MEASUREMENTS OF NO_y, NITRIC ACID, NO, AND PAN IN THE SOUTH COAST AIR BASIN

Final Report

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Disclaimer

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Abstract

NO_y–NO_y* analyzers and NO_2/PAN gas chromatographs were used in the continuation of a study to evaluate the concentrations of nitrogenous species in Azusa and Riverside. These two sites are generally on the same afternoon wind trajectory with Azusa, approximately 35 miles to the west-northwest, being upwind. NO_y-NO_y* instruments are chemiluminescent NO-NO_x analyzers equipped with dual converters, with one preceded by a NaCl-coated denuder to measure nitric acid by difference. NO_2/PAN gas chromatographs separate NO_2 and quantify the amount using luminol detection. This selective method of measuring NO_2 and PAN is used to quantify the amount of these species contained in the NO_y. The analyzers were operated from May 2001 through December 2002. Data were compiled, validated, and submitted for all of 2002. Data from 2001 were submitted as unvalidated data. In 2002 NO_y values at Riverside ranged up to 250 ppb, and values at Azusa reached up to 500ppb. The diurnal pattern of nitric acid was observable nearly every day, although at each site one of the two collocated NO_y-NO_y* instruments was biased low, most likely due to a slight converter efficiency mismatch. While there was significant scatter in the nitric acid measured by all of the instruments, the concentrations at Riverside ranged up to about 5 ppb while maximum values at Azusa were 20 ppb. The lower concentrations at Riverside were expected since the afternoon wind trajectory from Riverside passes over dairy operations emitting large amounts of ammonia, which would remove nitric acid as ammonium nitrate. The conclusion was that nitric acid concentrations could be characterized, although the accuracy could not be established. In Riverside, the PAN concentrations typically peaked at 1 ppb, although concentrations of 4 ppb were observed in August. In Azusa, a more limited amount of data from the NO_2/PAN GC showed PAN concentrations to be nearly a factor of two higher than in Riverside.

Executive Summary

A NO_2/PAN gas chromatograph and a pair of collocated NO_y-NO_y* analyzers were installed at both the South Coast Air Quality Management District's Azusa air monitoring facility and the CE-CERT Atmospheric Chamber Facility in Riverside. These two sites are generally on the same afternoon wind trajectory with Azusa, approximately 35 miles to the west-northwest, being upwind. Azusa is more characteristic of a source region while Riverside is primarily a receptor region. NO_y-NO_y* instruments are chemiluminescent NO-NO_x analyzers equipped with dual converters with one channel fitted with a NaCl-coated fabric denuder to selectively remove nitric acid. Since the instrument automatically cycles between the two channels, the difference is a measure of nitric acid. NO_2/PAN gas chromatograph separates NO_2 and PAN, and quantifies the amounts of each using luminol detection. A major advantage of this PAN measurement technique is that it is not necessary to generate PAN synthetically in order to perform calibrations.

The inlet for the NO_2/PAN GC and the converters for the NO_y-NO_y* analyzers were mounted in insulated boxes 1.5 m above the roofs of both buildings while the analyzers were installed inside the air-conditioned building. Automated zero checks were conducted five times a day, each period lasting 30 minutes. Data was logged at 10-minute intervals. Site checks were performed on a weekly basis in the smog season.

The analyzers were operated from May 2001 through December 2002. To conserve resources instruments were routinely maintained only during the "smog season" (April-October). Data were compiled and validated for all of 2002. Data from May-November were not fully validated and were submitted as "unvalidated" after obviously bad data were removed. Only 2002 data are described in this report.

For 2002, NO_y values at Riverside ranged up to 250 ppb, and values at Azusa reached up to 500ppb. The diurnal pattern of nitric acid was observable nearly every day, although at each site one of the two collocated NO_y-NO_y* instruments was biased low, most likely due to a slight converter efficiency mismatch. While there was significant scatter in the nitric acid measured by all of the instruments, the concentrations at Riverside ranged up to about 5 ppb while maximum values at Azusa were 20 ppb. The lower concentrations in Riverside were expected because the air trajectories were like to pass over the dairies to the east, which are a major source of ammonia, a species that reacts with nitric acid to form particulate ammonium nitrate. The conclusion was that nitric acid concentrations could be characterized, although the accuracy could not be established. In Riverside, the PAN concentrations typically peaked at 1 ppb although concentrations of 4 ppb were observed in August. In Azusa, the amount of data from the NO_2/PAN GC were limited due to servicing difficulties, but the concentrations appeared to be nearly a factor of two higher.

This contract included an additional task of preparing NO_y analyzers for the Lake Tahoe Atmospheric Deposition Study (LTADS). Three NO_y analyzers were refurbished and evaluated for performance and converter efficiency. Three calibrators were also calibrated. A class was given to LTADS site operators in NO_y analyzer maintenance and technical assistance was provided as needed.

1.0 Introduction and Objectives

1.1 Background

Oxidized nitrogenous species play a critical role in the formation of ozone and particulate matter in the atmosphere. The term NO_y has been used to describe the total reactive nitrogen oxides, or odd nitrogen, but the operational definition is the response of a chemiluminescent NO analyzer after the sample is treated with a converter that reduces more highly oxidized species to NO. It is generally agreed that NO_y consists primarily of nitric oxide (NO), nitrogen dioxide (NO_2), peroxyacyl nitrates (PAcNs), nitric acid (HNO_3), particulate nitrate, and nitrous acid (HONO), roughly in that order of concentration in ambient photochemical air pollution. Commercial converters have been shown to readily reduce these gaseous species while they have no efficiency for N_2O or organic nitro compounds, which are not considered photochemically reactive (Winer et al., 1974).

To measure NO_y accurately, it is necessary to minimize adsorption losses in the sampling line. Nitric acid has been shown to adsorb and desorb with temperature and humidity changes on all types of surfaces including the generally inert PFA tubing used for sampling NO_X. Since commercial NO_X analyzers require temperature-controlled shelters, sample lines are needed to draw sample from ambient air to the analyzer. During this transport, the temperature and relative humidity can change drastically. Since peak nitric acid is generally found during warm days, the sudden cooling and resultant increase in RH within the sample line when entering an air-conditioned shelter causes a significant adsorption of nitric acid. To avoid these adsorption losses, NO_y analyzers are configured such that the converter of a NO_X analyzer is placed in ambient air while the detector assembly remains in an air-conditioned environment. In the converter, NO_y components are reduced to NO, a species that has little affinity for adsorption to surfaces. In addition, a particulate filter is not used prior to entry into the converter to further minimize the adsorption of NO_y components.

Nitric acid has been shown to be a key NO_y component that is generally the final oxidation product of NO. This species readily deposits to surfaces affecting biological systems. In addition, it reacts rapidly and reversibly with ammonia to produce particulate ammonium nitrate with sub-micron aerodynamic diameters. Over the past twenty years, considerable efforts have gone into the development and testing of field methods for the analysis of nitric acid in ambient air. Due to its sorptive properties and equilibrium with ammonium nitrate, nitric acid has proven to be a difficult species to quantify in ambient air.

The present methods for measuring nitric acid include spectroscopic techniques and an array of filter pack and denuder difference systems. Despite moderate success during their application in short-term monitoring programs, none of the methods has become widely accepted as meeting the combined criteria of high sensitivity, accuracy, portability, and consistency of performance. Nitric acid is most commonly measured by collecting it on a diffusion denuder coated with a material that is specific for adsorbing this acid. The time resolution of this technique is several hours. Direct spectroscopic measurements with higher time resolution can be made using a long path Fourier Transform Infrared (FTIR) or tunable diode laser absorption spectrometer (TDLAS). These instruments, however, are expensive and labor-intensive.

A number of studies have been reported comparing these techniques via collocated ambient air comparisons (Spicer et al., 1982, Anlauf et al., 1985, Hering et al., 1988, Fox et al., 1988, and Tanner et al., 1989). Methods that include a pre-filter are expected to be subject to volatilization of collected ammonium nitrate, which would bias the measurement high, and the adsorption of nitric acid on the collected particulate matter, which would bias the measurement low. Therefore, it is possible that the biases may at times cancel each other out. In the first major comparison study (Spicer et al., 1982), the results were inconclusive for two reasons: Several of the methods in the developmental stage showed consistency problems, and for a number of sampling intervals benchmark data from a long-path FTIR instrument were unavailable due to the rather high detection limit of 6 ppb.

In October 1993, a side-by-side comparison of nitric acid measurements was conducted in Azusa, CA, between a tunable diode laser absorption spectrometer (TDLAS) (Mackay and Schiff, 1987) and two denuder difference samplers of the type employed during the California Acid Deposition Monitoring Program (the CADMP sampler) (Watson and Chow, 1991). The average CADMP measurements were approximately half those obtained by the TDLAS method. Based on previous observations of daytime nitric acid to ozone ratios in Azusa and other locations in the South Coast Air Basin (Anlauf et al., 1991; Tuazon et al., 1995), the TDLAS nitric acid measurements in Azusa during the 1993 study were significantly higher than expected. A review of the above TDLAS data found no tractable instrumental or operator errors (Tuazon et al., 1995). The TDLAS nitric acid time profiles, when examined with those of the concurrent ozone and peroxyacetyl nitrate profiles, showed no evidence of nitric acid adsorption/desorption process occurring along the sampling train nor evidence of nitric acid vaporization from particulate on the Teflon front-filter. The possibility of interferences on the spectroscopic measurement was raised but has remained a speculation.

The CADMP denuder sampling arrangement itself has its own shortcomings. Fitz and Hering (1996) have shown that nitric acid is reversibly adsorbed by the PFA-Teflon-coated surfaces of the housing for the size-selective inlet and the sampling plenum as a function of temperature, humidity and prior exposure. The overall loss of nitric acid to these surfaces was found to average 15%, although short-term concentration variability due to changes in temperature and humidity would vary by nearly 100% higher or 100% lower. In addition, Fitz and Hering (1996) noted that the nitric acid denuder may become saturated with nitric acid to such a degree that it could function as a source. The consistency in performance of the CADMP design as affected by the above variables was put in question during the 1993 Azusa study, where measurements by one of the two collocated CADMP samplers had a high probability of being correct while results from the other sampler were found erroneous (Tuazon et al, 1995).

In a recently reported study (Fitz et al. 2002), a CADMP denuder difference sampler has been deployed again in the field in Claremont, CA along with the TDLAS instrument as part of an extended comparison which included a kilometer-pathlength FTIR spectrometer (Biermann et al., 1988), a denuder difference sampler designed by the South Coast Air Quality Management District (SCAQMD) for its Enhanced Fine Particulate Monitoring Program (PTEP), and a newly developed coated-fabric direct denuder (Fitz and Motallebi, 2000). The FTIR was operated only during the daytime and provided reference data for the 1100-1700 PDT sampling period. The highest daytime correlation ($r^2 = 0.76$) was found between the FTIR and the fabric direct denuder measurements. The nitric acid measured by the TDLAS was poorly correlated with the PTEP sampler during the daytime, but was highly correlated ($r^2 = 0.90$) for samples collected at night (1700-1100 PDT). The nighttime data, however, showed the TDLAS measurements to be an average of 33% higher. The CADMP sampler correlated poorly overall, with the problem traced to the aluminum-based denuder having lost much of its removal efficiency. Although gaps in the data precluded more extensive direct comparison, none of the other three methods for nitric acid measurement showed high correlation with the TDLAS measurements during the daytime sampling periods. On average the results from all three were 22-33% lower than the TDLAS.

By equipping a chemiluminescent NO_y analyzer with dual converters and selectively scrubbing one channel of nitric acid, the concentration of nitric acid is measured by difference. We refer to this instrument as a NO_y / NO_y* analyzer. The focus of this report is to evaluate the performance of this measurement approach.

NO_2 is usually measured as the difference between NO and NOx using chemiluminescent NO_x analyzers. The U.S. Environmental Protection Agency has established a primary standard based on this technique. To measure NO_2, the air must first be passed through a thermal catalytic converter that reduces NO_2 (and other NO_y species) to NO. Since the response is then to both NO and NO_2, the NO must be subtracted from the total. This usually is accomplished by alternately sampling air that has and has not been directed through the converter. The difference, therefore, is due to the response from NO_2. Since these instruments respond to other NO_y species in the "NO_x" mode, the NO_2 concentrations will be biased high using this approach. More NO_2-specific converters based on the photolysis of NO_2 to ozone and NO have been reported, but their successful use depends on estimating the rate of oxidation back to NO_2, and this depends on the concentrations of several co-pollutants.

1.2 Objectives

The following were the objectives for this study:

- Operate pairs of NO_y-NO_y* analyzers for eighteen months at both Riverside and Azusa, CA.
- Operate NO_2/PAN GCs for eighteen months at both Riverside and Azusa, CA.
- Prepare NO_y analyzers for the Lake Tahoe Air Quality Study and provide operator training.

2.0 Approach

2.1 Monitoring Locations

These two sites are generally on the same afternoon wind trajectory with Azusa, approximately 35 miles to the west-northwest, being upwind. Azusa is more characteristic of a source region while Riverside is primarily a receptor region. Ambient data were collected at the CE-CERT laboratory in Riverside, and at the air monitoring site operated by the South Coast Air Quality Management District at 825 Loren Avenue in Azusa. Until March 2002, the roof of the CE-CERT at 1200 Columbia Avenue was used; after that time, the roof of the new facility at 1086 Columbia Avenue was used. The roof at the first CE-CERT site was 8 m above the ground, and the second was 13 m above the ground. The Azusa site was 4 m above the ground. Pairs of identical dual-converter ThermoEnvironmental NO_y analyzers were installed at each facility. At both locations, the converter boxes were located approximately 1.5 m above the roof. Approximately 10 m of ¼ inch OD PFA Teflon tubing was used to attach the converter box to the main analyzer unit. At both sites similar Teflon tubing was used to bring the calibration gas to the NO_y inlet. Separate Teflon lines were used to bring ammonia and nitric acid to the inlet for QC checks.

2.2 NO_y Instrumentation

The NO_y instruments were manufactured by ThermoEnvironmental (model 42CY) and based on its model 42S high sensitivity ambient NO_X analyzer. Figure 2-1 is a schematic drawing of how the analyzer was configured. The external converter housing was a stainless steel box with fiberglass insulation. The box was, therefore, slightly warmer than ambient air due to the heat released by the two converters. No filter was used prior to the sampled air entering the converter. A sodium chloride-coated fabric denuder was used to selectively remove nitric acid from one channel, allowing all other NO_y components to pass unattenuated, including particulate nitrate.

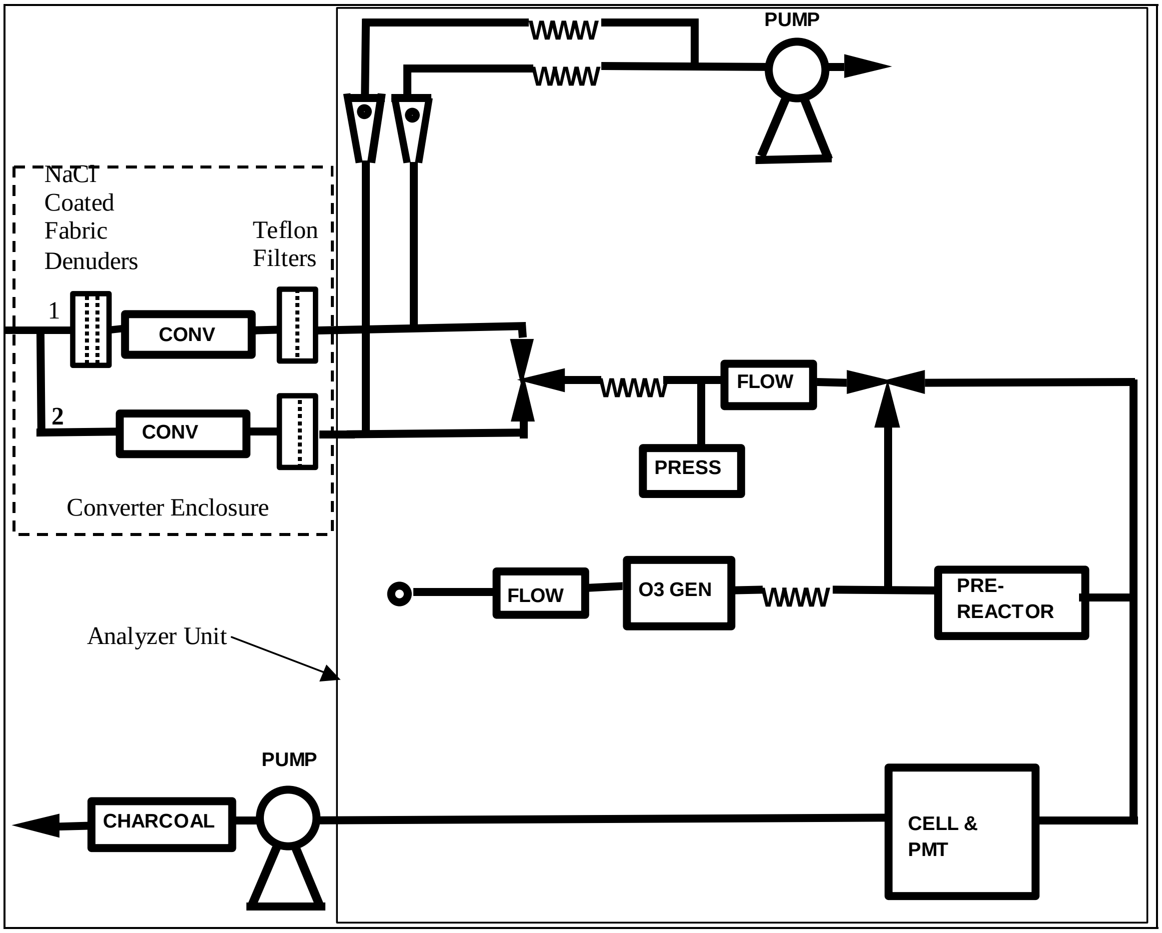


Figure 2-1. Schematic of the dual channel NO_y-NO_y* analyzer

A SOP was developed during the previous contract period to provide guidance for all QC procedures and documentation. Since an objective of this study was to test operational consistency of these analyzers, special QC steps were included as follows:

