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Climatology of Diurnal Trends and Vertical Distribution of Ozone in the Atmospheric Boundary Layer in Urban North Carolina

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ABSTRACT

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. During summer 1993, 1994, and 1995, ozone was monitored at ground level, 250 m, and 433 m. Boundary layer wind, temperature, and other meteorological variable profiles were determined from balloon soundings. During summer 1996 and 1997, ozone was monitored at ground level, 76 m, 128 m, and 433 m.

This paper presents the analysis and discussion of the five-year data. The evolutions of the convective boundary layer during daytime and the stable nocturnal boundary layer (NBL) were found to have marked impacts on ozone concentrations. A strong diurnal pattern, with an afternoon maximum and an early morning minimum, was dominant at ground level, but it was much weaker at elevated levels and insignificant above the NBL at night. Ozone deposition velocities at night during the measurement periods were estimated to range from 0.09 to 0.64 cm/sec. We found evidence of regional transport of ozone and/or its precursors from northwest and north of the site, which may play a role in high ozone events in the Raleigh-Durham area.

Ozone concentrations between the various elevated levels were well correlated, while correlations between the ground and upper levels were much weaker. However, a strong correlation was found between the nighttime and early morning ozone concentrations ($\overline{C}_R$) in the residual layer above the NBL and the maximum ground level concentration ($\overline{C}_{o\ max}$) the following afternoon. Based on this correlation, the latter may be predicted by an observational model $\overline{C}_{o\ max} = 27.76e^{0.016\,\overline{C}_R}$.

IMPLICATIONS

Knowledge of the vertical distribution of ozone in the planetary boundary layer (PBL) is essential to develop an effective SIP for ozone control. Vertical measurements of ozone in and above the surface inversion layer are needed as inputs to the urban airshed model (UAM). The distribution of ozone in the PBL is irregular due to localized production zones and the dynamic processes of the region. The irregular features in the production are due to the variation in afternoon solar ultraviolet flux, caused by absorption and scattering of clouds, and to emission and redistribution of precursor chemicals caused by localized sources and dynamic redistribution. The summer afternoon periods that are most conducive to ozone production are also periods of intense convective mixing in the PBL. Precursor chemicals are drawn into turbulent eddies from localized sources and from horizontally advected sources located near the top of the boundary layer or folded into the boundary layer by meteorological processes. The irregular nature of the summer afternoon ozone distribution can be observed in vertical profiles and time sequences of ozone measurements. At other times of the day, the stable nocturnal boundary layer may exhibit almost constant ozone values.

INTRODUCTION

Ozone, an important photochemical air pollutant, plays an important role in tropospheric chemistry. It is produced in the troposphere from the reactions between ozone precursors, nitrogen oxides (NO_x), and nonmethane hydrocarbons (NMHCs) in the presence of sunlight. Based on the absorption characterization of the major atmospheric pollutants, nitrogen dioxide (NO_2) is the most efficient absorber of the fraction of the sun's UV radiation between 290 and 380 *n*m.

Over the past few decades, much research has been done on the formation and analysis of ozone in the troposphere,[1-4] and ozone behavior under specific meteorological conditions such as nocturnal boundary layer (NBL) has also been well characterized.[5-9] However, most of the studies are limited to the ground level. Aneja et al.[10] and Aneja and Li[11] studied the ozone behavior at high elevations in the eastern United States and found that ozone concentrations and trends are significantly different at high elevations than at low-elevation continental sites. There has been little information[12] on the typical pattern of vertical ozone profile at low elevations in the atmospheric boundary layer as a function of meteorological variables and season.

In the troposphere, measurements of ozone include balloon radiosondes, aircraft, and surface measurements. For a long time record, airborne measurements (e.g., radiosondes and aircraft) over a short time interval seem impractical because of high cost and other limitations. A 610-m television broadcasting tower located about 15 km southeast of Raleigh, NC, provided the opportunity to perform multi-elevation atmospheric sampling. Ozone data were collected 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). Vertical measurements of ozone in and above the surface inversion layer were needed as inputs to the urban airshed model (UAM); these were made from the 610-m tower. Boundary layer wind, temperature, dew point, and mixing ratio profiles were determined by balloon soundings.

Ozone was sampled at ground level (about 97.5 m above sea level), middle level (250 m), and high level (433 m) during summer 1993, 1994, and 1995, and also at ground level, 76 m, 128 m, and 433 m during summer 1996 and 1997. In this paper, the five-year data set is analyzed to investigate the climatology of ozone concentrations and their diurnal patterns at different heights. The vertical distributions of ozone in the planetary boundary layer (PBL) and correlations between concentrations at the ground and elevated levels are also examined. These are explained in terms of the diurnal evolution of the PBL and the transport, production, and deposition processes that influence ozone concentrations. A simple method of predicting the maximum ground level ozone concentration is suggested from the data analysis.

EXPERIMENT

During summer 1993, three ozone monitors, three hydrocarbon samplers, and three carbonyl samplers were operated at ground level, middle level (250 m), and upper level (433 m). Sampling began on July 23 and continued until September 3. These observations were repeated in summer 1994, when sampling began on June 24 and ended on September 9. In summer 1995, only ozone was monitored at the tower, and the sampling began May 16 for ground and 250-m levels, and on May 25 for 433-m level, and continued until October 2. During 1996 and 1997, two new measurement levels at 76 m and 128 m replaced the 250-m level. In 1996, sampling started at ground level on May 30, at 76 m on May 24, at 128 m on May 23, and at 433 m from May 17; sampling ended September 19. In 1997, all levels started sampling May 15 and ended September 11, except for ground-level sampling, which ended October 31.

Samples were collected at 10 m, 250 m, and 433 m on the Auburn Transmitter Tower, a 610-m multicommunications tower located near the town of Auburn, NC (N Latitude 35° 40’ 35”; W Longitude 78° 32’ 09”) The sampling site is ~15 km (10 miles) east-southeast of downtown Raleigh, NC (population ~250,000). The site is close to major highways, most notably U.S. Highway 70 and Interstate 40.

From a base elevation of 96 m above mean sea level (MSL), the tower rises over 600 m. The adjacent fetch can be described as a mixture of cleared farmlands and small forest plots composed of a mixture of deciduous and coniferous trees. Situated between low-rolling hills of the Uwharrie mountains (elevation 180–275 m), approximately 100 km to the west, and the flat topography of the coastal plain to the east, the geography of the experiment site near the tower is fairly uniform, with small changes (30 m or less) in elevation.

