Pergamon

Chemosphere, Vol. 34, No. 3, pp. 611-623, 1997

0045-6535/97 $17.00+0.00

PII: S0045-6535(96)00393-1

TRENDS AND ANALYSIS OF AMBIENT NO, NO_y, CO, AND OZONE CONCENTRATIONS IN RALEIGH, NORTH CAROLINA

Viney P. Aneja[1]*, Deug-Soo Kim[2], William L. Chameides[3]

[1]Department of Marine, Earth and Atmospheric Sciences
North Carolina State University
Raleigh, NC 27695 -8208 USA
[2]Department of Environmental Engineering, Kunsan National University,
Kunsan, Chonbuk 573-701, KOREA
[3]School of Earth and Atmospheric Sciences, Georgia Institute of Technology,
Atlanta, GA 30332-0340 USA

(Received in USA 13 November 1995; accepted 23 September 1996)

ABSTRACT

Ambient concentrations of NO and NO_y as well as O_3 and CO were measured during August 19 to September 1, 1991 in downtown Raleigh, North Carolina as a part of the Southern Oxidants Study-Southern Oxidants Research Program on Ozone Non-Attainment (SOS-SORP/ONA). These measurements were made in an effort to provide insight into the characteristics of nitrogen oxides and their role in the formation of ozone in the urban Southeast U.S. environment. NO and NO_y showed bimodal diurnal variations with peaks in the morning (06:00 - 08:00 EST) and in the late evening (21:00 - 23:00 EST). These peaks at this urban site correspond to the coupled effects of rush hour traffic and meteorological conditions (i.e., variation of mixing height and dispersion conditions). The overall average NO and NO_y concentrations were found to be 6.1 ± 5.4 ppbv (range: 0 to 70 ppbv) and 14.9 ± 8.1 ppbv (range: 0.3 to 110 ppbv), respectively. Average daily maxima of NO and NO_y (18.3 ppbv and 27.4 ppbv) occurred during the morning. O_3 showed a diurnal variation with a maximum in the afternoon between 14:00 and 16:00 EST; and a mean concentration 20 ± 10 ppbv (range: 1 to 62 ppbv). Maximum O_3 and CO concentrations during weekdays result from NO and CO emitted from mobile sources during the morning rush hour. Background CO concentration at Raleigh was estimated to be ~ 470 ± 52 ppbv. A linear correlation of $r^2 = 0.53$ between CO and NO_y was observed. The ratio of CO to NO_y (~ 16) at the Raleigh site suggests that mobile sources are the major contributor to NO and NO_y concentrations at the site.

1. INTRODUCTION

In the lower atmosphere, nitric oxide (NO) is emitted both from anthropogenic sources i.e., stationary and mobile sources (Logan et al., 1981; Logan, 1983); and natural sources i.e. lightening and soil (Aneja, 1984). NO, in turn, is converted to nitrogen dioxide (NO_2) by reaction with peroxy radicals (RO_2) or ozone (O_3). RO_2 are produced mostly by the reaction of hydroxyl radical (OH) with reactive hydrocarbons; and carbon monoxide (CO), and the photolysis of aldehydes which have both natural and anthropogenic origins. NO_2 is then photolyzed in the atmosphere, and the atomic oxygen released combines with molecule oxygen (O_2) to form ozone (O_3). While carbon monoxide and the hydrocarbons are consumed in these processes, NO_x acts as a catalyst. The primary source of the hydroxyl radicals in the troposphere involves ozone itself (Finlayson-Pitts and Pitts, 1986). However, in urban atmosphere, the reaction of hydroperoxyl radical (HO_2) and NO also produce OH radical and contribute to increased OH concentration because of the presence of abundant formaldehyde, NO and sunlight. The major source of HO_2 in the urban environment during the daylight hours may be the photolysis of formaldehyde.

It is believed that a significant fraction of the O_3 in the atmosphere is photochemically produced in situ (Chameides and Walker, 1973; Fishman et al., 1979; Logan et al., 1981). Efforts to reduce ozone concentration, especially in urban areas, have focused on control of total nonmethane hydrocarbon (NMHC) emissions for the past 20 years. There is, however, no clear evidence that the expected decrease in ozone concentration has been achieved. Over sixty areas in the United States remain classified by the U.S. Environmental Protection Agency (EPA) as ozone non-attainment areas; twenty four of these areas are in the South. It is not clear whether the failure to decrease O_3 concentration is in the basic control strategy, or an inability to reduce total NMHC emissions by the necessary amount to reduce O_3 concentration. The interaction between nitrogen oxides, NMHC and their intermediate oxidation products is complex. In general, the relationship between the formation of ozone and its precursors is non-linear. This non-linearity makes the development of an effective ozone control strategy difficult. Recent work suggests that emissions of other precursor , such as those of the nitrogen oxides, should be considered in ozone control strategy (Milford et al., 1989; Cardelino and Chameides, 1990). There is also experimental evidence to suggest that ozone production in the troposphere is limited by the availability of NO_x (= $NO + NO_2$) (Logan et al., 1981). Completion of a successful budget for tropospheric ozone, therefore, requires additional information on the fate and distribution of nitrogen oxides species (Ridley and Robinson, 1992).

The diurnal patterns in the ambient concentrations of NO, total reactive nitrogen species ($NO_y = NO + NO_2 + NO_3 + N_2O_5 + HNO_3 + PAN + HNO_2 + NO_3^- +$ organic nitrates), CO, and ozone measured during late summer at Raleigh, North Carolina are presented. Temporal variations in the concentration of these O_3 precursors is related to mobile sources associated with the morning and evening rush-hour traffic. Statistical correlations between NO_y and CO are also examined and discussed. This work is part of the Southern Oxidant Study-Southern Oxidants Research Programs on Ozone Non-Attainment (SOS-SORP/ONA) sponsored by the U.S. EPA. The SORP/ONA focuses on elucidating the processes responsible for the formation of ozone and other photochemical oxidants in urban and industrial centers in the Southern United States (Southern Oxidants Study Report, 1990).