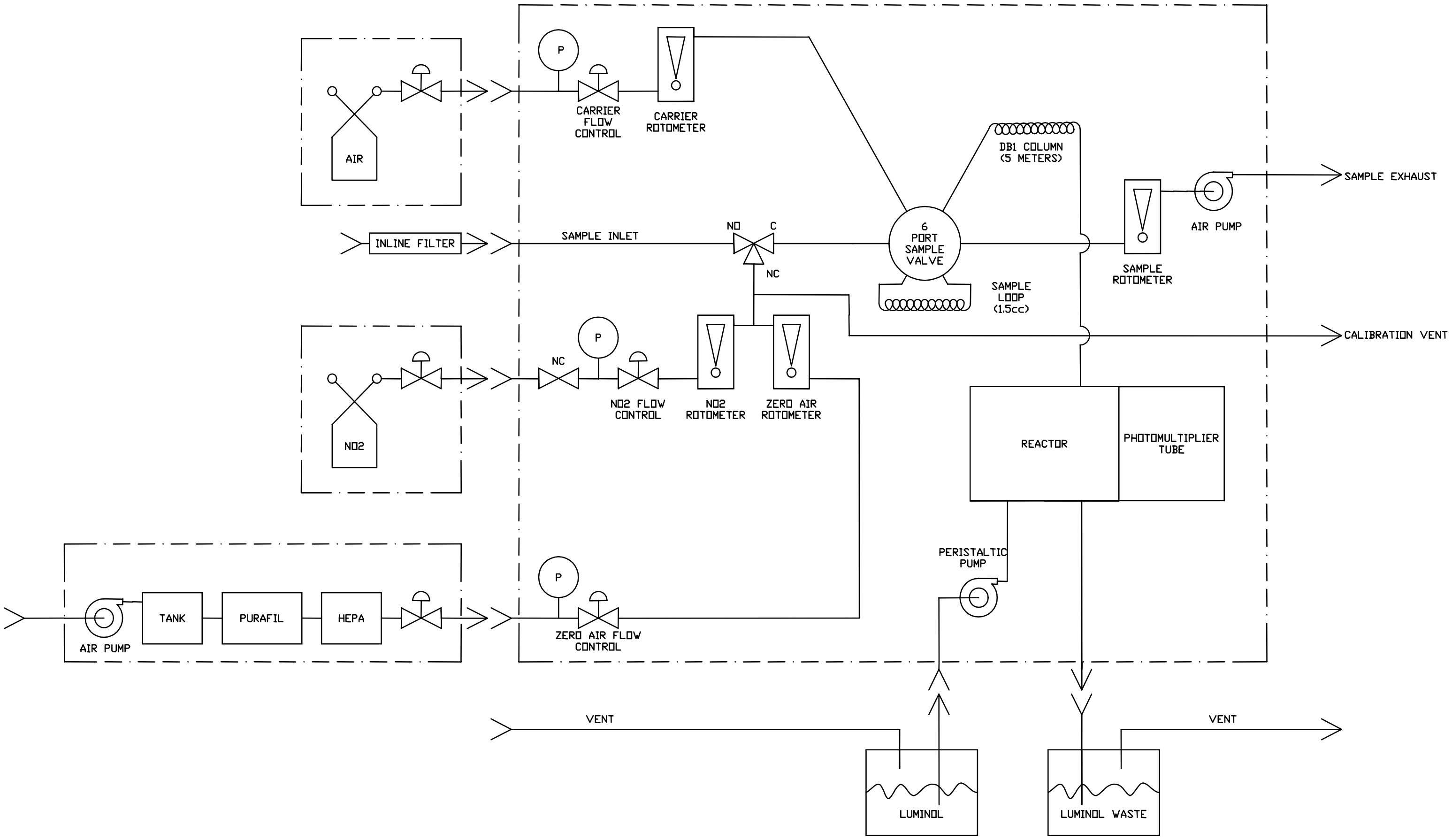
- The instruments were collocated to determine consistency relative to each other.
- Zero checks were performed five times a day. At Riverside, the pure air was produced with an Aadco 747 generator, while at Azusa an air compressor with a Purafil scrubbing cartridge was used.
- Weekly QC checks included the following:
  - Span check with NO produced by dilution of NO in N_2 from a certified compressed gas cylinder with zero air using a ThermoEnvironmental model 146 dilution calibrator.
  - Converter check with NO_2 generated by gas-phase titration of NO with ozone by the ThermoEnvironmental model 146 dilution calibrator.
  - Converter check with NPN produced by dilution of NPN from a certified compressed gas cylinder with zero air using a ThermoEnvironmental model 146 gas calibrator.
  - Challenge with nitric acid from a permeation tube source diluted with zero air.
  - Challenge with ammonia. The source of ammonia was a permeation tube at the Riverside site and a certified compressed gas cylinder in nitrogen at the Azusa site. This was necessary, as converters have been found to convert higher percentages of ammonia as they age, which could potentially bias the results when comparing two converter channels.
  - Challenge with air from which only nitric acid was removed using sodium chloride coated filters.

2.3 NO_2/PAN Gas Chromatograph

Figure 2-2 is a schematic of the instrument. A room temperature (25 ± ^{o}C) chromatographic column is operated on a carrier stream of zero air at a flow rate of about 40 ml/min. The column effluent passes through a luminol detector. Ambient air is drawn through a sampling loop connected to a six-port GC injection valve. The ambient sample is injected at 1-minute intervals (i.e., the sample switched briefly into the carrier stream). PAN elutes from the column several seconds after NO_2. Excess luminol in the detector reacts quantitatively with NO_2 and with PAN, generating light that is detected by a photo multiplier tube. The intensity of the light is proportional to the amount of NO_2 or PAN reactant present in the detector. The output of the PMT is amplified and fed to the NO_2/PAN GC computer data acquisition and analysis system, which stores and analyzes one complete chromatogram every minute. The NO_2 and PAN peaks in the chromatogram are processed to generate peak areas, a calibration factor is applied, and the resulting ambient NO_2 and PAN concentrations in ppb are stored on the NO_2/PAN GC computer along with the original chromatogram. The NO_2 and PAN concentrations are also sent to the monitoring station data logger, along with sample mode information.

An SOP was developed during the previous contract period to provide guidance for all QC procedures and documentation. QC consisted of zero checks that were done automatically in conjunction with the NO_y-NO_y* analyzers. In addition, weekly checks included challenging the instrument with NO_2. PAN has been found to give twice the response of NO_2, therefore it was not necessary to perform routine PAN calibrations. Occasional PAN tests were performed using synthesized PAN injected into a Teflon bag. The PAN concentration was determined by measuring NO_y with a chemiluminescent analyzer and measuring NO_2 with the calibrated NO_2/PAN GC. PAN concentrations were calculated by subtracting the NO_2 (the primary interferent in the synthesis) from the NO_y concentrations.

Figure 2-2. Schematic diagram of the NO_2/PAN gas chromatograph.



3.0 Results and Discussion

3.1 Preparation of NO_y Analyzers for the LTADS

Three ThermoEnvironmental NO-NO_y analyzers were renovated after use in the CCOS monitoring study. All were missing one or more components that were replaced. The analyzers were thoroughly cleaned, leak checked, zero adjusted, and spanned. The operating parameters were adjusted so that they were all the same. The analyzers' noise and sensitivity were determined and found to be within specifications. Their responses to NO_2, PAN, nitric acid, nitrous acid, and n-propyl nitrate (NPN) were determined and the converter temperatures were adjusted for 100% response to all of those species. The response to 60 ppb of ammonia was found to be less than 1 ppb.

The calibration of the mass flowmeters of three ThermoEnvironmental 146 calibrators were checked against our bubble and mass flow meters. The resulting calibration was posted on each calibrator.

A one-day workshop was presented to LTADS operators on maintaining NO_y analyzers. This primarily involved a detailed discussion of the SOP. Appendix A contains a copy the syllabus and the slides used.

3.2 Operation of a NO_y and Nitric Acid Measurement Network

3.2.1 Standard Operating Procedures

The standard operating procedures (SOPs) for operating the NO_y-NO_y* analyzer were those used in the previously (Fitz, 2002), while the one for the NO_2/PAN was the one prepared for the Central California Ozone Study (CCOS). These documents contain all the details for operating the analyzers and performing routine quality control checks. The heart of these documents is the weekly checklist, which provides for all the QC steps required for proper maintenance. Figures 3-1 and 3-2 show the checklist forms that were used.

Figure 3-1. Checklist used for NO_y/NO_y-NA Analyzers.

TEI Model 42CY Weekly Checklist - CE-CERT Site

Date: __________ Site ________________
Technician: __________
Time: __________ PDT/PST

Dilution Calibrator Information			**NO**			**NPN**		
SN			NO Cyl ID			NPN Cyl ID		
Cert Date			Cyl Conc		ppm	Cyl Conc		ppm
Dilution Flow		l/min	NO Flow		ml/min	NPN Flow		ml/min
O3 Setting		%	Calc Conc		ppb	Calc Conc		ppb

Permeation Calibrator Information

NH3 Perm Flow		ml/min
NH3 Dilution Flow		L/min
HNO3 Perm Flow		ml/min
HNO3 Dilution Flow		L/min
Water Bath Setpoint		C
Water Bath Temp		C
Fill Water Bath?		y/n

Check Parameter	**SN:CTL42** **NOy-NA**	**NA**	**NOy**	**Other**	**SN:CTL42** **NOy-NA**	**NA**	**NOy**	**Other**
Range, ppb				***********				***********
Averaging Time	***********	***********	***********		***********	***********	***********	
Calibrate, Factors, bkg		***********		pre:_____		***********		pre:_____
Calibrate, Factors, coef				***********				***********
Calibration, zero	***********	***********	***********	pre:_____	***********	***********	***********	pre:_____
Cell Pressure	***********	***********	***********		***********	***********	***********	
Internal T	***********	**********	**********		***********	**********	**********	
Chamber T	***********	**********	**********		***********	**********	**********	
Cooler T	***********	***********	***********		***********	***********	***********	
Converter T		***********		***********		***********		***********
Converter Set		***********		***********		***********		***********
Ozonator Flow	***********	***********	***********		***********	***********	***********	
Sample Flow	***********	***********	***********		***********	***********	***********	
Bypass Flow		***********		***********		***********		***********
Changed Filters?		***********		***********		***********		***********
Changed Denuders		***********	***********	***********		***********	***********	***********

Calibration Parameter	**Stabalized Digital Readout (ppb)**				**Stabalized Digital Readout (ppb)**			
Zero Air				***********				***********
NO				***********				***********
GPT				***********				***********
NPN				***********				***********
HNO3-Free Ambient				***********				***********
HNO3				***********				***********
NH3				***********				***********

COMMENTS

Figure 3-2. Checklist used for the NO_2/PAN GC.

CE_CERT PAN/NO2 GC Weekly Checklist (page 1 of 2)

Date:			**Project:**	18392
Technician:			**Site:**	CE-CERT
Time:		PDT/PST	**S/N:**	

NO Cylinder ID			**Calibrator SN**	
ID:			NO Flow	
NO conc:		ppm	Dilution Flow	
Cert date:		< 6 months	Ozone Setting	

Cylinder Pressures

NO cylinder pressure:		(psi)	>500
NO regulator pressure		(psi)	15 +/- 1

SAMPLE Mode checks

Sample Air flow rate		ccm	100
Carrier gas front panel pressure		(psi)	25 +/- 1
Carrier gas flow rate			30
Chromatogram shape normal?		yes/no	yes
Baseline flat?		yes/no	yes
Baseline raw level		counts/100 ms	<1000

Analyzer Responses

Mode	BKG counts	NO2 counts	PAN counts	NO2 ppb	PAN ppb
SAMPLE					
ZERO					
SPAN					

Span Calculation

NO2 response ppb/NO2 setpoint ppb		ratio	1 +/- 0.05

CE_CERT PAN/NO2 GC Weekly Checklist (page 2 of 2)

Maintenance information:

Teflon filter date:		Date last changed	< 30 days
Zero Air Purafil Date		Date last changed	< 90 days
Zero Air filter date:		Date last checked	< 90 days
Luminol Level		% of bottle	90% of bottle

Analyzer Sofware Settings

Cycle Timing (seconds)		**Calibration Factors**	
start	0	A_NO2	
Sample load		B_NO2	
Cycle		A_PAN	
NO2 start		B_PAN	
NO2 stop		A_Bg_NO2	
PAN start		B_Bg_NO2	
PAN stop		A_Bg_PAN	
BKG start		B_Bg_PAN	
BKG stop			
cal factors			

		Cal Schedule	
gate time (msec)		Every (hr):	
		Zero (min):	
		Span (min):	
		Transition cycles (#):	

Identification

3.2.2 Siting and Installation

Riverside

The installation included the following equipment:

- Two ThermoEnvironmental Instruments model 42CY dual converter NO_y, NO_y-NA analyzer (SN 58440 and SN 58441).
- One NO_2/PAN Gas Chromatograph.
- ThermoEnvironmental Instruments model 146 Calibrator. The calibrator was used manually for calibration checks.
- Scott Marrin NO in N_2 certified calibration gas.
- Permeation bath with NH_3 and HNO_3 permeation tubes (constantly purged with N_2).
- Campbell CR10 Data Logger. The data logger was programmed to collect data averaged for 10 minutes. The data logger was programmed to supply zero air five times a day for 30-minute intervals (at 04:00, 09:00, 14:00, 19:00, 23:00 hrs).
- Zero air supplied by an Aadco purification system.

Azusa

The installation included the following equipment:

- ThermoEnvironmental Instruments model 42CY dual converter NO_y, NO_y-NA analyzer (SN 58313).
- One NO_2/PAN Gas Chromatograph.
- ThermoEnvironmental Instruments model 146 Calibrator. The calibrator was set up to perform zero and span checks on the NO_y analyzer 5 times a day for 50 minutes each time (at 03:00, 7:00, 11:00, 16:00, and 22:00 hours).
- Scott Marrin NO in N_2 certified calibration gas.
- Scott Marrin NH_3 in N_2.
- Campbell CR10 Data Logger programmed to collect data averaged for 10 minutes.
- Zero air source consisting of a diaphragm compressor, holding tank, and Purafil adsorption tower.

3.2.3. Network Operation

Sites checks were performed at approximately weekly intervals in Riverside during the summers of 2001 and 2002. Site checks were not performed and the instruments were shut down from November 2001 through March of 2002 to conserve resources and avoid instrument damage.

3.2.4 Data Management

Data Collection

The NO_y data were collected using Campbell CR10 digital data loggers as 10-minute averages. The data logger initiated automatic zero air checks every four hours and flagged these periods. The date/time stamp for the raw data were “time ending” in Pacific Standard Time. The NO_2/PAN GC data were taken from the data stored in its computer, which consisted values for each 2-minute analysis sequence. Data were reviewed and downloaded weekly, and maintained in a networked PC that was backed-up weekly.

Data Validation

Data were validated for the year 2002 only and submitted to the ARB. Data from the period from May to December 2001 were not validated due to insufficient record keeping by the site operator that made data validation difficult, if not impossible, to perform adequately. For the 2001 data set, periods where the instruments obviously were not working were removed, as were obvious outliers (negative values greater than 1 ppb and values more than twice the peak 2001 concentrations). The data were submitted as “unvalidated”.

The data validation process consisted of ten steps:

1. Identify measurement period and period to be processed.
2. Obtain log books, check lists and calibration records and summarize.
3. Describe the instruments, data collected, etc.

4. Combine site data into files for each site for each year (or less, if >65,000 rows/year).
5. Calculate 10-minute medians from the 2-minute GC data and add these to the NOx data files.
6. Generate new spreadsheets that shift time/date indicated to beginning time, PST.
7. Apply outlier codes to data based on log entries, data logger programming, and obvious malfunctions (Level 0 validation) to data and output files.
8. Apply calibration factors to the data and output the data as Level 0.
9. Screen valid coded data for outliers and determine validity (Level 1 validation).
10. Evaluation by the Principal Investigator.

