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Vertical distribution of oxides of nitrogen in the semi-urban planetary boundary layer: mixing ratios, sources and transport

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Importance of this paper: Increasing nitric oxide (NO) emissions, in the presence of hydrocarbons and sunlight, are thought to be the cause of increased regional levels of tropospheric ozone and other photochemical oxidants. Knowledge of the vertical distribution of ozone and NO in the planetary boundary layer (PBL) is essential to develop effective ozone control strategies. To date, there is still disagreement in the scientific community as to whether NO_X *is mixed upward or downward through boundary layer processes. This paper considers one semi urban/rural location and examines which process (upward or downward) dominates.*

Abstract

Measurements of the mixing ratios of tropospheric NO and NO_Y (defined as nitric oxide (NO) + nitrogen dioxide (NO_2) + peroxyacetyl nitrate (PAN) + nitric acid (HNO_3) + particulate nitrate (NO_3^-) + ⋯) were made over a semi-urban area of central North Carolina at the surface (10 m) and on a tower at heights of 250 m (820 ft) and 433 m (1420 ft) above ground level (AGL) from December 1994 to February 1995. These measurements were compared with synoptic weather data and regional and local upper air soundings in an effort to characterize NO and NO_Y in the planetary boundary layer in terms of their vertical distributions, diurnal profile, and related transport mechanisms. A pronounced decreasing vertical gradient in both NO and NO_Y mixing ratios was observed, with a distinct diurnal cycle and nocturnal minimum. Furthermore, the results suggest that NO and NO_Y were mixed upward from the surface during passage of synoptic meteorological features (and their associated vertical motions). Most importantly, the data reveals that mixing ratios of NO and NO_Y at the elevated heights did not exist in sufficient concentrations above the inversion layer in the nocturnal boundary layer to be mixed downward upon breakup of the nocturnal inversion and affect surface measurements. Instead, concentrations of NO and NO_Y were apparently mixed upward during the morning and midday hours by vertical boundary layer processes. Thus, the association of observed increases in surface NO and NO_Y mixing ratios based solely on downward mixing processes is not justified in all cases, and other sources and processes for these increases must be considered, particularly over rural areas.

Keywords: NO; NO_Y; Downward mixing; Fumigation; Planetary boundary layer

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1. Introduction

The family of reactive nitrogen species, composed primarily in the lower troposphere of nitric oxide (NO) + nitrogen dioxide (NO_2) + peroxyacetyl nitrate (PAN) + nitric acid (HNO_3) + particulate nitrate ($NO_3^- + \cdots$) (Fahey et al., 1986; Trainer et al., 1991; Parrish et al., 1993; Aneja et al., 1996), and referred to here as NO_Y, plays a major role in the chemistry of the troposphere. In particular, the source species for the NO_Y family, NO and NO_2 ($NO + NO_2 = NO_X$; the remaining members of NO_Y are known as the oxidized species, or $NO_Z = NO_Y - NO_X$) play a predominant role as a precursor in the in situ production of tropospheric ozone (O_3) (a primary constituent of photochemical "smog") through the photooxidation of carbon monoxide, methane, and other reactive hydrocarbons (Fishman et al., 1979; Logan et al., 1981). Reactions 1, 2, and 3 in Table 1 outline these reactions.

Human activities have caused increases in O_3 precursor concentrations, which in turn, have resulted in a global increase of the tropospheric O_3 concentration (Hough and Derwent, 1990; Finlayson-Pitts and Pitts, 1993). Relatively high concentrations of ozone continue to be a major environmental and health concern in the United States despite 20 years of considerable regulatory and pollution control efforts (National Research Council, 1992). It has also been shown that many rural areas are just as susceptible to elevated ozone concentrations as urban areas, and more importantly, that most of this ozone is being produced photochemically from ozone precursors emitted within the region (Kelly et al., 1984; Liu et al., 1987; Chameides et al., 1992; Aneja et al., 1996).

The origin of tropospheric ozone precursors in rural areas (away from anthropogenic precursor sources) is attributed to a number of precursor sources, including natural emissions, horizontal advection, vertical mixing, deposition, and chemical production. In particular, however, much consideration has been given to the process known as "downward mixing", or fumigation of a plume of pollutants (such as NO_X) during breakup of the nocturnal inversion layer after sunrise. This downward mixing of pollutants from the plume can result in an increase in ground level mixing ratios (and resulting "peaks" in measured ambient profiles) of pollutants such as NO_X. For example, Trainer et al. (1987, 1991) postulate that increases in surface NO_X mixing ratios after sunrise over a rural area in Pennsylvania are attributable to the horizontal transport of NO_X above the nocturnal inversion layer and its subsequent downward mixing to the surface during the morning hours. Here, the authors state that the exact height of the NO_X emission layer is not critical, provided it is above the inversion layer.

In an effort to characterize the ability of such downward mixing processes to transport NO and NO_Y to the surface under varying conditions, mixing ratios of NO and NO_Y were continuously measured on two stationary platforms on a transmitter tower over a semi-urban area of central North Carolina at heights of 250 m (820 ft) and 433 m (1420 ft) above ground level (AGL). In addition, surface measurements (10 m) were made in a nearby mobile laboratory. The measurements of NO_Y mixing ratios during this study can be used as a surrogate for measurements of NO_X mixing ratios and discussion of their subsequent transport mechanisms

Table 1
Chemical reactions of major reactive nitrogen species in the atmosphere

	Rate constant[a]
Photostationary state	
(R1) $NO_2 + h\nu(\lambda \leqslant 420\ \text{nm}) \rightarrow NO + O(^3P)$	3.5×10^{-3}
(R2) $O_2 + O(^3P) \xrightarrow{M} O^3$	6.2×10^{-34}
(R3) $NO + O_3 \rightarrow NO_2 + O_2$	$2.3 \times 10^{-12} \exp(-1450/T)$
Peroxy radical disruption of photostationary state	
(R4) $NO + HO_2 \rightarrow NO_2 + OH$	$4.3 \times 10^{-12} \exp(+200/T)$
(R5) $NO + RO_2 \rightarrow NO_2 + RO$	8.0×10^{-12}
Formation and destruction of nitrous and nitric acid	
(R6) $NO + OH \rightarrow HONO$	5×10^{-12}
(R7) $HONO + h\nu \rightarrow NO + OH$	8.4×10^{-4}
(R7) $NO_2 + OH \rightarrow HNO_3$	1.3×10^{-11}
(R8) $HNO_3 + h\nu \rightarrow OH + NO_2$	1×10^{-7}
Formation and thermal decomposition of PAN, and loss of PAN with NO	
(R8) $CH_3CO_3 + NO_2 \rightarrow CH_3CO_3NO_2$	6×10^{-12}
$CH_3CO_3NO_2 \rightarrow CH_3CO_3 + NO_2$	$1.12 \times 10^{-16} \exp(-13330/T)\ s^{-1}$
(R9) $CH_3CO_3 + NO \rightarrow CH_3 + CO_2 + NO_2$	1.4×10^{-11}

[a] Reaction rate units are s^{-1} for unimolecular processes, cm^3 $molecules^{-1}$ s^{-1} for bimolecular processes, and cm^{-6} $molecules^{-2}$ s^{-1} for termolecular processes; T in degrees Kelvin. *Source*: Logan et al., 1981; Singh, 1987; Warneck, 1988.

during the early morning hours (0600–0900 local time) due to the fact that major NO_Y constituents such as PAN and HNO_3 are at a diurnal minimum during this time (Warneck, 1988; Aneja et al., 1994), and thus it is probable that NO_Y consists mainly of NO and NO_2 (or NO_X) during this time (Aneja et al., 1996). Observed NO and NO_Y mixing ratios were compared with synoptic scale meteorological features in order to determine possible transport mechanisms. In addition, the observed values of NO and NO_Y mixing ratios were then compared with nocturnal and morning boundary layer structures obtained from analysis of upper air soundings (produced locally at North Carolina State University (NCSU) or regionally by the Greensboro, NC National Weather Service (NWS) office) to characterize their possible transport processes. The results of these comparisons are conclusive in their agreement that during this study, NO and NO_Y did not exist in sufficient quantities above the nocturnal inversion to affect the surface mixing ratios after sunrise via downward mixing ratios; instead the results suggest that NO and NO_Y were mixed *upward* from the surface during the morning hours by vertical boundary layer processes.

