EVALUATION OF NO_y AND NITRIC ACID MEASUREMENT METHODS AND COLLECTION OF AMBIENT DATA

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Abstract

California has an ambient air quality standard for nitrogen dioxide (NO_2), and oxides of nitrogen are also critical participants in atmospheric photochemistry to form ozone. Ambient air quality monitoring networks use chemiluminescent analyzers that alternately measure NO and all nitrogenous species that are converted to NO by a heated catalyst. The difference is defined as NO_2. In the atmosphere these nitrogenous species (NO_y) consist of, in addition to NO and NO_2, nitrogenous acids (nitric and nitrous), ammonia (NH_3), and organic nitrates. Dual converter NO_x analyzers were used during SCOS97-NARSTO to measure NO_y and nitric acid. These instruments were refurbished by replacing or reactivating their reduction converters and thoroughly evaluating their efficiency to convert nitrogen-containing species. These instruments are equipped with dual converters with one channel fitted with a NaCl-coated fabric denuder to selectively remove nitric acid (NO_y*). Since the instrument automatically cycles between the two channels, the difference is a measure of nitric acid. A pair of collocated analyzers was set up at the CE-CERT laboratory in Riverside and a single analyzer was installed in Azusa at the monitoring site operated by the South Coast Air Quality Management District (SCAQMD). Data collection started April and October 2000, respectively, for the Riverside and Azusa measurement sites.

Data were compiled and validated until April 2001. NO_y values at Riverside ranged up to 300 ppb, and values at Azusa reached up to 500 ppb. The Azusa NO_y and NO_x reported by the SCAQMD compared quite closely. Since it was not possible to have both analyzers sample the same span gas, the significance of differences between the two approaches could not be evaluated. The diurnal pattern of nitric acid was observable nearly every day during the smog season. The concentrations at Riverside ranged up to 6 ppb in the summer. Despite the measurement period at Azusa not including the summer smog season, nitric acid concentrations as high as 8 ppb were observed.

A thermoevolution denuder (TED) to measure nitric acid was evaluated under laboratory conditions. This device uses a special ceramic fabric denuder coated with sodium chloride to selectively remove nitric acid. Since this fabric strongly adsorbs microwave radiation at the same wavelength as that for cooking, the fabric can be heated rapidly and controllably to high

temperatures using a standard microwave oven. This heating will decompose the collected sodium nitrate to NO_x. While this design allowed the denuder to adsorb nitric acid, the amount recovered was low and variable. We found that the denuder was not evenly heated, and the amount recovered when drops of dilute nitric acid were placed on the denuder depended on the location on the denuder that was used. It was likely that the microwave oven, which was a consumer product, was not designed to produce a uniform microwave field. We concluded that additional research was needed before the system was ready to evaluate with other methods of measuring nitric acid.

This report included the initial year of NO_y and nitric acid data. We continued to maintain the NO_y analyzers and added NO_2/PAN gas chromatographs at both sites. These chromatographs separate NO_2 and quantify the amount using luminol detection. This selective method of measuring NO_2 will be used to quantify the amount of NO_2 contained in the NO_y. Under additional funding these instruments will be maintained until October 2002. The results from this period will be the subject of a final report for the second period of funding.

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Executive Summary

California has an ambient air quality standard for nitrogen dioxide (NO_2), and oxides of nitrogen are also critical participants in atmospheric photochemistry to form ozone. Nitric acid (HNO_3) can react with ammonia (NH_3) in ambient air to form ammonium nitrate as a fine particle. Ambient air quality monitoring networks use chemiluminescent analyzers that alternately measure NO and all nitrogenous species that are converted to NO by a heated catalyst. The difference is defined as NO_2 although included in this measurement are other nitrogenous species such as nitric acid, organic nitrates, nitrous acid and other nitrogenous species (roughly in that order of concentration). Ammonia, often found at concentrations in excess of nitric acid, can also be partially converted to NO and therefore included in NO_2 measurement. NO_2 measurements, therefore, are bias high using this method.

The primary objective of this study was to use modified chemiluminescent analyzers to quantitatively measure NO_y and to evaluate their performance in measuring nitric acid. To evaluate the concept of complementing routine NO/NO_x monitoring stations, analyzers were used to make continuous measurements at two sites in the south coast air basin that have been shown to have some of the highest NO_y concentrations in California. The NO_y–NO_y* analyzers used during SCOS97-NARSTO were refurbished by replacing their reduction converters and thoroughly evaluating their efficiency to convert nitrogen-containing species. These instruments are 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. A pair of collocated analyzers was set up at the CE-CERT laboratory in Riverside, and a single analyzer was installed in Azusa at the monitoring site operated by the South Coast Air Quality Management District (SCAQMD). The converters were mounted in insulated boxes 1.5 m above the roofs of both buildings while the analyzers were installed inside the air-conditioned shelters. Automated zero checks were conducted five times a day at Riverside and six times a day at Azusa, each period lasting 20 minutes. Data was logged at either 10- or 15-minute intervals. Site checks were performed on a weekly to monthly basis. NO_y and nitric acid data was collected at the Riverside site starting

April 2000, and at the Azusa site starting October 2000. NO_y and nitric acid data were reported for a year period starting April 2000.

Data for the one-year period were compiled and validated. NO_y values at Riverside ranged up to 300 ppb and for Azusa up to 500 ppb. The major cause of missing data was vacuum pump failure of the analyzers. The Azusa NO_y and NO_x reported by the SCAQMD compared quite closely, generally within 10%. Based on a linear regression, the NO_y analyzer values were 15 percent higher than the NO_x. Since it was not possible to have both analyzers sample the same span gas, the significance of differences between the two approaches could not be evaluated. Analysis of the data showed that the analyzers sporadically produced erroneous data, with the nitric acid values being a large fraction of the total NO_y at times when it was physically unrealistic. The cause of this was found to be the operation of the channels at different ranges to maximize the data collection sensitivity. This occurred only with certain combinations of the two channels (NO_y and NO_y without nitric acid). This occurred despite the manual indicating that the range for each channel could be selected independently.

After removing most of the erroneous nitric acid data, we found that the diurnal pattern of nitric acid was observable every day during the smog season. The concentrations at Riverside ranged up to 6 ppb in the summer. Despite the measurement period at Azusa not including the summer smog season, nitric acid concentrations as high as 8 ppb were also observed. The nitric acid data included outliers that did not follow the smooth diurnal pattern. The two likely causes of this are not filtering out all of the erroneous data, or the analyzer measuring nitric acid by taking the difference of two often large numbers relative to nitric acid that did not correspond exactly in time.

A thermoevolution denuder (TED) to measure nitric acid was evaluated under laboratory conditions. This device uses a special ceramic fabric denuder coated with sodium chloride to selectively remove nitric acid. Since this fabric strongly adsorbs microwave radiation at the same wavelength as that for cooking, the fabric can be heated rapidly and controllably to high temperatures with a microwave oven designed for heating food products. This heating will decompose the collected sodium nitrate to NO_x. A sampling system with a nitric acid source was

designed and built to evaluate this concept for measuring nitric acid. The TED sampling and analysis was automated and controlled with a data logger. The original denuder holder and sampling assembly was constructed from borosilicate glass to withstand the high heat and allow microwave radiation to pass unattenuated. This material was found to adsorb nitric acid strongly. Replacement of glass with quartz also led to unsatisfactory results, since this material also adsorbed nitric acid. The final design incorporated PFA Teflon tubing to bring the sample to close proximity of the ceramic denuder. While this design allowed the denuder to adsorb nitric acid, the amount recovered was low and variable. We found that the denuder was not evenly heated and the amount recovered when drops of dilute nitric acid were placed on the denuder depended on the location on the denuder. It was likely that the microwave oven, which was a consumer product, was not designed to produce a uniform microwave field. We concluded that additional research was needed before the system was ready to evaluate with other methods of measuring nitric acid.

An initial objective of this study was to compare nitric acid measurements using four different approaches: dual converter NO_y, thermoevolution denuder (TED), tunable diode laser absorption spectrometer (TDLAS), and fabric sodium chloride denuders extracted with water with assay of nitrate by ion chromatography. The TED was not found reliable enough to provide useful data when sampling ambient air, and the TDLAS suffered major failure due to leakage of the cold head in which the lasers were installed. The TDLAS, therefore, required a major repair that was beyond the scope of this project. Without these two instruments further comparisons would not be useful and were not attempted.

This report includes the initial year of data. We continued to maintain the NO_y analyzers and added NO_2/PAN gas chromatographs at both sites. These chromatographs separate NO_2 and quantify the amount using luminol detection. This selective method of measuring NO_2 will be used to quantify the amount of NO_2 contained in the NO_y. Under additional funding these instruments will be maintained until October 2002. The results from this period will be the subject of a final report for the second period of funding.

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; 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. It is also possible that the denuder of the CADMP lost some efficiency to collect nitric acid or that there were losses in the sampling line. Both processes have been shown to occur with this sampler (Fitz and Hering, 1996).