Data status flags used were as follows:

Codes	Definition
0	Analyzer not present
1	Valid ambient data
2	Valid auto zero data
3	Zero/Span check or calibration
4	Transition (from auto zero, calibration, etc.)
5	Maintenance, data not valid
6	Missing data
7	Invalidated by Level 0 or Level 1 validation
8	Auto span
9	Unknown status

The code value “-1” was placed in the data field for all cases when the data code was not “1” or “2.”

The logbooks, checklists and calibration records were used to provide “Level 0” corrections to the data collected at each site. Each of the Level 0 data corrections was documented in specific “data validation log” for each site. These preliminary data were output as “step 7” data.

A computerized “outlier screening” was performed on the Level 0 data. The screening looked for excessively high or low data values, as well as abnormal rate of change from one hour to the next to “flag” data as possibly erroneous. The actual checks included:

- Flagging data less than -1 ppb.
- Flagging NO_y data greater than 200 ppb.
- Flagging PAN data greater than 10 ppb
- Flagging nitric acid data greater than 5 ppb
- Flagging data when absolute value of the difference between the NO_y, NO_y-HNO_3 or HNO_3 of the first analyzer was more than 5 ppb different from that for the same parameter on the second analyzer, when the first analyzer’s NO_y value was at least 30 ppb.

A “Level 1” data review was performed on these flagged data. The flagged data were assessed to determine whether they were likely valid data or invalid. A log was kept for all data that were reviewed. The review log included the period of time affected, the outlier screen routine that “flagged” the data, a brief data review note, and final data disposition (whether the data were kept or invalidated). The data designation code “7” was used for most data invalidated by this outlier screening.

The Principal Investigator reviewed the data resulting in the following data being invalidated:

CE-CERT Data	Reason
NOy1,2; NA1,2 4/29/02 07:10-07:50	Calibration, not flagged correctly
NOy1,2; NA1,2 6/1902 07:50-08:20	Calibration, not flagged correctly
NA2 7/4/02 @7:10-8:10	Suspect NO_y-NA Converter failing
NA2 7/6/02@ 20:30 to 7/8/02@ 10:00	NO_y-NA Converter failing
NOy1,2; NA1,2 8/14/02 15:20-17:10	Calibration, likely notation error in logbook
NOy1,2; NA1,2 8/27/02 09:50-18:50	Calibration, likely notation error in logbook
NOy1,2; NA1,2 9/4/02 09:50-16:10	Calibration, notation error in logbook
NOy1,2; NA1,2 11/05/02 15:30-17:00	Calibration, not flagged correctly

Azusa Data	Reason
NA1 6/25/02 09:40	Very high, data after this point not code 1
NA1 10/06/02 0:50-2:50	High and erratic, NOy1>>NOy2
NA1 11/25/02 1510-1520	High and erratic, NA2 is also a bit erratic
NA2 05/27/02 12:10-14:40	High and erratic, NA1 low and steady
NO_2/PAN 7/31/02 11:10-11:20	Calibration, not flagged correctly
NO_2/PAN 8/06/02 08:20:18:50	High and erratic compared to NO_y/NA, Instrument malfunctioned after 18:50

Note: The occasional high and erratic NO_y and NA observed concurrently with both analyzers indicate a local source of HNO_3 –like species at Azusa.

The “final” validated data is included with this report and used in the data analysis in this report are the data from the data processing step 9, Level 1 validation.

3.3 Results

3.3.1 Riverside (CE-CERT)

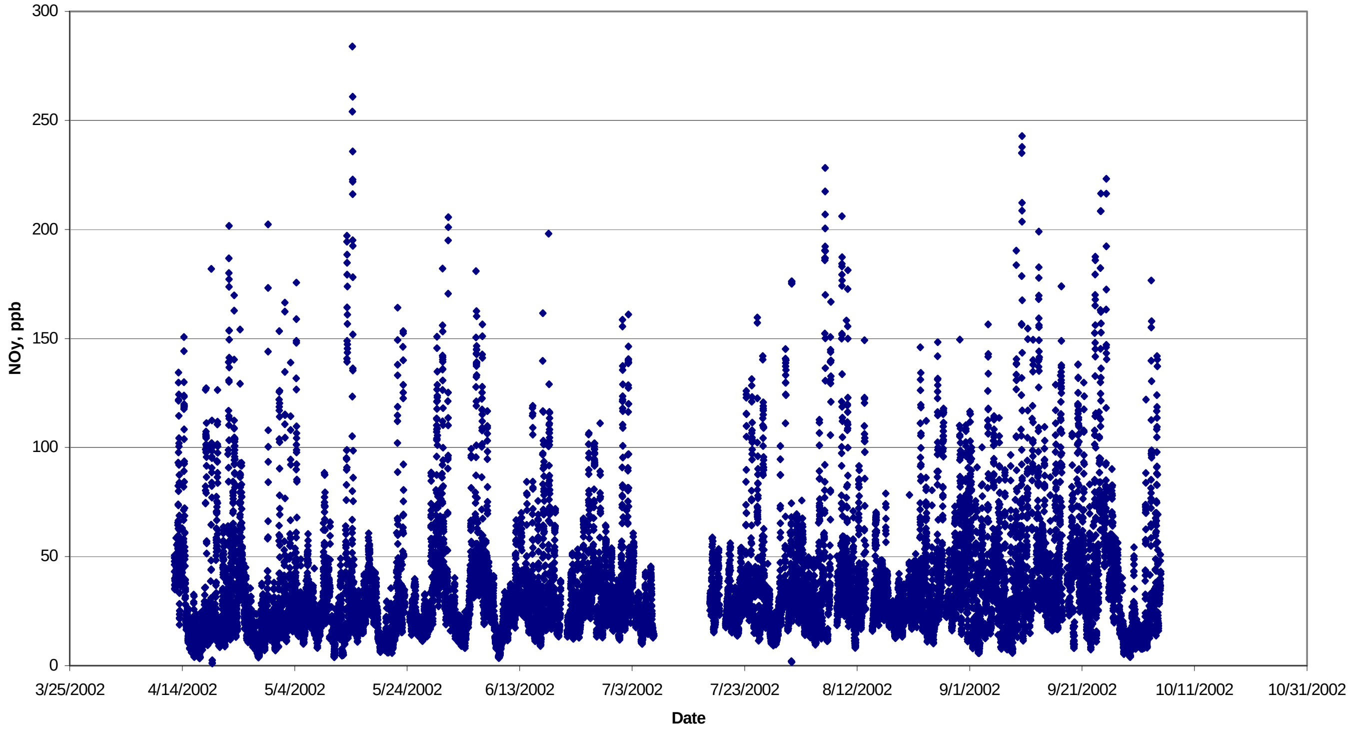
Figure 3-3 summarizes the NO_y data for both analyzers at Riverside for the entire measurement period. Each data point represents a 10-minute average. The analyzers respond approximately the same for the periods with peak concentrations of about 250 ppb. Figure 3-4 is a plot of the NO_y data from one analyzer versus the other for all periods when validated data are available from both instruments. The two are in good agreement for most of the period.

Figure 3-5 is a time series plot of the corrected nitric acid for both instruments. Note that there are sporadic outliers for which removal could not be justified. There also does not appear to be much of a seasonal variation. Analyzer 58440 appears to be biased low relative to analyzer 58441. This is likely due to a small converter mismatch causing negative values for nitric acid (which were removed in the data processing). On the other hand, analyzer 58441 may be biased high for the same reason since values are often non-zero for days at a time when it has been shown that nitric acid concentrations should be near zero most nights.

Figure 3-6 shows the time series for both analyzers during July 2002 when nitric acid concentrations are expected to be relatively high compared with the rest of the year. The diurnal variation is quite distinct for both analyzers, especially for analyzer 58441. The low bias of analyzer 58440 is clearly evident. Figure 3-7 shows the nitric acid concentrations for one typical day, July 22, 2002. The nitric acid follows the expected diurnal variation, peaking at 16:00 hours. Figure 3-8 is a plot of nitric acid concentrations measured by one analyzer versus the other when both produced validated data. The correlation is quite poor. We conclude that it is possible to measure nitric acid, although the measurement is far from reliable.

Figure 3-3. (a) NO_y concentrations for SN58440 (NO_y1). (b) NO_y concentrations for 58441(NO_y2).

a.



b.

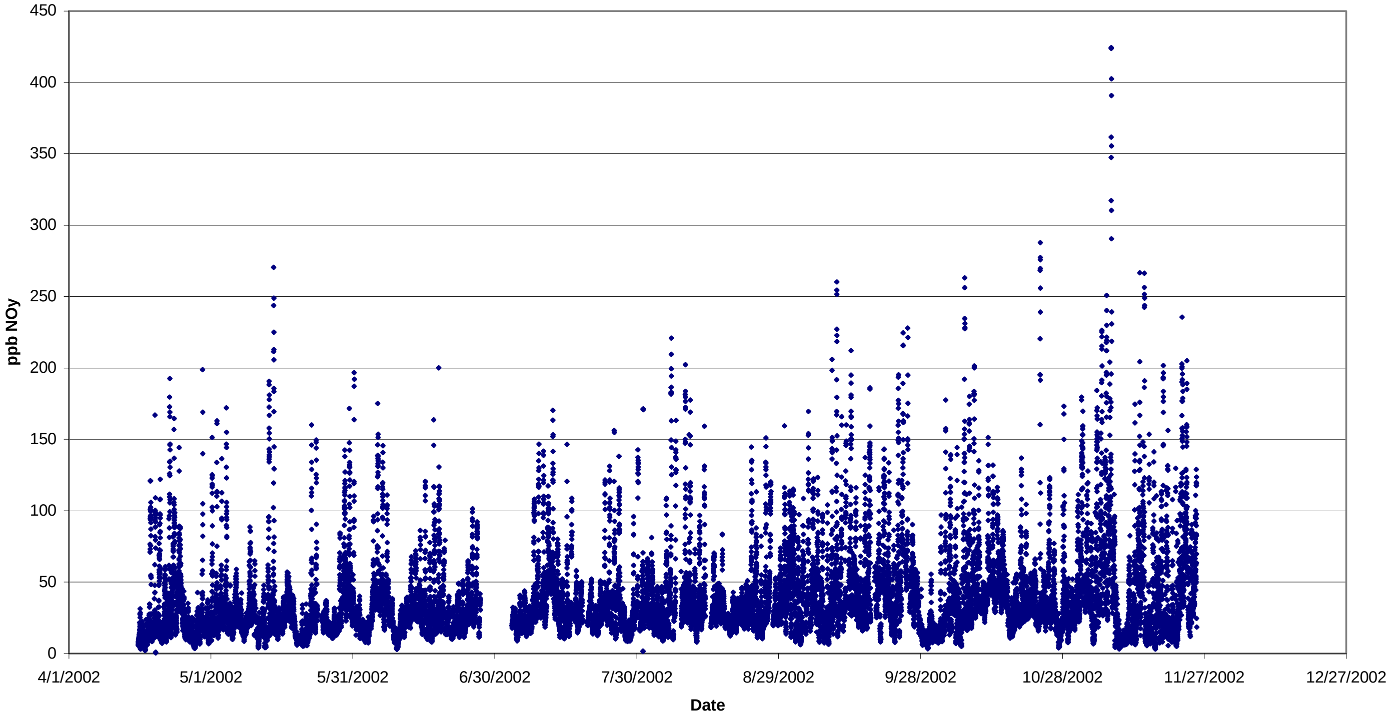


Figure 3-4. Comparison of NO_y between analyzers 58440 and 58441 (NOy1, NOy2).

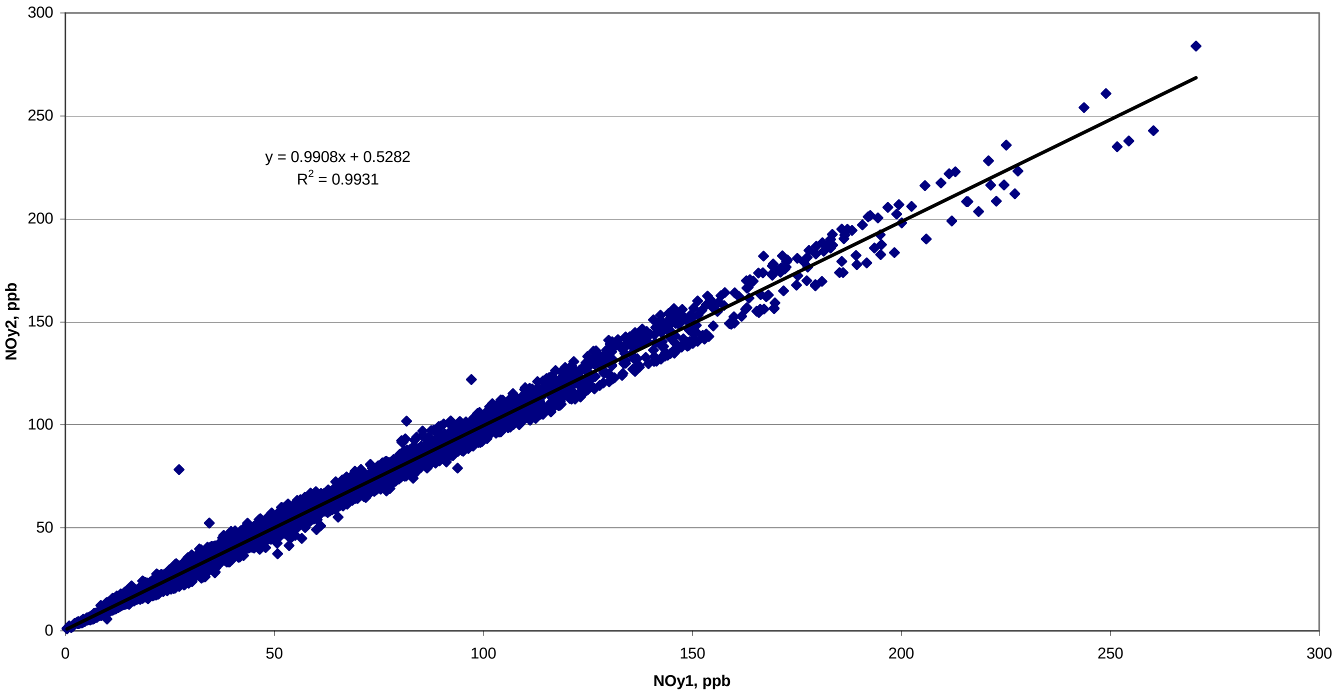


Figure 3-5. (a) HNO_3 concentrations for 58440 (NA1). (b) HNO_3 concentrations for 58441NA2).