2. Experimental

Measurements of NO and NO_Y mixing ratios were made at 250–433 m on the Auburn Transmitter Tower, a multi-communications tower located over a mixture of cleared farmlands and small forest plots near the town of Auburn, North Carolina (N latitude 35° 40″ 35′; W longitude 78° 32″ 09′), approximately 15 km (9.2 miles) east-southeast of downtown Raleigh, NC (tower location indicated by the star in Fig. 1). The tower is located approximately 1 km (0.6 mile) southwest of US-70 and approximately 3 km (1.8 miles) east of I-40, and there are several large NO_X point sources (such as power plants) within a 200 km radius (Aneja et al., 2000). Surface (10 m) mixing ratios of NO were measured over an agricultural field near the base of the transmitter tower. The measurements of NO and NO_Y mixing ratios were made on the tower across three months during the winter of 1994–1995; specifically, at the height of 433 m AGL, 7–16 December 1994 and 12–25 January 1995; and at 250 m AGL, 2–23 February 1995. The surface NO mixing ratios were measured at various times between 20 January 1995 and 16 February 1995. Data from these periods are not continuous due to malfunctions in the recording devices. Predominant winds, as indicated by the climatological record at RDU, indicate predominant northwesterly surface winds during this time of the year.

Detection of the NO mixing ratios at all heights was carried out by using TECO 42S (Thermal Environmental Instruments) chemiluminescence high sensitivity NO–NO_Y analyzers. The detection limit for this instrument is cited at 0.05 parts per billion volume (ppbv) NO (Thermal Environmental Instruments, 1992), however, individual determination of the instruments' detection limits were calculated for each run, as outlined below.

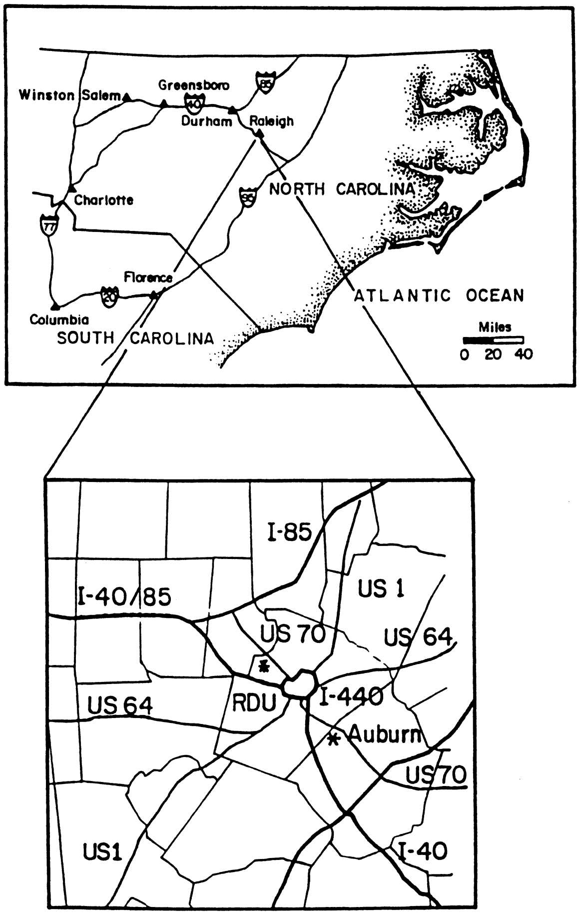

Fig. 1. Map of experimental area, showing major population centers within 200 km and major highways (research tower location is indicated by the star).

The TECO 42S instruments were zeroed and calibrated using a TECO 146 gas dilution/titration instrument, a standard containing 614 ppbv NO in N_2 (NIST traceable, Scott Specialty Gases, Plumsteadville, PA), and compressed zero air (National Welders, Raleigh, NC). A multipoint calibration was performed in the NCSU Air Quality laboratory and internal instrument settings were noted prior to the installation of each instrument on the tower.

After each intensive (which ranged in duration from one to three weeks), the TECO 42S was brought down from the tower and checked for drift against the NO standard. The measured deviation was less than 3%. In addition, discussion with engineers at TECO Instruments indicated that the difference in the standard atmospheric pressure between the calibration at the surface and placement of the instrument at 1500 ft should result in no more than a 4% loss of chemiluminescence detection of NO [Richard Kuran, personal communication].

To determine 42S NO–NO_Y instrument detection limits for NO mixing ratios, the standard deviation was calculated from a series of instrument readings ($n > 200$) of the lowest recorded signals (which occurred for NO during the night), and a value of three times this standard deviation was assigned as minimum detection limit (Taylor, 1987). The instrument's minimum detection limit while at 250 m was calculated to be approximately 0.04 ppbv; thus the data from 250 m are presented with a 0.04 ppbv cutoff. The instrument also produced a minimum detection limit of 0.04 ppbv during the January intensive at 433 m, however, the instrument performed erratically during the December intensive at 433 m (possibly due to interference with the data recording device), producing a minimum detection limit of approximately 0.23 ppbv. The compiled NO data for 433 m (December and January) is therefore shown with a 0.23 ppbv minimum detection cutoff. For the NO–NO_Y analyzer located at the surface (10 m), the calculated minimum detection limit was calculated to be 0.10 ppbv NO.

The NO–NO_Y analyzer and its pump and filters were placed in a weather-proof steel chamber located on platforms at the previously mentioned heights (tower measurements) or in a mobile laboratory (surface measurements); heat from the pumps kept the environmental temperature (as measured by the data logger case temperature) within the operating range of the instruments (10–30°C). The tower air sample was pulled at 1.5 liters per minute (lpm) through a length (6–12 m) of partially shielded 1/8 in. inside diameter perfluoroalkoxy (PFA) Teflon tubing that was attached to a metal bar which extended horizontally 1–2 m from the transmitter tower structure. The surface air sample was pulled through an 18 m (60 ft) length of PFA Teflon tubing attached to a 10 m mast.

Each TECO 42S was set to output data in 1 min rolling averages every 10 s (each average is thus composed of six observations). These output data were then collected in 15 min binned averages by two different data loggers. For the December tower intensive and all surface measurements, the output data were collected by a Toshiba Model 4700 CS laptop computer loaded with Labview for Windows software (Version 2.5.2, 1992; National Instruments). For the January and February tower intensives, the data were recorded by a Campbell Scientific Instruments Model 21 XL Datalogger.

The existence of synoptic meteorological features (for comparison with observed NO and NO_Y mixing ratios) was identified through the study of NWS daily surface weather maps for each intensive, and verified for the time of local area passage (in relation to the research tower) by comparison with Raleigh–Durham airport (RDU) NWS hourly and special surface weather observations for the research period. RDU is the closest reporting station to the tower, located about 17 miles to the northwest. The term "synoptic" is used here to define meteorological phenomena that have a time scale of 1–5 days, a length scale of 100–1000 miles, and in this case, those phenomena that involve upward vertical motion (such as low pressure systems, fronts, and troughs). Changes in such parameters as wind speed and direction, temperature, pressure, and cloud cover in the RDU observations were used as indicators of frontal or trough passage.

Using the definition and descriptions of the stable or nocturnal boundary layer given by Stull (1988) as a guide, determination of the vertical structure of the local nocturnal and early morning boundary layer was made through careful analysis of upper air soundings from the NWS office in Greensboro, NC (GSO) (N latitude 36.1°, W longitude 79.9°; 270 m above mean sea level (MSL)), about 85 miles northwest of the tower (see Fig. 1). These soundings were produced from the launch of a pilot balloon (PIBAL) equipped with a VIZ B Artsonde rawinsonde at 1100Z (0600 Eastern Standard Time (EST)), or approximately one hour before local sunrise during the research period.

Similarly, using the definition and descriptions of the mixed layer (ML) given by Stull (1988) as a guide, the growth of the local ML was analyzed from upper air soundings produced from locally launched PIBALs equipped with atmospheric instruments research (AIR) products instrument sondes. These sondes can detect and transmit atmospheric temperature and water vapor content data (but not wind data), and were launched from an agricultural field located approximately 2 miles east of tower during the month of December, and from the top of Jordan Hall (33 m AGL) on the NCSU campus, about 20 km (12 miles) northwest of the tower, during the months of January and February. An AIR products automated atmospheric data acquisition system (ADAS) receiver routed height, temperature, and water vapor data transmitted by the sonde to a Toshiba Model 3100 laptop for data acquisition. In a few cases, range, direction and azimuth of the launched balloon were manually tracked via theodolite to provide wind speed and direction calculation. For each run, the ADAS was calibrated with temperature and humidity data recorded by meteorological instruments located on the roof of Jordan Hall, or with handheld instruments at the field site.