The tower has platforms at various levels. Access to the levels is by a two-person elevator in the center of the tower’s tripod configuration. These platforms are large enough to support several small cabinets to house monitoring and testing equipment. The cabinets were used for hydrocarbon and carbonyl samplers. Ozone monitors and calibrators were located in a temperature-controlled building at the base of the tower. Ozone sampling was done using 15.9-mm i.d. sample lines of FEP Teflon tubing connected to a high-volume pump. The residence time in the sample line was less than 20 sec for ground level, 1.68 min for 76 m, 2.43 min for 128 m, 4.2 min for 250 m, and 6.85 min for 433-m level. The ambient air was withdrawn from the sample line by the ozone analyzers at ground level. Access to the tower was limited to Tuesday through Friday.

The sample probe assembly at each level included a 90-mm Teflon filter holder with a Teflon particulate filter. Each probe arm, made of stainless steel tubing, extended approximately 2 m from the tower platform, with about a 60° downward bend on the arm to minimize precipitation entering the probe line. The probes were located on the southwestern part of the tower for best exposure to the predominant southwesterly summer winds. A tower rigger was contracted to install the sample lines and probes on the tower.

Ozone was measured using the UV photometric detection principles. A Dasibi 1003 AH analyzer was used at each level. The instrument is designated as "equivalent methods" by the U.S. Environmental Protection Agency (EPA). A single, photometer-type calibrator was used to calibrate and check all three monitors daily to minimize variability in calibrations. The output of the monitors was connected to a data logger and to a backup data system to minimize data loss.

Ozone was monitored continuously for 23 hr/day, with 1 hr set aside for automated zero/span checks in the early morning hours between 3:00 and 6:00 a.m. EST. These check results and the hourly ozone averages were reviewed daily via modem at the main office of the Division of Air Quality. The zero/span check was used to determine whether a site visit was needed for further checking. To perform automated zero/span checks, a zero-air and one-span concentration were introduced into each analyzer. The span gas concentrations were 70–90% of the analyzer's nominal operating range (0.50 parts per million by volume [ppmv]). During routine sampling and automated zero/span checks, the monitors' span numbers were based on the statewide average barometric pressure corrected for elevation above ground level. The calibrator span number was based on the statewide average barometric pressure.

Frequent manual zero/span checks were used to determine the need for analyzer adjustments. No adjustments were needed during any of the five measurement seasons. To perform the manual zero/span checks, zero air and span concentration (0.35–0.45 ppm) were introduced into each analyzer through the 47-mm particulate filter. During these checks, the analyzers operated in their normal sampling modes, but the span numbers for the two monitors were adjusted to reflect average ground barometric pressure for the checks. Precision checks were performed in the same manner as manual span checks, except the precision check concentration was 16–20% of the analyzer's full-scale range (0.08–0.10 ppm). The gaseous standards for span and precision concentrations were obtained by an ozone generator, with ozone concentrations determined by a certified ozone transfer standard.

Accuracy audits were performed by the Division of Air Quality, usually at the beginning and the end of each measurement period, to document the difference between the analyzer response and the reference value obtained during the multi-point instrument audit. The differences resulting from accuracy audits were less than 8%.

To minimize line loss, the 15.9-mm i.d. sample lines were conditioned with 2 ppmv of ozone for seven days at a flow rate of 5 Lpm several days prior to the installation on the tower. Teflon inlet filters were used on the line near the intake on the tower to prevent particulate matter from entering the sample lines. These filters were also conditioned with ozone to minimize the potential ozone scavenging. Tests for line loss or gain were conducted near the beginning, in the middle, and at the end of each measurement period, by taking a certified calibrator to each level. At each level, 30 readings were taken from the calibrator while sampling ambient air. All values were corrected for zero offset of the instruments. The average results from the calibrator were compared to the appropriate monitor average response to approximate the loss of ozone in the sample lines.

During the 1993–1995 measurement periods, meteorological variables were obtained by using radiosondes attached to balloons, which were generally launched at 7:00 a.m., 1:00 p.m., and 7:00 p.m. each weekday; additional balloons were launched at 10:00 a.m. and 4:00 p.m. on days when ozone concentrations were predicted to be high. The variables measured from the radiosondes included dry and wet bulb temperatures and atmospheric pressure; these were used to compute mixing ratio and potential temperature. A theodolite was used to determine wind speed, wind direction, and the height of the balloon. Azimuth and elevation angle measurements were taken every 30 sec from the time of launch.

RESULTS AND DISCUSSION

Seasonal and Interseasonal Ozone Variations

Hourly ozone concentrations at the ground and elevated levels were used to calculate monthly averages for each year. Table 1 gives summary results of mean and maximum ozone concentrations for the summer months during 1993–1997. Mean concentrations at the ground level were generally lower than those at higher elevations in the mixed layer. The differences in the maximum concentrations at different levels were less discernible.

Figure 1 illustrates the frequency distributions of hourly ozone concentrations from 1993 to 1997. In 1993, the maximum frequency of hourly ozone concentration shifted from 25–35 parts per billion by volume (ppbv) (frequency 23%) at the ground level to 65–75 ppbv (27 and 28%) at the two upper levels. In 1994, ozone concentrations were evenly distributed in the range of 15–55 ppbv (14–17%) at the ground level, 25–55 ppbv (about 20%) at 250 m, and 35–55 ppbv (27%) at the uppermost level. In 1995, even distribution of ground ozone, ranging from 5 to 85 ppbv (about 10%), was also found, but the concentrations reached higher values of 65–75 ppbv, with 25% at 250 m and 33% at 433 m.

In 1996, the maximum frequency of ozone concentrations, 15–25 ppbv (18%), shifted to 45–55 ppbv (about 21%)

at 76 and 128 m, and to 45–65 ppbv (26%) at 433 m. In 1997, the dominant concentrations at ground level ranged from 15 to 55 ppbv (13–17%), increasing to 25–65 ppbv (14–17%) at the 76-m level, 35–65 ppbv (17–19%) at the 128-m level, and 45–75 ppbv (18–23%) at the 433-m level. We noticed that generally the most frequent occurrence shifted from lower to higher ozone concentration with the increase of elevations.

Effects of Meteorological Conditions on Ozone Concentrations

Meteorological conditions play an important role in the formation and destruction of ozone. Over the past two decades, the effects of meteorology on ozone formation have been studied.[5-10] The most frequent investigation has involved the relationship between ozone concentration and atmospheric temperature, but the relationship between daily ozone maximum concentrations and maximum temperatures has also been examined.[13]

Figure 2 shows the correlation between hourly ground-level ozone concentrations and temperatures in July and August 1993–1995. Ozone concentration generally increased with

Table 1a. Mean and maximum ozone concentrations (ppbv) during summers 1993–1995.

	Ground Level		250 m		433 m	
	Mean	Max	Mean	Max	Mean	Max
1993						
July	38	88	49	103	57	105
Aug	34	94	60	107	61	105
1994						
June	43	75	46	76	54	79
July	32	97	39	73	47	94
Aug	36	99	48	97	44	76
1995						
June	35	93	48	100	47	87
July	40	107	53	104	54	99
Aug	41	114	50	120	48	101
Sep	30	76	46	87	49	86

Table 1b. Mean and maximum ozone concentrations (ppbv) during summers 1996–1997.