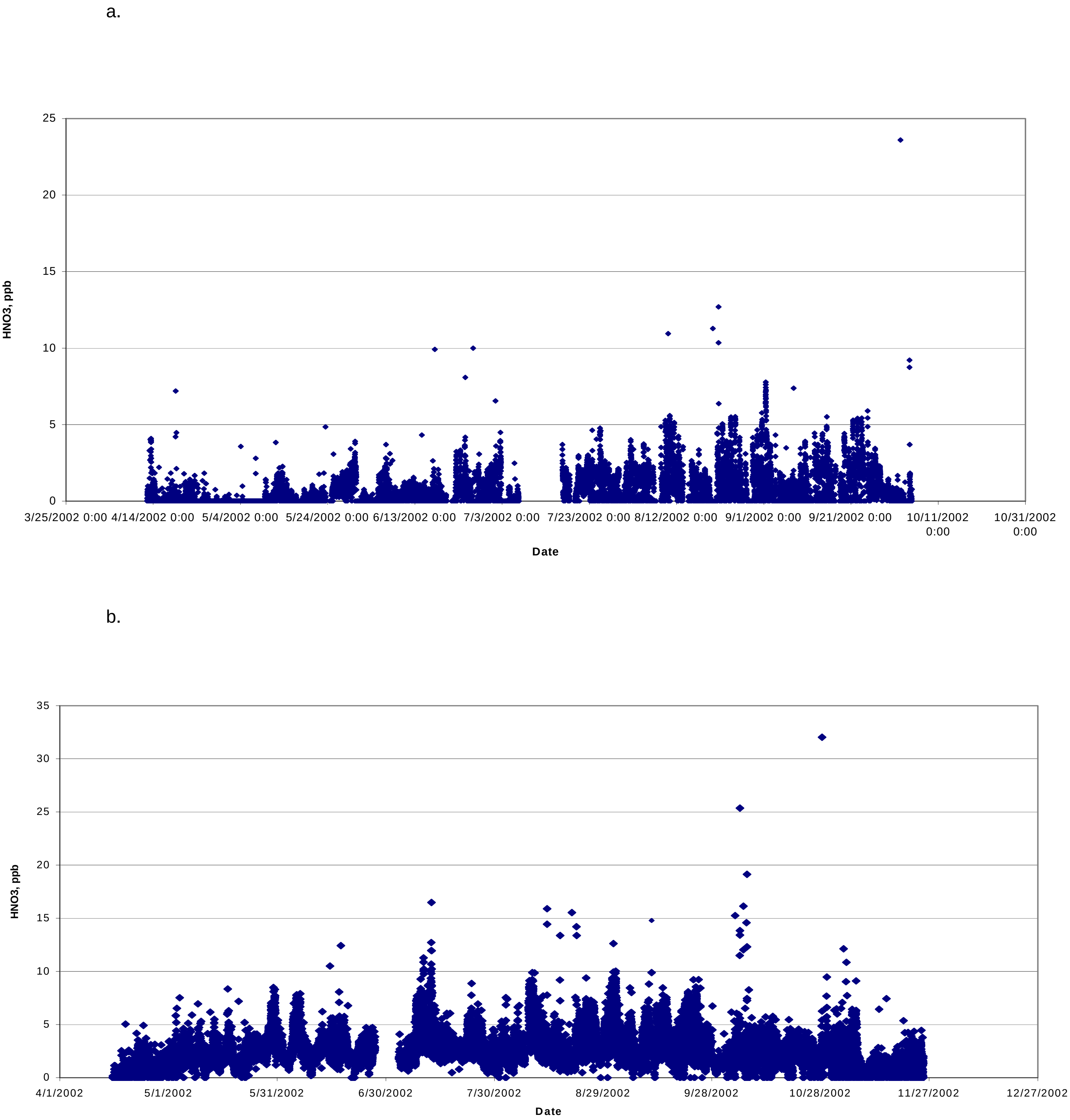
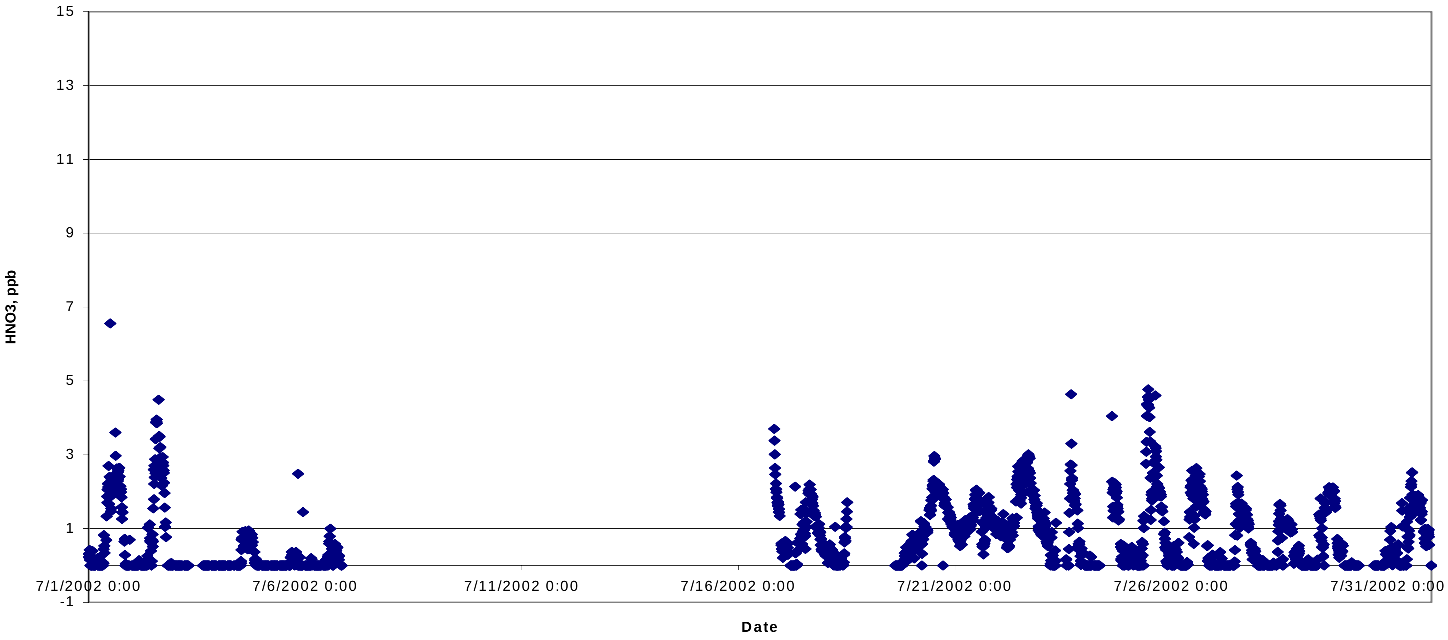


Figure 3-6. (a) Time series of nitric acid at Riverside during July 2002, Instrument 58440. (b) Time series of nitric acid at Riverside during July 2002, Instrument 58441.

a.



b.

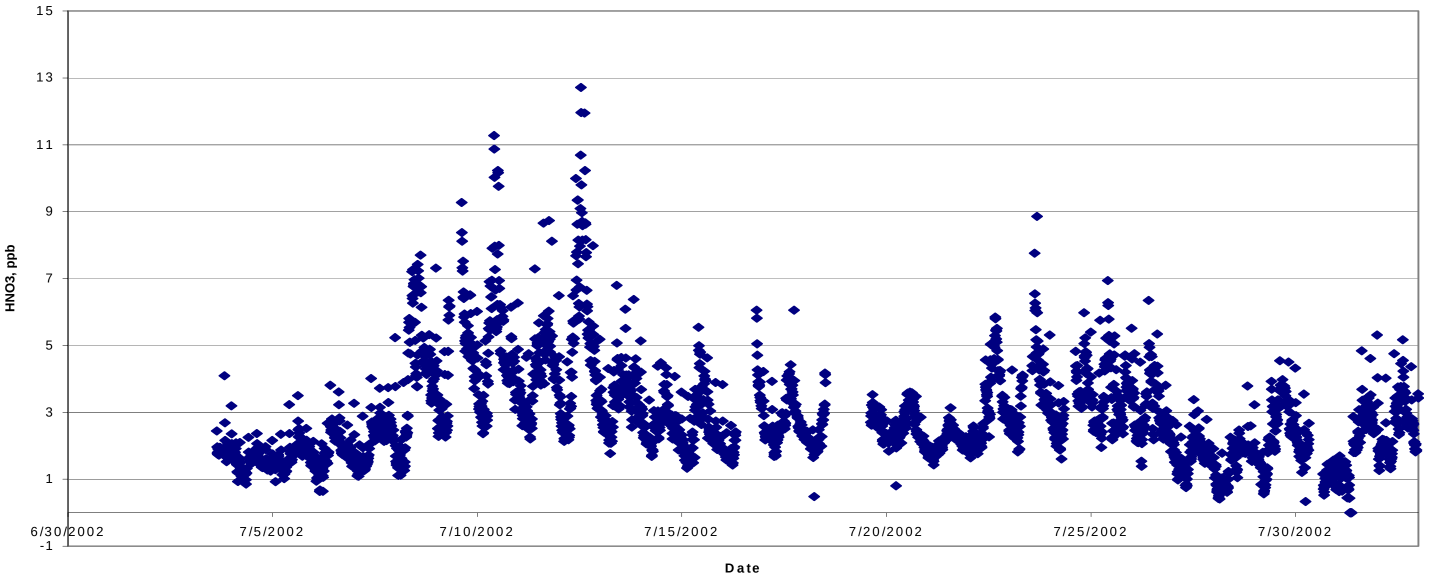
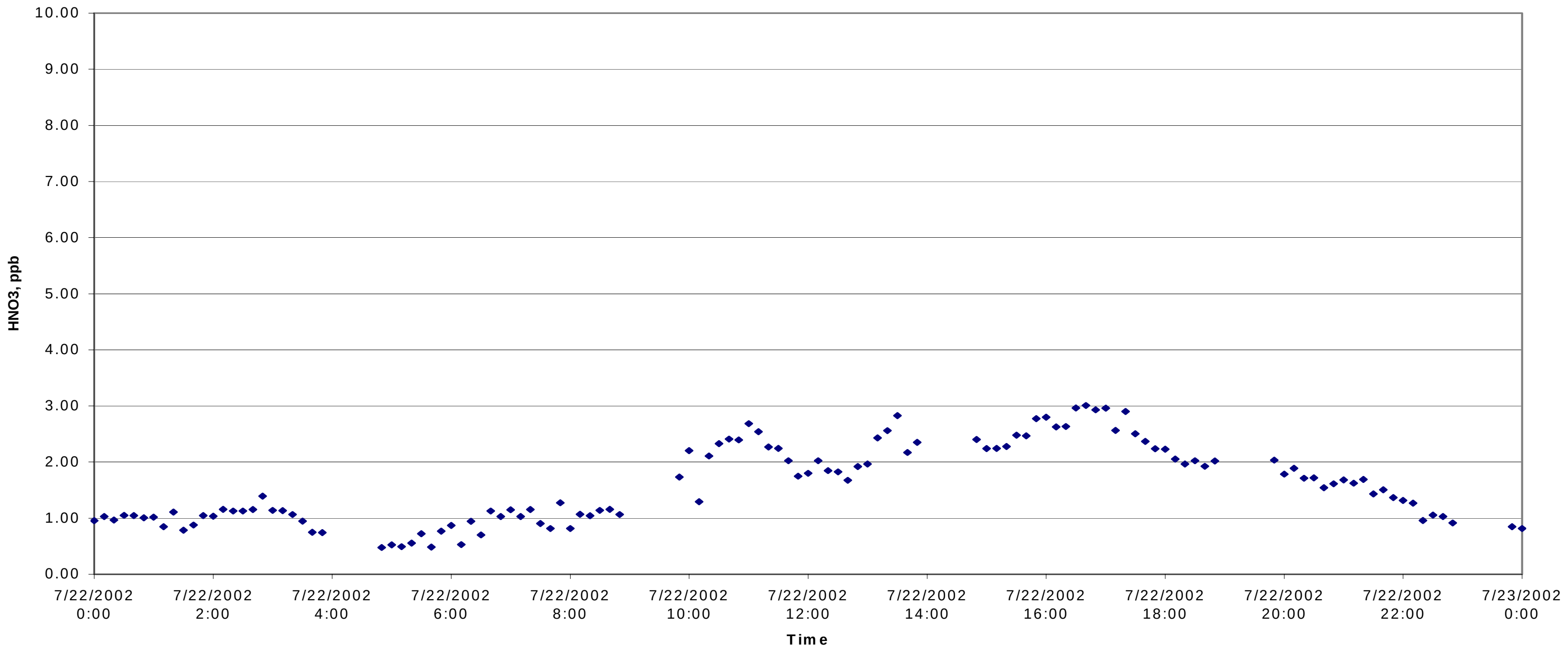


Figure 3-7. (a) Time series of nitric acid at Riverside during July 31, 2002, Instrument 58440. (b) Time series of nitric acid at Riverside during July 31, 2002, Instrument 58441.

a.



b.

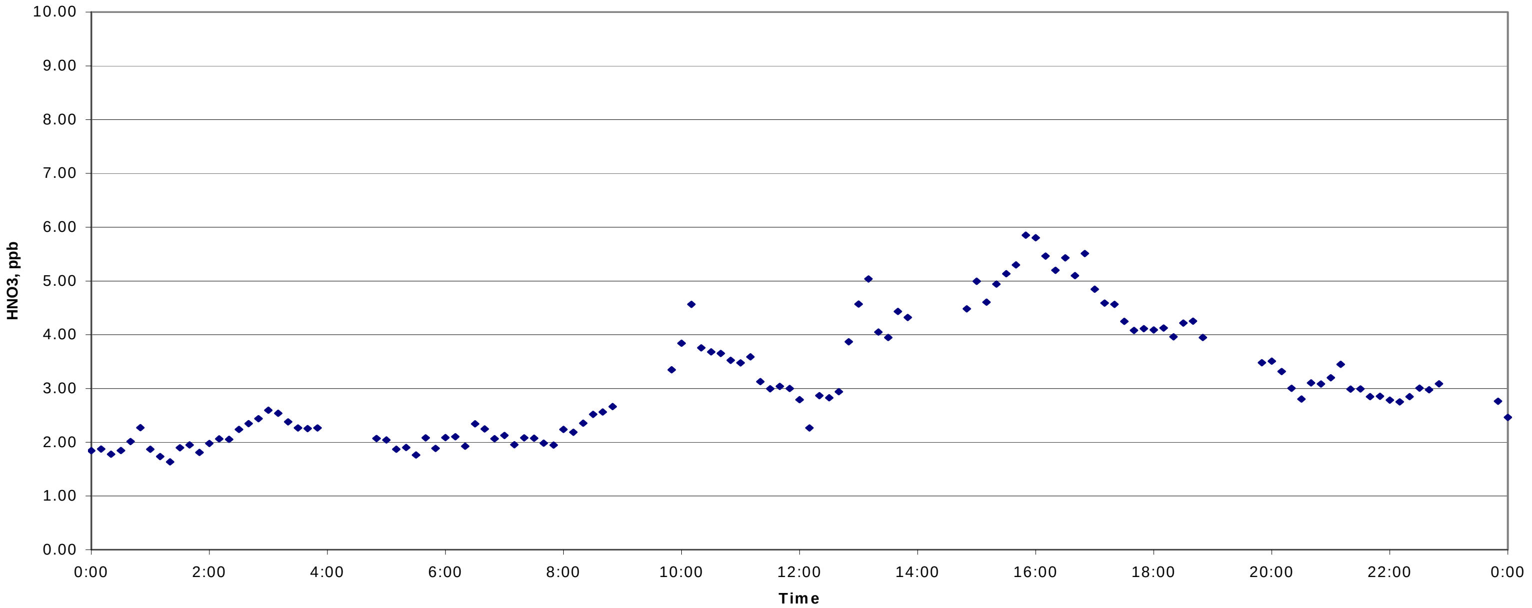


Figure 3-8. Comparison of HNO_3 measured by both analyzers at Riverside.

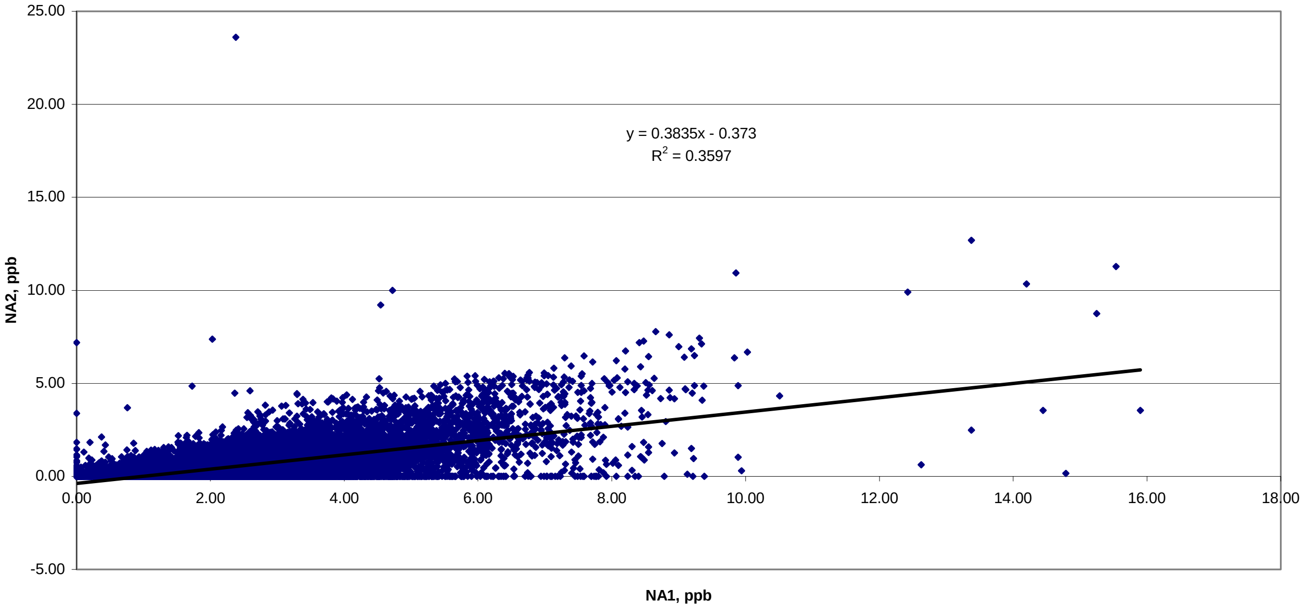
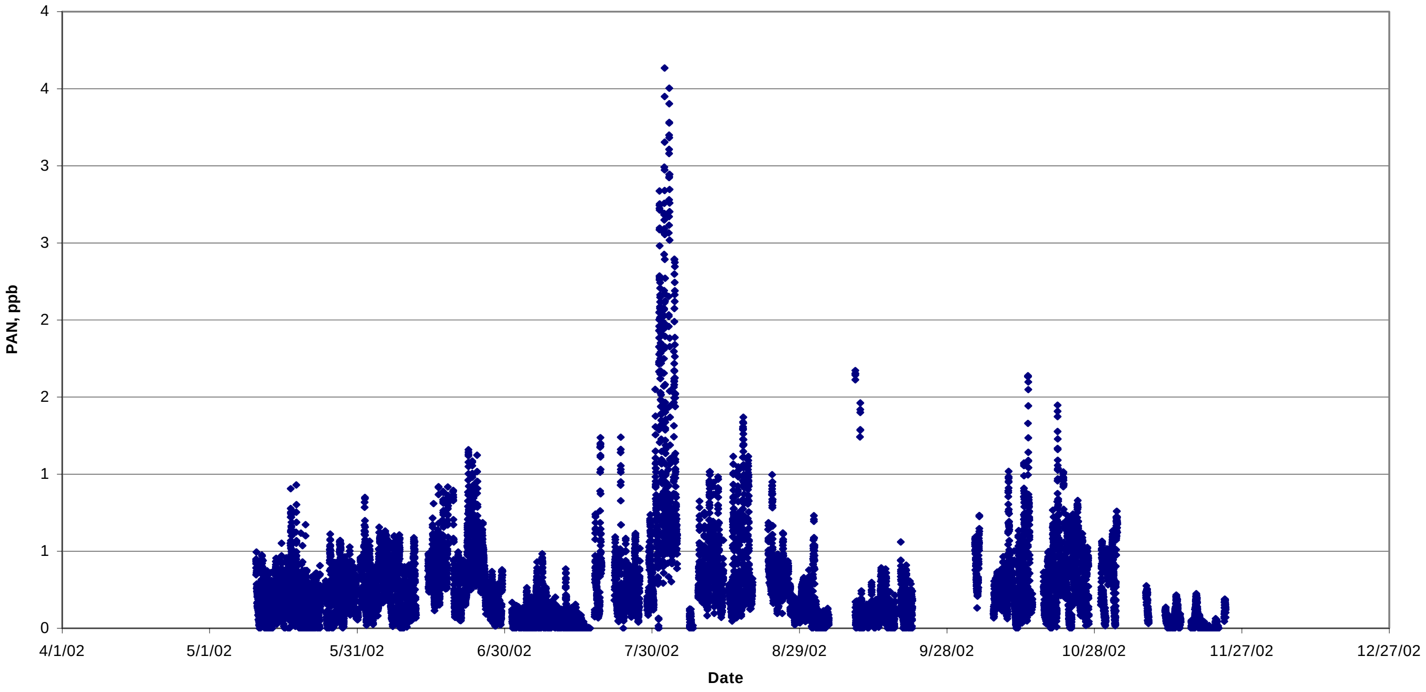


Figure 3-9 shows a time series of PAN and NO_2 concentrations from the NO_2/PAN GC for the measurement period. Peak PAN concentrations were typically one ppb, although an episode of 4 ppb occurred in early August. Figure 3-10 shows the month of July 2002. The diurnal distribution is clearly shown. Figure 3-11 shows a single day, July 22, 2002, in which the diurnal distribution can be seen in detail. PAN shows two maxima, one at noon and the other at 4 p.m. This is the expected behavior in Riverside, the first peak being due to locally generated secondary pollution and the second due to transport from the west.