The NO and NO_Y mixing ratio data for particular elevations or time periods is presented in terms of the mean ± one standard deviation (median in parentheses) for each population; differences between two populations are statistically validated via the *t*-test method at the 0.05 significance level. The *t*-tests and their results presented here are assumed valid through the central limit theorem (Snedecor and Cochran, 1989; Dickey, 1995).

3. Results and discussion

3.1. Vertical gradients and diurnal profiles of NO and NO_Y mixing ratios

The distribution of the measured NO mixing ratios at all heights displays a strong vertical gradient during both the daytime and the nighttime hours as shown in Table 2 (daytime is defined as the hours from 0615 EST to 1800 EST; nighttime is defined as the hours from 1815 EST to 0600 EST). Table 2 consists of both composite data from the entire research period, and also data that were collected concurrently at two different heights. Significant differences exist between the composite and concurrent mean NO mixing ratios at the surface and the NO mixing ratios at both heights during the day; during the night there are significant differences between the composite mean NO mixing ratios at the surface and 433 m, and between the concurrent mean NO mixing ratios at the surface and 250 m. Finally, the data show a 17% decrease in mean daytime composite NO mixing ratios from 250 to 433 m. These results suggest very strongly that a decreasing vertical gradient of NO exists during both the day and night. This observed nocturnal NO mixing ratio minimum is consistent with the predicted nocturnal atmospheric chemistry of NO, in which the titration of NO by residual ozone, (O_3) and by the OH radicals during the nighttime would be expected to lead to low or nonexistent mixing ratios of NO (in the absence of horizontal transport of NO) (Finlayson-Pitts and Pitts, 1986; Warneck, 1988).

The mean values in Table 2 also suggest a pronounced diurnal cycle with a nocturnal NO mixing ratio minimum at each height. Given that a high percentage (≈86%) of the nighttime readings were below instrument detection limits, and that the mean nocturnal NO mixing ratios are at least an order of magnitude lower than their daytime counterparts, the result is a strong composite diurnal profile for each height. The existence of both the vertical gradient and diurnal profile of NO mixing ratios is highlighted in Fig. 2 which shows the composite mean diurnal NO mixing ratio profile at each height for the measurement period. The NO mixing ratio usually peaked in magnitude around noon and began a slow decline throughout the afternoon hours. This profile is somewhat obscured in the surface (10 m) data which shows a pronounced morning and late afternoon peak. The majority of this morning and afternoon increase is believed to be the result of increased vehicular traffic during rush hour, as the site is located adjacent to a nearby highway. There is a sharp drop in the NO mixing ratio at sunset, indicative of the effects of both photochemistry and boundary layer transport processes on NO mixing ratios.

In contrast to NO mixing ratios, NO_Y mixing ratios at 250 and 433 m remained well above the instrument minimum detection limit (the lowest values recorded were around 1 ppbv. The mean values shown in Table 2

Table 2
Mean, standard deviation and (median) of observed NO and NO_Y mixing ratios: surface (10 m), 250 and 433 m (December 1994–February 1995)[a]

Height (m)	Day	Night	Dates
Composite NO mixing ratios			
10	8.07 ± 13.33 (3.67)	0.32 ± 1.27 (0.00)	2 January–16 Februay 1995
250	1.56 ± 3.23 (0.69)	0.22 ± 1.46 (0.00)	2–23 February 1995
433	1.30 ± 3.03 (0.00)	0.06 ± 0.23 (0.00) (min)	7–16 December 1994 and 12–25 January 1995
Composite NO_Y mixing ratios			
250	12.12 ± 7.67 (10.46)	9.48 ± 7.22 (7.93)	2–23 February 1995
433	9.27 ± 6.28 (7.22)	7.31 ± 4.92 (5.74)	7–8 December 1994 and 12–25 January 1995
Concurrent NO mixing ratio data between 10 and 250 m			
10	8.60 ± 15.30 (4.00)	0.29 ± 0.89 (0.00)	Days: 3–4,6–8,10,13–14,16 February 1995
250	1.89 ± 3.47 (1.29)	0.05 ± 0.09 (0.00)	Night: 3–4, 10 February 1995
Concurrent NO mixing ratio data between 10 and 433 m			
10	9.67 ± 8.20 (6.84)		Days 18, 24–25 January 1995
433	2.12 ± 3.05 (0.28)		

[a] Units are ppbv.

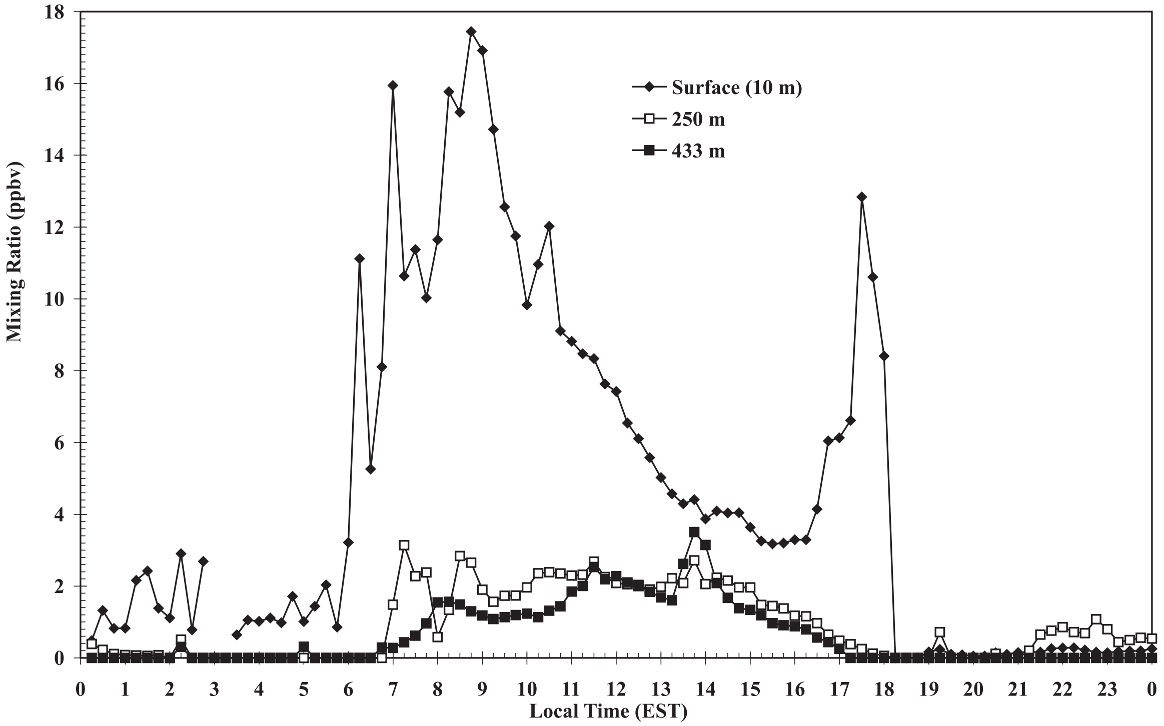

Fig. 2. Composite diurnal profiles of mean NO mixing ratios, three heights (December 1994–February 1995).

suggest that a vertical gradient between 250 and 433 m existed for NO_Y mixing ratios that is comparable to the observed gradient in the NO mixing ratios. In this case, there was a significant difference of 20–25% between the 250 and 433 m mean NO_Y mixing ratios during both the day and night, suggesting a strong decreasing vertical gradient. As with the NO measurements, the mean NO_Y mixing ratio data also show a strong diurnal profile, with mean NO_Y mixing ratio values decreasing between 20% and 25% from the daytime maximum to the nocturnal minimum at both heights (Table 2). Fig. 3 shows a comparison of the composite mean diurnal NO_Y mixing ratio profiles for both heights, and a diurnal cycle is clearly indicated. The mean NO_Y mixing ratios begin to rise sharply from the overnight minimum between approximately 0700 and 0715 EST, and reach a maximum around midday. The difference between the mean diurnal minimum and maximum measurements can be as high 7.59 ppbv (433 m), and are two to four times the difference between the mean daytime and nighttime measurements at the respective heights. This indicates that while some of the NO_Y measured during the day at each height was conserved or formed in the boundary layer during the previous night, an equal or larger portion (45–60%) was transported upward to and/or formed at these heights during the morning hours after sunrise.

