

## Comparisons of in situ and long path measurements of NO<sub>2</sub> in urban plumes

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[1] Measurements of NO<sub>2</sub> were taken at Cornelia Fort Airpark in Nashville, TN, during the 1999 Southern Oxidant Study using three different techniques: photolysis to NO followed by chemiluminescence (PCL), laser-induced fluorescence (LIF), and differential optical absorption spectroscopy (DOAS). This was an informal comparison of these techniques conducted during the 1999 Southern Oxidant Study. The PCL and LIF instruments were connected to a common manifold that sampled at the top of a 10-m-walkup tower. The DOAS instrument sampled over a 1.37-km-long light path with end points at 2 and 35 m above ground. The range of NO<sub>2</sub> mixing ratios measured was 0.75 ppbv to over 60 ppbv and the median value was nearly 3 ppbv. While preliminary data analysis showed overall agreement between the LIF and PCL instruments to within 1% (least squares slope = 0.99;  $r^2 = 0.98$ ), subsequent analysis revealed a discontinuous shift of about 12% in the PCL data, which was confirmed by comparison to the DOAS data. A leak in the PCL inlet system was the likely cause. After adjustment of the affected PCL data, a comparison of all the coincident measurements showed high correlation ( $r^2 > 0.99$ ) and overall agreement to within 5%. Analysis of the ratios of PCL NO<sub>2</sub> to LIF NO<sub>2</sub> showed that greater than 90% of individual data points agree to within the total combined instrumental uncertainties. However, the comparison over short time periods is more precise than the average over the campaign. We attribute this to the need for improved PCL instrument data reduction procedures. The two in situ instruments were also operated side by side a year later in Houston, TX, with similar results. *INDEX*

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### 1. Introduction

[2] The nitrogen oxides NO and NO<sub>2</sub> (NO<sub>x</sub> = NO + NO<sub>2</sub>) directly regulate O<sub>3</sub> production rates and indirectly influence aerosol abundances in the urban, rural, and remote troposphere. Emissions of NO<sub>x</sub> are thus responsible for the

major components of photochemical smog [NRC, 1991], the greenhouse forcing of tropospheric O<sub>3</sub> [e.g., Mickleby *et al.*, 1999], and maintaining the oxidizing capacity of the atmosphere [e.g., Logan *et al.*, 1981]. Nitric acid produced by NO<sub>x</sub> oxidation via OH + NO<sub>2</sub> is a significant component of atmospheric acid deposition, damaging many ecosystems [e.g., Durka *et al.*, 1994]. Nitrogen oxide deposition may also act as fertilizer enhancing carbon uptake and indirectly affecting global CO<sub>2</sub> abundances [Holland *et al.*, 1997].

[3] Nitrogen dioxide is the primary constituent of NO<sub>x</sub> in the planetary boundary layer. At high concentrations NO<sub>2</sub> and NO are toxic, and in the U.S., federal regulations such as the National Ambient Air Quality Standard (NAAQS) require that the annual arithmetic mean concentration of NO<sub>2</sub> not exceed 53 ppbv in an inhabited location [e.g., USEPA, 1997]. Currently, there is a substantial effort, known as the NO<sub>x</sub> State Implementation Plan (SIP) Call [Federal Register, 1998], to reduce ozone production and transport in the midwestern and eastern U.S. by reduction of emissions of NO<sub>x</sub>. The effect of regulated NO<sub>x</sub> reductions

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on O<sub>3</sub> will be predicted with photochemical transport models and evaluated by comparison to future observations of O<sub>3</sub> and NO<sub>x</sub>. However, monitoring requirements for NO<sub>2</sub> NAAQS compliance will not satisfy the need for high quality NO<sub>2</sub> data for this effort [McClenney *et al.*, 2002]. Indeed, one estimate [Tonnesen and Dennis, 2000] suggests the need for NO<sub>2</sub>-specific (i.e., not NO<sub>x</sub>) monitoring data at a total uncertainty of no more than 10%. Routine measurements of NO<sub>2</sub> at this level from monitoring networks currently are unavailable in part due to the lack of NO<sub>2</sub>-specific measurement techniques.

[4] Observation of NO<sub>2</sub> is challenging because of the large dynamic range of mixing ratios encountered: from low (<0.1 ppbv) levels in rural and remote locations to high (>100 ppbv) levels typical of urban areas, rapid temporal variation, and the difficulty of clearly discriminating against the wide array of other important atmospheric species that contain the NO<sub>2</sub> moiety (e.g., PAN, HNO<sub>4</sub>, HNO<sub>3</sub>). Detection of NO<sub>2</sub> has most often been accomplished via conversion to NO, a species that can be sensitively and specifically determined in the atmosphere. Conversion of NO<sub>2</sub> to NO, though, has been an area of concern. The use of metal compounds, such as FeSO<sub>4</sub> [Kelly *et al.*, 1980] and heated molybdenum, has had limited success primarily due to significant conversion of other nitrogen-containing species. On the other hand, conversion by photolysis has been shown to be reasonably specific [Kley and McFarland, 1980], and this technique has undergone substantial improvements in recent years [Ryerson *et al.*, 2000]. Direct detection of NO<sub>2</sub> has been limited primarily to spectroscopic techniques using wavelengths either in the infrared region (in situ tunable diode laser, TDLAS) [Schiff *et al.*, 1990] or in the UV (long-path differential optical absorption, DOAS) [Stutz and Platt, 1996; Harder *et al.*, 1997a]. Recently, an improved version of the laser-induced fluorescence (LIF) technique for direct detection of NO<sub>2</sub> has been reported [Thornton *et al.*, 2000]. This instrument has improved sensitivity and lower detection limit compared to the TDLAS instrument and makes in situ measurements, in contrast to the long paths generally required of DOAS systems.

[5] During the 1999 Southern Oxidants Study (SOS99) two in situ NO<sub>2</sub> instruments (photolysis-chemiluminescence, PCL, and LIF) and one remote sensing NO<sub>2</sub> instrument (DOAS) were deployed at Cornelia Fort Airpark (CFA), a site downwind of the Nashville urban plume. Though SOS99 was designed primarily to evaluate the factors that affect air quality in Nashville, TN, for these large field studies an effort is always made to incorporate intercomparison activities not only for data quality assurance purposes, but also as a venue for critical evaluation of current instrumentation. In this paper we report results from an informal intercomparison of measurements of NO<sub>2</sub>. These instruments were also operated a year later in Houston, TX, as part of the Texas Air Quality Study.

## 2. Previous NO<sub>2</sub> Comparisons

[6] The three NO<sub>2</sub> detection techniques described here, LIF, PCL, and DOAS, have been employed, though not simultaneously, in previous instrument comparison experiments [Fehsenfeld *et al.*, 1990; Gregory *et al.*, 1990;

Harder *et al.*, 1997a; Zenker *et al.*, 1998; Del Negro *et al.*, 1999; Alicke *et al.*, 2000; Kim and Kim, 2001]. However, the specific instruments deployed at Cornelia Fort have not been subject to such comparisons. Previous NO<sub>2</sub> instrument comparisons have demonstrated the need to discriminate against interferences [Fehsenfeld *et al.*, 1987; Gregory *et al.*, 1990] and have shown in general good agreement between techniques for NO<sub>2</sub> concentrations greater than 200 pptv [Fehsenfeld *et al.*, 1990; Gregory *et al.*, 1990; Harder *et al.*, 1997a; Zenker *et al.*, 1998] but poor agreement when NO<sub>2</sub> mixing ratios are less than 50 pptv [Gregory *et al.*, 1990; Atlas *et al.*, 1996; Zenker *et al.*, 1998]. Data from the Green Mountain Mesa, Boulder, CO, and the CITE 2 campaign showed that detection of NO<sub>2</sub> by reduction of NO<sub>2</sub> to NO on FeSO<sub>4</sub> followed by NO + O<sub>3</sub> chemiluminescence is subject to significant interferences from PAN (as much as 80% of PAN conversion to NO<sub>2</sub>) relative to the photolytic conversion of NO<sub>2</sub> to NO [Fehsenfeld *et al.*, 1987; Gregory *et al.*, 1990]. During CITE 2, comparison of flight data from a PCL instrument [Ridley *et al.*, 1988], Photo-Fragmentation NO Laser-Induced Fluorescence (PF-LIF) instrument [Sandholm *et al.*, 1990], and a TDLAS instrument [Schiff *et al.*, 1990] showed that all three instruments agreed to within 30–40% for NO<sub>2</sub> concentrations between 50 and 200 pptv. Comparisons when NO<sub>2</sub> mixing ratios are below 50 pptv have shown inconsistent levels of agreement between these instruments, ranging from no correlation between data sets obtained during CITE 2, PEM-West, and MLOPEX 2 campaigns [Gregory *et al.*, 1990; Atlas *et al.*, 1996], to agreement within the standard deviation of measurements (2.6 pptv) between the PCL (ground based) and PF-LIF (aircraft based) instruments during the PEM-West and MLOPEX 2 campaigns [Atlas *et al.*, 1996]. A recent ground-based study (BERLIOZ) demonstrated agreement to within <1% between a PCL system and a folded-path (open White cell) DOAS instrument for NO<sub>2</sub> mixing ratios greater than ~1 ppbv [Alicke *et al.*, 2003].