2. METHODOLOGY

2.1 Sampling Site

The sampling site is in an open field (~ 1600 m^2) on the St. Augustine's College campus, which is less than one mile north of the center of downtown Raleigh, North Carolina (35.9° N, 78.7° W, 126.8 m MSL). Raleigh is the capital of North Carolina and most of the state government office buildings, legislature, and capital buildings are concentrated in a one square mile area. In additions, a number of municipal buildings and several federal government buildings are present. Several major state highway arteries crisscross the downtown area leading to substantial traffic flow throughout the day as well as during the peak rush hours. Located within 3 miles of the downtown area are several colleges, one university, the county hospital, as well as a number of county public schools and shopping complexes. Surrounding inner Raleigh is a four-lane highway complex approximately 10 miles in diameter. This outer loop services traffic from several interstate highways and local commuters. There are no industrial, or municipal power emission sources (i.e., no major point sources) within 10 miles of the downtown area.

2.2 Analytical instrumentation

Ambient NO and NO_y concentrations as well as meteorological parameters (temperature, wind speed and wind direction) were monitored during the period August 19, 1991 to September 1, 1991. The hourly averaged concentrations of CO and O_3 were measured at the same site by North Carolina Department of Environmental Health and Natural Resources (NC DEHNR). All species were sampled at ~ 10 m height above the ground and all instruments for NO, NO_y, O_3 and CO measurement were kept in a temperature controlled mobile laboratory. NO and NO_y were measured simultaneously using a modified two channel commercial chemiluminescent NO/NO_x detector (TECO 14B/E, Thermo Electron) (Delany et al., 1982; Dickerson et al., 1984). The instrument is based on the reaction between NO and reagent O_3 which produces a chemiluminescence that is detected by a photo multiplier tube. The analyzer's heated (~375° C) molybdenum catalyst, which converts most NO_y species such as NO_2, HNO_3, N_2O_5 and PAN to NO (Delany et al., 1982; Dickerson et al., 1984), was mounted to the gas inlet at 10 m. This type of converter has been shown to convert all tested NO_y compounds, with low interference form NH_3 or other species under typical tropospheric conditions (Williams, 1995; Honrath and Jaffe, 1990; Fehsenfeld et al., 1987). N_2O, N_2, and NH_3 are not converted to NO to any appreciable degree at this temperature (Delany et al., 1982). The inlet line to the external converter was cut as short as possible to minimize the loss of nitric acid (HNO_3) on the inlet. For the laboratory operating conditions, the instrument detection limit was 0.1 parts per billion volume (ppbv) for both NO and NO_y (Delany et al., 1982; Dickerson et al, 1984). Instrument calibration was accomplished by standard addition of NIST traceable NO in N_2 (Scott Specialty Gases, Inc., Plumsteadville, PA) via a Multigas Calibration System Model 146 (Thermo Environmental Instruments Inc.; Franklin, MA). To examine the conversion efficiency of NO_y to NO for the molybdenum converter, NIST traceable NO_2 in N_2 standard was used to calibrate the response of the instrument. Conversion efficiency of NO_2 was calculated to be >98% for the entire field study. Raw data was corrected using the NO calibration results and the NO_y raw data was also corrected for converter efficiency. During each 30 minute period, NO and NO_y measurements were made for 25 minutes, and the instrument zero was checked in the 5 minutes before and after the NO and NO_y measurements. Allowing zero air flow through the pre-reaction chamber sets the instrument zero.

3. RESULTS AND DISCUSSION

3.1 Diurnal Variations of NO, NO_y and O_3

NO and CO may be the most abundant primary air pollutants in an urban environment. To investigate the urban photochemistry, the averages of these species together with O_3 and their diurnal variations may give us information relating to the photochemical activities and the production of secondary pollutants.

The mean, standard deviation of the mean, and range in hourly averaged concentrations of NO, NO_y, O_3 and CO are presented in Table 1. The mean of NO, NO_y and O_3 during this period were 6.1 ± 5.4 ppbv (n = 306), 14.9 ± 8.1ppbv (n = 307) and 20.1 ± 10.4 ppbv (n = 312), respectively. Concentrations of NO and NO_y ranged from less than 1 ppbv to 70 ppbv for NO, and from 1 ppbv to 110 ppbv for NO_y. O_3 concentrations ranged from 1 ppbv to 62 ppbv. The meteorology parameters were indicative of late summer at this location with relatively hot afternoon temperatures of ~30 ^{o}C, relatively low wind speeds averaging about 1.5 m/sec, and prevailing surface winds from southwest.

Composite diurnal profiles of NO, NO_y and O_3 are shown in Figure 1. O_3 displayed the typical diurnal variation with maximum concentration in the afternoon between 14:00 and 16:00 EST, and minimum concentration early in the morning (~ 06:00 EST). The increase in O_3 during the morning hours coincides with the decrease in NO

Table 1. Statistical summary of NO, NO_y, CO, O_3 and meteorological parameters measured at Raleigh, NC (Aug. 19, 1991 to Sept. 1, 1991).

