JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 99, NO. D5, PAGES 10,553–10,563, MAY 20, 1994

Observations and tropospheric photochemistry in central North Carolina

O. Poulida,[1] K. L. Civerolo, and R. R. Dickerson

Department of Meteorology, University of Maryland, College Park, Maryland

Abstract. The southeastern U.S. environment exhibits some of the highest average O_3 concentrations in the nation, especially during the summertime. Reactive nitrogen compounds and carbon monoxide were monitored for 2 weeks in rural North Carolina in August 1991 as part of the Southern Oxidants Study. The daytime (0600-1900 EST) mean NO concentration was ~200 parts per trillion (ppt), and nonzero abundances, probably due to soil emissions, were observed at night (mean NO ~ 60 ppt). Total reactive nitrogen compounds (NO_y) ranged between 1.5 and 12 parts per billion (minimum and maximum hourly observed averages). Back trajectories suggested the potentially important impact of power plants northwest of the site. The mean contribution of nitrogen oxides (NO_x) to NO_y during our experiment was 26% (±5% at $\pm1\sigma$ level of significance), with the diurnal variation of all trace gases strongly affected by the evolution of the planetary boundary layer. The good agreement between the observed O_3 production and the results of a simple physical/chemical scheme based on deviations from the $NO/O_3/NO_2$ photostationary state provides confidence in the reliability of a photolytic NO_2 converter. The same scheme indicated the enormously misleading conclusions that may result from the use of an inappropriate technique for monitoring NO_2.

1. Introduction

Ozone (O_3) controls the oxidizing capacity of the atmosphere and therefore the habitability of the planet. It is dangerous for humans [e.g., *Folinsbee et al.*, 1988] and deleterious to plant life [e.g., *Heck et al.*, 1984]. Monitoring of its precursors, such as nitrogen oxides (NO_x = nitric oxide (NO) + nitrogen dioxide (NO_2)), carbon monoxide (CO), and nonmethane hydrocarbons, is necessary for the calculation of in situ photochemical ozone production.

Nitric oxide reacts rapidly with ozone to form nitrogen dioxide, which in turn is photolyzed during daytime, regenerating ozone:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (R1)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (R2)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (R3)$$

where M represents a third body (typically N_2 and O_2). The above sequence of reactions illustrates a photostationary balance among NO, NO_2, O_3, and UV radiation [*Leighton*, 1961; *Stedman and Jackson*, 1975]. This null cycle by itself neither produces nor destroys ozone, and the photostationary state ratio ϕ should be equal to unity:

$$\phi = \frac{J_{NO_2} \times (NO_2)}{k_1 \times (NO) \times (O_3)} = 1 \qquad (1)$$

where the parentheses represent molecular number densities, k_1 is the rate of (R1) (k_1 = $2.0 \times 10^{-12}\exp(-1400/T)$ [*Jet Propulsion Laboratory* (*JPL*), 1992] in cubic centimeters per molecule per second, where T is the temperature in Kelvins), and J_{NO_2} is the photolysis frequency of NO_2. However, in rural or remote environments there is no a priori reason to expect (1) to be satisfied. Hydroperoxy radicals (HO_2), methyl peroxy radicals (CH_3O_2), and other organic peroxy radicals (denoted here as R_iO_2) can also efficiently oxidize NO to NO_2 by the reactions

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (R4)$$

$$CH_3O_2 + NO \rightarrow NO_2 + CH_3O \qquad (R5)$$

$$R_iO_2 + NO \rightarrow NO_2 + R_iO \qquad (R6)$$

without consumption of O_3. The peroxy radicals are produced during the oxidation of CO and hydrocarbons by the hydroxyl radical OH. Net ozone production occurs by peroxy radicals reacting with NO (reaction (R4)), whereas HO_2 reacting with O_3 causes destruction of ozone. Reaction (R4) dominates when the concentration of nitric oxide is sufficiently high ([NO]≥10 parts per trillion by volume (ppt)) [*Crutzen*, 1973; *Chameides and Walker*, 1973; *Fishman and Crutzen*, 1978; *Liu et al.*, 1987; *Lin et al.*, 1988].

In the presence of significant amounts of peroxy radicals, (R1)-(R6) give

$$J_{NO_2}\frac{(NO_2)}{(NO)} = k_1\,(O_3) + k_4\,(HO_2) + k_5\,(CH_3O_2) + \Sigma k_{6i}\,(R_iO_2) \qquad (2)$$

---

[1] Now at Institute of Environmental Physics, University of Bremen, Bremen, Germany.

Paper number 94JD00404.
0148-0227/94/94JD-00404$05.00

Equation (1) can then be modified as

$$\phi - 1 = \frac{k_4\,(HO_2) + k_5\,(CH_3O_2) + \Sigma k_{6i}\,(R_iO_2)}{k_1\,(O_3)} \qquad (3)$$

The rate constants k_4, k_5, and k_{6i} are relatively similar [*Atkinson and Lloyd*, 1984], so measurements of ϕ can be used to estimate an effective total peroxy radical concentration, which will be referred to as "equivalent $[HO_2]$," or $[HO_2]_{eq}$:

$$[HO_2]_{eq} = \frac{(\phi - 1) \times k_1 \times [O_3]}{k_4} \qquad (4)$$

where the square brackets represent mixing ratios, and $k_4 = 3.7 \times 10^{-12}\exp(250/T)$ in cubic centimeters per molecule per second [*JPL*, 1992].

The NO_2 produced from (R4)-(R6) is photolyzed and leads to O_3 production. Then the photochemical ozone production rate $P_{chem}(O_3)$ (in parts per billion (ppb) per second) is given by

$$P_{chem}(O_3) = (\phi - 1) \times k_1 \times [NO] \times [O_3] \qquad (5)$$

indicating that the rate of the photochemical formation of O_3 depends on the NO_x concentrations. The regional distribution of NO_x within the rural South is almost completely unknown [*Rodgers and Chameides*, 1988], since there have been few measurements of ozone precursors. The present monitoring system is inadequate for determining NO_x, because the system consists of commercial instruments, which suffer from interferences from HNO_3 and peroxyacetyl nitrate [*Fehsenfeld et al.*, 1987]. The U.S. Environmental Protection Agency (EPA) has approved the use of the molybdenum converter as a reference method for the measurement of NO_2 (designated reference method number RFNA-1289-074) in an urban environment to verify compliance with the air quality standards for NO_2, but as will be shown in the following section, the use of such a method yields unreasonable estimates of ozone mixing ratios.

In August 1991 our group participated in the Southern Oxidants Study (SOS) by using instruments of increased sensitivity and chemical specificity to monitor nitrogen compounds in rural North Carolina. The purposes of the experiment were to advance our knowledge of the regional distribution of NO_x within the southeastern United States and to test the reliability of our new NO_2 photolytic converter.

2. Measurement Site

The field experiment was carried out ~10 km south of the town of Candor, located in the Central Piedmont region of North Carolina, at the SONIA (Southeastern Oxidant and Nitrogen Intensive Analysis) site from August 7 to 18, 1991. There are only small residential towns around the area. The sampling site (35.26°N, 79.84°W; 198-m elevation; Figure 1) is situated in an open field (~10^4 m^2) surrounded by mixed deciduous and pine forest. The field was previously used to grow soybeans (N fixers). The ALCOA aluminum plant in the city of Badin, 40 km NW of Candor, and the Carolina Solite Co. in the town of Norwood, 28 km WSW of our site, do not appear to contribute significantly to the local air pollution. Pollutants may be transported to the region from the urban areas of Raleigh-Durham and Charlotte, located within a 130-km radius from the site (Figure 1).

