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New Technology Research & Development Program
Grant Contract 582-5-70807-0015

Task 1 Deliverable

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Progress Report, Task 1

TCEQ – NTRD Grant 582-5-70807-0015, Amendment No. 1

TAMU Research Foundation Award No. 467691-002-CA

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0. Scope of Work list

For this report, the scope of work was defined as listed on the following page:

GRANT ACTIVITIES

Article 1. Objectives

1.1. The objective for this work is: to install, instrument, maintain, and make available an air quality monitoring tower suitable for long-term rural air quality measurements as well as special research-quality measurements from time to time. The tower would be a facility available to all researchers, including TCEQ personnel, who wish to make measurements at such a site. The tower will be deployed and available during the Second Texas Air Quality Study (TexAQS-II), and will be a key component of the statewide monitoring network supporting the study.

Article 2. Scope of Work

Task 1: Construction of test site and infrastructure development

2.1. Task Statement: The PERFORMING PARTY will complete construction of the physical infrastructure and install all instrumentation needed to perform testing at test site.

2.1.1. The PERFORMING PARTY will complete preparation of the test site for physical infrastructure.

2.1.2. The PERFORMING PARTY will procure instrumentation for the test site.

2.1.3. The PERFORMING PARTY will procure tubing, fencing, and other needed materials for the physical infrastructure of the test site.

2.1.4. The PERFORMING PARTY will install the tower used for testing.

2.1.5. The PERFORMING PARTY will install and test the basic instrumentation will be installed over an eight-week period to ensure that the data is of sufficiently high quality for use by researchers and the State of Texas.

2.1.6. The PERFORMING PARTY will make the data available in near-real time on a web site hosted by Texas A&M University.

2.1.6.1. The PERFORMING PARTY will provide ftp or equivalent access available to TCEQ and other parties who wish to receive all the data as soon as it becomes available.

2.1.6.2. The PERFORMING PARTY will develop the web site and ftp with input from TCEQ personnel.

2.1.7. Schedule: The PERFORMING PARTY shall complete this task within 11 months of the signed Notice to Proceed Date as issued by TCEQ.

2.1.8. Deliverables: The PERFORMING PARTY shall submit a detailed list of instrumentation, photos of the completed physical infrastructure, a report detailing testing procedures and results, a copy of the interlocal agreement with the City of Collage Station for use of test site property, and access to a

functioning web site to the TCEQ.

1. Site and installation description

A 22 m tall aluminum walk-up tower with a 2×1 m footprint was erected in September 2005 on the north side of Lick Creek Park, College Station, TX, near the park's equestrian entrance. The coordinates of the tower are 30°34'7" N and 96°12'57" W. An aerial view is provided in *Plate 1*, which shows that the site has a mostly natural fetch for >2 km in the south, where air is advected over the park, a natural post oak woodland. Clearly visible to the west is the College Station subdivision Pebble Creek. Another, new subdivision is currently developed to the northwest and north of the site. Few developments are visible in the eastern directions. The strongest anthropogenic influence comes from the subdivisions and from highway 6 to the southwest. Rock Prairie Road and the park's equestrian entrance and parking lot are used to access the site.

