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

Tasks 2, 3 & 4 Deliverable Report
Final Report

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by the State of Texas through a Grant from the
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Final Report, Task 2

TCEQ – NTRD Grant 582-5-70807-0015, Amendment No. 2

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0. Scope of Work list

For this report, the scope of work was defined as Task 2:

Task 2: Commission the site Quality-assure data and maintain site

2.2. Task Statement: The PERFORMING PARTY shall conduct testing at the test site.

2.2.1. The PERFORMING PARTY will activate the site and data will become available through the web site and by other means.

2.2.2. The PERFORMING PARTY will collect routine data at the site and will undergo standard quality assurance. The quality-assured data will be available from the same web site as the near-real time data.

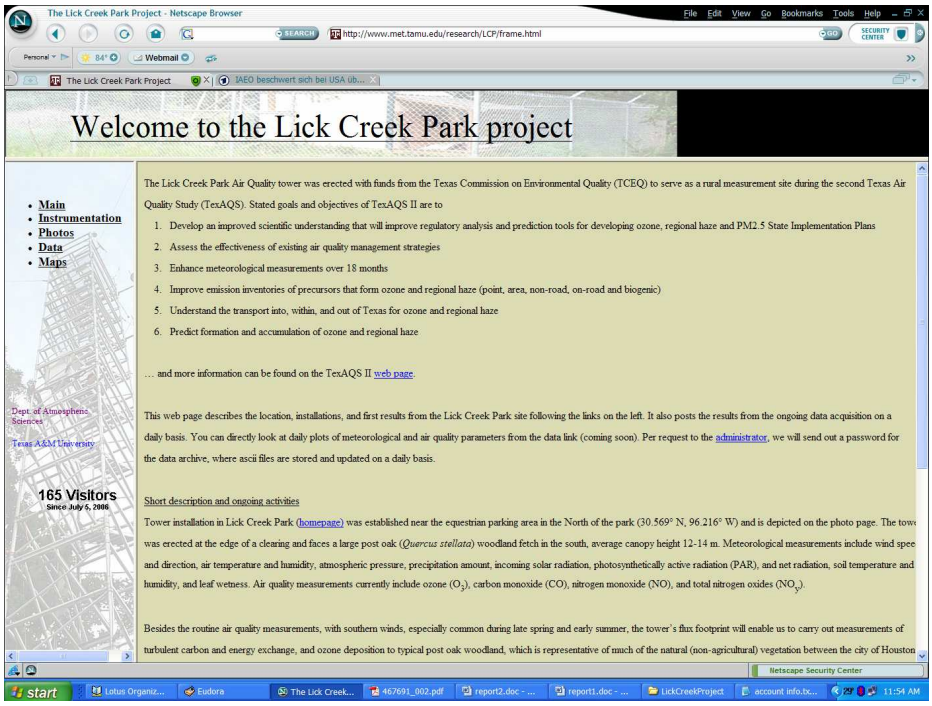
2.2.3. The PERFORMING PARTY shall complete this task within 13 months of the signed Notice to Proceed Date as issued by TCEQ