The CADMP denuder sampling arrangement itself has its own shortcomings, as 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 (multiple pass optics with a 25m basepath) 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 a pair of NO_y-NO_y* analyzers for a year at both Riverside and Azusa, CA.
- Develop and evaluate a nitric acid analyzer based on the thermal evolution denuder (TED), a nitric acid analyzer based on collection on a ceramic denuder followed by thermal evolution and quantification in a NO_y analyzer.
- Perform limited comparisons of nitric acid measurements between the NO_y-NO_y* method, a tunable diode laser absorption spectrometer, the TED, and a fabric diffusion denuder.

2.0 Approach

2.1 Monitoring Locations

Ambient data were collected at the CE-CERT laboratory, 1200 Columbia Avenue, Riverside, and at the air monitoring site operated by the South Coast Air Quality Management District at 825 Loren Avenue in Azusa. The roof at the Riverside site was 8 m above the ground. The Azusa site was 4 m above the ground. A pair of identical dual-converter NO_y analyzers were installed at the CE-CERT laboratory, while a single instrument was used in Azusa for this first year of monitoring. The second instrument for Azusa suffered from many breakdowns during laboratory checkout and spent much of the first year being repaired. 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 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 is 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.

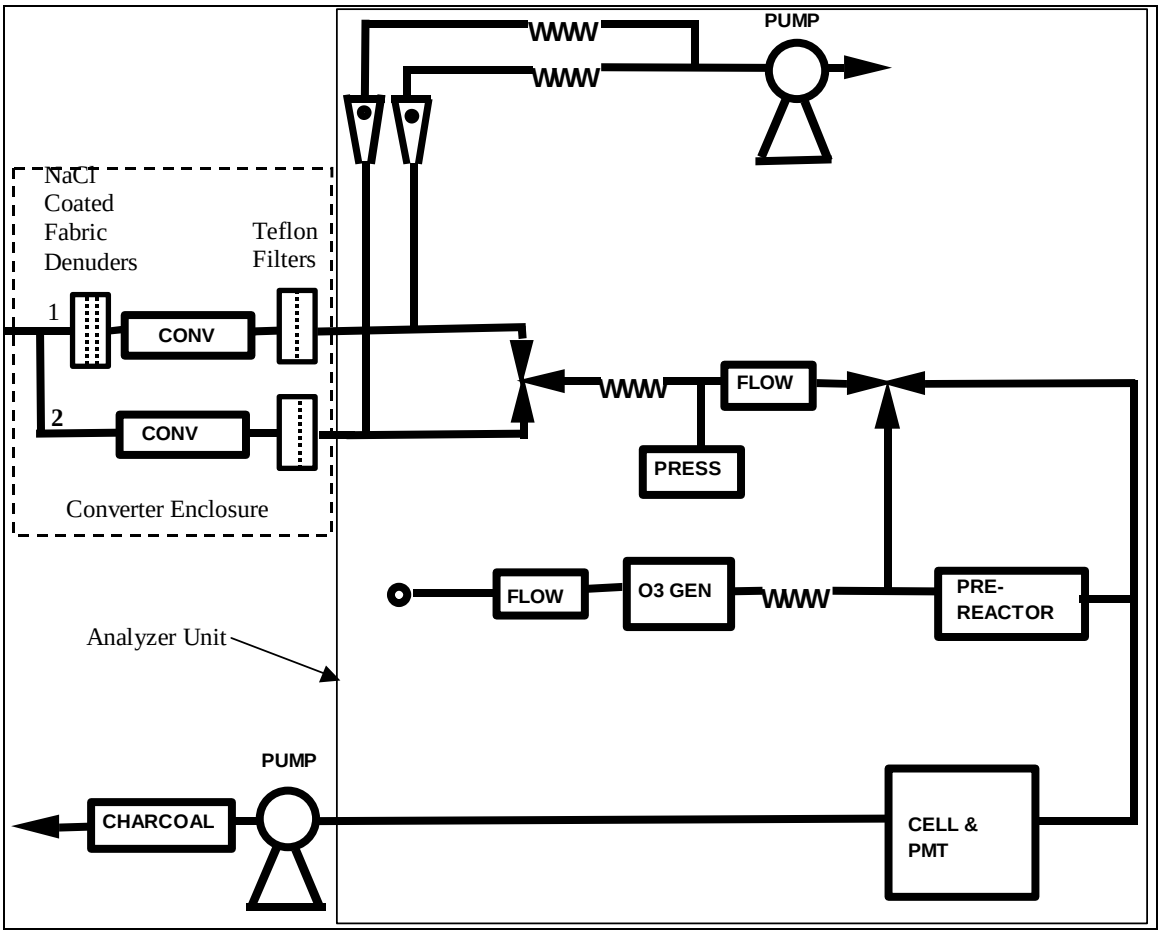


Figure 2-1. Schematic of the dual channel NO_y-NO_y* analyzer

An SOP was developed 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 every four hours. 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.
- Challenge with air from which only nitric acid was removed using sodium chloride coated filters.

Thermal Evolution Denuder

The thermal evolution denuder was conceived at the CE-CERT laboratory and initially developed and tested as an objective of this project. In this approach to measure nitric acid, a ceramic fiber denuder is coated with NaCl and placed in an open-face glass filter holder. The holder is then placed in a small microwave oven cavity with variable power control. The holder is plumbed so that it can automatically either sample air or be purged with purified air that is directed to a commercial NO-NO_x analyzer. Nitric acid is selectively removed by the denuder as sodium nitrate. After purging with purified air, the denuder is heated to decompose the sodium nitrate to NO_2. The NO_2 released is then quantified with a Thermo Environmental Instruments model 42 chemiluminescent NO/NO_x analyzer operated in the NO_x mode. A data logger is used to control the switching between sampling and purging and integrating the response of the NO_x channel.

The setup in Figure 2-2 was configured so the initial experiments could be conducted with a degree of flexibility in a manual mode. The normal mode had the NO_x analyzer with corresponding NO_y converter set up to sample zero air. The thermal evolution denuder could sample whatever was presented to it via the normally open port of valve 3. It should be noted that valves V1, V3, and V4 were Galtek PFA ¼-inch orifice solenoid valves, model #203-3414-215. PFA surfaces are known to have the least effect on HNO_3 and all surfaces that came in contact with the sample gas were made of PFA.

The microwave was a commercially available version from Sharp Electronics, Model #1000W. Holes were inserted into the microwave (Figure 2-3) for the denuder assembly and the sample line to the NO_x analyzer. A shield was placed around the denuder assembly and sample lines to prevent leakage of microwaves to its exterior (Figure 2-4). The denuder assembly contained a borosilicate conical reducer that was attached to a long borosilicate tube. The Pyrex tube contained two ports at its top for the inlet of sample gas and to facilitate changes of the ceramic denuder. The ceramic denuder was placed in the denuder assembly directly above the conical glass reducer, where a ridge was formed. The ridge located the denuder and facilitated easier installation and removal.

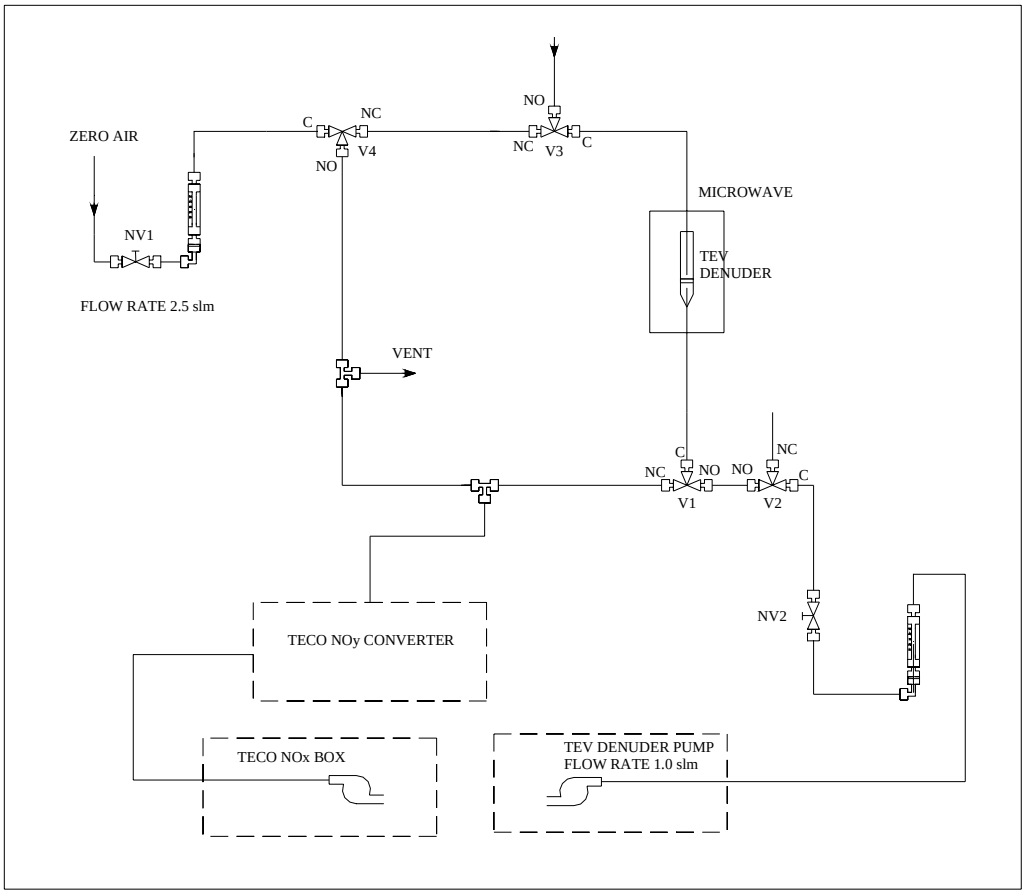


Figure 2-2. Schematic of the thermal evolution denuder (TED) nitric acid measurement system.

