

The Role of Vertical Mixing in the Temporal Evolution of Ground-Level Ozone Concentrations

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ABSTRACT

Aircraft measurements taken during the North American Research Strategy for Tropospheric Ozone-Northeast field study reveal the presence of ozone concentration levels in excess of 80 ppb on a regional scale in the nocturnal residual layer during ozone episodes. The air mass containing increased concentrations of ozone commonly is found on a horizontal spatial scale of about 600 km over the eastern United States. The diurnal variation in ozone concentrations at different altitudes, ozone flux measurements, and vertical profiles of ozone suggest that ozone and its precursors trapped aloft in the nocturnal residual layer can influence the ground-level ozone concentrations on the following day as the surface-based inversion starts to break up. A simple one-dimensional model, treating both meteorological and chemical processes, has been applied to investigate the relative contributions of vertical mixing and photochemical reactions to the temporal evolution of the ground-level ozone concentration during the daytime. The results demonstrate that the vertical mixing process contributes significantly to the ozone buildup at ground level in the morning as the mixing layer starts to grow rapidly. When the top of the mixing layer reaches the ozone-rich layer aloft, high ozone concentrations are brought down into the mixing layer, rapidly increasing the ground-level ozone concentration because of fumigation. As the mixing layer grows further, it contributes to dilution while the chemical processes continue to contribute to ozone production. Model simulations also were performed for an urban site with different amounts of reduction in the ground-level emissions as well as a 50% reduction in the concentration levels of ozone and its precursors aloft. The results reveal that a greater reduction in the ground-level ozone concentration can be achieved by decreasing the concentrations of ozone and precursors aloft than can be achieved from a reduction of local emissions. Given the regional extent of the polluted dome aloft during a typical ozone episode in the northeastern United States, these results demonstrate the necessity and importance of implementing emission reduction strategies on the regional scale; such regionwide emission controls would reduce effectively the long-range transport of pollutants in the Northeast.

1. Introduction

Ozone is a secondary pollutant formed in the atmosphere through photochemical reactions involving nitrogen oxides (NO_x) and volatile organic compounds (VOC) in the presence of sunlight. The temporal evolution of ozone concentrations at the ground level is controlled strongly by the diurnal variation of the atmospheric boundary layer. The entrainment and the fumigation processes in the convective boundary layer can influence the vertical distribution of the pollutant concentrations. Under certain meteorological conditions, ozone can be formed and accumulated in the daytime boundary layer with concentration levels that exceed the 1-h National Ambient Air Quality Standard of 0.12

parts per million (ppm). The radiative cooling at night leads to the formation of the stable surface layer near the ground. Above the stable surface layer and under the upper-level inversion, the characteristics of the atmosphere are relatively uniform; this layer is called the nocturnal residual layer. If elevated nitric oxide (NO) emission sources such as tall industrial smokestacks are not present, ozone concentrations in the residual layer remain high, since deposition and other removal processes that occur near the surface are absent aloft. In the nocturnal residual layer aloft, pollutants can be transported during the night over long distances with the prevailing winds. In the morning as the sun starts to heat up the ground, convective thermals and eddies initiate from the surface, forcing the growth of the mixing layer. As the mixing layer grows, pollutants trapped aloft in the residual layer can be entrained downward into the mixing layer; this fumigation effect leads to a rapid increase in pollutant concentrations at ground level. Also, pollutants emitted or formed near the ground can be mixed into upper levels of the atmosphere. If a

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stagnant weather system persists for several days, a polluted dome with elevated concentrations (relative to background values) of ozone and its precursors can be formed on a regional scale.

The meteorological conditions conducive to the long-range transport and accumulation of ozone on regional scales have been investigated over the eastern United States (Vukovich et al. 1985; Ozone Transport Assessment Group 1997; Rao et al. 1997, 1998a; Brankov et al. 1998) and in western Europe (Guicherit and van Dop 1977). Clarke and Ching (1983) analyzed the regional-scale aircraft sampling data over the eastern United States and pointed out that boundary layer ozone and ozone precursors may be vented above the mixing layer by cumulus activity, transported, and brought back into the mixing layer by subsidence and entrainment. Recent studies reveal that ozone transport aloft over the southern California air basin makes a significant contribution to the ground-level ozone concentration at a nearby downwind area on the following day (Bigler-Engler and Brown 1995). Observations and modeling studies on the Swiss plateau by Neu et al. (1994) show that between 50% and 70% of the daily maximum surface ozone concentration can be linked to ozone trapped aloft in the overnight residual layer.

The North American Research Strategy for Tropospheric Ozone (NARSTO) program is a collaborative research endeavor involving government, industry, and academia in the United States, Canada, and Mexico. As an element of NARSTO, a public-private consortium has initiated the NARSTO-Northeast (NARSTO-NE) air quality study. The NARSTO-NE field observations were taken in the summers of 1995 and 1996 and provide an extensive surface and upper-air meteorological and air quality database on the three-dimensional distribution and transport of ozone and its precursors in the northeastern United States. The database is maintained and updated regularly (Korc et al. 1996). Aircraft measurements taken during the NARSTO-NE summer 1995 field campaign indicate that ozone concentrations in the nighttime residual layer are in excess of 80 parts per billion (ppb) on a regional scale during ozone episodes. Using a photochemical box model [Ozone Isopleth Plotting Package, Research-Oriented version (Gery and Crouse 1991)], Zhang et al. (1998) showed that ozone aloft in the nighttime residual layer is an important contributor to the ground-level peak ozone concentration observed on the following day.

In this paper, the role of vertical mixing initiated by convective and turbulent processes on the temporal evolution of the ground-level ozone concentrations is discussed. Both observational and modeling analyses are presented to illustrate the linkage between the ground-level ozone and ozone trapped aloft in the nighttime residual layer. Since vertical mixing and chemical transformation are competitive processes in dictating the magnitudes of pollutant concentrations in the atmosphere, the relative contributions of vertical mixing and

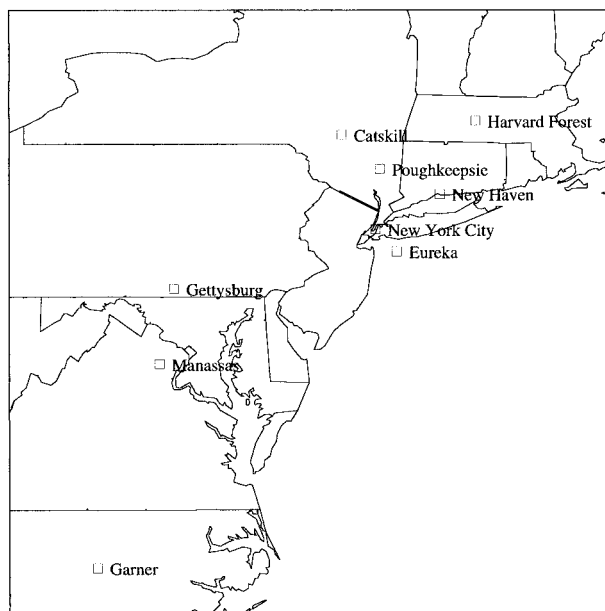


FIG. 1. Locations of monitoring sites in this study.

photochemical reactions are examined through a simple modeling approach to identify their respective roles in the ozone accumulation process.

2. Observations

a. Rate of change in ground-level ozone concentrations

The location of the monitoring stations in this study is depicted in Fig. 1. To identify the processes that govern the temporal evolution of the ground-level ozone concentrations, the rate of change in the ground-level ozone concentrations (the ozone tendency) is examined. To this end, an urban site located in downtown New York City and a rural site located in Catskill, New York, are selected, and the rate of change in the ground-level ozone concentrations at each site is calculated using all available observations from the summer of 1995 (June–August). The average-rate-of-change curves, presented in Fig. 2, indicate that the peak at the rural site occurs around 0900 EST (1400 UTC), which is 2–3 h earlier than the peak observed at the urban site. After 0600 EST, ozone concentrations at the rural site increase dramatically, while the rates of change remain negative at the urban site until 0700 EST because of NO titration in the urban area. After 0700 EST, the ground-level ozone concentration at the urban site increases at a rate greater than that at the rural site. The photochemical processes during the daytime help maintain the positive rate of change in ozone concentrations at both sites. The peak values of the rate of change in the ground-level ozone in the early morning time at the rural site suggest that vertical mixing might be the dominant factor in-

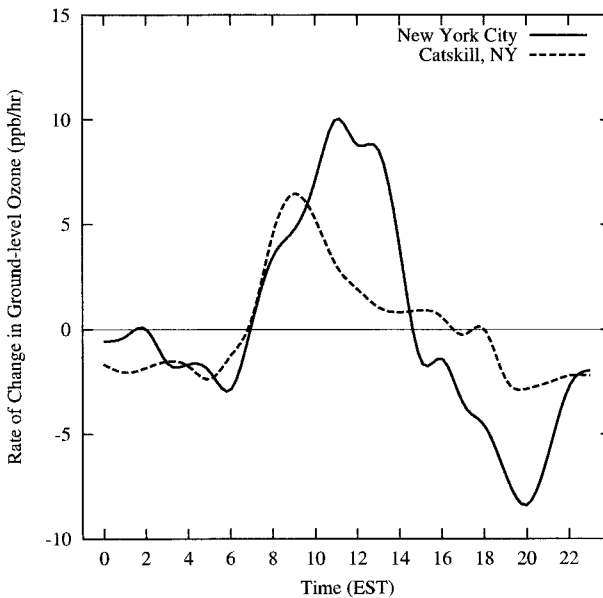


FIG. 2. Rate of change in ground-level ozone concentration (ozone tendency) during summer 1995.

creasing the ground-level ozone concentrations, because of the ozone-rich air mixing downward from aloft.

b. Observations at different altitudes

The characteristics of the ozone distribution in the vertical are related strongly to the temporal evolution of the atmospheric boundary layer. As an example, ozone concentrations measured at ground level and at 433 m above ground level (AGL) on a television tower located at a rural site in Garner, North Carolina (78.55°W, 35.68°N), during 7–18 July 1995 are presented in Fig. 3. The diurnal pattern that is obvious in the ground-level ozone concentrations is not evident at the 433-m level. Ozone concentrations at ground level decrease after sunset to very low values at nighttime due to NO titration and deposition processes and increase dramatically in the morning, reaching a maximum value in the afternoon. The difference in the ozone concentrations between the 433-m level and ground level reveals that the vertical gradient in ozone concentrations reaches its maximum at night. After sunrise, the vertical gradient in ozone concentration begins to decrease and by noon the ground-level ozone concentration becomes equal to or greater than that at the 433-m level. This profile suggests that the vertical mixing processes in the daytime convective boundary layer can bring ozone that is trapped aloft down to the ground in the morning. Also, the growing mixing layer in the morning leads to the up-mixing from the surface of air with low ozone and high NO concentrations, causing an intermediate decrease in ozone.

