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Evaluation of Ozone Production Efficiency in an Urban Plume Using a Lagrangian Box Model

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SOS 1999 FIELD CAMPAIGN

1. INTRODUCTION

A practical motivation behind many air quality field campaigns has been to elucidate the relation between volatile organic compounds (VOCs), nitrogen oxides ($NO_x = NO + NO_2$) and ozone (O_3). Part of the developing knowledge of various processes relating these species includes estimates from field observations of the ozone production efficiency (OPE) from the NO_x/VOC photochemistry and the associated NO_x loss rate in a complex urban plume. In this study, we consider observational and modeling techniques to evaluate OPE, making use of aircraft and ground measurements of O_3, VOCs, NO_x and NO_z taken in the Nashville urban plume on the afternoon of June 22, 1999 as part of the 1999 Southern Oxidant Study field campaign in Nashville, Tennessee.

2. OZONE PRODUCTION EFFICIENCY (OPE)

The OPE is defined as the number of O_3 molecules produced by a molecule of NO_x before it is lost from the $NO_x - O_3$ cycle due to oxidation and dry deposition.

LAGRANGIAN OPE

To quantify the efficiency of O_3 production in a parcel of air as it travels downwind, one must evaluate the "**Lagrangian OPE**," which can be viewed from two perspectives – *instantaneous* and *cumulative*.

$$Instantaneous\ Lagrangian\ OPE = \frac{(d[O_3(t)]/dt)_{\text{chem+dry dep}}}{-(d[NO_x(t)]/dt)_{\text{chem+dry dep}}} \quad (1)$$

$$Cumulative\ Lagrangian\ OPE = \frac{\Delta[O_3(t)]_{\text{chem+dry dep}}}{-\Delta[NO_x(t)]_{\text{chem+dry dep}}} \quad (2)$$

Furthermore, it is also useful to know the "**Chemical OPE**." The instantaneous and cumulative chemical OPEs are defined in the same way as their Lagrangian counterparts, but exclude the dry deposition term

3. LAGRANGIAN BOX MODEL

We use a 0-dimensional Lagrangian Box Model that includes photochemical reactions, dry deposition, and allows for horizontal dilution in a fully developed boundary layer:

$$\frac{dC_i}{dt} = R_i - \lambda(C_i - C_{i,b}) + \frac{E_i}{H(t)} - \frac{v_{d,i}}{H(t)}C_i \quad \text{for } \frac{dH}{dt} \le 0 \quad (3)$$

C_i = concentration of species i (molec cm^{-3})
$C_{i,b}$ = background concentration of species i (molec cm^{-3})
R_i = net rate of chemical reaction of species i (molec cm^{-3} s^{-1})
E_i = emission rate of species i (molec cm^{-2} s^{-1})
$v_{d,i}$ = dry deposition velocity of species i (cm s^{-1})
$H(t)$ = height of mixed layer at any time t (cm)
λ = dilution rate (s^{-1})

The dilution rate can be estimated from plume cross-section area (A) broadening as a function of time:

$$\lambda = \frac{1}{A}\frac{dA}{dt} = \frac{d\ln A}{dt} = \frac{\Delta \ln A}{\Delta t} = \frac{\Delta \ln(W \times H)}{\Delta t} \quad (4)$$

where W and H are the plume width and height, respectively.

4. EPISODE OF JUNE 22, 1999

METEOROLOGY

The weather on June 22 was characterized by light southeasterly flow at 850 mb with high dew-points and sparsely scattered cumulus throughout the region. Figure 1 shows the evolution of wind and boundary layer height from the radar wind profiler at Cornelia Fort Airpark (CFA)

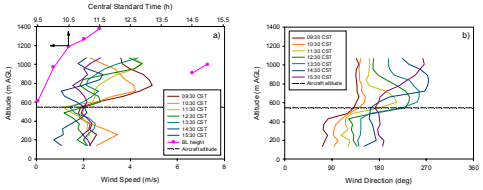

Figure 1: Evolution of the boundary layer height and wind speed and direction in the Nashville area on June 22, 1999 (W. Angevine, personal communication).

NASHVILLE URBAN PLUME: G1 AIRCRAFT MEASUREMENTS

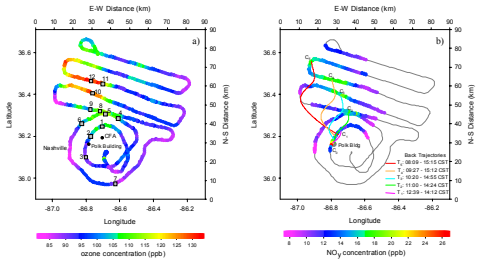

Figure 2: a) G-1 aircraft measurements of O_3 along the flight path. Numbered squares indicate locations where VOC canister samples were collected; **b)** NO_y measurements along the flight path. Lines from the plume centerline points (C_0 - C_5) are back-trajectories of air parcels that passed over the downtown area (calculated using the wind profiler data at CFA shown in Figure 1).

DOWNTOWN NASHVILLE: POLK BUILDING MEASUREMENTS

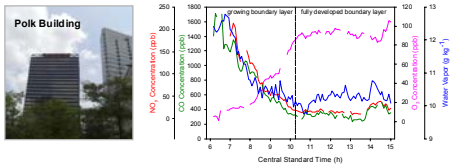

Figure 3: Evolution of O_3, NO_y, CO and H_2O observed atop the Polk Building in downtown Nashville (K. Olszyna, personal communication). Note that concentrations of all four quantities underwent rapid changes in the growing boundary layer until ~10:15 CST when it was fully developed. Relatively uniform profiles thereafter indicates that these and presumably other species were well mixed in the boundary layer.