## 3. Site Description

[7] CFA is located ~8 km NE of downtown Nashville, TN, in the floodplain of the Cumberland River. The area immediately around the sampling location was pasture with patches of mixed-hardwood forest. The forest canopy height was estimated at 12–15 m. The Airpark is a small general aviation facility with residential areas to the north and west. To the east (~1 km) is the Cumberland River and beyond that (0.1–0.2 km) is the Briley Parkway, a major thoroughfare (four-lane divided highway) running approximately North-South. Aircraft activity at the Airpark was sporadic, averaging only 4–5 flight operations daily. Vehicular traffic on the Briley Parkway was always present, peaking at the normal weekday morning and evening rush-hour periods. Winds at the site were typically light and variable. However, one recurring mode is apparent in the data: a southerly component from late night to midday with wind speeds generally less than 4 m s<sup>-1</sup>. Although another component is apparent as a peak in wind speed from the northeasterly sector, this wind direction occurred at all times of the day. Generally, wind from the east-southeast was very light. Daytime boundary layer (BL) heights ranged from 0.3–

0.5 km in the early morning to 1.5–2.0 km in midafternoon [Angevine *et al.*, 2003] and were significantly influenced by the proximity of the site to the Nashville urban center. Nocturnal BL heights at the site were highest (0.1–0.2 km) in the early morning hours prior to the transition to convective activity [White *et al.*, 2002]. There was also evidence for drainage flow along the river channel. During the sampling period of 15 June–15 July 1999, the average daily temperature ranged from 21° to 30°C. Relative humidity was on average 95% at night and 65% during the day, with a range of 30–100% during the day.

#### 4. Instrumentation

[8] The two in situ instruments in this study were an NO<sub>2</sub> LIF instrument developed and built at the University of California, Berkeley, and a custom-built NO<sub>2</sub> photolysis-NO chemiluminescence (PCL) instrument deployed by the Aeronomy Laboratory of the National Oceanic and Atmospheric Administration. The remote sensing instrument (DOAS) was deployed by a joint effort of the University of Heidelberg and the University of California at Los Angeles. The relative locations of the instruments are shown in Figure 1.

[9] For the in situ measurements air was brought down from the top of the 10 m high sampling tower at ~200 L/min through a 1.6-cm i.d. Teflon PFA tube (0.5–0.6 s residence time) common to both instruments that were located in adjacent trailers at the bottom of the tower. Both the LIF and PCL instruments had similar residence times in the plumbing from the sample point to the detection axes (~1 s). The LIF instrument drew off the main flow approximately 5 cm downstream of the PCL instrument through a stainless steel pinhole in a stainless steel fitting located at the common sampling point. The primary purpose of the pinhole was to affect a pressure drop to about 4 torr (1 torr = 101,325/760 Pa) in the detection chamber of the LIF instrument.

##### 4.1. LIF Instrument

[10] The LIF instrument uses a pulsed, tunable dye laser to excite a specific narrow (585 nm) rovibronic transition in NO<sub>2</sub>. Red-shifted fluorescence (>700 nm) is detected after optical and temporal filtering by counting single photons using a thermoelectrically cooled Ga-As photomultiplier tube. Calibrations of the LIF instrument were performed every 3–4 hours by introducing mixtures of an NO<sub>2</sub> standard (Scott Specialty Gases, 5.08 ppmv NO<sub>2</sub> ± 10%) in ultrapure synthetic (zero) air. The NO<sub>2</sub> calibration standard used during this study was the “reference” standard for a group of standards used by the UC, Berkeley team with mixing ratios ranging from 2 to 49.9 ppmv. The mixing ratios of these standards were routinely checked by comparison to the reference standard prior to, during, and after the SOS99 study. Deviation from the specified mixing ratios were no more than 5%. We use these standard intercomparisons to reduce the 10% uncertainty specified by Scott Specialty Gases. We assume an uncertainty of 5% in our calibration standard based on the results of these comparisons. Standard additions of an NO<sub>2</sub> reference gas to the sample stream were also done every 15–20 hours. Mixing ratios of NO<sub>2</sub> during a calibration ranged from ~100 to

**Table 1.** Detection Limit, Accuracy<sup>a</sup> (1 $\sigma$ ), and PRECISION<sup>a</sup> (1 $\sigma$ ) for the Three Instruments During SOS99<sup>b</sup>

Instrument	Detection Limit,		Precision
	pptv	Accuracy	
PCL	50	(5% + 16 pptv)	5% <sup>c</sup>
LIF	<4	5%	2% <sup>d</sup>
DOAS	400	8%	200 pptv

<sup>a</sup>Accuracy and precision values reported are 1 $\sigma$  at NO<sub>2</sub> mixing ratios typical of Cornelia Fort (i.e., >1 ppbv).

<sup>b</sup>See accompanying text for instrument-specific definitions of these values.

<sup>c</sup>Average for range of NO<sub>2</sub> mixing ratios observed over the campaign (see text).

0 ppbv in steps of ~25 ppbv over a 6-min time period. The instrumental zero was monitored every 0.75–3 hours by flowing ultrapure synthetic air through the detection system. The LIF instrument collected data at 1 Hz and submitted 1-min averages to the SOS99 data archive.

[11] The detection limit, accuracy, and precision for this instrument as deployed during SOS99 are summarized in Table 1. We define the detection limit as the uncertainty in the instrument zero which we estimate by the 1 $\sigma$  variation in the difference between adjacent zero measurements. This variation captures random and systematic changes in the mean instrument zero, which are not explained by photon counting statistics, and represents the largest contributions to its total uncertainty. This uncertainty then limits our ability to distinguish true NO<sub>2</sub> signal from the instrumental zero. The LIF precision was assumed to be dominated by shot-noise associated with single-photon counting techniques, i.e., percent error  $\sim 100\sqrt{S(\text{NO}_2, t)}/S(\text{NO}_2, t)$  where  $S(\text{NO}_2, t)$  is the signal count rate for a given NO<sub>2</sub> mixing ratio and integration time. For an LIF calibration factor on the order of 60 counts/ppb NO<sub>2</sub>/s, typical for data collected at Cornelia Fort, 1 ppbv of NO<sub>2</sub>, and a 60-s integration time, the shot-noise related precision is ~2% (1 $\sigma$ ) [Thornton *et al.*, 2000]. For the vast majority of NO<sub>2</sub> concentrations observed at Cornelia Fort the LIF precision was therefore better than 2% (1 $\sigma$ ) for 1-min averages. The instrument was calibrated by addition of a known amount of NO<sub>2</sub> in zero air and applying a correction for the effect of water vapor quenching on the excited NO<sub>2</sub>. The magnitude and form of the water vapor quenching effect are found elsewhere [Thornton *et al.*, 2000]. The correction factor for Cornelia Fort data was determined on a point-by-point basis using simultaneous measurements of relative humidity and temperature and was typically 6% (corresponding to an atmospheric water mole fraction of 0.024). A single calibration constant was used for the entire campaign as individual calibrations varied randomly by ±2% (1 $\sigma$ ) about the average value. A discussion of the LIF instrument, accuracy, and short-term and long-term precision can be found in the work of Thornton *et al.* [2000].

##### 4.2. PCL Instrument

[12] The NOAA/AL implementation of the PCL technique employs two NO chemiluminescence instruments [Williams *et al.*, 1998], one to measure NO and the other to measure NO plus a fraction of NO<sub>2</sub> photolyzed to NO (referred to as NX) by the UV portion of broadband

illumination (320–1400 nm) from a quasifocused 500 W Xe lamp (EX500-10F; ILC Technology, Sunnyvale, CA). Greater than 90% of the light output from the lamp is focused approximately 1 cm from the face of the lamp. A quartz flow cell (1 cm i.d. × 30 cm long) is positioned at this point to capture as much of the photon flux as possible. A UV-reflecting mirror is positioned at the opposite end of the cell, and the cell barrel is wrapped in aluminum foil to maximize internal reflection. The barrel of the cell assembly is encased in a recirculating water bath with the cell ends extending about 1.5 cm out on either end. For the cell temperature (35°–40°C), pressure (700 torr), and sample flow (2000 sccm) conditions during this study the average gas sample residence time in the photolysis cell was 0.5–0.6 s and the efficiency of NO<sub>2</sub> conversion (conversion fraction, CF) was 0.45–0.70. Because the calculation of NO<sub>2</sub> mixing ratios from these instruments requires that the NO data be subtracted from the NX data, the flow paths of the two NO chemiluminescence systems were closely matched to eliminate sampling lags and differential data smoothing. This required that an identical flow cell be installed in the sample plumbing of the NO instrument. This cell was completely wrapped with black electrical tape to eliminate NO<sub>2</sub> photolysis. Both NO instruments were calibrated from the same primary standard (~5 ppmv NO in N<sub>2</sub>, Scott-Marrin). The NO<sub>2</sub> calibration standard was derived from the same primary NO standard via O<sub>3</sub> gas-phase titration (~98% complete). Every 5 hours both chemiluminescence instruments were calibrated by standard addition of NO to the ambient air sample, and the NO<sub>2</sub> CF was evaluated via standard addition of NO<sub>2</sub> calibration gas. Also, the instrument backgrounds were determined at these times by routing the sample air into a prereactor through which reagent O<sub>3</sub> flowed. Because these calibrations are standard additions to ambient air, chemiluminescence quenching by water vapor is taken into account automatically. For the Nashville site this frequency of calibration (every 5 hours) was sufficient to capture almost all of the variations in water vapor, except for frontal passages. Periodically, the instruments sampled zero air in order to determine the level of NO and NO<sub>2</sub> artifacts (i.e., residual NO or NO<sub>2</sub> signals when sampling NO<sub>x</sub>-free air). The average of these artifacts was subtracted from all of the data and the standard deviation of the average included as an additional uncertainty.