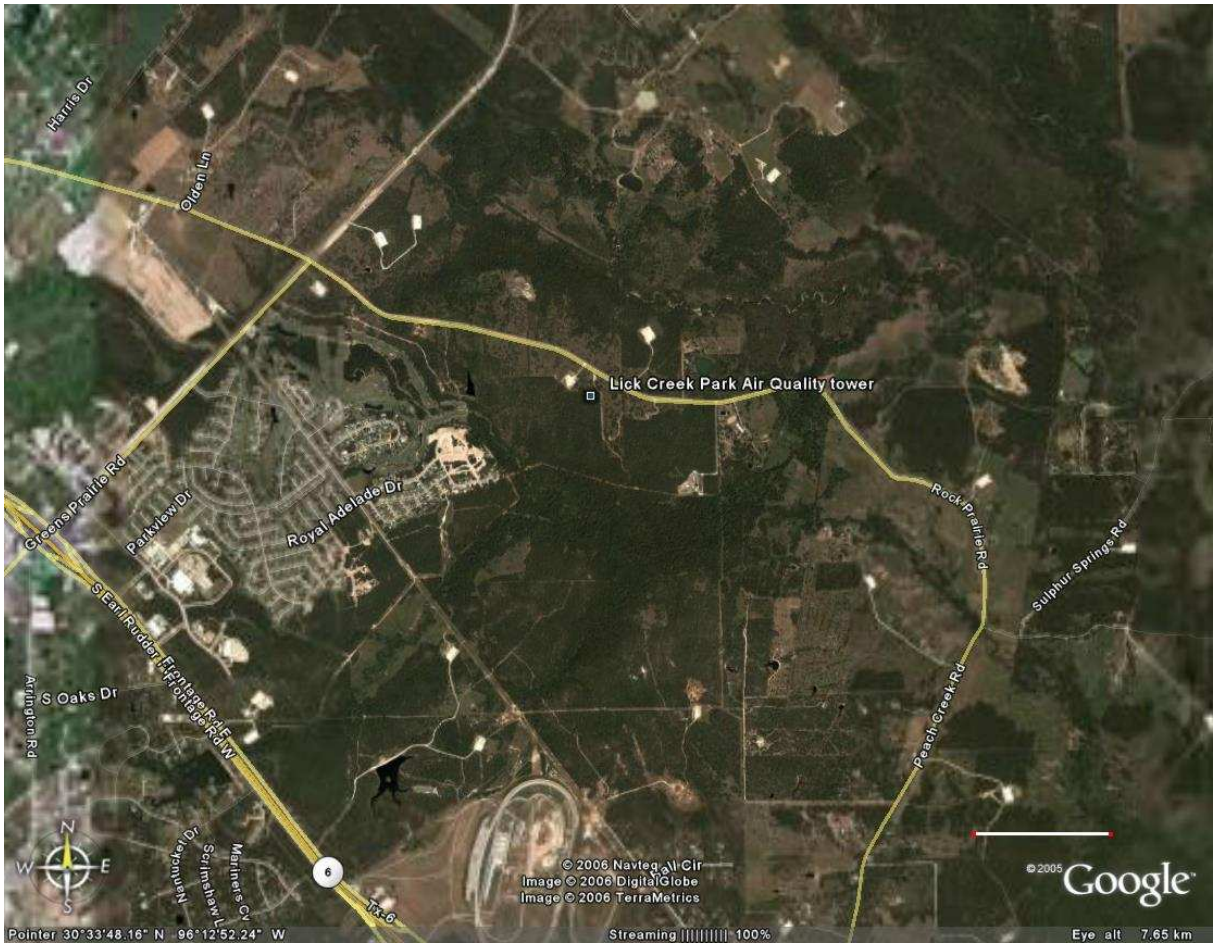


Plate 1: Location of the measurement site. White bar represents 1 km scale.

The walk-up tower consists of 11 separate, rectangular sections of 2 m height each. The top platform carries a railing of 1.5 m height only. Each leg of the lowest section rests on a concrete foundation. The tower is guyed at three anchor points on all four legs. A small shed of 3×2 m footprint was assembled next to the tower, and equipped with line power and air conditioning. Power comes from a pole next to Rock Prairie Road, where it is metered, and was run ~200 m underground to the site. Air conditioning is provided by a … BTU wall unit. *Plate 2* shows the tower and building after construction. They were later surrounded by a barb-wired fence for security and to deter park visitors from climbing the tower (*Plate 3*). The gate in the fence is chain-locked, and the building, which has all air quality instrumentation in it, is locked as well. Keys are available from the project PI. Total occupied ground space is approximately 12×8 m City of College Station park property.

Plate 2: Walk-up tower and instrument shed.

Plate 3: Perimeter fence.

2. Instrumentations list

Instrumentation procured for this project is part of two categories:

I. meteorological instrumentation
II. air quality instrumentation

I. The meteorological instrumentation purchased and installed on the tower includes:

- a wind speed and direction sensor, model 034B from MetOne
- cup anemometers, model 014A from MetOne
- temperature/humidity sensors, model 50Y from Vaisala, installed in aspirated radiation shields, model 075B from MetOne
- a tipping bucket rain gage with 6” orifice, model TR-525I from Texas Electronics
- a pyranometer for total down welling radiation, model PYR-P from Apogee Instruments Inc.
- a PAR sensor, model QSO-SUN from Apogee Instruments Inc.
- a net radiation sensor, model NR-LITE from Kipp & Zonen
- a barometer, model Setra 278 from Campbell Sci.
- two soil heat flux plates, model HFP01SC from Campbell Sci.
- soil moisture sensors, model EC-20 from Decagon
- soil temperature sensors, model 108-L from Campbell Sci.
- leaf wetness sensors, model 237-L from Campbell Sci.
- a CR1000 data logger from Campbell Sci. with power supply, a 32-channel multiplexer and 8-channel switch closure module, installed in a 16”×18” outdoor enclosure, all from Campbell Sci.

Table 1 contains a list of the most relevant sensors and their measurement precision.

Cables from all sensors installed on the tower were routed to the data logger (DL) enclosure on the 5th level of the tower. The DL records data from all sensors except the barometer at 10 second intervals then saves 1 minute averages to its storage module. The barometer is only read every 30 min. A serial cable is run from the DL to a PC inside the shed (photo), which automatically downloads data from the DL once a week.

Table 1: Important meteorological sensors used at the Lick Creek Park site.

Parameter	*Sensor Model*	*Manufacturer*	**Precision**
WS/WD	034B	MetOne	±0.1 m s^{-1}, ±4°
WS	014A	MetOne	±0.1 m s^{-1}
T/RH	HMP50Y	Vaisala	±0.5°C, ±3%
Rain	TR525I	Texas Electronics	±1- -5% @ 25-75 mm h^{-1}
Pressure	278	Setra	±1 mb @ 0-40°C
T (soil or air)	108-L	Campbell Sci.	±0.2°C
Soil moisture	ECH_2O-20	Decagon	±3%
Solar radiation	PYR-P	Apogee Instr.	±1-4% @ 45-75°

The combined wind speed and direction sensor has been installed at an elevation of 26 m above ground since 4 June 2006. The cup anemometers and T/RH sensors are installed at different tower levels with above-ground elevations of 22, 18, 14, 10, and 6 m. The radiation sensors are installed at 22 m, as is the tipping bucket rain gage.

II. The air quality instrumentation installed inside the shed and on the tower includes

- a model 42C NO/NO_x analyzer from Thermo Electron Corp.
- a model 48C-TLE CO analyzer from Thermo-Electron Corp.
- a model 400E ozone analyzer from Teledyne API

The instruments' specifications are summarized in *Table 2*.

Table 2: Air quality instrumentation used at the Lick Creek Park site.