3.2. Correlation of observed mixing ratios with synoptic features

A detailed review of combined time sequences of the diurnal profiles of the NO mixing ratio (250 m) reveals a series of somewhat periodic maxima and minima interspersed with aperiodic peaks (Fig. 4). Since these periodic maxima usually occur before or around midday, it is hypothesized that they are the result of upward transfer of NO and NO_Y from the surface via boundary layer processes (which will be discussed further in Section 3.3) and that the nocturnal minima are the result of the depletion of NO and NO_Y by various chemical reactions as discussed earlier. These maxima and minima will be referred to as the "diurnal maximum and minimum" for clarity. Furthermore, it is hypothesized that the aperiodic peaks (different from the diurnal maximum and minimum) observed at various times during the intensive are the result of synoptic scale meteorological processes that involve upward motion and therefore vertical lifting of NO and NO_Y from the surface. To test this hypothesis, measured values of NO and NO_Y at the 250 and 433 m heights were compared with synoptic/large mesoscale meteorological features that passed through central North Carolina during the measurement period.

Generally, the nocturnal NO mixing ratios were below instrument detection limits during periods of high

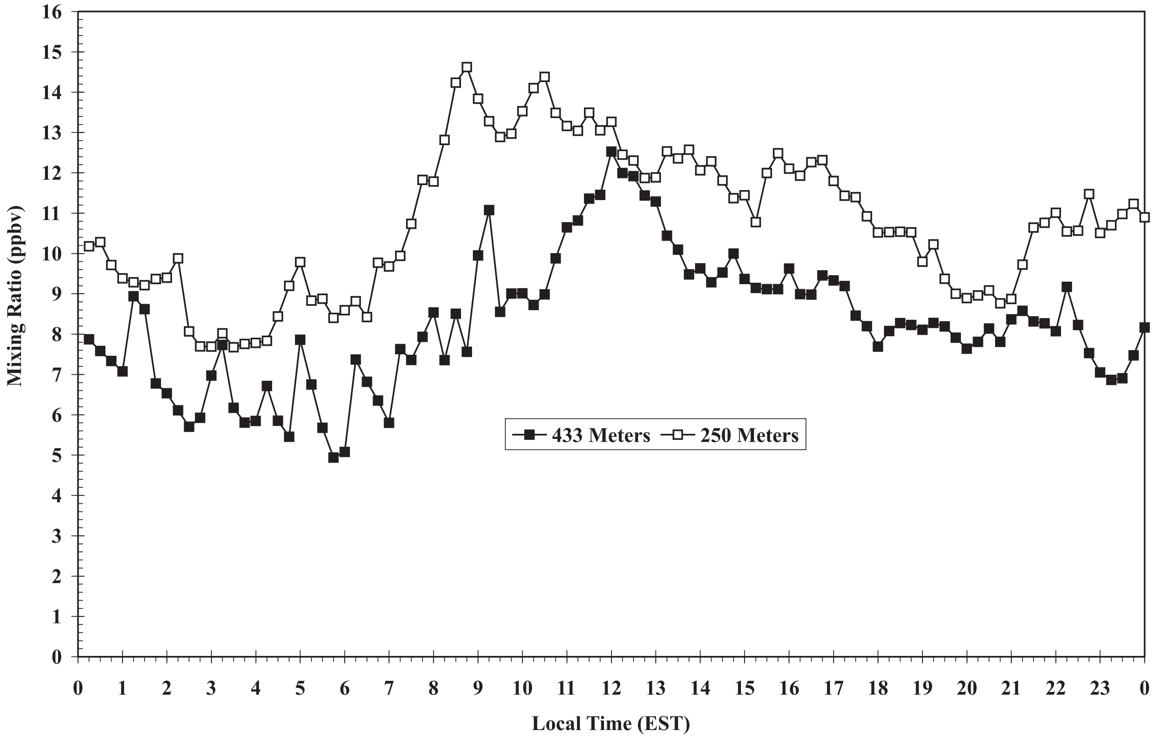

Fig. 3. Composite diurnal profiles of mean NO_Y mixing ratios, two heights (December 1994–February 1995).

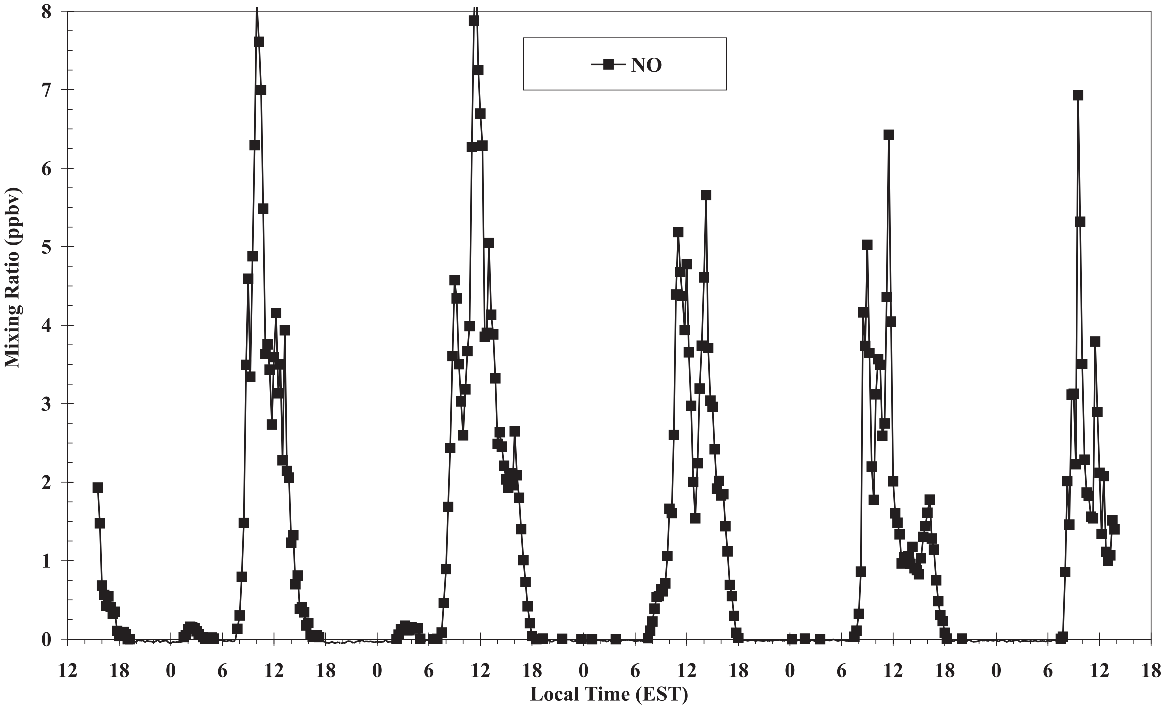

Fig. 4. Diurnal variation of observed NO mixing ratios, 250 m AGL (2–7 February 1995).

pressure (and thus periods of subsidence, or sinking atmospheric motions). However, during the passage of a front, low pressure or trough (and thus periods of rising atmospheric motions), the NO mixing ratios rose above minimum instrument detection limits. These increases above minimum instrument detection limits have varying magnitudes and time scales, but nevertheless are consistent phenomena. For example, Fig. 5(a) shows the diurnal variation of the NO mixing ratio at 433 m, overlaid with synoptic meteorology, on 7–10 December 1994. Here, it is evident during the night of 9 December, the NO mixing ratio fell below instrument detection limits, and NWS maps and RDU observations indicated a lack of synoptic forcing (weak high pressure). During the day on 9 December, NO mixing ratios rose above instrument minimum detection limits around midday (possibly due to boundary layer processes, discussed in further detail later). Then, in contrast to the previous night, NO mixing ratios remained above detection limits off and on during the night of 10 December. On this night, NWS surface maps and RDU observations indicated the passage of a cold front after sunset, and then a continued presence of a stationary front in the area. More importantly, during the early afternoon hours on 10 December, the 15 min mean NO mixing ratio (433 m) increased from 0.88 ppbv at 1315 EST on to 23.46 ppbv at 1330 EST and then to 40.78 ppbv at 1345 EST (Fig. 5(a)). A comparison with the surface maps and the RDU observations indicates that the passage of a warm front through the region occurred on that date between 1300 and 1400 EST. The NO mixing ratio had increased to a diurnal maximum of 1.29 ppbv at 1200 EST and was decreasing towards the diurnal minimum when the front came through and brought the large increase in NO mixing ratio. A similar event occurred on the evening of 16 February (Fig. 5(b)), when NO mixing ratios began falling after sunset, as usually observed, but abruptly rose from 0.24 ppbv at 2100 EST to a value of 14.88 ppbv at 2200 EST. Here, a comparison with surface maps and RDU observations indicate that a cold front moved through the region between 1900 and 2000 EST on that date. The resolution of the synoptic meteorological data does not allow for the calculation of the exact time of frontal passage at the tower, which may explain the apparent time lag in the increase of NO mixing ratios.

