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Ozone patterns for three metropolitan statistical areas in North Carolina, USA

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Abstract

As part of an effort by the state of North Carolina to develop a State Implementation Plan (SIP) for 1-h peak ozone control, a network of ozone stations was established to monitor surface ozone concentrations across the state. Between 19 and 23 ozone stations made continuous surface measurements between 1993 and 1995 surrounding three major metropolitan statistical areas (MSAs): Raleigh/Durham (RDU), Charlotte/Mecklenburg (CLT), and Greensboro/High Point/Winston-Salem (GSO). Statistical averages of the meteorological and ozone data were performed at each Metropolitan Statistical Area (MSA) to study trends and/or relationships on high ozone days (days in which one of the MSA sites measured an hourly ozone concentration $\geqslant 90.0$ ppbv). County emission maps of precursor gases, wind roses, total area averages of ozone, total downwind averages of ozone deviations, upwind averages of ozone, and a modified delta ozone analysis were all obtained and analyzed. The results of this study show a reduction in the delta ozone relative to an earlier study at RDU, but no average significant change at CLT (no comparison can be made for GSO). The statistical data analyses in this study are used to quantify the importance of local contributions and regional transport, to ozone air pollution in the MSAs.

Keywords: Urban ozone; Pollutant transport

1. Introduction

Ambient ozone concentrations found in the lower troposphere continue to be a major air pollution problem in the United States (Logan et al., 1985; NRC, 1991; Aneja et al., 1992; Sillman et al., 1993; Vukovich, 1994). Areas that violated the previous hourly National Ambient Air Quality Standard (NAAQS) of 0.12 parts per million by volume (ppmv) for ozone, as set by the US Environmental Protection Agency (EPA), were designated as non-attainment for ozone control (EPA, 1993). A day in which any 1-h average ozone concentration was greater than 0.12 ppmv was considered an exceedance day. An area which produces four or more exceedances over a 3-year period is considered in violation of NAAQS (EPA, 1993). The ozone standard has been revised more recently to 0.08 ppmv for the 8-h averaged concentration.

Ozone, a secondary pollutant, is designated as a criteria pollutant under the Clean Air Act Amendments (CAAA) of 1990 (EPA, 1993). In 1989, the EPA estimated that 67 million people lived in areas of NAAQS exceedances for ozone (NRC, 1991). Health effects of high ozone concentration exposure include eye irritation (NRC, 1991) and breathing trouble for asthmatics (EPA, 1994). Crop losses from high ozone exposure are estimated to be \$1 to \$2 billion annually in the US (EPA,

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1996). Additionally, non-crop losses have been documented by Moy et al. (1994), who report an alarming decrease of white pine trees at Shenandoah National Park in rural Virginia attributed to elevated ozone concentrations.

Tropospheric ozone is produced through reactions of hydrocarbons (HCs), (commonly referred to as volatile organic compounds or VOCs), nitrogen oxides (NO_x = NO and NO_2) and ultraviolet solar radiation ($h\nu$). In regions of high VOC concentrations (primarily through production of mobile, biogenic and industrial source emissions and transport of these species by the prevailing wind), a disruption in the photostationary state of ozone production occurs.

The ozone production cycle is driven by sunlight ($h\nu$); however, other meterological parameters, such as cloud cover, air temperature, relative humidity, atmospheric pressure, and wind speeds influence the kinetics for ozone production and distribution (Aneja et al., 1994). Furthermore, this reaction is maximized during the summertime, when the incoming solar radiation is greatest together with high temperatures.

High ozone concentrations in the southeastern United States continue to be a pervasive problem for both the previous 1-h NAAQS and the newly revised 8-h NAAQS. (In addition to the change in averaging time, the new standard was lowered to 0.080 ppmv over this 8-h period.) Wind direction associated with synoptic-scale weather patterns is important everywhere; for the Southeast US, ozone and its precursors can be transported primarily from the Northeast, Midwest, as well as other regions (Vukovich, 1994).

2. Background

North Carolina has three Metropolitan Statistical Areas (MSAs) that periodically experience high concentrations of ozone: Raleigh/Durham (RDU); Charlotte/Mecklenburg (CLT); and, Greensboro/High Point/Winston-Salem (GSO) (Fig. 1). Table 1 gives the number of 1-h NAAQS ozone exceedances over a 12-yr period for each of these MSAs. In 1990, the CLT MSA was designated as a non-attainment area for ozone. Two years later (June 1992), GSO and RDU were similarly designated. However, all three MSAs are currently considered to be attainment/maintenance areas with respect to the recently revised NAAQS (EPA, 1998).

According to the NAAQS, ozone control strategies were to be formulated at the state level. For our study

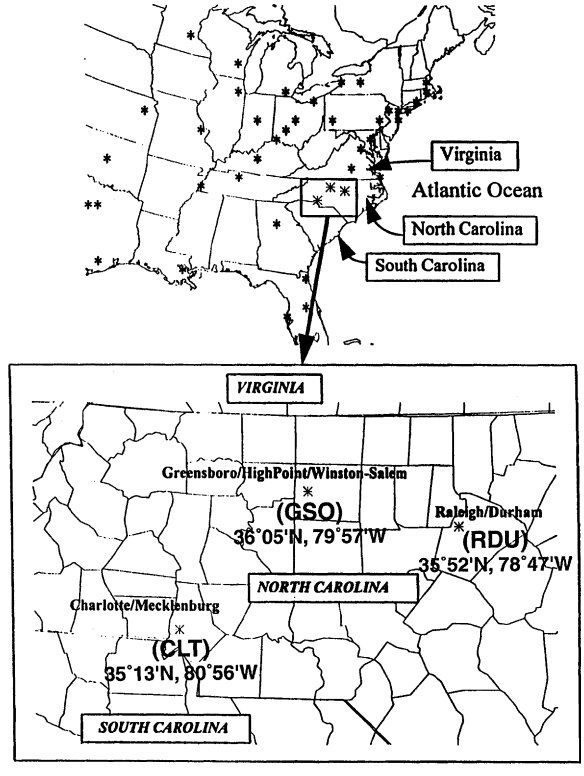

Fig. 1. Locations of the three North Carolina MSAs used in the study. Asterisks (*) indicate MSAs greater than 900,000 people. (Source: US Census).