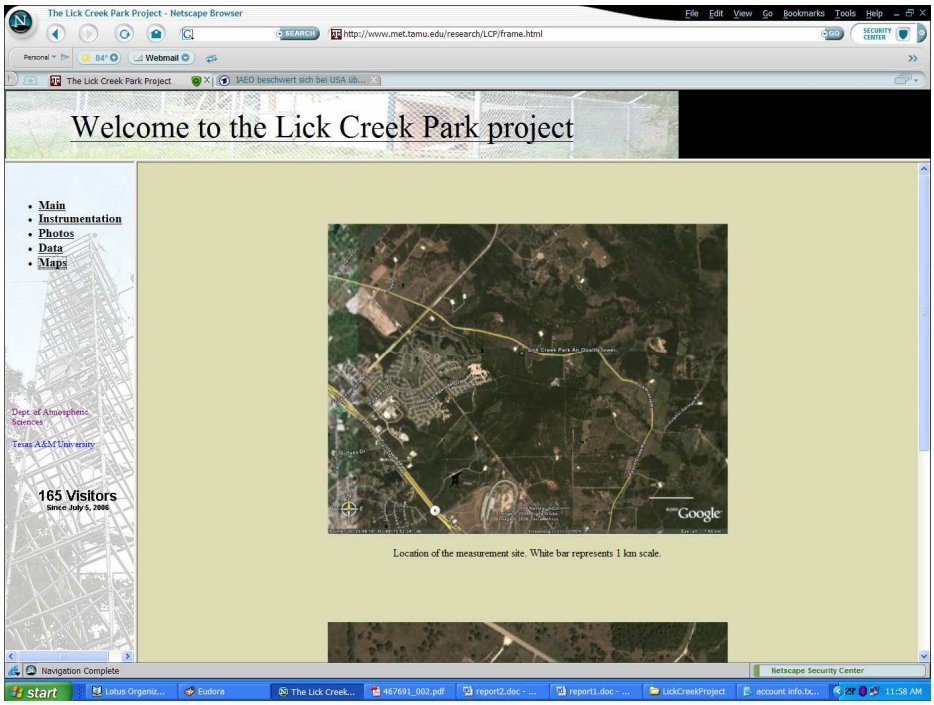
2.2.4. The PERFORMING PARTY shall submit a final report to the TCEQ on results of test data generated from the test site including all quality-assurance data.

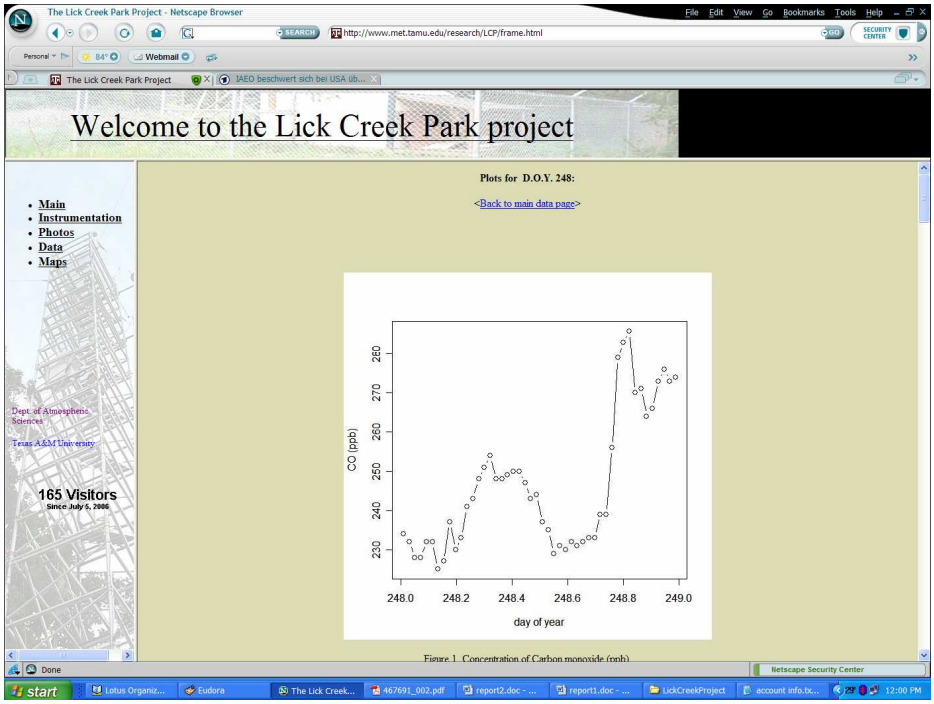
This Report therefore includes a description of the web page, a description of the data processing routines using R-language, other quality assurance measures, and an overview of the quality assured data attached to this report in ASCII format.

1. Web site overview

The internet portal for site description, data display, and data dissemination was first posted in early July 2006 at http://www.met.tamu.edu/research/LCP/frame.html. It contains a description of site location and activities, as well as a data page. The screenshots below depict some relevant pages.







Access to the data archive is achieved through a user name and password. Anyone with a vested interest in the data will be given access after contacting us via e-mail.