[13] The PCL NO<sub>2</sub> data were collected at 1 Hz, but 1-min averages were submitted to the SOS99 data archive. The detection limit, accuracy, and precision for these measurements are summarized in Table 1. The detection limit is defined as approximately three times the uncertainty in the NO<sub>2</sub> artifact. For this study the NO<sub>2</sub> artifact ranged from 0.051 to 0.094 ppbv with an average of 0.071 ppbv and a standard deviation of 0.016 ppbv. Since all NO<sub>2</sub> mixing ratios were greater than about 0.8 ppbv at the CFA site, this was not a concern. Accuracy is determined by a propagation of errors calculation that includes all uncertainties known to contribute significantly to the determination of absolute NO<sub>2</sub> mixing ratios. These include calibration gas, mass flow controllers, and the artifacts discussed above. Because the NO<sub>2</sub> mixing ratios are calculated from a difference of two measured mixing ratios (from both NO and NX instruments), the uncertainty in NO<sub>2</sub> depends on

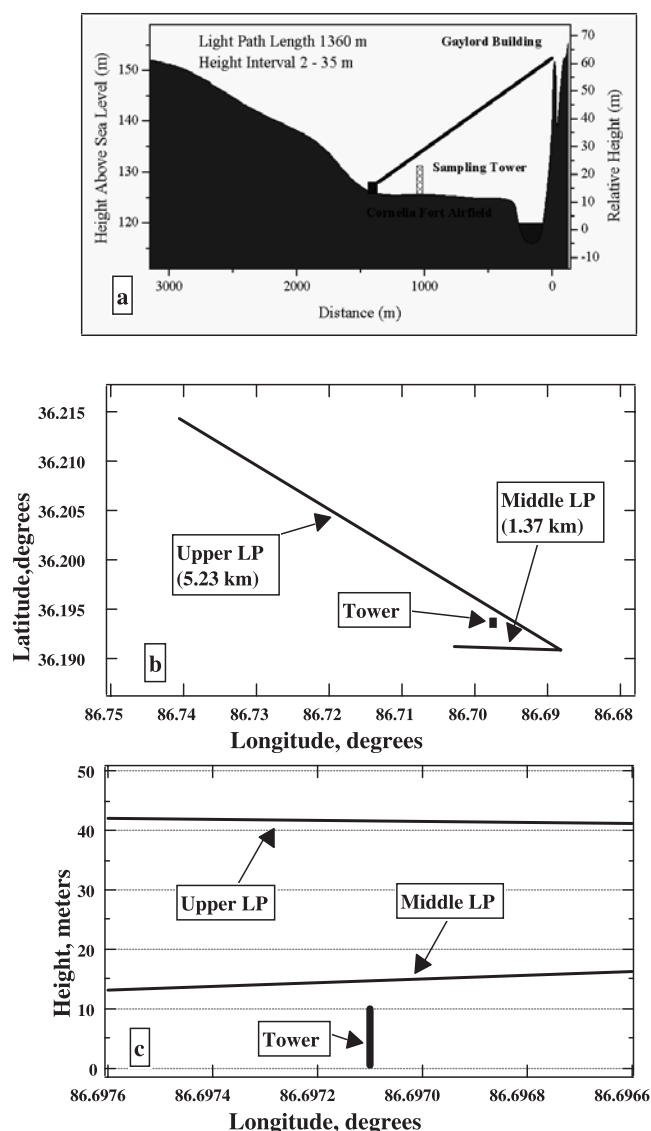
the ratio of NO<sub>2</sub> to NO. The value quoted in Table 1 (±5%) is for NO<sub>2</sub>/NO > 3 which is reasonable for all measurements not near sources. When NO<sub>2</sub>/NO = 1 the uncertainty is approximately ±9%, and for NO<sub>2</sub>/NO = 0.5 the uncertainty is approximately ±13%. Short-term precision is approximately 2% and is calculated as the relative standard deviation of measured mixing ratios from periods when NO<sub>2</sub> levels were constant; that is, when atmospheric variability was not expected to contribute to fluctuations in mixing ratios. The analysis described below shows that there is additional imprecision associated with variations in the measured Xe lamp CF. This is not due to fluctuations in lamp intensity, but instead results from the determination of the CF via standard addition to sometimes large and rapidly varying ambient NO<sub>x</sub>. Traditionally, this error was included as an inaccuracy term of approximately 4%, but the results from this study make it clear that this error should be considered an additional, long-term, imprecision.

### 4.3. DOAS Instrument

[14] The DOAS technique measures the spectrally resolved absorption features in a beam of white light that is folded once by an array of retroreflectors located at some distance from the instrument. The absorption features measured in the returning light beam correspond to a convolution of all the absorption bands in that wavelength region due to absorbing molecules that are present at any point in the beam path. Two such instruments measured over two different light paths at Cornelia Fort. A sketch showing the relationship of the DOAS middle beam path to the sampling tower and surrounding topography is shown in Figure 1a (note scale aspect ratio of ~60:1). The second and third panels of Figure 1 show that neither of the DOAS beams was in close proximity to the measurement tower.

[15] The two DOAS instruments used in this study are similar to the one described by *Alicke et al.* [2002]. Each instrument uses a double Newtonian telescope to send and receive a beam of white light from a Xe-arc lamp through the atmosphere. The receiving part of the telescope is coupled to a Czerny-Turner spectrograph with a focal length of 0.5 m ( $F = 6.9$ , 600 grooves/mm grating, thermostated to  $+30^\circ \pm 0.3^\circ\text{C}$ ) by a 200- $\mu\text{m}$  diameter quartz fiber. A photodiode array detector (Hoffmann Meßtechnik, using an array from Hamamatsu S5931-1024N; 1024 diodes of 25  $\mu\text{m}$  center to center spacing, height, 2.5 mm) was used for the detection of the spectra. Spectra were recorded at a spectral resolution of 0.55 nm. Sophisticated computer software extracts simultaneously from each measured spectrum the identity and concentration of all of the absorbing species present in the path of the beam solely based on well-characterized published absorption cross-section data. A calibration of the instrument is not necessary. Besides NO<sub>2</sub>, other species determined at CFA by this system included O<sub>3</sub>, SO<sub>2</sub>, CH<sub>2</sub>O, NO<sub>3</sub>, and HONO.

[16] The DOAS instruments had a variable data collection rate (5–30 min) depending on atmospheric opacity and NO<sub>2</sub> mixing ratios. The accuracy of the DOAS system for NO<sub>2</sub> is 8%, which is the accuracy to which the NO<sub>2</sub> absorption cross section is known [*Harder et al.*, 1997b]. Detection limit and precision both scale with the path length for the DOAS instrument. For SOS99 the detection limit shown in Table 1 is the average over the entire campaign. The precision of the



**Figure 1.** (a) Schematic of the middle UCLA DOAS light path in relation to the in situ measurement tower at Cornelia Fort; (b) plan view showing horizontal separation distances; (c) close-up elevation view showing vertical separation distances.

NO<sub>2</sub> concentration determined by the DOAS system is determined by the statistical uncertainty calculated by the spectral fitting routine during the analysis of each measured absorption spectrum. The average  $1\sigma$  precision uncertainty during SOS99 was 200 pptv, which results in a precision of 20% at 1 ppbv NO<sub>2</sub>. The UCLA DOAS instruments, the analysis methods used to calculate concentrations, and the error analysis are described in more detail elsewhere [Stutz and Platt, 1996, 1997; Alicke et al., 2002].

## 5. Results

[17] Mixing ratios of NO<sub>2</sub> (1-min averages) were  $\sim 2$ –5 ppbv during midday and reached as high as 65 ppbv at night. Much of this variation was due to boundary layer dynamics. The lowest NO<sub>2</sub> concentration was 0.735 ppbv,

remaining there for only a 5-min period. The level of NO<sub>x</sub> was consistently greater than 80% of the total nitrogen oxide (NO<sub>y</sub> = NO<sub>x</sub> + peroxy nitrates + alkyl nitrates + NO<sub>3</sub> + 2N<sub>2</sub>O<sub>5</sub> + HNO<sub>3</sub> + particulate NO<sub>3</sub><sup>-</sup>) budget at night and ranged from as low as 30% to as high as 90% of NO<sub>y</sub> during the day.

