

6.2 Revised INITIAL APPLICATION OF A COUPLED LES-PHOTOCHEMICAL MODEL
TO EXAMINE NEAR-SOURCE OZONE PRODUCTION FROM INDUSTRIAL EMISSIONS

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1. INTRODUCTION

Within the influence of urban areas and industrial complexes, surface ozone (O₃) monitors have revealed rapid O₃ formation and sharp “spikes” in measured O₃ concentrations. These extreme O₃ phenomena are apparently not being reproduced by coarse grid State Implementation Plan (SIP) models or by typical regional air quality prediction systems.

The co-emission of nitric oxide (NO) and volatile organic compounds (VOCs) into the large eddy structure of the convective boundary layer (CBL) has been hypothesized to produce reactant covariances that could effectively increase the mean rates of reaction over those produced in a coarse grid first-order closure SIP model. Reactive turbulence theory suggests that the effective reaction rates could be altered by correlation terms which are neglected in current models. From Sykes *et al.* (1994), the average reaction rate of two reactants *A* and *B* is given by

$$k\overline{AB} = k(\overline{AB} + \overline{A'B'}) \quad (1)$$

where *k* is the reaction rate coefficient, the overbar represents a spatial or temporal ensemble average concentration, and the prime indicates a fluctuation, or deviation, from the average. The concentration covariance term $\overline{A'B'}$ arises due to the Reynolds averaging required in constructing grid scale models. Typical coarse grid first-order closure models neglect this term and assume that the mean reaction rate is approximated by the product of the grid cell average concentrations of each reactant. Sykes *et al.* (1994) introduced an intensity of segregation *I_s* by rewriting Equation 1 in the following form

$$k\overline{AB} = k(1 + I_s)\overline{A}\overline{B} \quad (2)$$

where

$$I_s = \frac{\overline{A'B'}}{\overline{A}\overline{B}} \quad (3)$$

The intensity of segregation *I_s* denotes the importance of the concentration covariance term $\overline{A'B'}$ relative to the mean chemistry term $\overline{A}\overline{B}$. If the reactants are well-mixed, then *I_s* = 0 and the mean reaction rate is proportional to the product of the mean reactant concentrations. However, as the concentration

fluctuation covariance becomes significant, *I_s* deviates from zero in either a negative or positive sense. Reactants that remain correlated can cause effective reaction rates to be significantly changed. The present study is focused on the positive *I_s* case where coherent large eddy structures in the CBL may cause co-emitted reactants to remain positively correlated.

2. INDUSTRIAL PLUME SIMULATION APPROACH

Initial numerical experiments have been conducted to examine whether fine scale modeling and inclusion of turbulent-chemical interactions can accelerate the chemistry and impact the ozone production rates and concentration. The present study utilized an online coupled large-eddy simulation (LES)–photochemical model called LESchem (Herwehe, 2000). LESchem was built by integrating the second-generation Sparse Matrix Vectorized Gear (SMVGEAR II) chemistry solver (Jacobson, 1998) into the Regional Atmospheric Modeling System (RAMS) mesoscale model (Pielke *et al.*, 1992) configured to run in LES mode. The current photochemical mechanism used by LESchem is the updated Carbon Bond Mechanism IV (CB4) from Gipson and Young (1999) which solves 80 kinetic and 12 photolysis reactions for 38 chemical species. The LES dynamics and chemical reactions are solved together for each time step. The height- and time-dependent photolysis rates (*J* values) are computed in advance (offline) using the Tropospheric Ultraviolet and Visible (TUV) radiation model from NCAR (Madronich and Flocke, 1998).

The idealized coupled simulations of a hypothetical industrial plume were performed on a 20 km × 10 km × 4 km high domain with 200 m horizontal and 100 m vertical grid spacing. A mean westerly wind of 1 m s⁻¹ was specified. Periodic lateral boundary conditions were specified and a wall with a decaying Rayleigh friction layer controlled the domain top. The flat horizontally-homogeneous bottom surface of roughness length 7 cm was the location of the background trace gas emissions and dry deposition. The Mahrer and Pielke radiation scheme in conjunction with a moist soil model was used to compute the surface energy budget and drive the convection. The LES dynamics were computed using a fixed time step size of 3 s, while the chemistry solver employed variable time step sizes.