Figure 3-9. (a) CE-CERT PAN and (b) NO_2 concentrations 2002 time series

a.



b.

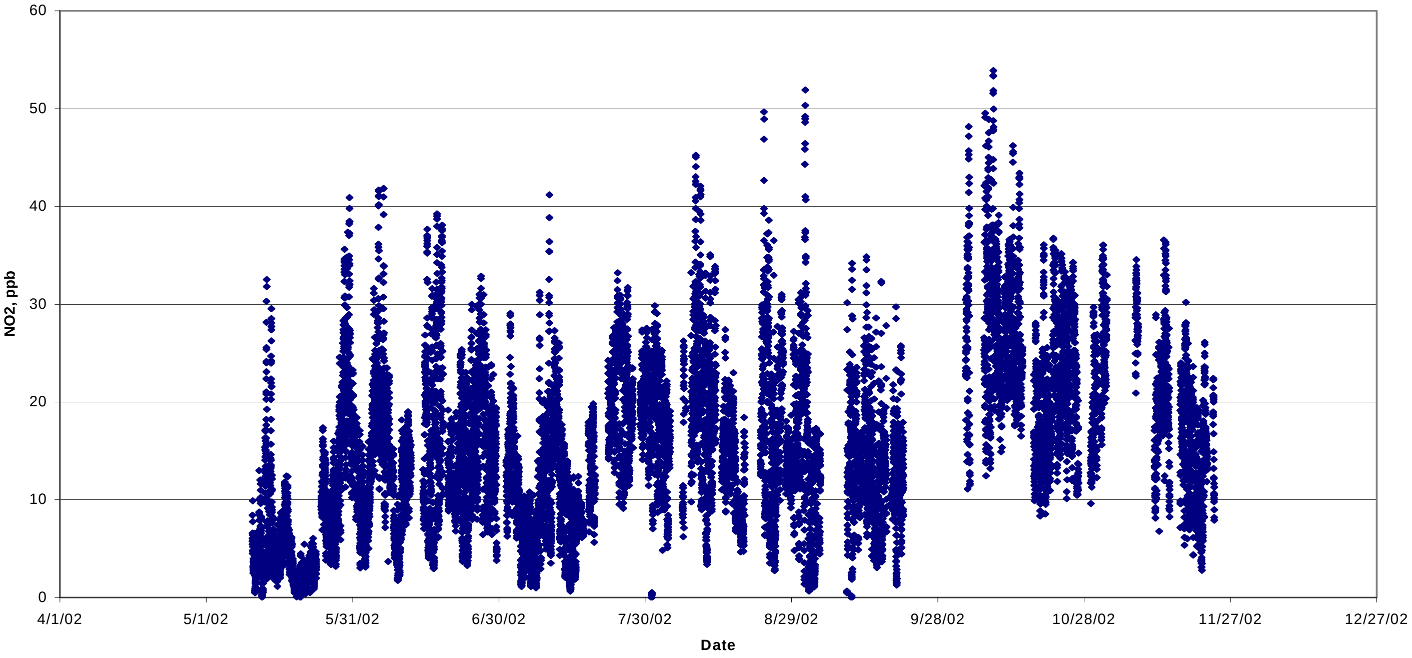
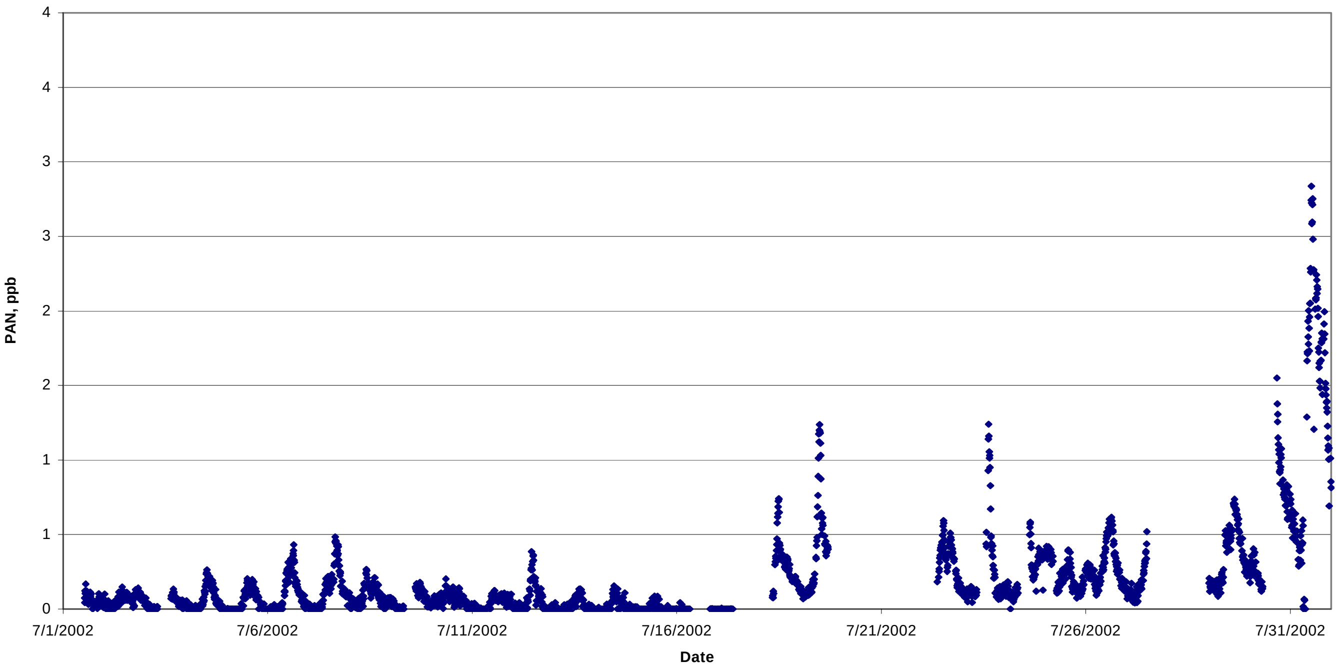


Figure 3-10. (a) CE-CERT PAN and (b) NO_2 concentrations July 2002 time series

a.



b.

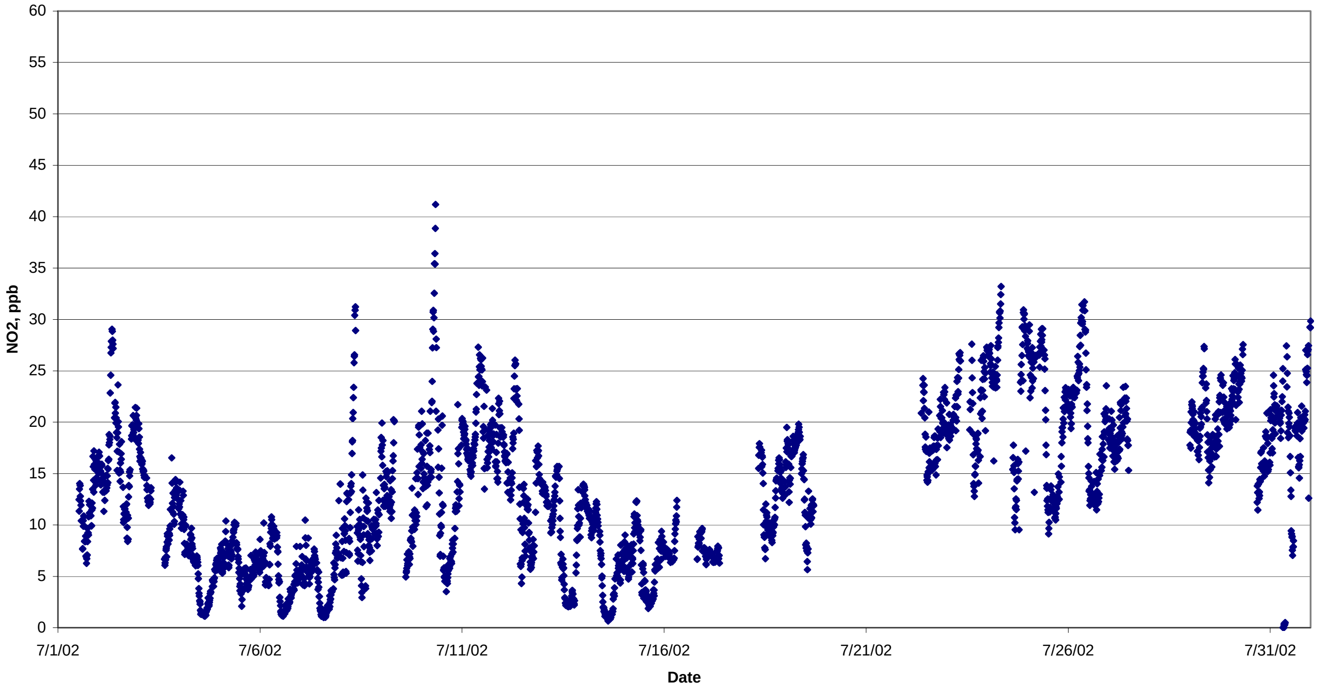
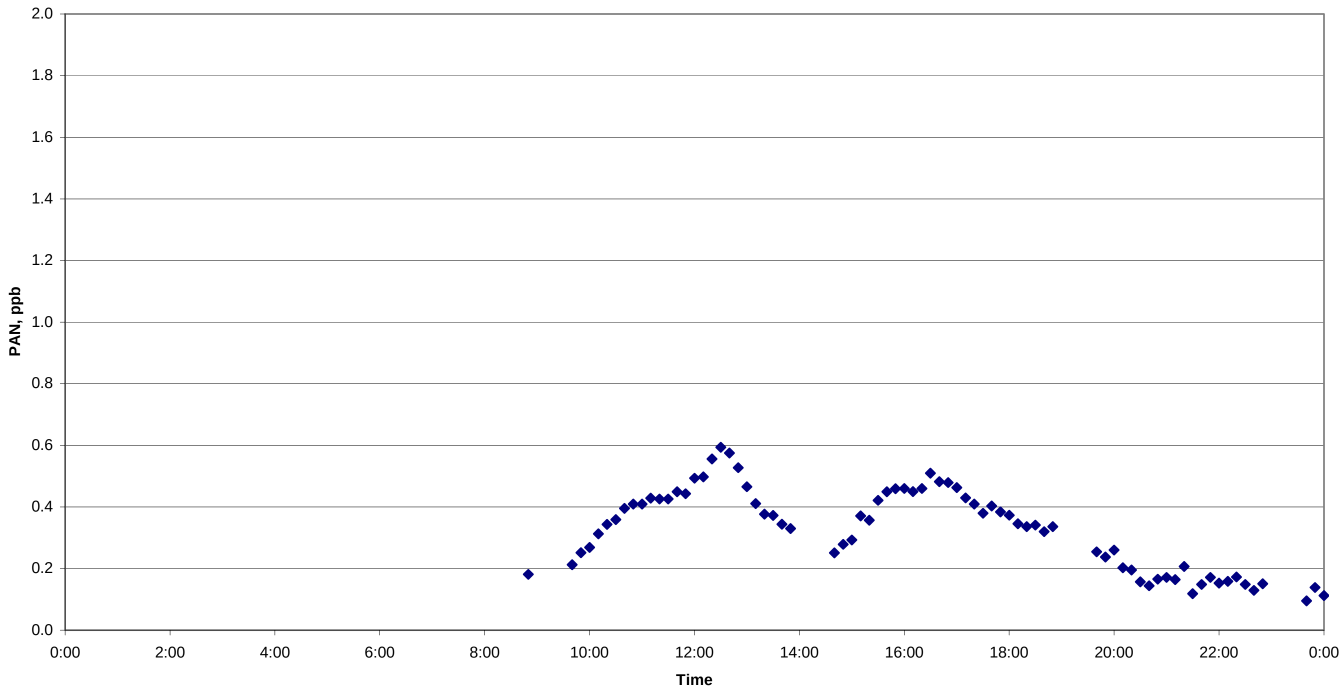
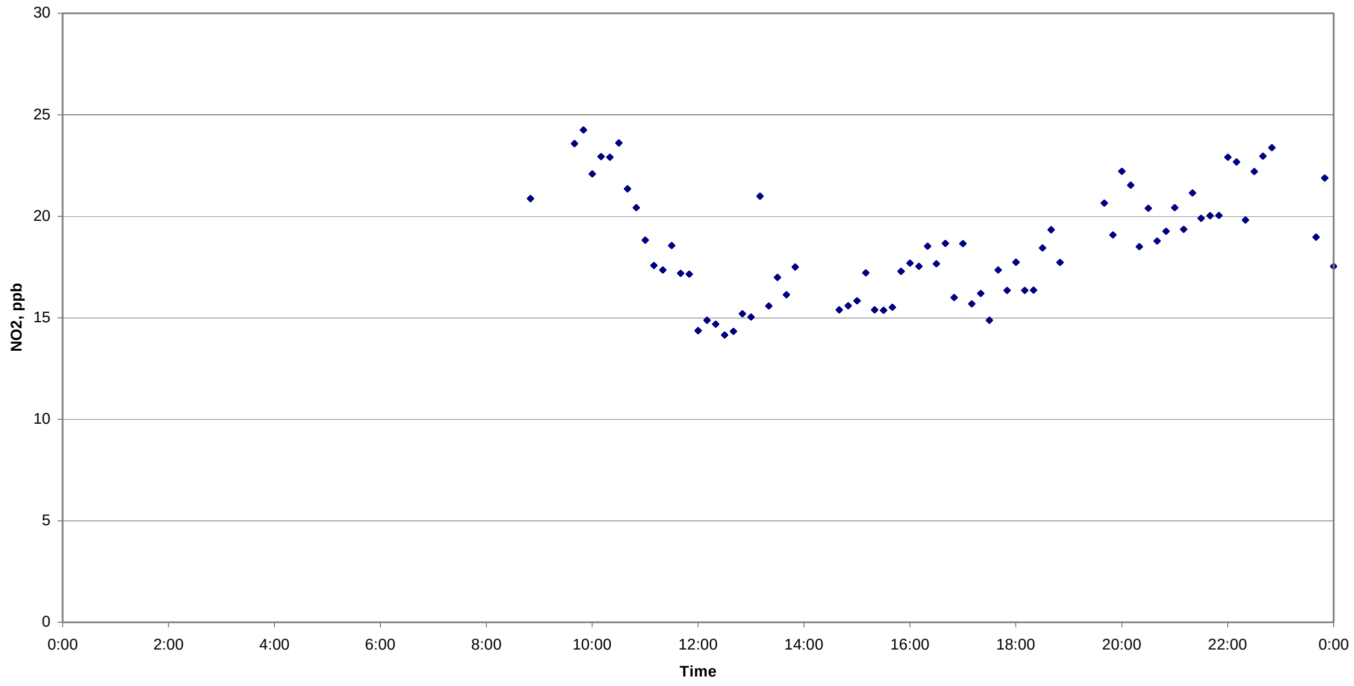


Figure 3-11. (a) CE-CERT PAN and (b) NO_2 concentrations July 22, 2002 time series

a.



b.



