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Coupling the Vertical Distribution of Ozone in the Atmospheric Boundary Layer

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Vertical measurements of ozone were made on a 610 m tall tower located about 15 km southeast of Raleigh, NC, as part of an effort by the State of North Carolina to develop a State Implementation Plan (SIP) for ozone control in the Raleigh Metropolitan Statistical Area and other metropolitan areas in the state. Ozone was monitored at 10, 250, and 433 m height levels during the summer months of 1993−1995 and at 10, 76, 128, and 433 m height levels during the summer months of 1996−1997. A regional atmospheric chemistry/transport model, called Multiscale Air Quality Simulation Platform (MAQSIP), was also employed to simulate three-dimensional O_3 distribution over the eastern United States for a 2-month period (June 1−July 31, 1995). Through complementary analyses of the 5-year data and the modeling results, this paper examines the vertical distribution of ozone concentrations in the atmospheric boundary layer with the emphasis on the contribution of residual ozone aloft to the ground level ozone enhancement during the daytimes. Both the observation and the model results show a strong correlation between the nighttime and early morning ozone concentrations ($\bar{C}_R$) in the residual layer above the nocturnal boundary layer (NBL) and the maximum ground level concentration ($\bar{C}_{omax}$) the following afternoon. On the basis of this correlation, an observational model for maximum ozone $\bar{C}_{omax} = 27.67 \exp(0.016\bar{C}_R)$ is proposed, where concentrations are expressed in parts per billion by volume (ppbv). Model results indicate, however, that both the coefficient representing the regional background ozone concentration and the exponent in the above relationship may vary considerably over the eastern United States.

Introduction

Knowledge of the vertical distribution of ozone in the planetary boundary layer (PBL) is essential in developing effective abatement strategies for ozone control. Vertical measurements of ozone in and above the surface inversion layer are also required as inputs to three-dimensional atmospheric chemistry transport models. The distribution of ozone in the boundary layer is influenced by localized production zones, the dynamical and photochemical processes in the troposphere over the region (*1*−*3*), and the vertical downward transport of ozone from the stratosphere (*4*). The irregular features in the ozone production are caused by the variation in solar ultraviolet radiation flux caused by absorption and scattering by clouds, redistribution of precursor chemicals emitted by localized sources, efficiency of ozone production (*5*), and transport processes in the PBL (*4*). Measurement of spatial and temporal variations of ozone concentration, transport winds, temperatures, and other meteorological variables in the PBL can be used to study these processes. The summer afternoon periods that are most conducive to ozone production are also periods of intense convective mixing in the boundary layer. Precursor chemicals are drawn into turbulent eddies from localized sources, horizontally advected from sources located in upwind region, or mixed down from the residual layer or free atmosphere into the boundary layer by entrainment and diffusion processes. The irregular nature of the summer afternoon ozone distribution can be observed in vertical profiles and time sequences of ozone measurements (*6*). During the nighttime, the stable nocturnal boundary layer may exhibit quite different ozone profiles in the absence of local production and dry deposition at the surface.

In general, the surface ozone exhibits strong diurnal variation with a mid-afternoon maximum and an early morning minimum (*7, 8*). Concentrations in daytime are much larger than those at nighttime (see, for example, Figure 1). At nighttime, the presence of temperature inversion isolates the surface level ozone from that of upper levels, as there is little or no vertical mixing between the surface layer and levels above the nocturnal boundary layer (NBL). Surface ozone is partly removed by deposition and reaction with nitric oxide (NO). Since no ozone is produced in the absence of sunlight at night, ozone concentrations begin to decrease after sunset, reaching minimum in early morning before sunrise.

After sunrise, the height of the unstable boundary layer begins to increase as the surface is heated and the nocturnal inversion is destroyed. This results in downward mixing of ozone from aloft (*9*). Surface ozone is also locally generated by reactions of nitrogen oxides with volatile organic compounds (VOCs) in the presence of sunlight (*4, 10, 11*). Consequently, ozone concentrations increase rapidly from early morning to about noon. By noon, the mixing height typically exceeds 1000 m and ozone is well mixed within the mixing layer. Strong photochemical production and strong convection in the mid-afternoon period cause ozone concentrations to reach peak values in the late afternoon. Thereafter, ozone production decreases with diminishing intensity of sunlight, resulting in a decrease of concentrations with time. At the time of sunset, concentrations decrease substantially below the afternoon maximum value. As a new NBL begins to form in the evening, ozone concentrations near the surface continue to fall due to surface deposition and reaction with NO.