	NO (ppbv)	NO_y (ppbv)	CO** (ppmv)	O_3** (ppbv)	Temp. (C)	WS (m/s)	WD (deg.)
Mean	6.1	14.9	0.7	20.1	26	1.5	196
S.D.*	±5.4	±8.1	±0.1	±10.4	±3	±0.5	±16
Range	0 - 70.7	0.3 - 111	0.2 - 2.6	1.0 -62.0	21 - 36	0.1 - 3.4	20 - 301
N*	306	307	325	312	239	239	239

* S.D. represents standard deviation.
N; number of observations.
WS; wind speed
WD; wind direction

** CO and O_3 were measured by North Carolina Department of Environmental Health and Natural Resources.

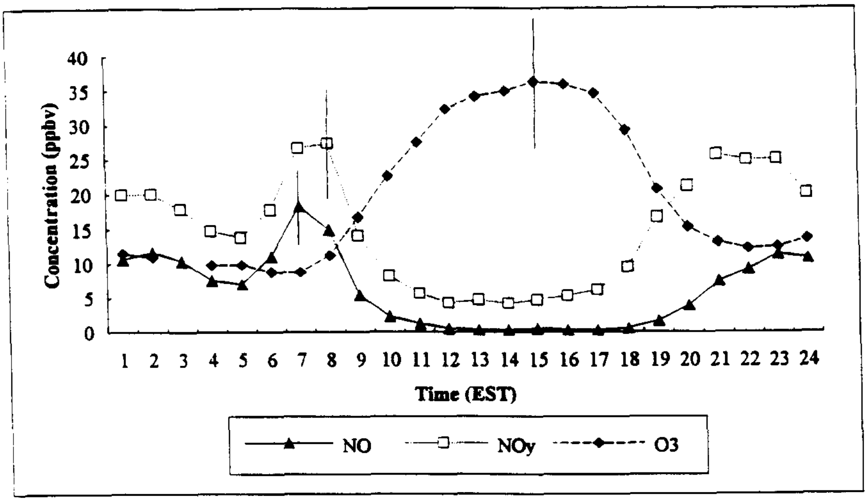

Figure 1. Composite diurnal profiles of NO, NOy and O3 at Raleigh, N.C.

concentration. According to NO_x-O_3 photostationary state analysis, ratio of K [NO][O_3] to J [NO_2] should be unity under photostationary state assumption where K is the rate constant of NO and O_3 reaction; J is the NO_2 photolysis rate. In the Raleigh area using the average NO, NO_y and O_3 concentrations measured, the value of photostationary state constant (K [NO][O_3]/J [NO_2]) is less than unity (~0.04); suggesting that the air contains significant amounts of new emissions that have not reached steady-state. This behavior is consistent with the photochemical production of O_3 from locally emitted precursor species. The decrease in O_3 concentration in the evening probably is the result of dry deposition under the subsiding boundary layer and titration with NO. The average daily maximum concentration of O_3 was 36.4 ± 14.7 ppbv.

Peak in the concentrations of NO and NO_y coincided with the morning rush-hour traffic (Figure 1). The morning peak was relatively short lasting between 06:00 - 08:00 EST. Average daily maximums of NO and NO_y during this period were 18.3 ± 23.7 ppbv and 27.4 ± 24.4 ppbv, respectively. The peaks associated with evening rush hour started around 18:00 EST, reaching a maximum at 21:00 EST. Average daily maximums of NO and NO_y between 21:00 - 23:00 EST were 11.5 ppbv and 25.8 ppbv, respectively. The ratio of NO to NO_y during the morning peak periods (~ 0.7) was higher than the ratio for the remainders of the day (ranged from 0.1 to 0.5). NO is emitted primarily by mobile sources during these peak periods and is converted to NO_2 and other oxidized nitrogen products in the air.

It was found that NO/NO_y ratios show a maxima during both morning and night time, with the night time values being a little lower than the morning value. This difference is the result of continued automotive emissions of NO during the morning. One also would expect a higher contribution of NO to NO_y during these high NO emission periods. Lower mixing depth and reduced dispersive conditions during these morning and night peak periods may also contribute to the increase of NO and NO_y for a short time period.

Similar diurnal pattern of NO has been observed at urban sites such as West London, Glasgow, and Billingham in the U.K. (Bower et al., 1991), and for Atlanta, GA in U.S.A. (data analysis from database of Summer 1990 Atlanta Ozone Precursor Study conducted by U.S. EPA). Diurnal variations of NO in Bower et al.'s measurements show that peaks during evening hours (18:00 ~ 20:00 h local time) are significant in winter months, but not as pronounced in summer months. This is probably due to the generally better-mixed conditions and hence improved dispersion during the afternoon and early evening (Bower et al., 1991). In our measurements, NO maximum during evening hours may be associated with a combination of meteorology and chemistry, as well as direct emission from rush hour traffic. Concentrations of both NO and NO_y increase gradually after the evening rush hour (~17:00 EST) and into night (~23:00 EST). The abundance of NO emitted from rush hour traffic may directly increase NO concentration in ambient air. However, no NO peak was found at the evening rush hour. This is attributed to immediate loss of NO by reaction with O_3 which is abundant during the evening rush hour and/or dry deposition. The decrease of O_3 after rush hour is thought to be evidence of this fact (Figure 1).

In order to examine the contribution of NO emitted from the rush hour mobile traffic to the NO peak concentration, mean diurnal variation of NO, NO_y and O_3 on weekdays and weekends are presented in Figure 2. On weekends, there were no significant variations of NO and NO_y concentrations. Only a relatively small variation of O_3 between day and night were found. Both NO and NO_y mean concentrations were significantly reduced on weekends (0.3 ± 0.1 ppbv for NO, and 4.8 ± 0.2 ppbv for NO_y) from the daily means for the entire measurement period (6 ppbv for NO and 15 ppbv No_y).

