Measurements of primary trace gases and NOY composition in Houston, Texas


ABSTRACT

Concentrations of CO, SO2, NO, NO2, and NOY were measured atop the University of Houston’s Moody Tower supersite during the 2006 TexAQS-II Radical and Aerosol Measurement Project (TRAMP). The lowest concentrations of all primary and secondary species were observed in clear marine air in southerly flow. SO2 concentrations were usually low, but increased dramatically in sporadic midday plumes advected from sources in the Houston Ship Channel (HSC), located NE of the site. Concentrations of CO and NOx displayed large diurnal variations in keeping with their co-emission by mobile sources in the Houston Metropolitan Area (HMA). CO/NOx emission ratios of 5.81 ± 0.94 were observed in the morning rush hour. Nighttime concentrations of NOx (NOx = NO + NO2) and NOY (NOY = NO + NO2 + HOx + HNO3 + HONO + N2O5 + HO2NO2 + PANs + RONO2 + p-NO3 + ... ) were highest in winds from the NNW-NE due to emission from mobile sources. Median ratios of NOx/NOY were approximately 0.9 overnight, reflecting the persistence and/or generation of NOx (NOx = NO + NO2) species in the nighttime Houston boundary layer, and approached unity in the morning rush hour. Daytime concentrations of NOx and NOY were highest in winds from the HSC. NOx/NOY ratios reached their minimum values (median ca 0.63) from 1300 to 1500 CST, near local solar noon, and air masses often retained enough NOx to sustain additional O3 formation farther downwind. HNO3 and PANs comprised the dominant NOY species in the HMA, and on a median basis represented 17–20% and 12–15% of NOY, respectively, at midday. Concentrations of HNO3, PANs, and NOY, and fractional contributions of these species to NOY, were at a maximum in NE flow, reflecting the source strength and reactivity of precursor emissions in the HSC. As a result, daytime NO2 concentrations were highest in air masses with HSC influence. Overall, our findings confirm the impact of the HSC as a dominant source region within the HMA. A comparison of total NOY measurements with the sum of measured NOY (NOY = NO + NO2 + HOx + HNO3 + HONO + N2O5 + HO2NO2 + PANs + RONO2 + p-NO3 + ... ) yielded excellent overall agreement during both day ([NOY]ppb) = ([NOx]ppb)*1.03 ± 0.16 – 0.42; r² = 0.9933) and night ([NOY]ppb) = ([NOY]ppb)*1.01 ± 0.16 + 0.18; r² = 0.9975). A similar comparison between NOy–NOx concentrations and NOY–NOx yields good overall agreement during both day ([NOY]/[NOx]) = ([NO2]/[NOx])1.01 ± 0.30 + 0.044 ppb; r² = 0.8527) and at night ([NO2]/[NOx]) = ([NO2]/[NOx])1.12 ± 0.69 + 0.16 ppb; r² = 0.6899). Median ratios of NO2/NO2 were near unity during daylight hours but increased to approximately 1.2 overnight, a difference of 0.15–0.50 ppb. Differences between NO2 and NO2 rarely exceeded combined measurement uncertainties, and variations in NO2/NO2 ratios may have resulted solely from errors in conversion efficiencies of NOx species and changes in NOY composition. However, nighttime NO2/NO2 ratios and the magnitude of NO2–NO2 differences were generally consistent with recent observations of CINO2 in the nocturnal Houston boundary layer.

1. Introduction

The 2000 Texas Air Quality Study (TEXAQS-2000) was conducted in and around the Houston Metropolitan Area (HMA) in August–September 2000 to investigate the causes of Houston’s repeated non-attainment of federal air quality standards. A major finding of...
TEXAQS-2000 documented the unusually large abundance of highly reactive volatile organic compounds (HRVOCs) in the Houston atmosphere and their role in the rapid and efficient photochemical generation of $O_3$ in the region (e.g., Ryerson et al., 2003; Jiang and Fast, 2004; Daum et al., 2003, 2004; Kleinman et al., 2002). The second Texas Air Quality study (TexAQS-II) was conducted from January 2005 to December 2006 and was designed to document and assess changes to air quality in southeastern Texas since 2000. The TexAQS-II Radical and Aerosol Measurement Project (TRAMP) was conducted at the North Moody Tower “supersite” on the campus of the University of Houston as part of the intensive operations period within TEXAQS-II. The background and objectives of TRAMP have been reviewed in Cowling et al. (2007) and Lefer et al. (in this issue).

The link between $O_3$ and NO$_x$ (NO$_x$ = NO + NO$_2$) photochemistry has been extensively studied for decades. The fundamental characteristics of urban photochemistry are reviewed by Finlayson-Pitts and Pitts (2000) and references therein, and are described in relation to Houston’s unique chemical and meteorological environment by Flynn et al. (in this issue), Lefer et al. (in this issue), and Cowling et al. (in this issue). Briefly, net ozone production occurs when peroxy radicals (RO$_2$), formed from photochemical reactions involving the hydroxyl radical (OH) with VOCS, oxidize NO to NO$_2$. Subsequent photolysis of NO$_2$ generates a O($^1$D) atom, which reacts with O$_2$ to form O$_3$, and NO, which can go on to generate additional $O_3$ by repeated reactions with RO$_2$. Photochemical ozone generation is constrained by the competition for NO$_2$ between reactions which perpetuate the catalytic cycle of NO–NO$_2$–$O_3$ reactions and those which terminate that cycle by converting NO$_2$ to nitric acid (HNO$_3$). Interactions of organic free radicals with NO$_2$ can produce peroxyacetyl nitrate (PAN) and its homologues, but these species are thermally unstable and typically act as temporary reservoirs of NO$_x$ in the lower atmosphere. Nighttime reactions can generate other species such as nitrate radical (NO$_3$), nitrous acid (HONO), nitric acid anhydride (N$_2$O$_5$) and nitryl chloride (ClNO$_2$), the latter particularly in a marine environment (Osthoff et al., 2008). These species can liberate NO, OH radicals, and/or Cl radicals upon photolysis the following morning, thereby contributing to the daytime photochemical cycle.