Although the above diurnal pattern in the surface layer is obvious, it becomes less pronounced with increasing height and almost becomes insignificant above the level of surface inversion at night. Balloon observations (*12, 13*) have shown that the ozone above the surface-based inversion is effectively

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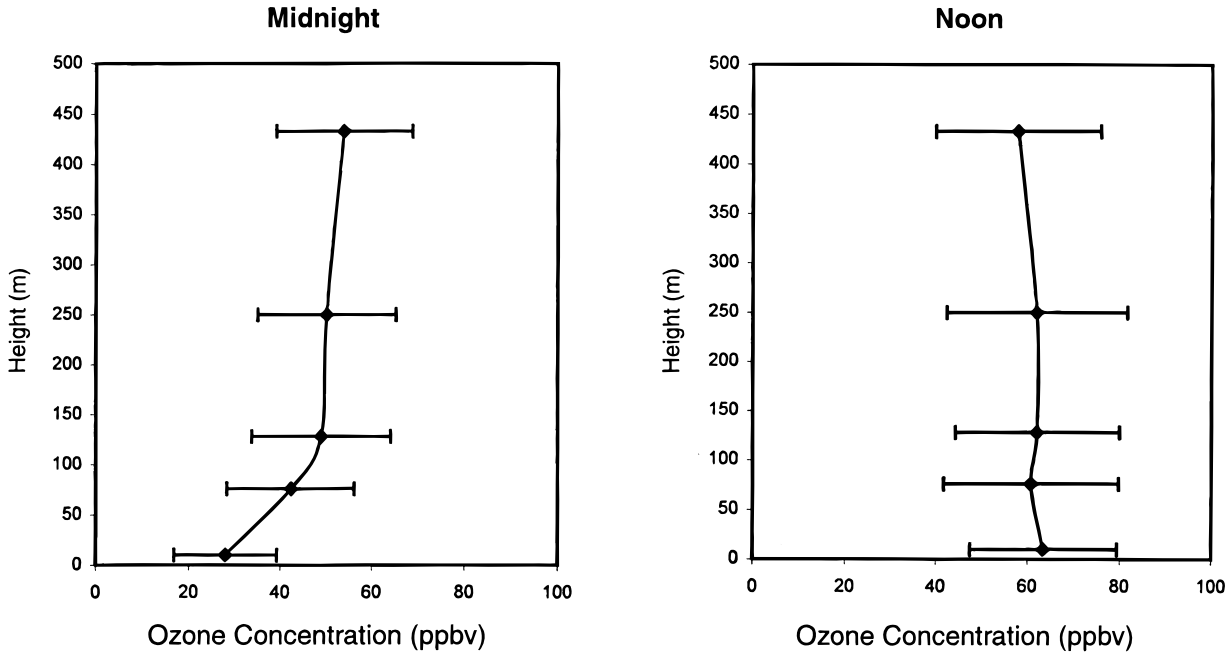

FIGURE 1. Mean ozone vertical profiles at 1200 (noon) and 0000 (midnight) EST during the summers of 1993−1997. The horizontal bars are ±1 SD.

cut off from all sinks while below the inversion it is removed by dry deposition. Investigations of high elevation ozone (*14*−*16*) have shown a reversed diurnal pattern of ozone at these high elevations that lie above the shallow NBL. Ozone at elevated levels above the NBL may not be influenced by surface deposition, so ozone levels at these elevations remain relatively high during nighttime. Fehsenfeld et al. (*17*) have found that the mid-morning ozone concentrations at high elevations in the Colorado mountains were typical of upper-air values. Harrison and Holman (*18*) suggested that these values were indicative of those arising from regional transport of ozone. Ozone in the residual layer representing the previous day's value may be comprised mainly of two parts: regional transport of ozone and local photochemical generation. Previous observations and model calculations (*19*) have indicated that local photochemical production of ozone was a very small part of the ozone increase in early morning. So it may be hypothesized that downward mixing of ozone from the residual layer is mainly indicative of the regional transport. Even under stagnant conditions at night near the surface, ozone can be transported by the nocturnal jet aloft.