Figure 2-3. Interior of the microwave and the glass enclosure around the ceramic denuder.

Figure 2-4. Microwave shielding tubes around the denuder assembly and sample line.

3.0 Results and Discussion

3.1 NO_y/Nitric Acid Analyzer Renovation and Evaluation

The converters of the four NO_y-NO_y* instruments were evaluated using the following nitrogenous gases:

- Nitrogen dioxide (NO_2)

  NO_2 was generated by the gas-phase titration with ozone using a commercial dilution calibration instrument equipped with an ozone generator and plumbed for performing gas-phase titration. Prior to dilution, NO in nitrogen was allowed to mix with air that had passed through an ultraviolet light-based ozone generator. NO_y is sampled with the light off and then with the light adjusted to titrate approximately 70% of the NO. The change in response to the change in NO_2 concentration is therefore a measure of converter efficiency.

- Nitric acid (HNO_3)

  Nitric acid vapor was generated by flowing clean, dry air past a permeation tube containing liquid nitric acid. The concentration is estimated by measuring the permeation and gas flow rates and verified with a NO_y analyzer whose converter efficiency was shown to be nearly 100%. The faction of nitric acid in the NO_y response was determined by placing a NaCl coated filter in the diluted air to remove nitric acid.

- Nitrous acid (HONO)

  Nitrous acid was generated by reacting hydrochloric acid with sodium nitrate in a stirred-flow reactor. (Febo et al., 1995). This has been demonstrated to be a clean and constant nitrous acid source. Dry nitrogen was passed through the reaction vessel and was then diluted with zero air. The concentration was determined using a NO_y analyzer with know high converter efficiency.

- Peroxyacetyl nitrate (PAN)

  PAN was prepared in solution by reacting peracetic acid with nitric acid (Holdren and Spicer, 1984) in a hydrocarbon solvent. The amount and purity in the solution was quantified by IR in a 0.25 mm liquid cell. An aliquot of the solvent was injected into a 100 liter Teflon chamber and allowed to vaporize. The PAN concentration is estimated from the IR absorbence and verified with a NO_y analyzer with known converter efficiency.

- n-propyl nitrate (NPN)

  This compound is known to be stable in compressed gas cylinders and is more difficult to reduce to NO than nitric acid (Bollinger et al., 1983). Diluting a compressed source of n-propyl nitrate, therefore, may provide a convenient and effective method of determining the efficiency of a NO_y converter. A commercially prepared and analyzed source of n-propyl nitrate in nitrogen is diluted with zero air. The concentration of the source is verified with a NO_y analyzer as described above.

- Ammonia (NH_3)

  Ammonia vapor was generated by flowing clean, dry air past a permeation tube containing liquid ammonia. The concentration was then estimated by measuring the permeation and gas flow rates and verified with a NO_y analyzer after conversion to NO by a high temperature (700-1000 ºC) stainless steel converter. The efficiency of this converter is verified by raising the temperature until no further conversion is observed.

The converters for the analyzers were found to have varying degrees of efficiency for nitrogenous species. None of them produced the expected conversion of 97% for NO_2.despite raising the converter temperature to 350 °C, the maximum allowed by the manufacturer at that time. Several of them were reactivated by passing hydrogen gas through the converter while they were heated to 350 °C. Four of the converters were replaced with new ones, but these did not perform with the expected efficiency at temperatures up to 350 °C either. After extensive testing by the manufacturer, we were able to achieve acceptable efficiency by raising the temperature up to a maximum of 380 °C. Starting with NO_2, the converter temperatures were adjusted so that near 100% conversion was achieved for each species. The temperatures were then be lowered until the

efficiency started to drop and then raised in 5 ºC increments until 100% efficiency is again achieved.

The problems encountered with NO_y converters led us to perform a detailed literature search to determine whether alternatives to the molybdenum converters were practical. The results were presented at the Combined US-German Ozone/Fine Particle Science and Environmental Workshop held in Riverside. Appendix A contains this paper as published in the proceedings of this conference. The conclusions were as follows:

- There are considerable conflicting reports with respect to converter efficiencies for NO_y and interfering compounds.

- Presently used converters can result in significant biases and interferences.

- Until better converters are developed, frequent zero checks as well as routine assessment of converter efficiencies for both NO_y species and ammonia should be performed.

The packaging of the instruments was improved by installing the bypass rotameters in the front of the instrument and the bypass pump inside the analyzer.

3.2 Evaluation of the Thermal Evolution Denuder

Initial Testing

The initial testing revealed a number of problems that needed to be solved. The first was that the ceramic denuder produced large NO_x responses without addition of any nitric acid. The response would not decrease despite repeated cycles of purging with purified air and heating with the microwave. Discussions with the manufacturer of the ceramic material revealed that nitric acid was used in the production process. The denuders were then heated to 1100°C overnight in a muffle furnace. This treatment resulted in the response dropping to levels near the detection limit of the NO_y analyzer. After this treatment, sampling with approximately 50ppb of nitric acid did

not result in any significant response from the NO_y analyzer. We then sampled nitric acid directly without a denuder and found no response. It appeared that the glass fabricated to hold the denuder was adsorbing the nitric acid. Quartz was found to adsorb nitric acid also. To test the feasibility of thermally desorbing nitric acid we performed an evaluation of adding liquid nitric acid directly to the denuder.

Recovery of Liquid Injections

A 1 mmol/l solution of nitric acid was prepared. One drop (~50 µl) of this solution was applied directly onto the denuder. This would be equivalent to sampling 30 ppbV of nitric acid at 4 l/min for 10 min. A new ceramic denuder, which was fired at 1100 °C and coated with NaCl, was placed in the sampling path inside the microwave. Zero air was sampled until the NO_x analyzer had a stable zero reading. The microwave was turned on repeatedly for 1-minute intervals to verify that the ceramic denuder itself did not give off NO_x. One drop of the nitric acid solution was applied directly onto the ceramic denuder using a long pipette. When applying the acid solution, the sampling line had to be opened to insert the pipette. This allowed ambient air that contained NO_x to enter the line. After the sampling line again was closed, it required about five minutes for the NOx analyzer to reach a stable zero reading. The microwave was subsequently turned on to heat the ceramic denuder and decompose the nitric acid. Approximately 30–40 seconds after turning the microwave on, the NOx analyzer showed a spike of NOx. Repeated heating did not result in further NOx production.

From the results of this experiment we concluded that irradiation times of 1 minute are sufficient to heat the denuder and remove all nitric acid as longer irradiation times did not result in higher NOx-peaks. The nitric acid removal is likely quantitative as repeated irradiations did not show any significant increase in NOx above zero except for the first irradiation after applying the nitric acid onto the denuder.

Other observations during the first experiment were that the denuder, irradiated by microwaves, became thermally hot, and required a minimum of 30 minutes to cool down again. Tests

indicated that if nitric acid was applied to the hot denuder, partial to complete decomposition occurred almost immediately. This resulted in a reduced or non-detectable NO_x peak during irradiation. It was also noticed that the microwave field across the denuder was inhomogeneous as the absolute intensity of the NO_x peak depended on where exactly on the denuder the nitric acid drop was applied.

Evaluation of Nitrate Thermal Decomposition Efficiency

For high and selective adsorption of nitric acid, the denuder must be coated with a chloride (or fluoride) salt so that HCl gas is released while forming a solid nitrate salt. Sodium chloride is normally used for coating standard diffusion denuders, but other chlorides such as ammonium may also be acceptable. Since the formation of sodium nitrate or ammonium nitrate results by (1) and (2) respectively, the second experiment was to observe whether the nitrates formed also decompose into NOx.

$$NaCl + HNO_3 \rightarrow HCl + Na\ NO_3 \qquad (1)$$

$$NH_4Cl + HNO_3 \rightarrow HCl + NH_4NO_3 \qquad (2)$$

One mmol/l solutions of sodium nitrate and ammonium nitrate, respectively, were prepared. One drop (~50 µl) of this solution applied directly onto the denuder is equivalent to sampling 30 ppbV of nitric acid at 4 l/min for 10 minutes on a denuder coated with either sodium chloride or ammonium chloride, respectively. A new ceramic denuder was placed in the sampling path inside the microwave, and the denuder was initially coated with NaCl. Zero air was sampled until the NOx analyzer had a stable zero reading. One drop of the nitric acid solution was applied directly onto the ceramic denuder using a long pipette. The microwave was subsequently turned on to heat the ceramic denuder and decompose the resulting nitrate. Approximately 30–40 s after turning the microwave on, the NOx analyzer showed a spike of NOx. A similar experiment was performed with NH_4Cl yielding congruent results. From the results it was clear that both salts decompose just as nitric acid itself from the microwave irradiation.