During the time period for which valid NO mixing ratio data was recorded at the two tower heights, there were approximately fourteen identifiable synoptic events that passed through the region, and all 14 produced observable increases in the NO mixing ratios (Figs. 5(a)–(j)). In addition, there were four peaks (5(b), (e), (i), (j)) in the NO mixing ratio during the nocturnal time periods that do not match up with identifiable synoptic scale events; these may be the result of small mesoscale (1–100 miles length scale, 1–10 h time scale) or smaller meteorological phenomena that provide some vertical lifting but were not identifiable with the given meteorological data. In particular, three of these peaks were observed at the time rain and/or drizzle were recorded by the RDU NWS, which are indicators of possible vertical motion in the atmosphere. Consistent with all these observations is the fact that the spikes or maxima occur without preference to wind direction, and that in most cases the maxima begins to decrease with time (and as the synoptic feature and its associated lifting move further away from the measurement site), even if the wind direction does not change. This supports the conclusion that upward vertical motions (and transport from the surface) are responsible for the noted increases in NO mixing ratios during synoptic event passage, and not horizontal transport.

The mixing ratios of NO_Y did not show as consistent an association with synoptic events as did the NO mixing ratios. For example, on the night of the 2 and 3 February 1995, a cold front passed through the local area of the tower just after midnight. During this time, the NO_Y mixing ratios (250 m) rose from 10.15 ppbv to a maximum of 33.68 ppbv at 0200 EST. Here it may be surmised that the vertical motion associated with the front transported NO_Y from the surface and was reflected in the increased mixing ratios. However, the very next night (3–4 February 1995) saw another cold front move through at 0300 EST, but the NO_Y mixing ratio (250 m) only rose from 3.75 to 5.98 ppbv by 0500 EST, before beginning to decrease again. The magnitude of this rise is within the usual nocturnal variation of NO_Y mixing ratios, and therefore cannot be attributed with certainty to an association with the synoptic event (cold front passage). There were approximately 10 identifiable synoptic features that moved through the local area of the tower during the times in which NO_Y mixing ratios were recorded, and seven of them were associated with increases in the NO_Y mixing ratios. The other three events did not seem to have an effect on the NO_Y mixing ratios. In addition, there were numerous instances of increases in NO_Y mixing ratios during the nocturnal hours that could not be associated with synoptic events. More comprehensive research is needed in this area to better understand the complex chemistry of nocturnal reactions involving NO_Y species.

3.3. Boundary layer formation and vertical transport processes

As outlined earlier, the formation of a nocturnal boundary layer, and in particular, the formation of separate stable and residual layers during the night, is a requirement for the vertical transport (downward mixing) of pollutants after sunrise (Trainer et al., 1987, 1991; Stull, 1988). Pollutants such as NO and NO_Y that

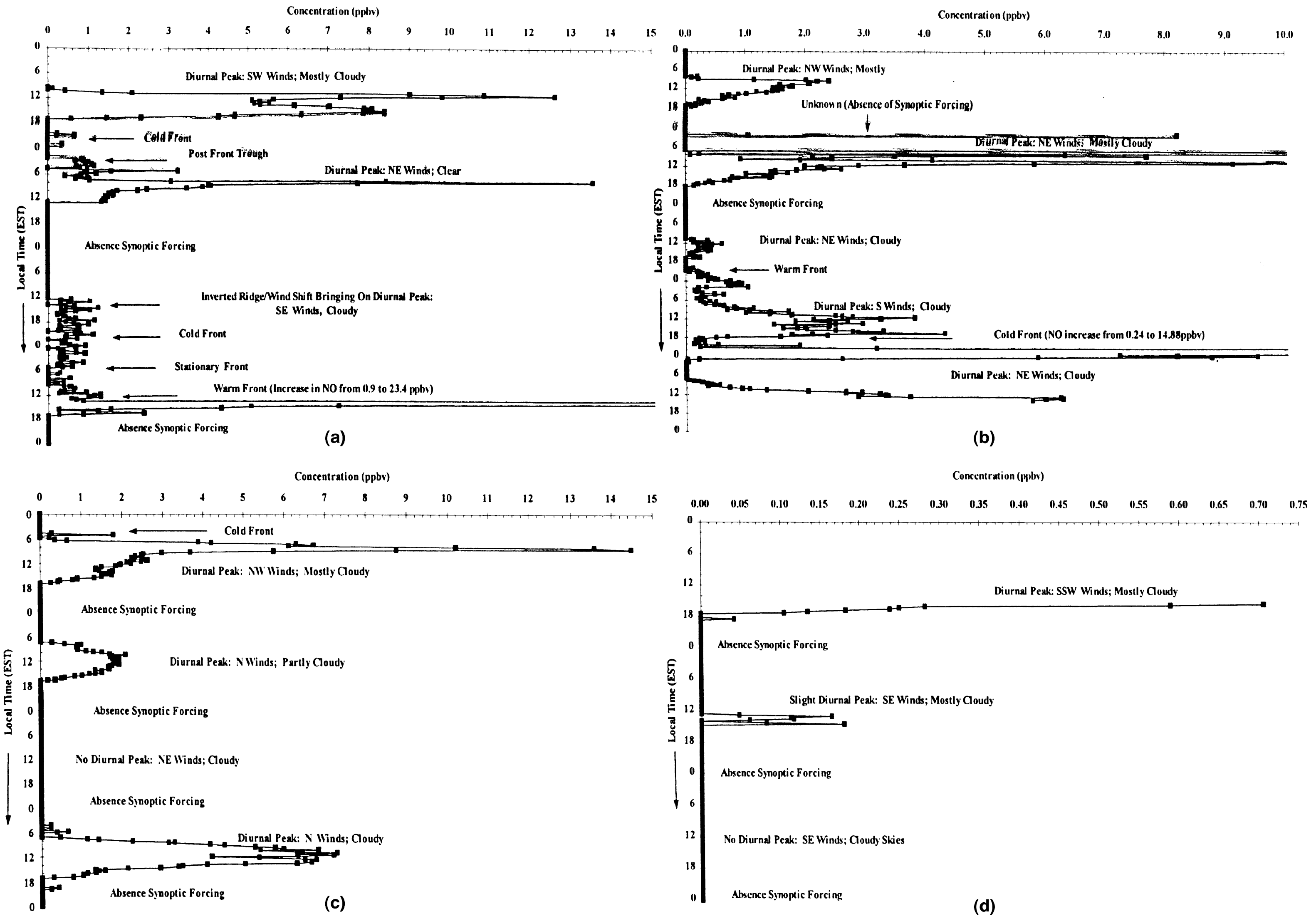

Fig. 5. (a) Diurnal variation NO concentration overlaid with synoptic meteorology, 433 m AGL (7–10 December 1994), (b) diurnal variation NO concentration overlaid with synoptic meteorology, 250 m AGL (13–17 February 1995), (c) diurnal variation NO concentration overlaid with synoptic meteorology, 433 m AGL (11–14 December 1995), (d) diurnal variation NO concentration overlaid with synoptic meteorology, 433 m AGL (12–15 January 1995), (e) diurnal variation NO concentration overlaid with synoptic meteorology, 433 m AGL (15–18 January 1995), (f) diurnal variation NO concentration overlaid with synoptic meteorology, 433 m (23–25 January 1995), (g) diurnal variation NO concentration overlaid with synoptic meteorology, 250 m AGL (2–4 February 1995), (h) diurnal variation NO concentration overlaid with synoptic meteorology, 250 m AGL (5–7 February 1995), (i) diurnal variation NO concentration overlaid with synoptic meteorology, 250 m AGL (8–11 February 1995), and (j) diurnal variation NO concentration overlaid with synoptic meteorology, 250 m AGL (20–21 February 1995).

