6.6 DIURNAL VARIATION OF NMHCs AT A DOWNTOWN SITE IN NASHVILLE: MODEL AND MEASUREMENTS

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1. INTRODUCTION

Diurnal variations in nonmethane hydrocarbon (NMHC) mixing ratios were measured in Nashville during the 1999 Southern Oxidant Study at a location near the top of a downtown highrise, the Polk Building. The diurnal variability in NMHCs at this location can be expected to be a function mainly of the diurnal variability of sources such as automobile emissions and biogenic isoprene emissions. These emissions would lead to an increase in the hydrocarbon mixing ratios during the daytime, with peak mixing concentrations occurring during the early morning and afternoon rush hour traffic patterns. The hydrocarbons that are not oxidized by OH during the daytime and subsequently become trapped in the nocturnal boundary layer can be expected to undergo further oxidation throughout the night by NO_3 and ozone. Because sources of hydrocarbons are limited in the nighttime hours, this depletion of the hydrocarbons would result in a minimum in the mixing ratios of the hydrocarbons in the hours before dawn. The measured diurnal variation of the hydrocarbons does follow this expected pattern. An exception was noted, however, on the night of 5-6 July 1999, when isoprene mixing ratios of up to 8 ppb were measured. The NO_x, NO_y, and CO mixing ratios for the same time period show unusual patterns (Fig. 1). Investigating the sources for this large measured isoprene mixing ratio during the night of 5-6 July and the possible effect this may have had on the following day's ozone mixing ratio is the subject of this research.

We have used a trajectory photochemical model to establish the possibility of regional-scale transport of isoprene into the Nashville urban airshed. Then a full-scale three-dimensional (3-D) model simulation of this region was made by using initially CMAQ (Community Model for Air Quality, Byun and Ching 1999) at a horizontal grid resolution of 30 km and later by a fine mesh simulation at a horizontal grid resolution of 4 km. Results of model calculations are interpreted to evaluate (a) the origins of the air measured atop the Polk Building during this period; (b) isoprene emissions from Biospheric Emission Inventory System version 2.0 (BEIS2) with a modified algorithm developed at Argonne, as compared with the measured ambient mixing ratios of isoprene; and (c) the contribution of isoprene to the elevated ozone concentrations observed during the episode.

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2. TRAJECTORY MODEL CALCULATIONS

In the trajectory model, a 0-D photochemical model is moved along a trajectory described either from a forecast meteorology model for the region or from interpolated wind, temperature, and dew point fields from the 4-D data assimilation analysis provided by NCEP (National Center for Environmental Prediction). Additional constraints include column ozone from Total Ozone Monitoring Spectrometer (TOMS) along the trajectory path for radiative flux calculations. The photochemical model has 79 species, 214 thermal reactions, and 32 photolysis rates. The model has full representation of inorganic gas-phase chemistry according to DeMore et al. (1997 and later revisions). The model is capable of treating heterogeneous chemistry and includes N_2O_5 hydrolysis reactions on ammonium bisulfate particles. The NMHC hydrocarbon chemistry follows the RACM (Regional Atmospheric Chemistry Mechanism) of Stockwell et al. (1997). The photolysis rates are calculated by using a two-stream radiative transfer model, with 128 bins for calculating absorption cross sections ranging from 170 nm to 450 nm. The chemical integrator uses the Gear method. For this calculation, back trajectories were obtained from the HYSPLIT model (Draxler and Hess 1997). These trajectories show that the origin of the air was to the south, in the high-isoprene source regions located in Alabama (BEIS2 estimates) for the night of 5 July and the early morning hours of 6 July.

A series of trajectory photochemical calculations was performed for one day starting at 16:00 hr local time on 5 July and ending at 16:00 hr local time on the 6 July. The calculations were designed to test the sensitivity of the plume to initial conditions (Fig. 2). These chemical trajectory modeling calculations suggest that the measured isoprene values are attainable if the air parcel trajectories have low NO_x