Experiment 3 looked at the effects that the sampling lines and the thermal evolution denuder glassware may have on gaseous nitric acid. The ceramic denuder was removed from the sampling line, and diluted gaseous nitric acid from a permeation tube was passed through the experimental setup. After about 4 hours, nitric acid was detected by the NO_y analyzer. The reading remained relatively constant over a 24-hour period, but lower than expected.

Collection and Desorption Efficiency of Nitrogenous Species

Gaseous nitric acid from a diffusion tube source, diluted with zero air resulting in approximately 30 ppbv, was passed through the experimental setup until the NO_x concentrations were constant. An uncoated ceramic denuder was then placed into the sampling line. After about 20 minutes the reading of the analyzer dropped to minimum detectable levels. Therefore, nitric acid was removed from the gas stream by the denuder, and the delay was likely an artifact of the NO_y setup as HNO_3 is known to stick to the walls of the NO_y converter. The collection efficiency of the uncoated denuder was then tested for NO_2 and NO by passing these gases through the experimental setup alone. NO_x concentrations were similar before and after the ceramic denuder.

The efficiency for nitric acid to pass through the experimental setup without the denuder in place was then evaluated for several configurations. Initially a gas stream containing 70 ppbV of nitric acid was passed through the system without the ceramic denuder, and no nitric acid was measured by the NO_x analyzer even after sampling for several hours. A piece of PFA tubing was then placed inside this glass tubing to replace the glass surface with a more inert PFA surface. The PFA tubing ended about 2 cm above the ceramic denuder. Results measured by the NO_y analyzer indicated that nitric acid was observed within 5 minutes after starting to sample from the source. The rise time to a stable reading required several hours. The nitric acid gas stream was diluted by a factor of 5 to 14 ppbV, more representative of ambient measurements, and the concentration of the NO_y analyzer stabilized within half an hour.

System Automation

The results from our initial experiments indicated that since microwave radiation could decompose HNO_3 deposited on a denuder, we could proceed to conduct experiments to see if that could work for ambient levels of HNO_3. To facilitate such a set of experiments, an automated sampling system was constructed to measure the HNO_3 injected into the denuder and compare that to how much the microwave irradiated denuder emitted. Figure 3-1 and 3-2 show the experimental setup for the automated experiments. The setup was configured so that there would be four modes of operation. The assembly required six valves; all were Galtek PFA ¼"orifice solenoid valves, model #203-3414-215 v, 3 rotameters with associated needle valves, a diffusion tube source for HNO_3, a sample pump and the NOx analyzer (TECO) with a NO_y converter.

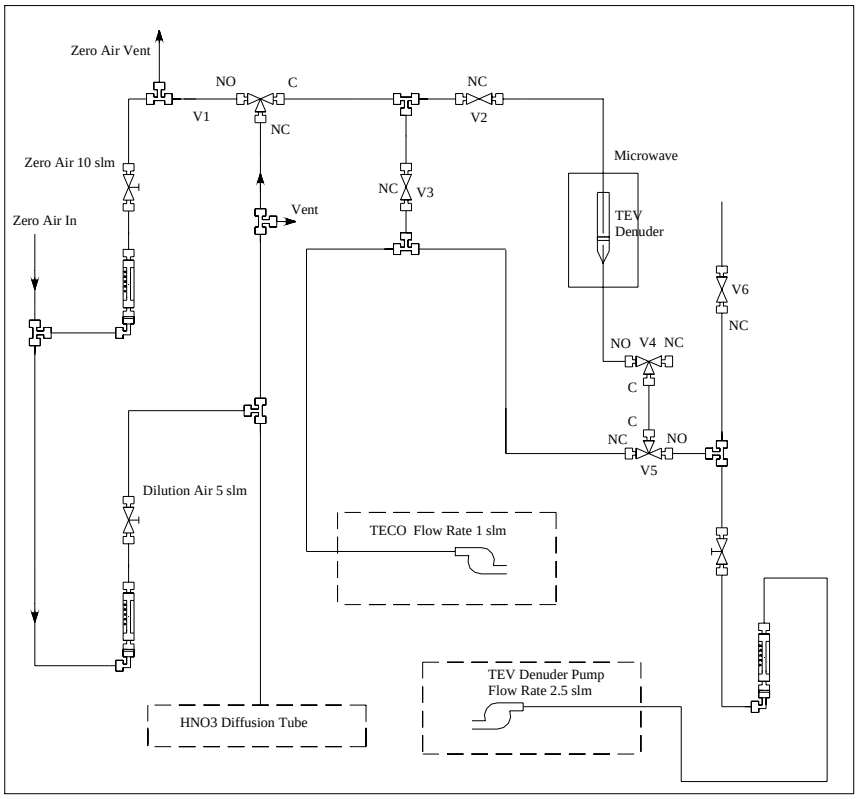


Figure 3-1. Schematic for automated TED experiments.

Figure 3-2. Photograph of the automated TED assembly.

The first mode was the Collection mode. In this mode the ceramic denuder collected ambient type level HNO_3 at the same time that it was being sampled by the NO_y analyzer. The HNO_3 source was a diffusion tube that contained 60% aqueous HNO_3 and was determined from pH titration to have a diffusion rate of 0.25 µg HNO_3 per minute. This yielded levels of approximately 50 ppbV NOx from the diffusion tube source when it was diluted with 5 l/min of zero air. Collection time was set to be 10 minutes.

The second mode was the zero mode for the NO_y analyzer. In this mode, the NO_y analyzer sampled only zero air to reduce the residual HNO_3 in the line, and that deposited on the surfaces of the NO_y converter. Although 4 minutes did not totally zero the level of the NO_y detector, it reduced the levels to less than 1 ppbV.

The third mode was the zero/heating mode in which the NO_y analyzer continued to sample zero air but the microwave was turned on for 1 minute.

The fourth mode was the TED measure mode. In this mode the NO_y analyzer sampled the microwave emitted NO_x that was diluted with zero air. The measure mode was 19 minutes. Modes 3 and 4 were repeated to ensure that there wasn't any residual HNO_3 on the surface of the microwave or in the sample lines.

A program using the Campbell CR10x data logging and control software was written to automate this sampling sequence. Table 3-1 lists the valve operation, microwave operation, and mode time for each of the four modes used.

Table 3-1. Modes -for TED automated sampling.

Mode	Description	V1	V2	V3	V4	V5	V6	Microwave	Time (min)
1	Collection	On	Off	Off	Off	Off	Off	Off	10
2	Zero	Off	On	Off	On	Off	Off	Off	10
3	Zero/heating	Off	On	Off	On	Off	On	On	1
4	TEV Measure	Off	Off	On	Off	On	Off	Off	19
3	Zero/heating	Off	On	Off	On	Off	On	On	1
4	TEV Measure	Off	Off	On	Off	On	Off	Off	19

For the automated experiments, a new ceramic denuder was heated for 3 hours at 1100ºC to remove contaminants. After it had cooled, the denuder was coated with 9% NaCl in water/methanol (50/50), dried in the laboratory hood, and mounted inside the microwave oven. To confirm that the denuder itself did not give off NO_y, the first experiments were conducted with NO_y-free zero air. Valve 1 was disabled, and zero air was sampled during the normal sampling cycle as described above. Figure 3-3 shows the results. The NO_y spikes occur after the microwave was turned on. Their intensity decreases within the first 4 cycles and stays constant for the following cycles. These minimum NO_y spikes are due to a small parcel of ambient air that is trapped between valves 4 and 5 during modes 3 and 4 and flushed out together with the decomposition products from the heated denuder onto the NO_y analyzer. The height of these ambient air peaks did not change significantly throughout the experiment and were thus regarded as a constant background. The broad steps in the plot are due to the instrument resolution of 1 ppb. The NO_y analyzer itself was operated with 10 seconds time resolution, but the analog signal was averaged by the data logging system for one-minute periods.

During the initial experiments high NO_y peaks of several hundred ppbV were observed immediately after the irradiation of the denuder. Consequently, the range of the NO_y analyzer was set to its maximum value of 1000 ppb, resulting in a concentration resolution of the analog output of 1 ppb. This causes the broad steps in the picture, while measuring at the very low end of the concentration range.

