PERGAMON

Chemosphere – Global Change Science 2 (2000) 157–165

CHEMOSPHERE– GLOBAL CHANGE SCIENCE

An observational based analysis of ozone trends and production for urban areas in North Carolina

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Received 8 September 1998; received in revised form 2 February 1999; accepted 11 August 1999

Importance of this paper: Ozone is a "criteria pollutant" in the United States necessitating its monitoring, and control of its precursor emissions. We have determined that ozone concentrations, [O_3], measured simultaneously upwind and downwind (along the predominant wind direction) of an urban area could be used to indicate the intensity of O_3 production in the urban area. The increase in O_3 in the urban center over the course of a day is due to photochemical production. This delta-ozone, $\Delta(O_3)$, defined as the difference between the daily maximum [O_3] measured downwind and that measured upwind of the urban center reflects the net increment of photochemical O_3 added to an airmass over the course of a day as it advects over the city.

Abstract

An observational based analysis of ozone production for Raleigh and Charlotte, North Carolina, was performed for the years 1981–1990. A trend analysis was carried out for the 10 yr period for Raleigh. The third quartile average for Raleigh indicated a slight upward trend of about 0.5 parts per billion by volume (ppbv) per year in ozone concentration, but this may not be statistically significant. During the period studied, Raleigh was designated as out of compliance for ozone, with a classification of moderate for non-attainment areas in 1989. There were three exceedences of the National Ambient Air Quality Standard (NAAQS) of 0.12 parts per million by volume (ppmv) each in 1980, 1983, and 1987; and 13 exceedences in 1988. Based on a regression analysis, it was identified that the variability in ozone concentration in the Raleigh area is best correlated with maximum temperature and solar radiation, and also weakly correlated with daily average wind speed and wind direction. But, the local meteorological parameters could only explain 35–53% of the total variance. A delta ozone analysis was performed to obtain an estimate of the contribution to the production of ozone made by the metropolitan areas of Raleigh and Charlotte, North Carolina. During the summer of 1989, the city of Raleigh provided an average of about 25 ppbv of additional ozone to air advecting over the city. The amount of ozone produced by the metropolitan area of Charlotte for 1984–1991 averaged about 10–15 ppbv with a slight upward trend in ozone production (1.34 ± 0.78 ppbv per year). These values are compared to a published value of 30–40 ppbv of ozone for Atlanta, Georgia, during 1979–1987.

Keywords: Urban; Ozone production; Meteorology; Analysis

1. Introduction

Ozone is the most abundant photochemical oxidant in the atmosphere and many measures have been enacted to control its production. Ozone is designated by the Clean Air Act as a criteria pollutant; with a primary and secondary National Ambient Air Quality Standard (NAAQS) (the erstwhile standard of an hourly ozone concentration of 0.12 parts per million by volume (ppmv) has now been revised to an 8-hr averaged value of 0.08 ppmv). Recent problems in compliance with the NAAQS along with the new compliance demands from

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1465-9972/00/$ - see front matter
PII: S1465-9972(00)00007-6

the 1990 amendments to the Clean Air Act have led to increased concerns for the control of ozone in Raleigh and Charlotte, North Carolina.

As a photochemical air pollutant, ozone is initially generated in the troposphere in the presence of sunlight from the photochemical reactions between ozone precursors nitrogen oxides (NO_x), and non-methane hydrocarbons (NMHC). Based on the absorption characteristics of the major atmospheric pollutants, NO_2 is the most efficient absorber of the fraction of the Sun's UV radiation between 290 and 380 nm (Leighton, 1961). Thus based on a complex set of photochemical reactions now identified, a general net mechanism for ozone production in the troposphere from the oxidation of a straight-chain alkane (for example) is as follows (Warneck, 1988):

$$R_1CH_2R_2 + 3NO + 3O_2 \rightarrow 3NO_2 + R_1COR_2 + R_1'CHO + H_2O \quad (1)$$

$$NO_2 + h\nu + O_2 \rightarrow NO + O_3 \quad (2)$$

where R_1 and R_2 are suitable alkyl group, and R_1' is an alkyl group containing one carbon atom less than R_1. The above net reactions convert one molecule of n-alkane into one molecule of ketone and aldehyde each, and it oxidizes three molecules of NO to NO_2. The subsequent photodissociation of NO_2 is the source of ozone. The complex chemical sequence of reactions is initiated by hydroxyl (OH) radical, which is regenerated so that it can continue the chain reaction.

A number of observers have demonstrated that ozone, in general, is formed near the urban and industrial areas with high levels of anthropogenic sources, and the long-range transport of ozone and its precursors from those regions may contribute to elevated ozone levels in downwind rural areas (Vukovich et al., 1977; Wolff et al., 1977, 1982; Wolff and Lioy, 1980).