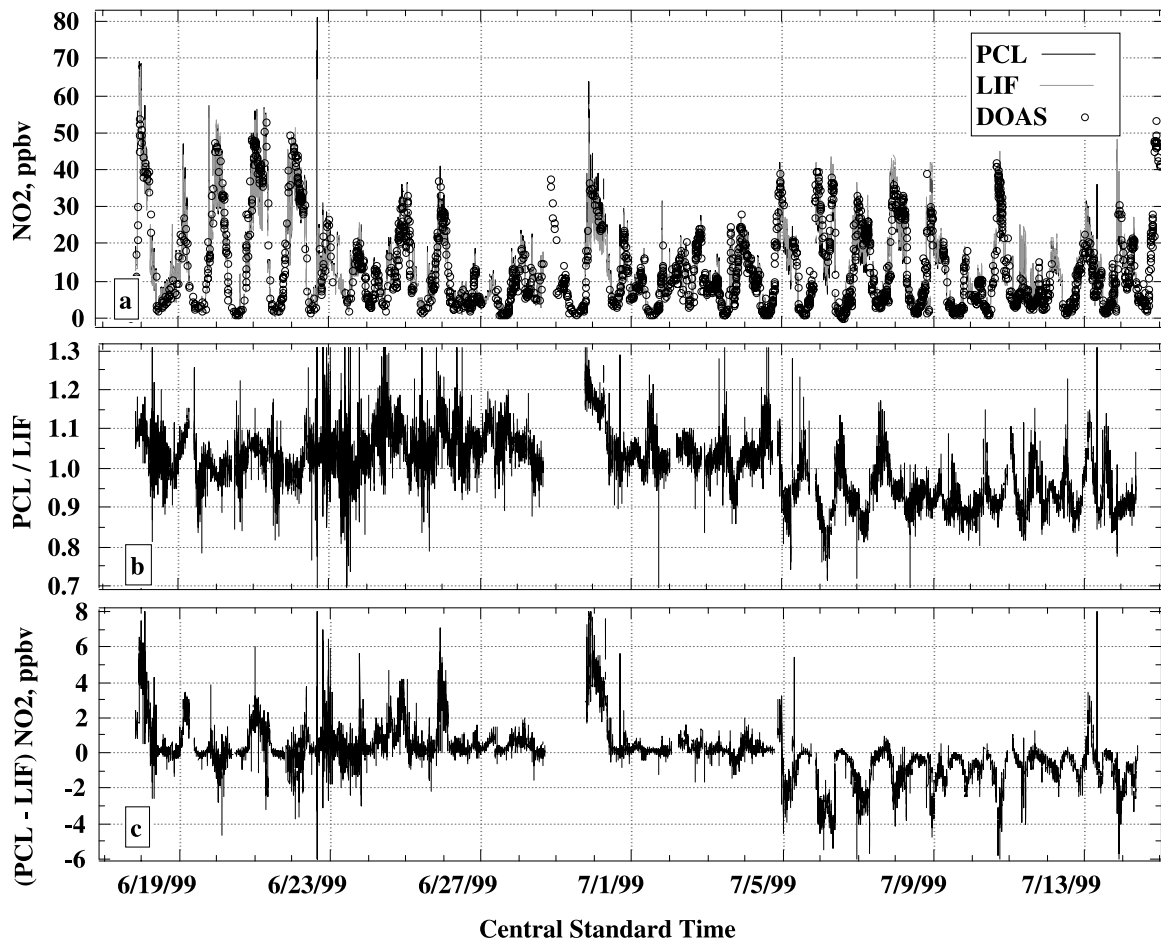
### 5.1. In situ Instruments Comparison

[18] The NO<sub>2</sub> mixing ratios measured at CFA by the LIF and PCL instruments were compared on a point-by-point basis. The time recorded by the Berkeley instrument was synchronized to the time-base of the NOAA instrument by comparing temporal structures in the 10-s average LIF data and 10-s average measurements of the PCL system. Because power failures and instrument maintenance resulted in the resetting of computer clocks more than once, several independent adjustments to the measurement time-base were made. Shifts on the order of 15–30 s optimized the coincidence between the data sets. Once the LIF measurement time-base was shifted to match the time-base of the PCL instrument, the 10-s measurements were then averaged to 1-min data for each instrument. Only coincident data were used for the analyses below.

[19] Figure 2a shows NO<sub>2</sub> mixing ratios observed by all three instruments for the entire study period: 17 June–14 July 1999. For most of the study period the data traces overlap on the scale shown. Figure 2b shows the ratio of PCL to LIF. The magnitude of the variation in the ratio reflects a combination of the short and long-term precision and accuracy of the instruments relative to each other. Effects due to sampling different air masses by the different instruments are eliminated since both sampled from the same fast flow line. The tight correlation between the 1-min average PCL and LIF data is evident. Shifts in the ratio on the order of 5–10% about the value 1 are readily detected. The vast majority of points (>98%) lie between 0.8 and 1.2 with the single point deviations reaching greater than 2 and less than 0.75 on a few occasions. Figure 2c shows the difference between the 1-min averages of PCL and LIF measurements. Most of the data cluster between  $\pm 2$  ppbv. In Figures 2b and 2c the structure of the data appears to be different after 4 July. This is discussed below.

[20] A log-log scatterplot of all NO<sub>2</sub> mixing ratios measured by the two instruments is shown in Figure 3a and the same plot on a linear scale is shown in Figure 3b. The solid lines show the 1:1 relationship. Bivariate weighted linear least squares analysis was performed on the data set where the weights used were the inverse of the squares of the precision uncertainties defined in Table 1. For the 27,350 coincident data points the slope of the regression line was 0.985 (std. err. =  $\pm 0.0005$ ) and the intercept was 0.055 (std. err. =  $\pm 0.002$ ), implying average agreement to better than 2% over the entire campaign. The unweighted squared correlation coefficient,  $r^2$ , value of 0.983 is provided to indicate the relative degree to which the data sets are correlated under the given conditions.

[21] Figure 4a shows the ratios of individual measurements with respect to the NO<sub>2</sub> level. The data cluster around the 1.0 line and, aside from slight curvature upward (to higher relative PCL values) at lower NO<sub>2</sub> values (<2 ppbv), there is no apparent trend in the plot. However, when the distribution of these data is plotted as a frequency histogram, as in Figure 4b (open circles), it is apparent that



**Figure 2.** (a) One-minute average NO<sub>2</sub> mixing ratios measured by the PCL (black trace) and LIF (gray trace), and DOAS (open circles) instruments for 18 June–14 July 1999; (b) ratio of PCL NO<sub>2</sub> to LIF NO<sub>2</sub> data for the same period; (c) difference of PCL NO<sub>2</sub> and LIF NO<sub>2</sub> data from same period.

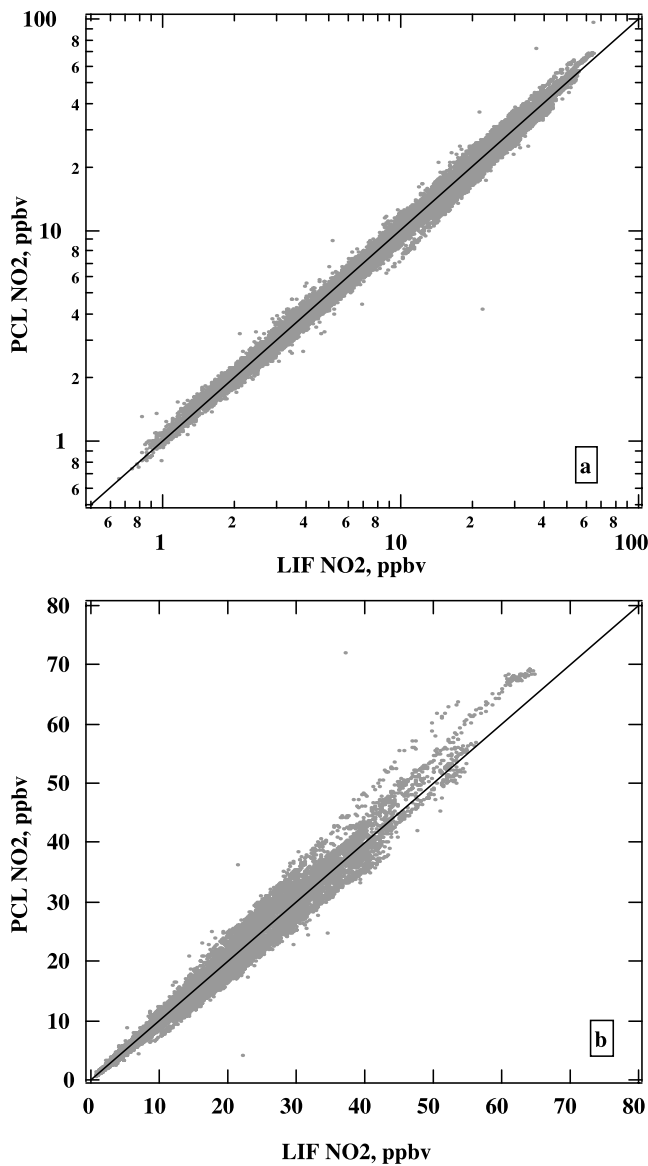
two populations of data are present. Examination of the time series data in Figures 2b and 2c shows a relative shift between the PCL and LIF data after 4 July. If the data in Figure 4a are segregated into these two time periods and plotted as frequency distributions, the histograms shown as gray lines in Figure 4b result, where the data from the earlier period have the higher mean value. Below, we use the DOAS data to ascertain whether the LIF data or the PCL data are responsible for the observed shift.

## 5.2. In situ Comparison to DOAS Data

[22] Comparison of the DOAS data to the LIF and PCL data for the entire campaign is shown in Figure 2a. The least squares fits of DOAS data to either the LIF or PCL data give a slope of 1.07 and high correlation ( $r^2 = 0.77$ ). However, data from the long path instruments are not fully included in this intercomparison because neither of the DOAS beam paths was coincident (or even nearly so) with the top of the sampling tower used by the two in situ instruments (Figure 1). Moreover, the atmospheric mixing and transport in the river valley where these measurements took place combined with strong and variable nearby sources contributed to highly variable NO<sub>2</sub> mixing ratios. Nevertheless, the comparison of the DOAS NO<sub>2</sub> data from the two light paths clearly shows periods when the local

environment was reasonably well mixed both in the horizontal and the vertical. We will use two such periods for comparison of the DOAS data to the two in situ instruments in order to determine the presence of any systematic differences in the latter. Ideally, we would use the DOAS data to determine problems in the in situ NO<sub>2</sub> data that might be due to sampling air through tubing, however inert, or to inaccuracies due to calibration standards. These effects can be discerned more easily by comparison of the in situ data sets to the DOAS data (rather than to each other) since the latter are not influenced by sampling plumbing and because the DOAS data should be as accurate as the NO<sub>2</sub> differential absorption cross section which is known to be 8% [Harder *et al.*, 1997b] and not subject to sampling interferences. Although the average agreement between the data sets is excellent (7%), transport effects preclude drawing detailed conclusions about sampling interferences and the precision of the DOAS instrument was not high enough to resolve the cause of discrepancies of order 5% between the in situ instruments.