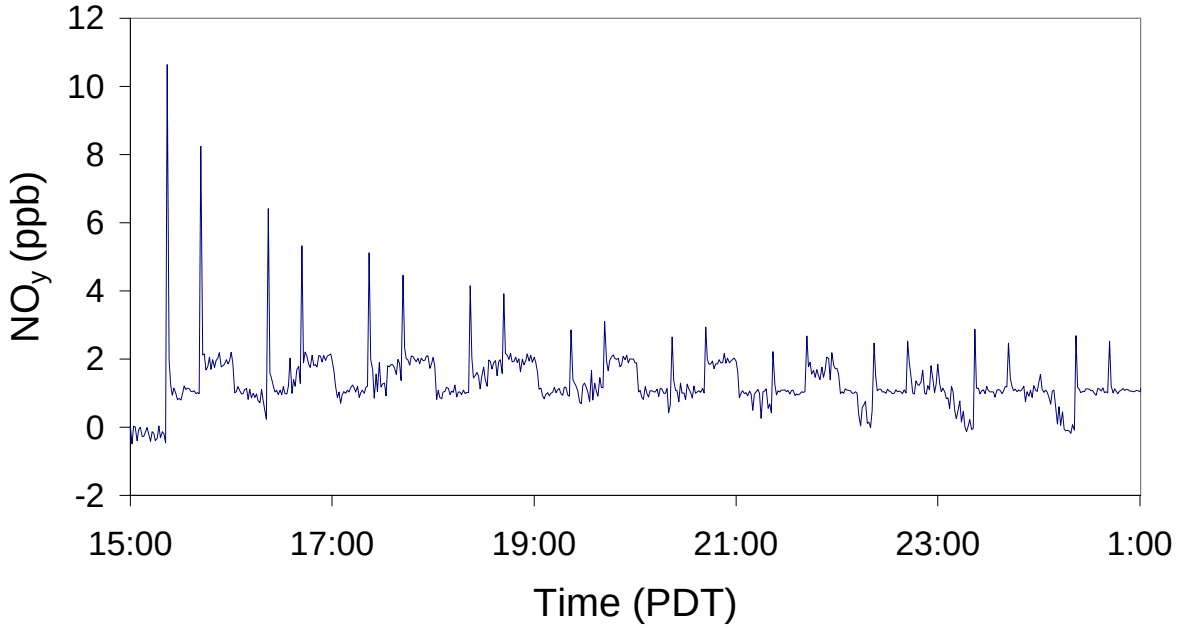


Figure 3-3. NaCl coated preheated denuder sampling zero air.

Once we had done preliminary tests to set up the range of the NO_x analyzer, we chose appropriate dilution flow of the diffusion tube source. Figure 3-4 is a plot showing the typical NO_y-readings for a 60-minute cycle.

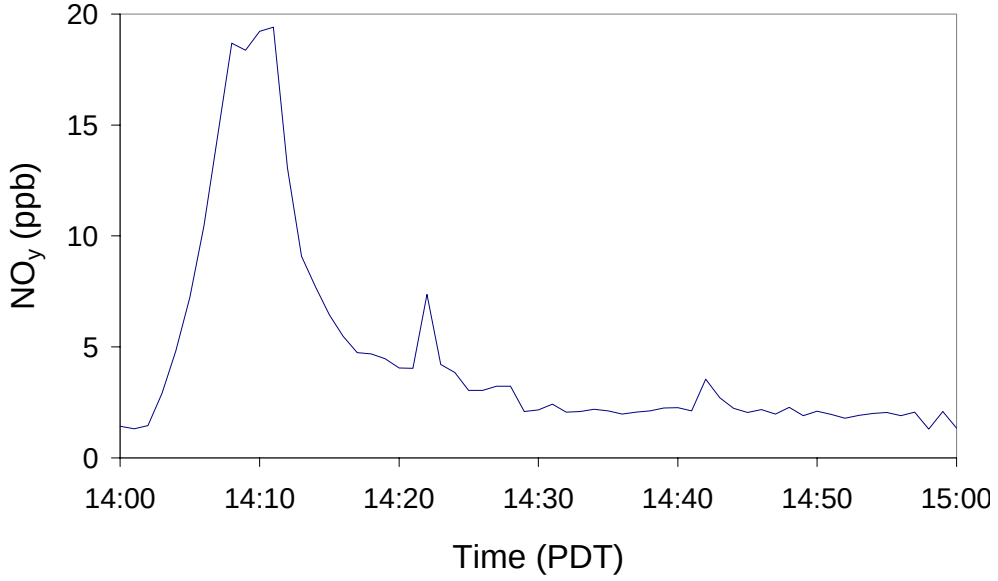


Figure 3-4. Typical NO_y concentrations for a 60-minute cycle.

The first large NO_y peak represents the collection period (mode 1) during which the analyzer is sampling the diluted nitric acid directly. As can be seen in the picture, the concentration stabilizes within the 10-minute duration of this mode. Simultaneously the same diluted nitric acid is passed through the ceramic denuder to collect the nitric acid. Since the denuder is coated with sodium chloride, the gaseous nitric acid is converted to solid sodium nitrate and gaseous hydrochloric acid. The former remains on the denuder whereas the latter evaporates and is carried away by the gas stream.

During the next 10 minutes (mode 2), the denuder is isolated from all flows, while the NO_y analyzer samples zero air, to return to a zero reading. Then the microwave is turned on for 1 minute to heat the denuder and decompose the formed sodium nitrate (mode 3). Immediately after this, the NO_y analyzer measures a peak in NO_y concentration. The heating is repeated once after 19 minutes and another smaller NO_y peak is observed.

Nitric Acid Recovery

During the first 10 minutes of the 60-minute cycle, diluted nitric acid was sampled. The measured NO_y concentrations show the maximum of nitric acid that can be collected on the ceramic denuder in the same time period. Averaging over 20 cycles gives a value of (0.62±0.07) μg HNO_3 where the error is one standard deviation.

Alkali metal nitrates decompose thermally to give mainly the metal oxides, nitrogen, and oxygen along with small amounts of nitrogen oxides, where the exact composition of the product mixture depends on the temperature. Previous studies, however, were all conducted under equilibrium conditions. By contrast, in the microwave setup employed in this study, the decomposition of the sodium nitrate occurs fast under non-equilibrium conditions and at an unknown temperature. Consequently, it is unknown how much of the nitrogen in the collected nitric acid is converted into nitrogen oxides and measured by the NO_y analyzer, and how much of it is converted into nitrogen giving no detector response.

The NO_y peak after the first heating of the ceramic denuder contains both the NO_y from the decomposition of the collected nitric acid as well as the NO_y from the trapped parcel of ambient air. The first laboratory experiments proved that a one-time heating of 1 minute was sufficient to remove nitric acid and nitrates quantitatively from the denuder. Thus the smaller peak after the second heating contains only the portion due to the trapped ambient air parcel, and the difference between both peaks is the NO_y formed by decomposition of the collected nitric acid/sodium nitrate. Again, 20 cycles were used to calculate the recovery rate. In detail, the difference in area between the first and second peak was determined and averaged, resulting in a value of (3.9±1.7) ppb NO_y·min, which correlates to $(1.00\pm0.45)\cdot10^{-5}$ μg HNO_3·min/cm^3. With a sampling rate of the NO_y analyzer of 1 l/min, the recovered nitric acid was $(1.00\pm0.45)\cdot10^{-2}$ μg HNO_3. Division by the maximum collectable amount of (0.62±0.07) μg HNO_3 results in a recovery rate of (1.6±0.7)%.

Conclusions

We have shown that the ceramic denuder material is able to quantitatively scrub nitric acid from air flowing through it, while letting nitrogen oxides pass. A single 1-minute irradiation of the ceramic denuder with microwaves quantitatively decomposes the collected nitric acid and/or the sodium nitrate that it is converted to. A fraction of the decomposition products are nitrogen oxides, which can be detected by a conventional chemiluminescence NO_y analyzer.

However, the observed peaks in NO_y upon heating of the denuder were very low. We attribute this mainly to the time resolution (averaging time) of the data logging system of 1 minute. The actual NO_y peak as observed directly on the display of the NO_y analyzer had a maximum of up to 900 ppb but lasted only a few seconds. Thus a data logging interval of 1 second instead of 1 minute should improve the signal to noise ratio significantly.

Another flaw of the used experimental setup was that a small parcel of ambient air was trapped between two valves, resulting in a substantial background signal.

Since the experiments presented here were designed to show the feasibility of the method, a commercial microwave oven was used to irradiate the denuder. As expected, the microwave field proved to be inhomogeneous. A commercial nitric acid analyzer based on this method would have to use a specifically designed microwave generator that focuses the microwaves only on the denuder.

Another problem that needs to be addressed is the cooling of the denuder after the irradiation. A microwave generator that focuses the irradiation only on the denuder would prevent the denuder holder from heating up unnecessarily, and less energy would need to be dissipated to cool the denuder to ambient temperature again.

3.3 Operation of a NO_y and Nitric Acid Measurement Network

3.3.1 Work Plan

A work plan was written to describe the measurement approach, quality control tests to be applied, and data quality objectives. Appendix B contains this work plan. A standard operating procedure (SOP) was written for the NO_y analyzers. This document, presented in Appendix C, contains all the details for operating the analyzers and performing routine quality control checks. The heart of this document is the weekly checklist, which provides for all the QC steps required for proper maintenance.

3.3.2 Siting and Installation

Riverside

The initial installation included the following equipment:

- Two ThermoEnvironmental Instruments model 42CY dual converter NO_y, NO_y-NA analyzer (SN 58440 and SN 58441).
- 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 or 15 minutes. The data logger was programmed to supply zero air every four hours for a 20-minute interval.
- Zero air supplied by an Aadco purification system.