3. Experimental Procedures and Data Reduction

A mobile laboratory and a removable tower supporting the sampling inlets were used for the realization of the experiment. The sampling inlets were located atop the mobile laboratory, about 8 m above the ground, and the sampling lines for all the detectors were approximately 10 m long.

Nitric oxide was measured simultaneously with two similar instruments employing a chemiluminescence reaction with O_3 (Thermo Environmental Corp., Franklin, Massachusetts, model 14B) modified for increased sensitivity [*Delany et al.*, 1982; *Dickerson*, 1984] and a noise-based detection limit (as configured for this experiment) of ~16 ppt (defined as a signal-to-noise ratio (S:N) of 1:1 at the $\pm 2\sigma$ noise level with a response time of 20 s). The absolute accuracy of the reported NO mixing ratios is no better than ~25 ppt as configured for these experiments. The sensitivity of both NO detectors was determined through calibrations at several NO concentrations generated by dynamic dilution of a known standard (Matheson; NO 2.2 parts per million by volume (ppm) in nitrogen) with compressed air. One of the NO detectors was operated in conjunction with a broadband UV NO_2 photolytic converter [*Kley and McFarland*, 1980; *Carroll et al.*, 1992], resulting in a NO/NO_x system, while the other was operated in conjunction with a hot molybdenum (Mo, 375°C) catalytic converter producing a NO/NO_y system. The Mo converter, which has a short glass inlet (<5 cm long), was mounted on the tower. Its conversion efficiency, determined through gas phase titrations, was found to be 98 (±1)% at $\pm 1\sigma$. The conversion efficiency of the NO_2 photolysis converter was determined through calibration with a NO_2 permeation tube and through gas phase titration and was found to be 60 (±7)% throughout the course of the experiment. Both the NO/NO_x and the NO/NO_y systems operated on 20-min cycles, producing a modulated signal, and were running in phase for simultaneous measurements of NO. The root-mean-square (rms) differences in the monitored concentrations averaged over 60 min were small and close to the limitations of the instruments; the difference in the mean daytime NO mixing ratios was 23 ppt, and the corresponding nighttime difference was 22 ppt.

Carbon monoxide measurements were made using a commercial nondispersive gas filter correlation analyzer (Thermo Environmental; model 48) modified for increased sensitivity [*Dickerson and Delany*, 1988] with a detection limit of about 24 ppb with S:N = 2:1 at the $\pm 1\sigma$ significance level and a 60-s time constant. The detector was calibrated using a transfer standard (Matheson; 5 ppm CO in N_2) and verified with a National Institute of Standards and Technology Standard Reference Material.

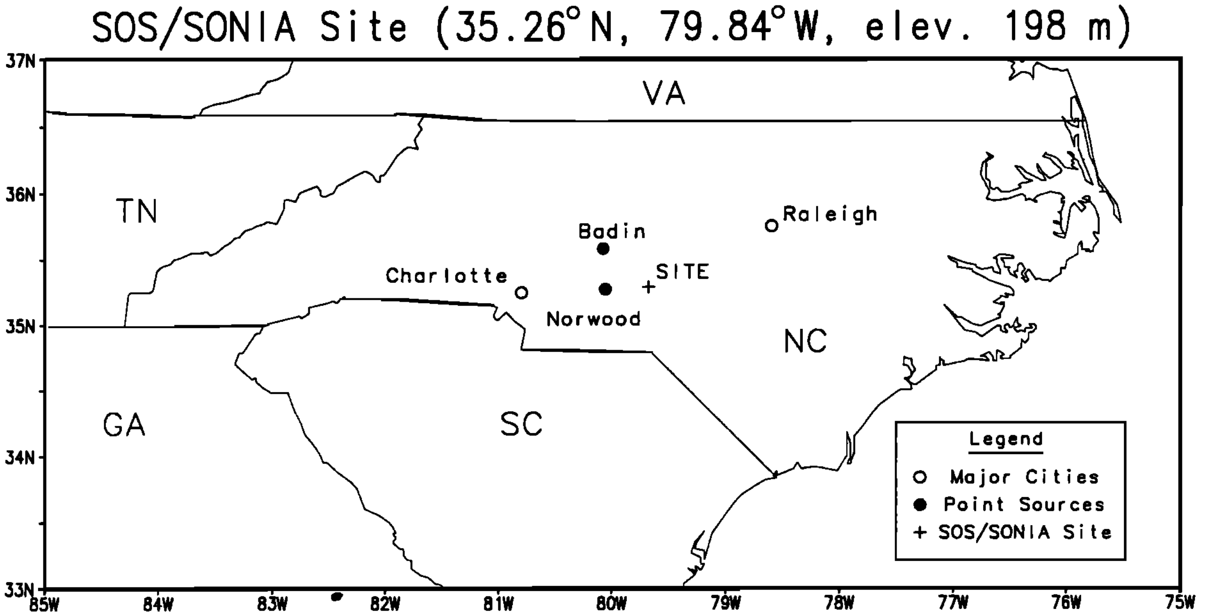

Figure 1. Map of North Carolina. The cross indicates the sampling site, and the open circles indicate locations of the major cities: Raleigh (130 km NE of the site; population 207,951) and Charlotte (110 km WSW of the site; population 395,934)

Total UV solar flux was measured with an Eppley radiometer mounted on top of our mobile laboratory. Information obtained recently from the manufacturer indicates that there is a loss of sensitivity on the order of 10% with increasing temperature for our experiment, during which the radiometer reached ~40°C. The photodiode has since failed, leaving the degree of this loss unknown.

The U.S. EPA operated a monitoring station adjacent to ours that measured standard meteorological parameters and O_3. The O_3 determination was based on a commercial instrument (Thermo Environmental; model 49) using absorption of 254-nm radiation. Hourly averages of O_3 concentrations were made available to us.

For a detailed description of all the detectors and of the sampling/calibration system the reader is referred to *Poulida* [1993]. Spikes due to electronic malfunctions or to local sources such as a car arriving at the site were eliminated, and hourly averages have been used for the analysis presented here. The total available CO data cover ~96% of the period of the experiment, the NO_x data cover ~87%, the NO_y data cover ~91%, and the UV data cover 100% of the second half of the experiment.

4. Results and Discussion

Table 1 includes some basic statistics for the monitored parameters. Although the nitric oxide concentrations are reported with parts-per-trillion precision, values below the detection limit of 25 ppt are not statistically significant.

4.1. Diurnal Variations

The chemistry of most reactive nitrogen compounds is determined by sunlight. In order to account for the different processes, the UV radiometer was used to separate periods of sunlight from dark. There are two interesting features in the mean diurnal variation of nitric oxide measured from the NO/NO_x and the NO/NO_y systems (Figure 2). Both instruments show a peak relatively early in the morning (0800 EST ± 1 hour) instead of around noon, when solar intensity is highest and therefore when the NO_2 photodissociation (R2) usually reaches its maximum. Similar behavior was observed at Wallops Island, Virginia [*Carroll et al.*, 1985; *Torres*, 1985], in Alabama during the Rural Oxidants in the Southern Environment (ROSE) experiment [*Cantrell et al.*, 1992], and in model calculations by *Fishman and Carney* [1984] for a summertime midlatitude planetary boundary layer (PBL), where the NO_x concentrations reached their maximum values at 0600 LT and then decreased to a minimum at 1500 LT because of mixing and conversion to HNO_3.