The primary time of interest is midday to mid-afternoon (11:00-15:00 LST). To obtain reasonable turbulent and chemical initial conditions for 11:00 LST, we: 1) computed a 9-h (06:00-15:00 LST) LES-only run

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initialized by a representative summer sunrise sounding, adjusting the soil model parameters to control the morning CBL growth and mid-afternoon mixed layer height; 2) simulated a 4-h LES (06:00-10:00 LST) on the full $20 \text{ km} \times 10 \text{ km}$ domain and saved final output for a simulation restart; 3) roughly spun up the chemistry by starting from typical tropospheric background mixing ratios at 06:00 LST, then simulated the morning 4-h period with background surface emissions on a small low-resolution (1 km horizontal spacing) domain; 4) combined the saved 10:00 LST LES output with the rough chemistry spin-up results for initial conditions to a full domain 200-m resolution 1-h (10:00-11:00 LST) coupled simulation, saving the final 11:00 LST results as initial conditions for the three 4-h coupled simulations discussed in the next section.

3. COUPLED LES-PHOTOCHEMISTRY RESULTS

The 11:00-15:00 LST LES dynamics in the coupled simulations described below were identical; only the chemistry scenarios were different. The strong summertime heating was evident by a CBL which grew from 1.2 km at 11:00 LST to about 2.6 km by 15:00 LST, rising 800 m in the first 90 min. Surface kinematic heat flux started a 0.25 K m s^{-1} , peaked around 0.39 K m s^{-1} at 12:40 LST before decreasing slightly after that, yielding a sensible heat flux estimate of $307\text{--}480 \text{ W m}^{-2}$ over the 4-h period. The convective velocity scale began at 1.9 m s^{-1} and reached a maximum of 2.9 m s^{-1} just before 14:00 LST. Thus, the convective time scale is in the range of 630-960 s for eddy overturning.

3.1 Background Chemistry without Plume

This 4-h coupled LES-photochemical “no plume” simulation acts as a “control run” for comparison with the subsequent plume simulations. Uniform and continuous surface trace gas emissions of NO, isoprene (ISOP), carbon monoxide (CO), and ethene (ETH) were specified as: 1) biogenic fluxes of $F_{\text{NO}} = 1.0 \times 10^{10}$ molecules $\text{cm}^{-2} \text{ s}^{-1}$ and $F_{\text{ISOP}} = 5.2 \times 10^{11}$ molecules $\text{cm}^{-2} \text{ s}^{-1}$; 2) anthropogenic fluxes of $F_{\text{NO}} = 1.6 \times 10^{10}$ molecules $\text{cm}^{-2} \text{ s}^{-1}$, $F_{\text{CO}} = 10 \cdot F_{\text{NO}}$, and $F_{\text{ETH}} = 0.08 \cdot F_{\text{NO}}$. Representative dry deposition velocities were specified for O_3 , NO, NO_2 , HNO_3 , H_2O_2 , FORM, ALD2, and PAN. Subsequent plume simulations used these background trace gas boundary conditions.

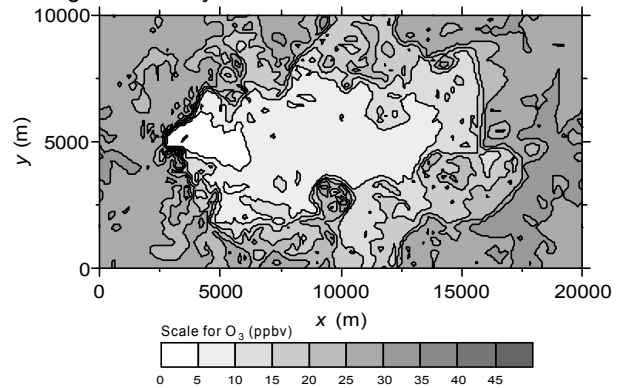


Figure 1. Surface (0 m AGL) ozone mixing ratio from the end (15:00 LST) of the high-NO/low-ETH source simulation.