[23] Despite these problems interpreting a campaign-length comparison, the multiple paths of the DOAS instruments did show that on at least two occasions a reasonably uniform air mass extended over the study region for a period of a few hours. Even though the two DOAS instruments



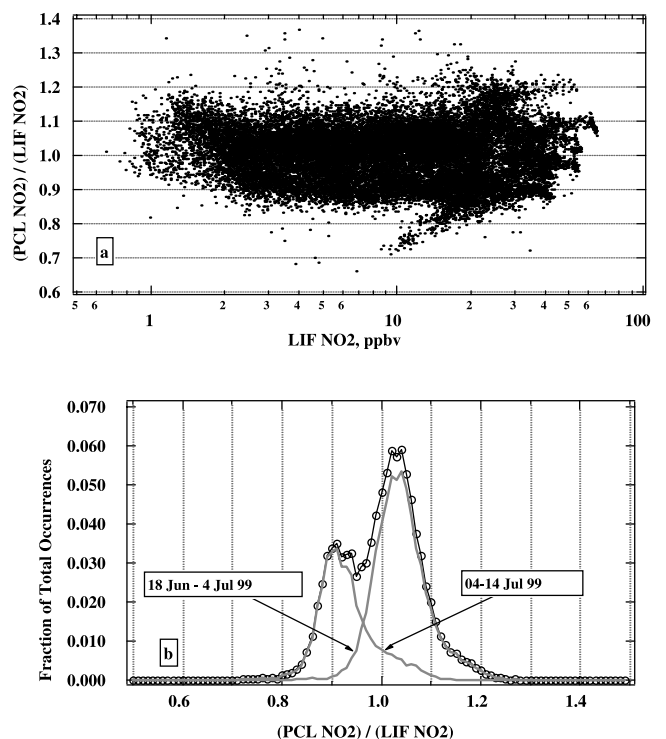
**Figure 3.** (a) Log-log scatterplot of all coincident PCL NO<sub>2</sub> data versus LIF NO<sub>2</sub> data with the one-to-one line shown in black; (b) same as Figure 3a but with linear axes.

used a common retro-reflector array, the light paths of the two instruments were substantially different (Figure 1). The upper path was at a higher altitude (end-points at 72 and 35 m above ground) than the middle path (end-points at 2 and 35 m above ground) and was also much longer (5.23 versus 1.36 km). The two paths were also divergent in the horizontal plane. We make the reasonable assumption that those periods when data from the two light paths are correlated in time and agree in magnitude for NO<sub>2</sub> are when the local atmosphere was well mixed. Comparisons made between in situ and DOAS data for these times will focus predominantly on measurement differences rather than sampling differences. Figure 5 shows the two comparison periods selected based on the upper path and middle path DOAS NO<sub>2</sub> data. Linear regressions of these upper and middle path NO<sub>2</sub> data sets (not shown) indicate reasonable correlation and overall agreement at 90% or better.

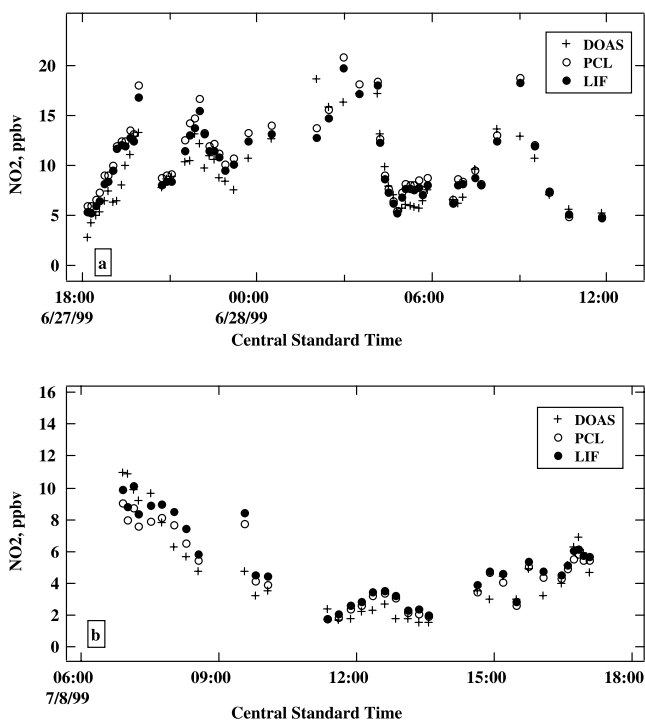
[24] For comparison of long path data to the tower data we use data from the middle beam because that one was most local to the tower. Those comparisons (DOAS to LIF or PCL) were done by integrating the 1 min in situ data over the corresponding (variable) sampling period of the long-path instrument and retaining only those data points that were concurrent (within 2 min) for all three instruments. This resulted in a total data set of 90 points which we emphasize are different from those data used in the other plots. These data are displayed in Figures 5a and 5b. Error bars for any of the points are of the order of the symbol size and have been left off the plots for clarity. Although scatter in these data is inevitable because of the sampling differences, unweighted linear regressions on these data sets (Table 2) show good correlation and provide confidence that the comparisons are meaningful. For the first period (27–28 June) there is a similar level of agreement between the DOAS and LIF data (slope = 0.89) and DOAS and PCL data (slope = 0.93). For the second period (8 July) the slope of the LIF versus DOAS line is 0.82, but the slope of the PCL versus DOAS line is 0.73. For both sets of comparisons, the intercepts and the  $r^2$  values are virtually identical. From this analysis it appears that the PCL data shifted to lower values by approximately 15%: from 4% greater than LIF to 11% lower. This is consistent with the ~12% shift to lower relative (to LIF) PCL values shown in Figure 4b.

### 6. Discussion

[25] The common sampling manifold used by the two instruments allowed for highly correlated ( $r^2 = 0.983$ ) NO<sub>2</sub>



**Figure 4.** (a) Ratio of all coincident PCL NO<sub>2</sub> and LIF NO<sub>2</sub> data plotted versus the LIF NO<sub>2</sub> mixing ratios; (b) histograms of the data in Figure 4a (line with circles) and of the ratio data prior to 4 July and after 4 July (gray lines).



**Figure 5.** Mixing ratios of NO<sub>2</sub> for (a) 27–28 June and (b) 8 July. Open circles are PCL data, closed circles are LIF data, and crosses are DOAS data.

measurements. The high correlation, together with the high precision (see Table 1) of each instrument allowed for shifts on the order of 5–10% in the relative calibration between the two instruments to be observed in the data on timescales as short as hourly as well as on average over the 4-week campaign. The causes of these calibration shifts are important to understand because in situ NO<sub>2</sub> measurements that are precise to 5–10% on the short term are necessary for accurate calculations of the sum total peroxy radical (HO<sub>2</sub> + RO<sub>2</sub>, where R is an organic moiety) concentrations from the NO<sub>x</sub> steady state [e.g., Cantrell *et al.*, 1997; Thornton *et al.*, 2002]. Long-term measurements of NO<sub>2</sub> that are precise to 1% are necessary for evaluating seasonal and multiannual trends.

[26] As discussed in section 5, a large systematic difference exists in the data that occurred after 4 July. The ratio PCL/LIF prior to 4 July averaged  $\sim 1.05$ . After 4 July there was a large shift of the ratio with strong diurnal variations for the first few days. After 8 July the diurnal variation dampened and the ratio settled at an average of  $\sim 0.93$ . Similarly, linear regression of the data obtained before 4 July gives the line  $\text{PCL} = 1.05\text{LIF} - 0.057$  ppbv with  $r^2 = 0.991$ , which is a higher correlation than the entire data set ( $r^2 = 0.983$ ). After 4 July the least squares fit yields a line  $\text{PCL} = 0.92\text{LIF} + 0.047$  ppbv with  $r^2 = 0.990$ . Finally, comparison of both PCL and LIF measurements to the DOAS data affirms that the PCL data decreased. The  $\sim 15\%$  change in the slopes of the PCL and LIF data relative to the DOAS data from before 4 July (PCL/LIF = 1.04; see Table 2) to after (PCL/LIF = 0.89) is consistent with the  $\sim 13\%$  shift in the ratio of PCL to LIF described above.

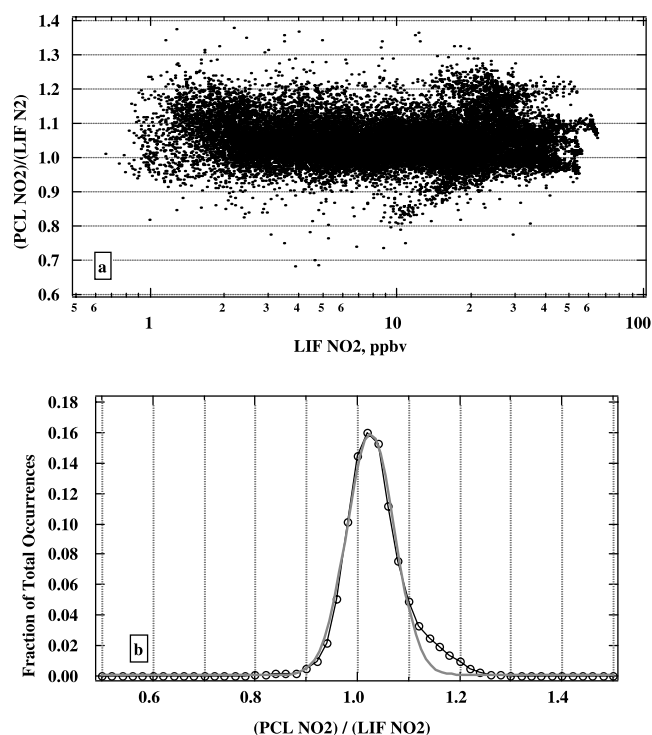
[27] These results suggest that a calibration shift occurred in the PCL data after 4 July. Examination of the PCL instrument sensitivities and backgrounds spanning the 4–5 July period showed no discontinuities or other exceptional behavior. Nor was there any indication of problems in the temperature, pressure, or flow data that are normally monitored during instrument operation. Clearly, there was no problem associated with the sampling manifold; otherwise, the LIF data would have been affected as well. However, the NOAA PCL instrument was taken off-line on 4 and 5 July for evaluation of the various gas standards that were used by the research groups. This effort involved replumbing the inlet systems of both the NO and NX instruments to accommodate NO and NO<sub>2</sub> standard gas cylinders. Thus a likely explanation for the change in the PCL NO<sub>2</sub> data was the presence of a leak in the inlet plumbing after the system was reassembled upon conclusion of the gas standards evaluation. A careful reevaluation of the NO<sub>2</sub> conversion fraction data over this period indeed shows an increase in the apparent level of added NO<sub>2</sub> calibration gas (but not NO calibration gas), which propagates directly to lower calculated NO<sub>2</sub> mixing ratios. This additional NO<sub>2</sub> source was likely instrument trailer air that was drawn into the NO<sub>2</sub> calibration line when the calibration valve opened, since the pressure in the sample line was lower than ambient due to the presence of the sampling manifold.