Nighttime nitric oxide was observed by both NO detectors during our experiment. Nitric oxide reacts with O_3 to form NO_2 within 2 min, typically, and reconversion is impossible without sunlight. Consequently, the NO mixing ratios are expected to be near zero during the nighttime in rural or remote sites unless a natural source exists. Several investigators [e.g., *McFarland et al.*, 1979] have used the nighttime NO signal as an indication of interferences of their detectors. Detailed analysis of the 10-s averages, recorded from our data acquisition system, suggest that the observed nighttime concentrations are real. The average nighttime NO mixing ratios recorded from the NO/NO_x and the NO/NO_y systems were 68 ppt and 46 ppt, respectively (Table 1). Nonzero but lower NO abundances were also observed at Wallops Island [*Carroll et al.*, 1985].

The O_3 concentrations (Figure 3a) showed the expected diurnal variation, with a minimum before sunrise and a peak late in the afternoon (1500 EST ± 1 hour). The mean difference between the daily minimum and max-

Table 1. Basic Statistics for Nitrogen Oxides, Total Reactive Nitrogen, O_3, and CO

	$NO_{daytime.1}$, ppt	$NO_{daytime.2}$, ppt	$NO_{nighttime.1}$, ppt	$NO_{nighttime.2}$, ppt	O_3, ppb	NO_2, ppb	NO_x, ppb	NO_y, ppb	CO, ppb
Mean	212	192	68	46	37	1.22	1.36	5.01	193
Minimum	41	5	9	0	2	0.33	0.40	1.41	141
25 percentile	103	67	45	8	23	0.58	0.70	3.51	173
Median	137	114	61	28	35	0.86	0.98	4.63	188
75 percentile	222	217	84	62	51	1.54	1.65	6.44	206
Maximum	1692	1901	157	251	86	5.52	7.22	12.07	285

Subscripts 1 and 2 indicate the NO chemiluminescence detectors of the NO/NO_x and NO/NO_y systems, respectively. Note the non-zero nighttime concentrations of NO.

imum was as high as 42 ppb, implying intense photochemical production of ozone during the day and/or strong destruction at night. For comparison, the corresponding amplitude observed at an 1100-m-altitude site in rural Virginia was only 8 ppb [*Poulida et al.*, 1991], demonstrating the substantial difference between a mountain and a flatland site. An elevated site is less affected by the evolution of the PBL, resulting in a diurnal variation weaker than that observed at low elevation sites.

For nonzero nighttime concentrations of O_3, NO should be depleted within a few minutes (reaction (R1)) unless there is a source of new NO. The very low concentrations of O_3 at night as well as the fact that soybeans (N fixers) had been grown in the field where our experiment took place strongly suggest that the nighttime measured NO is due to soil emissions.

At night, most of the NO_x is in the form of NO_2, which shows a mean diurnal variation (Figure 3b) similar to that of nitric oxide, with a peak at 0830 EST and a minimum late in the evening. The NO_y mixing ratios show a broad maximum just after sunrise (Figure 4a), following the variation of both NO and NO_2. The hourly mean carbon monoxide mixing ratios varied from 140 ppb to 285 ppb, with an overall mean value of 192 ppb and a standard deviation of only 28 ppb. It showed a weak diurnal cycle (Figure 4b), but its maximum coincides with the observed peak of the other trace gases, namely, early in the morning.

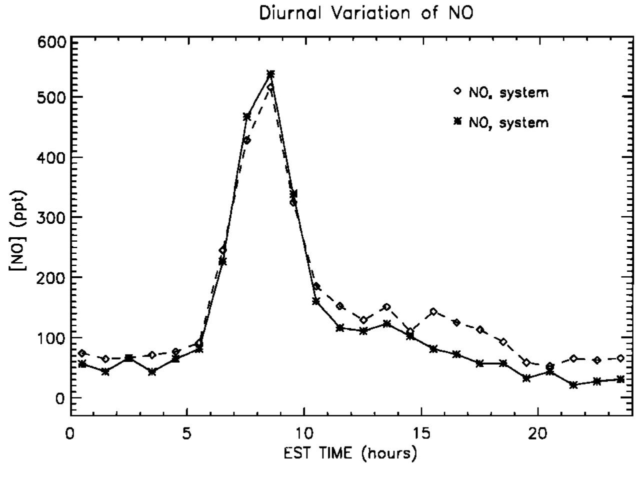

Figure 2. Overplotted diurnal variations of NO as monitored from the two chemiluminescence detectors. Notice the distinct morning peak and the nonzero nighttime NO abundances.

Notice that the mean hourly standard deviations of all the parameters are much smaller in the middle of the day than during the rest of the period, indicating that midday (1000-1700 EST) observations are more representative of regional air quality. The observed diurnal variation of the trace gases can be explained by the PBL evolution. Polluted air from sources located more than 10 km away is transported above the PBL into the area overnight. After the breakup of the nocturnal temperature inversion, atmospheric instability mixes air downward, resulting in the elevated concentrations of all trace gases. As the day progresses, the depth of the PBL increases, stronger dilution reduces the effects of these transported pollutants, and in situ photochemistry plays a significant role.

4.2. $[NO_x]$:$[NO_y]$ Ratio

A measure of the photochemical activity of NO_y in an air mass is the ratio $[NO_x]$:$[NO_y]$, which decreases with increased photochemical activity. When the ratio is equal to unity, there are no compounds in a more highly oxidized form than NO_2. Conversely, as the ratio approaches zero, all of the NO_x has been converted to some other form of reactive nitrogen. For example, fresh automobile exhaust shows a ratio near unity, but air parcels traveling over the Atlantic Ocean, being photochemically processed, show a ratio as low as 0.1 [*Carroll et al.*, 1992; Dickerson et al., submitted to *J. Geophys. Res.*, 1994].

During our experiment the $[NO_x]$:$[NO_y]$ ratio varied from 0.06 to 0.57 and the mean contribution of NO_x to NO_y was 26 (±5)%. The diurnal variation of the ratio (Figure 5) shows a maximum at 0800 (±1 hour) EST and a minimum at noon. The expected morning peak is due to relatively weak photochemistry. Later in the day, conditions are favorable for stronger photochemical processing and a more thoroughly mixed PBL. During the night, dry deposition removes HNO_3, which makes up about 30-45% of NO_y [*Buhr et al.*, 1990; *Doddridge et al.*, 1992; *Parrish et al.*, 1993], and soil emissions increase the $[NO_x]$:$[NO_y]$ ratio. The deviations of the ratio around the mean hourly values are at a minimum when the PBL height and photochemical activity are at a maximum (1000 to 1700 EST). The measurements taken during this period, which will be referred to as midday, will be used in the following section to characterize air of different geographic origin.

