layer in terms of a dimensionless entrainment velocity $\omega_e = w_e/w_*$[‖] and the differences between the concentrations in the free troposphere and those at a reference level ζ° inside the boundary layer. To proceed we need expression for w_e. The entrainment process at the top of the CBL is independent of the species, and, if we take the potential temperature as a marker, we have

$$\langle \vartheta w \rangle_h = -w_e \Delta\Theta, \qquad (108)$$

where $\Delta\Theta$ is the jump in potential temperature across the top h of the CBL. In (40) we have already assumed that $\langle \vartheta w \rangle_h = -0.2\, \langle \vartheta w \rangle_\circ$ so that

$$w_e = 0.2\, \frac{\langle \vartheta w \rangle_\circ}{\Delta\Theta}. \qquad (109)$$

The magnitude of the the jump has been estimated by Tennekes (1973) who expressed it in terms of the gradient Γ_Θ of the potential temperature in the free troposphere and h by

$$\Delta\Theta = \frac{1}{7}\Gamma_\Theta h. \qquad (110)$$

Inserting this result into (101), we get

$$w_e = 1.4 \frac{\langle w\vartheta \rangle_\circ}{\Gamma_\Theta h} = \frac{1.4}{1-b_1}\, w_* \left(\frac{\frac{g}{T}\Gamma_\Theta}{\frac{w_*^2}{h^2}} \right)^{-1}, \qquad (111)$$

where the fraction inside the parenthesis can be identified as a Richardson number based on the potential-temperature gradient in the free troposphere and free-convection turbulence in a CBL of depth h . With the typical values $\Gamma_\Theta = 10^{-2}$ K m^{-1}, $h = 10^3$ m, and $w_* = 1$ m s^{-1}, we find that $\omega_e = 7 \times 10^{-3}$.

Denoting concentrations in the free atmosphere by an asterisk superscript, we have:

$$\left\{\begin{array}{c} f_1^\circ \\ f_2^\circ \\ f^\circ \end{array}\right\} = \omega_e \times \left\{\begin{array}{l} S_1^\circ - S_1^* \\ S_2^\circ - S_2^* \\ S^\circ - S^*, \quad (i=3) \end{array}\right\}. \qquad (112)$$

We may reduce the degrees of freedom by assuming photostationary equilibrium Leighton (1961) between the three species:

$$k\tau \frac{[\mathrm{NO}]^*[\mathrm{O_3}]^*}{[\mathrm{NO_2}]^*} = \frac{S_1^* S_2^*}{S^*} = 1. \qquad (113)$$

We note that, the way the problem is now presented, it is symmetric in the indices 1 and 2. This means that we may always assume that $S_1^\circ \geq S_2^\circ$ at the reference level ζ° and in the free troposphere.

7. SAMPLE CALCULATION

Here we show a set of plots from a sample run of the model. The lower limit for the spatial integration cannot be zero because concentrations are not finite at $z = 0$. Therefore we have chosen the lower limit to be $\zeta_\circ = 10^{-5}$, which is consistent with surface layer formulations which are considered to be valid only down to a surface roughness length that is determined by the properties of the surface. As noted earlier, the top of the domain is at $\zeta^\circ = 1/1.2$.

[‖] By convention the entrainment velocity is positive when the flux is downward.

In figures 4, 5, 6, and 7 we use $\omega_e = 0.07$ and $\mathcal{D} = 4$, and the boundary conditions $S_1^* = 1$, $S_2^* = 0.01$, $f_1(\zeta_0) = -0.0036$, $f_2(\zeta_0) = 0.0049$, and $f_3(\zeta_0) \equiv f(\zeta_0) = -0.0001$. In the first two figures, the covariance term $\langle s_1 s_2 \rangle$ is set equal to zero, while in the second two figures the term is included. We see that there is a small, but significant, difference between the two sets of curves.

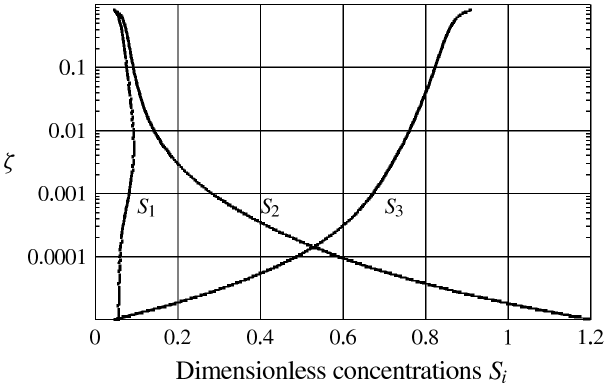

Figure 4: Concentration profiles with $\langle s_1 s_2 \rangle = 0$.

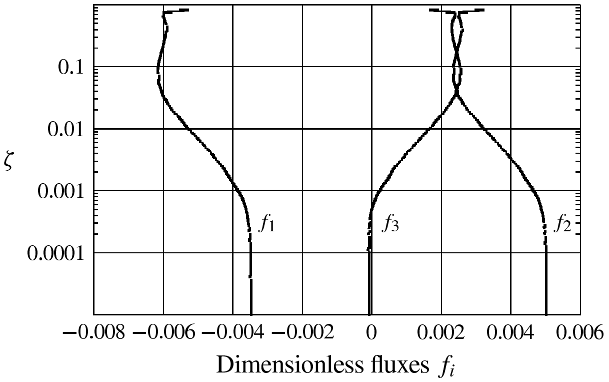

Figure 5: Flux profiles with $\langle s_1 s_2 \rangle = 0$.

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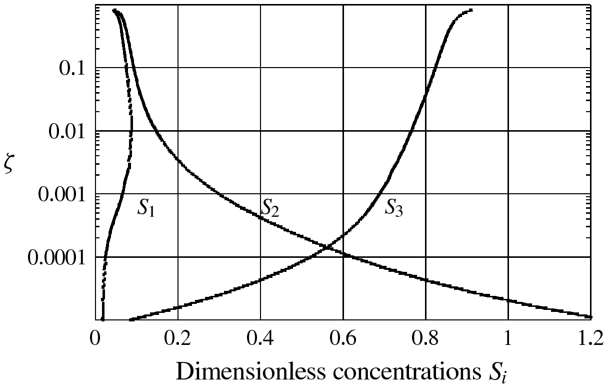

Figure 6: Concentration profiles with $\langle s_1 s_2 \rangle$ included.

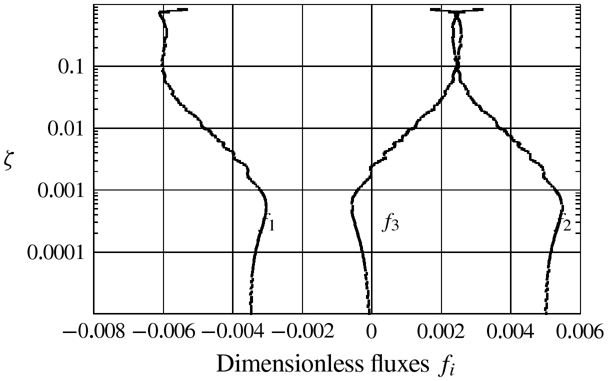

Figure 7: Flux profiles with $\langle s_1 s_2 \rangle$ included.

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