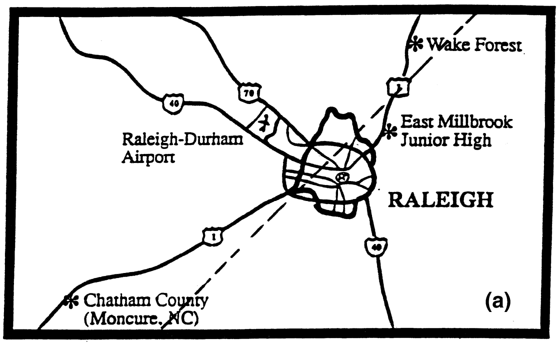
One can get an idea of the trend in ozone levels by performing various analyses on ozone data over many years. This can provide an insight as to whether the control measures have been effective in reducing ozone, or if adjustments are needed. Control measures have been enacted because ozone is a major component of photochemical smog, which can result in reduced visibility and injury to humans and vegetation.

The non-proportionality in ozone production with an increase in precursors, known as non-linearity, can result in problems in formulating control strategies. This relationship has been shown in the Empirical Kinetic Modeling Approach (EKMA), which shows that the ozone production does not increase linearly when the precursors are increased (Dimitriades, 1977). In studies by Laird et al. (1982) and Gradel et al. (1978), it was shown, using EKMA and other kinetic models, that as NO_x is reduced, the predicted photochemical production of ozone increases. Earlier, Fox et al. (1975) using smog chamber experiments reached the same conclusion that as precursor concentrations decrease ozone can be formed more efficiently. More recently, Liu et al. (1987) found that the ozone production per unit NO_x is actually greater at lower NO_x concentrations. Consequently, the better our understanding of the trends in the ozone levels and its precursors in cities, the better we can formulate effective ozone control strategies.

The purpose of this research was to discover the trends in ozone concentrations over the past 10 years for the Raleigh area, and to get an estimate of the contribution to regional O_3 concentrations made by the metropolitan area. This is done by performing various observational based trend analyses on the ozone data for the Raleigh area from 1981 to 1990. An estimate of the ozone production provided by the city area is obtained by performing a delta ozone analysis. The Raleigh ozone production is then compared to the values calculated for Atlanta, Georgia, by Lindsay et al. (1989), and for Charlotte, North Carolina, by this study. The comparison contrasts the estimate for Raleigh with the values for cities with larger metropolitan areas and greater photochemical precursor sources. Unfortunately, due to existing gaps in the data comparisons between the delta ozone values for the Raleigh area sites can only be performed for 1987–1990.

2. Ozone monitoring sites and periods

The locations and sites in Raleigh and Charlotte, North Carolina, are shown in Fig. 1. These sites are located along the predominant wind axis corresponding to two most frequent wind directions (southwest and northeast) in summer. The monitoring stations in the Raleigh area are: Chatham County, (Moncure) (CH) site, which is located about 43 km southwest of Raleigh in Wake County, East Millbrook Junior High (EM) and Wake Forest (WF) sites, which are located around 10 and 26 km northeast of the city center, respectively. The sites in Charlotte are all in Mecklenburg County with the Westinghouse Boulevard (WB) site about 15 km southwest of the city center while the Plaza Road (PR) and Route 29 North (RT) sites are located around 8 and 27 km northeast of the city center, respectively. Fig. 1 shows the three monitoring stations in each city, the major highways entering each region and the Raleigh–Durham and Charlotte–Douglas International airports. The metropolitan area of each city is outlined. There are suburban areas extending past the metropolitan area in both the cities. In the Raleigh area, the Chatham County and Wake Forest sites are considered rural and the East Millbrook site is considered suburban. In Charlotte, the Westinghouse Boulevard and Route 29 North sites are classified as rural and the Plaza Road site as suburban.



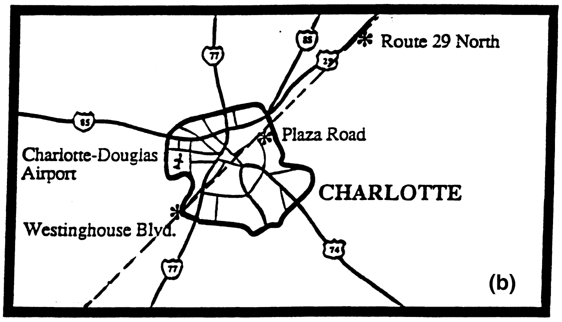
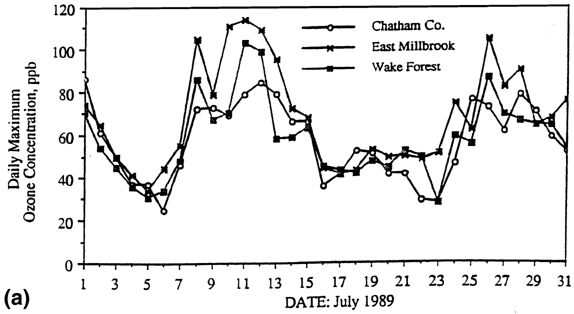


Fig. 1. The locations of the three sites along the predominant wind axis (- - - - -) (a) in Raleigh, North Carolina, and the location of Raleigh–Durham Airport, (b) in Charlotte, North Carolina, and the location of Charlotte–Douglas Airport.