Data collection started in April 2000.

Azusa

The initial installation included the following equipment:

- ThermoEnvironmental Instruments model 42CY dual converter NO_y, NO_y-NA analyzer (SN 58313).
- ThermoEnvironmental Instruments model 146 Calibrator. The calibrator was set up to perform zero check on the NO_y analyzer 6 times a day for 20 minutes each time.
- Scott Marrin NO in N_2 certified calibration gas.
- Scott Marrin NH_3 in N_2.
- Campbell CR10 Data Logger. The data logger was programmed to collect data averaged for 10 minutes.
- Zero air source consisting of a diaphragm compressor, holding tank, and Purafil adsorption tower.

Data collection started in October 2001 due to delays in having the instrument repaired by the factory. The problem was a failure in the analyzer's software that required evaluating it and sending it back to the manufacturer several times. Many of the analyzer's components were replaced, one by one, until the analyzer was finally shown to be reliable. The second analyzer was not available for use at this site since it was loaned, by ARB request, to Rich Barchett for use in an aircraft operated during CCOS.

3.3.3. Network Operation

Sites checks were performed at approximately weekly intervals in Riverside during the summer of 2000. Figure 3-5 is an example of a filled-in site check form.

TEI Model 42CY Weekly Checklist - CE-CERT Site

Date: 6-23-00
Technician: [illegible]
Time: 0814 PDT/PST

Dilution Calibrator Information
SN: [illegible]
Cert Date: [illegible]
Dilution Flow: 10.02 L/min
O3 Setting: ____ %

NO
NO Cyl ID: CC12880
Cyl Conc: 102.1 ppm
NO Flow: [illegible] ml/min
Calc Conc: 210 ppb

NPN
NPN Cyl ID: CC28549
Cyl Conc: 20.75 ppm
NPN Flow: 28 ml/min
Calc Conc: 180 ppb

Permeation Calibrator Information
NH3 Perm Flow: 47 ml/min
NH3 Dilution Flow: 8.4 L/min
HNO3 Perm Flow: 48 ml/min
HNO3 Dilution Flow: 8.1 L/min
Water Bath Setpoint: 45.0 C
Water Bath Temp: 46.0 C
Fill Water Bath?: Y y/n

Check SN:CTL42	58440				SN:CTL42	58441		
Parameter	NOy-NA	NA	NOy	Other	NOy-NA	NA	NOy	Other
Range, ppb	500.0	50.0	500.0	-------	500.0	50.0	500.0	-------
Averaging Time	-------	-------	-------	605	-------	-------	-------	
Cal Bkg	0.0	-------	0.0	pre: 0.0	0.0	-------	0.0	pre: 605
Cal Coeff	1.249	1.000	1.000	-------	1.192	1.000	1.000	-------
Cell Pressure	-------	-------	-------	255.3	-------	-------	-------	270.3
Internal T	-------	-------	-------	32.5	-------	-------	-------	34.2
Chamber T	-------	-------	-------	49.4	-------	-------	-------	48.9
Cooler T	-------	-------	-------	-11.7	-------	-------	-------	-10.6
Converter T	552		337	-------	366		372	-------
Converter Set	353		338	-------	368		373	-------
Ozonator Flow	-------	-------	-------	0.105	-------	-------	-------	0.104
Sample Flow	-------	-------	-------	0.296	-------	-------	-------	1.153
Bypass Flow	1.2	-------	1.4	-------	1.39	-------	1.38	-------
Changed Filters?	Y	-------	Y	-------	Y	-------	Y	-------
Changed Denuders	Y	-------	-------	-------	Y	-------	-------	-------

Calibration Parameter	Stabalized Digital Readout (ppb)				Stabalized Digital Readout (ppb)			
Zero Air	0.27	0.86	1.14	-------	0.41	0.96	1.38	-------
NO	211.9	0.4	212.3	-------	165.0	0.5	165.5	-------
GPT	208.4	(1.6)	210.4	-------	165.5	-0.4	165.1	-------
NPN	172.8	0.8	173.6	-------	138.4	0.6	138.9	-------
HNO3-Free Ambient	22.7	0.1	22.8	-------	18.95	0.93	19.68	-------
HNO3	1.68	4.24	5.92	-------	2.20	3.06	5.25	-------
NH3	0.36	0.85	1.21	-------	0.91	0.99	1.90	-------

COMMENTS

58441 pressure alarm after filter change. checked for leaks, changed teflon or denuder. Same Results, so let max press. to 400. (same as 58440)

Figure 3-5. Site check form.

3.3.4 Data Management

Data Collection

The air quality data were collected using Campbell CR10 digital data loggers. Data were reviewed and downloaded weekly and maintained in a networked PC that was backed up weekly. Initially, the data logger at the CE-CERT site processed the data into 15-minute averages. Effective 5/3/2000 at the CE-CERT site and when measurements commenced at the Azusa site (10/18/2000), the data were processed into 10-minute averages. These average data were retrieved by CE-CERT for review and further processing into the final validated data.

Data Validation

The date/time stamp for the raw data were "time ending" and for part of the year at the Azusa site, Pacific Daylight Time. The date/time for the data sets were "shifted" to "time beginning" and Pacific Standard Time. Periods of missing data (typically due to data logger failure) were identified. These preliminary, time corrected data, were output to files as "data processing step 6" data. The preliminary data include data status flags for each time period. The data flags used are:

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 1 validation
8	Invalidated by Level 2 validation
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 data greater than 100 ppb.
- Flagging data greater than 200 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 10 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.
- 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 4 ppb different from that for the same parameter on the second analyzer, when the first analyzer’s NO_y value was less than 30 ppb.
- Flagging data when the NO_y, NO_y-HNO_3 or HNO_3 value was greater than 2 ppb during an auto zero check.
- Flagging data when the logged HNO_3 value was not the same as the HNO_3 value calculated from the difference between the logged NO_y and NO_y-HNO_3 channel values.

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. For several periods, when the data assessment went further than to use just the immediate data trends near the affected periods (e.g., when the Azusa data were compared with the SCAQMD NO_x analyzer at the same site), the "Level 2," code "8" flag was used to identify data that were determined to be invalid. The validated data files for this processing step were output as "data processing step 9" data.

The "final," validated data 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.

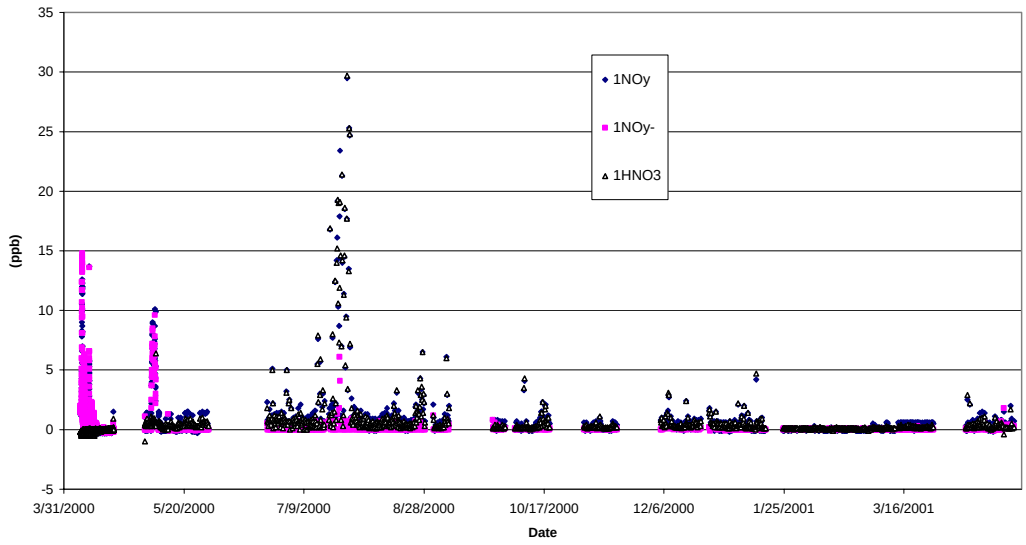
3.4 Results

3.4.1 Riverside (CE-CERT)

Automated Zero Checks

Figure 3-6 shows the automated zero checks that were performed during the entire period reported. Each point represents a 10- or 15-minute-averaged period selected in the middle of the zeroing period of 1 hour. The gaps in the data are periods when the instruments malfunctioned. Vacuum pump failure was the primary problem. Note that there are several periods when the zero is high for both of the instruments. Since both were affected, we suspect insufficient air was being supplied by the zero air source. The source was used for several other applications in the laboratory, and there were several periods when laboratory personnel apparently used too much during other procedures or that the main compressor for the "house" that supplied the air purification device malfunctioned. When insufficient zero air was available, the instrument sampled some or all ambient air. These periods are readily distinguishable in the time series plots of the Figure. The zero response of both the NO_y and NO_y- channels were very close to zero, typically less than 1 ppb. The zero for the NO_y was generally slightly larger. The converters of both analyzers had been renovated before the start of sampling, but very little of the previously reported "memory" effect was observed in contrast to the first year these instruments were used in the South Coast Air Basin.