Comparisons of measurements of total NO$_x$ (NO$_y$ = NO + NO$_2$ + NO$_3$ + HNO$_3$ + HONO + 2$^\circ$N$_2$O$_5$ + HO$_2$NO$_2$ + PANs + RONO$_2$ + p-NO$_3$ + ...) with the sum of individually measured component species constitute an important assessment of our ability to properly measure reactive nitrogen species and to close the reactive nitrogen budget. Such studies have been used to identify potentially important “missing” NO$_y$ compounds which may not be adequately measured by current analytical methods (Fahey et al., 1986; Buhr et al., 1990; Williams et al., 1997). Neuman et al. (2002) evaluated NO$_y$ composition as measured aboard the NOAA WP-3D aircraft during TEXAQS-2000 and found that the measured sum of NO$_x$, HNO$_3$, and PAN concentrations agreed with those of total NO$_y$ to within the combined uncertainties of the techniques.

In this paper we discuss measurements of primary trace gases (SO$_2$, CO, NO, NO$_x$, NO$_y$) with regard to local source regions. Observations are classified with respect to time of day and emission source regions inferred from wind direction data. Observations are used to derive CO/NO emission ratios from local sources; to identify potential local emission sources and source regions; and to assess the NO$_x$ budget at the Moody Tower supersite.

2. Experimental

Measurements of CO, SO$_2$, and reactive nitrogen compounds were made from August 15 to October 2, 2006 as part of the NOAA/Air Resources Laboratory's contribution to the TRAMP study. The inlet systems were mounted in a weather-tight NEMA enclosure at the top of a 10 m walk-up scaffold erected on the roof balcony of the North Moody Tower (MT: 29.718 °N, 95.341 °W) on the University of Houston (UH) campus. The measurement site is described in more detail in Lefer et al. (in this issue). By virtue of its sampling height (70 m above ground level) the site is more representative of emission sources in the wider HMA than of local street-level emissions. The MT site is located approximately 5 km SE of “downtown” Houston, 1 km SW of Interstate 45, and 3.5 km north of the South I-610 loop. The site is positioned 6 km SW and 25 km WSW, respectively, of the western and eastern edges of the petrochemical facilities in the Houston Ship Channel (HSC).

Detailed discussions of the instrumentation deployed in TRAMP appear in Luke et al. (2007) and will be only briefly reviewed here. The trace gas instruments were housed in an air conditioned trailer at the base of the walk-up scaffold. Heated (40 °C) and insulated PFA Teflon tubing was used for all calibration and sampling lines, and all instruments were calibrated at the inlet tip. Sampling lines were protected from particulate contamination with Teflon or other filter elements. Dynamic calibration gas mixtures were generated from NIST-traceable compressed gas standards in an excess flow of humidified zero air (all gases supplied by Scott Marrin, Inc., Riverside CA) using calibrated mass flow controllers (MFCs: Tylan General, Torrance, CA). Labview 8.0 software (National Instruments, Austin, TX) was used for data logging and instrument and calibration control. Analog signals were sampled at 5 s intervals; reduced output data were averaged over 1 min and 1 h time intervals.

2.1. Carbon monoxide, sulfur dioxide, and ozone

The CO and SO$_2$ detectors shared a common inlet and the combined sample flow passed through a Nafion dryer membrane (Model PD-625-24AIF, Perma Pure Inc., Toms River, NJ) to avoid condensation inside the trailer. Carbon monoxide was measured with a commercial non-dispersive infrared (NDIR), gas filter correlation spectrometer (Model 48S, Thermo Electron Corporation, Waltham, MA) modified for high sensitivity (Dickerson and Delany, 1988; Parrish et al., 1994). Sulfur dioxide was measured with a modified commercial pulsed fluorescence detector (Model 43S, Thermo Electron Corp.) (Luke, 1997; Luke et al., 2007). The CO and SO$_2$ detectors were calibrated every 1–3 days at concentrations of approximately 1000 and 60 ppb, respectively.

The uncertainty for 1 h average concentrations is estimated to be ±(0.07 ppb + 6% of reported concentration) for SO$_2$ and ±(10 ppb + 5% of reported concentration) for CO. Hourly averaged CO concentrations measured with the NOAA instrument agreed to within 3.0% of those reported by UH’s independent NDIR detector (Model 48C-TLE, Thermo Electron Corp.). The intercept of the regression was 2.0 ppb, and correlation between the detectors was excellent ($r^2 = 0.9870$). The contents of the NOAA CO calibration standard agreed to within 0.2 and 3.8% of two independent UH standards, respectively. Ozone concentrations were measured by scientists from UH using a commercial Thermo Electron Model 49C UV photometric detector. The uncertainty in $O_3$ concentrations is estimated to be the larger of ±5% or ±2 ppb.

2.2. Oxides of nitrogen (NO, NO$_x$, NO$_y$)

Reactive nitrogen compounds (NO, NO$_x$, NO$_y$) were measured with a two-channel ozone chemiluminescence detector. Major components of the NOAA-constructed detector were removed from two commercial detectors (Model 425, Thermo Electron Corp.) and repackaged into a single enclosure. The limit of detection (LOD) was 0.03 ppb NO (signal to noise ratio 2:1) for a 1 min integration time and was achieved by using a high-output silent-discharge ozone electrode (Ozonology, Inc., Northbrook, IL) and a high capacity Teflon diaphragm pump (DTC-120, Kurt J. Lesker Co., Clairton, PA).
A heated (350 °C) commercial molybdenum converter (Thermo Electron Corp.) was used to measure NOY continuously on the first channel. The converter was mounted in the NEMA enclosure to minimize adsorptive losses of NOY species. A MFC immediately downstream of the converter and protected from particulate contamination with a 60 µm mesh stainless steel filter maintained sample flow at 1 standard liter per minute (slm). NO and NOX were measured sequentially on the second detector channel using a photolytic converter mated to a separate inlet system and MFC. The converter was powered on and off at 1 min intervals with NO2 determined by difference. The design was based upon that of a solid-state light source converter (US Patent 7,238,328) developed by Air Quality Design, Inc. (Golden, CO). The NOAA converter consisted of a 225 cm² cylindrical quartz cell illuminated longitudinally with 2 UV LED arrays (λmax = 395 ± 5 nm; Opto Diode Corp., Newbury Park, CA) at each end. A custom power supply provided current control and thermal overload protection to each array. Highly reflective Teflon© (Gigahertz-Optik Inc., Newburyport, MA) was used on the outer cell surfaces to enhance photon reflectivity. At the normal sample flow of 1.5 slm and pressure of 100 torr, cell residence time was approximately 1.2 s; correction of NO and NOX values for variations in ambient O3 (e.g., Ridley et al. 1988) was not necessary. Potential interferences to the LED photolytic NOY and PAN measurement techniques are few. Only nitrous acid (HONO) has an appreciable absorption cross section near 395 nm; its photolysis potential (the product of the absorption cross section and photolysis quantum yield) is only 1.4% of that of NO2, but can be an order of magnitude larger at 385–390 nm. The maximum interference posed by N2O5 is 0.03% of NO2, assuming a quantum yield of 1.0 for the photolytic production of NO* and subsequent dissociation to NO (Finlayson-Pitts and Pitts 2000, and references therein). Artifact NOX2 formation arising from the thermal decomposition of PAN, N2O3, and H2O2NO should be negligible: the LED arrays impart little or no radiant heating to the quartz cell, and temperatures inside the converter were typically at or below outside (ambient) temperatures. PAN decomposition in the heated sample line was deemed to be negligible.