Table 1
Information on the three metropolitan statistical areas (MSAs) in North Carolina

MSA name	Population (as of 1995)	Number of NAAQS ozone exceedances (1980–1992)	Closest national weather service station	Latitude and Longitude of national weather service station
Raleigh/Durham (RDU)	1,000,000	23	Raleigh-Durham International Airport	35°52'N, 78°47'W
Charlotte/Mecklenburg (CLT)	1,200,000	72	Charlotte-Douglas International Airport	35°13'N, 80°56'W
Greensboro/High Point/Winston-Salem (GSO)	1,000,000	47	Piedmont-Triad International Airport	36°05'N, 79°57'W

Source: NC DEHNR.

period (1993–1995), there were 16 exceedances over 15 d in the North Carolina MSAs; RDU and GSO had three each, while CLT had 10 (there was one day in which RDU and GSO each had an exceedance).

The estimates of county mobile emissions of carbon monoxide, VOCs and NO_x for 1990 by US EPA (EPA, 1995) show that counties with high carbon monoxide emissions match favorably with the locations of the three MSAs and the highway links between Raleigh and Charlotte. The EPA considers a county to be high in emissions for CO, if the emissions are greater than 50 Mg d^{-1} (1 Mg $= 1 \times 10^6$ g). For a county to be high in VOC and NO_x, emissions must be greater than 10 Mg d^{-1}. The reason that CO is of interest is that carbon monoxide can be used as a tracer for mobile emissions and also acts as a precursor for ozone formation (Warneck, 1988). Along with the counties of high CO emissions, the mobile NO_x emissions and VOC emissions matched well with the highways and MSA locations, indicating that a major precursor gas for ozone formation can be attributed to these mobile emissions (Fig. 2).

Additionally, the 1990 EPA estimations of above average to high biogenic VOCs are strongly related to counties of heavy forest canopies in western and southern North Carolina. The EPA considers a county to have above average emissions of biogenic VOCs if emissions are greater than 50 Mg VOC d^{-1}, while high VOC county emissions are greater than 60 Mg VOC d^{-1} (EPA, 1995). Farming in south central North Carolina accounts for the above average to high biogenic NO_x. The EPA considers a county to be above average if biogenic NO_x emissions are greater than 1.1 Mg NO_x d^{-1}, while high indicates greater than 3 Mg NO_x d^{-1} (Fig. 3). In rural North Carolina, contributions of naturally-occurring VOCs, such as isoprene (Lawrimore et al., 1995) and NO_x from agricultural activity (Sullivan et al., 1996) also play an important role in ozone formation.

Due to the high emissions of naturally occurring NO_x and VOCs in the southeastern US, rural background concentrations of ozone are typically higher than those in other regions. Altshuller and Lefohn (1996) recently reported background ozone concentrations from across the US and Canada for inland sites of between 25 and 45 ppbv, for a specific 7-h time period from 0900 to 1559 Local Standard Time (LST). From their measurements at a rural site in central North Carolina, Aneja et al. (1996)

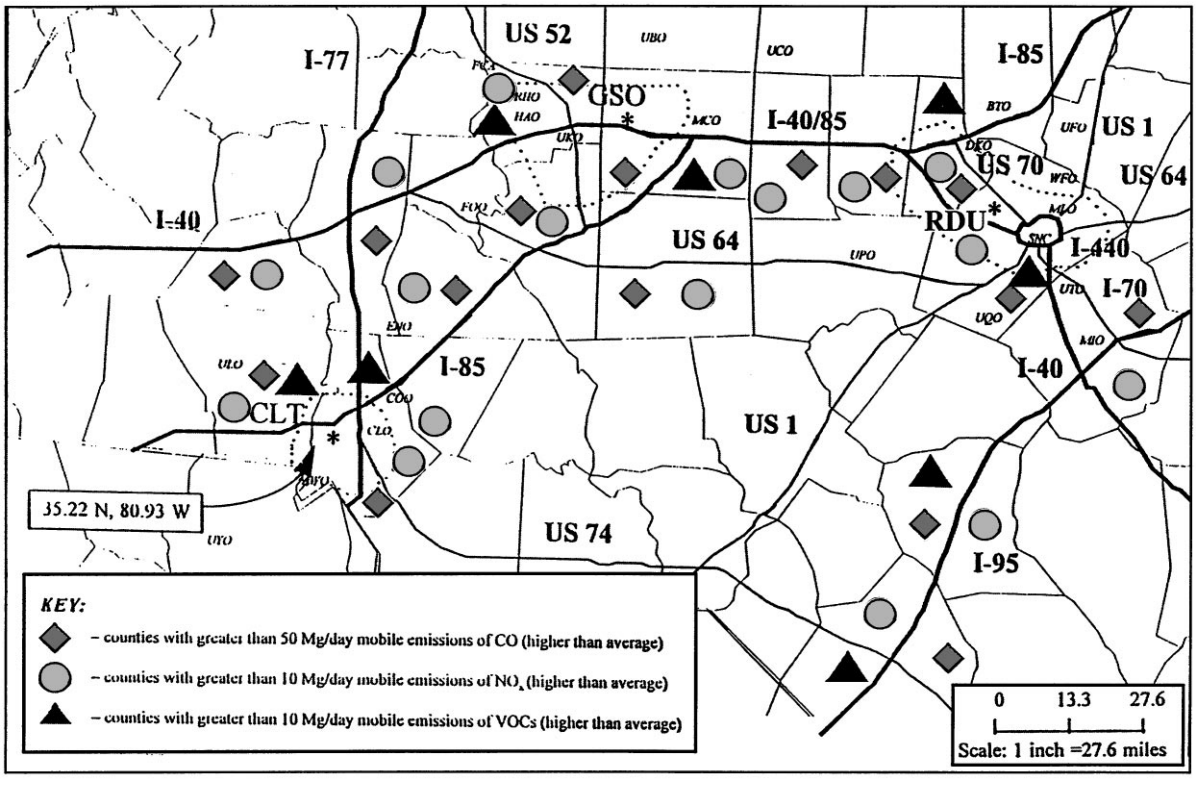

Fig. 2. County Mobile Emission Maps of CO, VOC, and NO_x. EPA estimates for mobile emissions of CO, VOCs, and NO_x by county. Asterisks (*) indicate National Weather Service stations. The ozone sites are in italics, interstates are denoted by thick lines, while US routes are denoted by thinner lines. Regions with high CO, VOCs, and NO_x match well with the three MSAs. (Source: NC DEHNR).