2. Quality assurance measures, R program routines

Data is downloaded by the field –PC each night after midnight. The following morning (except on weekends), it is transferred to our office PCs in Eller O&M Building on the Texas A&M main campus in College Station via a directional wireless antenna link (~8 miles line of sight). It is then read into R, a software for statistical computing and graphics, and processed to provide an output of half-hour averages for relevant meteorological and measured air quality data. The routines were programmed by Dr. Schade and are provided in the attached file “Rroutines.txt” for reference. The important operations be described here briefly:

- The function “GET” reads in a defined number of lines of the 1-minute resolution raw data created by the Campbell CR1000 data logger. It selects the most relevant meteorological data from the data frame and then creates a day-of-year (doy) vector from the time entries and attaches it to the data
- The function “COZERO” scans the carbon monoxide raw data in a predefined interval, extracts the lowest data during the hourly internal zero of the instrument, and eliminates all zero measurements from the ambient measurement series. It then linearly interpolates the zero data and subtracts that timeline from the ambient CO measurement timeline
- the function “NONOy” scans the NO/NO_y raw data and separates the fixed interval NO from the fixed interval NO_y measurements, then stores these data in a new matrix with their respective doy timeline
- the function “HHAVG” takes all raw meteorological and prepared air quality raw data and creates half-hourly mean, median, and sum parameters, excluding missing data. It also creates a daily plot for each quantity and a full 24-h data set in ASCII format

Posted data in the archive is spot-checked for inconsistencies, and was labeled missing or of questionable quality when sensors did not appear to have been working properly, which was most often the case for the wind direction sensor.

2.1 Calibrations

The most important quality assurance measures were regular onsite instrument calibrations. These included regular zero and span checks and adjustments for the NO_x and CO analyzers, and zero checks of the ozone analyzer. Table 1 below list all calibration checks and activities during the 8-week testing phase.

Table 1: Calibration details for the air quality instrumentation

action	*Date*	*NO*	*CO*	*O_3*	***Comments***
zero	13-Jun	0.4	290	---	no changes made
zero	20-Jun	2.2, 10.8	360	---	NO re-zeroed after span
span	20-Jun	101.5	785	---	PMT adjusted to -742 V
zero	27-Jun	1.3	414	---	NO & CO zeroed
span	27-Jun	97.8	428	---	no changes made
zero	4-Jul	---	106	0.3	NO out of order, only ozone zeroed
span	4-Jul	---	560	500	no changes made
zero	28-Jul	---	165	---	no changes made
span	28-Jul	---	625	---	no changes made
zero	8-Aug	---	365	---	NO instrument fixed and zeroed
span	8-Aug	---	825	---	NO span done
zero	11-Aug	-0.6	393	-0.9	only NO zeroed, catalyst temp = 390 C
span	11-Aug	90.6	873	---	only NO Span done
zero	17-Aug	0.2	490	-0.75	no changes made
span	17-Aug	99	960	---	no changes made
zero	22-Aug	0.2	550	-0.5	no changes made
span	22-Aug	98	1040	---	no changes made
zero	7-Sep	0	840	---	only CO zero done
span	7-Sep	98	490	---	CO span done

Note that internal CO zeros were carried out once an hour without letting the instrument carry out the electronic zero setting. We found the internal zero to be good (i.e. within 30 ppb of true zero) but quite unstable (±30 ppb) at times. Hourly electronic zeros could therefore have lead to an additional noise level in the data of this magnitude. In lieu, we devised the recording and post-processing method described above, in which each minimum value in a defined interval gets interpolated to the next one. This method successfully captured instrument drift and minimized zero noise. CO (and NO) instrument spans were only performed when the calibration gas value (added to zero) was

off by more than 10% (~50 ppb for CO, which also happened to be close to the CO instrument's stated precision level a the used averaging frequency of 20 s).

In addition to these direct calibrations, we have twice successfully challenged the NO_2 to NO "Molycon"-converter with low ppm levels (2-3 ppm) of NO_2 to arrive at a conversion efficiency of 91±3%. The actual conversion efficiency of NO_2 to NO at ambient levels, which are 10^2 to 10^3 times smaller at Lick Creek Park, is assumed to be over 90% at all times, the EPA acceptability limit for Molybdenum based catalytic converters. We have later increased the converter temperature from 330 °C to 390 °C in order to maximize NO_y to NO conversion. As the converter is installed only ~5 mL behind the gas inlet, which translates into a tubing residence time of <0.5 s, a successful conversion of all NO_y species is assumed and the measured "NO_x" is given as NO_y [1-4].