[28] A 12% correction to the PCL data after 4 July also is consistent with the comparison test of the standards used to calibrate each instrument. An evaluation of one of the LIF NO<sub>2</sub> standards by the PCL instrument on 5 July indicated a measured NO<sub>2</sub> mixing ratio of 42.3 ppmv (and 1.99 ppmv NO) compared to the value of 49.9 ppmv NO<sub>2</sub> expected for this tank. This discrepancy of  $-16\%$  (PCL/LIF) was originally attributed to insufficient time being allowed for equilibration of the LIF NO<sub>2</sub> cylinder/regulator combination to the PCL analysis system. However, if the NO<sub>2</sub> value determined by the PCL system is increased by 12% (from the above analysis) to 47.4 ppmv (49.4 ppmv NO<sub>x</sub>), then the standards are  $\sim 5\%$  different. If 47.4 ppmv were the true value for the standard and given no other errors, then the LIF data would be higher than the PCL data. Since the measurements show that the PCL data are higher than the LIF data by about 5%, some problem clearly remains with this comparison of the calibration standards. However, it is worth noting that the agreement between the PCL and LIF data presented here was obtained without using the results of this intercomparison of calibration standards.

[29] There is, of course, no way to correct for a problem such as a leak in the inlet system plumbing after the fact. However, if the PCL data after 4 July are increased by 12%

**Table 2.** Unweighted Least Squares Linear Regression Results ( $\pm 1\sigma$ ) From Comparisons of the DOAS Data to Data From the PCL and LIF Instruments for the Two Periods Shown in Figure 5

Parameter	27–28 June		8 July	
	PCL	LIF	PCL	LIF
Slope	0.93 ( $\pm 0.07$ )	0.89 ( $\pm 0.07$ )	0.73 ( $\pm 0.05$ )	0.82 ( $\pm 0.06$ )
Intercept	2.21	2.01	1.40	1.42
$r^2$	0.77	0.77	0.85	0.85
$N$		56		34



**Figure 6.** (a) Ratio of corrected coincident PCL NO<sub>2</sub> and LIF NO<sub>2</sub> data plotted versus the LIF NO<sub>2</sub> mixing ratios; (b) histogram of the data in Figure 6a (line with circles) and of the fitted normal distribution curve (solid line).

(calculated from the ratio of the means of the two distributions shown in Figure 4b), then the average ratio PCL/LIF becomes 1.047 for the entire data set and the unweighted linear regression equation becomes  $\text{PCL} = 1.049\text{LIF} - 0.038$  with  $r^2 = 0.991$ . These parameters are essentially identical to the data comparison for the period prior to 4 July and are probably more representative of the true comparison between the instruments. Figure 6 shows plots of the ratios and a histogram, similar to Figure 4, of the distribution of PCL/LIF using the data corrected as above. The histogram is an almost perfect Gaussian. These data were fit with the normal distribution (Figure 6b; solid line) with resulting fit parameters of mean = 1.032 and standard deviation of 0.045. From this it appears that NO<sub>2</sub> measured by these systems agrees to within 3% on average. However, this value includes a significant correction to a large fraction of the PCL data and thus is subject to considerable uncertainty. The value determined from linear regression analysis (5%) is virtually identical to the pre-4 July uncorrected data comparison and more likely reflects the true agreement. This value (5%) falls within the combined accuracy uncertainties listed in Table 1. From the histogram, the spread of these data (4.5%) is larger than expected based on short-term precision alone (2.8%), which indicates that long-term precision contributes significantly to the overall precision on the timescale of 1 month. Reevaluation of the PCL data reduction algorithms suggests that variation of the measured Xe lamp conversion fraction ( $\pm 4\%$ ) should be considered as an additional (long-term) imprecision and not (as currently) an inaccuracy for all data. The RMS overall precision uncertainty for the PCL system, then, is  $\pm 5\%$ . With preci-

sion uncertainties of 2% (LIF) and 5% (PCL), the standard deviation of normally distributed ratio data is expected to be less than 5.4% and greater than 4%, since the imprecision in the Xe lamp CF values will be independent of NO<sub>2</sub> mixing ratio. These expectations hold true. The skewness to the high-ratio side of the curve in Figure 6b also appears to be related to the variability in the Xe lamp CF values. The linear interpolation that is done between measured CF determinations during data reduction introduces variability, but there may be, as well, an influence here by the inlet system leak. All aspects of the PCL measurement systems and data reduction currently are being reviewed for possible improvements.

[30] One goal of this informal comparison was to assess the magnitude of interferences that might affect the PCL or LIF techniques differently. Though the analysis above suggests that such interferences, if any, are smaller than the combined instrument uncertainties, the evaluation for interferences could not be as rigorous as originally hoped for due to (1) problems with comparisons to the DOAS data and (2) the fact that the precision of the PCL system was not as high as the LIF system. Nevertheless, the data were examined for signs of interferences.

[31] Interferences may arise in both instruments from the conversion of nitrogen-containing species such as NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, PAN, HNO<sub>4</sub>, HONO, and HNO<sub>3</sub> to NO<sub>2</sub> (or to NO in the case of HONO) in the sample lines by thermal decomposition or surface-mediated processes [e.g., *Gao et al.*, 1994; *Bradshaw et al.*, 1999; *Ryerson et al.*, 2000]. The PCL instrument is further susceptible to interferences from the photolysis of these species to NO in the photolysis cell. The gas-phase thermal decomposition and surface-mediated conversion of nitrogen species should pose essentially the same interference in the LIF instrument given the similar residence time and sampling material. However, the LIF instrument is not susceptible to interferences from the photolysis of these species [*Thornton et al.*, 2000].

[32] The magnitudes of these potential interferences at Cornelia Fort are summarized as follows. Interferences from gas-phase thermal decomposition during transit of all the above species are calculated to be negligible assuming a 1-s residence time and a temperature of 300 K and using the rate constants of *Sander et al.* [2000 and references therein]. For example, thermal decomposition of PAN and its structural analogues would yield at most 2 pptv of NO<sub>2</sub> ( $\sim 0.1\%$  of PAN decomposes) for the experimental setup of the two instruments. Approximately, 10% of HNO<sub>4</sub> will thermally decompose which translates into a maximum 0.007 ppbv offset ( $\ll 1\%$  of NO<sub>2</sub>) at Cornelia Fort where we have estimated equilibrium HNO<sub>4</sub> concentrations from observed HO<sub>2</sub> and NO<sub>2</sub> concentrations and the equilibrium and formation rate constant (at 298 K and 760 torr) from *Sander et al.* [2000 and references therein]. Similarly, while approximately 4% of N<sub>2</sub>O<sub>5</sub> may thermally decompose, its estimated concentration at Cornelia Fort presents a negligible interference. There is no evidence that HNO<sub>3</sub> or PAN-type compounds are converted to NO<sub>2</sub> on PFA-Teflon surfaces. Measured NO<sub>3</sub> at CFA was a factor of 100–1000 lower than NO<sub>2</sub>, so even if quantitative conversion on tubing occurred the interference was negligible. Surface-mediated conversion of HNO<sub>4</sub> to NO<sub>2</sub> in PFA-Teflon tubing has not been experimentally determined, but if we again assume quanti-

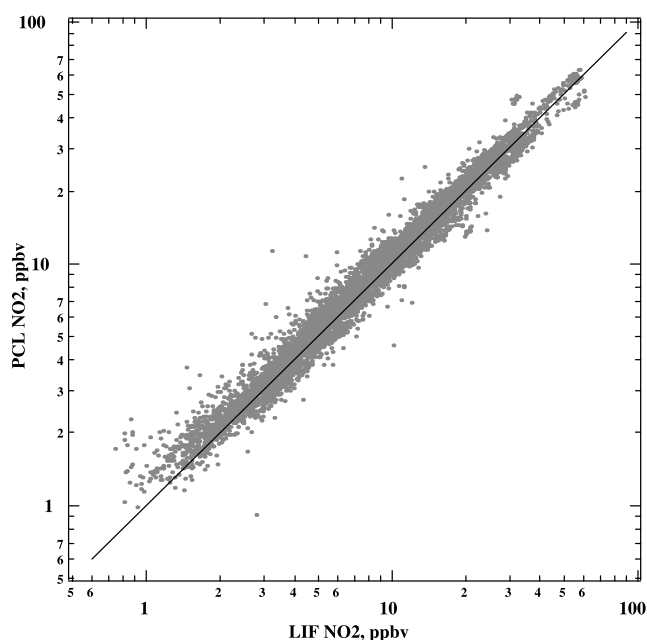
tative conversion, it is also a minor interference with an upper limit of a 0.07-ppbv positive bias ( $\ll 1\%$  typically).