Maximum ozone concentration at the surface is one of the most desired air pollution indices. Prediction of the same is of great importance to both public health and air quality. As discussed above, residual layer ozone may be indicative of the regional transport of ozone and/or its precursors that make significant contribution to the surface level ozone concentration. Here we have attempted to develop an empirical relationship to elucidate the effects of the previous night's ozone in the residual layer on the subsequent day's surface level ozone, based on the strong correlation between the two found from several years of monitoring data.

Experimental Procedures

Vertical measurements of ozone were made on a 610 m tall tower located at Auburn, NC, about 15 km southeast of Raleigh, NC (latitude 35°40′35″ N; longitude 78° 32′ 09″ W), as part of an effort by the State of North Carolina to develop a State Implementation Plan (SIP) for ozone control in the Raleigh Metropolitan Statistical Area (MSA) and other MSAs in North Carolina, as recommended by the Governor and approved by the U.S. EPA. During the summers of 1993−1995, ozone was monitored at ground level, 250. and 433 m. Boundary layer winds, temperatures, and other meteorological variable profiles were measured from balloon soundings at the tower site. During the summer months of 1996−1997, ozone was monitored at ground level, 76, 128, and 433 m. Ozone was measured using the ultraviolet photometric detection principle. A Dasibi model 1003 AH analyzer was used for each level. The instrument is designated by the U.S. EPA as an "equivalent method". The analyzers were multipoint calibrated daily. Note that the 433 m level falls frequently in the residual layer, sometimes near the nocturnal jet at night, and within the mixed layer of the afternoon convective boundary layer.

Results and Discussion

Here we present an analysis and discussion of the 5-year ozone data, examine the vertical distributions of ozone in PBL, and discuss correlations between concentrations at the ground and elevated levels. Figure 1 shows the vertical profiles of mean ozone concentration in the lower 433 m layer of the atmosphere, based on the 1993−1997 data set. These show the typical inverted profile at nighttime caused by dry deposition to the surface and reaction with NO and the typical daytime profile reflecting the important roles of both the local production and greater convective mixing in the vertical. Similar variability of ozone concentrations, indicated by bars representing ±1 SD, near the surface and at other levels aloft is due to the efficient mixing in the vertical during the daytime convective boundary layer.

Figure 2 shows a good correlation ($R = 0.64$) between the maximum ozone concentration at the ground between 10:00 AM and 4:00 PM and the average ozone concentration in the residual layer between midnight and 6:00 AM. On the basis of the 5-year (1993−1997) data set, the maximum ozone in surface layer $\bar{C}_{\mathrm{omax}}$ can be related to the previous night's average ozone concentration in the residual layer $\bar{C}_{\mathrm{R}}$ by an exponential empirical regression equation:

$$\bar{C}_{\mathrm{omax}} = 27.67 \exp^{0.016\bar{C}_{\mathrm{R}}} \qquad (1)$$

where ozone concentrations are in ppbv, and the intercept

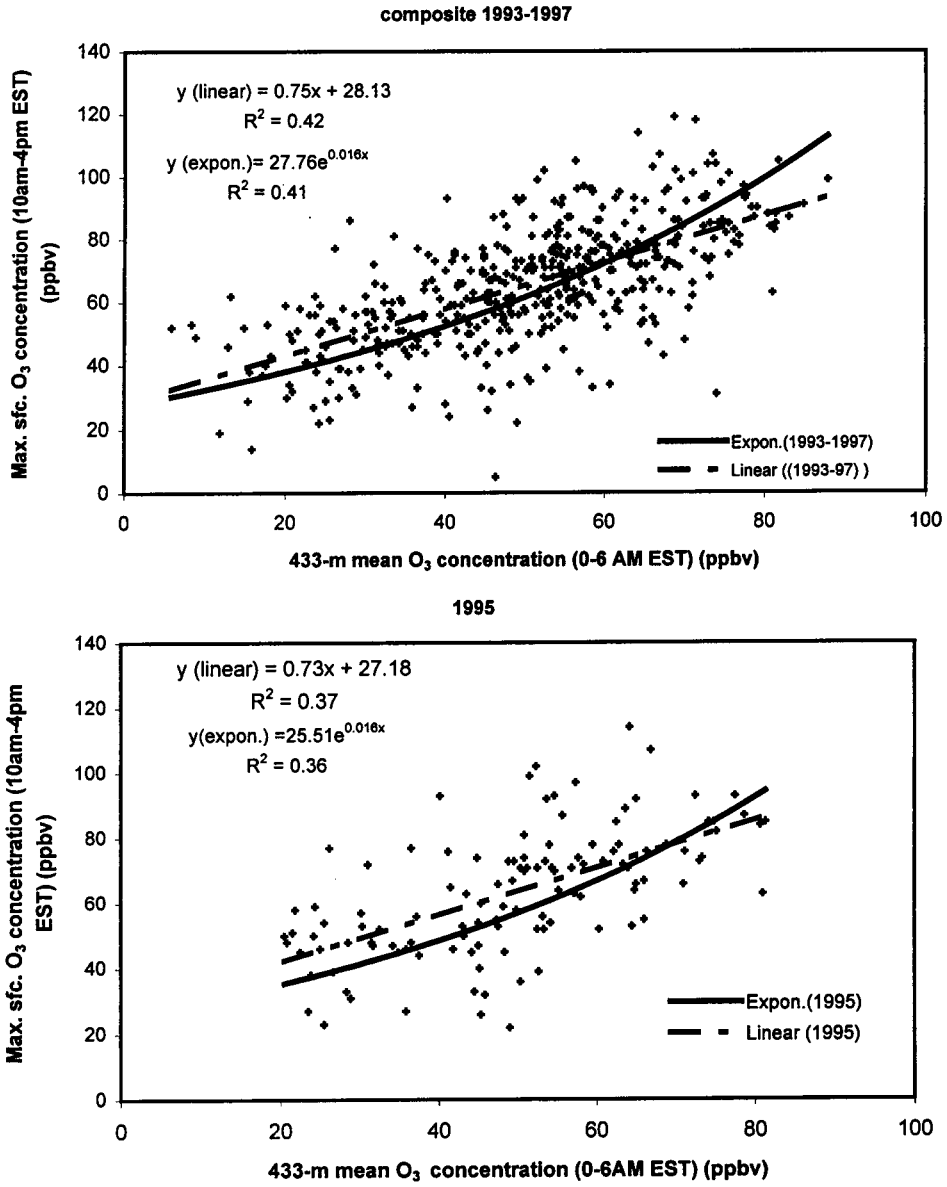

FIGURE 2. Correlation between maximum surface ozone (ppbv) and ozone concentration (ppbv) in the residual layer, based on 5 years (1993−1997) of observed data at Auburn, NC.

(27.67 ppbv) represents the nominal local background O_3 concentration in air not directly influenced by regional/long-range transport of ozone and/or its precursors. This is very similar to the ozone background at site SONIA (~27 ppbv) in Candor, NC, located in the central Piedmont region of North Carolina (*20*). The magnitude of the exponent (0.016) is the index of contribution of the residual ozone aloft from the previous night to the next day's maximum surface ozone and can be regarded as an indicator of the effects of regional transport of ozone and/or its precursors to the ground level ozone concentration. The greater its value is, the more contribution the regional transport makes to the surface ozone concentration. This value may vary from place to place and season to season depending on the meteorological conditions as well as local chemical characteristics. The overall correlation coefficient ($R = 0.64$) based on the 5-year data set is found to be quite consistent with correlation coefficients for the individual years, indicating the robustness of eq 1 as a predictive relationship. As an example, the scatter plot for the 1995 summer is also shown in Figure 2. Also shown in Figure 2 are the linear regression lines through the data that appear to fit as well if not better than the exponential relationship. Our main reason for preferring the latter is that the exponential relationship captures more accurately the observed behavior of surface ozone concentration at the higher concentration range.