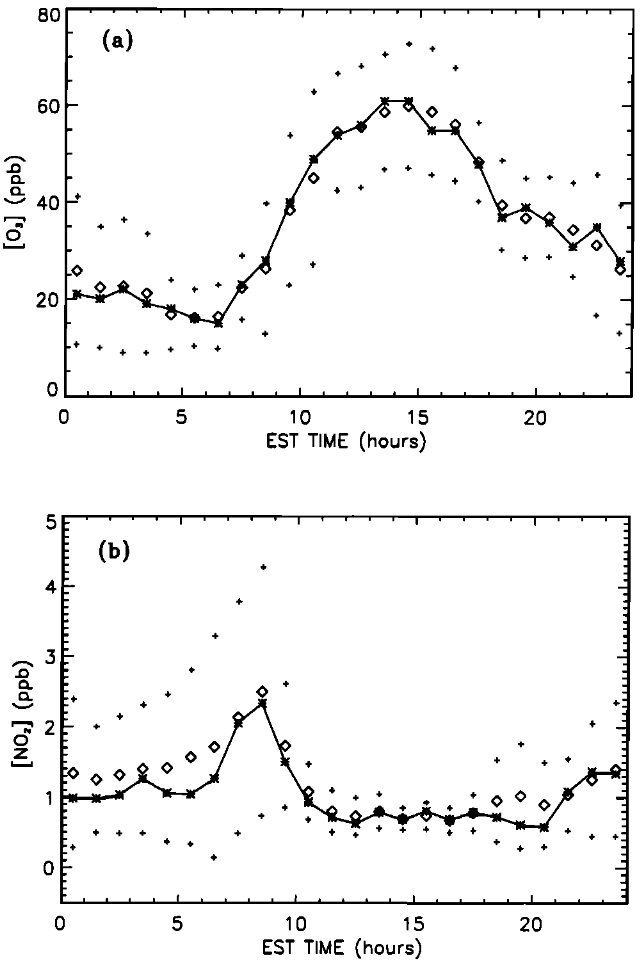

Figure 3. Diurnal variation of (a) O_3 and (b) NO_2 mixing ratios. The solid lines give the diurnal variations of the hourly medians, the diamonds represent the hourly averages, and the plus signs show ±1σ around the mean.

4.3. Back Trajectory Analysis

Knowledge of the origin of pollutants is essential to characterization of regional air quality. The measured levels of chemical constituents are directly related to the history of the air parcels arriving at the site. Local surface winds are inadequate for identification of the source of sampled air, since they are affected by the canopy of the surrounding vegetation. Therefore, the hybrid single-particle Lagrangian integrated trajectories (HY-SPLIT) model [*Draxler*, 1988] has been used to study the source of the air sampled at the site. The model uses the forecast wind fields predicted from the National Weather Service's nested grid model (NGM).

We ran two 48-hour back trajectories with ending points at 0900 EST and 1300 EST for each day of the experiment. The trajectories reflect the synoptic-scale meteorological patterns in which the air masses were embedded. No difference between the two sets of trajectories was observed, since no significant synoptic change (such as frontal passage) occurred in the two runs in the time interval 0900-1300 EST on the days studied. Table 2 shows the median of midday trace gas mixing ratios for the back trajectories ending at 1300 EST and the sector from which the back trajectories originate.

Mobile sources are rich in CO and NO_x, while point sources (such as power plants) are rich in SO_2 and NO_x but relatively poor in CO [e.g., *Parrish et al.*, 1991]. Air parcels polluted by power plants will exhibit smaller CO to NO_y ratios than those polluted by mobile sources. Air arriving at the site from the east and southwest shows the lowest NO_y concentrations and a high [CO]:[NO_y] ratio of ~43. On the other hand, air originating from the west to northwest sector or from the northeast shows very high mixing ratios of NO_y but only moderate concentrations of CO ([CO]:[NO_y] ratio ≈ 27). In two cases, both the CO and NO_y concentrations were high (with [CO]:[NO_y] ≈ 36), suggesting the combination of automobile and power plant emissions.

On the basis of midday NO_y and O_3 concentrations (Table 2), we grouped some of the days into two categories: "clean" days, and "dirty" days. Figures 6a and 6b give the 48-hour back trajectories for these two categories. The first category is characterized by air parcels originating from the NE to SSW sector, and the second one is characterized by air parcels from the W to NW sector. The morning peak in NO_y for the dirty days is quite enhanced. The difference in the [NO_y] between the morning peak and the observations just before dawn is ~5 ppb, but the corresponding difference for the clean days is only 1 ppb, indicating the importance of the transport mechanism discussed in the previous section.

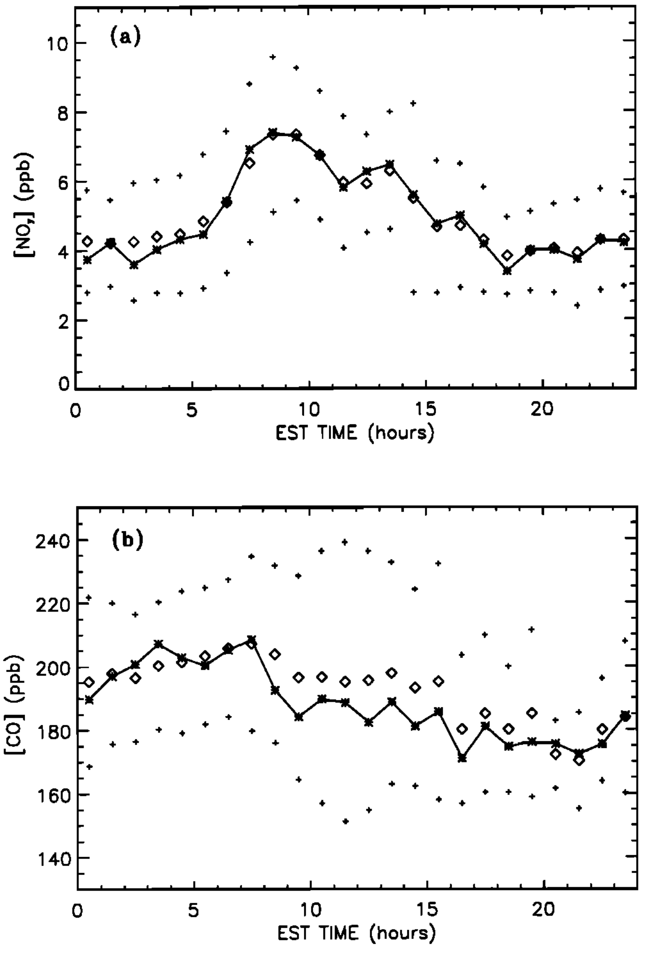

Figure 4. Diurnal variation of (a) NO_y and (b) CO mixing ratios. The symbols are as in Figure 3.

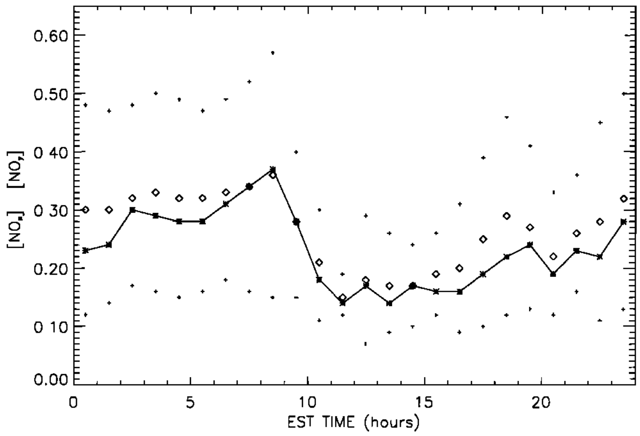

Figure 5. Diurnal variation of the NO_x to NO_y ratio. The symbols are as in Figure 3.

The history of the air parcels and their effects on the rural environment are directly related to the rate of O_3 production and consequently to the pollution control strategies that should be followed. The results of a simple photochemical/physical scheme for the estimation of the rate of O_3 formation are presented in the next section.