[33] The magnitudes of potential photolytic interferences for the PCL technique are described in detail by *Ryerson et al.* [2000]. Although the bandwidth of radiation used by the PCL instrument in this study is much wider than that used by *Ryerson et al.* [2000], the photolysis of HONO still presents the largest potential interference since its absorption cross section strongly overlaps that of NO<sub>2</sub> in the UV. Measured HONO was often greater than 1 ppbv at night and reached a maximum of 3 ppb, but was negligible during the day ( $\ll 0.1$  ppb) [*Alicke et al.*, 2000]. Assuming 37% photolytic efficiency [*Ryerson et al.*, 2000], conversion of HONO to NO in the photolysis chamber of the PCL instrument translates into a maximum potential error of  $\sim 1$  ppbv in the PCL data. But typically this results in an error of less than 2% since the ratio of HONO to NO<sub>2</sub> rarely exceeded 6% at Cornelia Fort [*Alicke et al.*, 2000]. The Xe lamp used in this study also emits radiation in the visible, which will photolyze NO<sub>3</sub>. However, photolysis of NO<sub>3</sub> is a negligible interference since NO<sub>2</sub>/NO<sub>3</sub> was always greater than 100. The LIF instrument is not susceptible to interferences from photolytic reactions producing NO<sub>2</sub>.

[34] Conversion of NO to NO<sub>2</sub> via reaction with O<sub>3</sub> in sampling tubing can be an interference for both PCL and LIF systems. The effect typically is  $\sim 2\%$  of ambient NO, assuming 40 ppbv O<sub>3</sub> (mean value at CFA), a 1-s residence time, and standard conditions. For the simultaneously measured NO and O<sub>3</sub> concentrations at Cornelia Fort, this interference was never larger than 0.55% of the observed NO<sub>2</sub>. The PCL data set was corrected for this NO + O<sub>3</sub> interference as a part of the data reduction process [*Fehsenfeld et al.*, 1990]. An additional consequence of this reaction involves HONO decomposition to NO during transit (i.e., surface mediated) followed by conversion to NO<sub>2</sub> by O<sub>3</sub>. However, even if quantitative HONO conversion occurs, it will be a negligible ( $\ll 1\%$ ) interference at the NO<sub>2</sub> mixing ratios measured at CFA. Also, the LIF instrument uses a pinhole to effect a pressure drop in the detection cell which reduces the rate of the reaction NO + O<sub>3</sub> during transit and further reduces any potential interference from this reaction.

[35] We examined the comparison data to determine if times of disagreement were correlated to any of the above species or processes. For example, in Figure 2 the agreement between PCL and LIF data appears to exhibit a diurnal trend most noticeably in data prior to July 2. The PCL/LIF ratio is on average 1.05 at night and 1.00 around noon for this subset of data. The  $1\sigma$  variation is larger than these deviations in the mean. However, individual days show the ratio deviating as much as 10–15% between night (midnight-morning) and day (morning to midnight). Scatterplots of both the difference between the LIF and PCL data and of the ratio of the two data sets versus the rate of the NO + O<sub>3</sub> reaction show no trend. In addition, the difference and ratio of the PCL and LIF NO<sub>2</sub> data versus the concentrations of PAN, NO<sub>3</sub>, HONO, and NO<sub>y</sub>-NO<sub>x</sub> measured at CFA, as well as versus relative humidity, temperature, and water vapor mole fraction showed no evidence of correlations with the entire data set or specific subsets such as prior to 2 July. The reasons for the apparent diurnal behavior in the PCL/LIF ratio remain unclear.

[36] Finally, as a gauge of how representative the SOS99 NO<sub>2</sub> comparison was, we show NO<sub>2</sub> data taken by the



**Figure 7.** Scatterplot of NO<sub>2</sub> mixing ratios measured at La Porte, TX, during the TEXAQS 2000 (15 August–13 September 2000) study by the PCL instrument versus the LIF NO<sub>2</sub> data. The solid line is a 1:1 relationship.

NOAA PCL and Berkeley LIF instruments during the Texas Air Quality Study (TexAQS) from 15 August to 15 September 2000. Both instruments were located at a site in La Porte, TX, which is approximately 30 km SE of downtown Houston and sampled from the same walkup tower but from opposite sides of the tower, not from a common manifold as at Cornelia Fort. The calibration methods, sampling methods, and detection apparatus of both instruments, while having been disassembled and reassembled since the previous measurement campaign, were essentially identical to those used at Cornelia Fort a year earlier. However, during TexAQS, the Berkeley LIF instrument was dedicated to measuring total peroxy nitrates, alkyl nitrates, and HNO<sub>3</sub>, in addition to NO<sub>2</sub> [*Day et al.*, 2003]. Another robust inter-comparison between the PCL and LIF was not the focus of this study; nonetheless, the available simultaneous NO<sub>2</sub> measurements provide a test for the reproducibility of the agreement obtained at Cornelia Fort. The 1 min data were synchronized to a common time and coincident data points retained; no other filtering was done. Figure 7 shows a comparison plot of NO<sub>2</sub> measured by the PCL instrument versus NO<sub>2</sub> measured by the LIF instrument. A 1:1 line is plotted for comparison. An unweighted linear regression of the 8341 data points yields the line  $PCL = 1.017LIF + 0.40$  with high correlation ( $r^2 = 0.973$ ). These comparison results are essentially the same as those achieved at Cornelia Fort and suggest that the long-term variability (i.e., campaign to campaign) between these two instruments is less than 5%.

## 7. Conclusions

[37] This informal comparison of NO<sub>2</sub> measurements made by a photolysis/chemiluminescence (PCL) instrument and a LIF instrument has shown agreement to within 5% on

average, indicated by linear regression analysis after correction of PCL data taken after 4 July. Although the original overall agreement between the two instruments was excellent, as shown by a linear regression line slope of 0.99, a discontinuity was apparent in the data time series. For the first half of the campaign the PCL instrument measured ~5% higher than the LIF instrument, but for the second half of the campaign the PCL instrument measured ~8% lower than the LIF instrument. That the shift was due to the PCL instrument was confirmed by comparison of both PCL and LIF data to NO<sub>2</sub> data from a long-path instrument (DOAS) before and after the discontinuity appeared. The cause for this data shift was likely the presence of a leak in the inlet system of the PCL instrument. If the PCL data after the discontinuity are increased by 12%, then the overall agreement (5% by linear regression analysis) of the two data sets is essentially identical to that seen prior to the data shift. A fit of the normal distribution to the ratios of PCL NO<sub>2</sub> data to LIF NO<sub>2</sub> data produced a mean value of 1.032, which is similar to that seen from linear regression (5%) but is more uncertain due to the significant correction applied to a large fraction of the PCL data.

[38] The 5% overall agreement from linear regression of the data is within the combined uncertainties of ±5% for the accuracy of each instrument. The normal distribution fit to the ratios of the observations produced a standard deviation of 4.5%, which is consistent with the combined 1σ precision uncertainty estimated to be 5.4%. Since the estimated total uncertainty (RMS of combined accuracy and precision uncertainty estimates in Table 1) of any data point pair is ~9%, then greater than 90% (i.e., two times the observed standard deviation) of all measurements agree to within the estimated total instrumental uncertainties at the 1σ level. A comparison between these same instruments a year later produced the same overall level of agreement (5%), which indicates the long-term stability of these systems and provides confidence in the robustness of the present results.

[39] The high levels of NO<sub>2</sub> (>1 ppb) characteristic of the Nashville urban area did not provide a test of the detection limits of either instrument, and no evidence of interferences was found. We suggest that future comparison experiments aimed at understanding instrumental differences on the order of 5–10% include daily comparison both of the collected data and of calibration standard(s) in order to monitor relative calibration shifts between instruments. Further, an increased emphasis on long-term precision would be fruitful for more rigorous evaluation of these instruments. This comparison has confirmed that NO<sub>2</sub>-specific (i.e., not NO<sub>x</sub>) measurements can be made with total uncertainty of 10% or less at levels typical of urban/suburban locations. Though the instruments deployed here were research-grade techniques that required constant attention for the relatively short duration of this study, it is likely that both the LIF and the PCL techniques can be used effectively in monitoring networks. For example, simplified approaches to LIF measurements have recently been described [Cleary *et al.*, 2002; Matsumi *et al.*, 2001]. Such methods will be required for robust evaluation of air pollution control strategies like the NO<sub>x</sub> SIP Call.