2.2 Other quality insurance measures

All data were screened for outliers, such as negative or consistently high mixing ratio data, and those section were set to NA. Also set to NA were any periods during which field calibrations were carried out, and any periods for which the respective sensor(s) are/were not working properly. Furthermore, data were removed (in the current file version) under circumstances where the above described data handling routines created erroneous output, which occurred in less than 5% of all cases and was often corrected for already through repeated raw data processing. Subsequent file versions will have more and more of these sections included as we continue to understand instrument and processing software behavior.

Special attention was paid to the wind direction data. We determined that wind direction was recorded erroneously on our data logger for most of the time. As it was seemingly not recoverable, we have set all wind direction data to "NA" and supplemented the dataset with available data from our sonic anemometer, which was operational for one of the two months data is reported on here.

3. Quality assured data

The attached file, **dat_LCP.v1.txt**, is a comma-delimited ASCII file that contains two months of quality-assured data between July 6 and September 6, 2006. Some examples out of that data set shall be described here.

Figure 1 shows meteorological data for a typical period during August 2006.

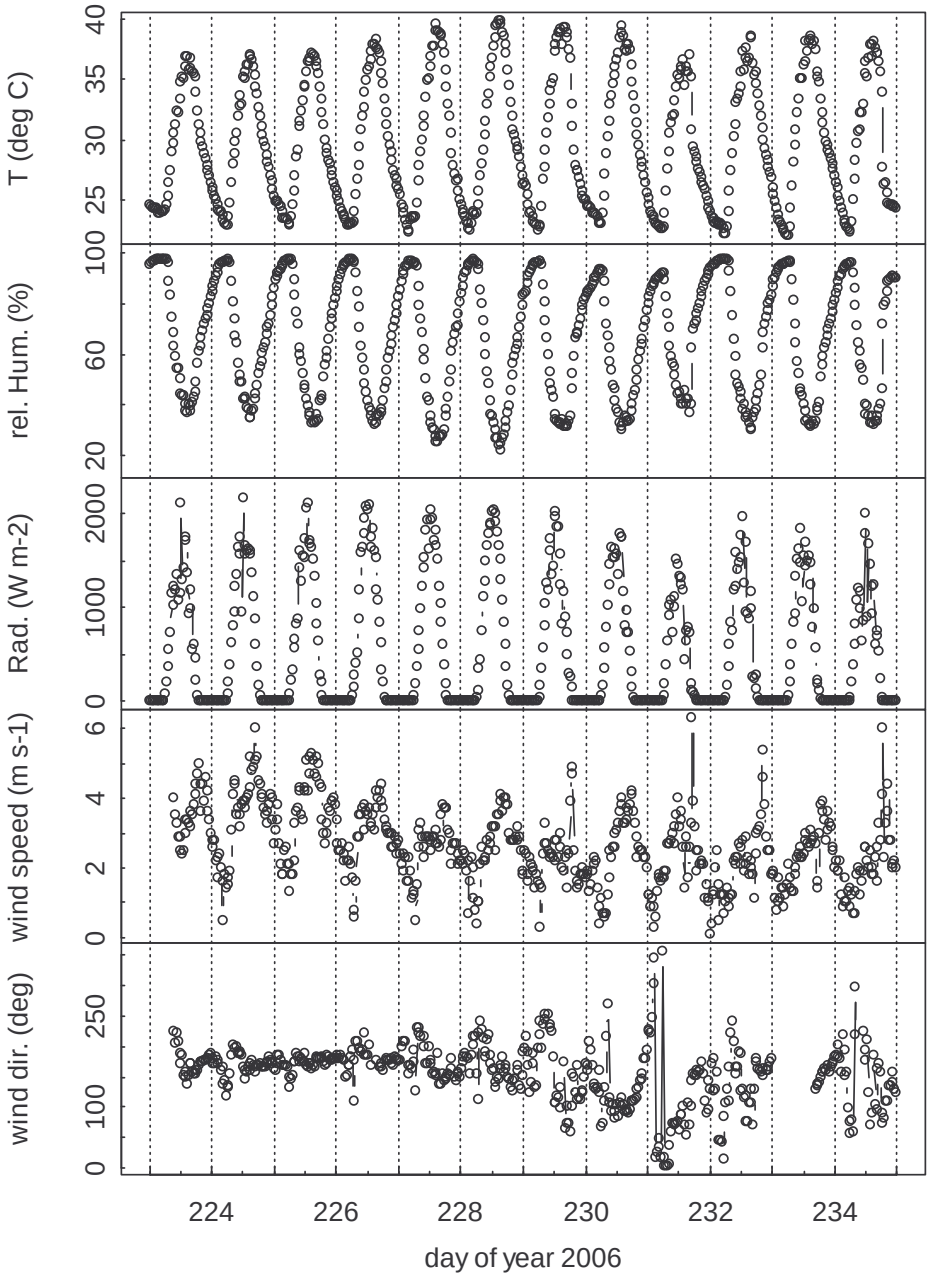


Figure 1: Meteorological data at Lick Creek Park for mid-August 2006.

Figure 2 shows the respective air pollution data for the same period:

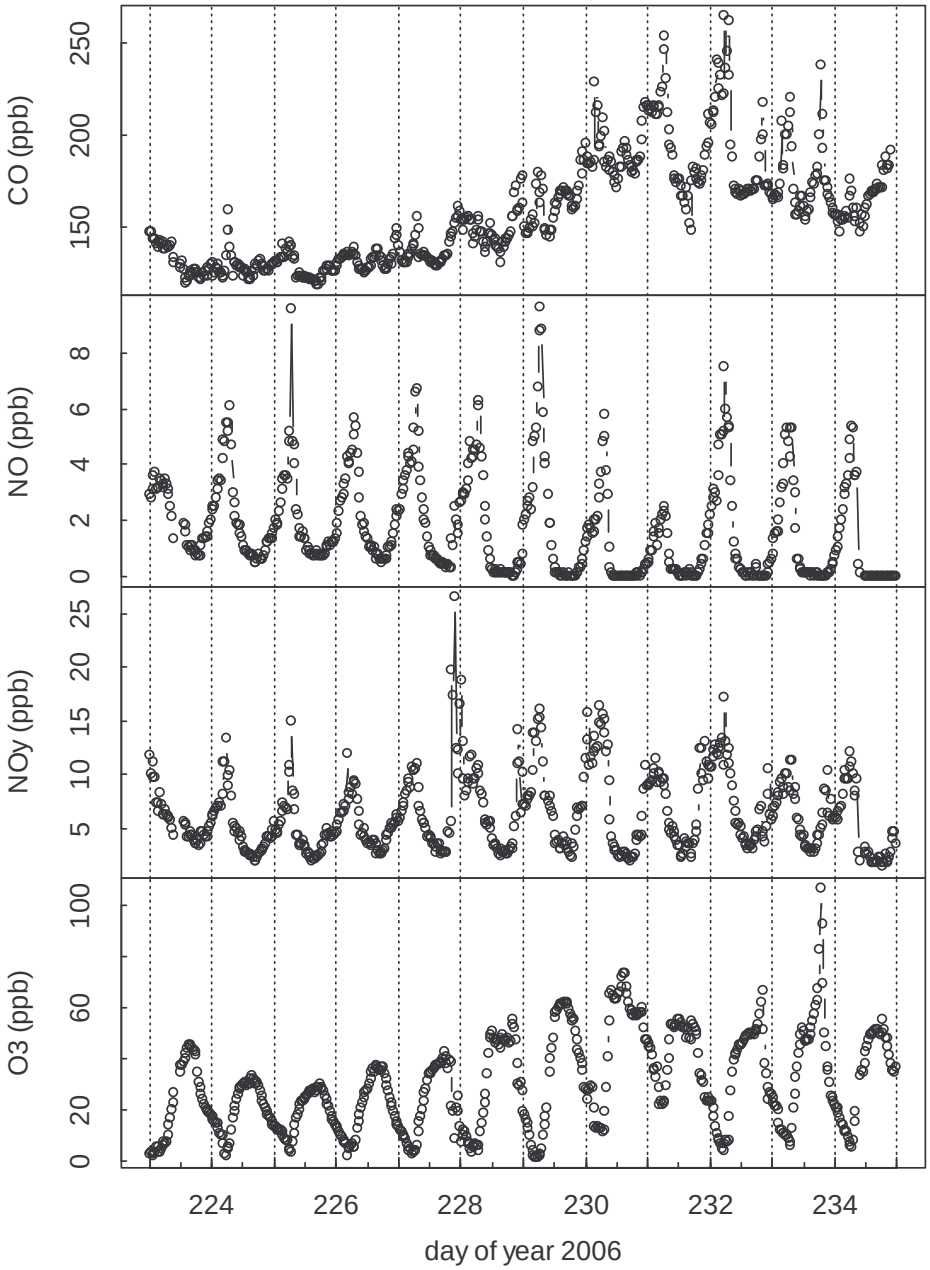


Figure 2: Air Quality data at Lick Creek park for the same period as in Figure 1.

Comparing Figures 1&2 shows that an initially relatively clean airmass (low CO, NO_y, and O_3) became higher polluted under progressively lower wind speeds under southerly wind conditions. Poorest air quality in terms of ozone (nearly 80 ppb) was reached on day of year 230 (August 18, 2006). A temporary wind direction change to northerlies drastically reduced the primary air pollutant CO and resulted in larger

nighttime ozone levels on day of year 231, indicating a cleaner background, possibly from aloft. However, southerlies were reinstated the following day, apparently reestablishing or recirculating the original air mass back to Lick Creek Park. On both days following the reestablishment of the original air mass, August 20&21, a late afternoon pollution event visible in the CO, NO_y, and ozone data indicates the arrival of the Houston urban plume, in one case pushing ozone over 100 ppb through an apparent plume excess of 40 ppb. Situations such as this one were the main reason this air quality station was supported for the TexAQS II study.

More generally, local air pollution meteorology can be characterized through long-term mean behavior of the measured pollutants. For this purpose we have aggregated the data into mean daily profiles. Figure 3 shows mean half-hourly air quality data along with a grey swath indicating the interquartile range during this analyzed two-month period. Most prominent are