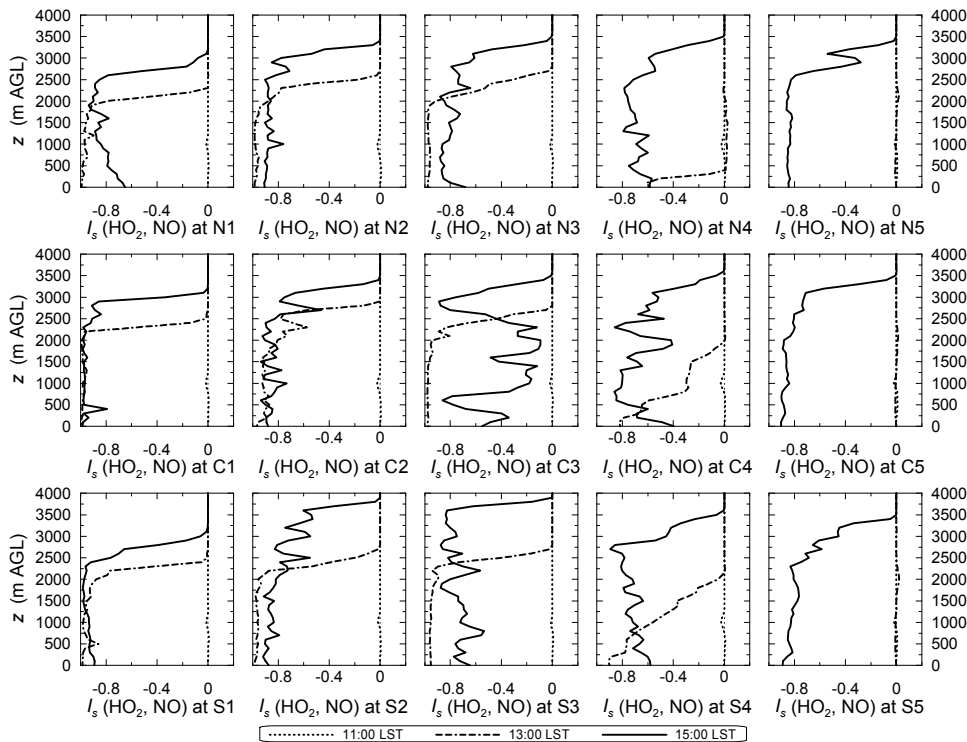


Figure 2. Horizontally-averaged (in $4 \text{ km} \times 4 \text{ km}$ sections) intensity of segregation profiles for the reactant pair HO_2 , NO at two-hour intervals from the high-NO/low-ETH source simulation.

No figures from this simulation are presented here, but growth of the CBL is clearly evident in most of the trace gas mean mixing ratio profiles. Surface ozone, 25 ppbv at 11:00 LST, decreases to 23 ppbv by 15:00 LST due to continued maturing of the chemistry, dry deposition, and a lack of strong NO_x ($\text{NO} + \text{NO}_2$) and VOC sources. Intensity of segregation values for most reactant pairs were negative and small, with not many less than -0.2, and usually close to 0 within the CBL.

3.2 High-NO/Low-Ethene Point Source

This first idealized 4-h plume simulation included a point source of NO and ETH co-emitting at typical emission inventory rates and representative of an industrial flare stack with efficient combustion. Located at $(x, y, z) = (2.8 \text{ km}, 4.8 \text{ km}, 350 \text{ m AGL})$, the stack emitted NO ($E_{\text{NO}} = 14 \text{ kmol h}^{-1}$) and ETH ($E_{\text{ETH}} = 0.01 \cdot E_{\text{NO}}$) continuously from 11:00-15:00 LST. In the LESchem model, the stack emissions came from a single $200 \text{ m} \times 200 \text{ m} \times 100 \text{ m}$ elevated grid cell volume, with E_{NO} translating to about 5.9×10^{11} molecules $\text{cm}^{-3} \text{ s}^{-1}$, for example. Background emissions were the same as for the control case.