On the other hand, significant diurnal variations of NO, NO_y and O_3 were observed on weekdays. NO and NO_y concentrations during daytime (10:00 to 18:00 EST) were low with average concentrations of NO and NO_y less than 0.5 ± 0.2 ppbv for NO and about 5 ± 1.7 ppbv for NO_y. Average NO and NO_y for the rest of hours were about 10 ± 4.2 ppbv for NO, and 20 ± 4.5 ppbv of NO_y. Peak NO concentration on weekdays was two orders of magnitude higher than peak NO concentration (0.2 ppbv) on weekends.

Low levels of NO during the day is probably due to photochemistry as well as enhanced dispersive conditions. NO reacts with peroxy radicals which are formed mostly from the oxidation of CO and hydrocarbons by OH attack and is converted to NO_2. Mixing height also is increased and well-mixed conditions exist during daytime. On the other hand, during night time, there is no photochemistry and more stable atmospheric conditions exist. A decrease of NO concentration is observed from 02:00 to 05:00 EST. This decrease is mainly due to the reaction of NO with ozone.

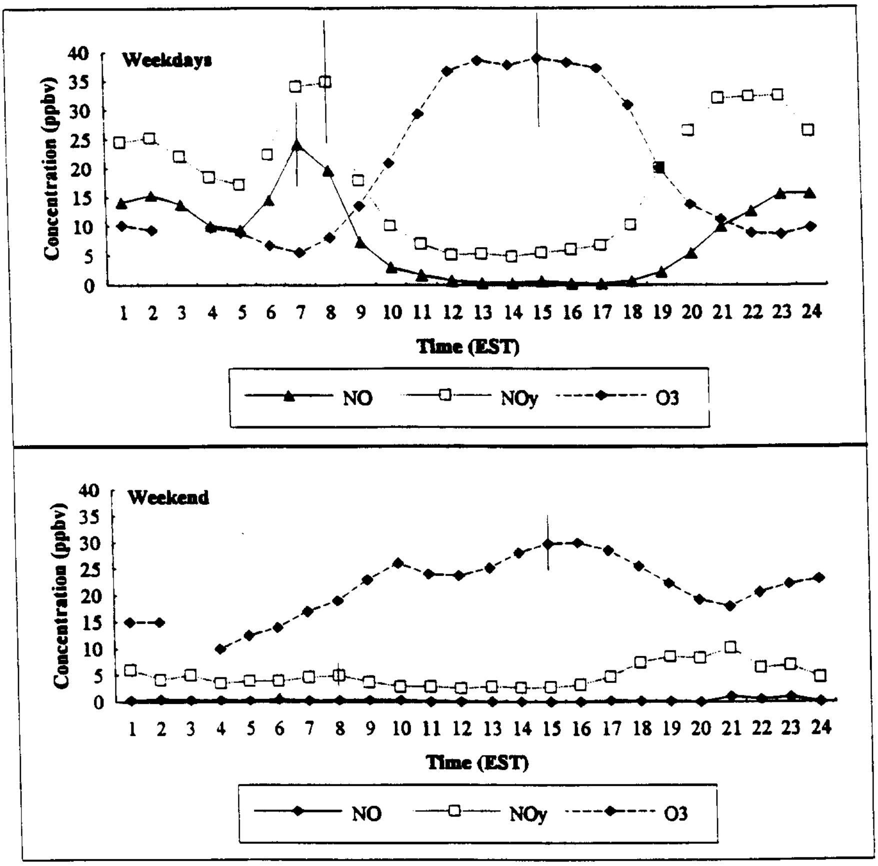

Figure 2. Composite diurnal profiles of NO, NOy and O3 for weekdays and weekend at Raleigh, N.C. Bars indicate 1 standard deviation.

Daily averaged maximum of O_3 concentration on weekdays was found to be ~10 ppbv higher than that on weekends (Table 2). This difference could be from the different production rate of O_3 between weekdays and weekend days. High NO concentration on weekday mornings may result in greater NO_2 concentration by reaction with peroxy radicals at the site. The level of CO and hydrocarbons in such an urban area may provide enough peroxy hydroxyl radical concentration to oxidize NO. Approximately 1 ppmv of CO concentration was observed during weekdays morning hours. Thus, this increase of the maximum O_3 on weekdays is thought to be due to the high NO emission locally emitted from automobiles during weekday mornings.

3.2 CO trends and their relation to NO_y and O_3 concentrations

The hourly averaged CO concentrations during the measurement period vary from 0.2 ppmv to 2.6 ppmv, and the mean and standard deviation was 0.7 ± 0.1 ppmv (Table 1). CO data measured at the site show the average CO level is higher in the morning and through the night than atmospheric during day time. Minimum CO concentration

Table 2. **The maximum concentrations of NO, NO_y, CO and O_3 for periods of weekdays and weekends.**

Periods	NO* (ppbv)	NO_y* (ppbv)	CO* (ppmv)	O_3** (ppbv)
Weekdays	22.0 ± 3.2	34.4 ± 0.6	0.9 ± 0.1	38 ± 1
Weekends	0.3 ± 0.1	4.8 ± 0.2	0.4 ± 0.1	28 ± 1

* averages during peak emission hours (06:00 ~ 08:00 EST)
** averages during peak photochemical hours (14:00 ~ 16:00 EST)

