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1. INTRODUCTION

A comprehensive treatment of turbulent mixing and chemistry is important in modeling a number of atmospheric chemistry processes in the planetary boundary layer (PBL). For gases such as O₃, NO, NO₂, peroxyacetyl nitrate (PAN), and a significant number of highly reactive nonmethane hydrocarbons, the turbulent mixing times and their reactive loss times in the boundary layer are of comparable magnitude. The physical process of mixing competes with chemical reactions to establish the vertical distribution of these gases. Evaluation of turbulent mixing and chemistry in a boundary layer is also of critical importance in the interpretation of fluxes obtained from measurements on towers or from aircraft. The heterogeneity of the surface covered by the footprint of the measurement results in the heterogeneity in sources and sinks. Thus, for trace gases with lifetimes close to the mixing times and under the influence of either a source or sink heterogeneity, model-based estimates of fluxes can be greatly in error if the physics and chemistry of the turbulent reactive mixture are not taken into consideration. A third and more complex issue is turbulence inside a canopy and the resulting segregation of gases. This segregation could have a significant effect on estimates of the amount of gases emitted from the surface (e.g., NO) and plants (e.g. isoprene) and available for mixing into the rest of the boundary layer, thus affecting the production and loss of oxidants above the canopy.

A parameterized turbulence scheme and a chemistry-transport equation with second-order closure assumptions was used by Gao et al. (1993) to model measured isoprene, NO_x, and O₃ vertical profiles in and above a forest canopy. The turbulence flow variables were prescribed by using known parameterizations. Several recent studies have adopted LES (large eddy simulation) models to describe the turbulent convective boundary layer (Petersen et al. 1999; Weil 1990; Sorbjan 1996). Though appealing in terms of its direct relation to eddy sizes in the flow, the LES approach yielded results similar to those from a one-dimensional (1-D) PBL model with second-order closure (Galmarini et al. 1998). An intermediate approach that might be

adequate to address this issue would use a 1-D PBL model with second-order or higher closure for the Reynolds stress terms and the full set of chemistry-transport equations.

We developed such an intermediate approach by using a 1-D PBL model with a 2.5-level turbulence closure model based on the K-ε theory. The fundamental aspects of this type of PBL model were discussed by Rodi (1985). This approach was used for modeling nocturnal boundary layers (Uno et al. 1989) and neutral and stable boundary layer (Duykerke 1988; Kotamarthi and Carmichael 1993). The photochemical model has 72 species, 132 thermal reactions, and 52 photolysis rates. The model has full representation of the inorganic gas phase chemistry based on DeMore et al. (1997 and later revisions). Heterogeneous chemistry including N₂O₅ on aerosol surfaces is also included in the model. The hydrocarbon scheme follows that of RACM (Regional Atmospheric Chemistry Mechanism) of Stockwell et al. (1997). The chemical integrator employs the Gear method. Photolysis rates are calculated by using a multi stream radiative transfer model, with 128 bins for calculating absorption cross sections ranging from 170 nm to 450 nm. Dry deposition losses for some of the gases are prescribed at the model surface to fixed values for the course of the simulation.

2. TREATMENT OF HIGHER ORDER TURBULENCE AND CHEMICAL REACTION CORRELATION TERMS IN THE MODEL

The evolution of a reactive trace gas distribution in the vertical direction in an evolving PBL can be expressed as:

$$\frac{\partial \langle C_i \rangle}{\partial t} = - \frac{\partial \langle w C_i \rangle}{\partial z} + \langle w R x n_i \rangle \quad (1)$$

where C_i is the concentration of trace gas i , z is the vertical axis, w is the wind velocity in the z direction, and $R x n_i$ is the reaction term involving species i . The terms $\langle C_i \rangle$, $\langle w C_i \rangle$, and $\langle R x n_i \rangle$ represent ensemble averages of the concentration, turbulent flux, and chemical reaction, respectively. To solve this equation, additional equations describing the flux term and the reaction term are required. The flux term is most commonly described in atmospheric chemistry models by using an eddy mixing coefficient in analogy to Fickian diffusion terms. The chemical reaction term, when expanded in terms of a mean and a fluctuating component about the mean as

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is done during the “Reynolds averaging” process, corresponds to covariance terms such as $\langle C_i \rangle \langle C_j \rangle$ for a reaction involving two gas phase components i and j . The second-order equation describing the flux term takes the form

$$\frac{\partial \langle wC_i \rangle}{\partial t} = - \langle w^2 \rangle \frac{\partial C_i}{\partial z} - \frac{\partial \langle w^2 C_i \rangle}{\partial z} \quad (2)$$

$$+ \frac{g}{\theta} \langle C_i \theta \rangle - \frac{1}{\rho} \langle C_i \frac{\partial P}{\partial z} \rangle + \langle wRxn_i \rangle \quad (3) \quad (4) \quad (5)$$

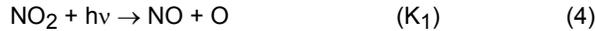
Here term (1) is the diffusional transport term; (2) is the vertical gradient of the turbulent flux; (3) is the change due to buoyancy (G); (4) is known as the pressure scrambling term and represents correlations of pressure fluctuations with concentration (P); and the (5) term represents the effect of change in flux due to chemical reactions.