Another case is presented in Fig. 3 to show the temporal variation in the mixing heights and ozone con-

centrations using observations from 17 June 1995 at the World Trade Center (457 m AGL) and at Greenpoint (3 m AGL), in downtown Manhattan in New York City. The mixing heights are estimated by the method suggested by Berman et al. (1997) using the rawinsonde data at Brookhaven, New York, and surface temperature at La Guardia Airport in New York City. The vertical ozone profile at 0400 EST over Poughkeepsie, New York, the nearest location for which aircraft spiral measurements are available, reveals a sharp vertical gradient in the surface stable layer and ozone concentrations in excess of 80 ppb aloft in the residual layer (Zhang et al. 1998). At nighttime, ozone concentrations at the World Trade Center are approximately 30 ppb higher than at Greenpoint. The mixing layer heights, presented in Fig. 3b, suggest that Greenpoint is in the relatively stable surface layer, while the World Trade Center monitoring site is in the nocturnal residual layer. In the morning, the mixing layer height increases dramatically from 350 m to 2500 m during the period between 0800 and 1200 EST. The ground-level ozone concentration also increases rapidly after 0900 EST when the mixing layer height rises above the top of the World Trade Center and reaches the altitude where ozone concentrations are enhanced. Ozone concentrations at the World Trade Center remain relatively constant until 1000 EST and start to grow after that. From 1200 to 1600 EST, ozone concentrations at both sites match closely, with little gradient in the vertical. The temporal profile of mixing height suggests that both monitoring sites are within the daytime mixing layer during 1200–1600 EST. While ozone concentrations after 1600 EST remain high at the top of the World Trade Center, they continue to decrease at Greenpoint soon after the collapse of the mixing height (Fig. 3b).

c. Harvard Forest meteorological and trace gas measurements

The Harvard Forest environmental measurement site, located in central Massachusetts, was established in October 1989. At this site, the concentrations and fluxes of reactive nitrogen (NO_x), carbon dioxide, water, ozone, and carbon monoxide have been measured since 1990 (Munger et al. 1996). The daytime mixing layer contains eddies of different sizes, ranging from small to large eddies consistent with the scale of mixing layer height. To study the mixing process in the subcanopy layer, eddies consistent with the scale of the surface layer depth are considered. The meteorological and trace gas measurements on a 30-m tower at the Harvard Forest site provide evidence for the contribution of the vertical mixing processes to the ground-level ozone concentration for the subcanopy in the atmospheric surface layer. The following discussion is based on the measurements that were taken during 9–12 August 1995.

Meteorological observations indicate a light southwesterly flow at the 29-m level above the ground (10

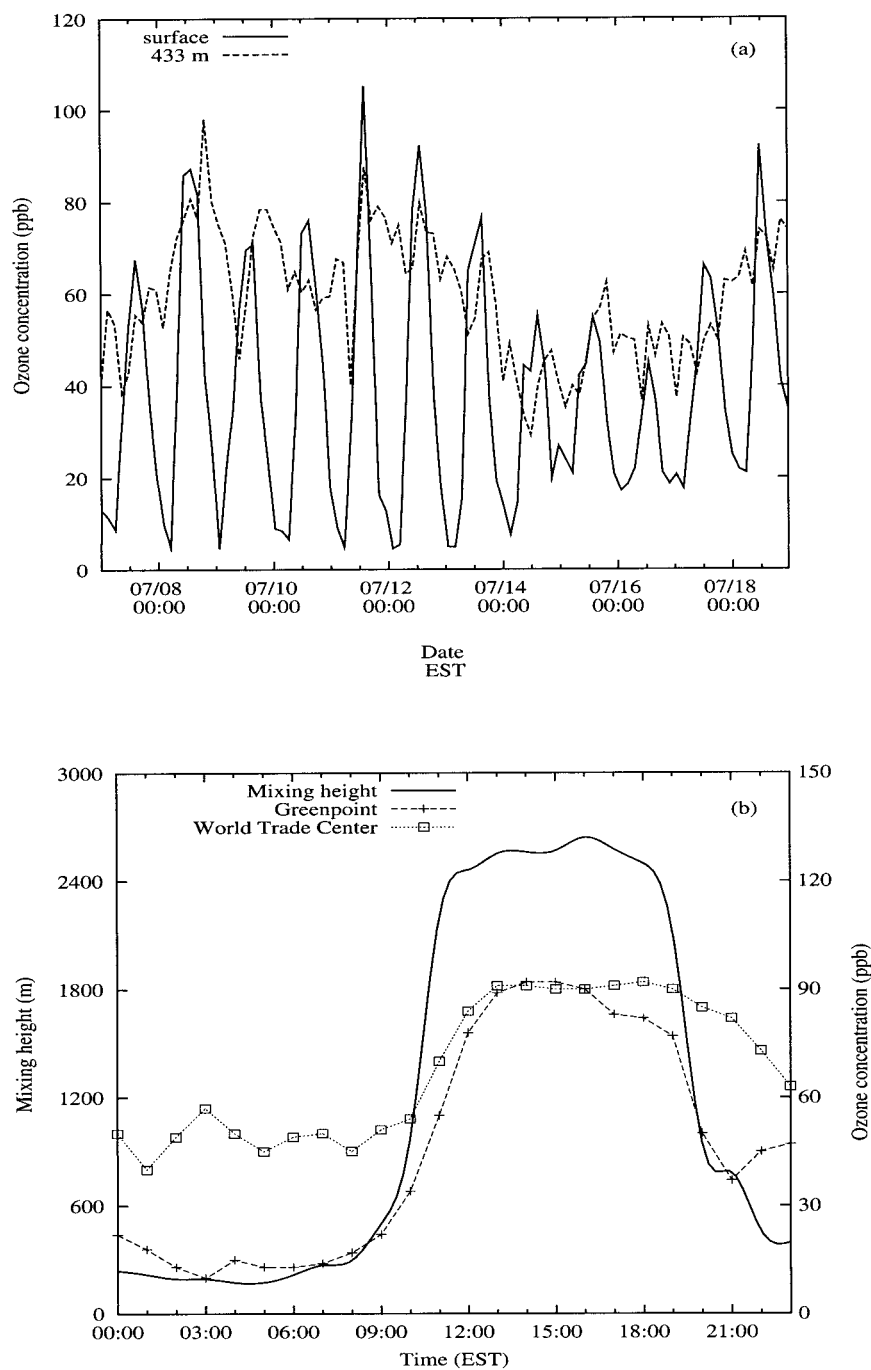


FIG. 3. (a) Ozone concentrations measured on a television tower at Garner, North Carolina, from 7 to 18 July 1995. The solid line is ozone concentration at ground level; the dashed line is ozone concentration at the 433-m level. (b) Mixing height calculated for New York City and ozone concentration measured at the World Trade Center and at Greenpoint, New York City, on 17 June 1995.

m above the canopy) during this period. The diurnal variation in ozone concentrations at the 29-m level can be discerned from Fig. 4. The peak ozone concentration on 10 August 1995 is in excess of 100 ppb during the afternoon. The flux measurements of heat, momentum,

ozone, and NO_y at the 29-m level are plotted in Fig. 4. Upward heat flux from surface heating by solar radiation increases during the daytime, reaching a maximum around noon, and decreases after sunset, with a small, negative value during the night. Downward momentum

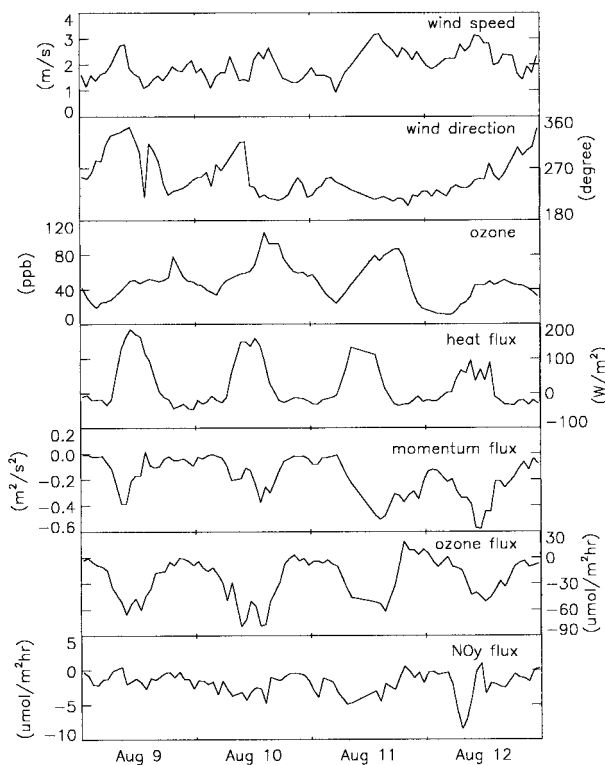


FIG. 4. Wind speed, wind direction, ozone concentration, and fluxes of heat, momentum, ozone, and NO_y measured on a 30-m tower at Harvard Forest for 9–12 August 1995.

flux increases as the convective mixing layer grows in the morning. Both ozone and NO_y flux measurements at 29 m clearly indicate the presence of strong downward transport during the daytime. The downward flux starts increasing in the morning, corresponding to the change in the momentum flux when convective activity is initiated, reaching its maximum value around noon, and then decreases in the afternoon, with almost no fluxes during the nighttime. Munger et al. (1996) indicated that the opening and closing of the stoma can regulate the ozone flux observed at Harvard Forest. Similar conclusions were drawn based on observations for a variety of forest types by Baldocchi et al. (1987) and Padro (1993).

At the Harvard Forest site, ozone concentrations were measured at eight levels (29.0, 24.1, 18.3, 12.7, 7.5, 4.5, 0.8, and 0.3 m) on the tower. Figure 5 shows the diurnal variation of ozone at three levels (29.0, 18.3, and 7.5 m) on 10 August 1995. The large rates of change in the ozone concentration (ozone tendency) at 7.5 and 18.3 m in the early morning before 0800 EST clearly illustrate the contribution from the mixing process and leaf-open/close activity to the ozone buildup at ground level; this pattern of diurnal variation is consistent with the earlier observations of Galbally (1968) in England.