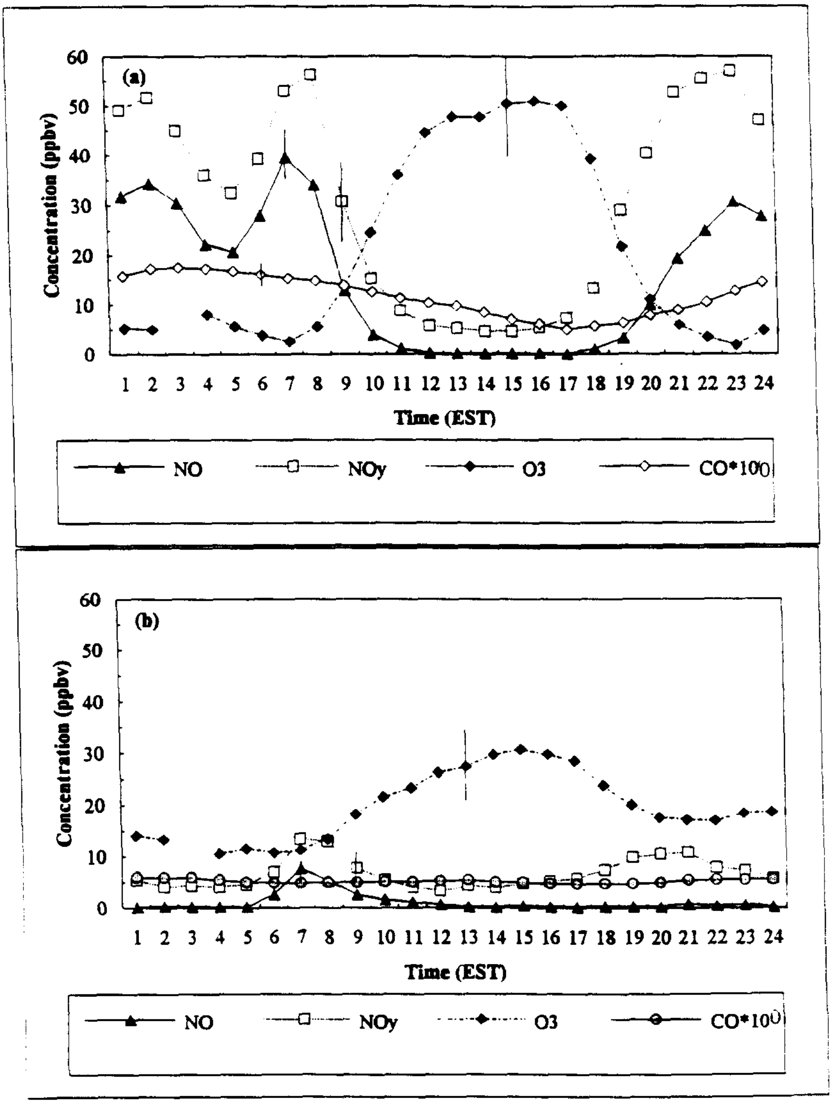

Figure 3. Composite diurnal variations of NO, NOy, O_3 and CO for (a) high CO and (b) low CO conditions at Raleigh, N.C. Bars indicate 1 standard deviation.

occurs around 16:00 EST when photochemical activity and dilution effect are strong during the day; HO_2 is produced in the oxidation of CO to CO_2 and leading to additional ozone formation (Figure 3).

Examination of hourly averaged CO concentrations during the measurement period show apparently different emission level of CO during morning rush hours. CO concentrations higher than 1.2 ppmv were observed during morning rush hours of the 22^{nd}, 23^{rd} and 29^{th} August, 1991 while CO concentrations below 0.6 ppmv were measured on the rest of the measurement days. During high CO days, significantly high O_3 and NO_y concentrations were also observed. Hourly averaged wind data and temperature measured at the site were examined. Temperature changes were not significant. Wind directions were drastically changing from NW to S or SE (downtown side), and magnitude of wind speed was relatively low on high CO days. Relatively high polluted air plume from center of the downtown area under low wind speed conditions should effect on O_3 chemistry through oxidation involving radicals and nitrogen oxides in ambient air (Finlayson-Pitts and Pitts, 1986). Atmospheric chemistry behavior including O_3 and NO may differ depending on CO concentration, i.e., under high CO conditions and under low CO conditions. High CO conditions are defined for this study as days where the morning peak time CO concentration is above 1.2 ppmv. Low CO conditions are defined as days where the morning peak time CO concentration is below 0.6 ppmv. A statistical summary of NO, NO_y, O_3 and CO over the period for high and low CO conditions is presented in Table 3. The mean of CO concentration during the high CO conditions (1.2 ± 0.4 ppmv) is about twice that during low CO conditions (0.5 ± 0.1 ppmv). Mean NO and NO_y concentrations in high CO conditions (15.7 ± 14.2 ppbv for NO and 31 ± 20 ppbv for NO_y) are significantly higher than those in low CO conditions (1.2 ± 1.8 ppbv for NO and 6.7 ± 2.9 ppbv for NO_y).

Table 3. The maximum and mean concentrations of NO, NO_y, CO and O_3 for the high and low CO conditions at Raleigh, North Carolina, during measurement period.

Condition	NO (ppbv)		NO_y (ppbv)		CO (ppmv)		O_3 (ppbv)		NO/NO_y	
	Max*	Mean	Max*	Mean	Max*	Mean	Max!	Mean	Max*	Mean
High CO	39.5	15.7	53	31	1.5	1.2	51	21	0.76	0.36
S.D.		±14.2		±20		±0.4		±19		±0.27
Low CO	7.6	1.2	13.5	6.7	0.5	0.5	30	19	0.56	0.15
S.D.		±1.8		±2.9		±0.1		±6		±0.15

* Maximum of hourly averaged values during morning rush hours (06:00 - 08:00 EST).
! Maximum of hourly averages during peak photochemical hours (14:00 - 16:00 EST).
High CO conditions; CO during morning rush hours > 1.2 ppmv
Low CO conditions; CO during morning rush hours < 0.6 ppmv
S.D.; standard deviation of the mean.