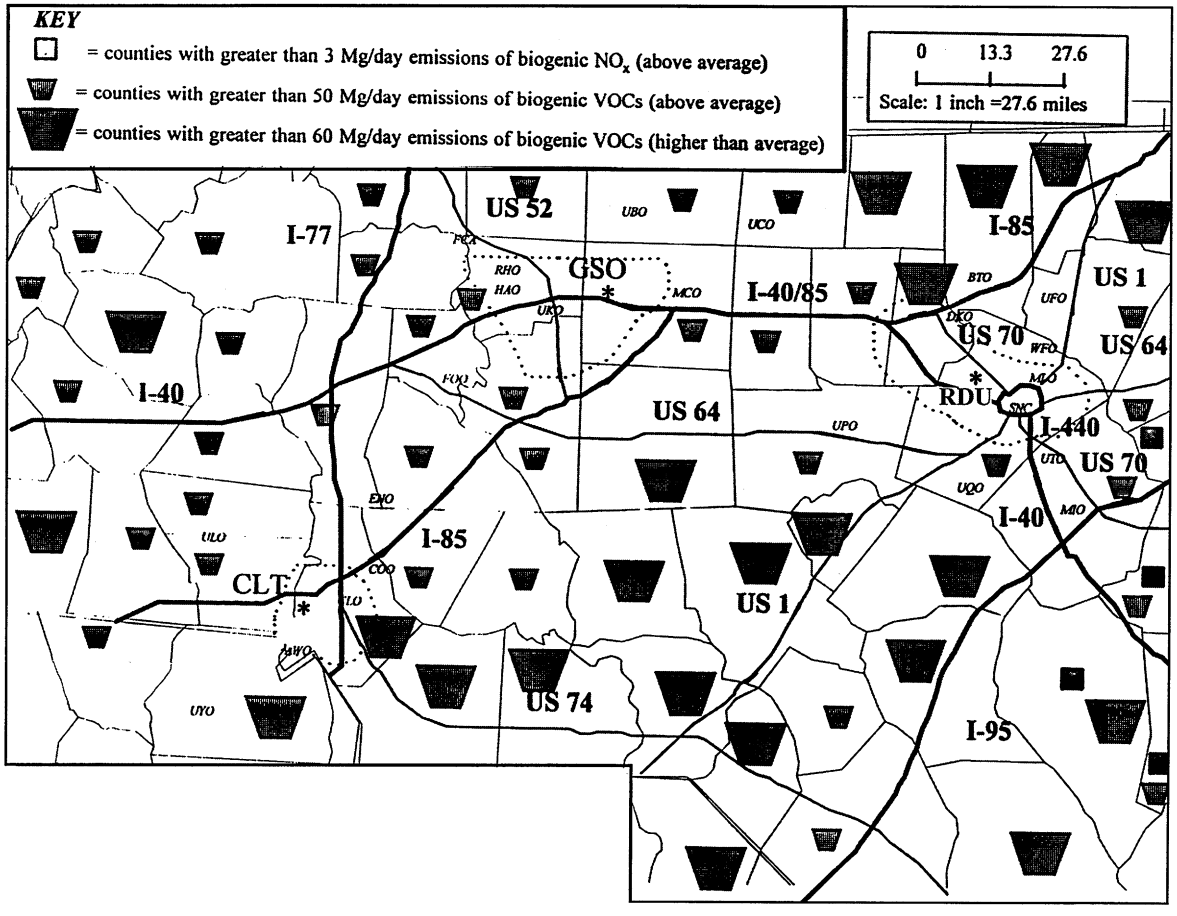

Fig. 3. County Mobile Emission Maps of VOC, and NO_x. EPA estimates for biogenic emissions of VOCs, and NO_x by county. Asterisks (*) indicate National Weather Service cations. The ozone sites are in italics, interstates are denoted by thick lines, while US routes are denoted by thinner lines. Most of south central NC has above average to high emissions of biogenic VOCs, while biogenic emissions are low. (Source: NC DEHNR)

obtained an average background ozone concentration of 27 ppbv for the daytime period in summer.

The North Carolina Department of Environmental and Natural Resources (NC DENR), formerly known as North Carolina Division of Environment, Health, and Natural Resources (NC DEHNR), in response to ozone exceedances at RDU, GSO, and CLT, expanded its statewide monitoring network from exclusively within the MSA to include more sites downwind of the three MSAs. During the years 1993, 1994, and 1995, there were 18, 21, and 22 active ozone stations in and around the three MSAs, respectively (Table 2). The purpose for the additional sites was to measure ozone concentrations at optimal downwind locations in order to develop a North Carolina State Implementation Plan (SIP) for ozone control. A site in York County, SC was added for this study. This location is southwest of the CLT MSA.

This study examines the ozone episodes experienced by the three MSAs and attempts to determine the role of local contributions versus regional transport of ozone and its precursors in producing high ozone levels within and downwind of the MSAs in NC. The methods used in support of this objective are: (1) to examine surface wind fields at the three MSAs; (2) to compare these wind fields, within an appropriate transport range of each MSA, in relation to precursor source locations; and (3) to examine the changing ozone concentrations as air masses move over the MSA.

3. Data retrieval and reduction

The three MSAs provided ideal locations for an ozone study because in the center of each MSA is a National

Table 2
Ozone monitoring sites in the Raleigh/Durham (RDU), Greensboro/High Point/Winston-Salem (GSO), and Charlotte/Mecklenburg (CLT) Metropolitan Statistical Areas (MSAs)