5. MODEL INITIALIZATION & INPUTS (T_3 TRAJECTORY)

INITIAL & BACKGROUND CONCENTRATIONS

O_3, NO_x, NO_y, CO, H_2O_2 and VOC concentrations measured at **Polk Building** around **10:20 CST** were used as initial concentrations for the **T_3 trajectory** shown in Figure 2b. Background concentrations were obtained from G-1 measurements outside the plume.

EMISSIONS & PHOTOLYSIS FREQUENCIES

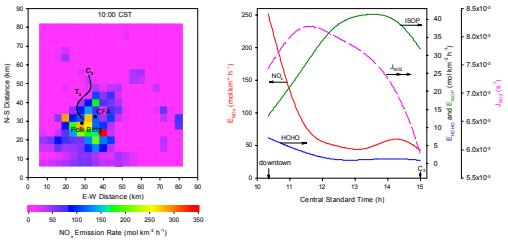

Figure 4: a) Example of NO_x Emissions inventory from SMOKE processor at 10:00 CST at 4-km resolution along with the back trajectory T_3; **b)** Examples of NO_2, HCHO, and ISOP emission rates along T_3 and smoothed clear-sky photolysis rate coefficient for NO_2 as a function of time.

PHOTOCHEMICAL MECHANISM

The gas chemistry is modeled with the photochemical mechanism CBM-Z (Zaveri and Peters, 1999), which is based on the widely used CBM-IV. CBM-Z contains 53 species and 133 reactions, and includes revised inorganic chemistry and organic chemistry.

DILUTION RATE

Assuming that the plume remained confined within the mixed layer of constant height, the dilution rate Equation (4) reduces to

$$\lambda = \frac{\ln(W_f / W_i)}{\Delta t} \quad (5)$$

where W_f and W_i are the final and initial plume widths, respectively, and Δt is the transit time. From Figure (2b) we estimate W_i = 12 km, W_f = 20 km, and Δt = 4.58 h. This gives an average dilution rate of $\boldsymbol{\lambda = 3.1 \times 10^{-5}\ s^{-1}}$.

6. MODEL EVALUATION

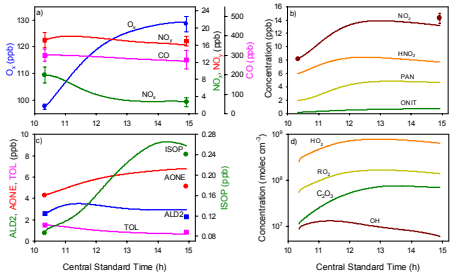

Figure 5: Simulated (lines) and observed (symbols) concentrations of some important trace species along T_3. Observations at the start of the simulation (at 10:20 CST) were made at the Polk Building and those at the end (at ~15:00 CST) were made by the G-1 aircraft. The error bars on some of the observed concentrations represent one standard deviation (σ).

7. MODELED RATES & LAGRANGIAN OPEs

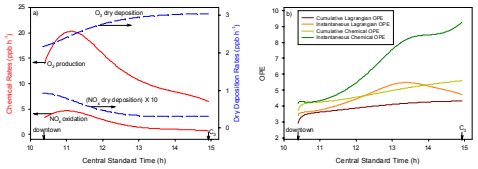

Figure 4: a) Simulated instantaneous chemical and dry deposition rates of O_3 and NO_x along T_3 as a function of time; **b)** Simulated Lagrangian and Chemical OPEs along T_3 as a function of time. The instantaneous quantities vary greatly with the time of day as well as the "photochemical age" of the air parcel.

8. SENSITIVITY STUDY

Sensitivity analysis was performed by scaling the T_3 trajectory (base case) emission rates of NO_x and anthropogenic VOCs by a scaling factor, S_j (where j = NO_x, VOC, or both), ranging from 0.5 to 1.5 (i.e., ±50%). The initial concentrations of NO_x and VOCs were also simultaneously scaled by the same factor on the assumption that they are linearly proportional to their emissions in a well-mixed layer near the source region. The results are summarized in Figure 5.

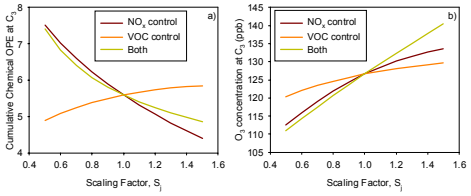

Figure 5: a) Sensitivity of the cumulative chemical OPE at C_3 to variations in NO_x and VOC emissions and initial concentrations as determined by the respective scaling factors; **b)** O_3 concentrations at C_3 as a function of these scaling factors.

9. CONCLUSIONS

1. The model-based instant0aneous O_3 production and NO_x oxidation rates along a selected air mass trajectory were strongly dependent on the time of day (photolysis rates) as well as the photochemical age of the air mass.

2. The associated instantaneous Lagrangian and Chemical OPEs increased rapidly as NO_x concentrations decreased due to oxidation, dilution, and dry deposition. However, the corresponding cumulative OPEs increased relatively slower due to decrease in both the O_3 production and NO_x oxidation rates as the air mass aged.

3. The sensitivity analysis showed that while different OPEs may serve as good indicators of the photochemical O_3 formation potential for a plume, they cannot be used to make decisions on emissions controls. Basing an ozone control policy solely on OPEs is equivalent to expecting that O_3 will respond linearly to a change in NO_x and/or VOC emissions, which is clearly not what happens.

10. ACKNOWLEDGEMENTS

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