the morning rush-hour starting around 6:30 am, and the nighttime increase of primary pollutants. The former is visible in both NO and CO, primary emissions from car traffic. The NO to NO_y ratio, depicted in Figure 4, shows that NO becomes up to 50% of NO_y during rush-hour, reflecting both the nearness to its major emission sources from southwest to northwest of the station and the low abundance of ozone at that time of day (Figure 3). The latter, the nighttime increase of NO, NO_y, and CO alongside a decrease of O_3, reflects continuing anthropogenic, and possibly also biogenic NO and CO emissions leading to a build-up in the shallow nighttime boundary layer. Emitted NO consumes nighttime ozone to below 10 ppb levels in the early morning hours, sometimes eliminating ozone from the boundary layer during rush-hour. This behavior is very similar to urban air quality data and characterizes Lick Creek Park more as an urban than rural measurement site, strongly influenced by anthropogenic primary pollutant emissions.

Generally, ozone values at Lick Creek Park do not show drastically elevated levels except in cases such as depicted above. Daytime ozone production leads to average levels around 40 ppb. While this is a typical rural background level, consecutive days under prevalent wind conditions lead to a day-to-day build-up of ozone as shown in Figure 2. Hence, in terms of daytime ozone, Lick Creek Park could be considered rural, but local and regional production has to be taken into account under recurring air mass patterns.