MSA	Downwind station identifier	EPA AIRS ID	Downwind station name	County	Land use	1993	1994	1995	Elevation (m)	Latitude North (DDMMSS)	Longitude West (DDMMSS)
RDU	BTO	37-077-0001	Butner	Granville	Residential	X	X	X	91	360827	784609
	UFO	37-069-0001	Franklinton	Franklin	Residential	X	X	X	135	360551	782749
	MIO	37-101-0099	Micro	Johnston	Agricultural	X	X		52	353411	781109
	JOO	37-101-0002	Johnston County	Johnston	Agricultural			X	127	353000	782615
	UQO	37-183-0016	Fuquay-Varina	Wake	Residential		X	X	117	353506	784741
	UPO	37-037-0004	Pittsboro	Chatham	Agricultural		X	X	400	354532	790955
	DKO	37-063-0013	Duke St.	Orange	Commercial	X	X	X	390	360208	785417
	SNC	37-183-0015	St. Augustine's	Wake	Residential		X	X	127	354718	783720
	MLO	37-183-0014	Milbrook	Wake	Residential	X	X	X	100	355122	783432
	UTO	37-183-0017	Auburn Tower	Wake	Agricultural	X	X	X	320	354100	783300
	WFO	37-183-2001	Wake Forest	Wake	Agricultural	X			87	355815	783927
GSO	MCO	37-081-0011	McLeansville	Guilford	Residential	X	X	X	229	360647	794216
	UCO	37-033-0001	Cherry Grove	Caswell	Agricultural		X	X	241	361810	792800
	UBO	37-157-0099	Bethany School	Rockingham	Agricultural	X	X	X	77	361832	795131
	FCA	37-067-0027	Hollyberry Lane	Forsyth	Agricultural			X	271	361411	802438
	RHO	37-067-0007	Rural Hall	Forsyth	Residential	X	X	X	295	360956	801413
	HAO	37-067-0022	Hattie Avenue	Forsyth	Residential	X	X	X	287	360638	801336
	UKO	37-067-1008	Piedmont Memorial	Forsyth	Residential	X	X	X	285	360303	800838
	FOO	37-059-0099	Fork	Davie	Agricultural	X	X		244	355201	802545
	GCO	37-067-0006	Goodwill Church	Forsyth	Residential	X			244	361259	800500
CLT	UYO	45-091-0006	York	York (SC)	Agricultural	X	X	X	222	345608	811342
	AWO	37-119-1005	Arrowwood	Mecklenburg	Industrial	X	X	X	195	350647	805511
	ULO	37-109-0004	Crouse	Lincoln	Residential		X	X	270	352618	811631
	CLO	37-119-0034	Plaza Rd	Mecklenburg	Residential	X	X	X	239	351455	804559
	COO	37-119-1009	County Line	Mecklenburg	Agricultural	X	X	X	216	352055	804137
	URO	37-159-0021	Rockwell	Rowan	Commercial		X	X	240	353454	802333
	ENO	37-159-0022	Enochville	Rowan	Residential			X	270	353205	804155
	LOO	37-109-0099	Lincoln County	Lincoln	Agricultural	X			351	352616	811038

Weather Service (NWS) reporting station, which records hourly meteorological surface observations. NWS data were retrieved from the meteorological archive at North Carolina State University (NCSU) and the participating NWS sites. Here, we assume that the measured wind speed and direction at the NWS reporting station are representative of the mean transport velocity within the specified distance from the NWS site. Hourly ozone data were obtained from the US EPA Aerometric Information Retrieval System (AIRS) for the study period. Additional ozone sites not in the AIRS database were obtained from NC DENR.

Ozone was measured by DENR site operators using the reference or equivalent ultraviolet photometric detection technique with Dasibi model 1003 AH ozone analyzers. These instruments and measurement technique are designated by the EPA as "equivalent reference methods". Precision and accuracy checks were done on a routine basis at each monitoring site.

A "mean %" is the average percent difference for all the precision or accuracy checks. For the entire statewide network, ozone data has a "mean %" accuracy (at the 5% significance level of 0.5% [$\pm$3.0%] in 1993, 0.2% [$\pm$4.5%] in 1994, and $-$0.1% [$\pm$3.1%] in 1995. This information was provided by NC DENR (Oommen, 1996).

3.1. High ozone day criteria

Because of the elevated background ozone concentration in the Southeast, it was necessary to identify an ozone concentration threshold which was distinguishable from the background value. Consequently, ozone data for this study were selected specifically for High Ozone Days (HODs), which met the criteria that at least one of the MSA ozone monitoring sites reported at least one hourly concentration greater than or equal to 90 ppbv and that this concentration occurred between 0900–1459 LST.

Previous studies have used lower threshold values such as 60.0 ppbv (Adams, 1992) and 80 ppbv (Lindsay et al., 1989). Even though the minimum threshold was 90 ppbv for our study, enough data were available to perform a statistically robust analysis. There were no HODs in October through March, and thus, data from these months were not used in this study.

While previous investigators have used different time periods such as 0700–1359 LST (Altshuller, 1988), 1100–1459 LST (Altshuller, 1986), and 1100–1559 LST (Lindsay et al., 1989; Adams, 1992), in this study we chose the 6-h period between 0900 and 1459 LST because this is typically the optimum time of day for ozone production due to high solar insolation. The ozone concentrations around the MSAs during this time period are generally higher than the background values reported by Altshuller and Lefohn (1996).

After the HOD criteria were met, vector-averaged wind speeds from NWS hourly observations for those days were computed for each 6-h period. Two 3-h time periods (0900–1159 LST and 1200–1459 LST) were established for determination of downwind effects and vector-averaged wind speeds for these periods for each HOD were also computed.

4. Results

4.1. Number of high ozone days

Even though the official ozone season in North Carolina is from April 1 to October 31, our study period focused from April 1 to September 30, for a total of 549 d between 1993 and 1995. For the three MSAs of interest, 1993 had the highest frequency of HODs (72/183, 39.3%) followed by 1995 (59/183, 32.2%) and 1994 (38/183, 20.7%). Thus there were a total of 169 HODs (169/549, 30.8%) during the study period when at least one of the three MSAs experienced high ozone concentrations. Additionally, there were 100 HODs (100/549, 18.2%) when at least two of the three MSAs experienced high ozone concentrations, and 46 HODs (46/549, 8.4%) when all three MSAs experienced HOD conditions.

Fig. 4 shows the inter-relationship of the 169 HODs for the three MSAs. During this period, there were 69 (69/549, 12.6%) days on which only one MSA had high ozone, and only one of these days had an MSA (CLT) exceeding the pre-existing 1-h NAAQS. There were 54 d (54/549, 9.8%) on which only two MSAs had high ozone, and on these days, there were only three NAAQS ozone exceedances (all in CLT). However, there were 46 d (46/549, 8.4%) on which all three MSAs experienced high ozone. On these days, there were 11 ozone NAAQS exceedances, suggesting that the greatest proportion of ozone exceedances occurred when all three MSAs experi-

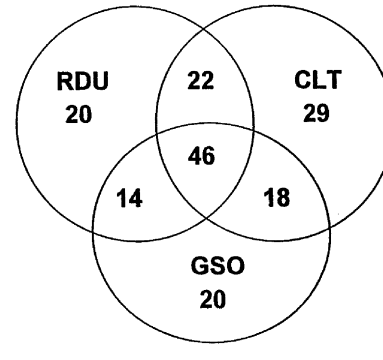

Fig. 4. Comparison of the number of high ozone days for RDU, CLT, and GSO for 1993–1995.

enced high ozone. This also suggests that the high ozone experienced by all three MSAs may be part of the regional pollution associated with synoptic scale weather patterns, rather than due solely to local production.