High NO concentrations coincident with high CO concentrations are expected because both CO and NO have similar anthropogenic sources (mainly mobile sources) in the urban areas. Figure 3 shows the diurnal variation of each species for both high and low CO conditions. Maximum ozone, in high CO conditions, is about 20 ppbv higher than during the low CO conditions. We hypothesize that the increase of maximum ozone concentration in high CO conditions is influenced by the following photochemical factors mainly; (1) the elevated anthropogenic hydrocarbon emissions during high CO conditions increase peroxy radical in urban atmosphere; (2) significantly higher ambient NO concentration during morning peak time in high CO conditions since NO and CO share sources and the NO is oxidized to form NO_2; and (3) high CO levels, since ozone can be produced by oxidation of CO in sufficient NO concentration.

The relationship between CO and reactive nitrogen species in Raleigh was investigated. A linear regression of hourly average CO and NO_y was performed and showed a strong correlation between CO and NO_y concentrations during the measurement period ($[CO] = 16.3[NO_y] + 470$; $r^2 = 0.53$). A scatter plot of the data is shown in Figure 4. The regression curve reveals a background CO concentration of 470 ± 52 ppbv at 95% confidence in the Raleigh urban area. It is not surprising that the background of CO at the Raleigh urban site is much higher than the value of 200 ppbv in clean air region of the northern hemisphere (Warneck, 1988), because the measurements were made near the downtown of the city where significant anthropogenic sources for CO are expected.

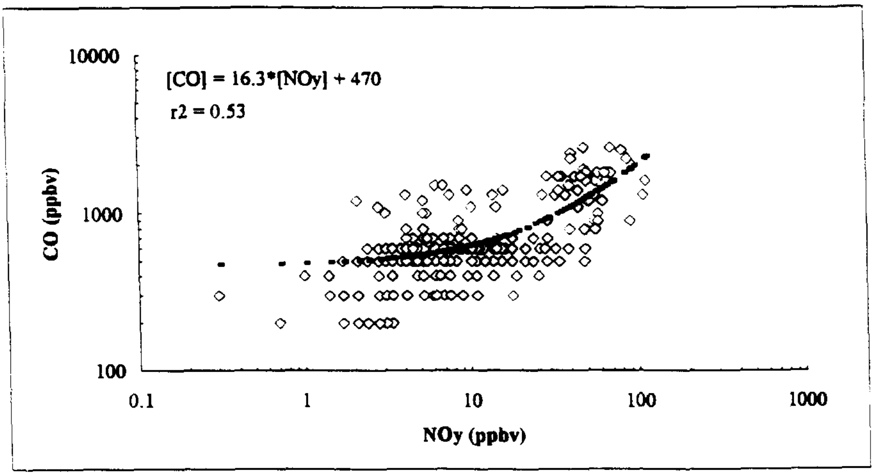

Figure 4. Correlation between [CO] and [NOy] on a log-log plot at Raleigh, North Carolina. Individual data points are from hourly averages during 8/19/91-9/1/91.

The ratio of CO concentration to NO_y concentration at Raleigh urban site (which is the slope of the regression curve in Figure 4) was 16.3. Parrish et. al. (1991) summarized average emissions of CO, NO_x and SO_2 in eastern United States using NAPAP Emission Inventory during summer, and reported the average emission ratio of CO and NO_y in eastern United States during summer as 4.3 with range from 1.0 to 8.4. The Raleigh, NC emissions inventory for 1990 (N.C. Division of Environmental Management, 1993) provides an average emission ratio of 7. A high emission ratio between CO and NO_y ($CO/NO_y > 7$) indicates mobile sources are dominant, while low emission ratios ($CO/NO_y < 1$) indicate that point sources are dominant. The ratio of 16.3 (based on measured concentrations) observed at Raleigh urban site, which is similar to the emission ratio of CO to NO_y (16.5) from the mobile source dominant Denver metropolitan area, suggests that Raleigh urban air mass is impacted mainly by mobile sources.

3.3 Relationship between NO_y concentration and O_3 concentration

Hourly averaged NO concentrations ranged from 0.3 ppbv to 70.7 ppbv during the high CO days, and ranged from 0.1 ppbv to 41.4 ppbv during the low CO days. Hourly average NO_y concentrations ranged from 2.1 ppbv to 111.0 ppbv during the high CO conditions and from 0.3 ppbv to 48.3 ppbv during the low CO conditions. During daytime hours the ratio of NO to NO_y is only about 0.05 (average = 0.26 during entire measurement period; 0.76 during morning rush hours) and CO concentration is about 1 ppmv. During nighttime hours, on the other hand, the average NO_y concentration is about 45 ppbv and the ratio of NO to NO_y is about 0.6 (Figure 3). The difference in NO_y concentration and ratio of NO to NO_y during the day and the night is caused by the coupled effects of photochemical activity and meteorological factors. During the daytime, photochemical activity is strong and NO and NO_2 is primarily transformed to HNO_3 and PAN. O_3 is also formed from NO_2 oxidation. However, during the nighttime, there is no photochemistry to produce O_3 from NO_2. However, enough O_3 exists an reacts quickly with NO released from mobile sources, converting it to other NO_y species. In addition, low mixing depth and non-dispersive conditions prevail.