	Ground Level		76 m		120 m		433 m	
	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.
1996								
June	40	105	54	113	55	108	58	117
July	40	119	49	122	51	118	53	112
Aug	34	96	49	94	54	93	57	85
Sep	25	77	38	83	42	86	44	86
1997								
May	44	91	51	91	56	100	51	84
June	37	96	47	98	50	104	49	99
July	49	118	54	112	58	108	64	105
Aug	45	104	53	99	61	115	63	104
Sep	39	96	39	90	58	107	56	90

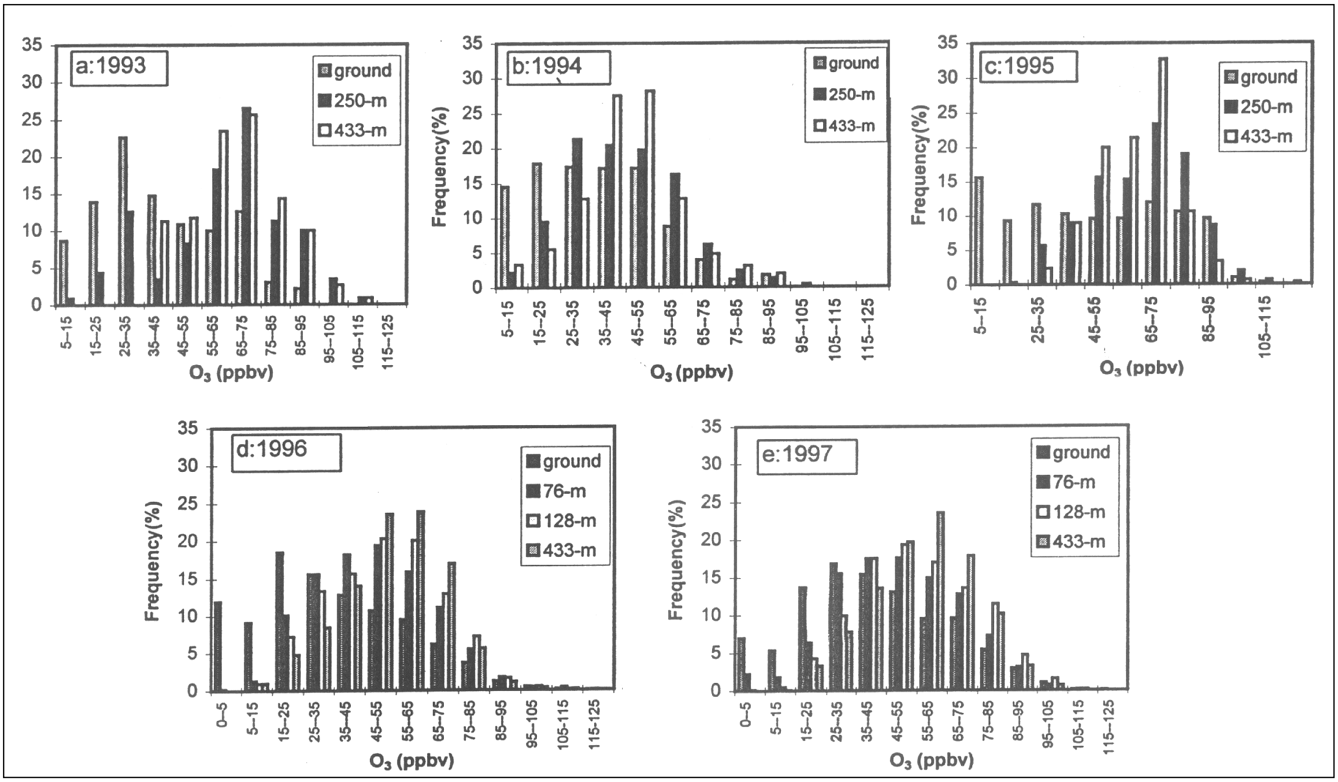

Figure 1. Frequency distribution of ozone concentrations measured at various heights during summers 1993–1997.

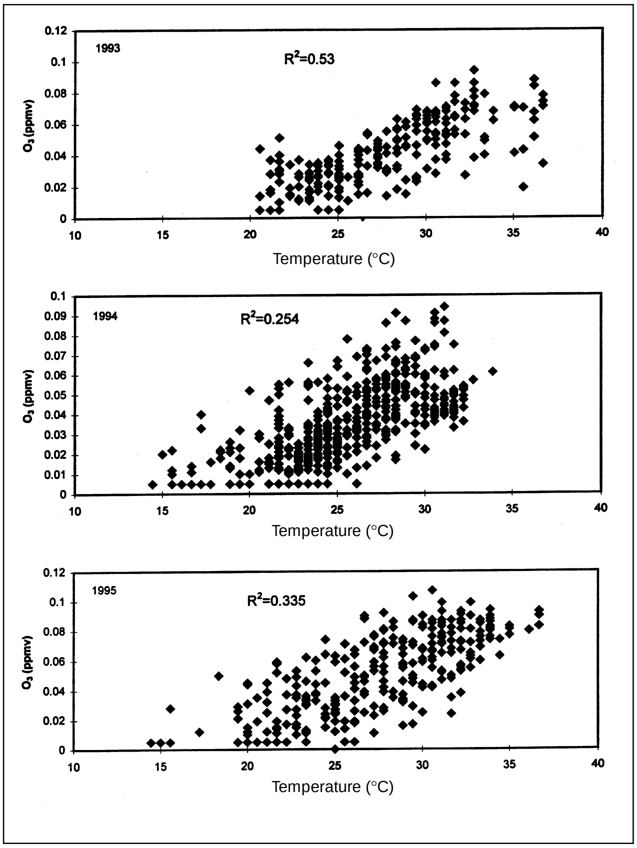

Figure 2. Ozone concentration versus temperature at ground level during summers 1993 to 1995.