Instrument	*Zero noise*	*LDL*	*Resolution*	**Precision**
48C-TLE CO	20 ppb @ 30 s	40 ppb	f(averaging time)	min ±1%
42C NO/NO_x	0.2 ppb @ 60 s	0.4 ppb	f(averaging time)	min ±1% or 0.4 ppb
400E O_3	0.3 ppb	< 1 ppb	1 ppb	0.5% of readout

The CO and O_3 analyzers pull sample air (total of ~1.5 L min^{-1}) at a TEE from the same ¼" OD Teflon PFA line, run ~24 m from the shed to the top level (22 m above ground) of the

tower. The inlet carries a 2 µm PTFE filter in a PFA filter holder, which is exchanged every 5-10 days.

The NO/NO_x analyzer samples air from its own ¼" OD Teflon PFA line at ~0.75 L min^{-1}. The Molycon catalytic NO_2 to NO converter and its 3-way selector valve from inside the model 48C was removed and the sample line directly connected to the photomultiplier tube. The catalyst and 3-way valve were installed in water-proof plastic housing on the top platform of the tower (22 m) by extending both the heater power and control thermocouple, and the valve power. The sample inlet is equipped with another 2µm PTFE filter in a PFA filter holder (also exchanged every 5-10 days), then immediately enters a TEE where the sample is routed either directly to the 3-way valve or through the Molycon converter. The common port of the 3-way valve is connected to the analyzer via ~24 m of the ¼" OD PFA line. The analyzer was put into "NO_x mode", providing power for the 12 V 3-way valve at all times. One power lead of the valve was directed through a solid state relay inside the DL enclosure that is switched on and off in a 6 minute cycle by the DL. The instrument's internal cycling of 12 seconds could not be set at a longer interval length, and, due to mixing in a long sampling line such as ours, could therefore not provide for independent NO and NO_2, respectively NO_y measurements. The current setup ensures that sample air comes in contact with the converter before significant sampling line losses can occur. The valve switching cycle was chosen to make sure that sample flow and data storage at 1-min intervals combine to an equilibrium output at the end of each 3-min interval.

Voltage signals from the instruments' analog output ports are measured every 10 s by one of the DL's input channels and stored as 1-min averages together with the meteorological data. The model 42C is set to output 0-10 V for 0-100 ppb NO_x. The model 400E ozone analyzer is set to output 0-5 V for 0-500 ppb O_3. The model 48C is set to output 0-10 V for 0-1000 ppb CO. The averaging times of the models 42C and 48C were set to 20 seconds.

3. Photos

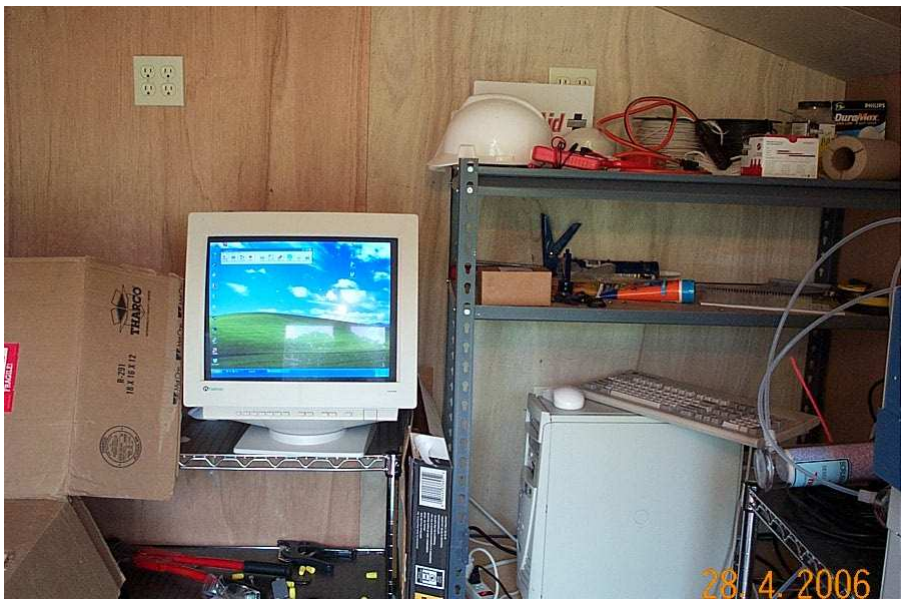
Pictures are provided of the tower setup (#1&#2), the inlets (#3), instruments (#4) and PC (#5). Picture 1 shows the north side of the tower, picture 2 the south side with the radiation sensors on the top level. Picture 3 shows the CO/O_3 inlet filter holder in the upper middle part and the NO/NO_x inlet filter holder in the lower left part of the picture.

#1

#2

#3

#4



#5

4. Testing procedures and Results

To test the air quality instrumentation, we have purchased three calibration gases and a zero air tank from Scott-Marrin, Inc., Riverside, CA. The calibration gases and their specifications are listed in *Table 3*.

Table 3: Calibration gas and zero air specifications

Cal-gas	*Concentration*	*Accuracy*	*Ref. standard (NIST)*
NO in UHP N_2	0.1 ppm	5%	SRM 2627a
NO_2 in UHP N_2	4.87 ppm	5%	SRM 2627a
CO in UHP air	0.454 ppm	2%	volumetric
Ultrapure air	CO <0.01 ppm, NO_x <0.001 ppm, 0 ppb O_3		

Zero air can also be generated onsite from an AADCO 737 pure air generator, specified at <1 ppb for both CO, NO_x, and ozone.

A. Zero- and span testing procedures

To test the analyzers' response for zero air, experiments were set up as recommended by the manufacturer by providing a flow of 1-2 L min^{-1} zero air independently at each analyzer's

sample port, letting the analyzer sub-sample from this flow at its own flow rate (<1 L min^{-1} for all three instruments) at a TEE. The zero was then either set manually at the instrument while in "calibration" mode (electronic zeroing), or recorded without electronic zeroing. For span checks or calibration, the procedure was identical, except that span gas was delivered at 1-2 L min^{-1} to the TEE for instrument sub-sampling. In addition, the 48C-TLE CO analyzer was programmed to carry out an internal zero check by routing sample air through a CO oxidation catalyst once every hour from 0-5 minutes of the hour.