4.4. Rate of Ozone Formation

To make a simplified calculation of the net rate of ozone production $P_{net}(O_3)$, we must consider the in situ photochemical rate of production (5), the rate of its destruction due to dry deposition and photochemistry, and the rate of transport from polluted areas. To a first approximation the photochemical destruction of ozone will be neglected, a deposition rate v_d of 1 cm s^{-1} will be applied, a linear rate of change of the height of the PBL will be considered, and no horizontal advection of ozone or transport from above will be assumed. The rate of the net photochemical production of O_3 is then given by the following expression:

$$P_{net}(O_3) = P_{chem}(O_3) - \frac{v_d}{H} \times [O_3] \tag{6}$$

where H is the height of the PBL during the considered time interval. The height of the PBL just after dawn was assumed to be 500 m [*Holzworth*, 1972], with a rate of increase of 100 m $hour^{-1}$ up to 1600 EST. Equation (6) can be used to estimate the rate of ozone production, provided that accurate measurements of NO, O_3, NO_2, and UV solar flux are available.

The use of the nitrogen dioxide photolytic converter during the field campaign offered the opportunity for interference-free measurements of NO_2 [e.g., *Fehsenfeld et al.*, 1990] and consequently the ability to address the rate of O_3 formation $P_{net}(O_3)$. The simple chemical/physical scheme described by (6) is used to investigate the reliability of our NO_2 converter and to demonstrate the severity of the misleading conclusions that can result from the use of inappropriate measuring techniques.

The scheme requires the use of the NO_2 photodissociation coefficient J_{NO_2} (in reciprocal seconds), and the empirical relationship given by *Madronich* [1987] is used for its estimation from the UV solar flux data:

$$J_{NO_2} = \frac{1.35 \times E}{(0.56 + 0.03 \times z) \times \cos\theta + 0.21} \ s^{-1} \tag{7}$$

where E is measured in watts per cubic centimeter and is given from the Eppley output, z is the station elevation above sea level in kilometers (z=0.198 km), and θ is the solar zenith angle. This formula applied for clear skies, a zenith angle of <60°, negligible local background, and moderate regional albedo yields estimates of J_{NO_2} with an absolute experimental accuracy of ±10%. For cloudy conditions the deduced uncertainties in the J_{NO_2} values could be as great as 50%.

Table 2. Midday Median Concentrations and Ratios

Day in August	Trajectory Direction	NO_x, ppb	NO_y, ppb	CO, ppb	O_3, ppb	NO_x:NO_y	CO:NO_y
08	NNW	---	7.36	274	71	---	37.2
09	WSW	1.09	6.67	242	51	0.16	36.3
10	NW	1.10	7.11	174	62	0.15	24.5
11	N	0.82	6.40	191	55	0.13	29.8
12	ENE	1.12	3.59	178	49	0.31	49.6
13	E	0.67	4.20	182	45	0.16	43.4
14	SW	0.94	4.72	183	34	0.20	38.8
15	W	0.93	6.18	177	61	0.15	28.6
16	WNW	0.77	6.10	158	66	0.13	25.9
17	NW*	0.64	6.63	173	68	0.10	26.1
Median		0.88	6.29	188	58	0.15	33.1

The concentrations can be compared with the corresponding median values for the entire period. Data are for back trajectories ending at 1300 EST.

* No NGM wind data were available for August 17. Therefore the surface and the 700-mbar maps were used to retrieve the origins of the air masses arriving at the site that day.

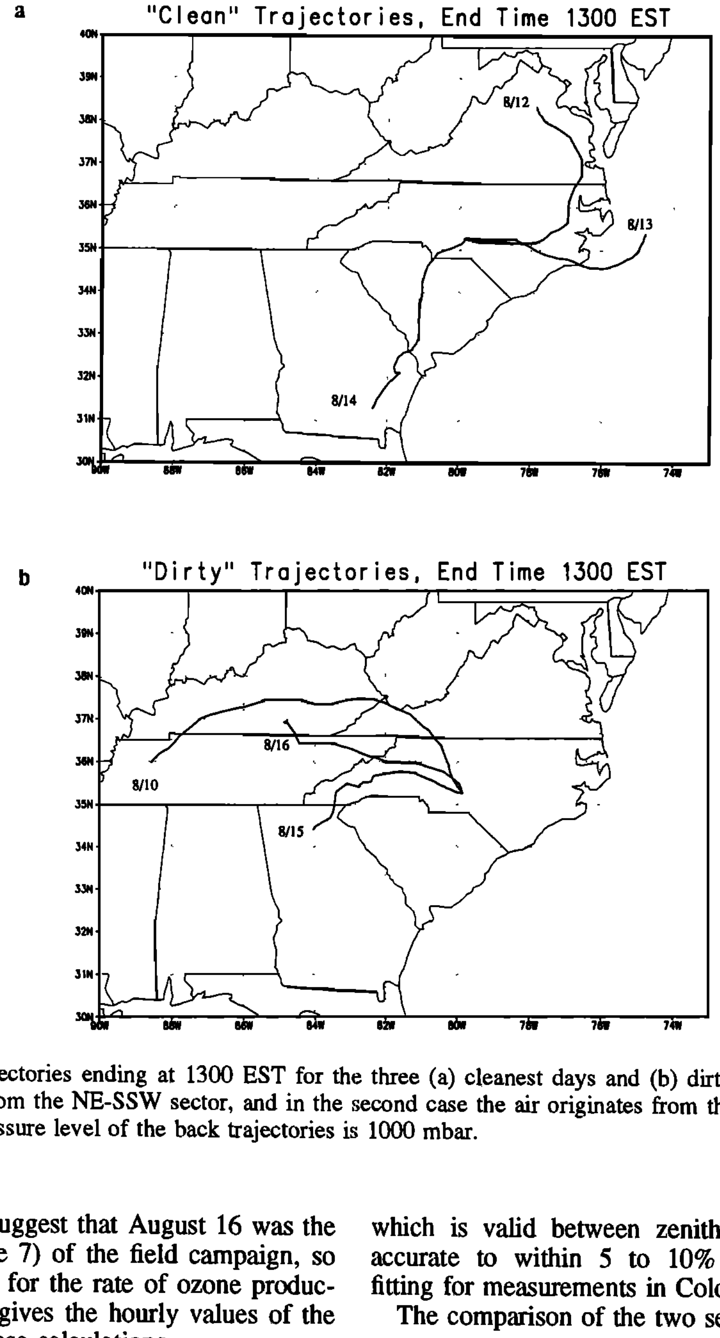

Figure 6. Back trajectories ending at 1300 EST for the three (a) cleanest days and (b) dirty days. In the first case air originates from the NE-SSW sector, and in the second case the air originates from the W to NW sector. The approximate pressure level of the back trajectories is 1000 mbar.

Our UV solar flux data suggest that August 16 was the most cloud-free day (Figure 7) of the field campaign, so it is considered appropriate for the rate of ozone production calculations. Table 3 gives the hourly values of the parameters necessary for these calculations.

One of the first interesting points is the relatively low UV flux observations. The Eppley radiometer was inspected and calibrated shortly before the field experiment. Direct measurements of J_{NO_2} (e.g., *Cantrell et al.* [1992] in Alabama) have shown that for $\theta < 25°$ and clear skies, the photolysis rate can be as high as 9.5×10^{-3} s^{-1}. However, our measurements never exceeded a value of 6.9×10^{-3} s^{-1}, suggesting attenuation of the solar UV flux. In order to get an estimate of the J_{NO_2} reduction due to the UV attenuation, we calculated the expected values of the photolysis rate for clear skies on the basis of the empirical formula given by *Dickerson* [1980], which is a function of zenith angle θ only

$$J_{NO_2} = 1.67 \times \exp(-0.575 \times \sec\theta) \times 10^{-2} \text{ s}^{-1} \qquad (8)$$

which is valid between zenith angles of 0 and 65°, is accurate to within 5 to 10% and describes the curve fitting for measurements in Colorado.