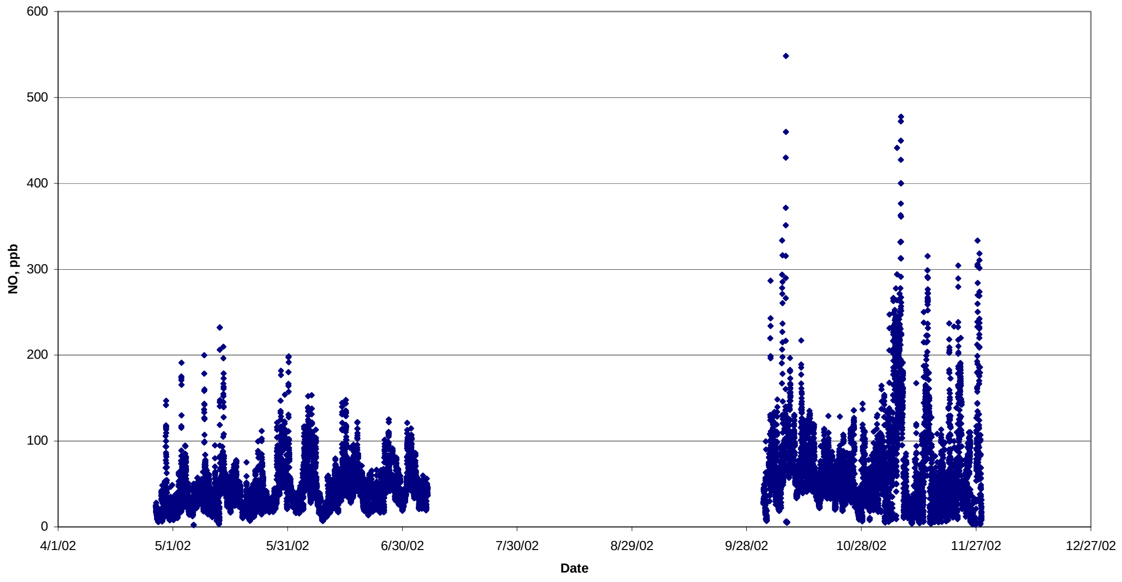
3.3.2 Azusa

Figure 3-12 summarizes the NO_y data for the analyzers at Azusa for the entire measurement period. Each data point represents a 10-minute average. This site was serviced primarily by student workers, and significant amounts of data were invalidated due to their repeated mistakes and inability to report instrumental problems. The most common mistakes were inadvertently disconnecting the instrument output leads during site checks and leaving the calibrator in the “zero” mode. Sample pump failures were also not noted. The peak concentrations were in the 500 ppb range, significantly higher than the peak values in Riverside.

Figure 3-13 shows a comparison between the two NO_y analyzers for periods when valid data were obtained from both. The very close agreement shows the quality of the validated data. Figure 3-14 summarizes the nitric acid data for both analyzers for the measurement period. As in the Riverside data, there does not appear to be any seasonal variation, rather a general spread of values from 0-10 ppb and one instrument appears to have a slightly high bias and the other slightly low. Figure 3-15 is a time series plot of nitric acid in May 2002. This is a month where data are generally available from both analyzers and when the higher nitric acid concentrations might be expected. The diurnal profile follows the expected curve, although analyzer 58438’s low bias clearly suppresses the nitric acid values obtained. It appears that analyzer 58313 is more accurately measuring nitric acid, and that peak values of 20 ppb were obtained. These peak values are typical of previous studies. These results are consistent with those observed in Riverside, where peak values are about half this concentration, mostly likely due to large sources of ammonia between Azusa and Riverside and the prevailing westerly winds in the afternoon. Figure 3-16 shows the detailed diurnal distribution of concentrations for a single day. While both show a peak near 14:00 hours, the low bias of analyzer 58438 is clearly evident. Figure 3-17 is a comparison of nitric acid measured by the two analyzers. The correlation is lower than that in Riverside, almost zero. We conclude that only one of the analyzers, 58313, was useful in measuring nitric acid. Peak concentrations were typically several hours earlier than Riverside, which is expected since that amount of time would be required for transport.

Figure 3-12. (a) Azusa NO_y concentrations at for SN58313. (b) NO_y concentrations for 58438.

a.



b.

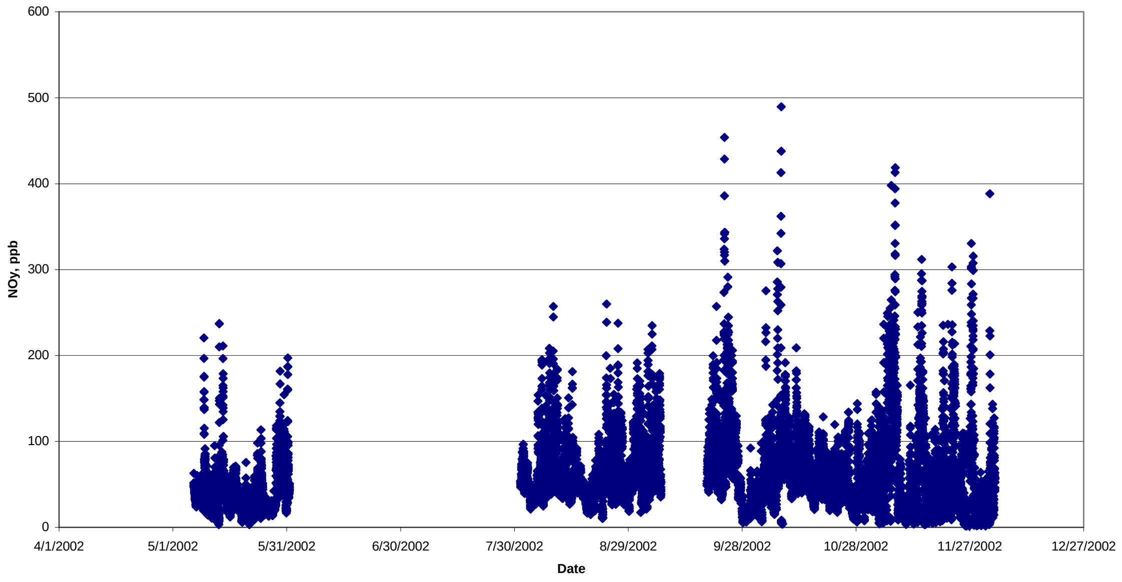


Figure 3-13. Comparison of NO_y at Azusa between analyzers 58313 and 58438.

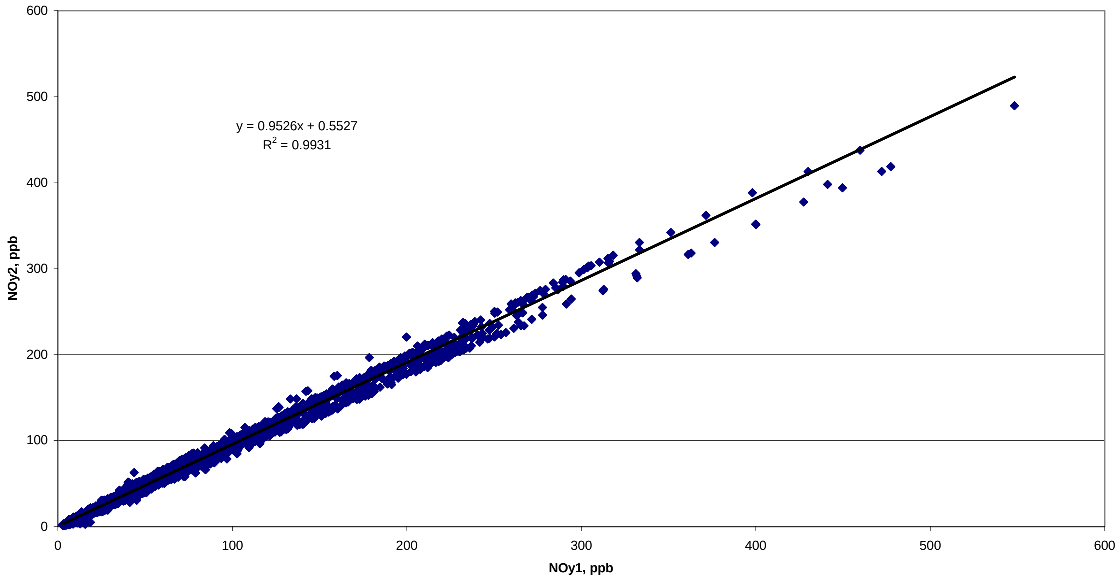
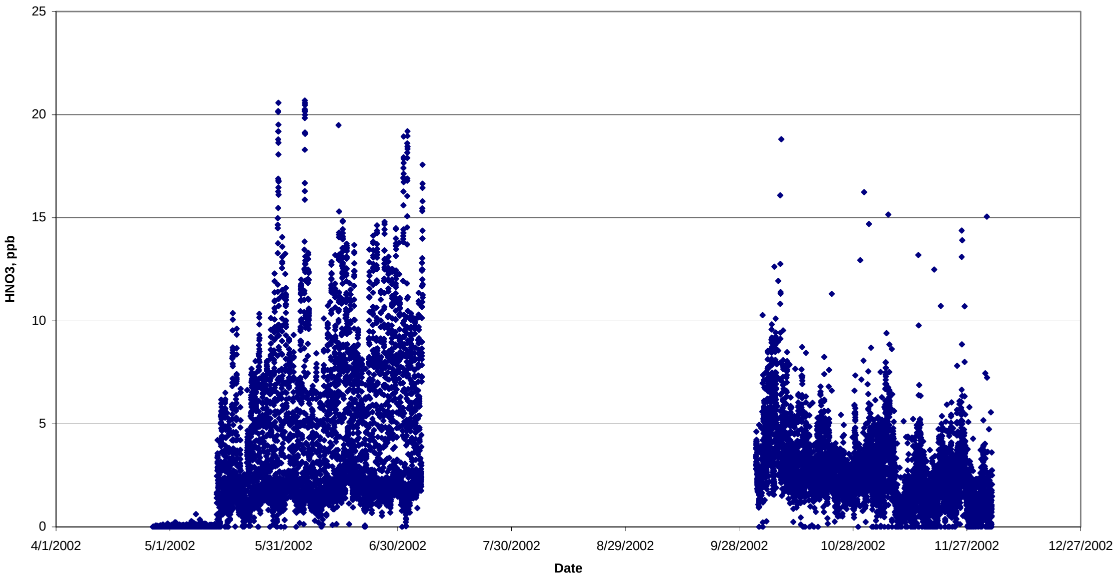


Figure 3-14. (a) Azusa HNO_3 concentrations at for 58313. (b) HNO_3 concentrations for 58438.

a.



b.

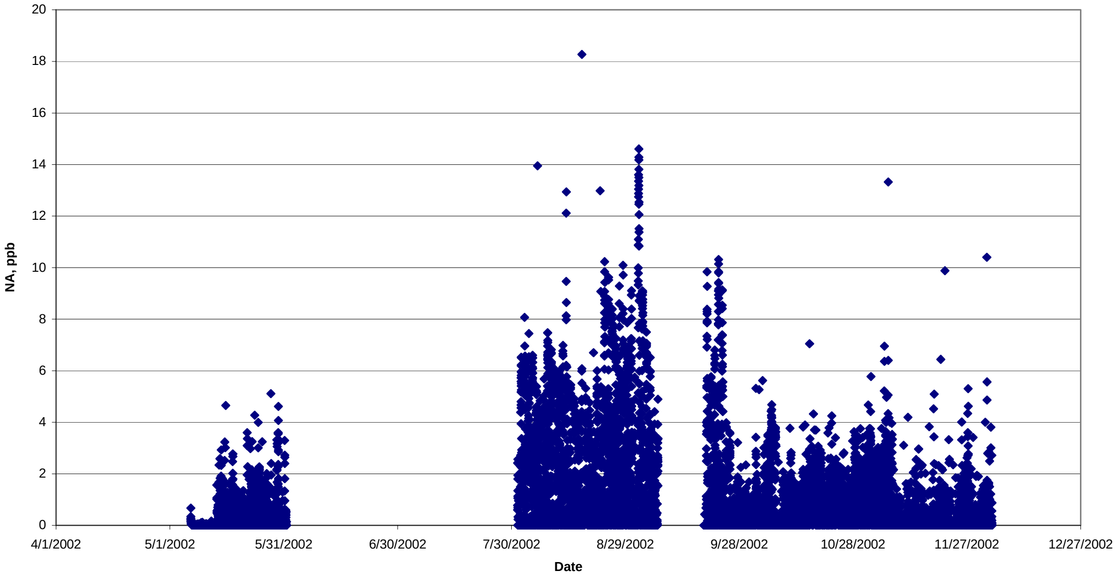
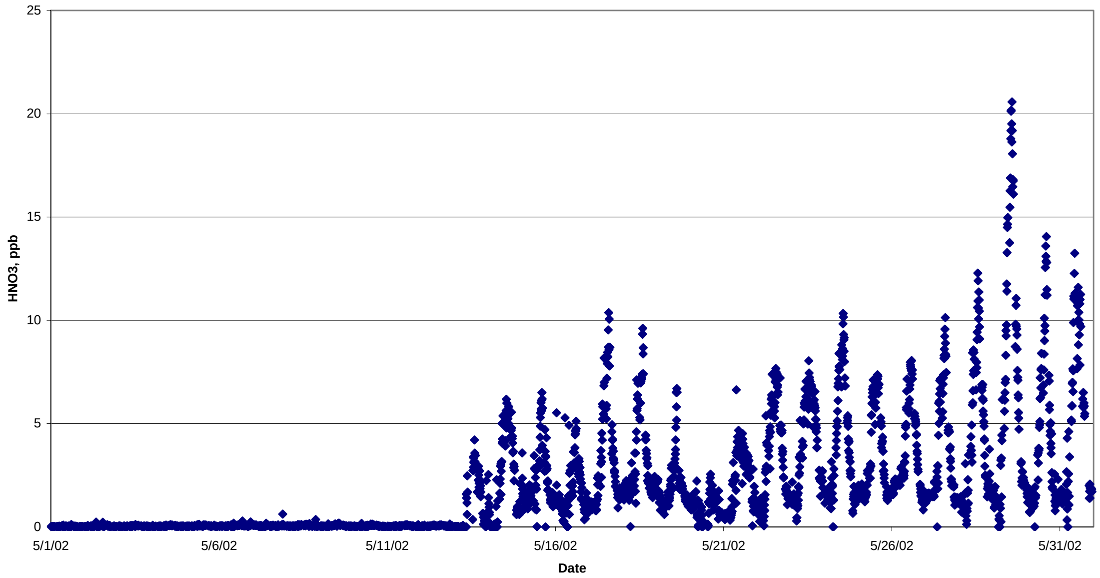


Figure 3-15. (a) Time series of nitric acid at Azusa during May 2002, Instrument 58313. (b) Time series of nitric acid at Azusa during May 2002, Instrument 58438.

a.



b.