The dynamic evolution of the 1-D PBL is described in the current model by using an algebraic stress model (ASM) assumption to close the second-order transport terms. This approach yields equations that would conform to a level-2.5 closure of the Reynolds averaged equation. We adopted a similar approach (ASM-like) and assumptions to close the second-order chemical equation. This yields the following equation for the flux term:

$$\frac{\langle wC_i \rangle}{2K} = - \frac{1}{\varepsilon} \frac{[\langle w^2 \rangle \frac{\partial \langle C_i \rangle}{\partial z} + \langle wRxn_i \rangle]}{2(C_{1t} + 2fC_{1tw}) + \frac{P+G}{\varepsilon} - 1} \quad (3)$$

Here C_{1t} and C_{1tw} are ASM constants, and f is the wall proximity function (Kotamarthi and Carmichael, 1993). This equation is similar to the one employed to close the second-order terms in the temperature equation, with an additional term in the numerator to account for second-order and higher-order correlation terms resulting from chemical reactions.

The reaction system involving NO, NO₂, and O₃ generally referred to as the photostationary system for O₃ production, can be used as an example.



For this system of three equations the correlation term $wRxn_{NO}$ would be

$$\langle wRxn_{NO} \rangle = K_1 \langle w\text{NO}_2 \rangle - K_3 \langle \text{NO} \rangle \langle w\text{O}_3 \rangle - K_3 \langle \text{O}_3 \rangle \langle w\text{NO} \rangle \quad (7)$$

where the respective correlation terms are derived as in (3). As is the usual practice in ASM-based modeling, the flux terms can now be represented in a form similar to the eddy mixing coefficient formulation, for example as follows:

$$\langle wC_i \rangle = \frac{2k}{\varepsilon A} \langle w^2 \rangle \frac{\partial C_i}{\partial z} \quad (8)$$

Here A is a constant derived from rearranging (2). This constant is dependent on the flow conditions and correlation terms discussed above.

The transport terms in the chemical tendency equations are solved by using a fully implicit finite difference scheme. The vertical grid employed has 45 levels laid out on a log-normal axis to give highest resolution in the lowest 50 m of the model. The model is solved with time step of 5 s for the chemistry and 5 min for the dynamic equations. The preliminary focus of these calculations is on evaluating the effect of chemistry on the calculated flux of NO from soil.

3. PRELIMINARY RESULTS

In this initial set of calculations, the mixing coefficient derived as described by (8) were employed in solving the transport equation for NO, NO₂, and O₃ keeping the eddy mixing coefficients for the rest of the 72 trace gases same as that calculated for the temperature in the model. This set of calculations is referred to as “with reaction.” In a second set of calculations, the eddy mixing coefficients for all of the trace gases in the model are set to those derived for the temperature and are referred to as “no reaction” in the following discussion. In both of these calculations, the entire complement of gas-phase reactions modeled is switched on. The only difference between the “reaction” and “no reaction” calculations are changes in prescribed eddy mixing coefficients for NO, NO₂, and O₃. Figure 1 shows the calculated flux of NO at three levels in the model, with reaction terms included in the calculation of the eddy mixing coefficients. The lowest layer of the model is at 1 m. The calculations were performed over a three day period starting at 8 p.m. For illustration purposes, the model surface was forced with a constant flux of NO of 300 ng N m⁻² s⁻¹ (higher by a factor 10 than the flux typically observed). The calculated fluxes at the three levels are smaller during nighttime than daytime. The variability in the calculated fluxes is also larger during daytime than nighttime. Figure 2 shows the O₃ flux at the 1-m level for the same calculation. The O₃ deposition rate is at a maximum during the early evening hours and is smallest during the middle of the day; this flux is driven mainly by the surface resistance.