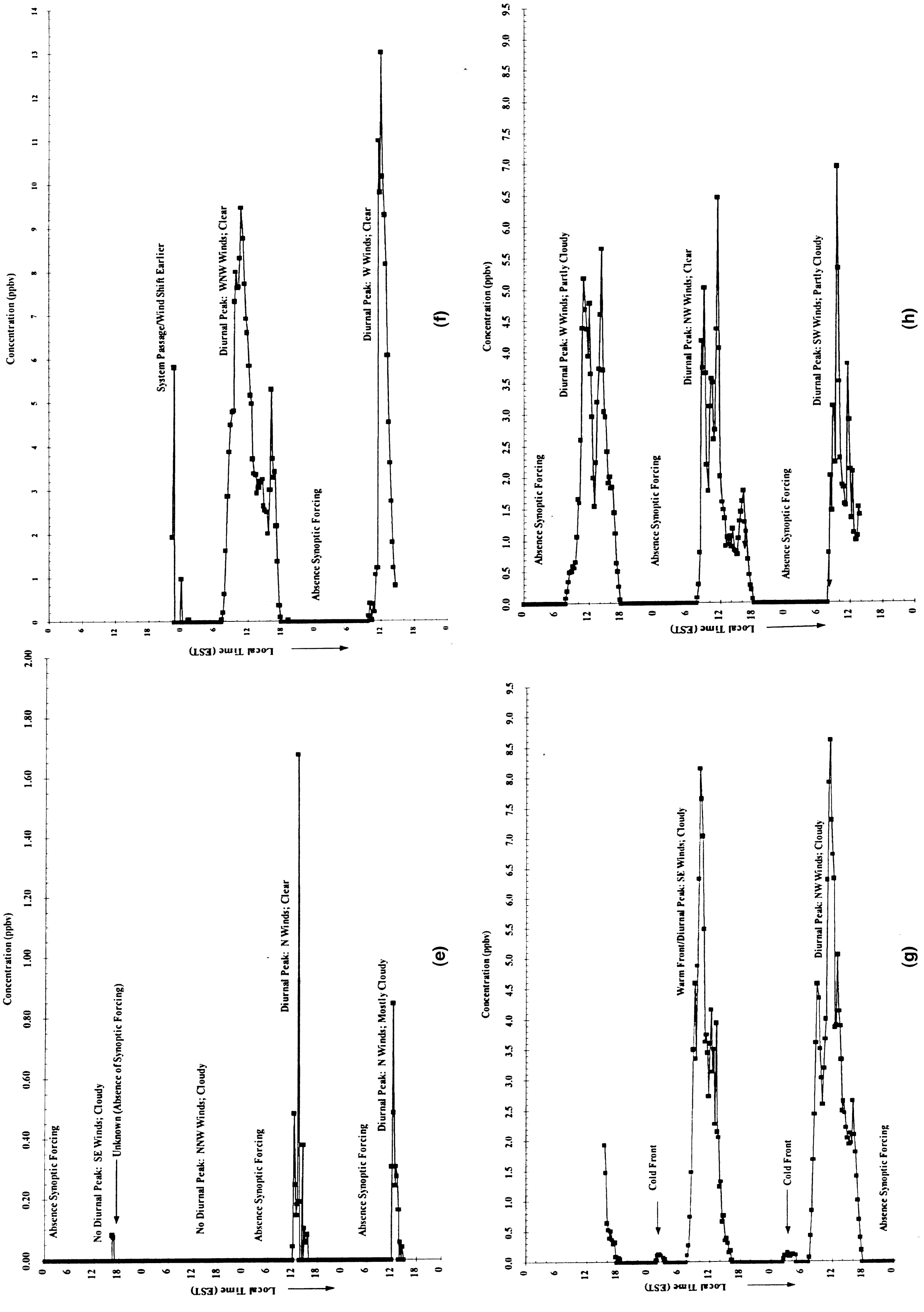

Fig. 5. (Continued).

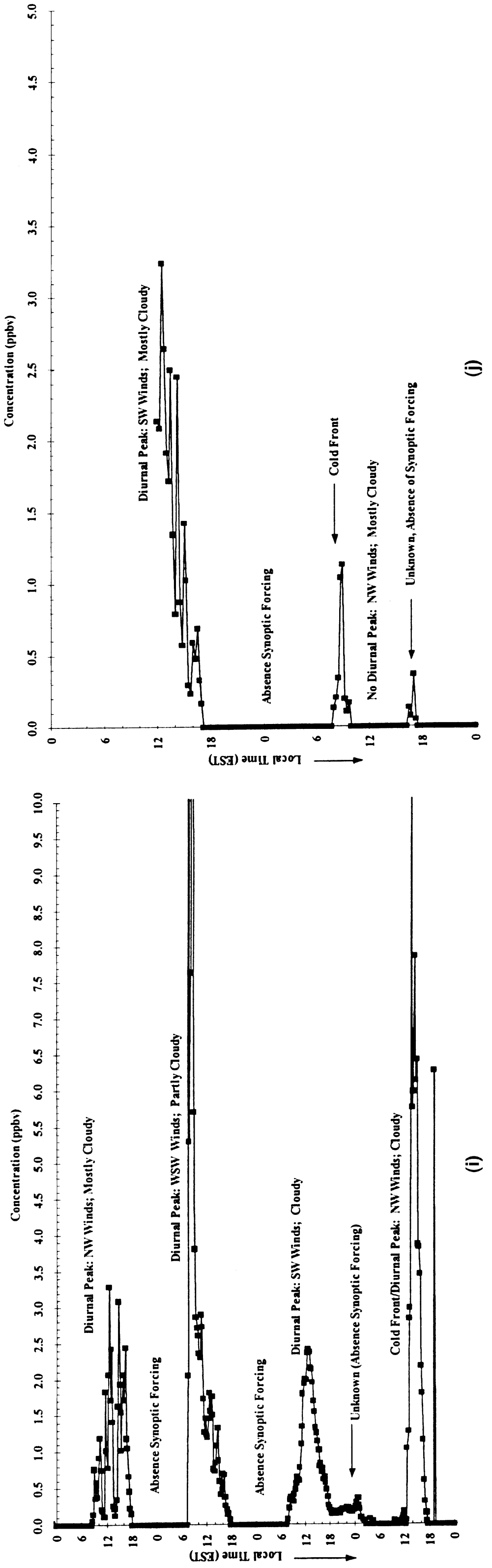

Fig. 5. (Continued).

are thought to be trapped at or above the interface of the residual and stable layers (and possibly transported by the low level jet usually found at this interface) can be mixed downward to the surface upon breakup of the nocturnal boundary layer in the morning. Investigation of the potential for the conservation and transport of NO and NO_Y in the nocturnal boundary layer was made by considering the following two processes: (1) formation of the nocturnal boundary layer (NBL) and possible conservation aloft of NO and NO_Y, and (2) growth of the mixed layer (ML) and possible mixing of NO and NO_Y (either upward or downward). These processes were then compared with the measured values of the NO and NO_Y mixing ratios at the two heights.

3.4. Nocturnal boundary layer

The presence of the nocturnal or stable boundary layer (NBL) was determined by the analysis of atmospheric conditions as given by meteorological data and upper air soundings collected during each measurement period; these were studied for evidence of the height of the stable layer through the temperature, dew point temperature and wind speed profiles. A thorough review of data gained during the course of this research revealed seven cases in which the NO–NO_Y analyzer was located at a height that was at or above the identifiable interface of the nocturnal boundary layer with the residual layer above it. In addition, in three of these seven cases, the instrument was located in an observed low level jet, or wind speed maximum. In all seven cases, measured NO and NO_Y mixing ratios were at or near their diurnal minimums.

For example, on the night of 3 February 1995, the RDU NWS recorded clear skies and winds of 6–10 kts after passage of a weak cold front at midnight, with temperatures dropping from 49°F at sundown to 33°F at 0600 EST. The upper air sounding (Fig. 6) at 0600 EST indicates a surface layer to about 35 m, a stable boundary layer to about 175 m, and a residual layer above the stable layer capped with an inversion beginning at approximately 800 m. A weak northeasterly low level jet maximum of 11 knots occurs between 250 and 300 m. The NO–NO_Y analyzer, located in the center of the low level jet and just above the stable boundary layer/residual layer interface, measured NO mixing ratios below instrument detection limits (0.04 ppbv) throughout the night until after sunrise (except during passage of cold front earlier in the evening as discussed in Section 3.3). NO_Y mixing ratios at 0600 EST, while higher than normal at 18.08 ppbv, were nevertheless at a nocturnal minimum, being lower than measurements at