Over the 3 yr period, CLT had the highest frequency of high ozone days, followed by RDU and GSO. In the RDU MSA, of the 549 total sampling days during the 3-y period, 102 d met the high (90 ppbv) ozone day criterion. This translates to about 18.6% of the days, or about one high ozone day for every 5 d. Similar, frequencies of HODs occurred in the other two MSAs; CLT and GSO experienced high ozone on 115 and 98 d (20.9% and 17.9%, respectively).

4.2. Determination of downwind sites using three-hour transport criteria

Eight wind direction regimes were established for the purpose of designating an ozone station as a downwind site. For each of these regimes, 3-h forward trajectories from near the center of the MSA (i.e., the airports) were constructed by vector-averaging the hourly winds in order to determine the range of air motion (Oommen, 1996). This procedure provided a rough check that the ozone sites used for statistical computations were all within the calculated range of downwind transport distances for parcels travelling from the MSA to the downwind ozone-monitoring site over a 3-h period. Table 3 summarizes these results, and identifies the downwind ozone-monitoring sites. Not all wind regimes could be included since not all had a suitable downwind ozone-monitoring site. Note that the distance of the downwind monitoring site from the airport was rarely below the minimum transport distance that an air parcel would travel in three hours.

The 3-h forward trajectories and ozone concentrations used in our study were averaged (vectorally for the winds; arithmetically for the ozone concentrations) and statistically analyzed using a student's t-test at the 5% significance level. Three-hour averaged ozone concentrations were calculated at each appropriate downwind site for each high ozone day. The time averaging reduced the variability of the ozone data and allowed enough time for the air to move from the MSA to the downwind station. All potential sites that met the transport criterion were used.

RDU had a potential maximum of seven sites outside of the MSA that could be designated downwind sites from the analysis, while CLT and GSO had four and five, respectively (Figs. 1 and 2). The corresponding wind directions are provided in Table 3. The average resultant wind speed for high ozone days was also calculated for each MSA. It should be noted that not all sites were at optimal spacing, but each site used for upwind and downwind analysis met the 3-h transport criterion.

5. Trends and/or relationships

Local and regional effects of winds, associated with high ozone days were studied utilizing a number of spatial averages and deviations. Wind roses were constructed on high ozone days, and were compared with climatological wind roses. Several types of ozone averages including area means and upwind–downwind differences were then computed at each MSA for high ozone days. Results were compared with the background ozone concentration determined by Altshuller and Lefohn (1996).

5.1. Meteorological 3-h wind roses

Three-hour transport wind roses were constructed for the three MSAs for high ozone days during the study period; these were compared with climatological wind roses (e.g., 1963–1992) provided by the National Weather Service (Oommen, 1996). Climatology for RDU, CLT, and GSO show peaks for south and southwest winds. Secondary peaks were associated with north and northeasterly winds at all three MSAs.

When examining all wind directions on high ozone days, there was a predominance of SW winds (Oommen, 1996). Some of the differences among the other wind directions may be explained by the upwind emissions. At RDU, the wind directions from the southwest and west likely result in the transport of polluted air from CLT and GSO. Combining these directional sectors at RDU accounts for over 41% of the high ozone days at RDU. From climatology, we should expect winds from those directions only 27% of the time. Thus, the air arriving from the directions of GSO and CLT is often enriched with ozone and its precursors.

The differences in wind roses are not as large for CLT. Days when the air is coming from the northeast and east into CLT account for almost 24% of all the HODs. This was very close to the climatological frequency (21.6%) for these winds. However, the number of days on which the air was coming from the southwest into CLT accounted for almost 26% of all HODs, which is significantly greater than what is expected from climatology (18.2%). Thus, it appears that a significant source of ozone precursors could be to the southwest of the CLT MSA. At GSO, the number of HODs when the air was coming from RDU (east) and CLT (southwest) accounted for nearly 35% of the total HODs, which is slightly higher than what is expected from climatology (27.3%), suggesting that some of the ozone or ozone precursors may come from CLT and RDU.

5.2. Total area averages

The total area average (TAA) is the spatial average of ozone for all sites in and surrounding the MSAs for all

Table 3
Results from the total area average (TAA), the total downwind average (TDA), the ozone deviation (OD), the upwind ozone concentration, and the modified delta ozone analysis (MDOA). The statistical averages for the above parameters are presented here. Values with statistically significant difference are indicated by asterisks (*). The standard error for each parameter is in brackets and was evaluated at the 95% confidence interval. The bold indicates the MDOA for each MSA

	TAA (ppbv)	TDA (ppbv)	Wind regime	Average wind speed (m/s)	Downwind Transport 3-h range (km)	Downwind station identifier	Downwind station name	OD (ppbv)	Upwind (ppbv)		MDOA (ppbv)
RDU	76.89 [0.19]	82.24 [0.58]	SW	3.0–3.7	32.5–40.0	UFO	Franklinton	4.50 [2.30]*	67.00 [4.00]		7.24 [2.94]*
			NE	2.0–3.3	21.5–35.8	UPO	Pittsboro	5.90 [4.70]*	69.00 [3.00]		14.06 [5.36]*
			S	2.2–3.0	24.0–31.9	BTO	Butner	6.50 [3.10]*	N/A		9.06 [10.49]
			N	2.4–4.8	25.9–52.0	UQO	Fuquay-Varina	8.12 [5.14]*	N/A		− 1.72 [14.65]
			NW	2.3–3.9	25.1–41.7	UTO	Auburn Tower	4.20 [9.20]	N/A		N/A
										average =	8.32 [3.97]*
CLT	77.29 [1.43]	83.87 [1.18]	SW	3.2–3.8	24.6–32.8	COO	County Line	10.48 [2.18]*	62.04 [4.44]		21.34 [3.94]*
			NE	2.3–3.0	34.0–41.4	UYO	York County	2.12 [2.67]	81.39 [4.69]		1.94 [4.69]
										average =	13.58 [4.10]*
GSO	75.17 [1.87]	81.50 [3.50]	W	1.7–2.5	18.6–26.5	MCO	McLeansville	12.21 [2.90]*	65.80 [9.25]		23.67 [8.10]*
			E	1.8–2.9	18.9–31.7	FCA	Forsyth County A	− 0.20 [5.90]	N/A		N/A**
			SW	3.1–3.8	33.8–49.2	UCO	Cherry Grove	5.67 [4.09]*	61.78 [2.81]		18.72 [10.67]*
			NE	1.3–2.2	14.4–23.9	FOO	Fork Recreation	0.52 [5.14]	N/A		N/A**
			S	1.9–3.2	20.5–34.1	UBO	Bethany School	2.86 [5.07]	N/A		N/A
										average =	16.71 [8.08]*