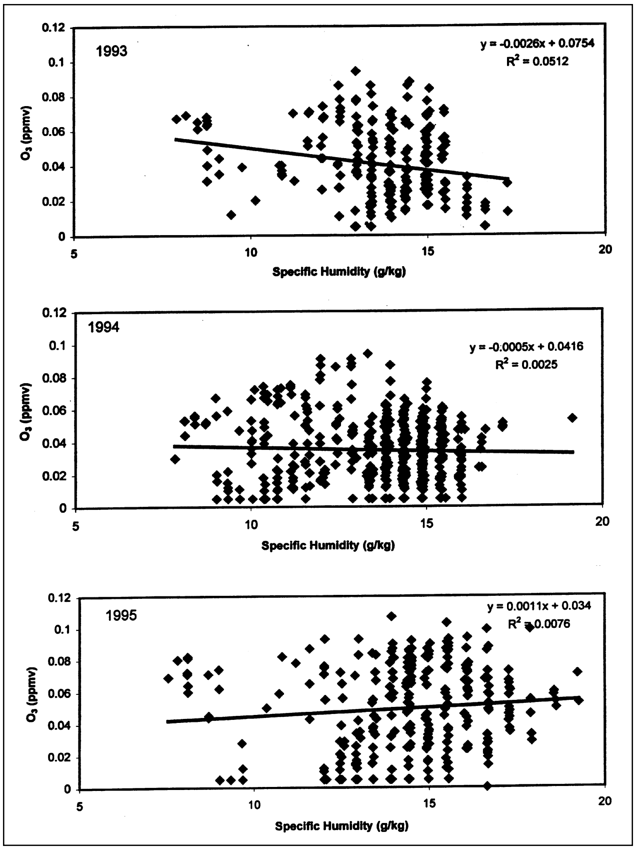

Figure 3. Ozone concentration versus specific humidity at ground level during summers 1993–1995.

increasing temperature (correlation coefficient, R = 0.50 – 0.73), which agrees with the results of previous studies and supports the notion that ozone formation kinetics intensifies with increasing temperature.

Humidity is also a factor that influences ozone formation. Water vapor in the atmosphere can enhance the removal of short-lived and highly reactive radicals (i.e., $HO_x = HO + HO_2$), which are important precursors for ozone formation. DeMore et al.[14] showed that HO_2 decreased dramatically with increasing water vapor concentration, which is consistent with the reaction: $H_2O + 2HO_2 \rightarrow H_2O_2 + O_2 + H_2O$.

Figure 3 illustrates the relationship between surface ozone concentration and specific humidity. We found no significant relationship between ozone concentration and specific humidity in 1993, 1994, and 1995 at our site.

In the eastern United States, high ozone is often associated with synoptic-scale high-pressure systems.[10,11,15-17] Figure 4 shows this general relationship between ground-level ozone concentration and the passages of high-pressure systems. We see that passages of high-pressure systems during the periods of July 11–14, 1995, and August 9–12, 1994, were associated with high ozone episodes (concentrations >100 ppbv on July 11, 1995 and >90 ppbv on August 10, 1994). In both cases, peak concentrations were attained almost two days prior to the peaking of pressure. Forty-eight-hr back trajectory analysis at 500 mbars was performed at the site during the high ozone events (Figure 5). This analysis shows that the high-ozone days were associated with northerly or northwesterly flow patterns, suggesting air mass sampled at the site passed through the Ohio Valley, exposing the air masses to high-ozone or ozone precursor sources, as it moved over the Midwestern states.

The dependence of seasonally averaged ground-level ozone concentration on wind direction is depicted in Figure 6, which indicates that ozone levels were higher when wind directions ranged between 270° and 360°, and between 0° and 90°. If the Raleigh-Durham area is located at the foreside (east) of a high-pressure system, the expected wind direction will be from the north. Based on these observations, we may conclude that the passage of high-pressure systems that transport ozone and/or its precursors from the northwest and north may be an important factor for high-ozone episodes in the Raleigh-Durham MSA.

Development of the PBL

The height of the PBL, also commonly known as the mixing height, is an important parameter in studying air

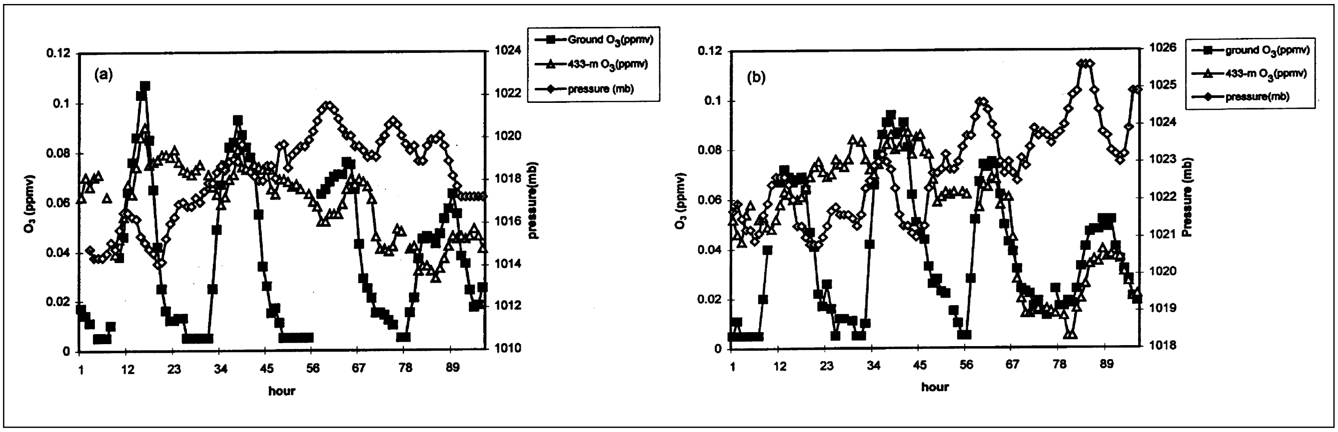

Figure 4. High ozone occurrence associated with high-pressure system passage during the periods of (a) July 11–14, 1995, and (b) August 9–12, 1994.

pollutant dispersion in the atmosphere. In the daytime unstable and convective boundary layer, air pollutant concentration and meteorological variables (e.g., potential temperature, mixing ratio, etc.) are distributed uniformly in a vertical direction. Mixing height is also an important parameter in modeling transport and the dispersion of chemical and photochemical pollutants on local/urban and regional scales. The height of the PBL was determined from profiles of temperature and mixing ratios obtained from radiosonde measurements during the 1993–1995 period, and the results for the three summer seasons are presented in Table 2. Following sunrise in early morning, the mixing height began to increase with the increase in surface temperature, reaching about 200 m at 7:00 a.m., which was still lower than the middle level of ozone measurement (250 m). At 1:00 p.m., the average of mixed height was about 1020 m, well above the upper level of ozone measurement (433 m). At 7:00 p.m., the average of PBL height further increased to 1270 m, near its maximum value for the day. Shortly after this time, the NBL began to form near the surface due to the cooling of the ground surface. There were no launches of radiosonde balloons at night.