Comparison with Model Simulation Results

To further examine the relationship between maximum surface O_3 concentration and that in the residual layer at other geographical locations, model predictions from a regional atmospheric chemistry/transport model, the Multiscale Air Quality Simulation Platform (MAQSIP), were examined. MAQSIP (MCNC) (*21*) is a modular air quality modeling system that has also served as a prototype for the U.S. EPA's Models-3 concept (*22*). The modeling system was configured to include detailed treatment of horizontal and vertical advection, turbulent diffusion based on K-theory, gas-phase chemical transformations using a modified version of the CBM-IV chemical mechanism (*23, 24*), anthropogenic and natural emissions, dry deposition, and mixing and attenuation of photolysis rates due to the presence of clouds. Seasonal simulations of tropospheric O_3 for the summer of 1995 have been recently performed with the modeling system for the eastern United States (*25*).

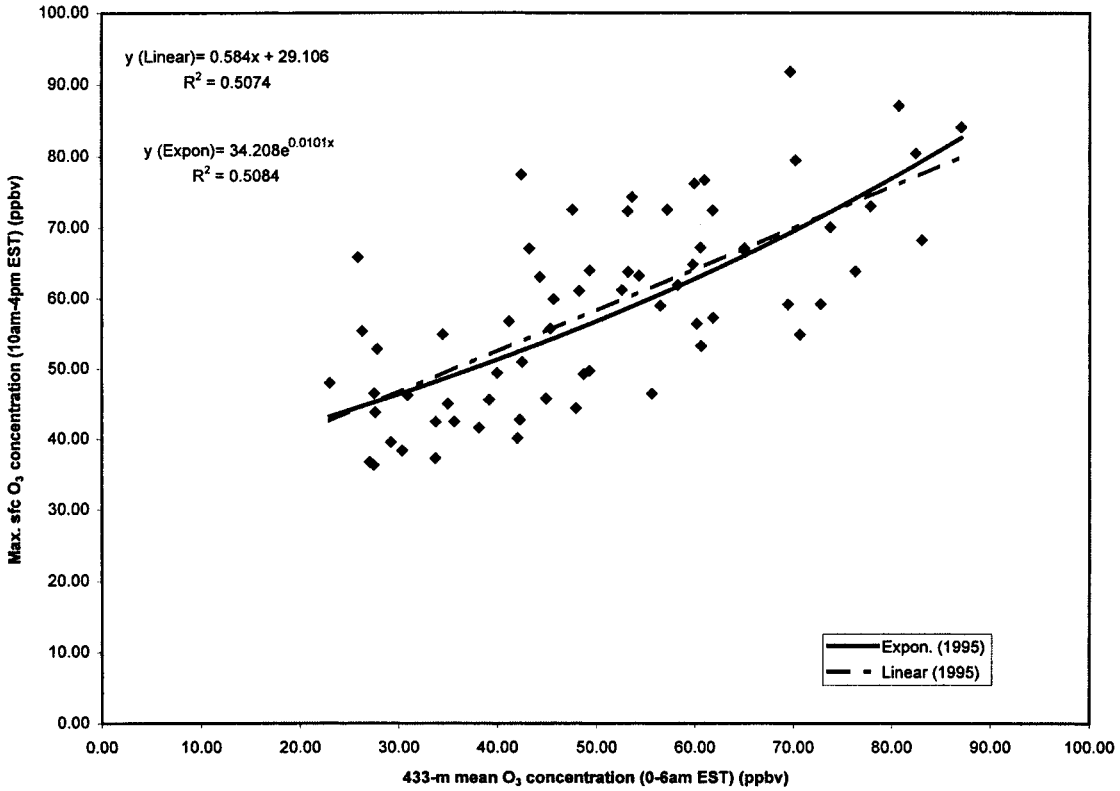

FIGURE 3. Correlation between maximum surface ozone (ppbv) and ozone concentration (ppbv) in the residual layer for the summer (June and July) of 1995 using model results at Auburn, NC.