**For each of the East and Northeast regimes in the GSO region, there was only one data point which fit the criteria of this study, and thus the student's t-test could not be calculated for these regimes. However, these data points were included in the overall GSO MDOA analysis.

HODs during the study period (Oommen, 1996). The TAA was calculated for RDU, CLT, and GSO MSAs (Table 3). These values are compared to the rural background values given by Altshuller and Lefohn (1996).

The TAA for RDU was calculated to be 76.89 ppbv [$\pm$0.19 ppbv]. The small confidence interval suggests that all the ozone sites surrounding the MSA were high, and not influenced by an anomalous measurement. This value is more than twice the rural background value of 35 ppbv [$\pm$10 ppbv] (Altshuller and Lefohn, 1996). Thus, there is a large difference between the RDU TAA and the background ozone value. Also of importance is that each TAA is a 3-h average, which indicates high exposure of ozone.

Similarly, the TAAs for CLT and GSO were not significantly different from RDU, but were nearly twice the rural background concentrations. Since the average values at all three MSAs were not significantly different from each other, this again suggests that high ozone days are a regional rather than a local problem, but each MSA adds substantially to the regional background ozone on these days.

5.3. Total downwind averages

The total downwind average (TDA) is computed at each MSA (Table 3) to determine if there was a statistically significant difference between the TAA and the TDA (Oommen, 1996). If the ozone concentration at the downwind site was equal to the TAA, then there is no net ozone being added by the city, suggesting that the rate of local production of ozone over the city is equal to the rate of destruction between the city and the downwind sites.

The TDA for RDU was computed to be 82.24 ppbv [$\pm$0.58 ppbv], which was statistically significantly higher than its TAA. Again, a small confidence interval suggests that all sites surrounding the MSAs were high. Similarly, the TDAs for CLT and GSO (see Table 3) were statistically significantly higher than their respective TAAs, but not statistically significantly different from RDU, again suggesting that the three MSAs are affected by similar synoptic-scale weather patterns. The consistently higher downwind averages suggest that each MSA does add to its downwind ozone level.

5.4. Ozone deviations

The idea of separating the downwind ozone averages by wind direction was then investigated to see if any particular wind direction produced a significantly higher downwind ozone average. Previous studies (Altshuller, 1988) have separated downwind ozone concentrations by wind direction. The difference between the downwind concentration for a particular wind regime and the TAA (Table 3) is called the ozone deviation (OD) (Oommen, 1996).

For RDU, the greatest ozone deviation occurs when the wind is from the north. That is, ozone concentration in an air parcel moving from the RDU MSA southward will increase by 8.12 ppbv [$\pm$5.14 ppbv] when measured at the downwind station. Other significant ozone deviations occur for S, SW, and NE wind directions. From the county precursor maps (EPA, 1995), there is strong evidence that the ozone precursors are being transported from the RDU MSA to regions downwind. Under the above wind regimes, biogenic VOCs and NO_x emissions are above average, but not high. However, mobile emissions of the precursor gases are high. A possible scenario is that as an air parcel leaves the RDU MSA, it is loaded with VOCs and NO_x due to mobile emissions. As this air parcel is transported by the prevailing wind, ozone is being produced giving large concentration at the downwind site.

For CLT, the SW direction was the only wind regime for significant ozone deviation. Ozone concentrations increased by an average of 10.48 ppbv [$\pm$ 2.15 ppbv] when the air parcel travels from the MSA to the downwind site. Anthropogenic emissions of VOCs and NO_x likely contribute to this high ozone concentration deviation. A major source for these precursors is likely the exhaust from mobile sources traveling along a highway. As the plume leaves the CLT MSA and moves northeastward, it is likely that the ozone precursors from the highway as a continuous line source (e.g., Interstate-85, which is oriented southwest-northeast) add to the plume (EPA, 1994). The ozone accumulation cycle is further disrupted, causing an increase in the downwind ozone concentration.

The highest ozone deviation for GSO occurs when the wind is from the west. That is, as an air parcel leaves the GSO MSA and travels eastward, 12.21 ppbv [$\pm$ 2.90 ppbv] of ozone is added, when measured at the downwind site. The only other wind regime for significant ozone deviation was SW. Like CLT, these increases are best explained by mobile emissions of VOC and NO_x (EPA, 1994). Interstate-40/85 is aligned east-west from the GSO MSA to the RDU MSA, while I-85 is oriented southwest-northeast into GSO from CLT. Emissions of the precursor gases from mobile sources on Interstate-40/85, and the subsequent conversion to ozone, could explain this increase on the eastern side of the MSA. Under a SW wind regime, this suggests that VOC and NO_x emissions from these highways may be transported into GSO, form ozone, and then are transported to the downwind site. This situation is also likely considering that the counties to the northeast of the GSO MSA do not emit high amounts of VOC and NO_x (EPA, 1995).

Transport of the VOC and NO_x gases in the MSAs appear to play an important part in the higher downwind ozone concentrations. Yet, an MSA is not the sole source for the high ozone downwind. If that were true, then all ozone concentrations at sites downwind should be

significantly higher than the corresponding TAAs. However, this is not the case, indicating the precursor gases are also being transported into the MSA from other regions.