The response of daily maximum O_3 concentration to maximum NO and NO_y concentration at rush hour in the morning, the ratio of NO and CO concentration to NO_y concentration ([NO]/[NO_y] and [CO]/[NO_y]) at morning peak hours are shown in Figure 5. Daily maximum O_3 concentrations in the Raleigh urban areas were found to be a function of elevated NO_y concentration in the morning from rush hour traffic, and the ratio of CO concentration to

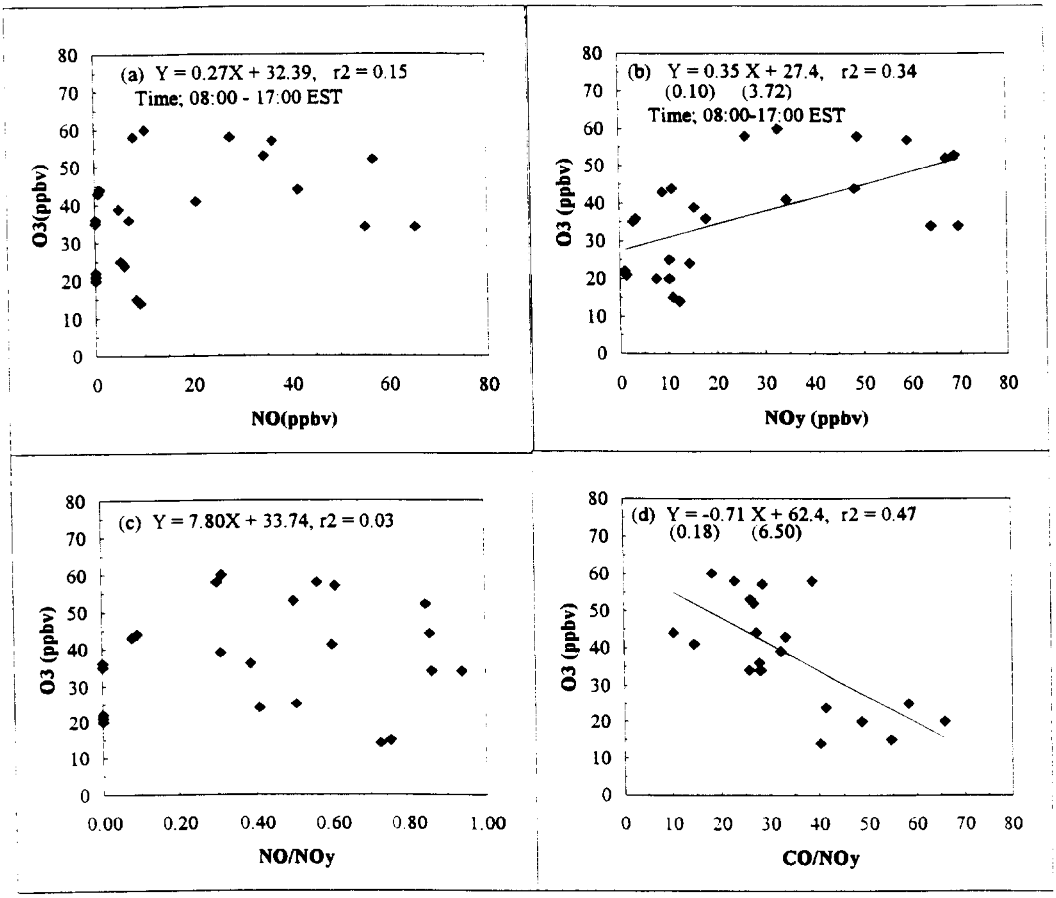

Figure 5. Correlations between daily maximum of [O_3] and (a) [NO], (b) [NOy], (c) the ratio of [NO] to [NOy] and (d) the ratio of [CO] to [NOy] at rush hour in the morning. The values in parenthesis are the standard errors for the constants.

NO_y concentration during the measurement period. Positive correlation between daily maximum O_3 concentration and the elevated NO_y concentration ($r^2 = 0.34$) was observed. The elevated NO_y concentration during the morning time was observed to be composed of over 60% of NO to total NO_y concentration. These observational-based results suggests that local production of NO from mobile sources at this location does contribute to the photochemical production of O_3.

4. SUMMARY AND CONCLUSIONS

These preliminary results have focused on an observational based analysis of reactive nitrogen species, and carbon monoxide in elucidating the processes responsible for the formation of ozone in an urban center (i.e. Raleigh, NC) in the southern United States. This will assist in the photochemical modeling and sensitivity analysis of ozone formation rate to changes in anthropogenic nitrogen oxide and CO concentrations/emissions.

The mean NO and NO_y concentrations were found to be 6.1 ± 5.4 ppb (ranged from 0 to 70 ppbv) and 14.9 ± 8.1 ppbv (ranged from 0.3 to 111 ppbv), respectively. Diurnal patterns of NO and NO_y observed at the Raleigh site is similar to those observed at urban cities in the U.K. (Bower et al., 1991); and Atlanta, GA in the U.S.(Atlanta Ozone Precursor Study, U.S. EPA, 1990). The peak of NO and NO_y in the morning was coincident to morning rush hours at the site; while the evening maxima is caused by the coupled effects of photochemical activity and meteorological factors. The average contribution of NO to NO_y concentration (NO/NO_y) was ~ 20 % during the entire measurement period; while the high contribution of NO to NO_y concentration (~ 70 %) during morning rush hours was attributed to the domination of mobile sources.

Different diurnal patterns of NO and NO_y between weekdays and weekends was attributed to emission from mobile sources. On weekends no morning peak was observed and both NO (0.3 ppbv), and NO_y concentrations (4.8 ppbv) were significantly reduced from daily mean concentrations for the entire measurement period (6 ppbv for NO, and 15 ppbv for NO_y). Daily averaged maximum of O_3 concentration during weekdays was found to be 10 ppbv higher than that during the weekends. Slight variations of hourly averaged CO concentrations was observed during entire measurement period (0.2 - 2.6 ppmv; mean and standard deviation = 0.7 ± 0.1 ppmv). However, relatively high CO concentrations above 1.2 ppmv during the morning rush hours were observed. Increase of maximum O_3 on weekdays may result from increase of photochemical formation of O_3 due to high NO, anthropogenic hydrocarbons, and CO level during morning automobile rush hours.