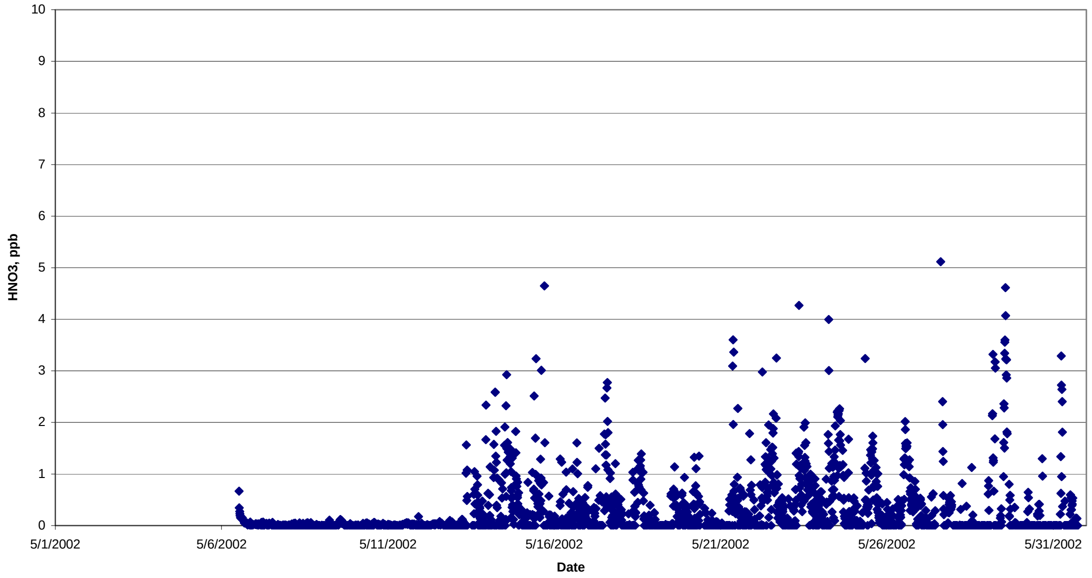
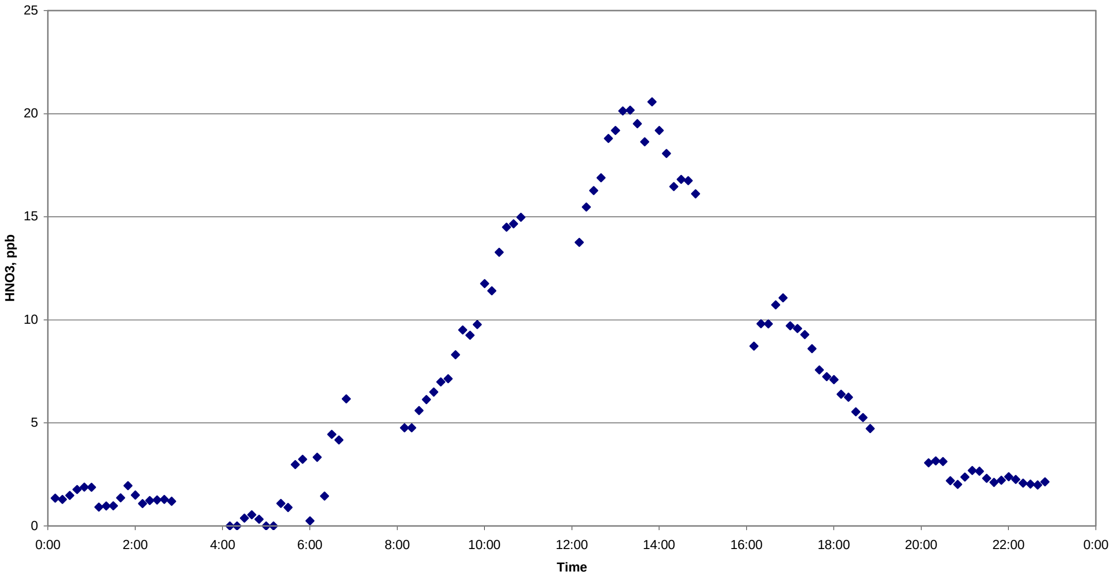


Figure 3-16. (a) Time series of nitric acid at Azusa during May 29, 2002, Instrument 58313. (b) Time series of nitric acid at Azusa during May 29, 2002, Instrument 58438.

a.



b.

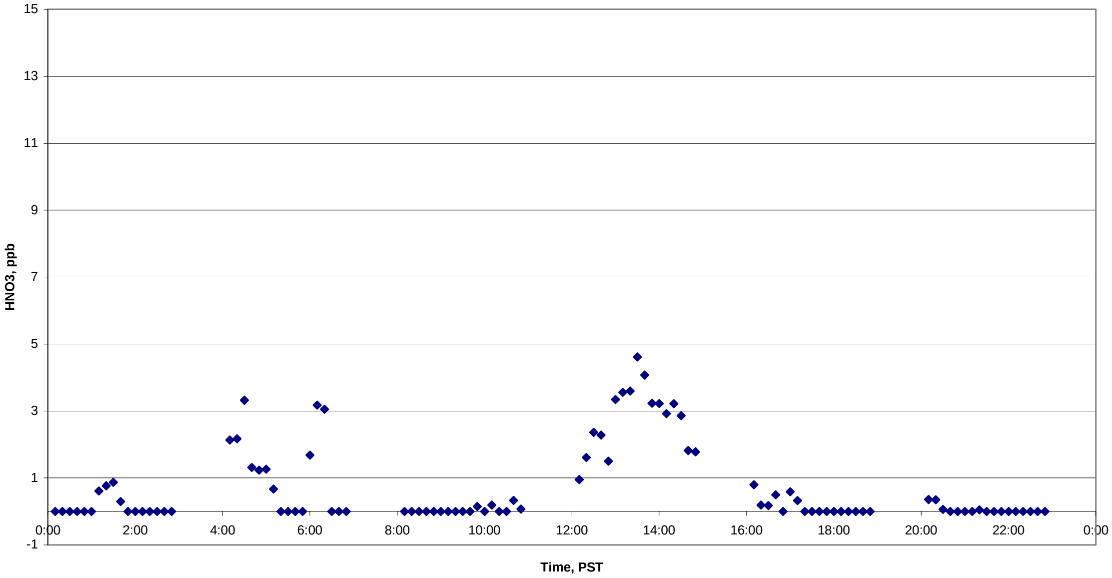


Figure 3-17. Comparison of HNO_3 measured by both analyzers at Azusa

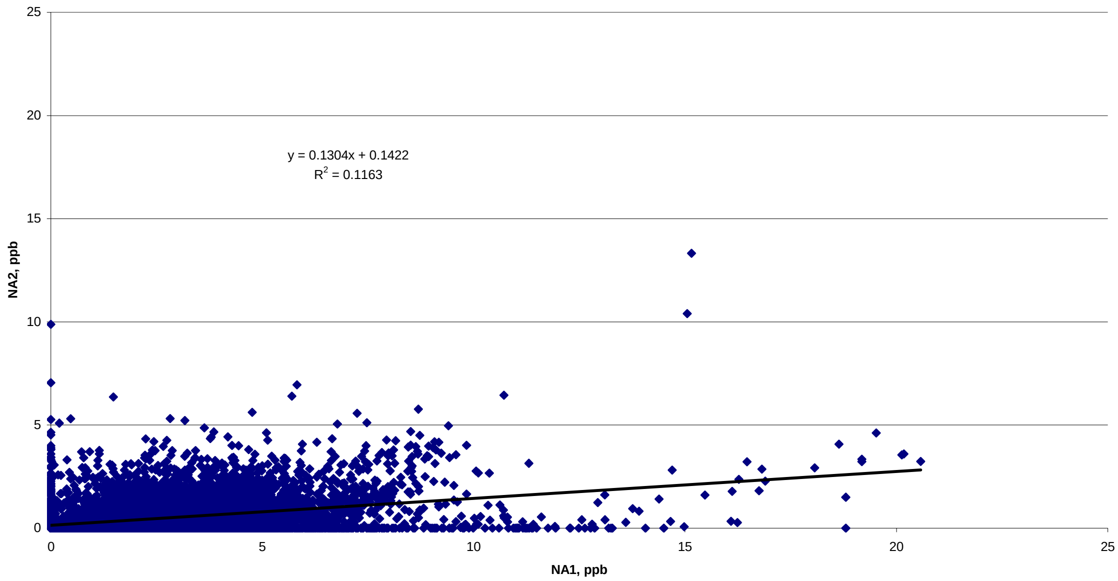
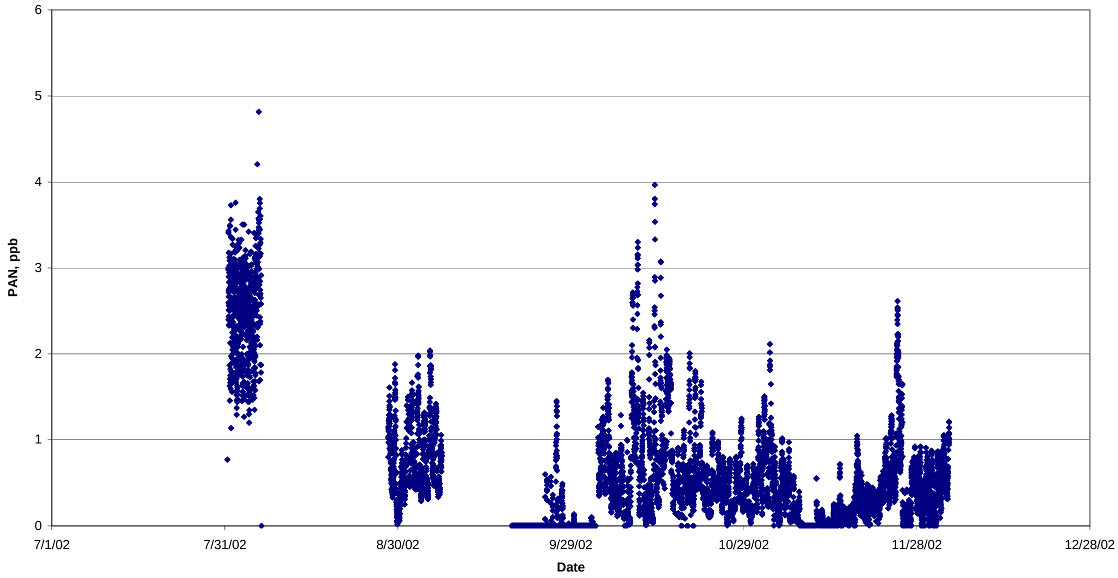


Figure 3-18 shows a time series of PAN concentrations for the measurement period. There was a great deal of missing data due to repeated failure of the computer that controlled the NO_2/PAN GC. Since resources were not available to repair the computer, we were required to wait until spare parts could be removed from another analyzer that had been assigned to another project. After that time significant amounts of data were lost due to the instrument's calibration drift between site checks and the operator error noted above, in leaving the system in the "zero" mode. Figure 3-19 shows the month of October. The diurnal distribution is clearly shown, and concentrations appear to be somewhat higher than Riverside. Figure 3-20 shows a single day in which the diurnal distribution can be seen in detail. The expected profile is observed although, unlike Riverside, the NO_2 and PAN often peak at about the same time of day.

Figure 3-18. (a) Azusa PAN and (b) NO_2 concentrations 2002 time series

a.



b.

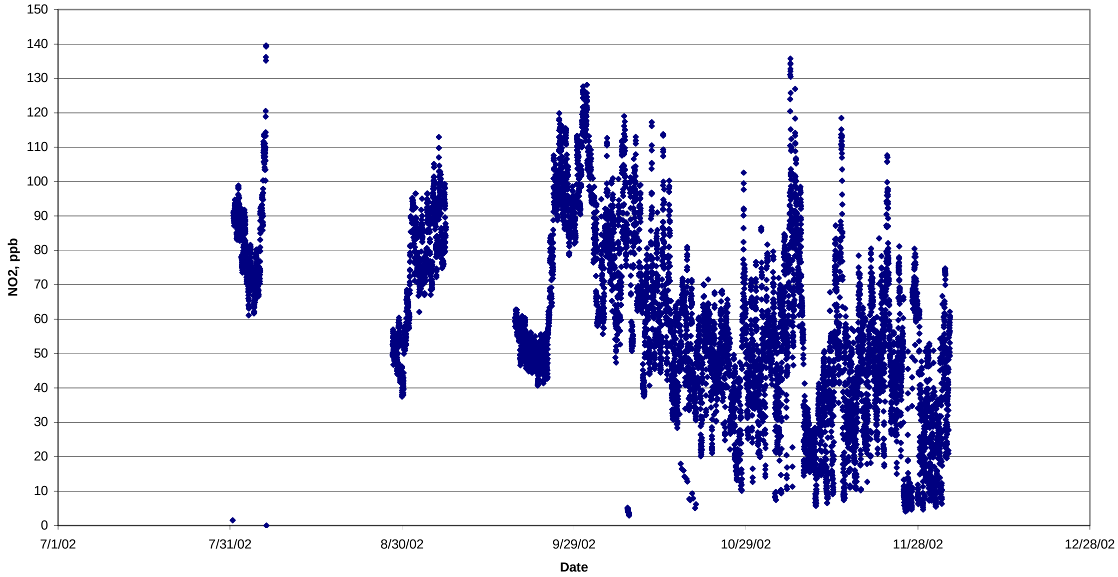
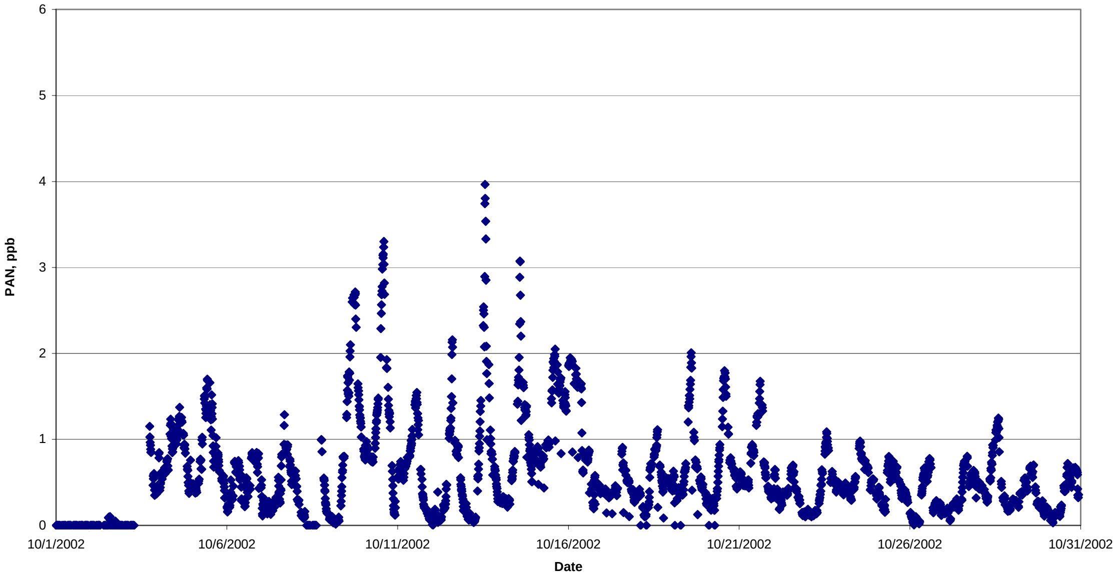


Figure 3-19. (a) Azusa PAN and (b) NO_2 concentrations October 2002 time series

a.



b.

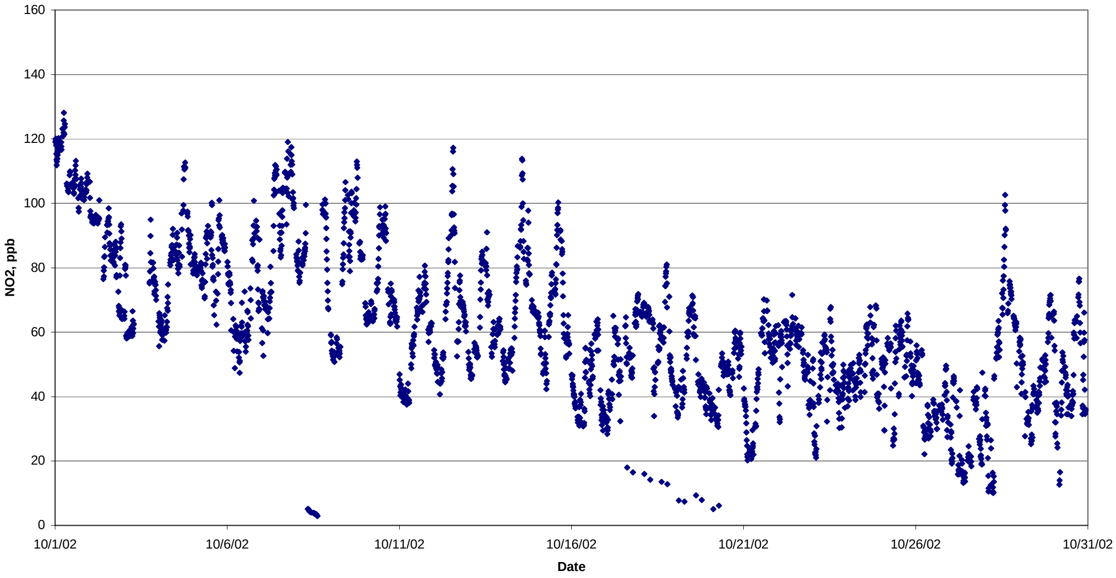
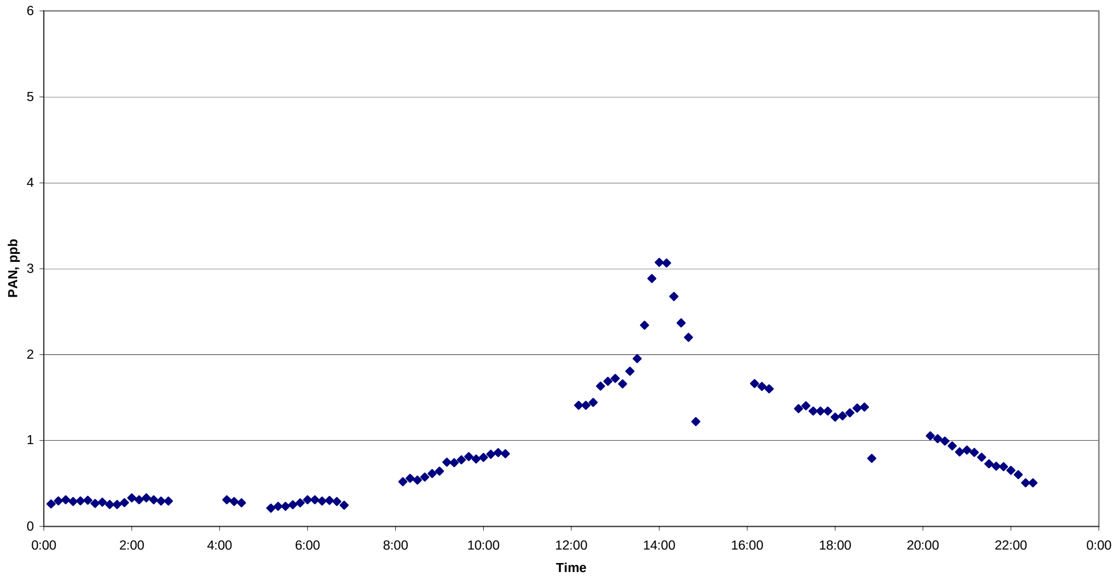
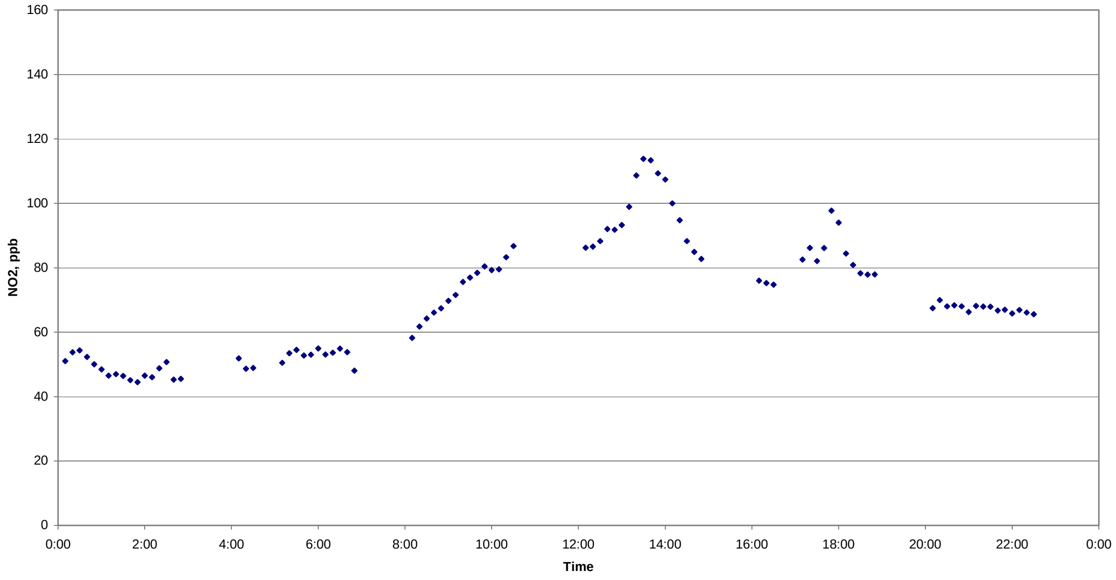