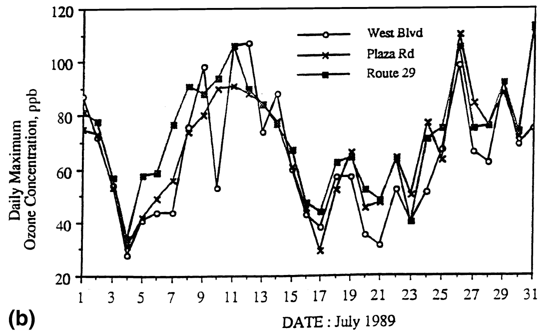


Fig. 2. (a) Daily maximum ozone concentrations at the three sites in Raleigh, North Carolina, for July 1989. (b) Daily maximum ozone concentrations at the three sites in Charlotte, North Carolina, for July 1989.

In both the cities, the sites located southwest of the city center will be called upwind sites because high ozone events are associated with winds from that quarter.

The hourly averaged ozone concentrations for all the Raleigh and Charlotte sites were provided by the erstwhile North Carolina Department of Environment, Health, and Natural Resources (NC DEHNR). However, ozone data for the Chatham County site were available only for 1987 and 1989 and for the East Millbrook Junior High site only for 1989 and 1990. The Wake Forest site in Raleigh and all the Charlotte sites were in operation over the entire 1981–1990 period. The meteorological data for Raleigh–Durham and Charlotte–Douglas International airports were obtained from the National Climatic Data Center (NCDC), Asheville, North Carolina.

3. Ozone data analyses

3.1. Time series of daily maximum concentration

The daily maximum ozone concentrations for the three sites in the Raleigh, North Carolina area for July 1989 are shown in Fig. 2(a). The ozone concentrations were plotted together to see if the three sites had similar temporal variations with good correlations between the sites. The summer of 1989 was chosen since it was the only year with data for all the three sites. The monthly minimum and maximum ozone concentrations occurred almost simultaneously (within a day), indicating that the three sites were experiencing the same overall photochemical activity. The graph also shows that the East Millbrook site generally had the highest daily maximum ozone concentration and the Chatham County site frequently had the lowest. Since Chatham County is considered a rural site and usually the upwind site, due to the predominant SW wind direction, it would be expected to have the lowest maximum ozone concentrations. Conversely, since Wake Forest is usually the farthest downwind site it might be expected to have the highest maximum ozone concentrations. However, Wake Forest is considered a rural site and situated about 26 km from the city center; frequently it might have been near the edge of the urban plume. East Millbrook is a suburban site, which is located only about 10 km from the city center, is more likely to be near the center of the urban plume and reflects the urban contributions to ozone production more accurately. In addition, the East Millbrook site is closer to high traffic areas which could also be adding to the local photochemical production of ozone. Similarly, strong correlations between the ozone concentrations at these sites, with some differences in magnitudes, were also found during the summer of 1991 (Adams, 1992).

The daily maximum ozone concentrations for the Charlotte, North Carolina, sites, also for July 1989, are shown in Fig. 2(b). Once again the monthly minimum and maximum ozone concentrations occured almost simultaneously, indicating similar overall photochemical activity at the three sites. None of the three sites, however, consistently had the highest daily maximum. The Route 29 North site, which was usually farthest downwind, generally experienced the highest concentrations. The suburban Plaza Road site experienced the highest concentration on several (5) days, while the Westinghouse Blvd. Site had the highest concentration on 4 d when it might have been the downwind site. The most unusual are the daily maximum concentrations for 11 July when both upwind and downwind rural sites experienced higher ozone levels than the suburban site in the middle. The most likely explanation for this is the presence of somewhat stagnant conditions within the Charlotte area under a stationary high-pressure system for several days. The central urban ozone including that at the Plaza Road was suppressed by fresh NO_x emissions.

The monthly minimum and maximum ozone concentrations occurred nearly coincident at the Raleigh and Charlotte sites. There were periods of very high ozone concentrations, such as 10–12, 26, and 31 July, while much lower concentrations were observed on 4–6, 16–17, and 21–23 July. The time series of daily maximum ozone concentrations for July 1989 (Fig. 2) show two broad periods (8–13 and 24–31 July) of high values and two broad periods (3–7 and 15–23 July) of low values. These are related to the same synoptic weather patterns affecting both the areas.