The comparison of the two sets of J_{NO_2} values resulting from (7) and (8) for August 16 showed an average reduction of the photolysis frequency by 24 (±6)%. The reduction is higher during the morning hours and decreases toward the afternoon. As mentioned above under Experimental Procedures and Data Reduction, there could be a 10-15% negative bias in the Eppley output due to elevated temperatures during the experiment. This drift could introduce a corresponding 10-15% reduction in the J_{NO_2} values. The rest of the attenuation in UV flux may be due to clouds or haze. *Shetter et al.* [1992] have observed only a 5% reduction of J_{NO_2} values due to aerosol scattering over Hawaii.

Concurrent clear-sky hourly averages of the available data (Table 3) are used for calculating the photostationary state ratio ϕ for each hour (1). For that period the ratio ϕ was generally higher than unity and lay between 0.53 and 1.42 (Table 4). The ratio ϕ shows a maximum just

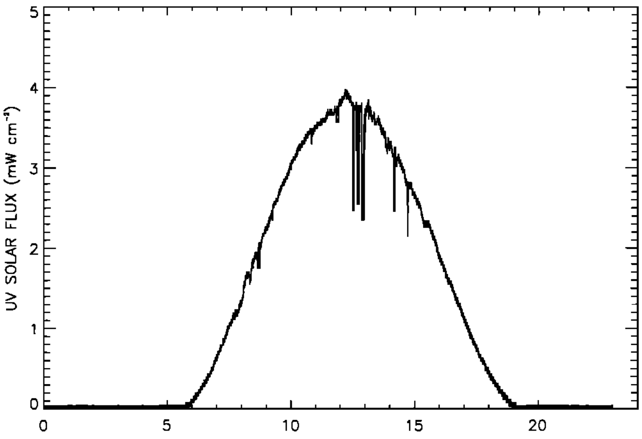

Figure 7. UV solar flux measurements for August 16. The Eppley radiometer output may have been reduced by 10-15% because of the temperature dependence in the calibration.

before noon and a minimum in late afternoon. The deviations of the photostationary state ratio from unity confirm the existence of other oxidants that convert NO to NO_2 without O_3 consumption. If these oxidants are represented by $[HO_2]_{eq}$, we can calculate the equivalent concentration of peroxy radicals from (4) for each hour (Table 4). The uncertainty deduced from known experimental errors is estimated to be ~31%, a value that does not include the unknown uncertainty due to the temperature sensitivity of the Eppley radiometer. The derived $[HO_2]_{eq}$ mixing ratios lie between <10 and 59 ppt, with a distinguishable maximum at 1030 EST and a minimum in late afternoon. At Mauna Loa, *Ridley et al.* [1992] estimated a maximum $[HO_2]_{eq}$ of ~70 ppt to occur at 1130 LT, and during the ROSE study in Alabama, *Cantrell et al.* [1992], using both experimental data and theoretical estimates, found a maximum $[HO_2]_{eq}$ of 150 ppt at solar noon.

The hourly rate of O_3 production $P_{net}(O_3)$ calculated from (6), shows a first maximum early in the morning. This morning maximum coincides with the observed morning peaks of all the measured trace gases. The rms difference between the calculated mixing ratio of O_3 based on the applied scheme and the observed ratio is ~ 26% (Figure 8), a difference well within the uncertainties introduced from the measurement techniques and the simplicity of the applied chemical/physical scheme. Both observed and calculated O_3 show the same trend: a sharp increase of O_3 early in the morning, a maximum mixing ratio at 1030 EST, and a slow decrease in the afternoon. It should be noted that during the hours centered on 1430 and 1530 EST, ϕ was less than unity. For these two hours, $P_{chem}(O_3)$ was assumed to be zero.

The high sensitivity of the calculation of the O_3 production to $[NO_2]$ is clear when measurements from a method designated by EPA were applied. We repeated the calculations of the O_3 production using values of NO_2 obtained from the hot Mo converter. The resulting rates of ozone formation are unrealistic, and the calculated hourly O_3 concentrations are nearly 2 orders of magnitude higher than observed (Figure 8).

5. Comparison With Other Measurements

One of the purposes of the experiment was to characterize the regional air quality at a rural site in the southeastern United States. In order to put the observations in North Carolina into perspective, it is necessary to compare them with summertime measurements in other rural environments.

Median concentrations of daytime NO and O_3 in North Carolina are very similar to those observed at an elevated site (elevation=1100 m) in the Shenandoah National Park (SNP) in rural Virginia in 1989 [*Poulida et al.*, 1991, *Doddridge et al.*, 1992], while the median summertime CO concentration in North Carolina is a little lower (188 ppb versus 211 ppb in SNP), probably because central North Carolina is a less populated area. However, the mean CO mixing ratio observed in rural North Carolina (193 ppb) was within the 1σ range of the summertime mixing ratios measured in SNP (232 ± 57 ppb). On the other hand, NO_y was about 25% higher in North Carolina than at SNP and was similar to the concentrations observed in Bondville, Illinois, and Scotia, Pennsylvania [*Parrish et al.*, 1993]. The Bondville site was fairly remote and was surrounded by agricultural land on which corn, soybeans, and alfalfa were growing during the field experiment, and the Scotia site was surrounded by a matrix of major industrial sources at distances of 100 km or more. The similarity of the median values suggests

Table 3. Hourly Data for Calculating Rate of O_3 Formation on August 16

Time, EST	UV, mW cm^{-2}	NO, ppb	NO_2, ppb	O_3, ppb	$J_{NO_2}\times10^{-3}$, s^{-1}	$k\times10^{-13}$, cm^3 $molecule^{-1}$ s^{-1}
0830	1.83	0.64	3.14	35	4.4	0.175
0930	2.65	0.47	2.66	56	5.6	0.182
1030	3.31	0.14	0.94	65	6.4	0.186
1130	3.65	0.15	0.77*	66	6.7	0.190
1230	3.51	0.12	0.60	68	6.5	0.192
1330	3.54	0.12	0.65	68	6.9	0.193
1430	2.95	0.14	0.57	68	6.3	0.194
1530	2.30	0.19	0.57	65	5.6	0.194

* No NO_2 data were available for the interval between 1100 and 1200 EST; therefore a linear interpolation between the surrounding time intervals was applied.

Table 4. Hourly Values of Photostationary Ratio ϕ, Rate of O_3 Production, and Equivalent $[HO_2]_{eq}$ on August 16

Time, EST	ϕ	P_{net} (O_3), ppb/hr	$[HO_2]_{eq}$, ppt
0830	1.39	12.6	28
0930	1.22	7.8	26
1030	1.42	3.9	59
1130	1.11	-0.6	16
1230	1.03	-1.8	<10
1330	1.10	-0.5	16
1430	0.77	-1.8	<10
1530	0.53	-1.7	<10

that the southeastern environment may be strongly affected by reactive nitrogen compounds that are transported over the area from point sources far away rather than from local natural sources. The spread of the NO_y data in North Carolina is significantly smaller than that in the data for the other two sites (Figure 9), implying that more uniformly mixed air was monitored during our experiment.