Figure 3-20. (a) Azusa PAN and (b) NO_2 concentrations October 14, 2002 time series

a.



b.



4.0 Conclusions

Given the limited resources for this project, a great deal of useful data was generated. The NO_y and component concentrations have been determined over an entire smog season for two important receptor sites in the south coast air basin. The stretching of resources to maintain a remote site, however, contributed to overall poorer data recovery. Figure 4-1 summarizes the concentrations measured at both sites.

The dual converter approach appears to be a viable method for measuring nitric acid, although the ambient measurements must be continually checked to determine performance. With these analyzers, QC checks using synthetically prepared gases does not appear to be sufficient to verify converter performance. It is necessary that a trained technician review the ambient data on a timely basis. It should be noted the dual converter method has been used for several years to measure concentrations in our smog simulation chamber and the results are in general agreement with those measured used a tunable diode laser absorption spectrometer (TDLAS) and those predicted from the SAPRC99 computer simulation model.

The NO_2/PAN GC has shown to measure the concentrations of these compounds with sufficient sensitivity for ambient measurements and with high sensitivity (due to chromatographic separation). Under the supervision of experience personnel, the instrument can perform reliably and with high data recovery

Table 4-1. Concentrations measured at (a) Riverside and (b) Azusa

a.

	NOy 58441			NA 58441			NO2			PAN		
2002	Max	Min	Med	Max	Min	Med	Max	Min	Med	Max	Min	Med
April	198.9	0.41	17.85	5.0	0.0	0.6	NA	NA	NA	NA	NA	NA
May	270.5	3.97	22.45	8.5	0.0	2.0	40.9	0.0	5.2	0.9	0.0	0.2
June	200.1	2.96	25.31	12.4	0.0	2.4	41.8	1.7	13.3	1.2	0.0	0.3
July	171.3	1.40	27.53	16.5	0.0	2.5	41.2	0.0	12.2	2.8	0.0	0.1
August	220.8	8.08	29.92	15.9	0.0	2.7	50.3	1.4	16.5	3.6	0.0	0.3
September	260.3	3.36	36.04	14.8	0.0	2.7	34.8	0.0	12.4	1.7	0.0	0.1
October	287.7	4.02	34.43	19.1	0.0	2.1	53.4	8.3	23.5	1.6	0.0	0.3
November	424.5	3.18	36.74	12.1	0.0	0.9	36.6	2.8	18.2	0.8	0.0	0.0

b.

	NOy 58313			NA 58313			NO2			PAN		
2002	Max	Min	Med	Max	Min	Med	Max	Min	Med	Max	Min	Med
May	232	2.18	35.25	20.6	0.0	1.1	NA	NA	NA	NA	NA	NA
June	232	2.18	42.71	20.7	0.0	3.0	IS	IS	IS	IS	IS	IS
July	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
August *	260	10.55	51.70	18.3	0.0	0.6	IS	IS	IS	IS	IS	IS
September*	454	5.54	69.43	14.6	0.0	0.0	127.6	40.7	80.5	2.0	0.0	0.0
October	548	5.22	56.02	18.8	0.0	2.7	128.1	2.9	58.5	4.0	0.0	0.5
November	478	2.56	39.86	15.2	0.0	1.8	135.7	4.1	42.7	2.6	0.0	0.2

* NOy and NA datafrom analyzer SN 58438
NA: No data available
IS: Insufficient data for monthly summary

5.0 Recommendations and Future Research Needs

We have shown that the dual converter approach appears to be a viable method of measuring nitric acid provided that QC checks are conducted to insure that ammonia conversion and the memory effect are minimized and that the ambient data are continually reviewed for performance.

There is still a large body of data from the 2001 smog season that might be recoverable if there is an interest in this year. Although it would not be possible to perform rigorous data validation, an experience data validator could likely be able to produce a useful data set.

In the future, it would be useful to compare the NO_2 measured by NO_x analyzers with that from the more specific NO_2/PAN gas chromatograph. To do this properly would require that the calibration of both instruments be traced to the same span gas.

6.0 References

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APPENDIX A: NO_y WORKSHOP PRESENTATION

NOy Workshop
February 20, 2002

10:00 –10:30 Instrument Overview
10:30 – 11:00 Installation
11:00 – 12:00 Quality Control
  zero checks
  span checks
  interference checks
  converter efficiency checks
12:00-1:00 Lunch
1:00 – 2:00 Demonstration
3:00 – 3:30 QA
2:30 – 3:00 Questions and Comments
3:00 CE-CERT Lab Tour

NOy Analyzer Work Shop
February 20, 2002

Dennis Fitz

College of Engineering-Center for Environmental Research and Technology

University of California, Riverside

Work Shop Schedule

10:00 - 10:30	Instrument Overview
10:30 - 11:00	Installation
11:00 - 12:00	Quality Control Steps
12:00 - 1:00	Lunch
1:00 - 2:00	Demonstration
2:00 - 2:30	Quality Assurance
2:30 - 3:00	Questions and Comments
3:00	CE-CERT Tour

Definitions

- NO_x: NO + NO_2
- NO_y:
  - – *Modeling Perspective*: All photochemically reactive odd nitrogen oxides (N_2, N_2O)
  - – *Measuring Perspective*: All oxidized nitrogenous species reduced to NO in a converter of a chemiluminescent NO-NO_x analyzer
- NO_z = NO_v - NO_x

NO_y Species

- **NO**
- **NO_2**
- **HNO_3**
- **PAcN**
- **HONO**
- **N_2O_5**
- **HO_2NO_2**
- **Organic Nitrates**
- **NO_3**
- **NO_3^-**

NO_y Analyzers

- Chemiluminescent NO Analyzer
- (NO_y) Converter to NO Located Outside Without an Inlet Filter (to reduce HNO_3 losses)
  - Heated Molybdenum (300°-350°C)
  - Heated Gold (400°C) + CO (or H_2)
  - Heated Vitreous Carbon (350°C)
  - Ferrous Sulfate

INTERFERENCES - HEATED CONVERTERS

- Variable Efficiency for Nitrogenous Species
- Ammonia Conversion at High Temperatures

MOLYBDENUM CONVERTER CHARACTERISTICS

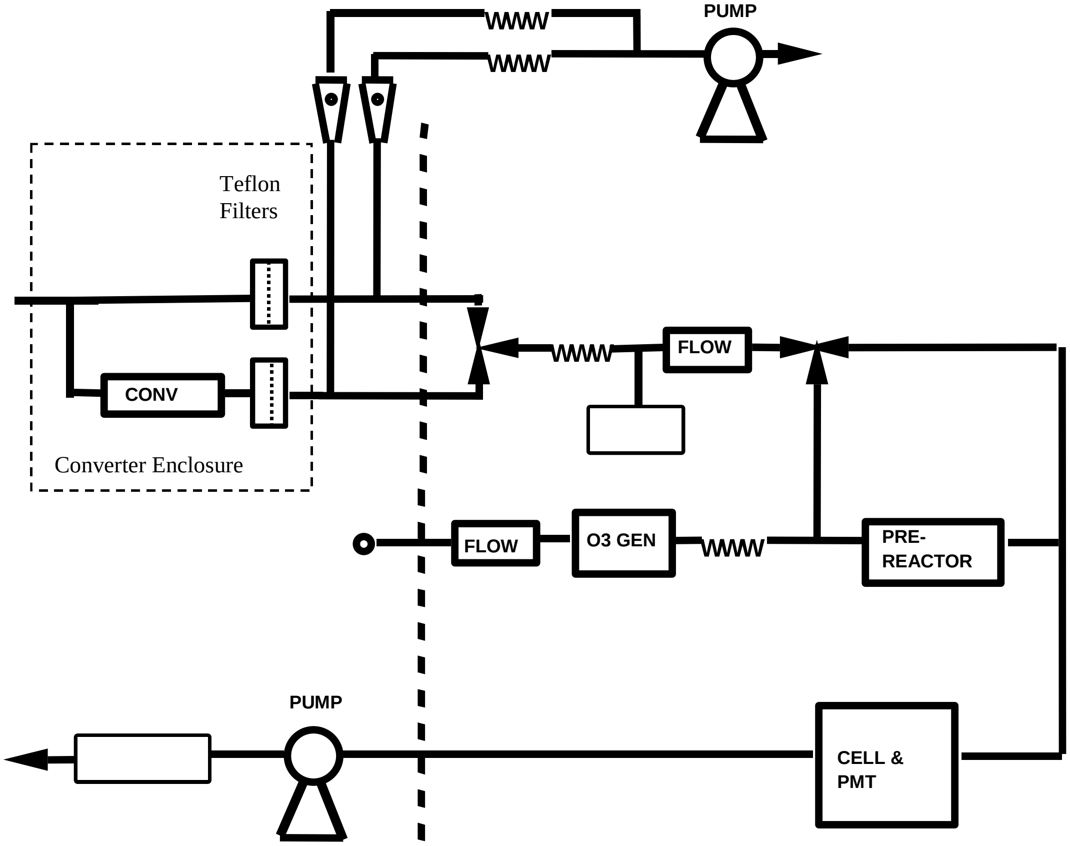
- Ammonia Conversion
- "Memory Effect" (High NO_y or Hydrocarbon Concentrations)
  - Long stabilization period
  - Elevated "zero" response
- Compound Selective Degradation
- Lowered Efficiencies at Atmospheric Pressure

AMMONIA COVERTER EFFICIENCY FOR THERMOENVIRONMENTAL MOLY CONVERTER

56 ppb Ammonia - Dry

% NH3 Conversion	Converter Temperature, C
14.8%	315
26.8%	313
5.2%	360
4.5%	376
26.6%	314
5.2%	370
9.5%	365
2.5%	301
11.9%	**Average**

NOy Analyzer Plumbing



Instrument Description

- Thermoenvironmental Model 42CY
  - – Permeation Dryer
  - – Internal Bypass pump and rotameters
- External Converter Box
- Otherwise Similar to Standard Model 42C

CE-CERT Evaluation

- LINEARITY TESTS (<1%)
- ZERO DRIFT-LDL /(.050 PPB
- SPAN DRIFT (<1%/24 HRS)
- CONVERTER EFFICIENCY TESTS
  - HNO3
  - NO2
  - PAN
  - HONO
  - N-PROPYL NITRATE (NPN)

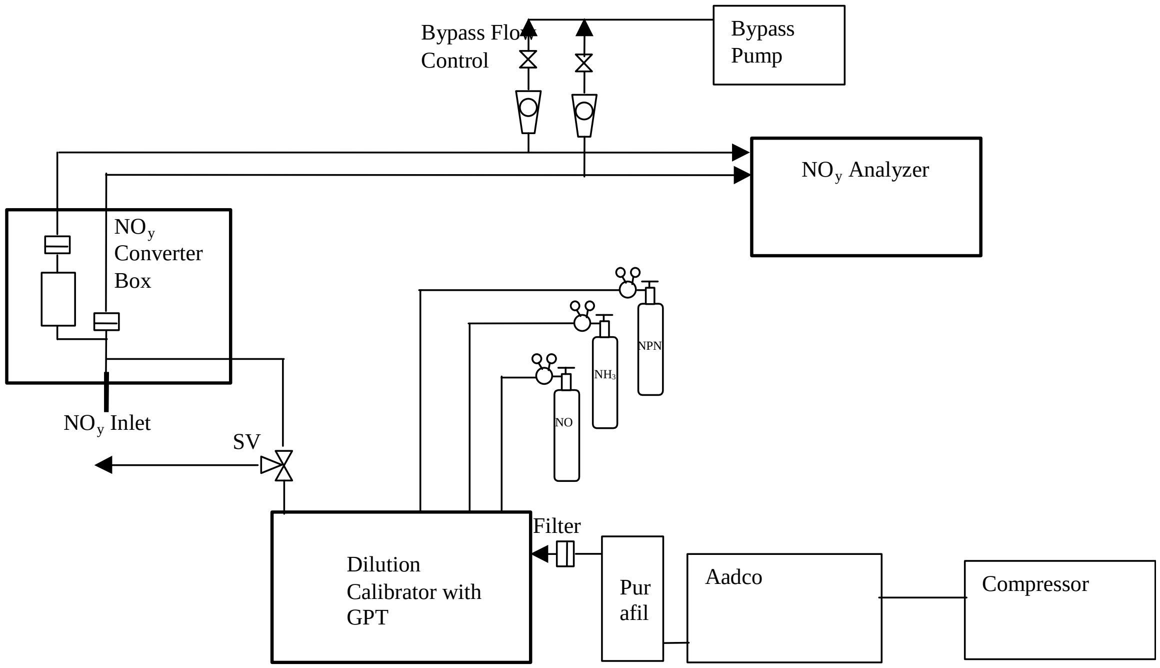
Installation

- Standard Siting Criteria
- Converter Box Attached to a 11/4 in OD pipe
  - “U” bolts supplied (if I send them out)
  - Mount 2 m above roof surface
  - Use 3/4 flexible conduit for electrical wires
  - Short (6 in) inlet line
  - Two 1/4 in Teflon sample lines
  - One 1/4 in Teflon calibration line

Installation Supplies

- 100 ft 1/4 OD PFA Teflon Tubing
- 1 1/4 OD Pipe and mounting hardware
- 30 ft 3/4 in Plastic coated flexible metallic conduit
- Programmable Dilution Calibrator with GPT
- Calibration Gases
  - – NO in N_2 (with SS regulator and tubing)
  - – NPN in N_2 (with SS regulator and tubing)
  - – NH_3 in N_2 (with SS regulator and tubing)
- Pure Air Source
- Data Acquisition System

Installation Plumbing



Installation Warnings

- Check to make sure the converter temperature is read out properly by the instrument
  - An open circuit will result in full heat on and **burn out** converter
  - Radio interferences can also burn out converter
  - At start up watch converter temp rise and **stabilize**
- Do not use the SS cross inside the converter box to connect calibration gas
  - It pressurizes the NO and NO_y lines differently leading to apparent mismatches in response characteristics

Calibration

- Same as Standard NO_x Analyzer
- If Converter efficiency is < 96/% for NO2 Raise Converter Temperature in 5ºC increments (~ 1/4 turn on trim pot on temperature controller board) up to 380ºC

Recommended Quality Control

- Automated Daily Zero/Span Checks (NO)
- Automated Daily NO_2 Converter Efficiency Checks
- Automated or Manual Weekly NH_3 Interference Checks
- Automated or ManualWeekly
- NPN Converter Efficiency Checks

Quality Assurance

- Follow NO_y SOP
- Audit by challenging with NO and NO_2 at the Converter Box Inlet
  - Optional NH3 interference check
  - Optional NPN converter efficiency check