In both cases, zero and span check/calibration, the instrument was allowed to sample zero/span gas for at least 5 minutes prior to calibration or recording, and was usually in equilibrium a that time. Independent zero/span checks were carried out approximately weekly during the testing phase after we had received the cal-gases in second week of May. A summary of readings is given in Table 3:

Table 3: Zero and span readings (in ppb) during the test phase

	Date	*NO*	*CO*	O_3	**Comments**
zero	19 May	-0.02	230	± 0.5	only ozone zeroed
span	19 May	20.4	775	---	CO set, NO not set
zero	19 May	---	130, 110	---	CO zeroed third time around
span	19 May	---	630, 455	---	new CO span coef. = 0.766
zero	23 May	6.8	120	---	NO PMT adjusted then zeroed
span	23 May	101	---	± 0.5	new PMT-voltage: -695 V
zero	2 June	0.0	220	---	no changes made
zero	13 June	0.4	290	---	no changes made
zero	20 June	2.2, 10.8	360	---	NO re-zeroed after span
span	20 June	101.5	785	---	PMT adjusted to -742 V

Our testing showed no significant difference in using bottled zero air versus the generator zero air for the analyzers reported on here.

The testing revealed that the CO analyzer, typical for the measurement principle of GFC IR absorption is less sensitive in the abundance range encountered at this site, i.e. less than 1 ppm. A 500 ppb standard was purchased for this reason and revealed a 25% lower sensitivity

compared to the factory calibration, which is usually done with a 10 ppm standard. Also visible is an upward drift of the analyzer signal, which we address by taking regular internal zero readings of the analyzer once an hour using the instruments own zero catalyst. Comparisons of those zero readings with our independent zero checks using bottled or generated air showed no significant differences at the instruments readout, but may not translate into proper corrections using the DL recorded, minutely values. We therefore intend to increase the length of the internal, hourly zero checks from five to eight minutes. In addition, when the analyzer moves "out of range", the zero value will have to be electronically reset.

The NO_x analyzer's NO response was incorrectly set out of the factory. We had to adjust the PMT voltage drastically to meet the required sensitivity. Data before May 23 2006 was a factor of five too low but could be adjusted backwards in time. The response of this analyzer also seems to show a trend in zero readings but less pronounced than that of the CO-analyzer. The 3-minute interval set for the catalyst-valve in order to measure NO versus NO_2/NOy assures that the sample line is cleaned at least ten times before a "final" reading is taken during the third minute of each sub-cycle stored to the DL. Whether just NO_2 or also higher oxidized NO_y species are converted by the Molycon catalyst near the inlet, was tested on 23 May, 2006 by increasing the catalyst's temperature in 20 K steps from its "normal" operating temperature of 326°C to 386°C while routing the air permanently through the catalyst after calibration. We found no change in the measured value of 7.1 ppb as would be expected for the case of conversion of higher oxidized NO_y species at higher catalyst temperatures. Hence, we conclude that indeed NO_y, not NO_x is measured in this setup. This experiment will be repeated, then also including a test in which we will completely remove the inlet filter in order to see whether HNO_3 is significantly retained by it. We have also not yet successfully performed a catalyst calibration by injecting our NO_2 standard at the sample inlet, because of lack of a functioning setup. This, however, will be carried out in the last week of June 2006.

An indirect calibration of the ozone analyzer on loan from the University of Texas has also not been performed. UV absorption ozone analyzers are known to be very stable, and, as they are based on a first principles measurement, rarely need calibration unless one or more of its internal parts are out of normal operating limits. We have zeroed the instrument and basically confirmed that its noise is below 1 ppb and its electronic zero is stable. We are not in

possession of an independent calibration device. However, we will carry out regular span checks using the instruments internal ozone generator in the future to confirm its normal operations.

B. Data examples

Figures 1 to 4 show a comparison between the NWS weather station hourly data from Easterwood Airport, College Station, TX, to our data for a week-long period in June 2006. Despite an offset in wind direction (not shown), which we will address in the coming weeks, the weather data at our site is in agreement with a nearby standard station. Expected differences are visible for pressure (the site lies ~30 m lower than Easterwood Airport), wind speed, as well as temperature and humidity due to the vegetational influences at Lick Creek Park (LCP). Note that the LCP data are minute averages, while the Easterwood Airport data are hourly values.