Stack emissions started at 11:00 LST. Thus, with a 1 m s^{-1} mean westerly wind, the average leading edge of the plume should be near $x = 10 \text{ km}$ by 13:00 LST and near $x = 17.2 \text{ km}$ by simulation end at 15:00 LST. Figure 1 shows the final surface level O_3 distribution. Because of the weak mean wind, convection is the dominant dynamical process and the plume often fumigates to the ground. The high-NO/low-ETH stack emissions have significantly reduced O_3 near the source due to titration by NO. This O_3 reduction was prevalent downwind throughout the CBL depth wherever the plume was present. At the turbulent edges of the plume, some O_3 production is evident with mixing ratios above 30 ppbv. In general, this VOC-limited plume has an impact similar to that of a power plant plume, where the eventual O_3 production would occur beyond the extent of the current domain.

Plume scenarios are heterogeneous by nature. Thus, an analysis method was devised whereby the $20 \text{ km} \times 10 \text{ km}$ domain was divided into 15 $4 \text{ km} \times 4 \text{ km}$ squares for discrete horizontal averaging of chosen quantities. Also, 4 km happens to be the typical fine resolution grid spacing for regional air quality models, so averaging LESchem results over $(4 \text{ km})^2$ areas allows direct comparison to single point values from a typical regional scale model. The 15 averaging squares were labeled by south-north location (S for southern tier, C for central, N for northern tier) and numbered 1-5 from west to east. There is no overlap between averaging squares in the west-east sense, but the C tier overlaps both the S and N tiers by 1 km each due to the 10 km south-north extent of the domain.

Intensity of segregation profiles for the HO_2 , NO reactant pair are shown in Figure 2 for each of the averaging squares. Both the growth of the CBL and the downwind extent of the plume can be seen. With I_s (HO_2 , NO) values approaching -1, HO_2 and NO are highly segregated from one another, thereby significantly reducing the average rate at which the

$\text{HO}_2 + \text{NO}$ reaction occurs. Several other reactant pairs from this high-NO/low-ETH plume simulation showed similar strongly negative I_s values.

3.3 High-NO/High-Ethene Point Source

To represent an industrial flare stack with inefficient combustion, the second idealized plume scenario specified a slightly greater NO emission and a much greater ETH emission. This high-NO/high-ETH point source was at the same location, but the NO and ETH emissions were $E_{\text{NO}} = 15 \text{ kmol h}^{-1}$ and $E_{\text{ETH}} = 3.6 \cdot E_{\text{NO}}$.

The sizable co-emission of NO and ETH from the point source produced copious amounts of O_3 as seen

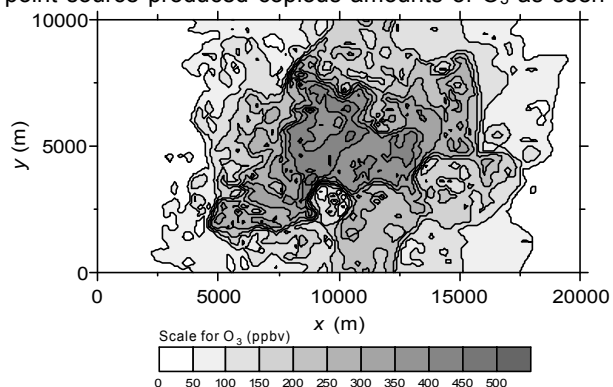


Figure 3. Surface (0 m AGL) ozone mixing ratio from the end (15:00 LST) of the high-NO/high-ETH source simulation.

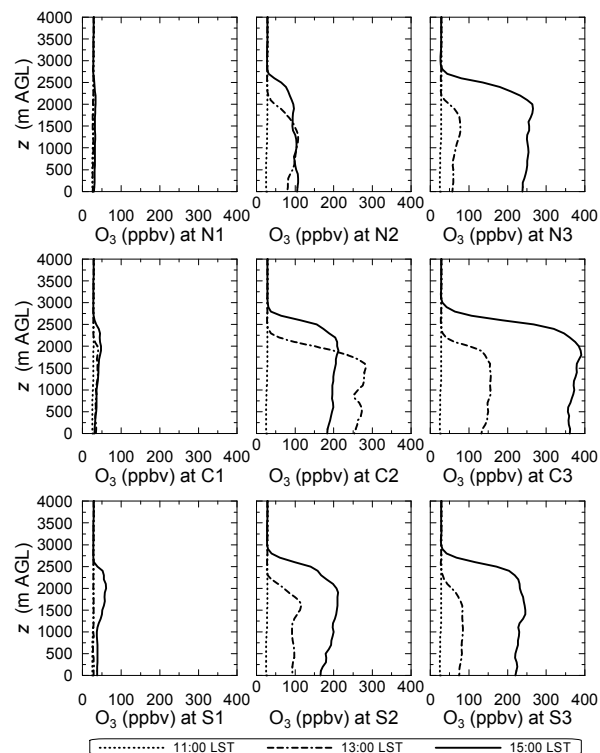


Figure 4. Horizontally-averaged (in $4 \text{ km} \times 4 \text{ km}$ sections) mean ozone mixing ratio profiles at two-hour intervals from the high-NO/high-ETH source simulation.