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## References

- Alicke, B., G. Hoenniger, U. Platt, and J. Stutz, *Measurements of O<sub>3</sub>, HCHO, NO<sub>2</sub>, HONO, and NO<sub>3</sub> by Differential Optical Absorption Spectroscopy During the 1999 SOS Field Study in Nashville*, AGU, Washington, D. C., 2000.
- Alicke, B., U. Platt, and J. Stutz, Impact of nitrous acid photolysis on the total hydroxyl radical budget during the Limitation of Oxidant Production/Pianura Padana Produzione di Ozono study in Milan, *J. Geophys. Res.*, 107(D22), 8196, doi:10.1029/2000JD000075, 2002.
- Alicke, B., A. Geyer, A. Hofzumahaus, F. Holland, S. Konrad, H. W. Pätz, J. Schäfer, J. Stutz, A. Volz-Thomas, and U. Platt, OH formation by HONO photolysis during the BERLIOZ experiment, *J. Geophys. Res.*, 108(D4), 8247, doi:10.1029/2001JD000579, 2003.
- Angevine, W. M., A. B. White, C. J. Senff, M. Trainer, R. M. Banta, and M. A. Ayoub, Urban-rural contrasts in mixing height and cloudiness over Nashville in 1999, *J. Geophys. Res.*, 108(D3), 4092, doi:10.1029/2001JD001061, 2003.
- Atlas, E., et al., A comparison of aircraft and ground-based measurements at Mauna Loa Observatory, Hawaii, during GTE PEM-West and MLO-PEX 2, *J. Geophys. Res.*, 101, 14,599–14,612, 1996.
- Bradshaw, J., et al., Photofragmentation two-photon laser-induced fluorescence detection of NO<sub>2</sub> and NO: Comparison of measurements with model results based on airborne observations during PEM-Tropics A, *Geophys. Res. Lett.*, 26, 471–474, 1999.
- Cantrell, C. A., R. E. Shetter, J. G. Calvert, F. L. Eisele, E. Williams, K. Baumann, W. H. Brune, P. S. Stevens, and J. H. Mather, Peroxy radicals from photostationary state deviations and steady state calculations during the Tropospheric OH Photochemistry Experiment at Idaho Hill, Colorado, 1993, *J. Geophys. Res.*, 102, 6369–6378, 1997.
- Cleary, P. A., P. J. Wooldridge, and R. C. Cohen, Laser-induced fluorescence detection of atmospheric NO<sub>2</sub> with a commercial diode laser and a supersonic expansion, *Appl. Opt.*, 41(33), 6950–6956, 2002.
- Day, D. A., M. B. Dillon, P. J. Wooldridge, J. A. Thornton, R. S. Rosen, E. C. Wood, and R. C. Cohen, On alkyl nitrates, O<sub>3</sub>, and the “missing NO<sub>y</sub>,” *J. Geophys. Res.*, 108, doi:10.1029/2003JD003685, in press, 2003.
- Del Negro, L., et al., Comparison of modeled and observed values of NO<sub>2</sub> and jNO<sub>2</sub> during the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission, *J. Geophys. Res.*, 104, 26,687–26,703, 1999.
- Durka, W., E. D. Schulze, G. Gebauer, and S. Voerkelius, Effects of forest decline on uptake and leaching of deposited nitrated determined from N15 and O18 measurements, *Nature*, 372, 765–767, 1994.
- Federal Register, 1998, 40 CFR Parts 51, 72, 75, and 96, Finding of Significant Contribution and Rulemaking for Certain States in the Ozone Transport Assessment Group Region for Purposes of Reducing Regional Transport of Ozone; Rule, vol. 63, pp. 57,356, Oct. 27 1998.
- Fehsenfeld, F. C., et al., A ground-based intercomparison of NO, NO<sub>x</sub> and NO<sub>y</sub> measurement techniques, *J. Geophys. Res.*, 92, 14,710–14,722, 1987.
- Fehsenfeld, F. C., et al., Intercomparison of NO<sub>2</sub> measurement techniques, *J. Geophys. Res.*, 95, 3579–3597, 1990.
- Gao, R. S., E. R. Keim, E. L. Woodbridge, S. J. Ciciora, M. H. Proffitt, T. L. Thompson, R. J. McLaughlin, and D. W. Fahey, New photolysis system for NO<sub>2</sub> measurements in the lower stratosphere, *J. Geophys. Res.*, 99, 20,673–20,681, 1994.
- Gregory, G. L., et al., An intercomparison of airborne nitrogen dioxide instruments, *J. Geophys. Res.*, 95, 10,103–10,127, 1990.
- Harder, J. W., E. J. Williams, K. Baumann, and F. C. Fehsenfeld, Ground-based comparison of NO<sub>2</sub>, H<sub>2</sub>O, and O<sub>3</sub> measured by long-path and in situ techniques during the 1993 Tropospheric OH Photochemistry Experiment, *J. Geophys. Res.*, 102, 6227–6243, 1997a.
- Harder, J. W., J. W. Brault, P. V. Johnston, and G. H. Mount, Temperature dependent NO<sub>2</sub> cross sections at high spectral resolution, *J. Geophys. Res.*, 102, 3861–3879, 1997b.
- Holland, E. A., et al., Variations in the predicted spatial distribution of atmospheric nitrogen deposition and their impact on carbon uptake by terrestrial ecosystems, *J. Geophys. Res.*, 102, 15,849–15,866, 1997.
- Kelly, T. J., D. H. Stedman, J. A. Ritter, and R. B. Harvey, Measurements of oxides of nitrogen and nitric acid in clean air, *J. Geophys. Res.*, 85, 7417–7425, 1980.
- Kim, K., and M. Kim, Comparison of an open path differential optical absorption spectroscopy system and a conventional in situ monitoring system on the basis of long-term measurements of SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub>, *Atmos. Environ.*, 35, 4059–4072, 2001.
- Kley, D., and M. McFarland, Chemiluminescence detector for NO and NO<sub>2</sub>, *Atmos. Technol.*, 12, 63–69, 1980.

- Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Tropospheric chemistry: A global perspective, *J. Geophys. Res.*, *86*, 7210–7254, 1981.
- Matsumi, Y., S. Murakami, M. Kono, K. Takahashi, M. Koike, and Y. Kondo, High-sensitivity instrument for measuring atmospheric NO<sub>2</sub>, *Anal. Chem.*, *73*(22), 5485–5493, 2001.
- McClenny, W. A., E. J. Williams, R. C. Cohen, and J. Stutz, Preparing to measure the effects of the NO<sub>x</sub> SIP call—Methods for ambient air monitoring of NO, NO<sub>2</sub>, NO<sub>y</sub>, and individual NO<sub>z</sub> species, *J. Air Waste Manage. Assoc.*, *52*, 542–562, 2002.
- Mickley, L. J., P. P. Murtie, D. J. Jacob, J. A. Logan, D. M. Koch, and D. Rind, Radiative forcing from tropospheric ozone calculated with a unified chemistry-climate model, *J. Geophys. Res.*, *104*, 30,153–30,172, 1999.
- NRC, *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, Natl. Acad. Press, Washington, D. C., 1991.
- Ridley, B. A., M. A. Carroll, G. L. Gregory, and G. W. Sachse, NO and NO<sub>2</sub> in the troposphere: Technique and measurements in regions of a folded tropopause, *J. Geophys. Res.*, *93*, 15,813–15,830, 1988.
- Ryerson, T. B., E. J. Williams, and F. C. Fehsenfeld, An efficient photolysis system for fast-response NO<sub>2</sub> measurements, *J. Geophys. Res.*, *105*, 26,447–26,461, 2000.
- Sander, S. P., et al., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Eval. 13*, NASA Jet Propul. Lab., Calif. Inst. of Technol., Pasadena, Calif., 2000.
- Sandholm, S. T., J. D. Bradshaw, K. S. Dorris, M. O. Rodgers, and D. D. Davis, An airborne compatible photofragmentation two-photon laser-induced fluorescence instrument for measuring background tropospheric levels of NO, NO<sub>x</sub>, and NO<sub>2</sub>, *J. Geophys. Res.*, *95*, 10,155–10,161, 1990.
- Schiff, H. I., D. R. Karecki, G. W. Harris, D. R. Hastie, and G. I. Mackay, A tunable diode laser system for aircraft measurements of trace gases, *J. Geophys. Res.*, *95*, 10,147–10,153, 1990.
- Stutz, J., and U. Platt, Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least-squares methods, *Appl. Opt.*, *35*, 6041–6053, 1996.
- Stutz, J., and U. Platt, Improving long-path differential optical absorption spectroscopy with a quartz-fiber mode mixer, *Appl. Opt.*, *36*, 1105–1115, 1997.
- Thornton, J. A., P. J. Wooldridge, and R. C. Cohen, Atmospheric NO<sub>2</sub>: In situ laser-induced fluorescence detection at parts per trillion mixing ratios, *Anal. Chem.*, *72*, 528–539, 2000.
- Thornton, J. A., et al., Ozone production rates as a function of NO<sub>x</sub> abundances and HO<sub>x</sub> production rates in the Nashville urban plume, *J. Geophys. Res.*, *107*(D12), 4146, doi:10.1029/2001JD000932, 2002.
- Tonnesen, G. S., and R. L. Dennis, Analysis of radical propagation efficiency to assess ozone sensitivity to hydrocarbons and NO<sub>x</sub>, 1, Local indicators of instantaneous odd oxygen production sensitivity, *J. Geophys. Res.*, *105*, 9213–9225, 2000.
- U.S. Environmental Protection Agency, Office of Air and Radiation, in *Nitrogen Oxides: Impacts on Public Health and the Environment, EPA-452/R-97-002*, 1997.
- White, A. B., B. D. Templeman, W. M. Angevine, R. J. Zamora, C. W. King, C. A. Russell, R. M. Banta, W. A. Brewer, and K. J. Olszyna, Regional contrast in morning transitions observed during the 1999 Southern Oxidants Study Nashville/Middle Tennessee Intensive, *J. Geophys. Res.*, *107*(D23), 4726, doi:10.1029/2001JD002036, 2002.
- Williams, E. J., et al., Intercomparison of ground-based NO<sub>3</sub> measurement techniques, *J. Geophys. Res.*, *103*, 22,261–22,280, 1998.
- Zenker, T., et al., Intercomparison of NO, NO<sub>2</sub>, NO<sub>y</sub>, O<sub>3</sub>, and RO<sub>x</sub> measurements during the oxidizing capacity of the tropospheric atmosphere (OCTA) campaign 1993 at Izana, *J. Geophys. Res.*, *103*, 13,615–13,634, 1998.

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