The atmospheric processes such as horizontal advection, vertical mixing, photochemical reactions, and de-

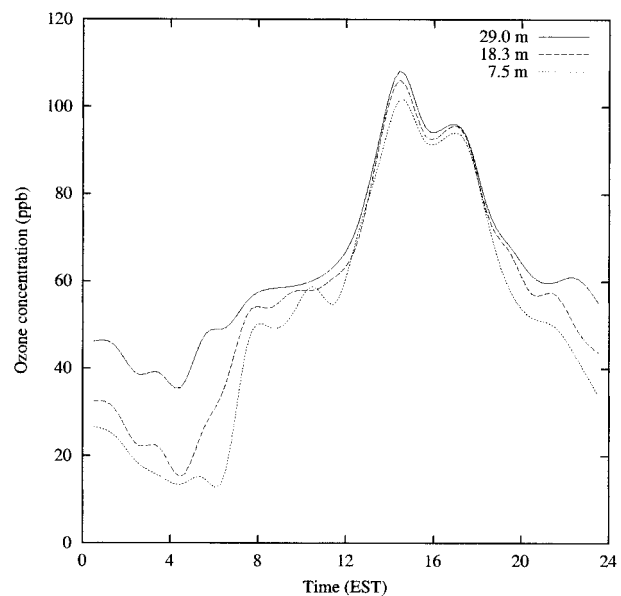


FIG. 5. Ozone concentrations measured at the 29.0-m, 18.3-m, and 7.5-m levels above ground at the Harvard Forest on 10 August 1995.

position dictate the ozone tendency in the subcanopy layer. To focus on the importance of transport of ozone trapped aloft downward to the subcanopy layer in the morning, the divergence of vertical ozone fluxes was examined. We assume that the local rate of change in the ozone concentration in the subcanopy layer is controlled solely by the vertical flux at the 30-m level and deposition in the canopy layer. As pointed out by Munger et al. (1996), the leaves dominate ozone deposition in the canopy. The values of deposition velocity (v_d) are taken from Padro (1993) and Baldocchi et al. (1987) observational studies for a deciduous forest in the summer during the daytime. The ozone tendency is calculated from

$$\frac{\partial[\text{O}_3]}{\partial t} = -\frac{w'[\text{O}_3]' - v_d[\text{O}_3]}{h_s}, \quad (1)$$

where h_s is the height of the subcanopy layer and $w'[\text{O}_3]'$ is the vertical flux of ozone. The observed ozone concentration at 24 m at 0600 EST for the period of 9–12 August 1995 is used as the initial value, and Eq. (1) is integrated over time. The temporal evolution of the ground-level ozone concentration determined from Eq. (1), presented in Fig. 6, agrees very well with the observations in the morning, indicating that the vertical transport of ozone from aloft is the major source for the ozone buildup at ground level. However, the curves start to diverge later in the day, indicating that contributions from photochemical production processes become important in the afternoon.

d. Vertical profiles of ozone

Atmospheric mixing height determines the depth through which the precursors emitted near the ground

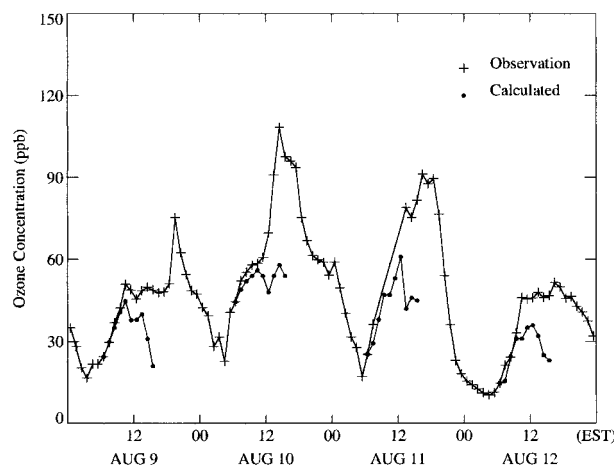


FIG. 6. Ozone concentrations at the 24-m level at the Harvard Forest site. Solid line with plus signs indicates observation, and solid line with dots represents calculated values using the flux divergence approach.

level are mixed and influences the amount of ozone that can be mixed downward to the ground. The average of all ozone vertical profiles from the nighttime aircraft spiral measurements over the Northeast during all summer 1995 ozone episodes, presented in Fig. 7a, reveals the presence of elevated ozone concentrations of about 80 ppb in the nighttime residual layer. Figure 7b shows the ozone profiles measured at Poughkeepsie, New York, around 0400 EST from 12 to 16 July 1995. The vertical structure of the atmospheric boundary layer can be discerned readily from the ozone profiles. In the nocturnal stable layer near the surface, ozone concentrations exhibit a sharp gradient in all five profiles because of the presence of removal processes such as deposition and NO titration near the surface. However, the ozone destruction processes are much slower in the residual layer; concentrations are relatively uniform and are higher than those at the ground. During the 12–16 July 1995 episode, ozone concentrations in the nighttime residual layer increase from approximately 60 ppb on 12 July to about 100 ppb on 14 and 15 July, and then drop back to 40 ppb on the night of 16 July after the passage of a cold front. The “ozone reservoir” of 80–100 ppb aloft is a regional-scale feature that plays an important role in increasing ground-level ozone concentrations on the following day (Zhang 1998; Zhang et al. 1998).

A comparison of the ozone profiles in the morning and afternoon at rural sites provides further insight on the impact of the vertical mixing process. Figure 8a shows temperature and ozone profiles at Manassas, Virginia, on 17 June 1995. The temperature profile in the early morning shows a stable boundary layer below 300 m with a low ozone concentration and a neutral layer above 500 m with 80 ppb of ozone. The temperature profile in the afternoon indicates a well-mixed boundary layer up to 1500 m. Ozone concentrations are relatively uniform in the mixing layer, with an average that is close

to the background value observed in the previous nighttime residual layer. In rural areas outside the impact area of urban pollutant plumes, the vertical mixing process might be the dominant mechanism for the buildup of ground-level ozone. For urban areas with high precursor emissions, ozone concentrations in the afternoon show a large increase in the mixing layer. For example, temperature and ozone profiles at New Haven, Connecticut, on the early morning of 14 July 1995 show a stratified structure in the boundary layer (Fig. 8b). In this case, ozone concentrations in the nighttime residual layer are quite high with a peak value of about 120 ppb. In the afternoon, ozone concentration in the mixing layer exceeds 120 ppb, reaching 160 ppb near the surface. Obviously, in addition to the vertical mixing processes, photochemical reactions and advection of urban plumes also are important contributors to the sharp increase in the ozone concentration in the mixed layer. Thus, at urban sites or downwind of urban sites, the incremental contribution by photochemical production to ozone in the boundary layer is significant.

Kleinman et al. (1994) analyzed ozone observations in rural Georgia and pointed out that, in the morning, concentrations of ozone increase because of entrainment of air aloft by the growing convective boundary layer. This increase is particularly strong on high ozone concentration days and almost nonexistent on days with low ozone concentrations. Approximately half of the steep increase in ozone in the early morning on high ozone days is attributed to entrainment and the other half is attributed to in situ chemical production.

To assess the relative contributions of chemical reactions and vertical mixing processes to ground-level ozone concentrations, a simple modeling approach is presented in the following section.

3. Modeling approaches

a. Lagrangian particle dispersion model

We use a Lagrangian Particle Dispersion (LPD) model (Uliasz 1994) to illustrate the regional-scale transport pattern during a typical ozone episode over the northeastern United States. The Regional Atmospheric Modeling System (RAMS; Pielke et al. 1992) with three nested grids was used to provide the 3D meteorological input fields for the Lagrangian particle model. Details on the RAMS setup and simulations can be found in Kallos (1997). Particles are released continuously with a rate of 240 particles per hour starting at 0700 EST 13 July 1995 from the $10 \text{ km} \times 10 \text{ km} \times 0.1 \text{ km}$ volume centered at four large urban areas: Pittsburgh; Philadelphia; Washington, District of Columbia; and New York City. Figure 9a shows the distribution of particles in the boundary layer up to 2 km during 0000–1200 EST on 14 July 1995. The particle plumes are dispersed and transported downwind over the northeastern urban corridor. The daytime convective thermals and turbu-