The daily maximum ozone concentrations for June 1982 and 1988 for the Wake Forest (Raleigh) site are plotted in Fig. 3(a). This was done to compare the daily maximum values for years with relatively low and high ozone concentrations. The range of daily maximum ozone concentrations for the month of June were 41–78 parts per billion by volume (ppbv) during 1982, and 44–157 ppbv during 1988. Also, there were 8d in June 1988 with an exceedence of the NAAQS for ozone of 0.12 ppmv, shown as the dashed line in Fig. 3(a), and none in 1982, when the highest daily maximum concentration was only 78 ppbv. The range of ozone values and the number of exceedences reflect the dependence of ozone production on the meteorological conditions. For the days with exceedences in 1988, the wind direction was from the south or southwest, the maximum temperature was 85 F or higher, and the percent possible sunshine was 90% or greater, except for 21–23 when the maximum daily temperature was in the mid-1990s. Also, 1988 was an unusually hot and dry summer in the Southeast US, which was characterized by anomalously high ozone concentrations.

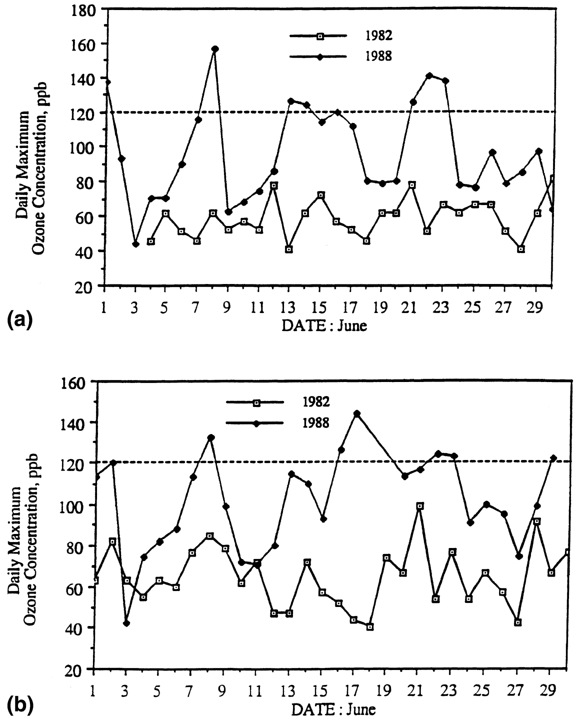


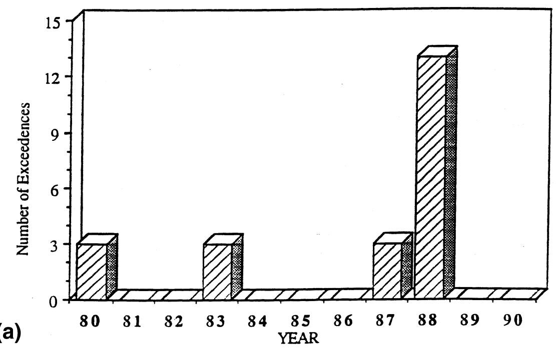
Fig. 3. (a) Daily maximum ozone concentrations at Wake Forest (Raleigh, North Carolina) for June 1982 and 1988. The dashed line represents the NAAQS of 0.12 ppm. (b) Daily maximum ozone concentrations at the Route 29 North site (Charlotte, North Carolina) for June 1982 and 1988. The dashed line represents the NAAQS of 0.12 ppm.

Similarly for Charlotte, North Carolina, the daily maximum ozone concentrations for June 1982 and 1988 are plotted for the Route 29 North site in Fig. 3(b). Ozone values were not available for the 18th, 19th, and 30th of June 1988 for this site. The range of the daily maximum ozone concentrations for the month of June were 40–99 ppbv during 1982, and 42–144 ppbv during 1988. These values are similar to the range of ozone values observed for Raleigh over the same time period. There were 7 d in June 1988 with an exceedence of the NAAQS shown as the dashed line in Fig. 3(b), and none in 1982, when the highest daily maximum ozone concentration was 99 ppbv. Thus, in both the cities, 1988 was characterized by anomalously high ozone concentrations, and 1982 with unusually low concentrations. High values were recorded in Raleigh and Charlotte on roughly the same days (1, 8, 16 and 17 and 21–23 June).

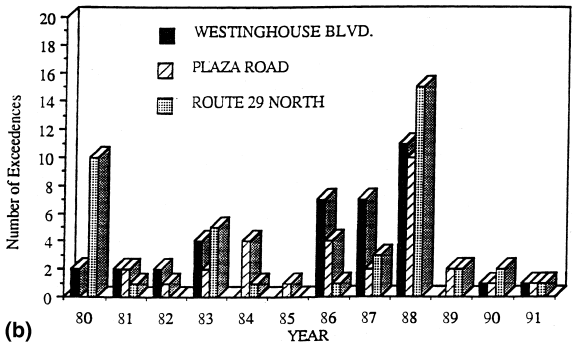
3.2. Number of exceedences

One of the factors the US Environmental Protection Agency uses to monitor ozone trends is the number of exceedences of the NAAQS per year. Fig. 4(a) shows the plot of exceedences per year for 1980–1990 at the Wake Forest (Raleigh) site. Although there is no discernible upward trend in the number of exceedences, there were three exceedences each in 1980, 1983 and 1987, while the worst year was 1988 with 13 exceedences. The maximum daily ozone concentration of 159 ppbv measured at the Wake Forest site for the period occurred in June 1988. Conversely, 1982, 1984, 1989 and 1990 were characterized by lower ozone concentrations, with the daily maximum ozone level for these years around 100 ppbv. 1981 and 1986 were close to exceedences with daily maximum ozone concentrations of 114 and 118 ppbv, respectively. The number of exceedences in 1987 and 1988, which constituted a violation, resulted in the Raleigh metropolitan statistical area to be classified as out of compliance for ozone.