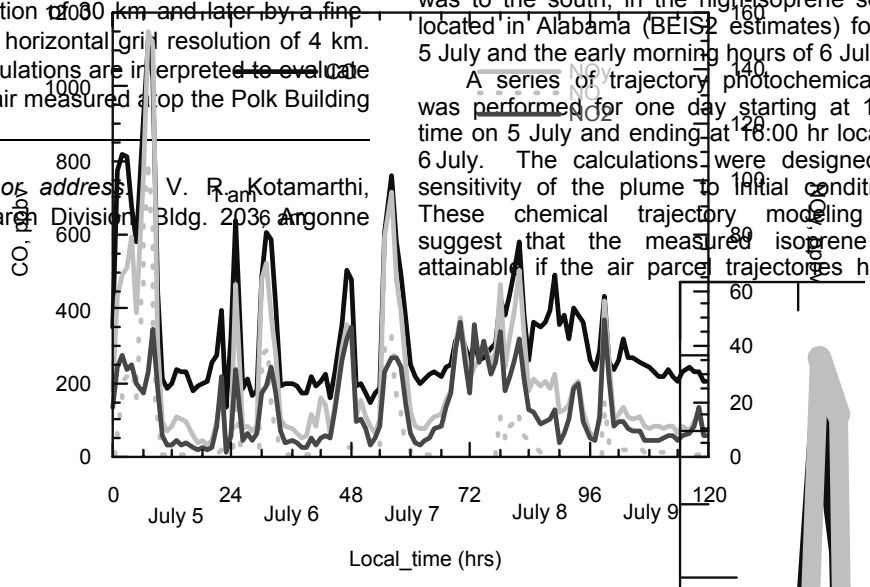

Fig. 1. Measurements of CO, NO_y, NO, and NO_2 made in 1999 at the top of the Polk Building in downtown Nashville.

Fig. 2. Sensitivity of isoprene concentrations calculated with the trajectory photochemical model to initial conditions of NO_x and ozone in the trajectory.

levels (2 ppb or less) and moderate ozone levels (~40 ppb). In contrast high ozone (> 80 ppb) and high NO_x (~10 ppb) in the air parcel originating from a isoprene source region several hundred kilometers away from the urban center will produce less than a few hundred ppt of isoprene near the Polk Building during the early morning hours.

3. 3-D MODEL CALCULATIONS

To evaluate this case in further detail, we followed the trajectory photochemical calculation with a full 3-D simulation with the CMAQ model. The source emissions for the model were generated by using the SMOKE (Sparse Matrix Operator Kernel Emission) model,

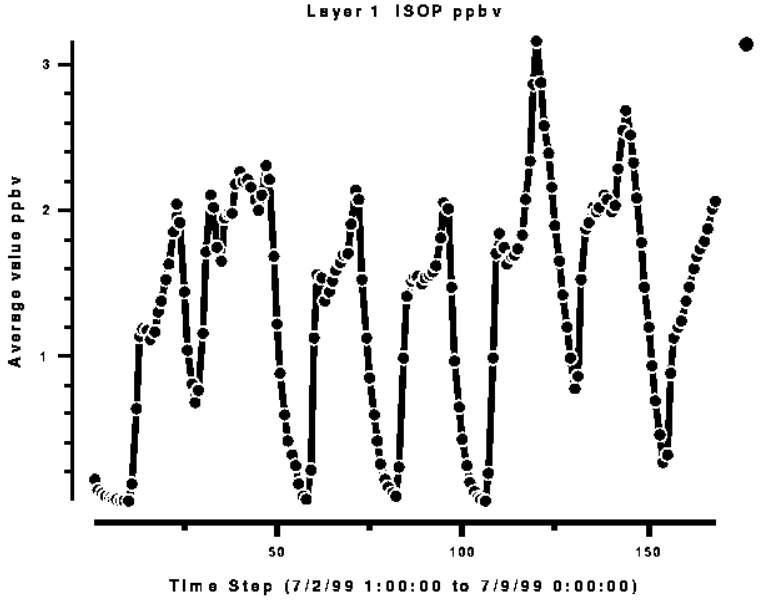

Fig. 3. Isoprene time series generated for the surface grid box over Nashville from a CMAQ simulation with a horizontal grid resolution of 30 km.

obtained from the North Carolina Supercomputing Center (http://envpro.ncsc.org/products/smoke), for the first 10 days of July 1999. The initial calculations employed a horizontal grid resolution of 30 km. The meteorology for the model simulations was generated by using Mesoscale Modeling System 5 (MM5) version 3 driven at the boundaries with the NCEP 4-D reanalysis data set for this period.

The model results for isoprene extracted from the CMAQ results for the Nashville region for the first week of July 1999 are shown in Fig. 3. The model results follow the expected patterns with low mixing ratios of isoprene during the nighttime and peak values at approximately 16:00 hr. However on two nights the isoprene stayed above 1 ppb in this simulation. The highest isoprene at nighttime in this simulation is only 1 ppb, compared to 6-8 ppb measured atop the Polk Building during the night of 5 July and the early morning hours of 6 July. We are now attempting to refine these calculations further using a finer resolution CMAQ run (4 km horizontal resolution) and an estimate of biomass emissions obtained with new parameterizations being developed at Argonne and using the BEIS2. Results from this calculation will be presented, along with a more detailed comparison of model calculations and measurements of a number of NMHCs, NO_x, NO_y, CO and O_3.

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