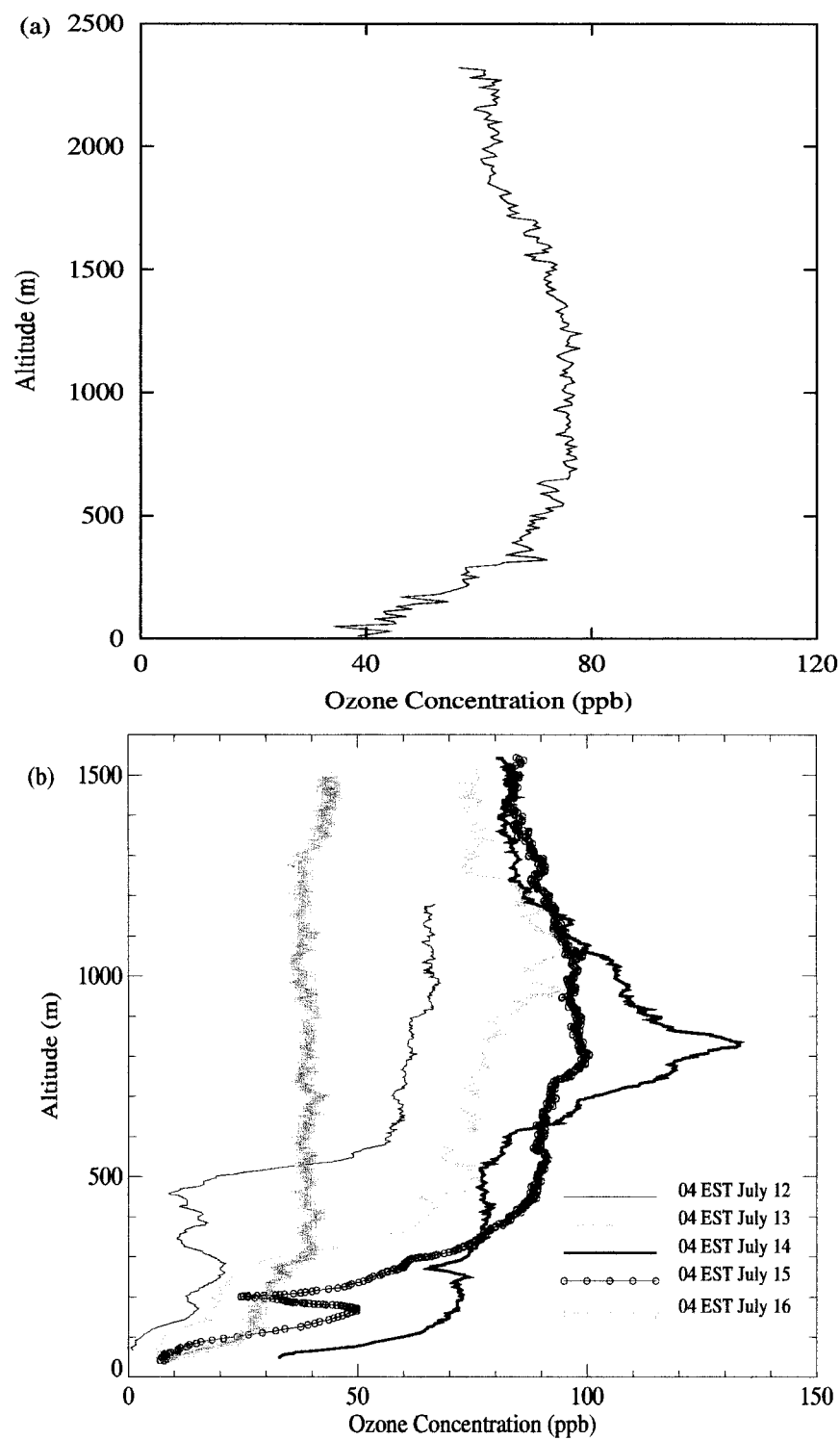


FIG. 7. (a) Average nighttime ozone profile over all NARSTO-NE aircraft measurements taken during summer 1995 ozone episodes. (b) Ozone profiles measured by aircraft over Poughkeepsie, New York, at 0400 EST during 12–16 July 1995.

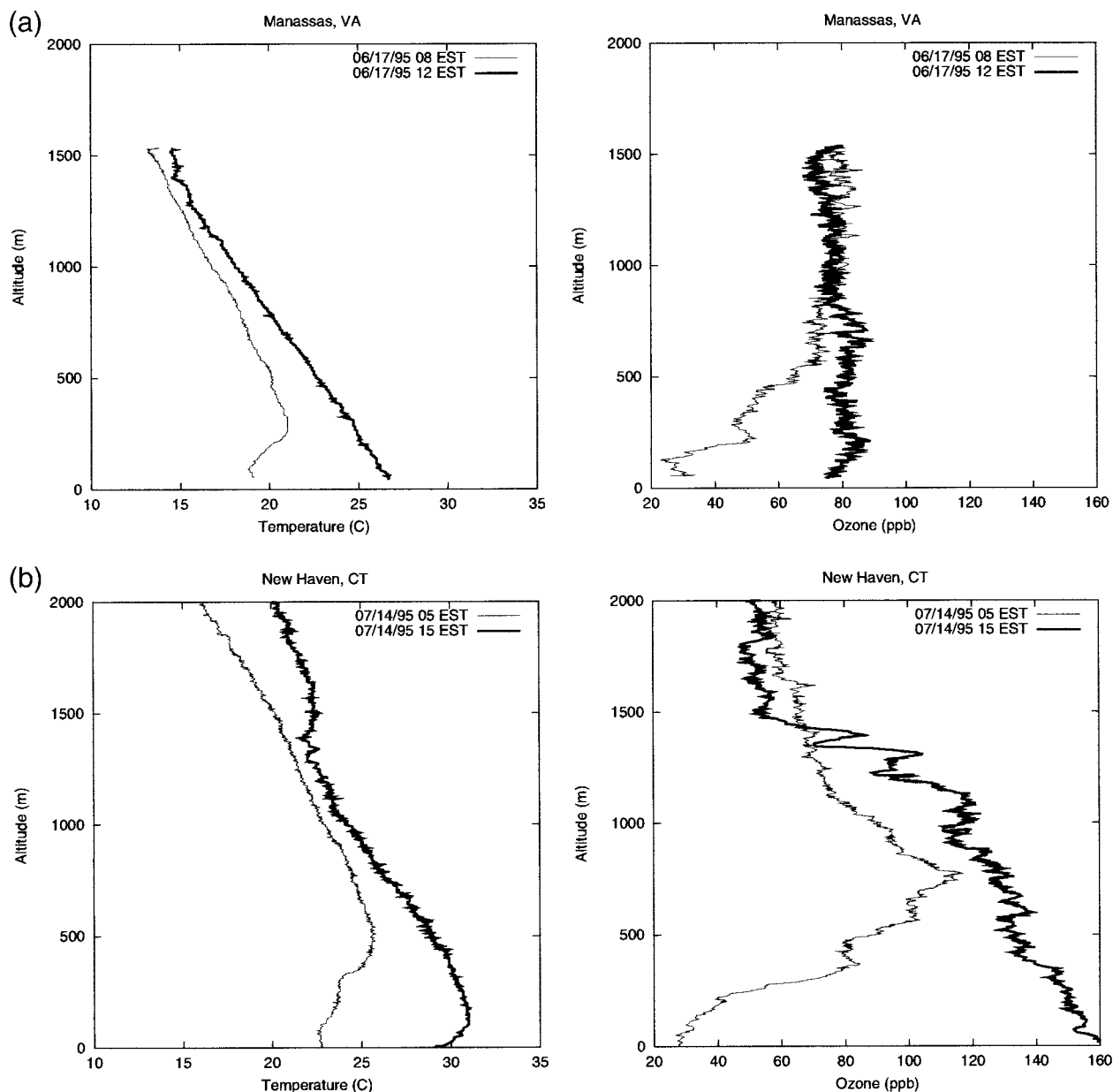


FIG. 8. Aircraft measurements of temperature and ozone profiles at (a) Manassas, Virginia, on 17 June 1995 and (b) New Haven, Connecticut, on 14 July 1995.

lence transport the particles to the upper levels of the atmospheric boundary layer. These particles remain aloft in the nighttime residual layer (Fig. 9b). The vertical distributions of particles, projected onto the x - z plane, are presented in Fig. 9c. At night and in the early morning, the new releases of particles are confined to the stable layer near the surface, while particles injected into the upper level by daytime convection travel farther downwind. The aged particles aloft are brought down into the mixing layer on the next day by the fumigation process, as is evident in Fig. 9c. Although ozone and its precursors are reactive pollutants rather than passive

particles, model calculations presented here nevertheless demonstrate the potential for the regional-scale transport of pollutants released at ground level.

b. One-dimensional integrated boundary layer model

Comprehensive photochemical models have been applied extensively to study the urban and regional-scale ozone problem and the efficacy of emission control strategies in reducing ozone exceedances (e.g., Rao et al. 1996). Although ozone air quality models, such as the Urban Airshed Model (Morris et al. 1991), include

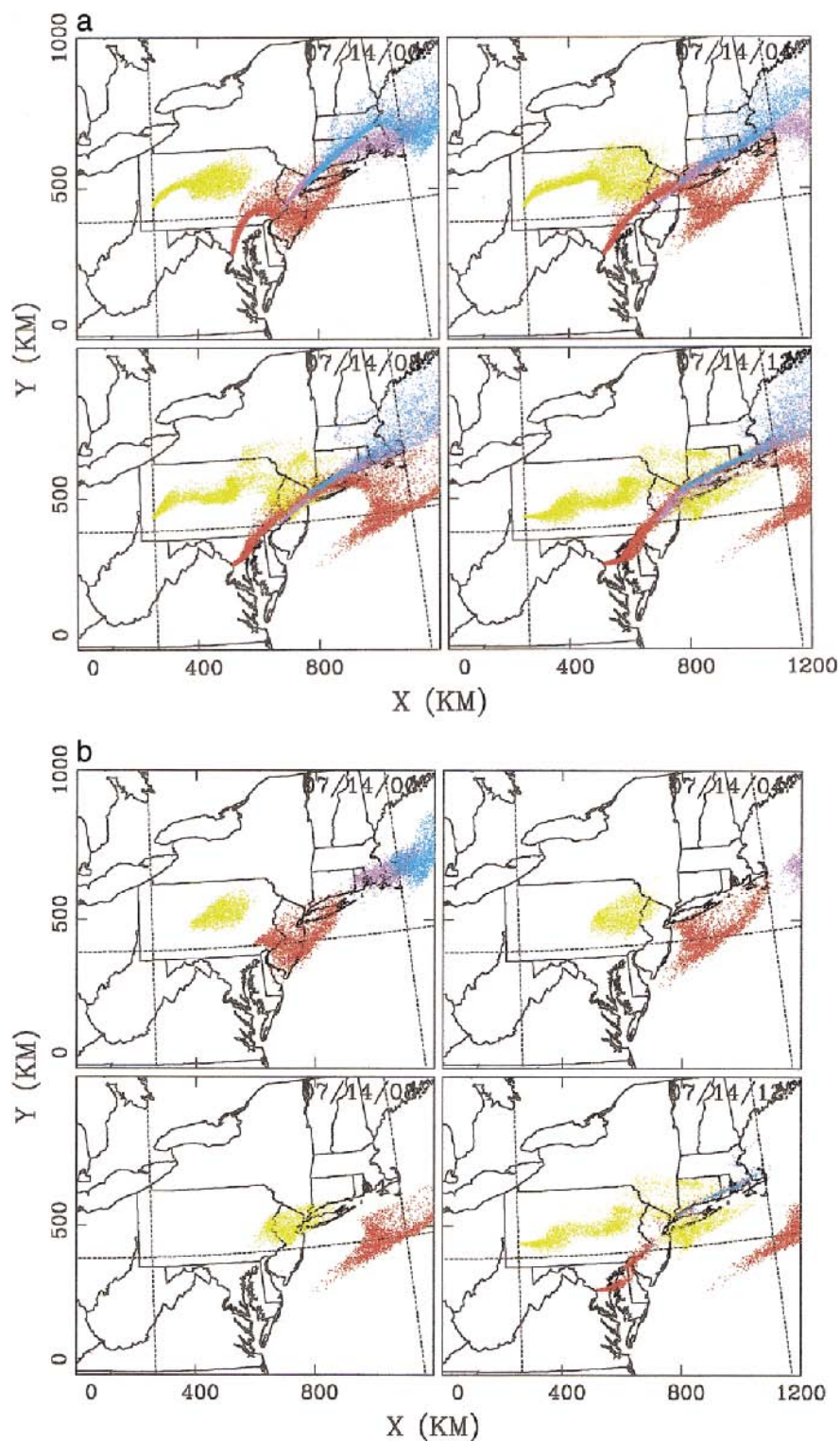


FIG. 9. (a) Particle distributions simulated by LPD model in the boundary layer (0–2 km) from 0000 to 1200 EST 14 July 1995; (b) particles aloft from 0.5 to 2 km during the same period; (c) particle distribution projected to the x - z plane during the same period.