5.5. Upwind averages

Upwind averages were also computed for the delta ozone analysis (Table 3). The upwind averages were all significantly higher than the background ozone values computed by Altshuller and Lefohn (1996), indicating that transport of ozone and its precursors provides the elevated upwind values for high ozone days. The upwind average values were not significantly different from each other (between 61 and 69 ppbv), except for the much larger value of 81.4 ppbv for the northeasterly wind into CLT. This high value further indicates that ozone might be transported from a region further upwind of CLT.

5.6. Modified delta ozone analysis

To further understand transport of ozone and its precursors, a modified delta ozone analysis (MDOA) was performed for the three MSAs. Such an analysis was performed by Lindsay et al. (1989) to determine if emission controls were working for the Atlanta, Georgia (GA) MSA, where ozone concentrations have been among the highest in the country. Delta ozone, $\Delta(O_3)$, is defined as the difference between the ozone concentration measured at a downwind site and that measured at an upwind site. This should reflect the net increment of photochemical ozone added to an air parcel as it moves over the city. Lindsay et al. (1989) found that the city of Atlanta added from 30 to 40 ppbv for southwest winds as an air parcel passes through the city. Adams (1992) performed a similar analysis on ozone data for Raleigh from 1981 to 1991, which showed that about 19 ppbv of ozone was added to the air parcel as it moved over the city under southwest winds.

In 1990, the Clean Air Act Amendments (CAAA) set tighter standards for ozone control. Primarily through more stringent inspection/maintenance (I/M) programs, emissions of the precursor gases (from mobile sources) were to be reduced significantly. A modified delta ozone analysis was performed, using the 1993–1995 data from the three MSAs in the current study (Oommen, 1996). Several modifications have been made to the original delta ozone analysis of Lindsay et al. (1989). First, we used 90 ppbv as a minimum (threshold) hourly ozone concentration for defining a high ozone day whereas Lindsay et al. (1989) and Adams (1992) used 80 and 60 ppbv, respectively. Second, our MDOA uses a different averaging period (0900–1459 EST), as compared to 1000–1559 LST used by Lindsay et al. (1989) and Adams (1992). This modified time period is centered around noon and probably better represents the solar insolation around its maximum value, but still avoids the morning and evening heavy traffic periods. The time also starts late enough in summer for the ozone in the residual layer to be mixing downward into the unstable boundary layer (Oommen, 1996), while the boundary layer growth rate may not reach its maximum (Stull, 1988). Third, more wind direction regimes were used in this study, when compared to the work of Lindsay et al. (1989), which restricted their study to only two wind regimes. It is important to recall that not all wind directions had ozone monitoring sites which fit the 3-h transport criterion; further, not all sites which fit this criteria were suitable for the modified delta ozone analysis in this study. Additional sites provided four wind regimes for the 1993–1995 RDU and GSO data sets, which were found suitable for the modified delta ozone analysis, whereas CLT still had two suitable wind directions. It should be noted that the downwind ozone sites may not have optimum locations for the specified wind directions, but the sites used are within the estimated range of the downwind transport distances.

The MDOA does show that the Raleigh/Durham MSA on average added 8.32 ppbv [$\pm$ 3.97 ppbv] as an air parcel passes through the MSA for all suitable wind directions. The above average value of delta ozone is about half of that found in the earlier analysis performed by Adams (1992), who calculated an average value of about 15.00 ppbv [$\pm$ 10.00 ppbv]. Differences in the threshold ozone concentrations, averaging periods, and monitoring sites used in the two studies could explain the observed differences.

There are four wind regimes (N, NE, S, and SW) which have been used in our delta ozone analysis. When the wind is from the NE, the RDU MSA adds 14.06 ppbv [$\pm$ 5.36 ppbv] of ozone (Table 3), whereas it adds only half that amount for a southwesterly wind. Adams (1992) also separated the total delta ozone analysis into southwesterly and northeasterly wind regimes, but found quite different delta ozone values for southwesterly (19.00 ppbv [$\pm$ 7.00 ppbv]) and northeasterly (4.00 ppbv [$\pm$ 1.00 ppbv]) winds. However, it is important to note that the downwind site for the Adams study utilized the Wake Forest (WFO) station. This station stopped taking measurements after the 1993 ozone season. Further, this site does not fit the 3-h transport criterion for a southwest wind. This site is approximately 23 km from RDU's NWS station. For our study period, the Franklinton (UFO) station, a site further downwind, was utilized (Figs. 2 and 3).

Only emissions of biogenic VOCs are high to the northeast of RDU, yet the MSA adds approximately 14 ppbv of ozone when the wind is northeasterly. Medium to long-range transport of NO_x and additional VOCs from regions northeast of RDU are plausible explanations. Similarly, biogenic VOC emissions to the southwest of RDU are high, which makes it harder to distinguish between urban/anthropogenic transport from

CLT or transport from the biogenic-rich regions of VOCs.

There is no significant contribution to delta ozone when winds are from the north, but southerly winds give an average delta ozone of 9.06 ppbv [± 10.49 ppbv]. The negative delta ozone for a north wind was a little surprising, but this value was based on only three data points and is not statistically significant. Adams (1992) did not consider north and south winds, so no comparison can be made with that study.

The MDOA showed that the CLT MSA adds on average 13.58 ppbv [±4.10 ppbv] of ozone as an air parcel passes through the MSA. This value shows a slight reduction from the mean delta ozone value of 17 ppbv [± 5 ppbv] reported by Adams (1992).

We separated our delta ozone analysis into two wind regimes (SW and NE). When the wind is from the southwest, the CLT MSA adds 21.34 ppbv [± 3.94 ppbv] of zone (see Table 3). This is much higher compared to the delta ozone value for the RDU MSA for a southwesterly wind. Adams computed a delta ozone of 17.50 ppbv [± 9.50 ppbv] for a southwesterly wind; however, this small difference is not statistically significant. The high amount of ozone being added by CLT suggests that VOCs and NO_x are transported medium to long-range via the prevailing winds from regions southwest of CLT. The average delta ozone for a northeasterly wind is much smaller and not statistically significant, but comparable to that reported by Adams (1992). Thus, there is no significant change in delta ozone at CLT between the two studies.

It is important to note that in this study, a site further to the southwest of the CLT MSA was chosen. Adams (1992) chose the Arrowood (AWO) site, which we considered to be within the CLT MSA (Figs. 3 and 4). Instead, we utilized the York County (UYO), South Carolina, site which is outside of the CLT MSA, but within the 3-h transport range. The differences in locations would probably explain the small differences in the average delta ozone values found in the two studies for the NE regime in the CLT MSA.