The NO/NOX/NOY detector was calibrated automatically every 11 h, and converter artifact levels were determined from extensive zero air flushes prior to calibration. Conversion efficiencies (CE) were measured by periodic gas phase titrations (GPT;Stedman, 1976) and verified frequently by calibrating with NO2. The NO2 CE of the molybdenum converter was 97.6 ± 0.6%, while that of the photolytic converter decayed from 56.2% to 51.7% during the study. The NOAA NO calibration standard agreed to within 2.5% of 0.22 ppb NO (0.015 ppb NO, plus 7% of reported concentration), ±(0.040 ppb + 12% of reported concentration), and ±(0.22 ppb + 10% of reported concentration), respectively.

2.3. Other reactive nitrogen species

Concentrations of NOY component species are discussed below in the context of NOY budget studies. Concentrations of peroxyacetyl nitrate (PAN), peroxyacryloyl nitrate (APAN), peroxypropionyl nitrate (PPN), peroxybutyryl nitrate (PBN), and peroxymethacryloyl nitrate (MPAN) were measured at 10 min intervals by UH using an automated GC/ECD technique (Leuchner and Rappenglick, in this issue; Rappenglick et al., submitted for publication). Measurement uncertainties are the larger of ±11.6% or ±30 ppt for PAN and PBN; ±12.3% or ±85 ppt for PBN; ±16.2% or ±100 ppt for MPAN; and ±22.3% or ±40 ppt for APAN. The University of New Hampshire (UNH) measured HONO and HNO3 at 5–10 min intervals using an automated mist chamber technique with ion chromatographic detection (Ziemba et al., in this issue; Stutz et al., in this issue). Overall uncertainties of both measurements are ±10%. Aerosol nitrate in particles smaller than 1 µm vacuum aerodynamic diameter was measured with an Aerodyne Research, Inc. (Billerica, MA) quadrupole mass spectrometer (Ziemba et al., in this issue); mass loadings were reported at 10 min intervals with an uncertainty of ±10%.

3. Results

The magnitude, variety, and geographical distribution of emission sources in the HMA complicate any analysis of observations there. Numerous petrochemical and other industrial facilities are found to the east of the MT site in the HSC, a region which dominates the emissions of NOX and VOCs in the metropolitan area (Daum et al., 2003, 2004; Ryerson et al., 2003; Leuchner and Rappenglick, in this issue; Cowling et al., 2007 and references therein). The numerous tanker and cargo ships in the HSC and turning basin emit NOX, CO, SO2, and carbonaceous aerosols to the HMA (e.g., Lack et al., 2008; Cowling et al., 2007; Williams et al., in press). Refineries and other industrial sources are located farther a field to the east and southeast in the Beaumont-Port Arthur and Texas City areas, respectively. The 3800 MW W.A. Parish electrical generating unit (EGU), approximately 35 km southwest of the Moody Tower, burns coal and natural gas. Its total net generating capacity is among the largest of all fossil fuel plants in the U.S. (data available at: http://www.eia.doe.gov/neic/rankings/plantsbycapacity.htm) and the plant emits approximately 5000 tons NOX per year (data available at: http://www.epa.gov/cleaneenergy/energy-resources/egrid/index.html). Numerous smaller EGUS are located well to the north of Houston. Finally, a series of interstate highways and heavily traveled main roads ring the city and the MT site.

Time series plots of measured CO, SO2, and NOX appear in Fig. 1a–c and reflect the complexity of emissions in an urban environment. Emissions from local sources were superimposed on background concentrations which varied with wind direction and upwind emission source intensity. The prevailing meteorology during TRAMP is reviewed in Lefer et al. (in this issue). During the 6-week study, winds were typically from the eastern sector (39.5% from the NE, 27.6% from the SE) with westerly winds less frequent (6.6% from the NW, 26.3% from the SW). Low concentrations of primary and secondary trace species, as well as increased cloud cover and precipitation, were observed in clean southerly flow from the Gulf of Mexico from August 25–28, Sept. 15–18, and Sept. 22–23 (Lefer et al., in this issue). Higher concentrations were measured following frontal passage in the area (Rappenglick et al., submitted for publication), when persistent northerly winds transported natural (biomass burning) and anthropogenic (point-source and urban) emissions from upwind continental sources into the HMA. Under these conditions, local emissions were superimposed on a background of elevated concentrations of CO, SO2, and reactive nitrogen species, as may be seen by inspection of Fig. 1a–c. Recirculation of polluted air in the land-breeze/gulf-breeze circulation under weak synoptic flow was responsible for elevated O3 observed on August 31–Sept. 1, and on Sept. 7, 12, and 26 (Lefer et al., in this issue; Rappenglick et al., submitted for publication).

A summary of the trace gas observations, segregated into day (0800–2000 CST) and night (2000–0800) time periods, appears in Table 1. Median concentrations were typically higher at night in the shallow nocturnal boundary layer (BL); during the day, convective mixing increased BL heights and diluted emissions throughout a larger volume of the lower troposphere (Day et al., in this issue). Fumigation of the Moody Tower by SO2-rich plumes: titration of NO by O3 at night; and photochemical generation of NOX oxidation products (NO2) account for the observations of higher concentrations of SO2, NO, and NO2, respectively, during the daytime (Table 1).
nitrogen compounds were observed in southerly flow. Day and nighttime CO concentrations were highest in winds from the NW-NE (ca 315°–45°) and were well correlated with NOx, likely reflecting the co-emission of CO and NOx in the morning rush hour from mobile sources travelling the interstate highways and arterial roads north of campus. This interpretation is supported by a source apportionment study of VOC compounds measured during TRAMP (Leuchner and Rappenglu¨ck, in this issue), which found that the source factor associated with vehicular emissions was elevated in winds from all northerly directions, from the west through the ENE. Northerly winds also brought continental emissions into the HMA. Overall correlation of NOx and CO concentrations from all wind sectors, day and night, was quite good ($r^2 = 0.7253$).