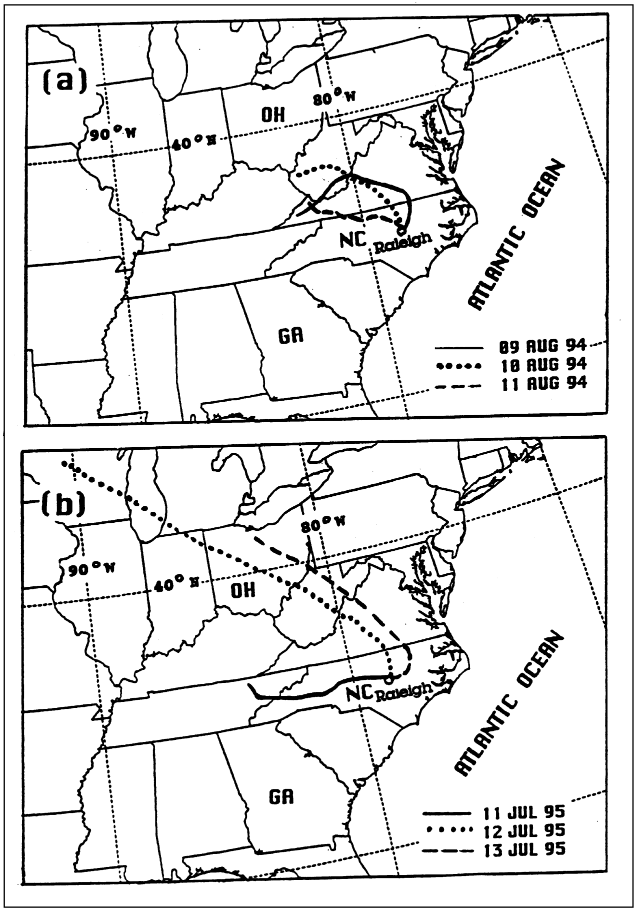

Figure 5. Forty-eight-hr back trajectory analysis ending at 1200 EST at 500 mbars at Auburn, NC (N Latitude 35° 40' 35"; W Longitude 78° 32' 09") during the periods of (a) August 9–11, 1994, and (b) July 11–13, 1995.

We may assume, as suggested by Arya[18] on the basis of sounding data from other locations at night, that the mixing height (or depth of NBL) was in the range of 50–200 m. Oommen[19] examined ozone concentrations, PBL heights, and meteorological variables including temperature, mixing ratio, dew point, and potential temperature within the PBL in 1993, 1994, and 1995, showing that there were no significant differences among these three years, except that the average dry bulb temperature was significantly higher in summer 1993 than in the other two years. This probably was an influencing factor for high ozone concentrations in 1993.

Ozone Concentrations in the PBL and the Surface Flux/Deposition

Figure 7 shows the diurnal variations of ozone concentrations at different measurement levels. The surface ozone exhibited the largest diurnal variations, with mid-afternoon maxima of 68 ppbv (1993), 57 ppbv (1994), 78 ppbv (1995), 60 ppbv (1996), and 67 ppbv (1997), and early morning minima within a narrow

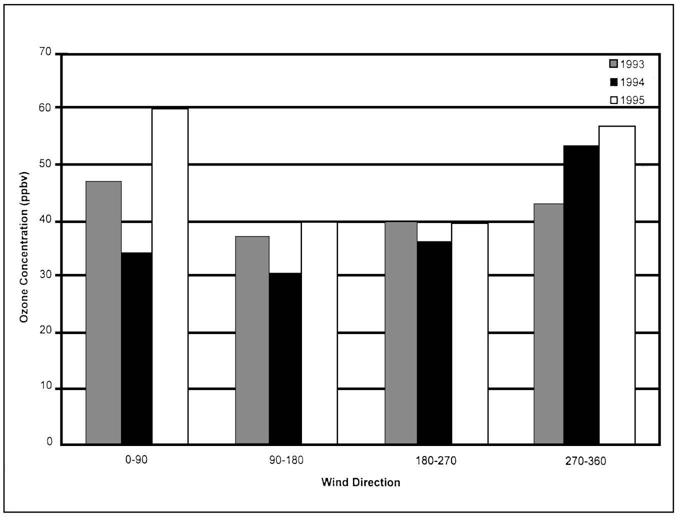

Figure 6. Ground-level ozone concentration versus wind direction during summers 1993–1995.

range of 14–18 ppbv. Notice that maximum ozone was significantly higher in 1995 than in 1994 by 21 ppbv, while minimum ozone concentrations were not significantly different between these years. Concentrations in daytime were typically three times as large as those at nighttime.

At nighttime, the presence of temperature inversion isolates the surface level ozone from that of upper levels, as there is no or very little vertical mixing between the surface layer and the levels above NBL. Surface ozone is partly removed by deposition and reaction with nitric oxide. Since no ozone is produced in the absence of sunlight, ozone concentrations began to decrease after sunset (about 8:00 p.m.), reaching minimum in early morning before sunrise (5:00 or 6:00 a.m., as shown in Figure 7). Assuming that dry deposition is responsible for most of the nocturnal ozone loss, ozone decay at nighttime due to first-order process can be expressed as[6]

$$-\frac{d[O_3]}{dt} = k[O_3] \tag{1}$$

where k is rate of ozone loss (sec^{-1}). It can be obtained by plotting $\ln[O_3]$ against time from 8:00 p.m. to 6:00 a.m. EST. The effective deposition velocity, v_d, can be determined from the loss rate, k. The estimated NBL depth, h, and the surface flux, F, can then be calculated from ozone concentration $[O_3]$ and dry deposition velocity, v_d, using the expressions[6,20]

$$v_d = k\,h \tag{2}$$

$$F = v_d\,[O_3] \tag{3}$$

Estimated deposition velocities ranged from 0.09 to 0.64 cm/sec, and agreed with those obtained by Kelly et al.[6] (0.06–0.34 cm/sec) and Colbeck and Harrison,[21] who used similar procedures. Surface ozone fluxes ranged from 0.37 to 6.66 × 10^{11} molecules/cm^2/sec, consistent with the results of Kelly et al.[6]

After sunrise, the mixing height began to increase as the surface was heated and the nocturnal inversion was