Figure 10 gives a graphical representation of the statistical distribution of the midday $[NO_x]$:$[NO_y]$ ratio in North Carolina compared to those at the sites in Illinois and Pennsylvania. The last two sites exhibited higher ratios than ours. In North Carolina the midday ratio ranged from 0.09 to 0.53 with a median value of 0.17, but it ranged from 0.04 to 0.70 in Bondville (the median ratio was 0.32) and from 0.11 to 0.84 in Scotia (the median ratio was 0.31) [*Parrish et al.*, 1993].

6. Conclusions

Too little is known about the regional distribution of NO_x within the rural southeastern U.S. environment. Therefore we participated in a field experiment held at the SONIA site near Candor, North Carolina, as part of the SOS project. One of the objectives of the project was to help establish the background concentrations of different chemical species for the southeastern states.

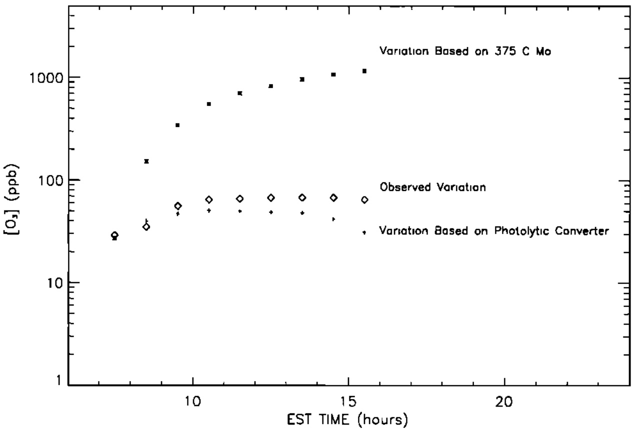

Figure 8. Intercomparison of the observed O_3 variation on August 16 with those calculated on the basis of NO_2 measurements with the photolytic converter and the hot molybdenum converter.

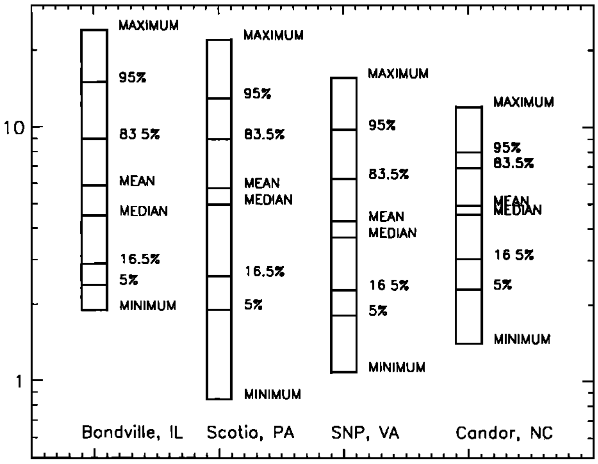

Figure 9. Intercomparison of the NO_y mixing ratios measured in rural North Carolina with those measured in other rural sites in eastern United States. The range, the mean mixing ratio, and the central 67% and central 90% are shown. The dashed lines represent observed median values. The data for Bondville and Scotia are adapted from *Parrish et al.* [1993], and the SNP data are adapted from *Doddridge et al.* [1992].

There was a significant spread of the data, especially of the NO and NO_y measurements. The dependence of the levels of the observed mixing ratios of CO, NO_x, and NO_y on the origin of the air arriving at the site suggests a potentially strong effect of power plants located in the industrial Midwest on the air quality of the southeastern environment. Concurrent measurements of SO_2 would have led to more definite conclusions on the relative impact of power plants and automobiles on the region.

The tendency of all the trace gases to show a distinguishable peak during the morning hours is directly related to surface deposition at night and to the transport of polluted air parcels over the PBL during the night and their downward mixing after the breakup of the nocturnal temperature inversion. Dynamical processes and soil fluxes dominate early in the morning and during the night, while photochemistry becomes more important when intense UV solar flux is present.

No ozone episode occurred during the course of our experiment, and the mean hourly daily maximum was only 63 ppb. The observed CO values were close to those monitored in rural Virginia, suggesting that CO mixing ratios of 200 ppb are representative of the rural continental environment during the summertime.

The NO observations at night were well above the detection limit of both chemiluminescence detectors and were not due to any known artifact of the sensors, suggesting that soil emission is a relatively strong nighttime source of nitric oxide for the area. These mixing ratios were as high as 200 ppt, with a mean value of ~60 ppt. In order to get an estimate of the importance of such a natural source for the southern environment, there is a need for soil flux measurements.

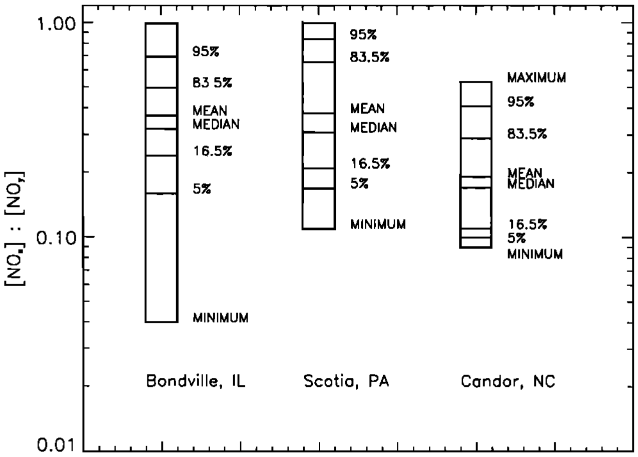

Figure 10. Intercomparison of the NO_x to NO_y ratios observed in rural North Carolina with those observed in Bondville and Scotia for midday (1000-1800 EST). The data for the last two sites are from *Parrish et al.* [1993]. The statistical representation is as in Figure 9.

Our measurements suggest that there are deviations from the photostationary state, implying the existence of oxidants that convert NO to NO_2 without O_3 consumption. The reasonable agreement between the observed and calculated values of O_3 production provides strong evidence for the reliability of our NO_x measurements and the good performance of the NO_2 photolytic converter. In contrast, the use of an EPA approved technique for NO_x measurements yielded totally unrealistic estimates of in situ O_3 production, since this technique overestimated the NO_2 mixing ratios in North Carolina by a factor of 4. Our test suggested that the NO_2 measurements taken in an urban environment with standard commercially available instruments cannot be used in an urban airshed model for the calculation of O_3 production and the establishment of pollution control strategies. Comparisons of these instruments with methods of proven specificity for NO_2 are needed.

Variations of the actinic flux are reflected in the J_{NO_2} values, and most of the existing empirical relationships for the calculation of the photodissociation frequencies are limited by the clear-sky conditions, introducing non-negligible uncertainties in the estimation of deviations from the Leighton relationship. Consequently, there is a continued need for direct measurements of the rate of photolysis of NO_2 and O_3 in order to obtain more accurate estimates of the potential for photochemical ozone production.

Acknowledgments. This work was supported by the Southern Oxidants Study (grant UCAR S59194) and by NSF (grant ATM-90-14841). Back trajectory calculations were supported by a grant to CICS from NOAA/ARL. The authors would like to thank M. Owens for helping in the field, L. Moy for help with the back trajectories model, B. G. Doddridge and K. P. Rhoads for help in preparation of the final manuscript, and M. A. Carroll for her suggestions in the design of the NO_2 photolytic converter.

References

Atkinson, R., and A. C. Lloyd, Evaluation of kinetic and mechanistic data for modeling of photochemical smog, *J. Phys. Chem. Ref. Data, 13,* 315-444, 1984.

