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 (O$_3$) monitors have revealed rapid O$_3$ formation and sharp "spikes" in measured O$_3$ concentrations. These extreme O$_3$ 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

$$ k \bar{A} \bar{B} = k (\bar{A} \bar{B} + \bar{A}' \bar{B}') $$

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 $\bar{A}' \bar{B}'$ 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

$$ k \bar{A} \bar{B} = k (1 + I_s) \bar{A} \bar{B} $$

where

$$ I_s = \frac{\bar{A}' \bar{B}'}{\bar{A} \bar{B}}. $$

The intensity of segregation $I_s$ denotes the importance of the concentration covariance term $\bar{A}' \bar{B}'$ relative to the mean chemistry term $\bar{A} \bar{B}$. 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 $\times$ 10 km $\times$ 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 km × 10 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 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 307-480 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 cm\(^{-2}\) s\(^{-1}\) and \(F_{\text{ISOP}} = 5.2 \times 10^{11}\) molecules cm\(^{-2}\) s\(^{-1}\); 2) anthropogenic fluxes of \(F_{\text{NO}} = 1.6 \times 10^{10}\) molecules cm\(^{-2}\) s\(^{-1}\), \(F_{\text{CO}} = 10 F_{\text{NO}}\), and \(F_{\text{ETH}} = 0.08 F_{\text{NO}}\). Representative dry deposition velocities were specified for O\(_2\), NO, NO\(_2\), HNO\(_3\), H\(_2\)O\(_2\), FORM, ALD2, and PAN. Subsequent plume simulations used these background trace gas boundary conditions.

![Figure 1](image1.png)

**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](image2.png)

**Figure 2.** Horizontally-averaged (in 4 km × 4 km sections) intensity of segregation profiles for the reactant pair H\(_2\)O\(_2\), 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 NOx (NO + NOy) 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 industrial flare stack with efficient combustion. Located at (x, y, z) = (2.8 km, 4.8 km, 350 m AGL), the stack emitted NO \( (E_{NO} = 14 \text{ kmol h}^{-1}) \) and ETH \( (E_{ETH} = 0.01 E_{NO}) \) 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 \( 5.9 \times 10^{11} \) molecules cm\(^{-3}\) 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 downward 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, \( 4 \text{ km} \) 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 \( I_x \) \( (HO_2, NO) \) values approaching -1, \( HO_2 \) and NO are highly segregated from one another, thereby significantly reducing the average rate at which the \( HO_2 \) + NO reaction occurs. Several other reactant pairs from this high-NO/low-ETH plume simulation showed similar strongly negative \( I_x \) 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 \( E_{NO} = 15 \text{ kmol h}^{-1} \) and \( E_{ETH} = 3.6 E_{NO} \).

The sizable co-emission of NO and ETH from the point source produced copious amounts of \( O_3 \) as seen...
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 \( I_s (\text{HO}, \text{NO}) \) 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.

Acknowledgments: This research was supported by the NOAA/ARL/Atmospheric Turbulence and Diffusion Division and a cooperative agreement with the University of Alabama in Huntsville. Thanks to Michael Trainer of NOAA's Aeronomy Laboratory for providing emission rates and plots of airborne observations.

5. REFERENCES