The number of exceedences of the NAAQS from 1980 to 1991 for the three sites in Charlotte are shown in Fig. 4(b). As with Raleigh, 1980, 1983, 1986 and 1987 were characterized by a high number of exceedences, with the highest number of exceedence occurring in 1988. Conversely, 1982, 1989, 1990 and 1991 were characterized by a low number of ozone exceedences of the NAAQS. The Route 29 North site had the highest number of exceedences over the period with 41, which was followed by Westinghouse Boulevard with 37, and Plaza Road with 30 exceedences.



(a)



(b)

Fig. 4. (a) The number of exceedences at the Wake Forest (Raleigh) site from 1980 to 1990. (b) The number of exceedences of the NAAQS at the sites in Charlotte from 1980 to 1991.

3.3. Third quartile average

Another statistic that can be employed to follow the long-term trends in ozone is the average of the third quartile of daily maximum ozone concentrations. The third quartile is the top 25% of the daily maximum ozone concentrations whose average is likely to be less sensitive to extreme values. Fig. 5 shows the average of the third quartile values for the Wake Forest (Raleigh) site for June–August of 1981–1990. As with the number of exceedences, the values of the third quartile averages were high in 1983, 1987 and 1988. Consistent with 1988 being characterized by anomalously high ozone concentrations, the average of the third quartile of ozone values for 1988 was greater than the NAAQS of 0.12 ppmv. 1982, 1984, 1989 and 1990 had much lower values for the third quartile average. There appears to be a slight upward trend of about 0.5 ppbv per year in the third quartile averaged ozone concentrations at this site over the 10 yr period, but this may not be statistically significant. The population of the Raleigh metropolitan area doubled during this period and vehicular traffic more than doubled. Thus, the production of ozone precursors in the area must have increased substantially inspite of the controls on tailpipe emissions.

3.4. Delta ozone analysis

Lindsay et al. (1989) introduced a method of estimating photochemical production of ozone in a metropolitan area. Their delta ozone method is an observational-based analysis of the ozone concentrations in an urban environment relative to those in the upwind rural environment. When winds are from the predominant wind direction (southwest and northeast for

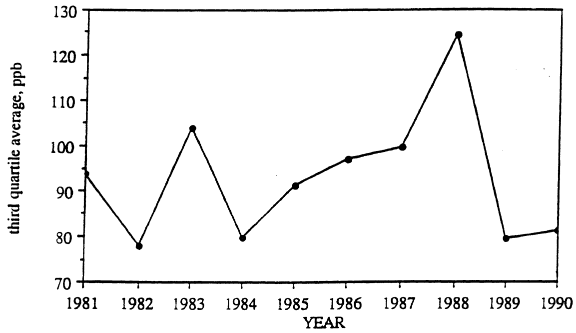


Fig. 5. The average of the third quartile of daily maximum ozone concentrations during June–August for the Wake Forest site.

Raleigh and Charlotte), the difference between the daily maximum ozone concentrations at the downwind and upwind sites should give an estimate of the ozone production over the area. In the Raleigh area, when the winds are from the southwest, the upwind site is located in Chatham County at Moncure (CH), and both the downwind sites are located in Wake County at East Millbrook Junior High (EM) and Wake Forest (WF). Similarly in Charlotte, where all sites are in Mecklenburg County, the upwind site is located at Westinghouse Boulevard (WB), and the two downwind sites are located at Plaza Road (PR) and Route 29 North (RT). The difference between the two sites (one upwind and the other downwind of the city) represents the difference in the concentrations of ozone entering and leaving the city area, and hence a measure of the amount of ozone that is produced over the metropolitan area (Lindsay et al., 1989). The wind and downwind sites for delta ozone analysis are reversed when the actual winds are from the northeast direction. An advantage of using a delta ozone analysis is that most of the variations due to meteorological factors are removed, since the upwind and downwind sites are generally influenced by the same synoptic and mesoscale meteorological conditions. Only those days when the wind speed was greater than 2 m s^{-1}, the wind direction was from the southwest or the northeast, and the ozone concentrations were greater than 60 ppbv at both the sites were included in our analysis. This method of analysis has been recommended because it is a more accurate indicator of trends in urban ozone production and allows one to evaluate the effectiveness of control measures in reducing ozone (Lindsay et al., 1989). The results of our delta ozone analysis are discussed in Section 4.