3.2. Sulfur dioxide

Concentrations of SO2 in the HMA were typically low; 597 of 1058 hourly averaged values were between 0 and 1 ppb. While median concentrations exhibited little diurnal variation (Fig. 3), inspection of 95th percentile concentrations reveals the occasional impact of SO2-rich plumes at the site, usually during midday. This behavior is also evident from inspection of Fig. 1b; SO2 concentrations were usually quite low but were occasionally perturbed by large increases in short-duration plume events. The highest SO2 concentrations were observed from 0600 to 1400 CST in winds influenced by emissions in the HSC (50°–110°; henceforth referred to as “NE flow”), although high [SO2] was also occasionally observed at night in winds from this sector; daytime and nighttime [SO2] averaged 9.31 ± 12.9 ppb in NE flow. Overall, correlation between CO and SO2 in these air masses was good ($r^2 = 0.6131$) only at SO2 concentrations exceeding 10 ppb. SO2/NOx ratios in NE flow averaged 0.438 ± 0.429 (max = 2.20), considerably higher than the ratio of 0.1–0.15 observed in winds from almost all other sectors. These observations begin to reflect the complex distribution of sources in the HSC; sporadic or episodic primary emissions from co-located or closely located sources in the HSC; and/or the occasional fumigation of the site by specific sources within the HSC possessing unique emissions characteristics.

Elevated SO2 concentrations were also measured during the day in southwesterly flow (220°–240°). In these air masses, high SO2 (>4 ppb) correlated well with NOx ($r^2 = 0.4706$) but not with CO ($r^2 = 0.0790$), which remained low and relatively invariant (161 ± 41 ppb). SO2/NOx ratios averaged 0.393 ± 0.773 (max 3.27) in winds from 220° to 240°, suggesting an emissions signature from EGUls southwest of the city (e.g., W.A Parish). Elevated SO2/NOx ratios were not observed in SW winds at night, however.

3.3. Reactive nitrogen compounds

Diurnal profiles of weekday NO, NO2, and NOY concentrations are shown in Fig. 4a–c, and like CO exhibited clear variations, with concentrations increasing dramatically during the morning rush hour. The growth of the convective BL in mid-late morning, coupled with enhanced photochemical transformations and depositional losses, acted to decrease concentrations throughout the day. Concentrations increased again at night, as late day and nighttime emissions were injected into the smaller volume of the nocturnal BL.

Like CO, diurnal variations of NOx and [NO2] were much smaller on weekends than during the week (Figs. 4 and 5). Concentrations of NO were often near zero at night due to rapid oxidation by O3 and conversion to NO2. However, occasional early morning (0300–0500 CST) releases of large amounts of NO from sources in the HSC were advected to the site in NE flow. These perturbations may be seen in Figs. 4a and 5a through examination of 75th and 95th percentile concentrations.

Note that the morning rush hour, assumed to be from 0500 to 0900 CST, spanned both day and nighttime periods.

3.1. Carbon monoxide

Median CO concentrations displayed a well defined diurnal variation, increasing during the morning rush hour and peaking at 346 ppb at 0700–0800 CST over all days of the study. Weekdays (Fig. 2a) exhibited a more pronounced diurnal variation than weekends (Fig. 2b) due to higher traffic volumes and greater regularity in variations of traffic density. Between 0600 and 0700 CST, median [CO] peaked at 432 ppb during the week, but only at 250 ppb on the weekends. CO typically remained near or below 200 ppb throughout the day on weekends.

A histogram of CO concentrations (not shown) displayed a bimodal distribution, with a mode at 120–140 ppb and a secondary peak at 180–200 ppb. The lowest concentrations of CO, SO2 and reactive
At night, concentrations of NO and NOY were highest in winds from the NNW-NE due to mobile source emissions in the morning rush hour (e.g., Leuchner and Rappenglück, in this issue). Emissions from upwind continental sources may also have contributed to increased background concentrations of NO and NOY in northerly flow, but this contribution was likely much smaller than for CO due to the shorter atmospheric lifetimes of reactive nitrogen compounds. SO2/NOX ratios averaged only about 0.1 in winds from 300° to 40°, suggesting that emission signatures from distant (ca 100 km) EGUs to the north of the HMA were not discernible.

Highest daytime concentrations of NO and NOY were observed in winds from the HSC. Source apportionment analysis (Leuchner and Rappenglück, in this issue) confirmed that the HSC is the dominant source region for VOC emissions to the HMA, and large VOC and NO emissions from petrochemical and other industrial facilities in the HSC have been well documented (e.g., Ryerson et al., 2003; Daum et al., 2003, 2004; Kleinman et al., 2002; Cowling et al., 2007 and references therein). Substantial NOX is also emitted in the diesel exhaust of tanker and cargo ships in the ship channel (Cowling et al., 2007; Williams et al., in press).

NOX concentrations were also elevated in winds from the south-east during the day and night. VOC composition reflected a variety of contributing source factors in SE flow, including biogenic emissions, fuel evaporation, vehicular exhaust, aromatic compounds, and natural gas and crude oil signatures. Mobile source emissions from the I-45 and South I-610 loop dominated the VOC emission signatures in SE flow, however, and refinery and other industrial emissions were less important (Leuchner and Rappenglück, in this issue). NOY concentrations were poorly correlated with the moderate levels of SO2 measured in SE flow (slope = 0.0388, r^2 = 0.0261), but were much better correlated with CO (slope = 5.123, r^2 = 0.4394), consistent with a mobile emission source.

NOX concentrations were slightly elevated in winds from the southwest, likely due to daytime emissions from upwind EGUs. Although relatively few observations were made under westerly flow, NOX and NOY concentrations were elevated in a broad sector from the SW-NW during the day, most likely from mobile source emissions (I-59, 288, Galleria area, Medical Center) without overlap of industrial sources. Concentrations of NOX and NOY were at a minimum in marine air in southerly flow.

### 3.4. NOX–CO correlations

The correlation of CO and NOX concentrations in the morning rush hour has been commonly used as a robust measure of molar

![Fig. 2](image-url)  
**Fig. 2.** Diurnal profiles of CO concentration (ppb): (a) weekday aggregated data, (b) weekend data. Horizontal bars represent median concentrations, rectangular boxes denote 25th and 75th percentile concentrations, and whiskers denote 5th and 95th percentile concentrations.