In the present study, model predictions for a 2-month period (June 1−July 31, 1995) were analyzed to further investigate the relationship between maximum surface O_3 concentration and that in the residual layer from the previous day and to compare it with that obtained from observations. Figure 3 shows the scatter plot of model-predicted concentration for the grid cell in which the observation site is located. Compared to the observed relationship, the model shows a relatively higher background value; this is consistent with the model initial and boundary conditions for O_3 mixing ratio that were specified at 35 ppbv. It may be noted that both the observed and the modeled ozone background values are consistent with values observed over the eastern United States (*26*). Also, it is noted that the magnitude of the exponent (0.010) is lower than that in the observed relationship (0.016). Examination of this value for other locations shows significant spatial variation and suggests that, while the surface concentrations are influenced by those in the residual layer through the diurnal evolution of the boundary layer, the relative contribution to surface enhancements leading to the maximum value is a function of local chemical and physical characteristics. In general, the model calculations suggest that the values of the exponent vary between 0.01 and 0.02 in the continental United States with R^2 in the range of 0.3−0.7 (Figure 4).

On the basis of the observed and modeled correlation analysis, we postulate that the magnitude of the exponent is related to the relative contribution of O_3 in the residual layer to the subsequent day's peak O_3. The strong correlation between maximum surface O_3 concentration and that in the residual layer further suggests the impact of regional transport on O_3 enhancement in the eastern United States. We also note that regions with high inferred background (> 40 ppbv) concentrations have associated with them lower values of the exponent and the correlation coefficient R and, therefore, are the regions where the proposed relationship is the weakest. These regions of enhanced ozone concentrations, relative to the model specified background value, probably correspond to areas with large local production or are in proximity of major sources and their clusters. Regions where the correlation is stronger (in larger exponent and R values) are characterized by lower inferred background values. In such regions, the enhancement, leading to the maximum surface ozone concentration, is probably more influenced by downward mixing of the residual ozone. We may, therefore, surmise that the proposed relationship is stronger in semi-urban and rural regions and weaker in large urban and industrial regions. Exceptions might be the periods of regional pollution episodes during which the regional ozone background may also rise, leading to higher values aloft. These high values can then be entrained to the surface the next day, leading to higher ground level concentration in all areas (rural, suburban, and urban). Thus, in episodic conditions, one might expect strong correlations even with higher background values.

Conclusions

The following conclusions can be drawn from our analyses of the 5 years (summer only) of measured ozone data from a tall tower and simulated concentrations from MAQSIP:

(a) The average vertical concentration profiles for the midnight and noon hours show nearly uniform concentrations above 125 m with slightly higher average value during the daytime. Ozone concentration increases sharply with height in the nocturnal boundary layer, while it slightly decreases with height in the daytime unstable surface layer.

(b) There is a fair to good correlation between the average O_3 concentration $\bar{C}_R$ in the residual layer during the previous night and the maximum surface concentrations $\bar{C}_{omax}$ during the following day. An exponential empirical regression equation of the form