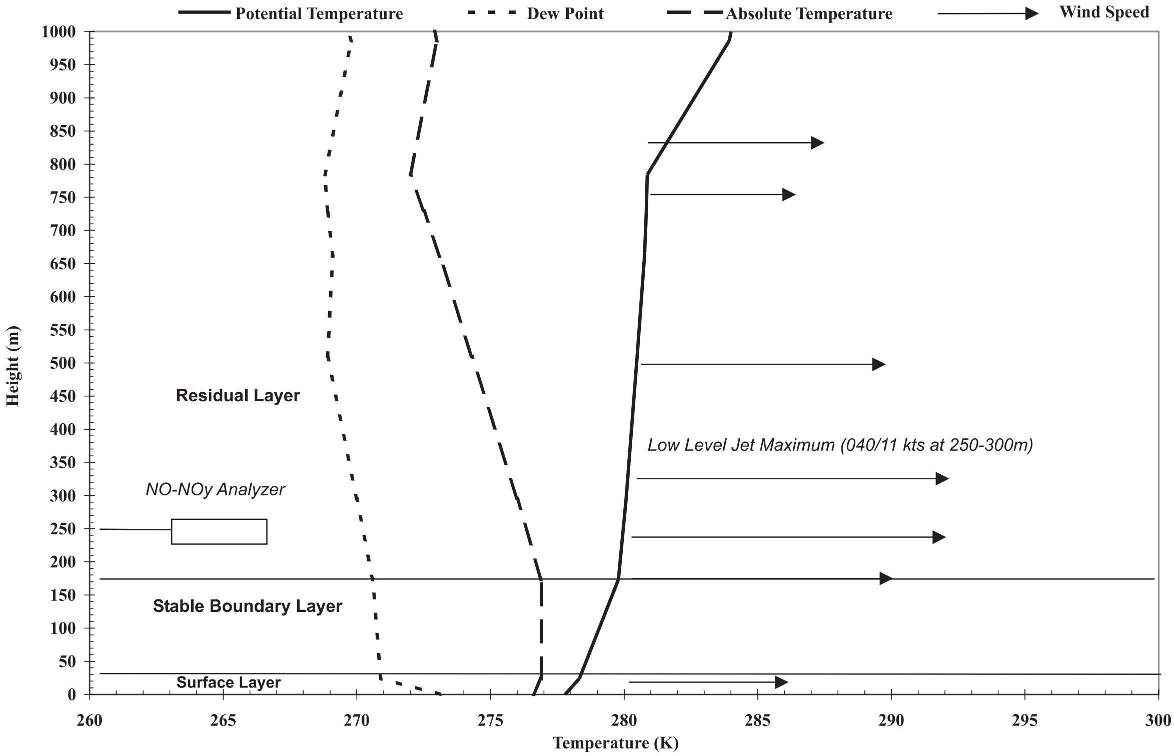

Fig. 6. Greensboro, NC NWS upper air sounding – 3 February 1995 (0600 EST). Arrows show relative wind speed at that height.

0145 EST (33.55 ppbv) during frontal passage and measurements during the subsequent diurnal peak (27.14 ppbv at 1000 EST).

In these seven cases, NO and NO_Y did not exist in sufficient quantities to affect surface mixing ratios upon being mixed downward. In addition, apart from the previously mentioned synoptic episodes, NO mixing ratios were, with one exception, *always* below instrument detection limits during the early morning hours just before sunrise, no matter what the state of the boundary layer. This includes 17 mornings at 433 m and 17 mornings at 250 m. The one exception occurred on 14 December 1995; NO mixing ratios ranging from zero to 0.66 ppbv were measured from 0415 to 0630 EST. In this case, however, rain and drizzle were recorded throughout the night at the RDU NWS office, indicative of possible small scale vertical lifting (not evident in the large scale resolution of the meteorological data). The NO_Y mixing ratios were, with three exceptions, at or near the nocturnal minimum values during the early morning hours just before sunrise, no matter what the state of the boundary layer; this includes 14 mornings at 433 m and 21 mornings at 250 m. Of the three exceptions, two were measured during periods of rain and drizzle (as recorded by the RDU NWS office) and hence were possibly affected by small scale vertical lifting. The final exception, for which no synoptic or precipitation events can be associated, occurred on 14 February 1995. In this case, the NO_Y mixing ratios reached a nocturnal minimum at approximately 0330 EST (3.83 ppbv) and then rose quickly to 20.70 ppbv at 0600 EST. The mixing ratios continued to rise, however, reaching a peak of near 50 ppbv between 0715 and 0800 EST (or after local sunrise).

3.5. Mixed layer growth

Although the mean diurnal profile indicates the average time of increase from the nocturnal minima for the NO and NO_Y mixing ratios at 250 and 433 m is between 0700 and 0800 EST (see Figs. 2 and 3), individual profiles show a wide variation in time of increase to the diurnal peak. It is hypothesized that this diurnal peak is related to the growth of the mixed layer and the subsequent "upward mixing" of NO and NO_Y from the surface via the convective eddies that make up the mixed layer. To test this hypothesis, NCSU upper air sounding data gathered at various times during six mornings within the research period were studied in order to compare the growth in the mixed layer heights with the observed diurnal NO and NO_Y mixing ratio increases. In general, these results indicate that the time of the diurnal peak of the mixing ratios of NO and NO_Y measured on the tower is dependent on the rate of growth of the mixed layer during the morning hours.

For example, on the night of 7–8 December, mostly cloudy skies and the passage of a cold front precluded development of a strong stable boundary layer, so that in the presence of partial sunlight and warming temperatures after sunrise, 0730 EST NCSU upper air sounding (Fig. 7) from the agricultural site indicates the mixed layer had risen to 525 m. The NO–NO_Y analyzer located at 433 m recorded a maximum diurnal mixing ratio (13.64 ppbv) at 0800 EST, or soon after the rise of the mixed layer past the height of the instrument. In contrast, NCSU soundings from the agricultural field site on the 13 December at 0815 EST (Fig. 8(a)) and 0915 EST (Fig. 8(b)) shows that the mixed layer had risen from about 310 m to about 340 m, or an increase in mixed layer height of only about 30 m in an hour. The instrument located at 433 m did not record a diurnal rise in NO mixing ratios above instrument detection limits during the morning hours, or even throughout the rest of the day. It is theorized that because of the lack of surface heating due to the heavy overcast and strong cold advection from the northeast (temperatures remained in the mid 30s (°F) throughout the day), the mixed layer never reached the height of the instrument (and subsequently never transported any NO up to that level for the instrument to record). NO_Y mixing ratios were not recorded on this date.

Overall, in five of the six cases where local upper air data were compared to measured NO and NO_Y mixing ratios, the values measured at 250 and 433 m were at a minimum *before* the mixed layer (as determined by PIBAL rawinsonde launch data) reached that height, and did not reach a peak until *after* the mixed layer has reached or surpassed that height. In the sixth case, the NO mixing ratios never rose above instrument minimum detection limits throughout the day (possibly due to heavy overcast limiting rise of the mixing layer, as described above). These results lead to the conclusion that in these cases, NO and NO_Y were mixed upward from the surface to the elevated heights, as opposed to being mixed down.

4. Summary and conclusions

The tropospheric boundary layer distributions of NO and NO_Y mixing ratios were measured over a semi-urban area of central North Carolina at the surface (10 m) and at two heights (250 and 433 m) on a tower for a period of nearly 45 days starting in December 1994 and continuing through January and February 1995. These measurements were then compared to synoptic/large mesoscale features and upper air meteorological data in order to characterize the diurnal variations of both NO and NO_Y mixing ratios in terms of temporal and spatial variations within the

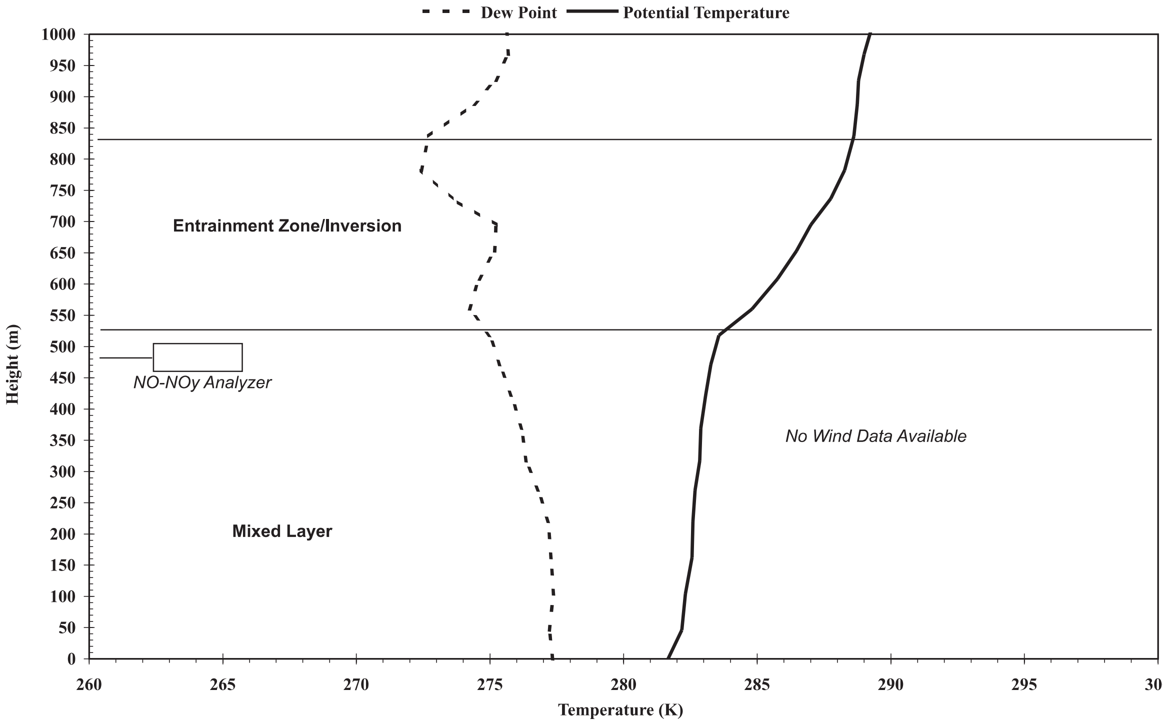

Fig. 7. NCSU upper air sounding – 8 December 1994 (0730 EST).