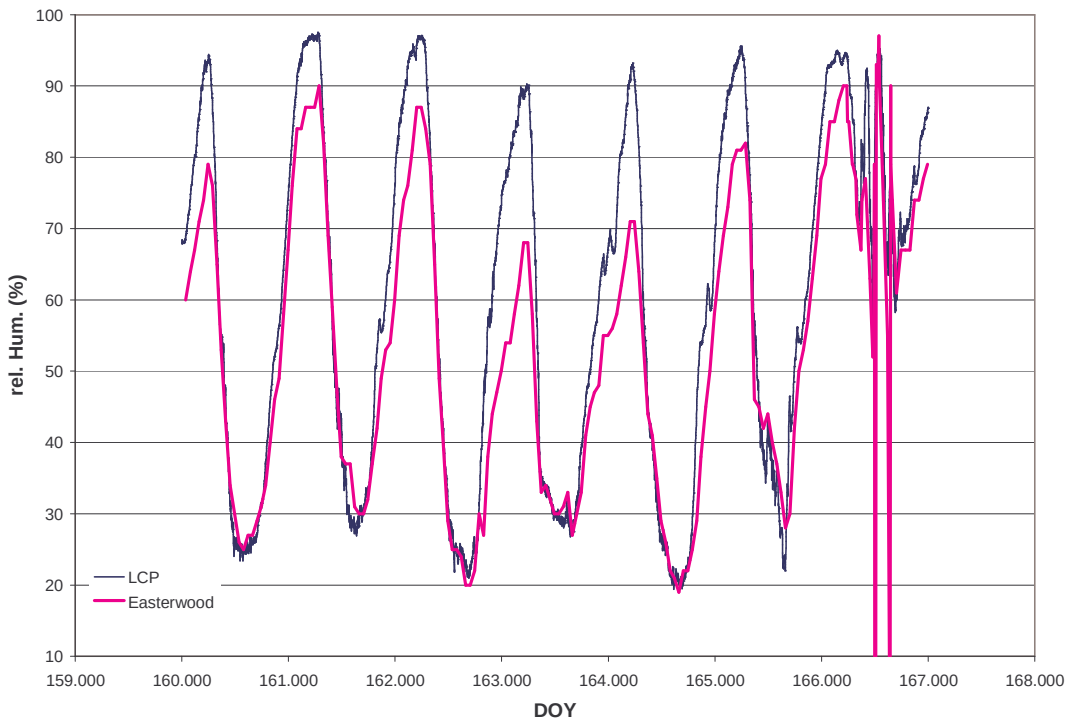


Figure 1: Relative humidity measurements at Lick Creek Park versus Easterwood Airport.

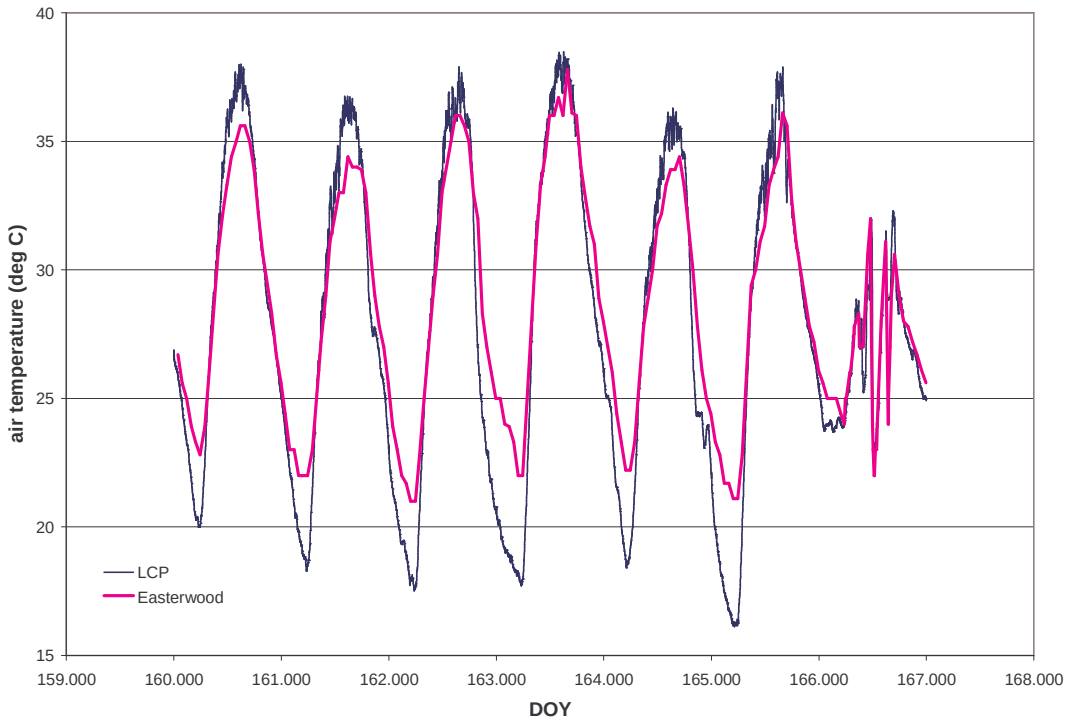


Figure 2: Air temperature measurements at Lick Creek Park versus Easterwood Airport.