a



b

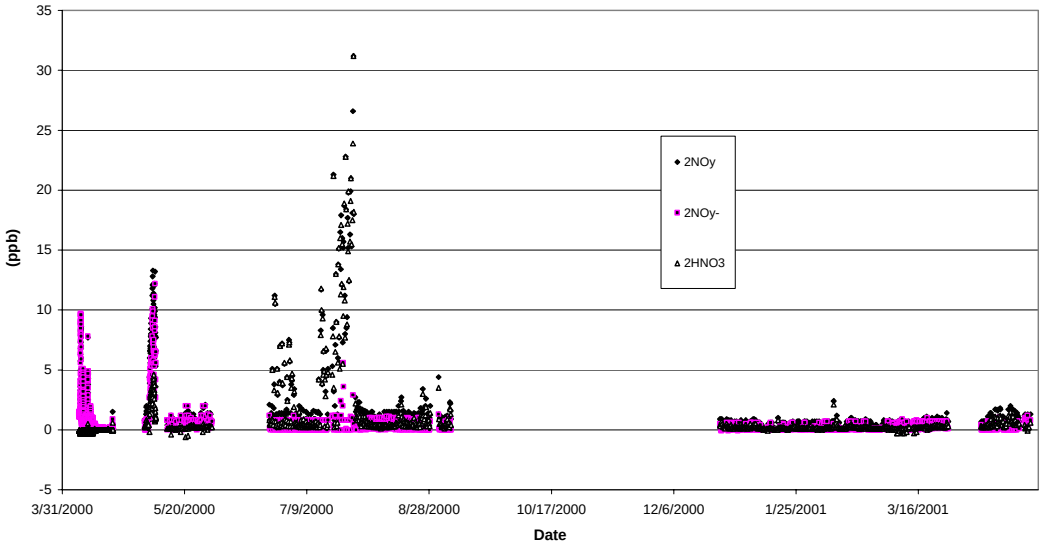


Figure 3-6. (a) Auto zero NO_y SN58440. (b) Auto zero NO_y 58441.

Data and Data Analysis

Figure 3-7 summarizes the NO_y data for both analyzers at Riverside for the entire measurement period. Each data point represents a 10- or 15-minute average. The analyzers respond approximately the same for the periods with peak concentrations of about 300 ppb. Figure 3-8 shows the percentile distribution of NO_y by month for both analyzers. For comparison, Figure 3-9 shows the percentile distribution of ozone concentrations at a nearby site located on the UC Riverside campus. This site is operated by the South Coast Air Quality Management District and is located approximately 3 miles to the south of the CE-CERT location. Figure 10 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, although Analyzer 58440 shows a period of decreased response. This was most likely when the vacuum pump started to fail but before the data were invalidated because of the failure. Figure 3-11 summarizes the nitric acid data from both analyzers for the measurement period. There appears to be periods when the nitric acid concentrations of both instruments were unrealistically high.

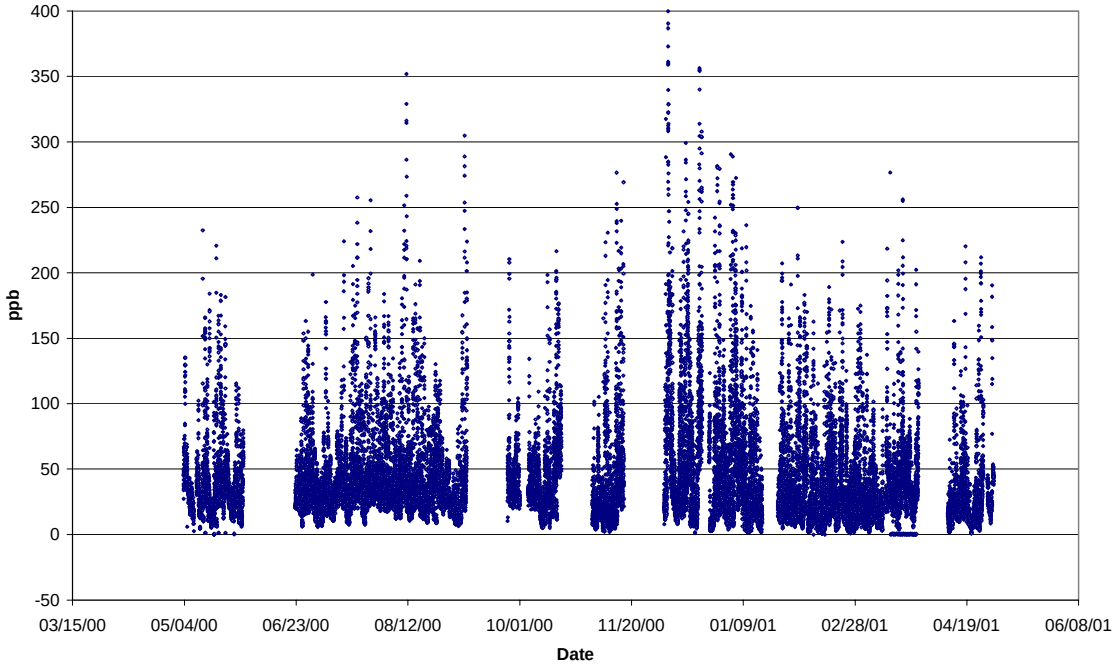
To further investigate the phenomenon of unrealistically high nitric acid concentrations, we plotted the nitric acid versus the NO_y concentration for each analyzer. The results (Figure 3-12) show two distinct relationships. For much of the time there does not appear to be a relationship between NO_y and nitric acid. There appear to be intervals for both instruments when the NO_y and nitric acid concentrations are nearly the same. There is also a very sharp demarcation line on the relationship with the higher nitric acid values. This demarcation line could not be the result of the actual ratio between NO_y and nitric acid. We believe that this is caused by a bug in the software of the analyzer that occurs under certain conditions. The NO_y and NO_y- channels were operated at 1ppm full scale while the nitric acid channel was operated at 50 ppb full scale. We have previously found in laboratory testing that a mismatch in full scales settings, even though all components should be within scale, can result in erroneous readings. This occurred only for certain combinations of values. We originally thought that this was a peculiarity of the analyzer as frequent checking of the ambient analyzers showed no problems. Until we analyzed the validated data set, these infrequent, but large excursions from the expected values were not noticed.

To correct for the erroneous nitric acid data we eliminated values that were above 5 ppb and were more than 30% of the concurrent NO_y value. This effectively removed many of the values corresponding to the points forming the relationship of high nitric acid to NO_y ratio without the bias of manual selection. Not all of these points could be removed since some data points were averages (10 or 15-minute) of periods when the analyzers were operating correctly and periods when they were not. This correction algorithm is therefore an approximation intended to removed the most serious and unrealistic outliers, a substantial number outliers therefore remained.

Figure 3-13 is a time series plot of the corrected nitric acid for both instruments. Note that the there does not appear to be any seasonal variation, rather a general spread of values from –1 to 4 ppb except for February. During this month there are high values in both analyzers that could not be explained. Figure 3-14 shows the percentile distribution of the nitric acid by month, again showing the high values in February. Figure 3-15 shows the time series for both analyzers during July 2000 when nitric acid concentrations are expected to be relatively high compared with the rest of the year. Although the plots show some outliers, the diurnal variation is quite distinct for both analyzers. Figure 3-16 shows the nitric acid concentrations for one typical day, July 30, 2000. Except for a few outliers, the nitric acid follows the expected diurnal variation, peaking at 14:00 hours. Although analyzer SN58440 generally gave lower concentrations, both showed a small shoulder at approximately 20:00 hours. We conclude that the instruments appear to be sufficiently sensitive to measure nitric acid in Riverside.