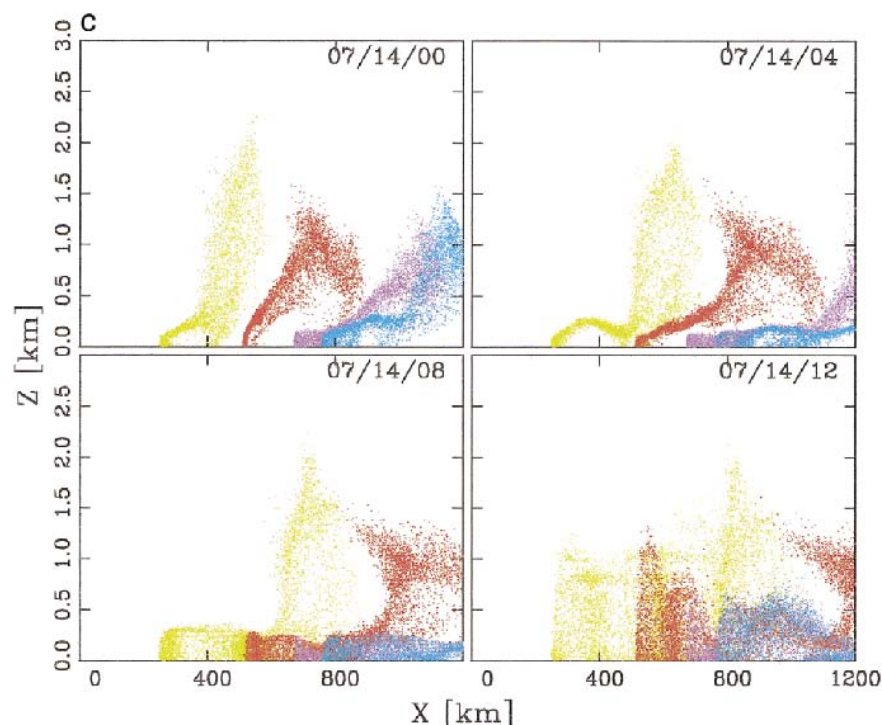


FIG. 9. (Continued)

sophisticated chemical mechanisms for species transformation, the representation of the atmospheric boundary layer turbulent mixing process in these models is often based on the concept of eddy diffusion or local first-order K theory. Modeling studies of chemical reactions in the atmospheric boundary layer have shown that the accuracy of simulated chemical fields is sensitive to the turbulent mixing scheme used in a model (Pleim and Chang 1992).

To examine the relative contribution of the vertical mixing and photochemical processes to ground-level ozone concentrations, an integrated one-dimensional (1D) time-dependent model was employed. The 1D model includes meteorological and chemical processes to simulate the atmospheric boundary layer up to 3 km. The 1D modeling approaches have been used in earlier studies to examine the photochemistry in the atmospheric boundary layer. For example, Trainer et al. (1991) used a 1D model with meteorological and photochemical components to study the reactive nitrogen photochemistry at a rural site in Pennsylvania. Also, Fish et al. (1999) used a 1D model to study the vertical distribution of nitrate radical (NO_3) in the boundary layer. The advantage of using a simple 1D model is that the key meteorological and chemical processes that affect the ozone distribution can be examined more easily than with a complex 3D model.

To emphasize the contribution of vertical mixing and photochemical production processes, horizontal advection and deposition are not considered in the current

model simulations. The model includes two soil layers, a surface layer of 30 m, and 30 layers above the surface layer with equal thicknesses of 100 m (Fig. 10a). The meteorological module is based on Blackadar's planetary boundary layer model (Blackadar 1979b; Zhang and Anthes 1982) and has been adapted in other 1D modeling applications (Trainer et al. 1991; Fish et al. 1999). Budgets are kept for heat, water vapor, and momentum in each layer. The force–restore method is used for surface energy budget. When the surface heating rate is large and the wind speeds are not large, the free convection regime prevails within the buoyantly driven mixing layer. Blackadar's nonlocal closure scheme is applied for the free convection regime (Blackadar 1979a). Thermals rise from the surface layer and exchange properties between the upper layers and the surface layer, as illustrated in Fig. 10b. The vertical mixing in this scheme is not determined by local gradients but by the thermal structure of the whole mixing layer. In the surface layer, the prognostic variables are solved by

$$S_a^{t+1} = S_a^{t-1} + \left(\frac{F_s z_1}{\bar{m} h^2} - \frac{F_s}{\bar{m} h} + \frac{F_1}{\bar{m} h} \right) \left[\exp \left(-\frac{\bar{m} h \Delta t}{z_1} \right) - 1 \right] + \frac{F_s \Delta t}{h}, \quad (2)$$

where S_a represents any prognostic variable in the surface layer, F_s is the surface flux, F_1 is the flux at the top of the surface layer, h is the mixing layer height, z_1

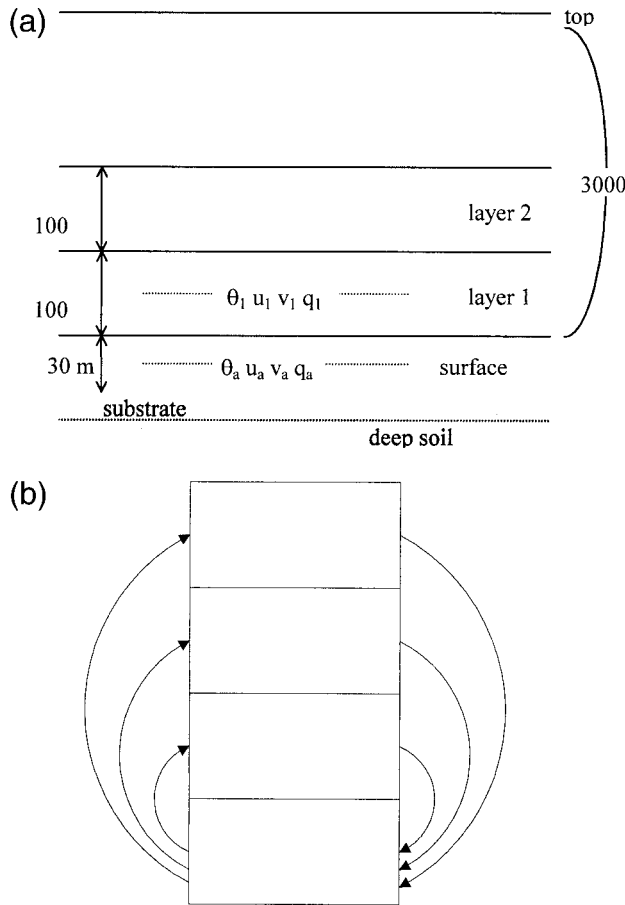


FIG. 10. (a) Vertical layer structure for the 1D model; (b) Blackadar's nonlocal closure scheme for free convection regime.

is the surface layer height, Δt is the time step, and mixing coefficient m is calculated by

$$\bar{m} = H_1 / \left\{ \rho_a c_p (1 - \varepsilon) \int_{z_1}^h [\theta_{va} - \theta_v(z')] dz' \right\}, \quad (3)$$

where ε is the entrainment coefficient, H_1 is the heat flux at the top of the surface layer, ρ_a is the density of air, c_p is the specific heat capacity, θ_v is the virtual potential temperatures, θ_{va} is the virtual potential temperature at the top of the surface layer, and z' is the height of the model layer. For the variables S_i in the mixing layer, the prognostic equation is

$$\frac{\partial S_i}{\partial t} = w(z) \bar{m} (S_a - S_i), \quad (4)$$

where $w(z)$ is a weighting function that accounts for the variation of exchange rate with height, either as a result of the size distribution of the convective eddies or the variation of the entrainment rate or both. Estoque (1968) suggested the form

$$w(z) = 1 - \frac{z}{h}. \quad (5)$$

TABLE 1. Chemical species in CBM-IV.

CBM-IV species	Species name
NO	Nitric oxide
NO ₂	Nitrogen dioxide
NO ₃	Nitrogen trioxide (nitrate radical)
N ₂ O ₃	Dinitrogen pentoxide
HONO	Nitrous acid
HNO ₃	Nitric acid
HO ₂ NO ₂	Peroxynitric acid
O(¹ D)	Oxygen atom
O	Oxygen atom
OH	Hydroxyl radical
O ₃	Ozone
HO ₂	Hydroperoxy radical
H ₂ O ₂	Hydrogen peroxide
CO	Carbon monoxide
FORM	Formaldehyde
ALD ₂	High molecular weight aldehydes (RCHO, R > H)
C ₂ O ₃	Peroxyacyl radical [CH ₂ C(O)OO]
PAN	Peroxyacyl nitrate [CH ₂ C(O)OONO ₂]
PAR	Paraffinic carbon bond (C–C)
ROR	Secondary organic oxy radical
OLE	Olefinic carbon bond (C=C)
ETH	Ethene (CH ₂ =CH ₂)
TOL	Toluene (C ₆ H ₅ –CH ₃)
CRES	Cresol and higher molecular weight phenols
TO ₂	Toluene–hydroxyl radical adduct
CRO	Methylphenoxy radical
OPEN	Aromatic ring fragment acid
XYL	Xylene [C ₆ H ₄ –(CH ₃) ₂]
MGLY	Methyl glyoxal [CH ₃ C(O)C(O)H]
ISOP	Isoprene
XO ₂	NO–NO ₂ operation
XO ₂ N	NO–nitrate operation

For other regimes, the turbulent exchange is controlled by the local gradients using the K theory. The local Richardson number, in accordance with the prevailing lapse rate and wind shear, determines the magnitude of the exchange coefficient.