![Fig. 3](image-url)  
**Fig. 3.** Same as Fig. 2, for all weekday and weekend SO2 data (ppb). Note that the concentration scale is logarithmic.
emission ratios from mobile sources (e.g., Fujita et al., 1992; Parrish et al., 2002). High vehicular traffic volumes and low BL heights in the morning tend to maximize pollutant concentrations. Morning NOx and CO concentrations should remain largely unperturbed by photochemistry and should accurately reflect emission ratios from nearby sources, although long-range transport can enhance [CO]. NOx emission from EGUs can confound the analysis, but since these emissions typically emanate from elevated stacks they should be transported aloft prior to the onset of convective mixing.

CO and NOx concentrations measured during the morning rush hour (0500–0900 CST) from all wind directions and for all days of the TRAMP study are plotted in Fig. 6. The CO/NOx emission ratio inferred from the fitted slope of a linear least squares regression is 5.81 ($r^2 = 0.8134$). The total uncertainty (0.94) in the calculated emission ratio is estimated by adding in quadrature the standard error of the fitted slope (0.31) and the combined uncertainties of the CO, NO, and NO2 measurements discussed above. Our ratio agrees almost exactly with 2006 ratios computed from ambient monitoring stations in the Houston area (Cowling et al., 2007; Parrish et al., 2009). The CO/NOx emission ratio determined from Moody Tower data reported by Parrish et al. (2009), 4.7, was calculated from an independent UH data set and included a relatively few observations of high [CO] and [NOx].

Fig. 4. Same as Fig. 2 for weekday data only: (a) NO (ppb), (b) NO2 (ppb), (c) NOY (ppb). Note that the ordinate for NO concentrations is a logarithmic scale.

Fig. 5. Same as Fig. 2, for weekend data only: (a) NO (ppb), (b) NO2 (ppb), (c) NOY (ppb). Note that the ordinate for NO concentrations is a logarithmic scale.
not detected by the NOAA instruments. Both the NOAA and UH NOx instruments measured NO and NO\textsubscript{2} sequentially, so reported concentrations may suffer from increased uncertainties under rapidly fluctuating conditions. At NO\textsubscript{x} concentrations below 70 ppb and under more quiescent conditions, CO/NO\textsubscript{x} emission ratios derived from the two data sets agreed more closely (NOAA: 5.52, UH: 5.32).

3.5. Photochemical processing

Diurnal profiles of NO\textsubscript{x}/NO\textsubscript{y} ratios are presented in Fig. 7a. Concentrations of NO\textsubscript{2} were calculated as the difference between NO\textsubscript{x} and NO\textsubscript{y} measurements; diurnal profiles are presented in Fig. 7b. (The designations NO\textsubscript{x} and NO\textsubscript{y} – NO\textsubscript{x} shall be used interchangeably in the discussion below.) Approximately 4% of the total 1049 hourly observations of NO\textsubscript{2} were slightly less than zero: 4 hourly observations were between −1 and −2 ppb, and 40 were between 0 and −1 ppb. NO\textsubscript{2} concentrations of −0.41 to −1.26 ppb were sometimes calculated late at night or during the morning rush hour, while slightly negative [NO\textsubscript{2}] (ca. −0.05 ppb) occasionally resulted from uncertainties in the molybdenum converter artifact at NO\textsubscript{y} concentrations of 1–2 ppb.

Median NO\textsubscript{x}/NO\textsubscript{y} ratios decreased through the morning and reached a minimum of approximately 0.63 near local solar noon (1300–1500 CST). Conversely, ratios of NO\textsubscript{z}/NO\textsubscript{y} were approximately 0.37 (median) and reached as high as 0.45–0.50 at the 25th percentile level at this time (Fig. 7c), with NO\textsubscript{z} concentrations approaching 5 to as much as 10 ppb (Fig. 7b). Although high concentrations of O\textsubscript{3} and NO\textsubscript{z} were often observed at the MT site, these measurements indicate that NO\textsubscript{x}–O\textsubscript{3} photochemistry was far from exhausted, with substantial levels of NO\textsubscript{x} still available for additional ozone generation farther downwind. NO\textsubscript{y}/NO\textsubscript{x} ratios increased during the evening and reached approximately 0.9 overnight, reflecting the persistence of NO\textsubscript{z} species in the nighttime BL. Ratios approached unity in the morning rush hour when fresh injections of NO\textsubscript{x} dominated the NO\textsubscript{y} distribution.

Fig. 8 presents a diurnal profile of median ratios of measured component NO\textsubscript{y} species to total NO\textsubscript{y}. Median, 25th percentile, and 75th percentile concentrations for all reactive nitrogen species are listed in Table 2 for rush hour, midday, and overnight periods. Although NO\textsubscript{x} constituted the majority of NO\textsubscript{y} throughout the day, HNO\textsubscript{3} was the dominant NO\textsubscript{y} species and constituted as much as 17–19.5% of NO\textsubscript{y} from 1300 to 1500 CST. Median HNO\textsubscript{3} concentrations during midday (1100–1700 CST) were 1.531 ppb (central range 0.377–3.270 ppb). The pronounced peak in HNO\textsubscript{3} and HNO\textsubscript{3}/NO\textsubscript{y} near solar noon (Fig. 8) reflects the importance of the NO\textsubscript{2} + OH reaction as the dominant HNO\textsubscript{3} production pathway. HNO\textsubscript{3} accounted for about 3% of total NO\textsubscript{y} at night, with a median concentration of 0.667 ppb from 2100 to 0500 (central range 0.141–1.197 ppb). Nighttime observations of aqueous NO\textsubscript{3} in the MC technique were assumed to arise from either N\textsubscript{2}O\textsubscript{5} (formed from the nighttime reaction of NO\textsubscript{2} and NO\textsubscript{3}) or HNO\textsubscript{3} (formed from N\textsubscript{2}O\textsubscript{5} hydrolysis in the gas and aerosol phase and from other heterogeneous reactions; Finlayson-Pitts and Pitts, 2000, and references therein). Peroxyacyl nitrates comprised the second most abundant NO\textsubscript{y} species, with median fractional contributions to NO\textsubscript{y} of 2.3–3.1% at night and in the early morning (excluding rush hour), and 12.0–14.8% at midday (Fig. 8). The median concentration of PAN and PAN...
Fig. 8. Median fractions of the indicated NO species to NO as a function of time of day, calculated from diurnally aggregated concentrations: HNO3/NOY (solid triangles), PANs/NOY (solid diamonds), HONO/NOY (solid circles), p-NO3/NOY (solid squares). NO3/NOY ratios (open squares) are keyed to right ordinate.