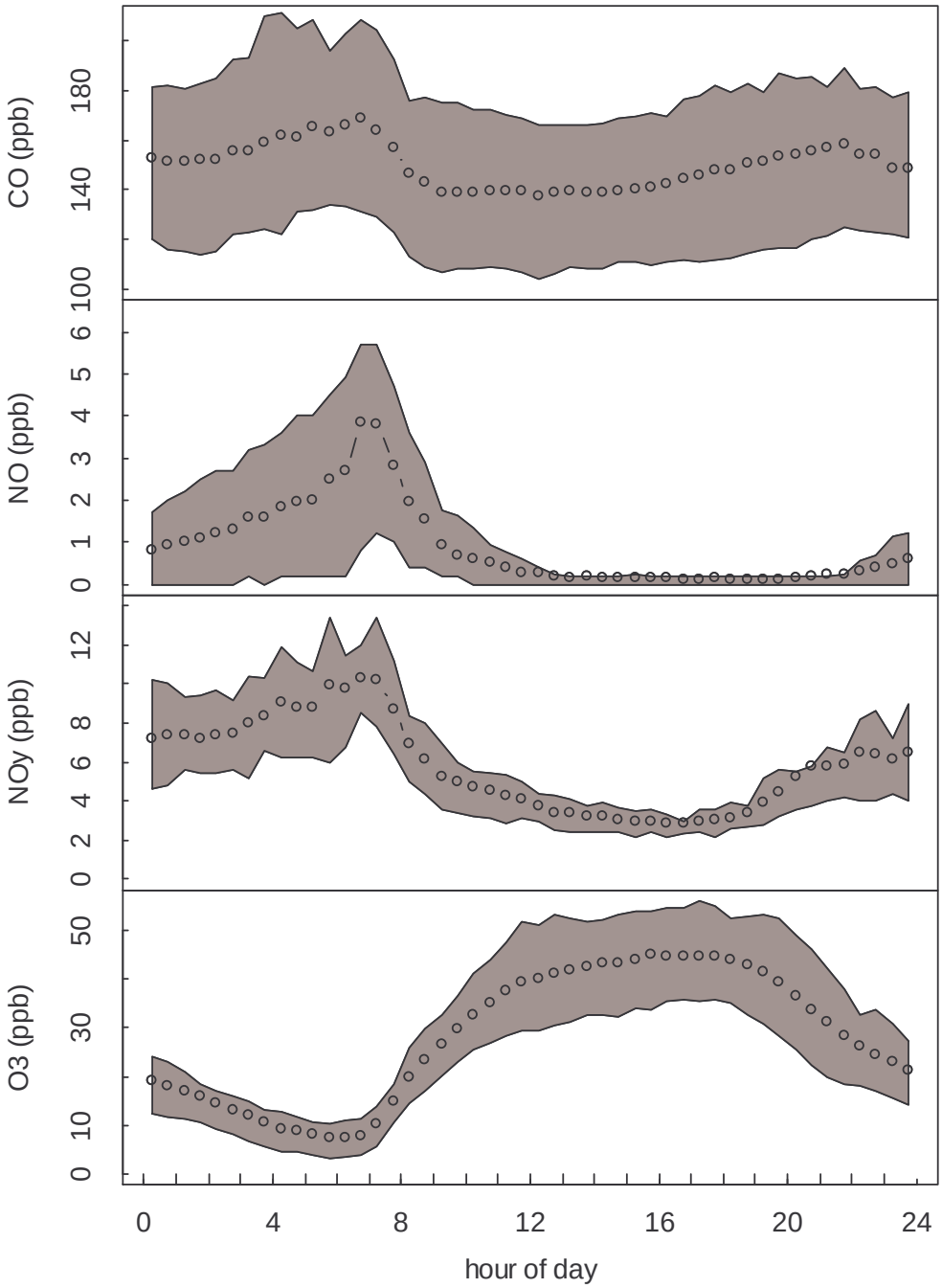


Figure 3: Air pollutant meteorology at Lick Creek Park depicted via diurnal means (open circles; lowest and highest 0.1 data quartile ignored) and interquartile ranges (grey swath).