The MDOA shows that the GSO MSA adds, on average, 16.71 ppbv [± 8.08 ppbv] of ozone as an air parcel passes through the MSA. This mean is the highest among the three MSAs and twice the mean delta ozone for the RDU MSA. When separating by wind regimes (Table 3), with the west wind the GSO MSA added 23.67 ppbv [± 8.10 ppbv] of ozone, whereas for the southwest wind, it added 18.72 ppbv [± 10.67 ppbv]. For the east and northeast winds, delta ozone could not be calculated for the lack of significant data. Because emissions of VOCs are above average and NO_x is low to the west of GSO (EPA, 1995), transport of VOCs and NO_x into GSO are considered the likely explanation for the high amount of ozone being added by the city. Under a southwesterly wind, there appears to be a mixture of medium to long-range transport from CLT, coupled with mobile emissions along Interstate-85.

6. Summary and conclusions

Statistical analyses were performed on hourly ozone concentration data from 1993 to 1995 for three metropolitan statistical areas (MSAs) in North Carolina: Raleigh/Durham (RDU), Charlotte/Mecklenburg (CLT), and Greensboro/High Point/Winston-Salem (GSO). The results of this study show that even though stricter regulations on emission controls for the precursors of ozone have been implemented, as a result of the 1990 CAAA, these MSAs still experience high ozone days (e.g., any hourly ozone concentration $\geqslant$ 90 ppbv) and exceedances of the previous 1-h NAAQS (e.g., hourly ozone concentrations $\geqslant$ 120 ppbv). The three MSAs had a total of 16 exceedances of the ozone standard over 15 d. Of the 549 d (April–September, 1993–1995) in the study period, there were 169 d which had high ozone (ozone concentration $\geqslant$ 90 ppbv) in at least one of the three MSAs. Wind field patterns and averages of ozone were analyzed in an effort to determine whether these high ozone days (HODs) occur due to local contributions versus regional transport.

Local processes of ozone formation were found to be important in determining HODs at the three MSAs, as there were significant emissions of VOCs and NO_x. County mobile precursor emission maps showed that the three MSAs have higher than average mobile emissions of VOCs and NO_x. Additionally, the three MSAs were above average in biogenic VOCs, but low in biogenic emissions of NO_x. Thus, the large amounts of precursors in these MSAs in conjunction with strong solar insolation and high daytime temperatures during late spring and summer periods accounted for the large number of HODs.

A comparison of the wind roses for high ozone days and those based on the climatology showed some interesting features of the three MSAs. On high ozone days, winds at RDU were frequently from the directions of CLT and GSO. Similarly, GSO measured a high percentage of its high ozone days when winds were from RDU and CLT. The frequencies of above wind directions on HODs were significantly greater than those obtained from climatology at both RDU and GSO. Yet, CLT's winds on high ozone days were similar to the climatological values. However, southwesterly winds at CLT on high ozone days were more frequent than the climatological value, indicating a significant source for CLTs high ozone comes from regions to the southwest of that MSA.

The total area average (TAA) for the three MSAs were significantly higher than the regional background value of ozone reported by Altshuller and Lefohn (1996),

indicating the importance of the local production of VOCs and NO_x in these MSAs, especially on those selected HODs. Both the regional transport and local production of ozone within the MSA contributed to the high ozone values downwind of the three MSAs, as the total downwind averages (TDAs) were significantly higher than their TAAs. However, there are no significant differences among either the TDAs or TAAs for the three MSAs. This suggests that the three MSAs are similar and, in general, high ozone concentrations occur under the same regional/synoptic conditions.

An analysis of ozone deviation showed the importance of photochemical production and regional transport of ozone from the MSA to the downwind site. Highest ozone deviations occurred at RDU under a north wind, CLT under a southwest wind, and GSO under a west wind. Significant deviations also occurred at RDU under S, SW, and NE winds and at GSO under southwest winds. Local emissions of anthropogenic VOC and NO_x from mobile sources contributed to these high ozone deviations. If the MSAs were solely responsible for the deviation, then all wind directions should have produced significant ozone deviations, whose magnitudes would depend on the spatial distribution of emission sources as well as on the transport distance over the MSA. Since this was not strictly true, regional, and potentially long-range transport of VOCs and NO_x might also be influencing the ozone deviations.

For all three MSAs, upwind ozone concentrations were found significantly higher than the regional background ozone value. Lower background concentration is a result of averaging in both space and time (this includes all days, not just the HODs). Much elevated upwind concentrations on HODs could be attributed to regional transport of ozone and its precursors (VOCs and NO_x) by the prevailing winds and conversion to ozone before reaching the upwind site. The upwind concentrations were significantly lower than the total area averaged concentrations, except for site northeast of CLT. The modified delta ozone was the contribution of the MSA to the local ozone production. The modified delta ozone analysis (MDOA) values at RDU and CLT were compared with those computed by Adams (1992) for an earlier (1981–1991) data set. The comparison showed a 50% reduction of delta ozone at RDU, but no significant change at CLT. The decrease in the RDU MDO may partly be attributed to the tougher emission standards as required by the Clean Air Act Amendments of 1990; however, 3 years of data is a short record from which to qualitatively make this decision. It is not clear why the same regulations did not reduce MDO at CLT. No comparison between the two data sets was made for GSO.

The MDOA was also separated by wind regimes at each MSA. At RDU, the highest MDO occurred under a northeast wind. Since only biogenic VOCs are high northeast of RDU, this suggests medium to long-range transport of ozone precursors from regions further northeast by the prevailing winds. For CLT and GSO, the highest MDOs occurred under southwest winds, although a west wind at GSO also gave a large MDO. Lower, county-averaged emissions of the precursor gases to the southwest of CLT and west of GSO may explain relatively large values of MDO for these MSAs under southwest winds.

We find that on the high ozone days experienced by the RDU, CLT, and GSO MSAs ozone pollution was influenced by the local production of VOCs and NO_x due to mobile sources, the interaction of the wind fields between the MSAs, and regional transport of the precursor gases. Additionally, upwind ozone averages were elevated even in regions where VOC and NO_x emissions were low, suggesting that long-range transport of precursor gases could occur from other regions, such as the mid-Atlantic, Ohio Valley, and to the southwest of the CLT MSA.

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