4. Results

The delta ozone analysis was performed for Raleigh and Charlotte, North Carolina, and then compared to values obtained by Lindsay et al. (1989) for Atlanta, Georgia. In the Raleigh area, the values at the Chatham County site are available only for 1987 and 1989, and the values at East Millbrook Junior High are available only for 1989 and 1990. Consequently, only a limited delta ozone analysis could be performed for the Raleigh area. However, for Charlotte a more extensive delta ozone analysis was performed for the period from 1980 to 1991. It should be noted that the locations of the sites in the two metropolitan areas might not be positioned optimally to obtain the best estimate of the maximum delta ozone.

Table 1 presents the average delta ozone values and their standard deviations calculated for the Raleigh area sites. There is considerable variation in the delta ozone values, so the standard deviations around the average values are large, and due to the small number of values used in some of these calculations the statistics are not very robust. Since the East Millbrook Junior High (EM) site is located closer to the city area and there are few emission sources between the Chatham County (CH) site and the city area, the delta ozone values between these two sites are considered to be the best estimators of ozone accumulation over the metropolitan area. When the winds are from the southwest, the average value of the concentration of ozone provided to air advecting over the city area is about 25.6 ± 12.8 ppbv. This can be compared to values between 30 and 40 ppbv obtained by Lindsay et al. (1989) for Atlanta, Georgia. The average delta ozone value for the northeast winds is only about 5.4 ± 6.1 ppbv. These rather infrequent winds in summer are often associated with low temperatures and overcast skies, which are not conducive to the local ozone production over the urban area. It should also be noted that the sites on either side of the urban area might not be optimally located to capture maximum delta ozone. For example, the Chatham County site is 43 km from the city center and any increase in ozone due to local production over the city may be considerably reduced due to dispersion and deposition. The urban plume may also miss the far downwind site on occasion when wind direction is off the line of sight. Since there is great distance between the Wake Forest (WF) and Chatham County (CH) sites and both are located in rural areas, the delta ozone values for WF–CH are expected to be even lower. The average delta ozone values for southwest winds were around 12 ppbv and for northeast winds were approximately 5 ppbv, with standard deviations larger than the above average values.

The delta ozone estimate for WF–EM is negative for both southwest and northeast winds, indicating that the daily maximum ozone concentration at East Millbrook

Table 1
Average delta ozone values and ± standard deviations for the Raleigh area sites for southwest and northeast winds[a]

Predominant wind direction	EM–CH (1989)	WF–CH (1987, 1989)	WF–EM (1989, 1990)
SW	$+25.6 \pm 12.8$ (9)[b]	$+11.9 \pm 15.4$ (34)	-19.7 ± 12.6 (23)
NE	-5.4 ± 6.1 (6)	-4.9 ± 7.6 (18)	-2.7 ± 5.1 (18)

[a] EM: East Millbrook Junior High, CH: Chatham County, and WF: Wake Forest.
[b] The values in parentheses are the number of days for each condition.

Junior High on an average was greater than the concentration at the Wake Forest site. This suggests that the Wake Forest monitoring site was probably outside or near the edge of the urban plume, and the effects of the metropolitan Raleigh area are less felt on the observed ozone concentrations there. The average delta ozone value for southwest winds during 1989 and 1990 indicate that the ozone concentration at the East Millbrook Junior High site is on an average around 20 ppbv greater than that at the Wake Forest site. When the winds are from the northeast, the average delta value is only about 3 ± 5 ppbv resulting from there being a few emission sources between the sites and the fact that both the sites are upwind of the city center and its precursor sources. The suburban site (EM) is more influenced by the traffic in the metropolitan area and shows somewhat higher concentrations, compared to those of the upwind site (WF).

The average delta ozone values for Charlotte are shown in Figs. 6(a) and (b) for the 8 yr period. Fig. 6(a) presents the trends in the annual average delta ozone values for PR–WB from 1984 to 1991 for southwest and northeast winds. The values of ozone production provided by the city area for southwest winds ranged from around 7 ppbv in 1990, to a high of almost 20 ppbv in 1984. The delta ozone estimates for northeast winds ranged from approximately 2.5 ppbv in 1984 and 1990 to a high of about 14 ppbv in 1988. The magnitudes of Charlotte delta O_3 for the two wind directions are much closer than those for the Raleigh area. However, the average delta ozone values for Charlotte are lower because the upwind site (WB) is not truly representative of background ozone concentrations; there are several sources near the city which could be elevating the upwind site's ozone concentrations. Although there is no significant trend in the delta ozone concentrations over the 7 yr period, the values for the SW and NE winds appear to be negatively correlated.