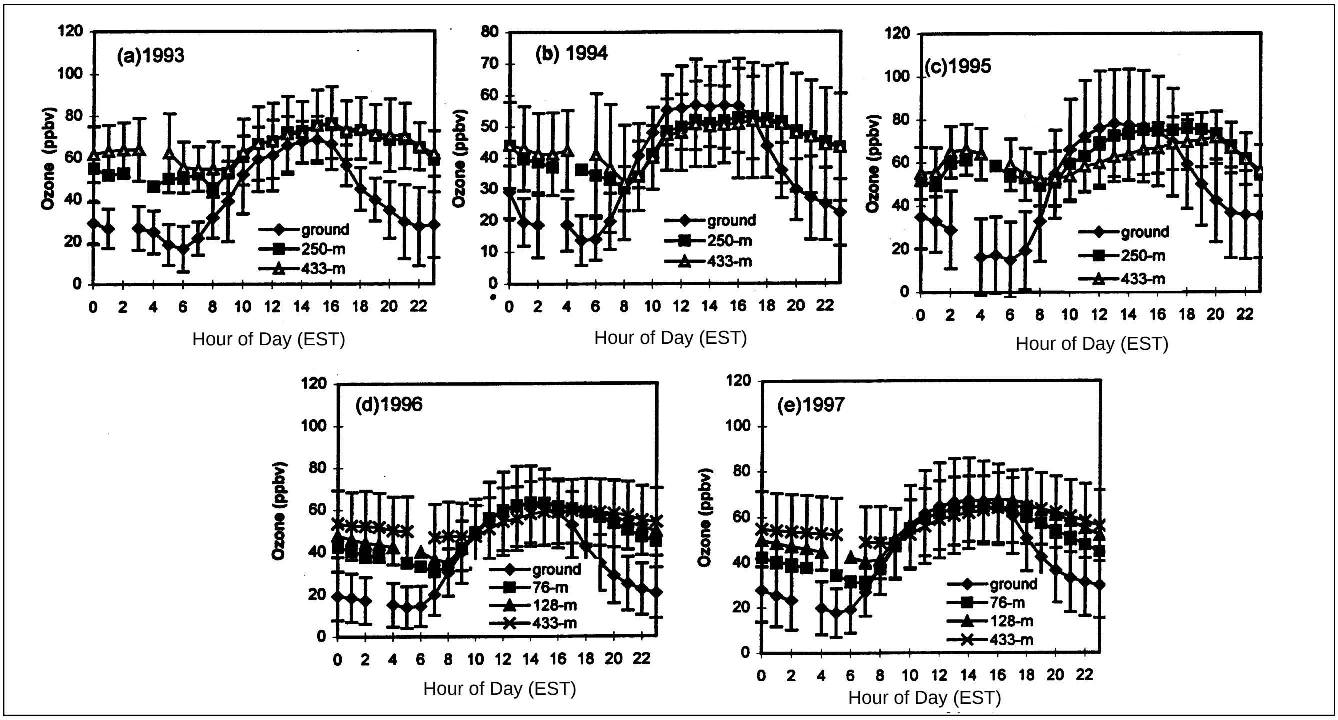

Figure 7. Diurnal profiles of ozone concentration during summers 1993–1997; vertical bars represent ±1 standard deviation for ground and 433-m levels.

Table 2. Means and standard deviations of the height of planetary boundary layer at different times of the day during summers 1993–1995. Values in parentheses stand for ±standard deviation.

Year	Number of Soundings at 7:00 p.m. EST	Mixing Height (m)	Number of Soundings at 1:00 p.m. EST	Mixing Height (m)	Number of Soundings at 7:00 p.m. EST	Mixing Height (m)
1993	19	195 (50)	17	1007 (136)	11	1384 (209)
1994	23	194 (34)	7	993 (169)	2	1610 (96)
1995	8	241 (99)	8	1076 (201)	8	1028 (96)
Total	50[a]	202 (61)	32[a]	1021 (169)	21[a]	1270 (134)

[a] Totals.

destroyed. This resulted in downward mixing of ozone from aloft. Surface ozone was also locally generated by reactions of NO_x with VOCs in the presence of sunlight, with concentrations increasing rapidly from 6:00 to 11:00 a.m., as shown in Figure 7. By 1:00 p.m., the average of mixing height exceeded 1000 m and ozone was well mixed within the mixing layer. Strong photochemical production and strong convection in the mid-afternoon period caused ozone concentrations to reach peak values in the late afternoon. Ozone production decreased with diminishing intensity of sunlight, resulting in a decrease of concentrations with time. At sunset, concentrations decreased to about half of the afternoon maximum value. As the new NBL began to form in the evening, ozone concentrations near the surface continued to fall due to surface deposition.

Although the diurnal pattern at the surface is obvious, it is less pronounced with increasing height and almost insignificant at the highest measurement level. We see from Figure 7 that the amplitudes of diurnal profiles at elevated levels were much less than those at ground level. Balloon observations[22,23] have shown that the ozone above the surface-based inversion is effectively cut off from all sinks, while below the inversion it is removed by dry deposition. Investigations of high-elevation ozone[10,11,24] have shown a reversed diurnal pattern of ozone at these high elevations, which lie above the shallow NBL. Ozone at elevated levels above the NBL may not be destroyed due to surface deposition combined with advective processes, so ozone levels at these elevations remained relatively high during nighttime (Figure 7). Figures 8 and 9 correlate ozone concentrations between different elevations; correlations between 250 and 433 m (R = 0.94) and between 76 and 128 m (R = 0.90) were the strongest, while those between ozone concentrations at the surface and higher elevations were much weaker (R = 0.60-0.73). Due to the strong correlation of ozone found between 250 and 433 m during earlier years, the 250-m measurement level was replaced by two new levels, 76 and 128 m, in 1996. The lower measurement heights were chosen so that one or both of them would lie within the NBL.

Recall that surface ozone concentrations increased significantly in the morning due to mixing down of ozone from the previous day's reservoir aloft, together with photochemical production from local sources of its precursors. The increases in concentrations from 7:00 to 11:00 a.m. averaged 38 ppbv in 1993, 36 ppbv in 1994, 53 ppbv in 1995, and 35 ppbv in 1996 and 1997. In the absence of horizontal advection, changes in concentrations in the atmospheric boundary layer are due to the vertical turbulent transport and chemical transformations.[25-27] The conservation equation describing the time rate of change of concentration can be expressed as

$$\frac{\partial \overline{C}}{\partial t} = -\frac{\partial \overline{w'c'}}{\partial z} + Q \qquad (4)$$

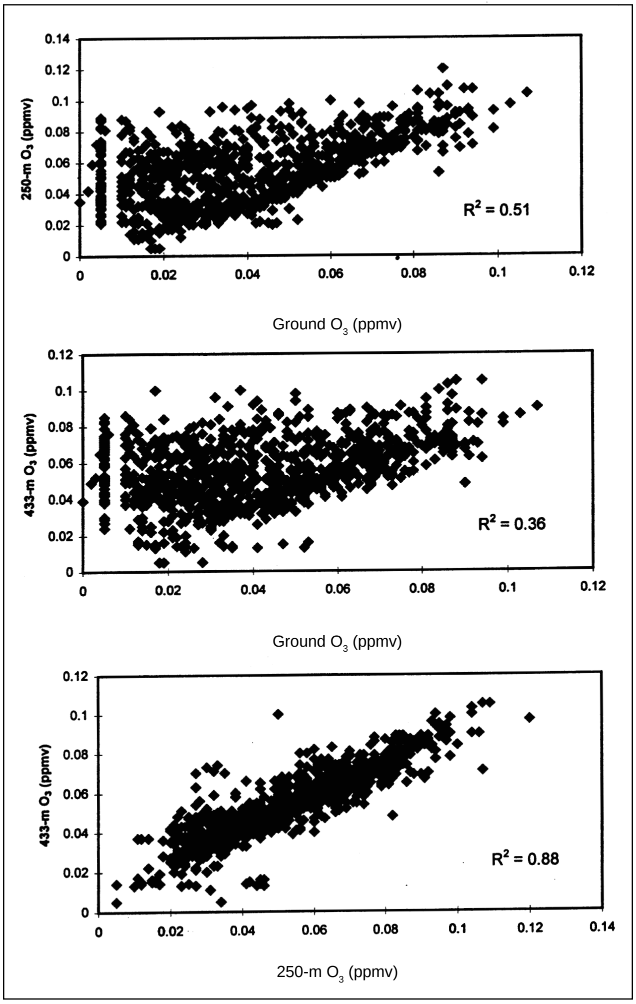

Figure 8. Correlation of hourly O_3 concentrations between different levels during summers 1993–1995.