various layers that make up the day and nighttime boundary layer. The NO mixing ratios showed a strong diurnal profile, with a negative gradient associated with height. In the absence of synoptic meteorological features, the mean nocturnal NO mixing ratios were below instrument detection limits, which ranged from 0.04 to 0.23 ppbv; in contrast the mean daytime NO mixing ratios were at least an order of magnitude greater than the mean nighttime NO mixing ratios. NO_Y mixing ratios measured at 250 and 433 m also indicated a negative or decreasing vertical gradient, as well as a 22% decrease from the mean daytime values to the mean nighttime values. More importantly, the large increase from the nocturnal minimum (usually just before sunrise) to the diurnal maximum peak indicated that only 40–55 % of the daytime increase is due to NO_Y being conserved or formed in the nocturnal boundary layer overnight; the rest is either transported to and/or formed at the height within the hours after sunrise. The results observed for both NO and NO_Y mixing ratios indicate the importance of the local surface (i.e., biogenic emissions) as a source for both constituents.

The passage of synoptic scale/large mesoscale meteorological features was related to increases in NO and NO_Y mixing ratios measured at the 250 and 433 m heights. In particular, the nocturnal passage of a synoptic feature capable of inducing upward vertical motion in the atmosphere, such as a front or trough, produced an identifiable increase in the NO mixing ratios above the detection limit of the instrument in every observable case. The relationship of the passage of these synoptic meteorological events with increases in NO_Y mixing ratios were less identifiable, possibly due to the more complex nocturnal chemistry and transport processes with which NO_Y is associated. However, the NO_Y mixing ratios did respond to the synoptic meteorological events in enough instances (70%) to validate that under certain circumstances, NO_Y is also transported upward by the vertical motion produced by the passage of synoptic features.

Most importantly, throughout the measurement period, diurnal minimum values of NO and NO_Y mixing ratios were recorded (except for the previously mentioned synoptic event induced increases) at heights of 250 and 433 m just before sunrise, regardless of the structure of the nocturnal boundary layer. Comparison with upper air soundings at 0600 EST indicate that in at least seven of these cases, the instruments were in the residual layer, and thus this research indicates that the residual layer cannot be assumed to act as a significant reservoir of either NO or NO_Y (or by association, NO_X) for downward mixing. Furthermore, in three of these instances, the analyzer was located directly in the low level jet just above the interface between the stable layer and the residual layer, but still

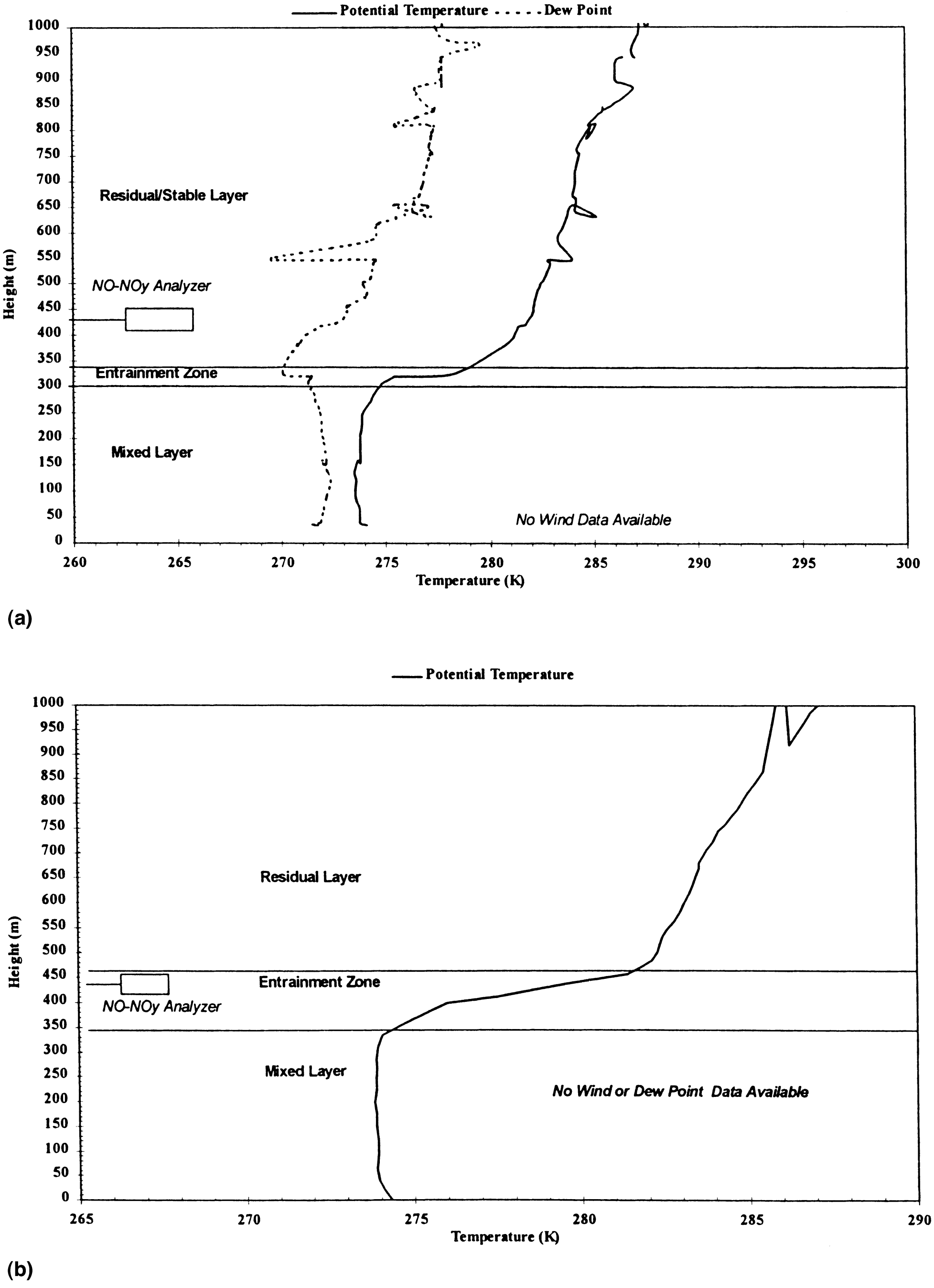

Fig. 8. (a) NCSU upper air soundings – 13 December 1994, 0815 EST, and (b) NCSU upper air soundings – 13 December 1994, 0915 EST.

recorded minimum values of NO and NO_Y. In these cases the low level jet evidently was not transporting a plume of NO and NO_Y that could be transported down or fumigated to the surface upon breakup of the inversion. Instead, comparison with upper air soundings taken at various times in the morning during the development of the mixed layer indicates that increases in NO and NO_Y mixing ratios (at the 250 and 433 m heights) are the result of the *upward* mixing of these gases from the surface.

In conclusion, it is felt that the knowledge gained during this study provides a better understanding of the vertical distribution and transport processes related to the mixing ratios of NO and NO_Y (and through NO_Y, the mixing ratios of NO_X). Furthermore, it points towards a rethinking of processes and sources related to rural surface mixing ratios of the oxides of nitrogen, and to that extent, the effectiveness of current NO_X emission and source control policies. Clearly, more comprehensive research into the role the various constituents of the oxides of nitrogen play in atmospheric chemistry and the production of ozone is necessary. Future work should consist of similar studies at different locations to determine whether these results can be extended to other locations, and to examine the contribution of factors such as emissions source distribution, in situ chemical processes, and transport.

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