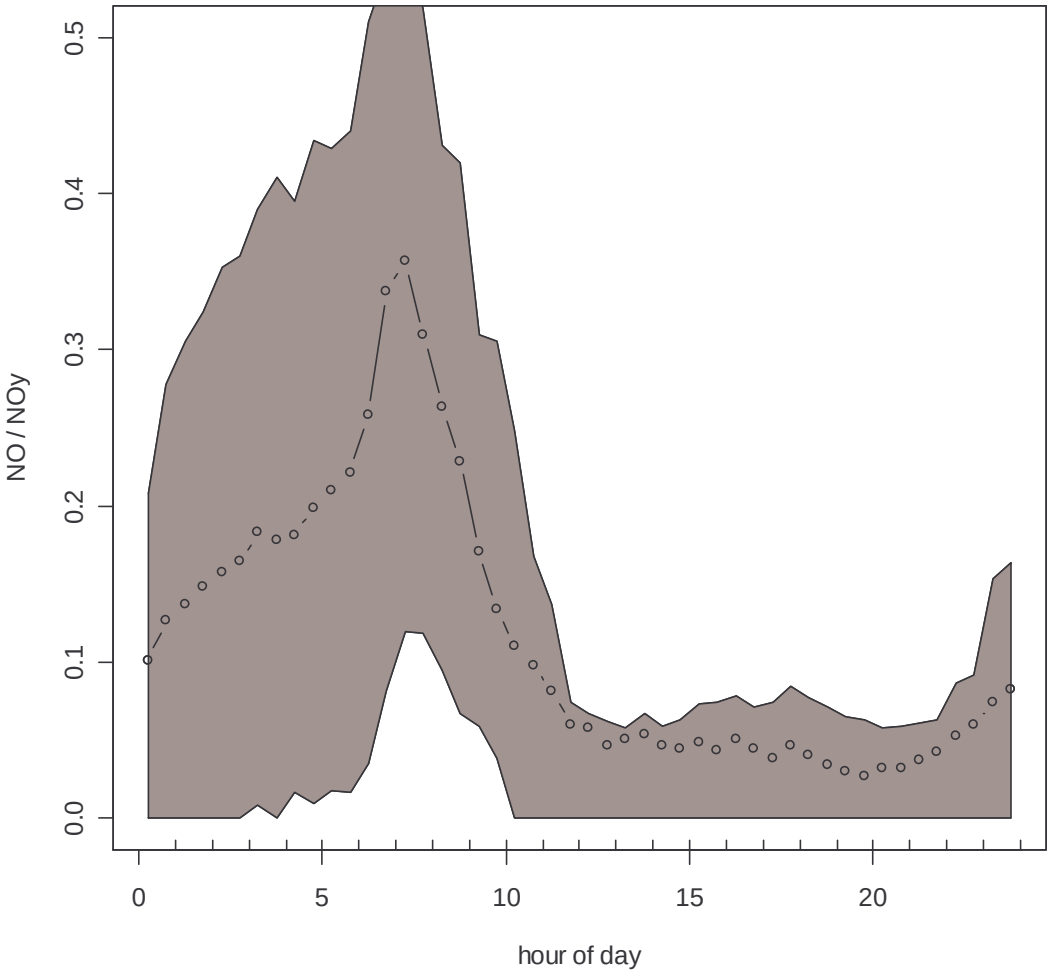


Figure 4: Mean (open circles) and interquartile range (grey swath of the NO to NOy ratio at Lick Creek Park.

4. Attachments

- Rroutines.txt (a text file with comments)
- dat_LCP.v1.txt (a comma-delimited ASCII file; the header contains: "doy" – time vector, "hour" –a fractional hour vector, "rad" – pyranometer radiation in W m^{-2}, "tair" air temperature in °C, "rh" – relative humidity in %, "ws" – wind speed from the cup anemometer in m s^{-1}, "wd" – wind direction from the wind vane in deg, "CO" – carbon monoxide in ppb, "NO" – Nitrogen oxide in ppb, "NOy" – sum of NO_x, HNO_3, HONO, PAN, alkyl nitrate, and higher

peroxynitrate species in ppb, "O3" – ozone in ppb, "ws.s" – wind speed from the sonic anemometer in m s^{-1}, "wd.s" – wind direction from the sonic anemometer in deg, "Ts" – virtual air temperature from the sonic anemometer in °C)

5. References

1. Roscoe, H.K. and K.C. Clemitshaw, 1997, *Measurement techniques in gas-phase tropospheric chemistry: A selective view of the past, present, and future.* Science. **276**(5315): p. 1065-1072.
2. Aneja, V.P., et al., 1997, *Trends and analysis of ambient NO, NOy, CO, and ozone concentrations in Raleigh, North Carolina.* Chemosphere. **34**(3): p. 611-623.
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4. Fehsenfeld, F.C., et al., 1987, *A Ground-Based Intercomparison Of NO, NOx, And NOy Measurement Techniques.* Journal Of Geophysical Research-Atmospheres. **92**(D12): p. 14710-14722.