Buhr, M. P., D. D. Parrish, R. B. Norton, F. C. Fehsenfeld, R. E. Sievers, and J. M. Roberts, Contribution of organic nitrates to the total reactive nitrogen budget at a rural eastern U.S. site, *J. Geophys. Res., 95,* 9809-9816, 1990.

Cantrell, C. A., et al., Peroxy radicals in the ROSE experiment: Measurements and theory, *J. Geophys. Res., 97,* 20,671-20,686, 1992.

Carroll, M. A., M. McFarland, B. A. Brian, and D. L. Albritton, Ground-based nitric oxide measurements at Wallops Islands, Virginia, *J. Geophys. Res., 90,* 12,853-12,860, 1985.

Carroll, M. A., B. A. Ridley, D. D. Montzka, G. Hubler, J. G. Walega, R. B. Norton, B. J. Heubert, and F. G. Grahek, Measurements of nitric oxide and nitrogen dioxide during the Mauna Loa Observatory photochemistry experiment, *J. Geophys. Res., 97,* 10,361-10,374, 1992.

Chameides, W., and J. C. G. Walker, A photochemical theory of tropospheric ozone, *J. Geophys. Res., 78,* 8751-8760, 1973.

Crutzen, P. J., A discussion of the chemistry of some minor constituents in the stratosphere and troposphere, *Pure Appl. Geophys., 106,* 1385-1399, 1973.

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

Dickerson, R. R., Direct measurements of ozone and nitrogen dioxide photolysis rates in the atmosphere, Ph.D. dissertation, Dept. of Chemistry, Univ. of Michigan, Ann Arbor, 1980.

Dickerson, R. R., Measurements of reactive nitrogen compounds in the free troposphere, *Atmos. Environ., 18,* 2585-2593, 1984.

Dickerson, R. R., and A. C. Delany, Modifications of a commercial gas filter correlation CO detector for enhanced sensitivity, *J. Atmos. Oceanic Technol., 5,* 424-431, 1988.

Doddridge, B. G., R. R. Dickerson, R. G. Wardell, K. L. Civerolo, and L. J. Nunnermacker, Trace gas concentrations and meteorology in rural Virginia, 2, Reactive nitrogen compounds, *J. Geophys. Res., 97,* 20,631-20,646, 1992.

Draxler, R. R., Hybrid single-particle lagrangian integrated trajectories (HY-SPLIT): Model description, *Tech. Memo. ERL ARL-166,* Natl. Oceanic and Atmos. Admin., U.S. Dept. of Commerce, Silver Spring, Md., 1988.

Fehsenfeld, F. C., et al., A ground-based intercomparison of NO, NO_x, and NO_y measurement techniques, *J. Geophys. Res., 92,* 14,710-14,722, 1987.

Fehsenfeld, F. C., et al., Intercomparison of NO_2 measurement techniques, *J. Geophys. Res., 95,* 3579-3597, 1990.

Fishman, J., and T. A. Carney, A one-dimensional photochemical model of the troposphere with planetary-layer parameterization, *J. Atmos. Chem.,* 351-376, 1984.

Fishman, J., and P. J. Crutzen, The origin of ozone in the troposphere, *Nature, 274,* 855, 1978.

Folinsbee, L. J., W. E. McDonnell, and D. H. Horstman, Pulmonary function and symptom responses after 6.6-hour exposure to 0.12 ppm ozone with moderate exercise, *J. Air Pollut. Control Assoc., 38,* 28-35, 1988.

Heck, W. W., W. W. Cure, J. O. Rawlings, L. J. Zaragosa, A. S. Heagle, H. E. Heggestad, R. J. Kohut, L. W. Kress, and P. J. Temple, Assessing impacts of ozone on agricultural crops, I, Overview, *J. Air Pollut. Control Assoc., 34,* 729-735, 1984.

Holzworth, G., *Mixing Heights, Wind Speeds, and Potential for Urban Air Pollution Throughout the Contiguous United States,* Environmental Protection Agency, Washington, D.C., 1972.

Jet Propulsion Laboratory (JPL), Chemical kinetics and photochemical data for use in stratospheric modeling, evaluation number 9, Publ. 90-1, Natl. Aeronaut. and Space Admin., Washington, D.C., 1992.

Kley, D., and M. McFarland, Chemiluminescence detector for NO and NO_2, *Atmos. Technol., 12,* 63-69, 1980.

Leighton, P. A., *Photochemistry of Air Pollution,* Academic, San Diego, Calif., 1961.

Lin, X., M. Trainer, and S. C. Liu, On the nonlinearity of the tropospheric ozone production, *J. Geophys. Res., 93,* 15,879-15,888, 1988.

Liu, S. C., M. Trainer, F. C. Fehsenfeld, D. D. Parrish, E. J. Williams, D. W. Fahey, G. Hubler, and P. C. Murphy, Ozone production in the rural troposphere and the implications for regional and global ozone distributions, *J. Geophys. Res., 92,* 4191-4207, 1987.

Madronich, S., Intercomparison of NO_2 photodissociation and U.V. radiometer measurements, *Atmos. Environ., 21,* 569-578, 1987.

McFarland, M., D. Kley, J. W. Drummond, A. L. Schmeltekopf, and R. H. Winkler, Nitric oxide measurements in the equatorial Pacific region, *Geophys. Res. Lett., 6,* 605-608, 1979.

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

Parrish, D. D., et al., The total reactive oxidized nitrogen levels and the partitioning between the individual species at six rural sites in eastern North America, *J. Geophys. Res., 98,* 2927-2940, 1993.

Poulida, O., Observations and photochemistry of reactive trace gases in the atmosphere, Ph.D. dissertation, Dept. of Meteorology, Univ. of Maryland, College Park, 1993.

Poulida, O., R. R. Dickerson, B. G. Doddridge, J. Z. Holland, R. G. Wardell, and J. G. Watkins, Trace gas concentrations and meteorology in rural Virginia, 1, Ozone and carbon monoxide, *J. Geophys. Res., 96,* 22,461-22,474, 1991.

Ridley, B. A., S. Madronich, R. B. Chatfield, J. G. Walega, and R. E. Shetter, Measurements and model simulations of the photostationary state during the Mauna Loa Observatory Photochemistry Experiment: Implications for radical concentrations and ozone production and loss rates, *J. Geophys. Res., 97,* 10,375-10,388, 1992.

Rodgers, M. O., and W. L. Chameides, Atmospheric photochemical oxidants: A southern perspective, report of a workshop held in Atlanta, Ga., Georgia Inst. of Technol., June 27-29, 1988.

Shetter, R. E., A. H. McDaniel, C. A. Cantrell, S. Madronich, and J. G. Calvert, Actinometer and Eppley radiometer measurements of the NO_2 photolysis rate coefficient during the Mauna Loa Observatory Photochemistry Experiment, *J. Geophys. Res., 97,* 10,349-10,360, 1992.

Stedman, D. H., and J. O. Jackson, The photostationary state in photochemical smog, paper presented at the Symposium on Chemical Kinetics Data for the Upper and Lower Atmosphere, symposium no. 1, Warrenton, Va., September 15-18, 1974.

Torres, A. L., Nitric oxide measurements at a nonurban eastern United States site: Wallops instrument results from July 1983 GTE/CITE mission, *J. Geophys. Res., 90,* 12,875-12,880, 1985.

K. L. Civerolo, R. R. Dickerson, and O. Poulida, Department of Meteorology, University of Maryland, 2213 Computer and Space Sciences Building, College Park, MD 20742-2425.

(Received August 26, 1993; revised January 28, 1994;
accepted February 7, 1994.)