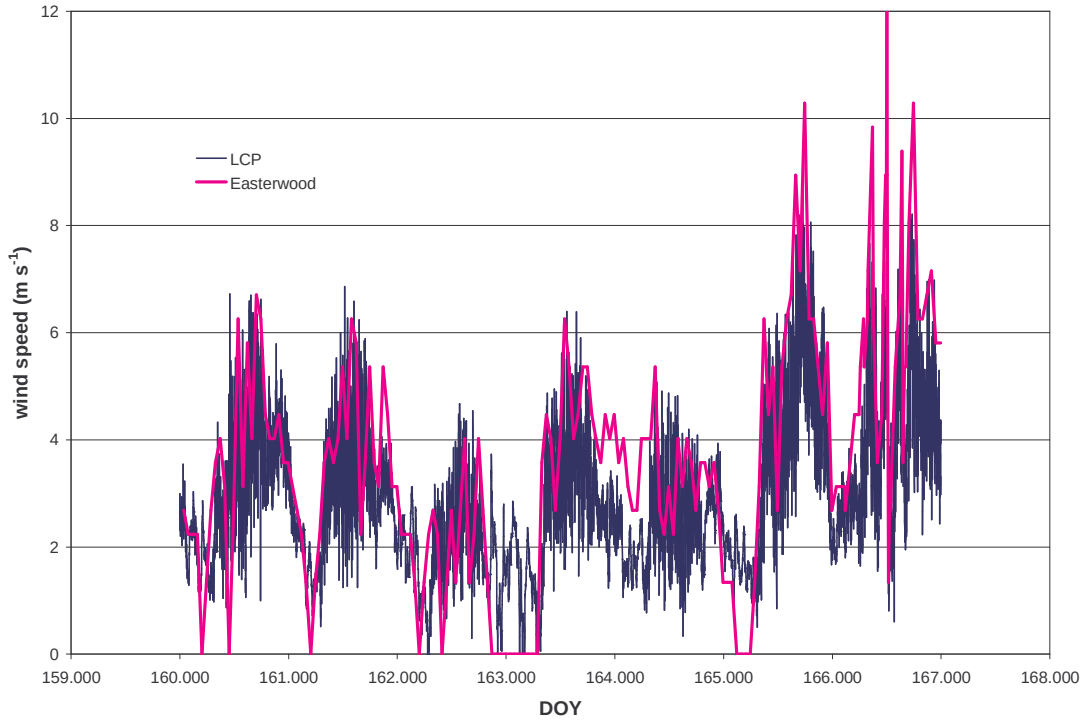


Figure 3: Wind speed measurements at Lick Creek Park versus Easterwood Airport.

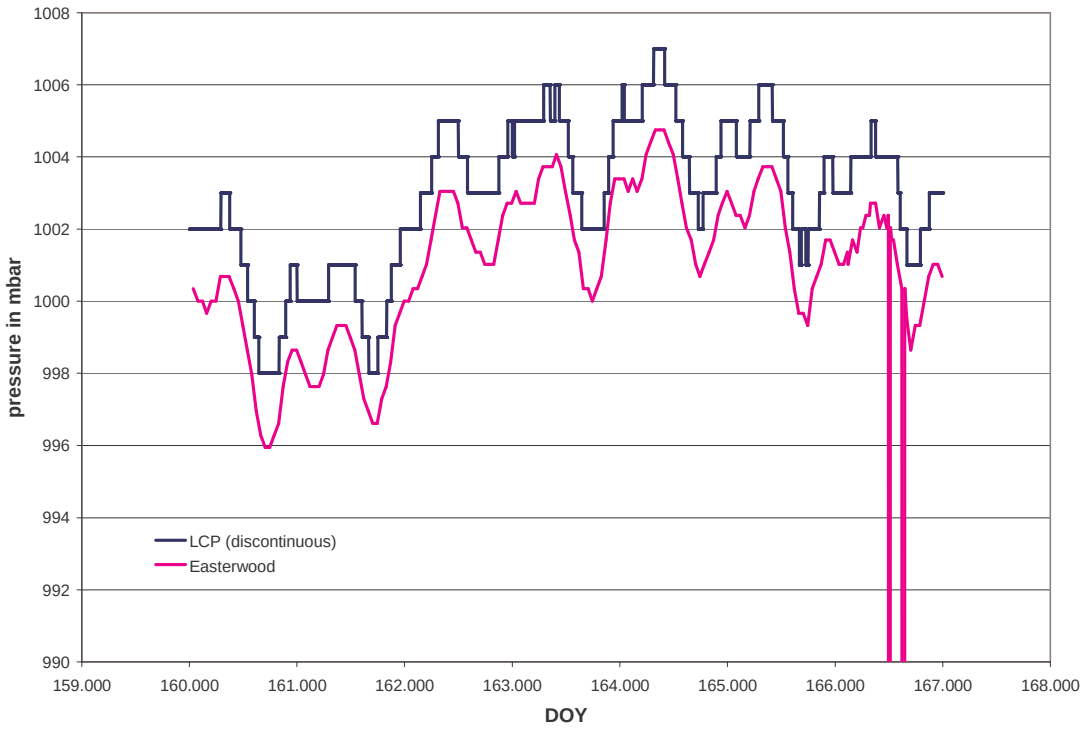


Figure 4: Pressure measurements at Lick Creek Park versus Easterwood Airport.

Figures 5 to 7 show an example week of air quality data from June 2006, and *Figure 8* shows an enlarged section of the NO/NO_y data to illustrate the instrument's 6-minute cycling.

Figure 5 shows the typical diurnal ozone cycling with maxima during the afternoon and minima in the early morning, at times (days 155 & 158) enhanced by either stomatal uptake in the canopy or local rush hour traffic NO emissions during the early morning when the nighttime boundary layer is still intact. This is followed by a rapid increase along with the daytime boundary layer growth, mixing high ozone levels from the nighttime residual layer aloft downwards. An additional ozone increase is seen during the late afternoons on days 155 and 158. Comparing that to Figures 6 and 7 reveals the advection of polluted air during these days, particularly visible on day 155 in both CO and NO_y.

Clear local traffic effects are visible in the regular morning spikes for CO and NO. In Figures 7&8, NO is represented by the minima, which is essentially the white space under the curve. As expected, very little if any NO is detected except during the hours of rush hour traffic or very low ozone levels.