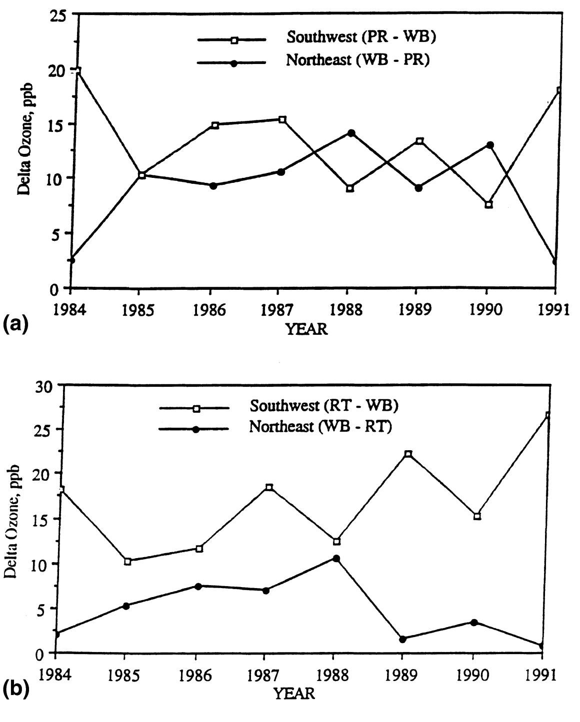


Fig. 6. Annual average delta ozone produced in Charlotte, North Carolina, for southwest and northeast winds. Only days when the stations recorded over 60 ppbv and winds averaged over 2 m/s were included in obtaining averages (a) for the Plaza Road and Westinghouse Boulevard sites, and (b) for the Route 29 North and Westinghouse Boulevard sites.

The values of delta ozone between the PR and WB sites were averaged over the entire 8 yr period to get an idea of the overall ozone production between the sites. The average delta O_3 concentration between the two suburban sites when the winds are from the southwest is around 14 ± 4 ppbv, and the value is about 9 ± 4 ppbv when the winds are from the northeast.

Fig. 6(b) shows the trend in the annual average delta ozone values between the rural and suburban sites from 1984 to 1991 for southwest and northeast winds. The delta ozone estimates when the winds are from the southwest ranged from about 10 ppbv in 1985 to approximately 26 ppbv in 1991. The values when the winds were from the northeast ranged from about 1 ppbv in 1989 and 1991 to around 10 ppbv in 1988. The delta ozone value averaged over the entire period for these sites was approximately 17 ± 6 ppbv when the winds were from the southwest and about 5 ± 3 ppbv when the winds were from the northeast. There appears to be a slight upward trend in ozone production (1.34 ± 0.78 ppbv per year) in Charlotte over the 8 yr period when the winds were from the southwest (Fig. 6(b)). However, there was no overall discernible trend in the delta ozone values over the period for Charlotte for the northeast wind direction. The delta ozone values for the SW and NE winds appear to be again negatively correlated. Overall the delta ozone estimates for Charlotte ranged from about 2 to 27 ppbv, which are quite similar to the values for the Raleigh area. But, both cities provide a smaller contribution to air advecting over the metropolitan area than Atlanta, Georgia, which can be explained simply in terms of differences in their sizes and emissions of precursor gases.

5. Correlations with meteorological variables

In order to study the possible relationships between the daily maximum ozone concentration and the various meteorological parameters, linear regression analyses were performed between ozone concentration as the dependent variable and one of the meteorological parameters as an independent variable. For the latter, we selected daily maximum temperature, percent possible sunshine, daily average dew point temperature, and daily average wind speed and direction. It has been hypothesized and confirmed by observations that ozone concentrations in urban areas reach high values on warm spring and summer days, usually under the influence of stagnant high pressure systems, which are characterized by bright sunshine, high temperatures, and low dew points and wind speeds. Ozone concentrations are usually much lower under the influence of low pressure systems which are often characterized by overcast skies, lower temperatures and higher dew points and wind speeds. In order to further test the above hypotheses and expectations based on observations elsewhere, we correlated the ozone data from the three Raleigh sites with the standard meteorological data from Raleigh/Durham Airport. The data were limited to late spring and summer months (May–August) of 1984–1991 for the Wake Forest site and only 3 yr for the other two sites. The results of the linear regression analysis, including scatter diagrams and correlation coefficients involving ozone and different meteorological variables, are given by Adams (1992). Here, we only give a brief summary of correlation coefficients (R). Note that R^2 represents the fraction of the variance of daily maximum ozone concentration that is due to the variability of the correlated meteorological parameter.

For all the sites in and around the Raleigh area, daily maximum ozone concentration is best correlated with either the daily maximum temperature ($R = 0.32$–0.49) or the percent possible sunshine ($R = 0.35$–0.50). Ozone at the urban site of East Millbrook Junior High is better correlated with daily maximum temperature, while that at the rural site in Chatham County is better correlated with the percent possible sunshine. These two parameters are of course interrelated and play an important role in the biogenic emissions of precursors and ozone formation. The other meteorological parameters examined turned out to be much less important in explaining the variability of daily maximum ozone concentration. The correlations with the daily average wind speed ($R = 0.22$–0.30) and wind direction ($R = 0.12$–0.29) are much weaker, but statistically significant at the 99% level. The urban site showed the best correlation of ozone with wind speed and wind direction. These correlations might have been higher if hourly averaged wind speed and wind direction at the time of maximum ozone concentration or mid-day (10 am–5 pm) average values were used instead of their daily averaged values.