homologues was 0.289 ppb (central range 0.190–0.607 ppb) from 2100 to 0500 CST and increased to 0.907 (central range 0.454–1.962 ppb) throughout midday, but increased slightly, along with [NOY] and NOY/NOX ratios in daytime NE flow implied by data in Fig. 9 are evident in Fig. 10a. Because HNO3 and PANs were the dominant NO2 species in the HMA, both [NO2] and NO2/NOY were also largest in air masses impacted by sources in the HSC; ozone concentrations followed this pattern (Fig. 10a). These results are consistent with the findings of the earlier TEXAQS-2000 study (Ryerson et al., 2003; Daum et al., 2003, 2004) where high ozone concentrations and rates and efficiencies of ozone production observed in the HSC were attributed to the magnitude and reactivity of VOC and NOX emission sources there. Aircraft flights in the 2006 TEXAQS-II campaign again confirmed the presence of large emission sources of NOX and HRVOCs and the rapid and efficient production of O3 in the HSC; followed by dispersion across the HMA (Cowling et al., 2007). Although data collected during TEXAQS-II suggest a reduction of approximately 40% in the emission of ethene and other HRVOCs from sources in the HSC (Cowling et al., 2007), our findings suggest that this region is still the source of maximum O3 production in the HMA.

Fig. 9. Scatter plot of NO2 and NOY concentrations (ppb) for day (0800–2000 CST; open diamonds) and, night (2000–0800 CST; solid circles) periods, and for midday (1100–1700 CST) conditions under northeasterly flow (solid squares).

Table 2
Trace gas concentrations (ppb) for select time periods.

<table>
<thead>
<tr>
<th>Species</th>
<th>0500–0900 CST</th>
<th>1100–1700 CST</th>
<th>2100–0500 CST</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Median</td>
<td>25th Pile</td>
<td>75th Pile</td>
</tr>
<tr>
<td>NO</td>
<td>6.741</td>
<td>1.860</td>
<td>16.785</td>
</tr>
<tr>
<td>HNO3</td>
<td>0.519</td>
<td>0.154</td>
<td>0.830</td>
</tr>
<tr>
<td>PANs</td>
<td>0.265</td>
<td>0.169</td>
<td>0.473</td>
</tr>
<tr>
<td>HONO</td>
<td>0.428</td>
<td>0.214</td>
<td>0.700</td>
</tr>
<tr>
<td>p-NO3</td>
<td>0.234</td>
<td>0.051</td>
<td>0.363</td>
</tr>
</tbody>
</table>

Ryerson et al. (2003) attributed higher PAN/NOY ratios in daytime NE flow to the HMA, and measured roughly equal concentrations of HNO3 and PAN compounds in aircraft transects of the HSC plume in 2000.

In order to investigate the dependence of NO2 species concentrations upon nearby source regions, we separated day and nighttime observations into 20° wind direction bins and calculated in each bin the median of the ratio of each species to NOY. Results are shown in Fig. 10a (day) and 10b (night). Median ozone concentrations for each wind direction bin are also presented.

Large HNO3/NOY and PANs/NOY ratios in daytime NE flow implied that this region is still the source of maximum O3 production in the HMA.
concentrations of NOY and NOZ were lower in westerly-northerly flow than in winds from the NE, and median O3 concentrations were less than 0.70 ppb and 50–70 ppb. Back trajectories associated with the remaining two episodes (HNO3/NOY ca 0.15, O3 ca 50–70 ppb on Sept. 6–7 and Sept. 13–14) suggested regional transport of polluted air masses from the north even though Sept. 6–7 was classified as a sea breeze day (Lefer et al., in this issue; Rappenglück et al., submitted for publication). It is possible that the 40 km EDAS model failed to resolve this fine scale recirculatory flow.

3.6. NOY composition and budget

Hourly averaged concentrations of NOY were compared to the sum of measured concentrations of individual NOY components (NOYi: NOYi = NO + HNO3 + PANs + HONO + p-NO3). NOY concentrations were measured with the solid-state photolytic converter described above. Hourly averaged concentrations of HNO3, PANs, HONO, and p-NO3 were calculated by adding in quadrature the measurement uncertainties in NO, NO2, and NOX concentrations. Measurement uncertainties in NO, NO2, and NOX concentrations were assumed to be half the stated LOD. AMS nitrate concentrations were converted to a mixing ratio equivalent assuming 298 K and 1 atm pressure. Nitrate radical (NO3) concentrations measured with a long-path DOAS averaged 20 ± 14 ppb (max 75.6 ppb) and 18.3 ± 20.6 ppb (max 98.2 ppb) from the lower and middle light paths, respectively (J. Stutz, personal communication), and were not considered. 697 h (338 day, 359 night) of data, covering approximately 60% of the total deployment period, were included in the analysis.

Results of the comparison between measured NOY and NOYi are shown for day and nighttime periods in Fig. 11a and in expanded scale in Fig. 11b. A least squares linear regression of nighttime data yields the following equation: NOY(ppb) = ([NOYi(ppb)]1.01) + 0.18 (r² = 0.9975). During daylight hours, the corresponding regression equation changed to: NOY(ppb) = ([NOYi(ppb)]1.03) - 0.42 (r² = 0.9933). At low concentrations ([NOY] < 0.15) measured [NOY] was larger than [NOYi] at night, but smaller than [NOYi] during the day. The total uncertainty in the fitted slope (0.16 day and night) is calculated by adding in quadrature the measurement uncertainties in NOY (±10%) and NOYi (±12%), obtained by weighting the uncertainty in each measured species by its average fractional contribution to NOY with the standard error in the fitted slope (±0.26% night, ±0.45% day). Overall, then, NOY and NOYi concentrations agreed well to within the combined uncertainties of the measurement methods. Ryerson et al. (2003) demonstrated similar closure of the NOY budget to within overall measurement uncertainties on all available flights of the WP-3D aircraft over Houston in 2000.

3.7. Budget of NOx oxidation products (NO2)

Because NO and NO2 constituted the overwhelming fraction of NOX during TRAMP (77.4 ± 17.1% during the day; 89.2 ± 10.3% at night), the NOX budget reflects primarily the measurement agreement for NOX. A more stringent assessment should focus instead on the budget of NO2 compounds. Measurement uncertainties in NO,
Calculated NO$_2$ concentrations are plotted against NO$_2$ concentrations (ppb) for daytime (1000–2000 CST) and nighttime (2100–0500 CST) time periods in Fig. 12. Statistical descriptors of calculated NO$_2$/NOZ ratios are presented in Table 3 for various time periods throughout the day. Because rapidly varying NO$_x$ and NOY concentrations can induce substantial errors in calculated NO$_2$ data collected during the morning rush hour and growth of the PBL (0500–1000 CST) were excluded from further analysis.