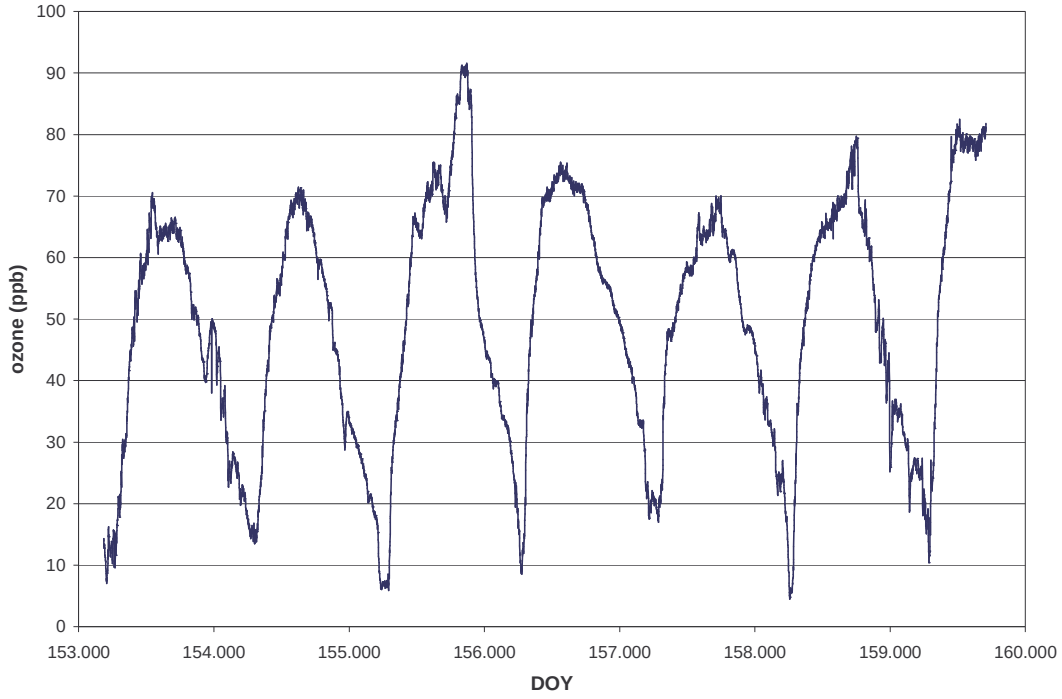


Figure 5: Ozone measurements at LCP.

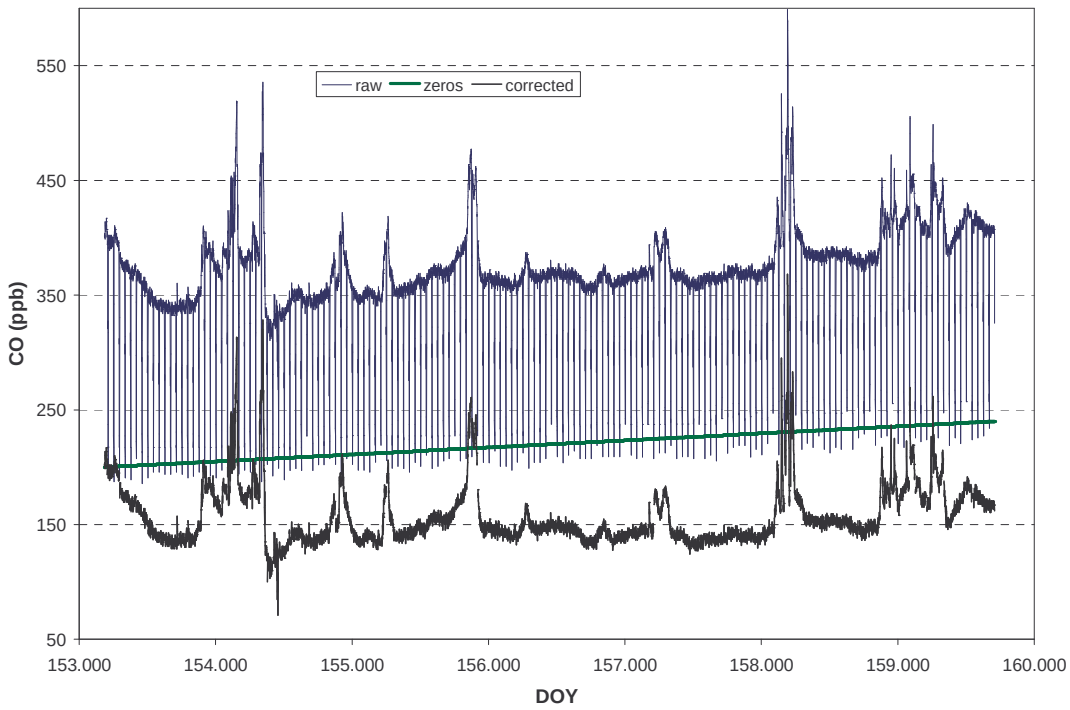


Figure 6: Carbon monoxide measurements at LCP, corrected for an estimated zero development from 200 to 240 ppb in this period.