Linear correlation between CO and NO_y concentrations ($r^2 = 0.53$) was found during the measurement period. The background CO concentration was estimated to be ~ 470 ± 52 ppbv. The observed ambient ratio of CO to NO_y concentration in Raleigh, 16.3, was similar to the measured automobile emission ratio of CO to NO_y (16.5) in the Denver metropolitan area (Parrish et. al, 1991). This observed ratio suggests that the air mass in urban Raleigh is influenced by mainly mobile sources. Daily maximums of O_3 were correlated to daily maximums of NO_y ($r^2 = 0.34$), and the $[CO]/[NO_y]$ ($r^2 = 0.47$) during the measurement period. These observational-based results suggest that local production of NO from the mobile sources contributes to the photochemical production of O_3.

These preliminary results from Raleigh urban site suggest that the emission of NO from mobile sources during morning rush hours may be an important source of atmospheric NO concentration, and that this locally produced NO concentration may increase the maximum O_3 during the day. Without hydrocarbon data analysis, however, there are uncertainties in the discussion of photochemical production of O_3. It is hoped that the analysis and discussions of the nitrogen oxides measurements made at Raleigh, N.C. will contribute to the development of improved methodologies for characterizing the causes of ozone non-attainment in urban areas of the southeast U.S.

5. ACKNOWLEDGMENTS

This research has been funded by the U.S. Environmental Protection Agency as part of the Southern Oxidant Study - Southern Oxidant Research Programs on Ozone Non-Attainment (SOS-SORP/ONA). We acknowledge Mr. G. Murray, NC DEHNR, Dr. W. Robarge, NCSU and Dr. H. Jeffries, UNC at Chapel Hill and members of our Air Quality group, Benjamin Hartsell, Zheng Li and Mita Das for their assistance and discussions on atmospheric oxidants; and Mrs. P. Aneja, Ms. M. DeFeo and Ms. B. Batts in the preparation of the manuscript.

Disclaimer - The contents of this document do not necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor the views of all members of the Southern Oxidant Study Consortia; nor does mention of trade names or commercial or non-commercial products constitute endorsement or recommendation for use.

REFERENCES

Aneja, V.P. (1984) Environmental Impact of Natural Emissions, Air Pollution Control Association, TR-2, p. 430.

Cardelino, C.A. and Chameides W.L. (1990) Natural hydrocarbons, urbanization, and urban ozone, *J. Geophys. Res.*, **95**, 13971 - 13979.

Chameides, W.L., and Walker J.C.G. (1973) A Photochemical Theory of Tropospheric Ozone, *J. Geophys. Res.*, **78**, 8751-8760.

Delany, A.C., Dickerson R.R., Melchior, Jr. F.L. and Wartburg A.F. (1982) Modification of commercial NO_x detector for high sensitivity, *Rev. Sci. Instrum.*, **53**, 1899 - 1902.

Dickerson, R.R., Delany A.C. and Wartburg A.F. (1984) Further modification of commercial NO_x detector for high sensitivity., *Rev. Sci. Instrum.*, **55**, 1995 -1998.

Fehsenfeld, F.C. et al. (1987) A ground-based intercomparison of NO, NO_x, and NO_y measurement techniques, *Journal of Geophysical Research*, **92**, 14710-14722.

Finlayson-Pitts, B.J., and Pitts J.N.; Atmospheric Chemistry, Wiley-Interscience Publication, John Wiley & Sons, New York (1986).

Fishman, J., Solomon S., and Crutzen P.J. (1979) Observational and Theoretical evidence in support of a significant in situ Photochemical source of Tropospheric Ozone, *Tellus*, **31**, 432-446.

Honrath, R.E. and Jaffe, D.A. (1990) Measurements of nitrogen oxides in the Arctic, *Geophys. Res. Lett.*, **17**, 611-614.

Logan, J.A., Prather M.J., Wofsy S.C., and McElroy M.B. (1981) Tropospheric chemistry; A global perspective, *J. Geophys. Res.*, **86**, 7210 - 7254.

Logan, J.A. (1983) Nitrogen Oxides in the troposphere: Global and Regional Budgets, *J. Geophys. Res.*, **88**, 10785-10807.

Milford, J.B., Russell A.G. and McRae G.J. (1989) A new approach to photochemical pollution control: Implications of spatial patterns in pollutant responses to reductions in nitrogen oxides and reactive organic gas emissions, *Environ. Sci. Technol.*, **23**, 1290 - 1301.

N.C. Division of Environmental Management (1993) The redesignation demonstration and maintenance plan for Raleigh/Durham and Greensboro/Winston Salem/High Point ozone nonattainment areas, Raleigh, N.C. 27603.

Parrish, D.D., Trainer M., Buhr M.P., Watkins B.A., and Fehsenfeld F.C. (1991) Carbon monoxide concentrations and their relation to concentrations of total reactive oxidized nitrogen at two rural U.S. sites., J. *Geophys. Res.* ,**96**,9309-9320.

Ridley, B.A. and Robinson E. (1992) The Mauna Loa Observatory photochemistry experiment, *J. Geophys. Res.*, 97, 10285-10290.

Southern Oxidant Study Report (1990) University Corporation for Atmospheric Research, August 1990.

Warneck, P.; Chemistry of the Natural Atmosphere, Academic Press, Inc., San Diego, California (1988).

Williams, E. (1995) NO_y Intercomparison Study, Southern Oxidants Study 1995 Data Analysis Workshop and Annual Meeting, Raleigh, NC.