Despite the considerable scatter in the data, the plot in Fig. 12 suggests that the budget of NO$_2$ compounds in the daytime data was generally closed to within the combined uncertainties of the techniques. Calculated concentrations of NO$_2$ agreed well with the measured sum of NO$_2$ components during the day: [NO$_2$] (ppb) = ([NO$_2$] (ppb)$^*$1.01) - 0.044 ppb ($r^2 = 0.8527$). The overall uncertainty in the daytime fitted slope, ±0.30, was calculated as the quadrature sum of the standard error of the fitted slope (±2.5%) plus uncertainties in NOZ and NOZi concentrations. Uncertainty in daytime NO$_2$ concentrations ranged from an average of ±175% at NOZ concentrations below 1 ppb, to ±44% at 1–3 ppb, ±25% at 3–5 ppb, ±18% at 5–7 ppb, and ±11% at concentrations greater than 7 ppb. A median uncertainty of ±28% was assumed. Uncertainty in NOZ$_i$ was calculated to be ±11% from the sum of the uncertainties of each measured component. Note that Stutz et al. (in this issue-a) deduced that daytime NOZ measurements of HONO may be plagued by interferences from photochemically produced species such as organic nitrates. Such compounds should also be converted to NO on hot molybdenum and pose no bias to NOZ/NOZ$_i$ ratios here, but daytime measurements of NO$_2$ may include compounds not currently accounted for in species-specific measurements.

Despite greater uncertainty in nighttime NO$_2$ concentrations, NOZ$_i$ also agreed well with the sum of NOZ$_i$ at night: [NOZ$_i$] (ppb) = ([NOZ$_i$] (ppb)$^*$1.12) + 0.16 ppb ($r^2 = 0.6899$) (Fig. 12). The overall uncertainty in the fitted slope was calculated to be ±0.69, reflecting the larger standard error of the slope (±4.7%) and the larger uncertainty in measured NOZ$_i$ concentrations, which ranged from ±165% at concentrations less than 1 ppb, to ±70% at 1–3 ppb, ±42% at 3–5 ppb, and ±32% above 5 ppb. A median uncertainty of ±61% in the nighttime NO$_2$ data was assumed.

While higher nighttime NOZ$_i$/NOZ$_i$ ratios may point to the presence of one or more unidentified photochemically labile NO$_x$ species, they may well arise from competing errors or artifacts in NOZ

![Fig. 11. Scatter plot of total NO concentrations (ppb) and the sum of NO$_x$ components (NO$_x$; ppb) for day (0800–2000 CST, open circles) and night (2000–0800 CST, solid circles) periods. A plot of the entire data set is presented in (a) and as an expanded scale in (b). The solid line denotes a 1:1 correspondence of the data. The equations of a linear least squares fit to the data are: ([NO$_x$] (ppb) = ([NO$_x$] (ppb)$^*$1.03 ± 0.16) - 0.42; $r^2 = 0.9933$) for daytime data and ([NO$_x$] (ppb) = ([NO$_x$] (ppb)$^*$1.01 ± 0.16) + 0.18; $r^2 = 0.9975$) at night.

![Fig. 12. Scatter plot of concentrations of NO$_2$ and the sum of HONO + PANs + HONO + p-NO$_3$ concentrations (ppb) for daytime (1000–2000; open circles) and nighttime (2100–0500 CST; solid circles) periods. Data collected from 0500 to 1000 CST were excluded. The solid line denotes a 1:1 correspondence of the data. The equations of a linear least squares fit to the data are: ([NOZ] (ppb) = ([NOZ] (ppb)$^*$1.01 ± 0.30) + 0.044 ppb; $r^2 = 0.8527$) during the day and ([NOZ] (ppb) = ([NOZ] (ppb)$^*$1.12 ± 0.69) + 0.16 ppb; $r^2 = 0.6899$) at night.]
measurement and changes in NOy composition from day to night. In any case, the small differences observed in day/night NOZ/NOz ratios inferred from the regressions above are well within the combined measurement uncertainties of the analytical methods and are not statistically significant. Therefore, the data must be compared with caution and any interpretation will remain speculative.

Diurnal profiles of NOz/NOz ratios (excluding data from 0500 to 1000 CST) are presented in Fig. 13. Diurnally averaged solar zenith angles calculated at the location of the Moody Tower appear as a solid line. Median ratios of NOz/NOz were very near to unity during the day, began to increase after sunset, and increased throughout the night to reach a maximum at 0300–0500 CST. Median values of the difference ([NOz]-[NOz]) ranged from 0.15 to 0.35 ppb at night and increased to ca 0.50 ppb at 0400–0500 CST. HNO3/NOx and PANs/NOx ratios were not very different between early evening and early morning time periods, however, suggesting that measurement artifacts may not have played a significant role in increases in observed NOz/NOz ratios. This is also demonstrated by data in Fig. 14, a plot of day and night NOZ/NOZi ratios as a function of NOx/NOY ratios; nighttime data exhibit slightly greater increases in observed NOZ/NOZi ratios. This is also demonstrated that measurement artifacts may not have played a significant role early evening and early morning time periods, however, suggesting that measurement artifacts may not have played a significant role in increases in observed NOz/NOz ratios. This is also demonstrated by data in Fig. 14, a plot of day and night NOZ/NOZi ratios as a function of NOx/NOY ratios; nighttime data exhibit slightly greater (though not significant) discrepancies between NOZ and NOZi ratios than daytime values at equivalent NOx fractions.

Hourly NOZ/NOz ratios were evaluated on an individual basis, and those hours for which differences between NOZ and the sum of NOZi exceeded the combined measurement uncertainties were examined more closely. In the daytime a total of 31 h were recorded in which the sum of NOZ exceeded NOZ by an amount greater than the combined measurement uncertainties (case 1); 29 h saw NOZ > NOZi and PANs/NOx ratios were not very different between early evening and early morning time periods, however, suggesting that measurement artifacts may not have played a significant role in increases in observed NOz/NOz ratios. This is also demonstrated by data in Fig. 14, a plot of day and night NOZ/NOZi ratios as a function of NOx/NOY ratios; nighttime data exhibit slightly greater (though not significant) discrepancies between NOZ and NOZi ratios than daytime values at equivalent NOx fractions.