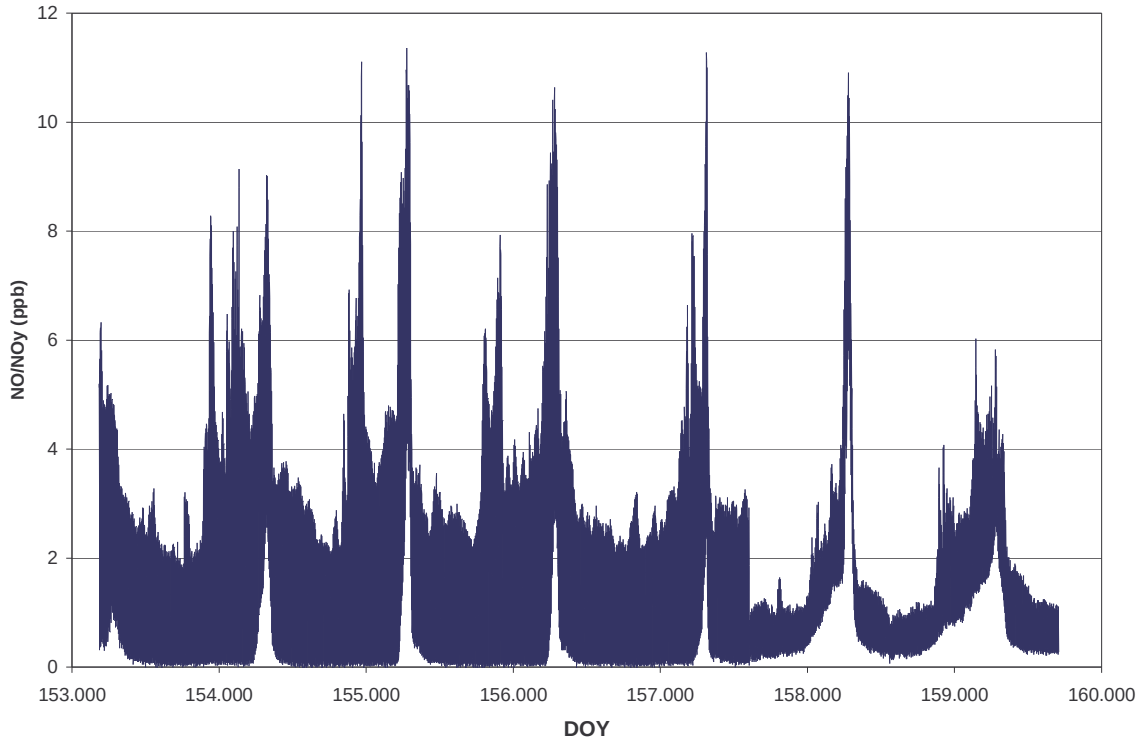


Figure 7: NO/NOy measurements at LCP for the same period shown in Figures 5&6.

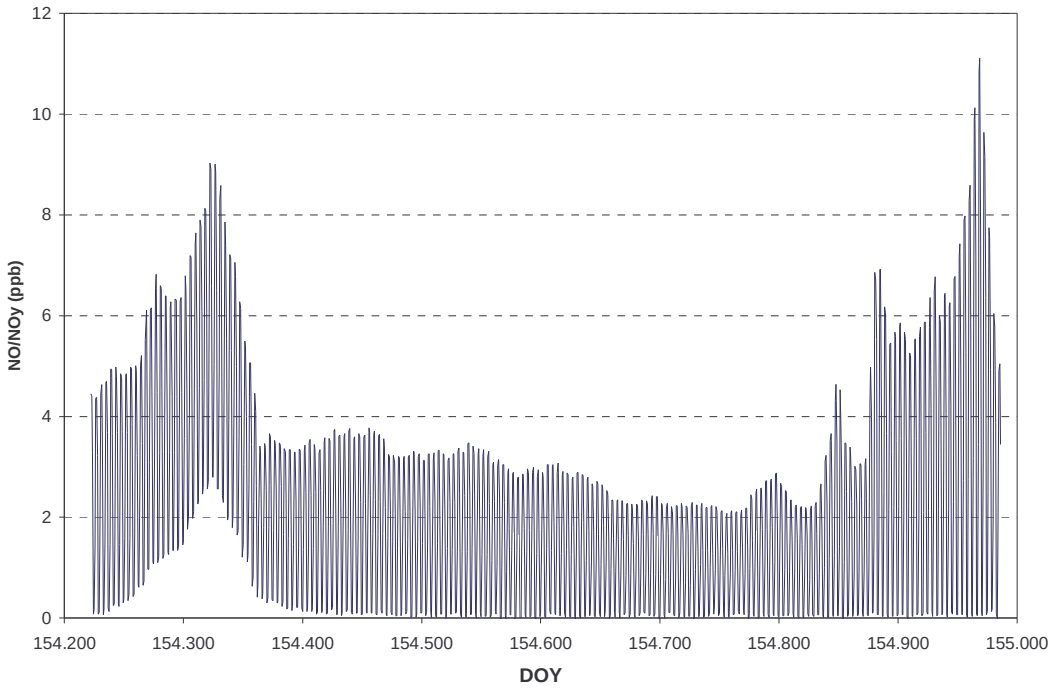


Figure 8: Same as Figure 7 but for only 21 hours to enhance visibility of NO.

C. Quality Assurance measures

To further ensure the quality of the collected data, the following active measures are currently being put in place:

- check on/correct wind direction sensor alignment
- 48C-TLE CO instrument:
  - increase the internal, catalytical zero measurement time to 8 minutes
  - install the CO standard gas line to the instrument's span gas valve and carry out a span gas injection and calibration check once a week
- 42C NOx analyzer:
  - install the NO-standard gas line to the instrument's span gas valve and carry out a span gas injection and calibration check every 2-4 days
  - install the zero air gas line to the instrument's zero gas valve and carry out a zero gas injection at least once a day as a check
  - install a new NO_2-standard gas line to the NO/NO_y inlet and carry out a bi-weekly check of catalyst activity
  - repeat catalyst temperature test to evaluate NO_x versus NO_y sensitivity with and without an inlet filter

5. Webpage

We have initialized a webpage at http://www.met.tamu.edu/research/LCP/frame.html that can be accessed directly or through the Departments front page under "Research Groups". It currently contains basic information and meteorological data examples. However, it will be filled in the beginning of July with the most recent data, and then updated once a day in the morning. To download ASCII data a password will be required that we will send out on request. Daily ½-h resolution data plots (in jpeg format or pdf) for wind speed and direction, temperature and relative humidity, solar irradiation and rain amount, and CO, NO, NO_y, and ozone will be freely accessible on the page from the data link.