In a recent study of the daily maximum and 8 h average ozone concentrations in Houston, Davis and Speckman (1999) found the best correlation ($R = 0.56$) of ozone with midday average winds. The correlations with the wind direction varied considerably among sites, which raises an interesting question about the origin of ozone at the rural sites. Wind direction can be more important in determining ozone concentrations at the rural sites, because it determines the transport of ozone and/or its precursors to those sites. Finally, ozone was not found to be significantly correlated with daily average dew point temperature, except for the rural Chatham County site ($R \simeq 0.2$). On the whole, the local meteorological parameters considered here could explain only 35–53% of the total variance of maximum ozone concentrations at the three sites. Long range transport, movement of synoptic and mesoscale weather systems, local production and regional transport of precursors (VOCs and NO_x) and the associated photochemistry are other confounding factors in the variability of urban ozone.

6. Conclusions

Our analysis of the summer (June, July and August) ozone data for Raleigh and Charlotte, North Carolina, from 1981 to 1991, indicates that, on an average, both cities can add up to 27 ppbv of additional ozone to air advecting over the city areas; the actual contribution strongly depends on the wind direction and possibly on other meteorological parameters and conditions. There appears to be a slight upward trend of about 0.5 ppbv per year on the average of the first quartile of daily maximum ozone concentrations for Raleigh, North Carolina, but this may not be statistically significant. The ozone concentrations at the East Millbrook Junior High site, which is located approximately 10-km northeast of the Raleigh city area, were generally the highest of the three Raleigh sites. The ozone concentrations were usually lower at the Wake Forest site, which is located about 26 km northeast of the city area, indicating that this site is more often near the edge of the urban plume for the prevailing southwest winds. During the prevailing SW winds, an upwind site in Chatham County, located 43 km southwest of Raleigh, had the lowest ozone values. The average delta ozone value, defined as the difference in ozone concentrations between the downwind and upwind sites, and reflecting the amount of ozone added primarily by the city area to air advecting over the region, was about 26 ppbv for 1989. For all the pairs of upwind and downwind sites in Raleigh, the annual average delta ozone values for both the prevailing southeast and southwest wind directions ranged from about 3 to 26 ppbv.

The annual average delta ozone values for Charlotte, North Carolina, during 1984–1991 for southwesterly winds ranged from around 8 to 27 ppbv, with a slight upward trend in ozone production; and for northeasterly winds they ranged from about 2 to 14 ppbv. The average delta ozone values for Charlotte for northeast and northwest wind directions were around 9 and 14 ppbv, respectively; and for Raleigh, these were about 5 and 26 ppbv. The values for Raleigh are based on just 1 yr's (1989) data which may account for the much higher value for the southwest winds. The delta ozone values, indicating the local production of ozone by the urban area, for the two cities in North Carolina are less than the values of 30–40 ppbv found by Lindsay et al. (1989) for Atlanta, Georgia, during the 1979–1987 period.

For the sites in and around the Raleigh area, the daily maximum ozone concentration is found to be best correlated with either the daily maximum temperature ($R = 0.32$–0.49) or the percent possible sunshine ($R = 0.35$–0.50). These two interrelated parameters play an important role in ozone formation. The correlations with the daily-averaged wind speed and wind direction are found to be much weaker ($R \leqslant 0.3$), but statistically significant. On the whole, meteorological parameters considered in our regression analysis could explain only one-third–one-half of the total variance of ozone concentrations.

The primary merits of our method of analysis of the daily maximum ozone concentration data in and around the two largest North Carolina cities (Charlotte and Raleigh) are its simplicity, requirement of only routine meteorological and daily maximum ozone data, and the use of simple statistics (e.g., averages, differences, and correlations). There are also some serious limitations of the data and methodology used here. These are: (1) the lack of detailed information on the emissions and transports of chemical precursors in the urban areas of interest; (2) non-utilization of any urban or regional photochemical models for ozone formation; (3) lack of more detailed analyses of the synoptic and mesoscale systems which might have responsibility of high ozone episodes, and (4) lack of more detailed correlation analysis utilizing hourly or midday average rather than daily average winds.

Acknowledgements

This research has been funded by the US Environmental Protection Agency through cooperative agreement with the University Corporation for Atmospheric Research (S9153) as part of the Southern Oxidant Study (SOS-SORP/ONA), and the Southeast Regional Climate Center (NA89AA-D-CP037). We thank Mr. Hartsell for his comments and Ms. DeFeo in the word processing of the manuscript. We also thank the North Carolina Department of Environment and Natural Resources for providing the ozone data.

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