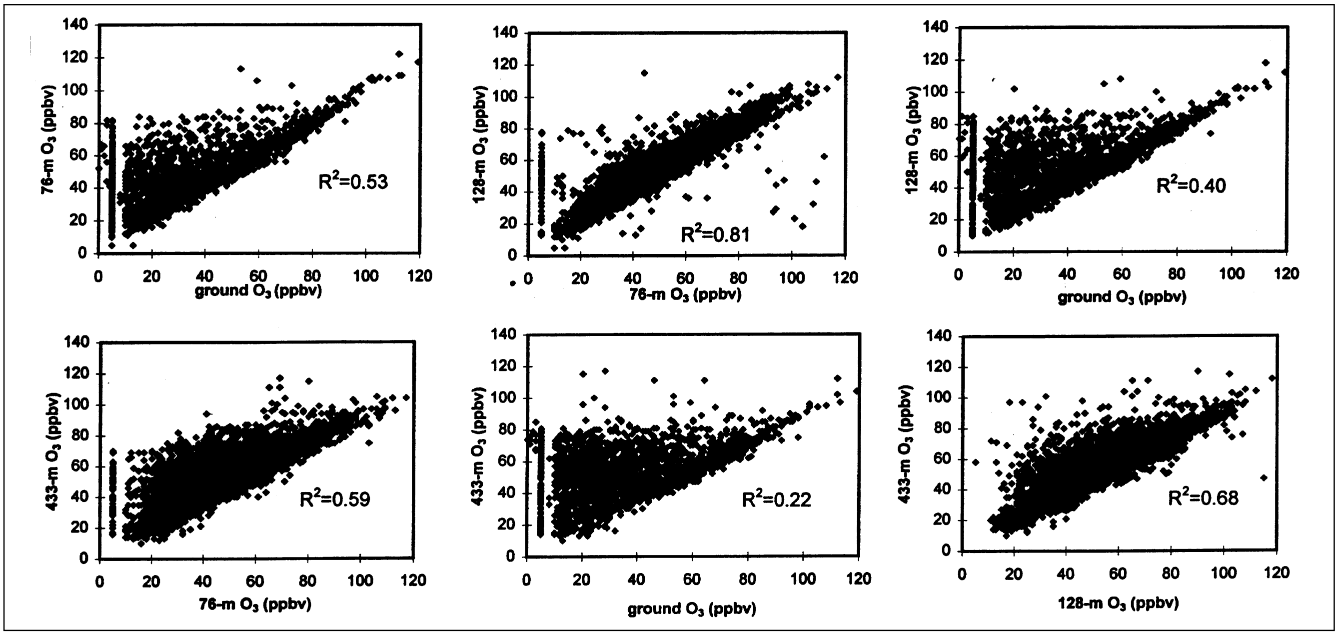

Figure 9. Correlation of hourly O_3 concentrations between different levels during summers 1996 and 1997.

where $\overline{C}$ is the mean ozone concentration, $\overline{w'c'}$ is the vertical flux of ozone, and Q represents the sink and source term. Integrating eq 4 with respect to time from t_1 to t_2, we have

$$d\overline{C} = V + P - L \tag{5}$$

Here, $d\overline{C}$ represents the change of concentration during the period of integration, V is the vertical transport, and P and L represent the production and loss, respectively, during this period. So $(P - L)/d\overline{C}$ will represent the net contribution of production and loss to the total concentration change, and $V/d\overline{C}$ stands for the relative contribution of vertical transport to the same.

Fehsenfeld et al.[8] found that mid-morning ozone concentrations were typical of upper-air values. Harrison and Holman[28] suggested that these values were indicative of those arising from long-range ozone transport. Recirculation and regional ozone buildup are other possible sources. Note that at 7:00 a.m., the mean mixing height was 202 m, and concentrations at 433 m represent the residual layer values. Assuming that ozone was mixed down later in the morning (7:00–11:00 a.m.), V values during this period can be estimated from the difference between the surface value and that in the residual layer at 7:00 a.m. The average differences between ground and 433-m concentrations at 7:00 a.m. were 33 ppbv in 1993, 19.6 ppbv in 1994, 35.2 ppbv in 1995, 26.7 ppbv in 1996, and 22.2 ppbv in 1997, which implies that about 87% (1993), 54% (1994), 67% (1995), 77% (1996), and 64% (1997) of the ozone increase from 7:00 to 11:00 a.m. came from downward mixing.

Ozone in the residual layer representing the previous day's value may derive mainly from two phenomena: regional transport of ozone and/or local photochemical generation. Observation and model calculation[6] 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, as corroborated by back trajectory analysis (Figure 5). Comparison of $V/d\overline{C}$ values indicates that contribution of transport in 1993 was significantly greater than that in 1994. Recalling that 1993 was a high ozone year and 1994 was a low ozone year, we may conclude that the main contributor to high ozone in 1993 was transport of ozone and/or its precursors from the northwest and the north (the predominant wind directions during the measurement period).

Figure 10 compares the differences in ozone concentrations between 433 m and ground levels for different years. Most ozone is believed to have been produced between 10:00 a.m. and 4:00 p.m. If downward mixing outweighs ozone production at the surface level, the differences will be positive; otherwise they will be negative. During the 10:00 a.m. to 4:00 p.m. period, the difference in 1993 was positive, with a mean value of 8 ppbv, while the differences in the other four years were negative. This implies that, locally, photochemical production in 1993 was less important than in 1994–1997, which in turn supports the idea that the role of transport in total ozone level in 1993 was more important than during the other four summers.