Table 3

<table>
<thead>
<tr>
<th>NOz/NOz</th>
<th>Day CST</th>
<th>Night CST</th>
<th>Dark CST</th>
<th>MidDay CST</th>
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</thead>
<tbody>
<tr>
<td>Average</td>
<td>1.053</td>
<td>1.275</td>
<td>1.189</td>
<td>1.029</td>
</tr>
<tr>
<td>Std. Deviation</td>
<td>0.516</td>
<td>0.569</td>
<td>0.528</td>
<td>0.496</td>
</tr>
<tr>
<td>Median</td>
<td>1.042</td>
<td>1.226</td>
<td>1.179</td>
<td>0.973</td>
</tr>
<tr>
<td>5th Percentile</td>
<td>0.199</td>
<td>0.460</td>
<td>0.225</td>
<td>0.216</td>
</tr>
<tr>
<td>25th Percentile</td>
<td>0.788</td>
<td>0.948</td>
<td>0.939</td>
<td>0.789</td>
</tr>
<tr>
<td>75th Percentile</td>
<td>1.286</td>
<td>1.519</td>
<td>1.467</td>
<td>1.247</td>
</tr>
<tr>
<td>95th Percentile</td>
<td>1.977</td>
<td>2.197</td>
<td>1.938</td>
<td>1.788</td>
</tr>
</tbody>
</table>

Fig. 13. Same as Fig. 2, for NOz/NOz ratios. Data collected from 0500 to 1000 CST were excluded. The solid line represents the calculated median zenith angle during the study period.

Fig. 14. NOz/NOz ratios as a function of NOx/NOy ratios for daytime (0800–2000 CST; open circles) and nighttime (2000–0800 CST; solid circles) periods.

4. Summary

Concentrations of CO, SO2, NO, NO2, and NOy were measured atop the University of Houston’s Moody Tower supersite during the 2006 TRAMP study, and their temporal variations reflected the interactions of multiple local sources characteristic of a large urban

4. Summary
environment. \( \text{SO}_2 \) concentrations were usually low, but increased dramatically at midday in sporadic plume events from sources in the HSC. Winds from the SW brought emissions from EGU's (W. A. Parish) into the HMA during daytime. The lowest concentrations of all primary and secondary species were observed in clean marine air in southerly flow. Concentrations of \( \text{CO} \) and \( \text{NO}_2 \) displayed large diurnal variations in keeping with their co-emission by mobile sources in the HMA. A \( \text{CO}/\text{NO}_2 \) emission ratio of 5.81 ± 0.94 was inferred from consideration of morning rush hour data.

Nighttime concentrations of \( \text{NO}_x \) and \( \text{O}_3 \) were highest in winds from the NNW-NE due to emission from mobile sources in the morning rush hour. Median ratios of \( \text{NO}_2/\text{NO}_x \) were approximately 0.9 overnight, reflecting the persistence and/or generation of \( \text{NO}_2 \) species in the nighttime Houston BL, and approached unity in the morning rush hour, when fresh emissions of \( \text{NO}_x \) dominated the \( \text{NO}_x \) budget. Daytime concentrations of \( \text{NO}_x \) and \( \text{O}_3 \) were highest in winds from the HSC to the NE. Occasional late-night and early morning releases of \( \text{NO}_x \) were observed in winds from the HSC, perhaps from refinery flares and/or emission from ships. \( \text{NO}_x/\text{NO}_y \) ratios reached their minimum values (median ca 0.63) from 1300 to 1500 CST, and air masses often retained enough \( \text{NO}_x \) to sustain additional \( \text{O}_3 \) formation farther downwind. \( \text{NO}_2 \) and PANs comprised the dominant \( \text{NO}_x \) species in the HMA, representing, on a median basis, 17–20% and 12–15% of \( \text{NO}_x \), respectively, at midday. Contributions from \( \text{HONO} \) and \( \text{p-NO}_3 \) were far smaller. Concentrations of \( \text{HNO}_3 \), PANs, and \( \text{NO}_2 \), and fractional contributions of these species to \( \text{NO}_y \) were at a maximum in NE flow, reflecting the source strength and reactivity of precursor emissions in the HSC. As a result, daytime \( \text{O}_3 \) concentrations were highest in air masses with HSC influence. Overall our findings confirm the impact of the HSC as a dominant source region within the HMA.

Variations of nighttime \( \text{NO}_2/\text{NO}_x \) ratios with wind direction were largely unremarkable, but increases in \( \text{O}_3 \) and \( \text{HNO}_3/\text{NO}_2 \) were noted in winds from the ESE \( (100°–140°) \), SW \( (200°–260°) \), and NW \( (300°–320°) \), suggesting the advection into the HMA of photochemically aged plumes. ARL's HYSPLIT model was used to calculate back trajectories and confirmed the recirculation of these parcels either over the HMA or nearby coastal Louisiana. In some instances, back trajectories suggested the transport of aged air masses from the DPW area as well as from Mexico.

A comparison of total \( \text{NO}_x \) measurements with the sum of measured \( \text{NO}_y \) species, \( \text{NO}_y \), yielded excellent overall agreement during both day \( (\text{NO}_y/\text{ppb} = [\text{NO}_y]_{\text{ppb}}/1.03 ± 0.16) \) and \( \text{night} (\text{NO}_y/\text{ppb} = [\text{NO}_y]_{\text{ppb}}/1.01 ± 0.16) \); \( \rho^2 = 0.9933 \) and \( \rho^2 = 0.9975 \). A similar comparison between \( \text{NO}_y/\text{NO}_x \) concentrations and the sum of \( \text{NO}_2 \) species, \( \text{NO}_2 \), also yielded good overall agreement despite the increased uncertainty inherent in calculated \( \text{NO}_x \) concentrations. \( \text{NO}_2/\text{NO}_x \) ratios increased to approximately 1.2 overnight, a difference of 0.15–0.50 ppb. While not statistically different from unity, nighttime \( \text{NO}_2/\text{NO}_x \) ratios were consistent with the presence of photochemically labile \( \text{NO}_x \) species, and the magnitude of \( \text{NO}_2/\text{NO}_x \) differences was generally consistent with recent observations of \( \text{CINO}_2 \) in the nocturnal Houston BL.

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References


Stutz, J., Wong, K.W., Lawrence, L., Flynn, J.H., Rappenglück, B., Lefer, B., Brune, W., Ziemba, L., Griffin, R. Nocturnal NO2 radical chemistry in Houston, TX, in this issue-b.