For the chemical module, the 1D model uses an extended version of the Carbon Bond Mechanism (CBM-IV) for solving the chemical transformation (Gery et al. 1989). CBM-IV has been proven to provide a good balance between chemical detail and computational cost (Derwent 1990). Organic species are grouped according to the carbon bond type, and a structured lumping technique is employed in CBM-IV. The chemical species considered here are listed in Table 1. A set of representative values of photolysis rates as a function of solar zenith angle (Systems Applications International 1995) is used for the photolysis reactions. The rate constants of other reactions are adapted from Svensson (1996). Following the computational approach of Morris et al. (1991), the time integration of the CBM-IV uses quasi-steady-state assumptions for species with large formation/removal rates and the Newton–Raphson algorithm for the remainder of the species.

A case study is discussed in the following for an urban site in the New York metropolitan area on 14 July 1995. The initial vertical profiles for the meteorological var-

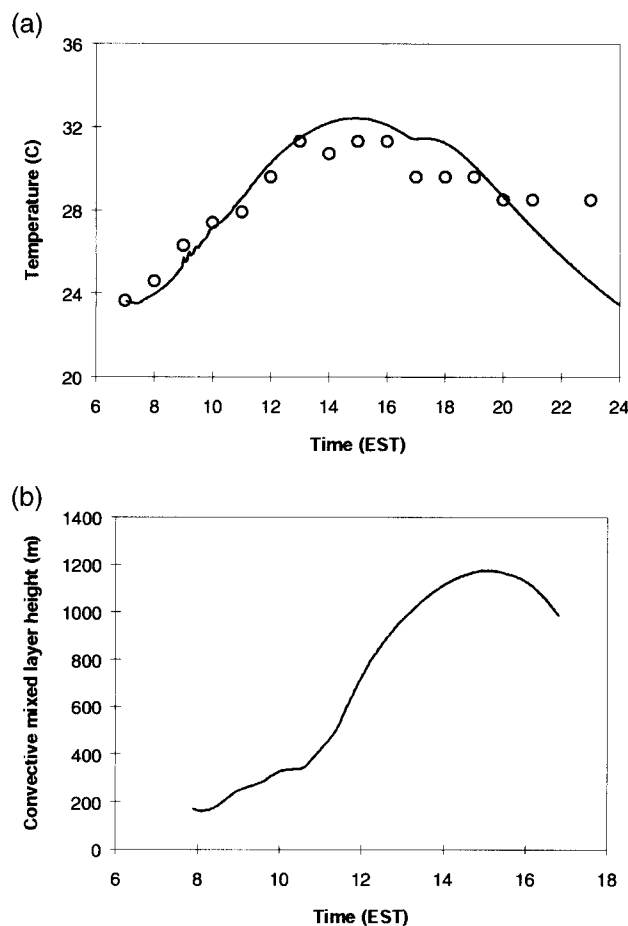


FIG. 11. (a) Ground-level temperature as simulated by the 1D model and measured at John F. Kennedy Airport, New York (open circles); (b) simulated convective mixing layer height, both on 14 July 1995.

ables are derived from the rawinsonde measurements at *Eureka*, off the New Jersey shore. Initial vertical profiles of chemical species are extracted and interpolated from the nearby grid cell of an Urban Airshed Model, Variable Grid version (UAM-V) simulation that had a horizontal resolution of 12 km and had seven vertical layers (Ozone Transport Assessment Group 1997). Simulations with the 1D model started at 0500 EST and continued until midnight. The model-simulated diurnal variation in air temperature near the surface agrees well with the nearby observation at John F. Kennedy Airport, New York (Fig. 11a). The model-simulated mixing layer height is presented in Fig. 11b. Potential temperature profiles as simulated by the model are shown in Fig. 12a. During the daytime, because of strong surface heating, a very shallow unstable layer exists near the surface. A well-mixed layer gradually develops throughout the day topped by an upper-level stable layer. Profiles indicate that the mixing layer reaches about 1200 m between 1400 EST and 1600 EST. The temperature profile at 2000 EST shows the formation of a surface-based

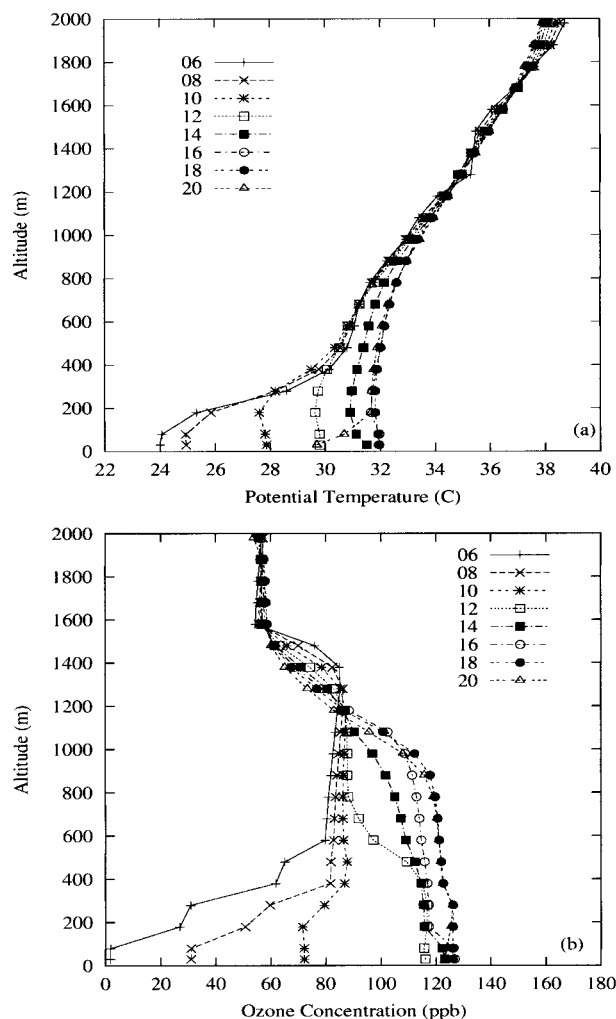


FIG. 12. (a) Simulated potential temperature profiles and (b) simulated ozone profiles for 14 July 1995.

stable layer detached from a neutral residual layer above the surface-based inversion because of radiative cooling.

The temporal evolution of potential temperature and ozone vertical profiles is shown in Fig. 12. The initial profile indicates a strong gradient in the stable layer near the surface, and a relatively uniform concentration of 80 ppb in the residual layer between 500 and 1300 m, and an average value of 60 ppb in the upper-level stable layer. The ozone concentration in the lower boundary layer starts increasing rapidly in the morning. The profiles at 0800 EST and 1000 EST show the gradual increase of ozone concentration in the lower atmosphere. As the top of the mixing layer reaches the ozone reservoir layer, ozone-rich air is entrained into the mixing layer to replace the air mass that had lower ozone concentrations, and the material is quickly redistributed in the mixing layer. Ozone concentrations at ground level increase rapidly because of this fumigation process. Ozone profiles in the afternoon are relatively uniform up to the top of the mixing layer. The tether-

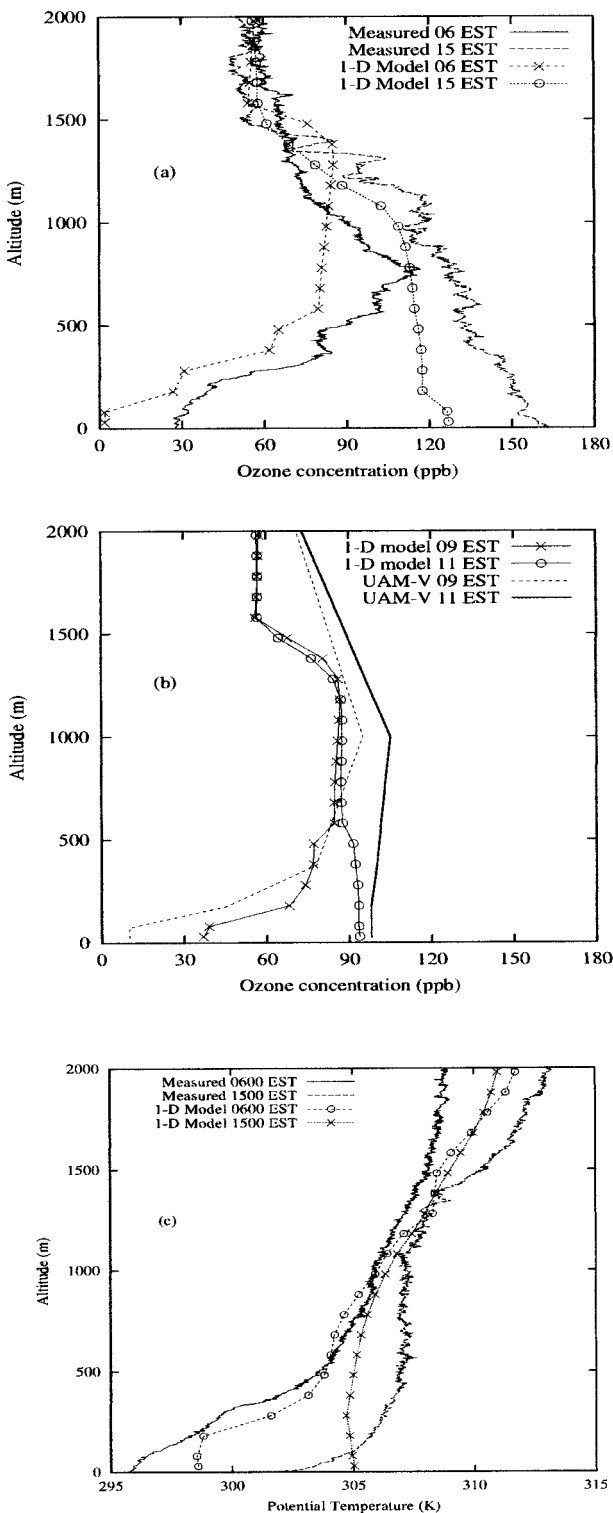


FIG. 13. (a) Comparison of ozone profiles simulated by the 1D model with those measured by the aircraft; (b) comparison of ozone profiles simulated by the UAM-V model with those from the 1D model; (c) comparison of potential temperature simulated by the 1D model with that measured by the aircraft, all on 14 July 1995.