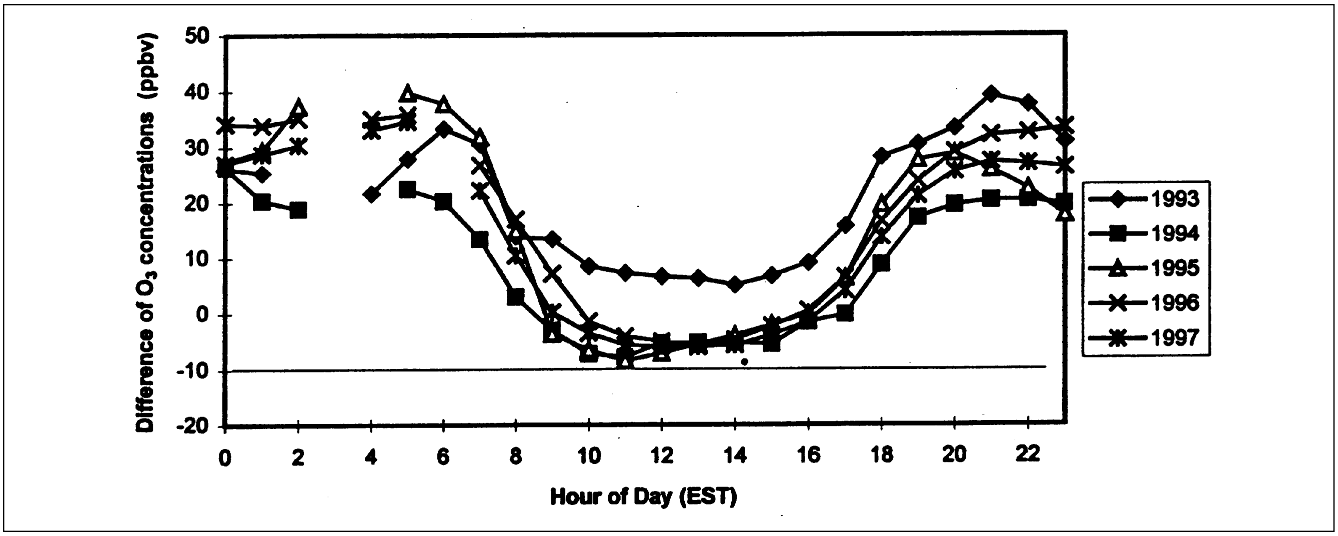

Figure 10. Difference between O_3 concentrations at 433 m and ground level during summers 1993–1997.

Prediction of Maximum Ozone Concentration at the Surface

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, the residual layer ozone may be indicative of the regional transport of ozone and/or its precursors, which contribute significantly to the surface-level ozone concentration. In an attempt to develop a model to predict the maximum surface-level ozone concentration in the afternoon using the ozone concentration in previous night's residual layer (midnight to 6:00 a.m.) as a predictor, we examined the possible correlation between the two. Figure 11 shows a good correlation ($R \cong 0.64$) between the maximum ground ozone concentration between 10:00 a.m. and 4:00 p.m. and the average residual layer ozone concentration between midnight and 6:00 a.m. Based on the five-year (1993–1997) data set, the maximum ozone in surface layer $\overline{C}_{o\,max}$ can be related to the previous night's average ozone concentration in the residual layer $\overline{C}_R$ by an observational model:

$$\overline{C}_{o\,max} = 27.76e^{0.016\overline{C}_R} \qquad (6)$$

where ozone concentrations are in ppbv, and the intercept (27.76 ppbv) represents the nominal local background O_3 concentration in air not directly influenced by regional transport of ozone and/or its precursors. This is very similar to the ozone background at site SONIA (~27 ppbv) in Candor, located in the central Piedmont region of North Carolina.[29] The overall correlation coefficient ($R = 0.64$) based on the five-year data set is quite consistent with correlation coefficients for the individual years, indicating the robustness of eq 6 as a predictive relationship.

SUMMARY AND CONCLUSIONS

Meteorological variables (temperature, dew point, mixing height, and passage of a synoptic high-pressure system) have varying influences on ozone concentrations in the atmospheric boundary layer. Analysis of 1993–1995 data has shown that surface ozone concentrations increased with increasing temperature but had an insignificant relationship to specific humidity. High ozone episodes associated with the passages of high-pressure systems suggested the importance of transport of ozone in the local ozone level. The mean heights of the mixing layer at measurement sites were estimated to be about 202 m at 7:00 a.m., 1021 m at 1:00 p.m., and 1270 m at 7:00 p.m., which followed the typical diurnal pattern observed at other homogeneous land sites.[18] Surface ozone also exhibited a typical diurnal pattern. The diurnal variations at elevated levels were much weaker because those levels were cut off from surface destruction processes of ozone at nighttime and were within the mixing layer in daytime. The correlations between ozone concentrations at the various elevated levels were fairly strong ($R = 0.77$-0.94), while those between the ground and upper levels wre slightly weaker ($R = 0.60$-0.73).

Deposition velocities at nighttime during measurement periods were estimated to range from 0.09 to 0.64 cm/sec, and surface fluxes of ozone ranged from 0.37 to 6.66×10^{11} molecules/cm^2/sec. From the observed increase in ozone concentration in the morning hours and the possible role of the mixing down of the ozone from the previous night's residual layer, we infer (based on back trajectory analysis) that regional transport plays a role in high-ozone events in the Raleigh-Durham area. Significant correlation between the concentration in the previous night's residual layer and the maximum ground level concentration on the following afternoon suggests a predictive capability based on an observation-based model derived from the data.

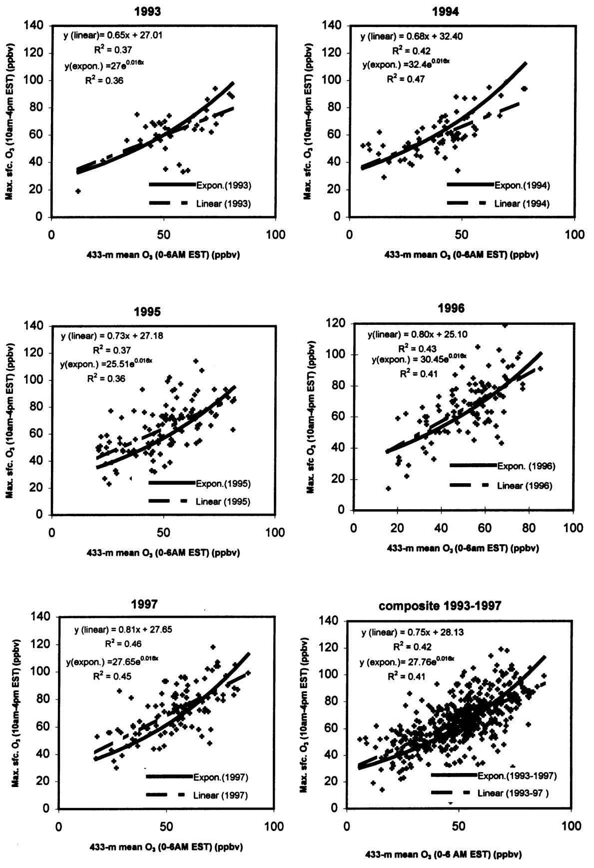

Figure 11. Prediction of maximum surface ozone (ppbv) using ozone concentration in the residual layer.

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