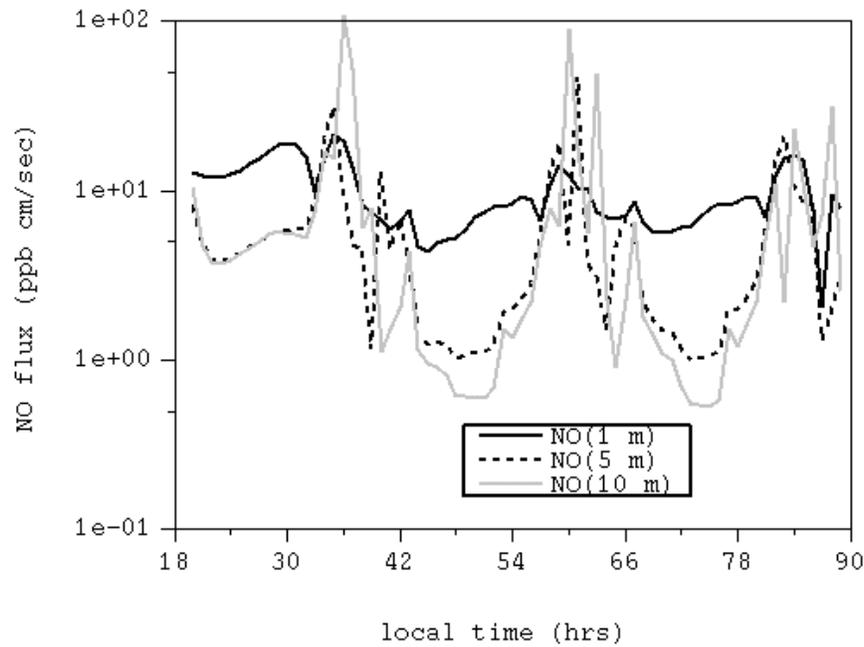


Fig. 1. Calculated flux of NO over a three day period starting at 20 hr local time (8 p.m.) with a fixed surface emission for NO. Fluxes were calculated with modified eddy mixing coefficients as discussed in the text.

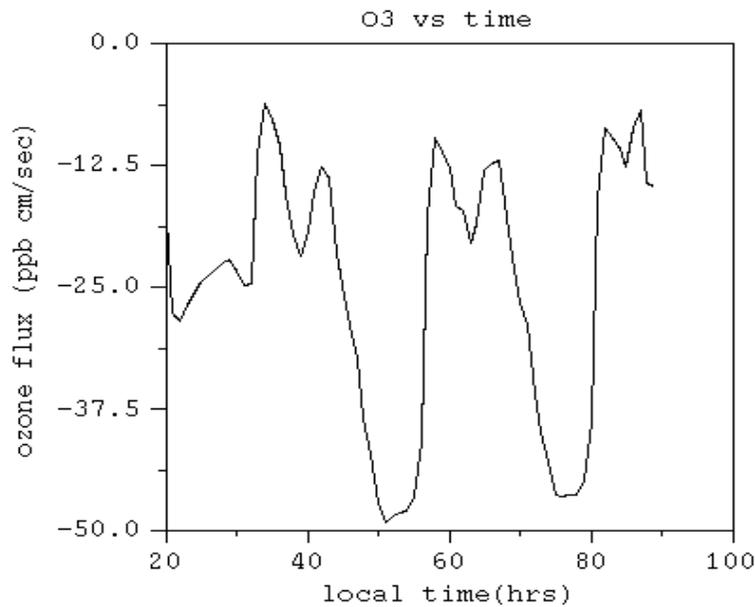


Fig. 2. Calculated O₃ flux at 1 m above the surface in the model for the same conditions as in Fig 1.

Figure 3 shows the ratio of NO flux calculated at 00 hr as a function of altitude and is typical of the model results for nighttime. The ratio compares the effects on the estimated fluxes of second-order reaction correlation terms of the chemical reaction in relation to a calculation where the effects of reaction correlation on the fluxes were ignored. The ratio is between 1 and 1.1 through

most of the lowest 10 m of the model and reaches a value of 1.3 at 10 m. This result reflect the stronger effect of the term involving NO during nighttime. As a result, the flux increases when the second-order reaction terms are considered in calculating the flux during nighttime.

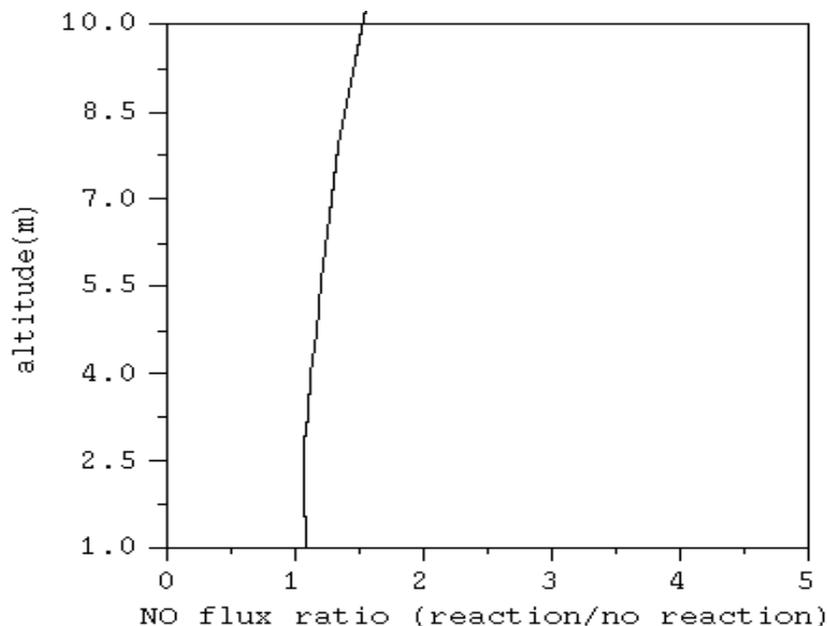


Fig. 3. The ratio of NO fluxes calculated for the lowest 10 m of the model.

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