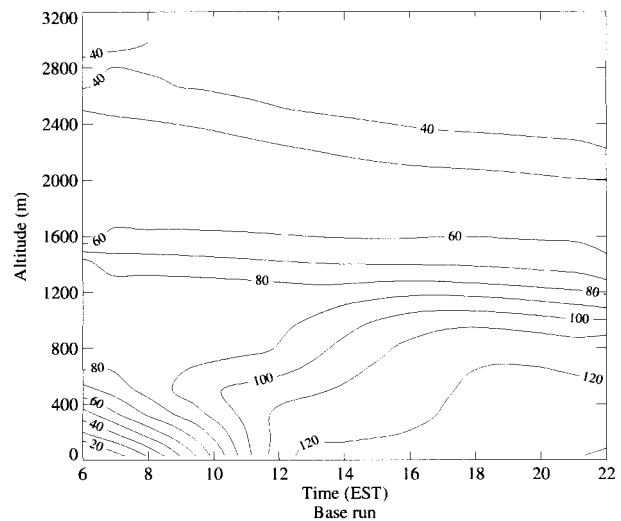


FIG. 14. Time-height cross section of simulated ozone concentrations for 14 July 1995.

sonde measurements of ozone up to a few hundred meters above the ground, taken during the NARSTO-NE summer 1995 field campaign, also reveal the presence of the high ozone concentrations above 150 m from the ground in the early morning; there is a rapid increase in ground-level ozone at a rate of about 15 ppb h^{-1} between 0700 and 0930 EST [see Fig. 12 in Zhang et al. (1998)]. Since the solar radiation and temperature during the early morning hours may not be sufficient to yield a rapid increase in ozone concentrations from photochemical reactions, the vertical mixing process might be a primary source for the observed rapid increase in the ground-level ozone concentrations during the early morning.

By noon, the ozone concentration in the newly formed mixing layer becomes higher than that aloft because of photochemical production (Fig. 12b). With further growth of the mixing layer, the convective mixing in the afternoon continues to ventilate ozone from the surface up to higher levels, as evidenced in Fig. 12b. This ventilation is consistent with data from aircraft measurements (Fig. 13a). To assess whether the 1D model is capturing the salient features of ozone behavior, the results of a 1D model were compared with those derived from a 3D photochemical model, UAM-V (Systems Applications International 1995). The ozone simulations with UAM-V for the summer of 1995 were discussed by Rao et al. (1998b). The vertical profiles of ozone as simulated by UAM-V, along with the aircraft measurements, presented in Fig. 13b, agree well with those derived from the 1D model. The potential temperature profiles as simulated by the 1D model are compared with aircraft measurements in Fig. 13c. The contours of ozone concentration in the time-height cross section, presented in Fig. 14, illustrate the temporal evolution of ozone concentrations in the vertical. The vertical gradient in the lowest boundary layer decreases in the day-

time convective mixing layer, but ozone concentrations above the maximum mixing layer height do not change much throughout the day. The slight decrease in the ozone concentration above 2000 m is caused by large-scale subsidence associated with the upper-level stable layer.

At ground level, the 1D model simulates higher ozone concentrations than those observed at Bronx, New York, before noon. This overprediction is attributable in part to the adoption of initial concentrations for the ground-level pollutants from the UAM-V simulation rather than from the observations. However, the growth rate curve of the ground-level ozone concentration simulated by the model matches well with the observations. The differences between the model simulations and observations become larger after 1800 EST, implying that those processes other than chemistry and vertical mixing, such as advection, deposition, etc., that are not included in the 1D model, become more important in the evening.

For each time step, the 1D model goes through both the chemical module and the meteorological module, and the rate of change for each time step for each process can be stored for further analysis. The rate of change in ground-level ozone concentration due to vertical mixing and chemical reactions, as well as the total rate are presented in Fig. 15a. It can be seen that the vertical mixing process produces a sharp increase in ozone concentrations as the mixing layer starts to grow and penetrate into the ozone-rich layer in the morning. The increment produced by vertical mixing processes reaches the maximum value between 1000 EST and 1100 EST. Further growth of the mixing layer causes a decrease in the ground-level ozone concentration; this decrease is because the ozone-rich air mass aloft has been entrained rapidly into the mixing layer, so the ozone concentration in the mixing layer already has reached the initial concentration aloft, and dilution will take effect with further growth of the mixing layer. The chemical production rate, however, starts increasing after sunrise and reaches its peak value at noon when solar radiation is most intense. Whereas the vertical mixing process in the morning dictates the overall shape of the total ozone tendency curve, both vertical mixing and chemical processes control it in the afternoon. The relative contributions of vertical mixing and photochemical processes to the ground-level ozone concentration for each hour are integrated according to their corresponding rates and are illustrated in Fig. 15b. These results indicate that the mixing layer growth rate as well as the maximum mixing layer height play at least an equal, if not more important, role in contributing to ground-level ozone concentrations. To assess whether the 1D model simulations are reasonable, the results of the 1D model were compared with the UAM-V simulations for the 10–18 July 1995 episode in Fig. 15c. Although the magnitudes of the rate of change simulated by the 1D and 3D models do not agree, there is good agreement between the shapes of the two curves. This

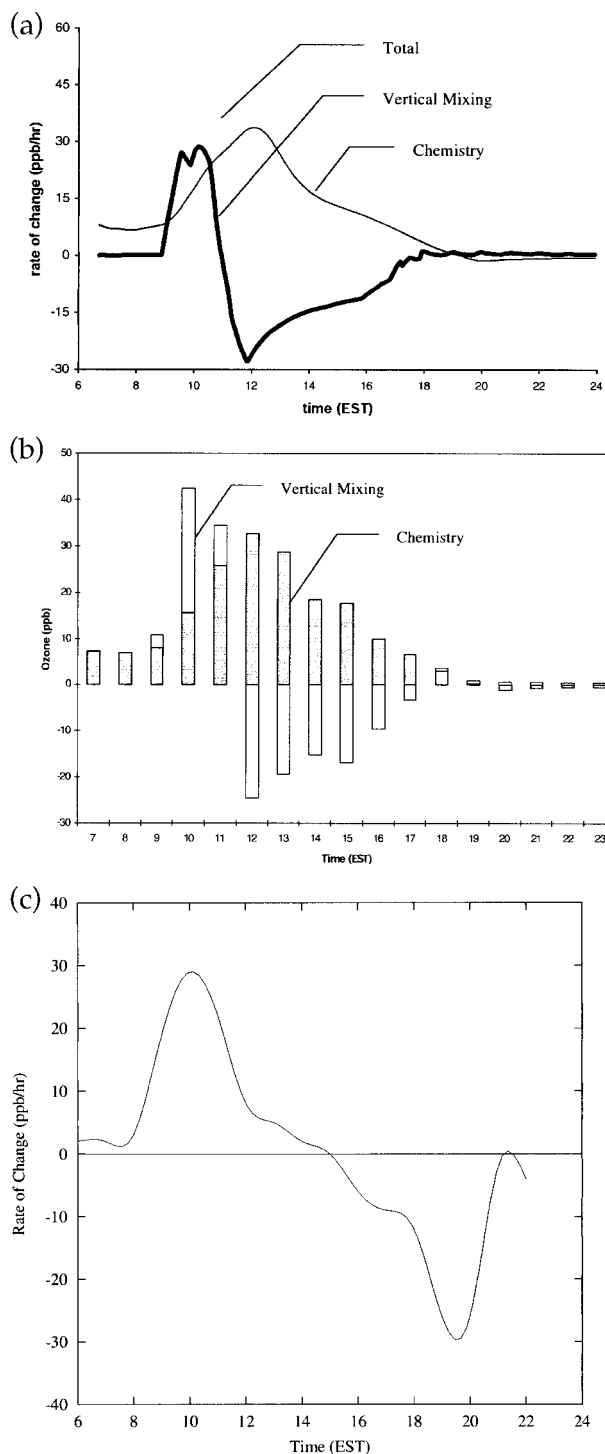


FIG. 15. (a) Rate of change in the ground-level ozone concentration for 14 July 1995. The thick dark line indicates the contribution from the vertical mixing process, the thin solid line represents the chemical contribution, and the gray line is for the total rate of change; (b) contributions from vertical mixing and chemical reactions to the ground-level ozone concentration within 1-h intervals for 14 July 1995; (c) rate of change in ground-level ozone concentration as simulated by the UAM-V model for 14 July 1995.

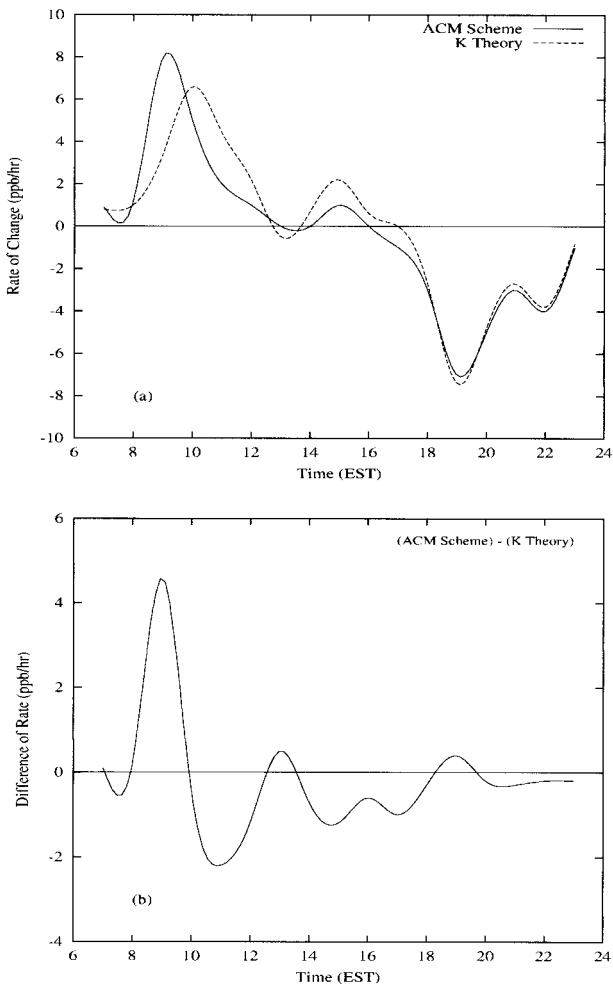


FIG. 16. (a) The rate of change in ground-level ozone concentration over an urban area simulated by the MAQSIP model for 13 July 1995 using two different vertical mixing schemes. (b) Difference between the two ozone tendencies.

agreement demonstrates that the 1D model is able to capture the salient temporal features of the ozone accumulation process.

c. Sensitivity test using 3D photochemical model

To examine the sensitivity of the model-simulated ozone concentrations to the vertical mixing schemes, a 3D photochemical model, the Multiscale Air Quality Implementation Platform (MAQSIP; Odman and Ingram 1996), is used with two different vertical mixing schemes: *K* theory and the Asymmetrical Convection Model (ACM). The MAQSIP modeling domain covers the states of Georgia and Alabama with a horizontal resolution of 18 km and 26 vertical layers. Two simulations were performed for 12–13 July 1995 using the *K* theory option and the ACM option in MAQSIP while keeping all model inputs, namely, meteorological and air quality data and the emissions inventory, the same.