$$\bar{C}_{omax} = \bar{C}_b \exp^{n\bar{C}_R} \quad (2)$$

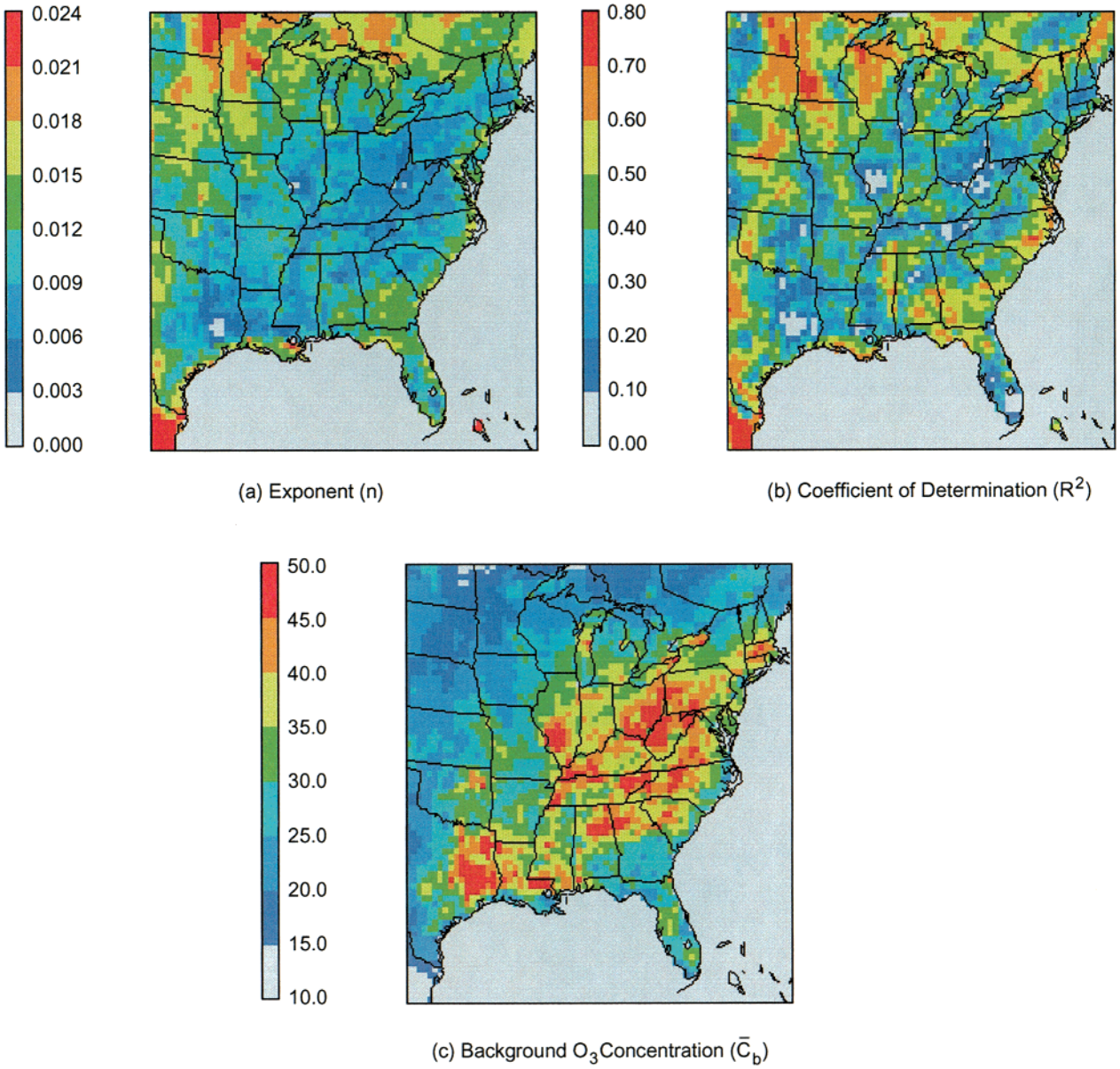

FIGURE 4. Model values of (a) magnitude of the exponent, (b) coefficient of determination, and (c) inferred background ozone concentrations. These values are based on an exponential fit between model-predicted maximum surface ozone and ozone in residual nocturnal boundary layer.

is proposed here for predicting $\bar{C}_{o\max}$ from the observed value of $\bar{C}_R$. In the proposed relation, $\bar{C}_b$ represents the regional background concentration of ozone, while the exponent n is a measure of the contribution of the residual ozone aloft from the previous night to the next day's maximum surface concentration. For our tower site near Raleigh, NC, $\bar{C}_b \simeq 27.7$ ppbv, $n \simeq 0.016$, and $R \simeq 0.64$. A linear regression equation can also be fitted as well, but eq 2 better represents the data during high ozone episodes and is preferred.

(c) Regional simulations of ozone concentrations for 2 months (June and July) in 1995 (with a comprehensive air quality model, MAQSIP) also show a good correlation, similar to that of observed data at the tower site. Model simulations over the entire eastern United States indicate, however, that both the coefficient ($\bar{C}_b$) and exponent (n) in the best-fitted regression eq 2 and the correlation coefficient (R) vary considerably spatially. But regions of high inferred background concentrations have associated with them lower values of n and R, implying that these are also the regions where the proposed regression relationship is the weakest. The proposed relationship appears to be stronger in semi-urban and rural regions where local ozone production is relatively small.

(d) The present analysis provides a basis for a better quantification of the effects of regional ozone transport and exchange processes associated with the breakup of the nocturnal inversion on the surface ozone concentration. Additionally, the complimentary analysis of modeled and observed data presented in this paper not only serves as a model evaluation activity but also supports the empirical relationship between ozone in the residual layer and maximum surface ozone derived from observations.

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