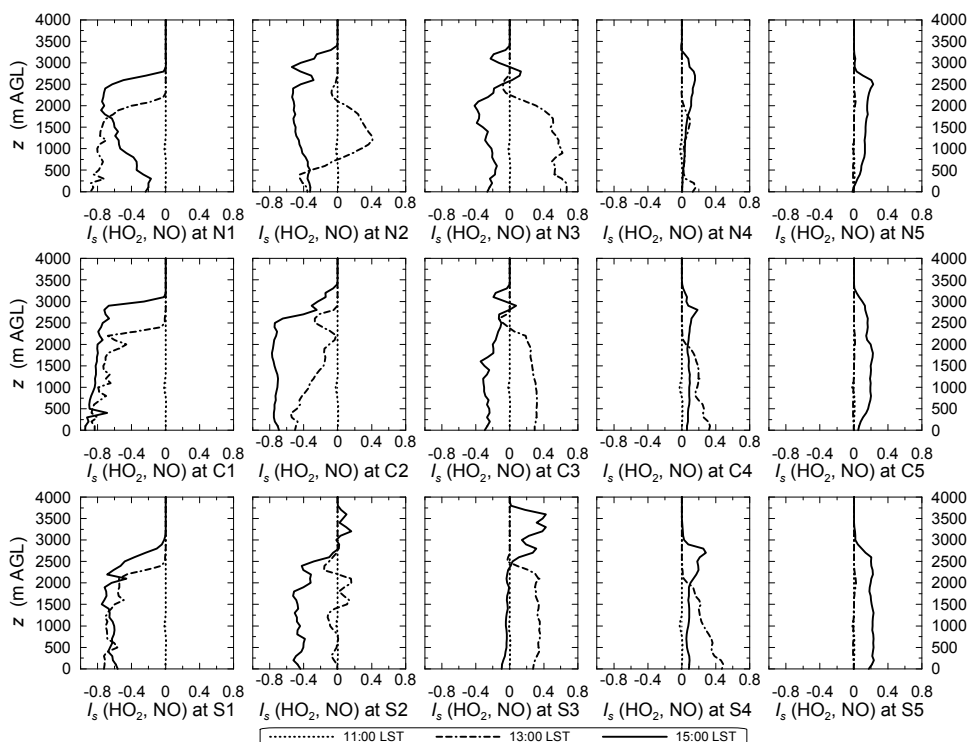


Figure 5. Horizontally-averaged (in 4 km \times 4 km sections) intensity of segregation profiles for the reactant pair HO₂, NO at two-hour intervals from the high-NO/high-ETH source simulation.

in Figure 3. Pockets of high O₃ concentration, which form rapidly and can occur at any altitude within the CBL, can be seen near the source. The vertical distribution of O₃ is represented in the mean O₃ mixing ratio profiles of Figure 4, computed from horizontal averages over near-source (4 km)² squares.

Figure 5 shows the I_s (HO₂, NO) values from the high-NO/high-ETH simulation. Quite different from the high-NO/low-ETH case, positive I_s values occur downwind of the point source. In fact, a few I_s values for reactant pairs important in determining O₃ loading show positive correlations near the source, indicating an increase in average reaction rates for many reactions.

4. CONCLUSIONS

These preliminary idealized plume experiments have not been rigorously checked for chemical consistency or compared against observations, but the results are consistent with the original hypothesis that coherent turbulent structures in plumes from co-emissions of NO and VOC can lead to rapid patchy ozone formation, usually within a few kilometers of the source. Simulations such as these could provide improvements to the reaction rate coefficients currently used in traditional models.

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