TABLE 2. Emission reduction simulation scenarios.

Run no.	Run description
Run 1:	Base run
Run 2:	Reduce all ground-level emissions
Run 3:	Reduce 50% of O_3 and precursors in the nighttime residual layer
Run 4:	Reduce 50% of ground-level VOC emission
Run 5:	Reduce 50% of ground-level NO_x emission

The ozone tendency at ground level over an urban area as simulated by MAQSIP for 13 July 1995 is illustrated in Fig. 16a and the difference between the rate of change from the two simulations is presented in Fig. 16b. These results reveal that replacing the treatment of vertical mixing by *K* theory with a more diffusive mixing module within MAQSIP has its greatest effect when the vertical mixing process is initiated for the day. The use of the ACM approach results in an earlier mixing down of ozone from aloft soon after sunrise. Thus, the simulations from a 3D model complement the results of the 1D model for the effects of the vertical mixing process on the ground-level ozone concentration.

4. Implications for emission control strategies

To reduce ground-level ozone concentrations in ozone nonattainment areas, various emission control strategies are being considered by policy makers. To examine the implications of the vertical mixing processes for designing emission control strategies, four additional simulations (Run 2–Run 5) have been performed for the above urban site, in addition to the base case run (Table 2).

The percentage ozone reductions relative to the base run (Run 1) are shown in Fig. 17. The ground-level ozone concentrations predicted under each scenario are shown also in Fig. 18. It can be seen that Run 3, for which ozone and precursors in the nighttime residual layer were reduced by 50%, provides the largest reduction in the ozone concentrations in the boundary layer and in the ground-level ozone concentration. Other cases, including even the elimination of all local precursor emissions, are less effective in reducing the ozone problem at local urban sites because of the presence of high concentrations of ozone and precursors aloft. Considering the regional nature of high ozone concentrations in the nighttime residual layer, the magnitudes of ozone and precursor concentrations aloft are dictated not only by local emission sources but also are impacted by transport from upwind source regions. The results about the importance of vertical mixing processes presented in this paper are consistent with those reported by Trainer et al. (1991) and Kleinman et al. (1994).

5. Summary

Comparisons of diurnal patterns of ozone concentrations at some elevated and ground-level sites suggest

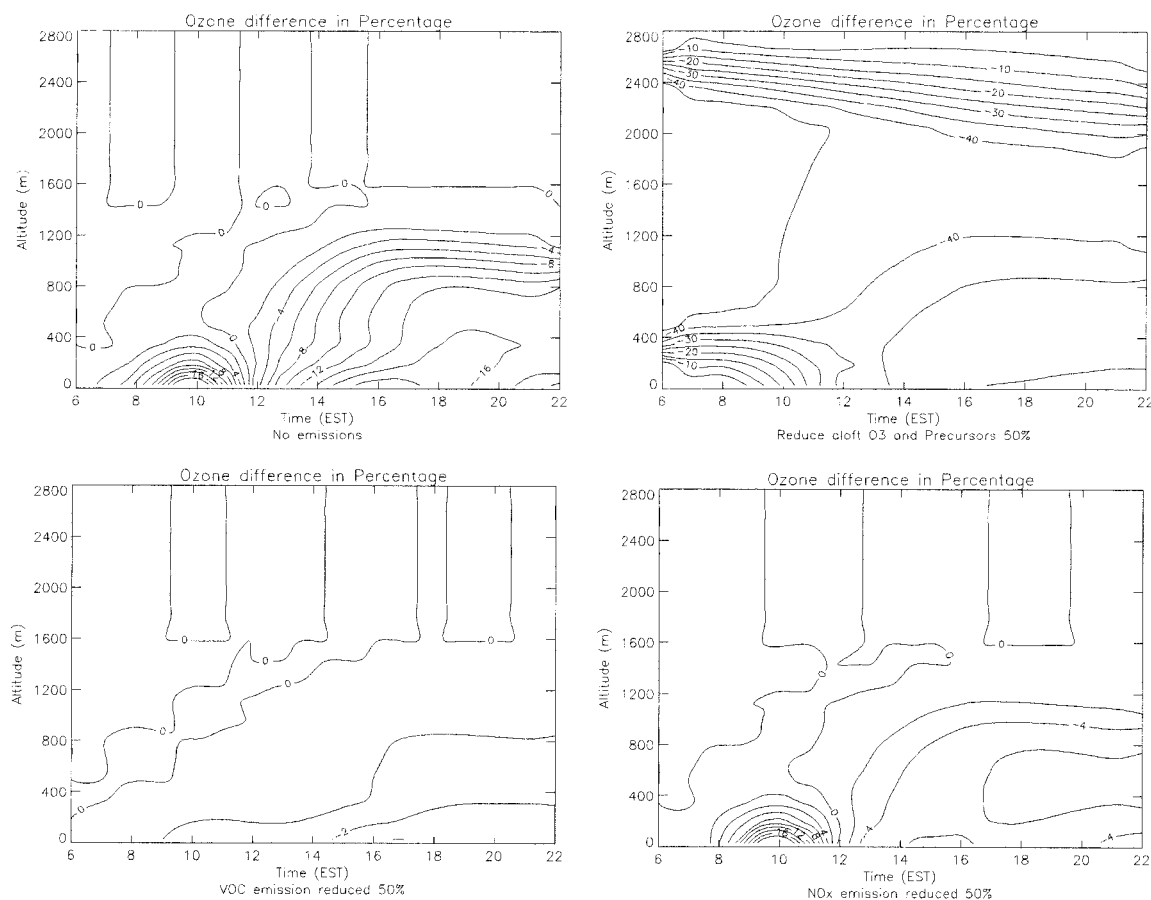


FIG. 17. Percent reduction in ozone from the base case over an urban area under different emission control strategies, as labeled.

that ozone aloft in the nighttime residual layer exerts a major influence on the temporal evolution of the ground-level ozone concentration through vertical mixing processes. Flux measurements of ozone, NO_x , heat, and momentum at the Harvard Forest site demonstrate the downward transport of ozone to the ground and its correspondence to the downward momentum flux and upward heat flux in the atmospheric surface layer during the daytime convective regime. For rural areas, calculations using flux divergence suggest that the vertical mixing process is the sole mechanism for increasing the ground-level ozone concentration in the morning. These results are consistent with aircraft measurements of ozone vertical profiles in the rural area. Ozone profiles over the urban area show that, in addition to the vertical mixing process, photochemical production in the daytime mixing layer also is important for the ozone accumulation at the ground level.

To assess the relative contributions of vertical mixing and chemical processes to the ground-level ozone concentrations, a 1D model that incorporates the boundary layer dynamics and photochemistry was used at an urban site for a typical ozone episode. The model simulation results indicate that photochemical ozone production gradually increases in the morning, reaches a

maximum in the midday, and then decreases. The vertical mixing process affects the ground-level ozone concentration in two ways. First, during the early stages of the mixing layer growth, vertical mixing contributes a large increment of ozone to the ground level, exceeding that from chemical production. Second, after the ozone concentration in the mixing layer becomes equal to or larger than that in the topped stable layer, further growth of the mixing layer leads to a strong dilution and thus a negative contribution to ground-level ozone concentrations as ozone starts to build up from photochemical production. The sum of the two contributions becomes smaller in the afternoon, leading to a much slower increase in the ground-level ozone concentration.

Model simulations with different levels of emission reduction and a 50% reduction in the levels of ozone and precursor concentrations in the nighttime residual layer aloft also were performed. These results indicate that a reduction of 50% in the levels of ozone and its precursors aloft leads to a greater improvement of ozone concentrations at ground level and in the boundary layer than that achieved from reductions in local emissions. Thus, a regionwide emission control strategy should be the most effective way to manage the ozone air quality problem in the northeastern United States. These results

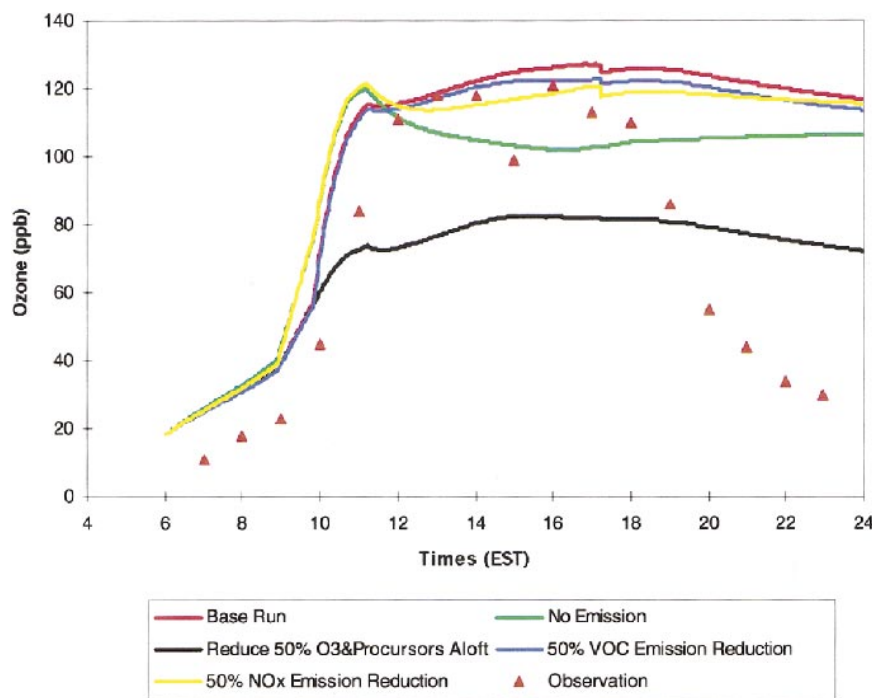


FIG. 18. Ground-level ozone concentrations for an urban area under different emission reduction scenarios, as labeled.

are consistent with previous studies on vertical mixing process and ozone transport and provide more evidence and support on air quality management for policy making.

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