Figure 3-17 is a plot of nitric acid concentrations measured by one analyzer versus the other after the application of the screening process. The response is linear, indicating that the instruments are measuring nitric acid, although values above 10ppb (mostly during February) are considered suspect as described above. The correlation is low in part because of a number of outliers that were not removed in the screening process.

a



b

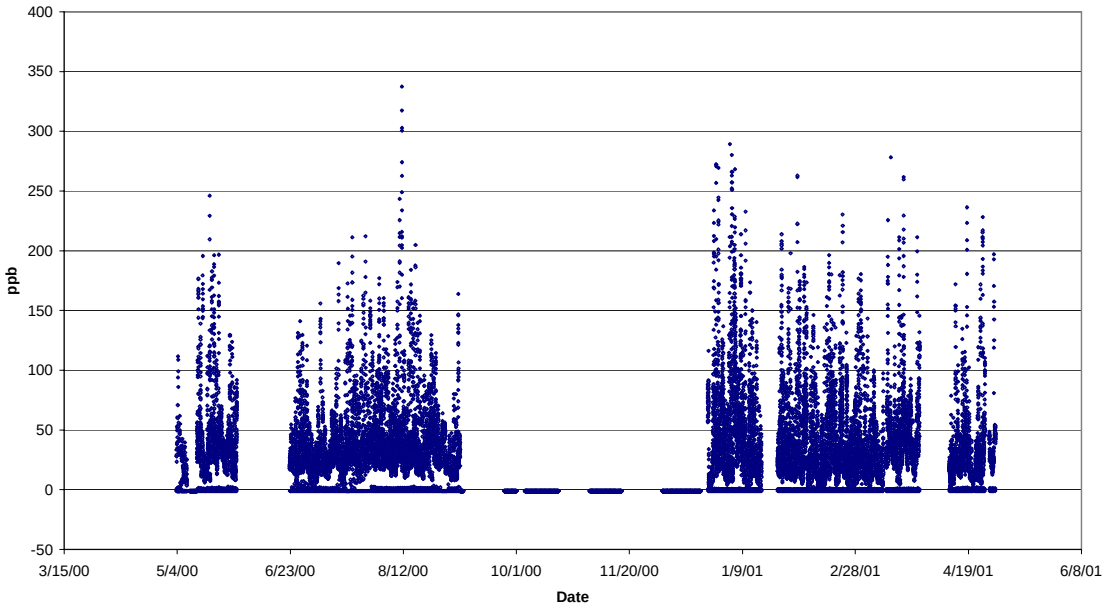


Figure 3-7. (a) NO_y concentrations for SN58440. **(b)** NO_y concentrations for 58441.

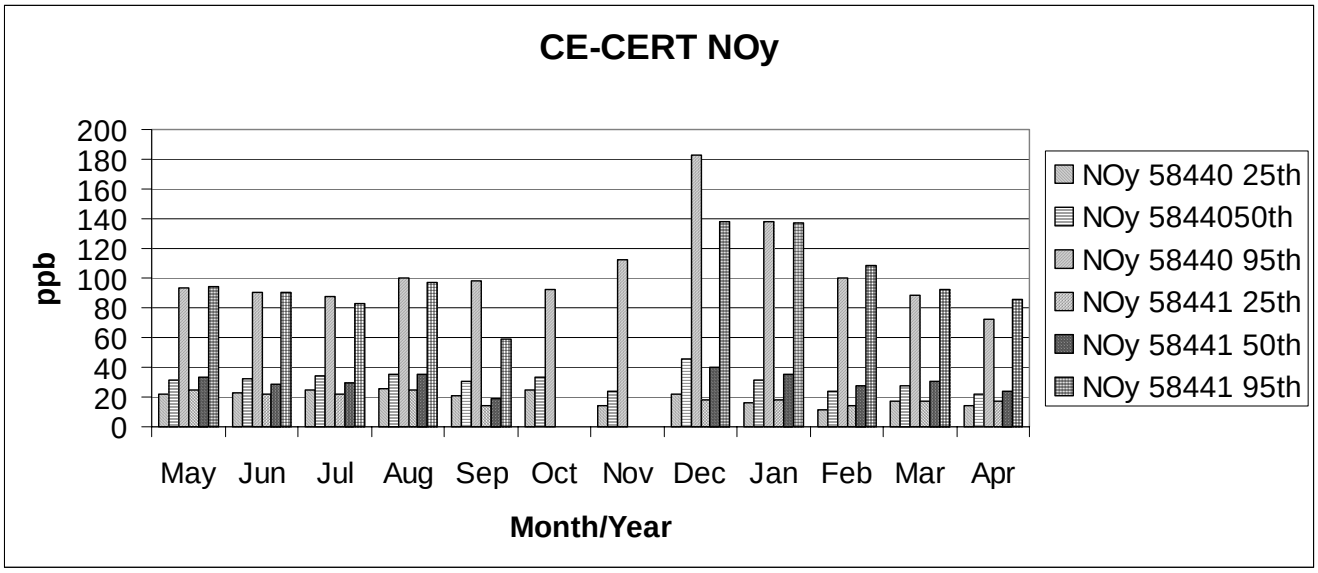


Figure 3-8. Percentile distribution of NO_y concentrations by month.

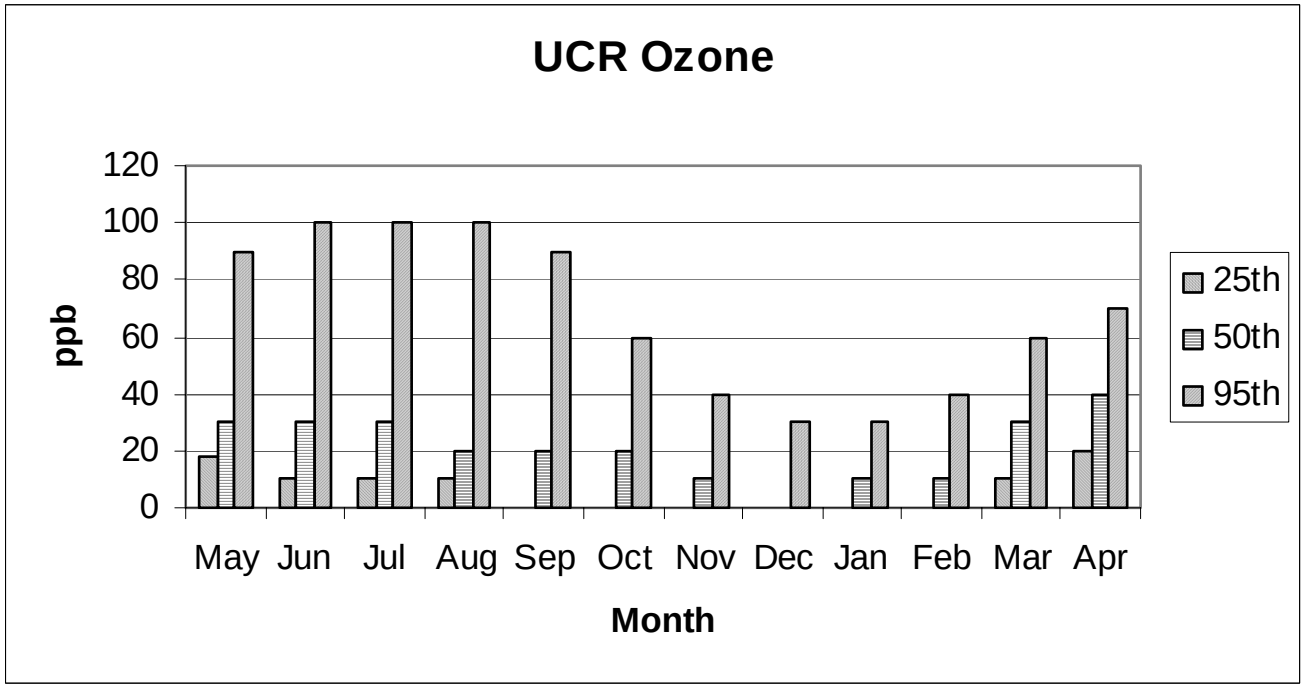


Figure 3-9. Percentile distribution of ozone concentrations from UCR SCAQMD-operated site.

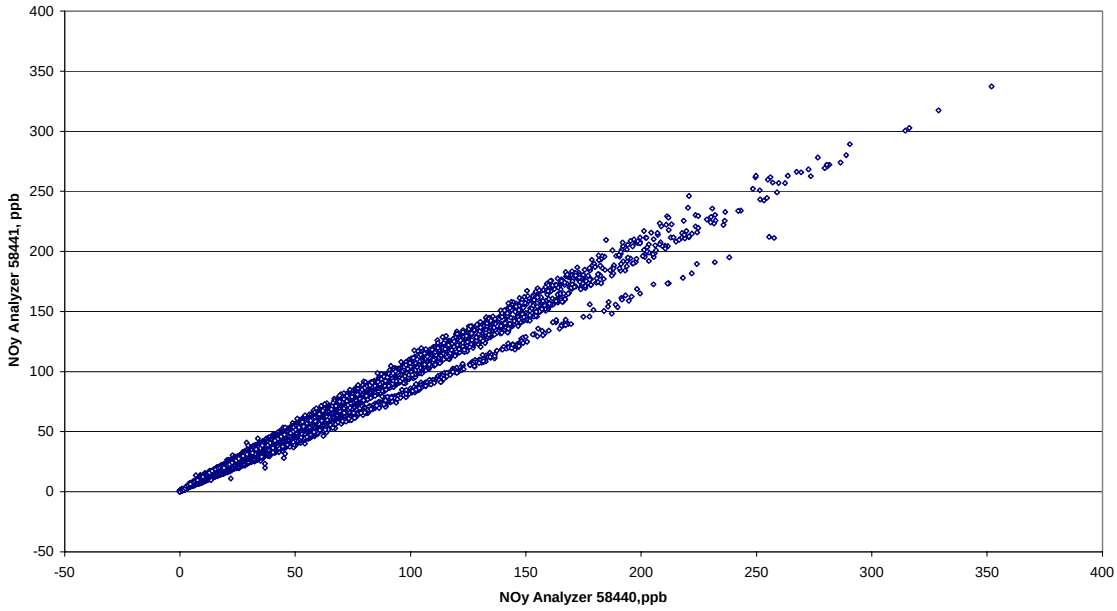
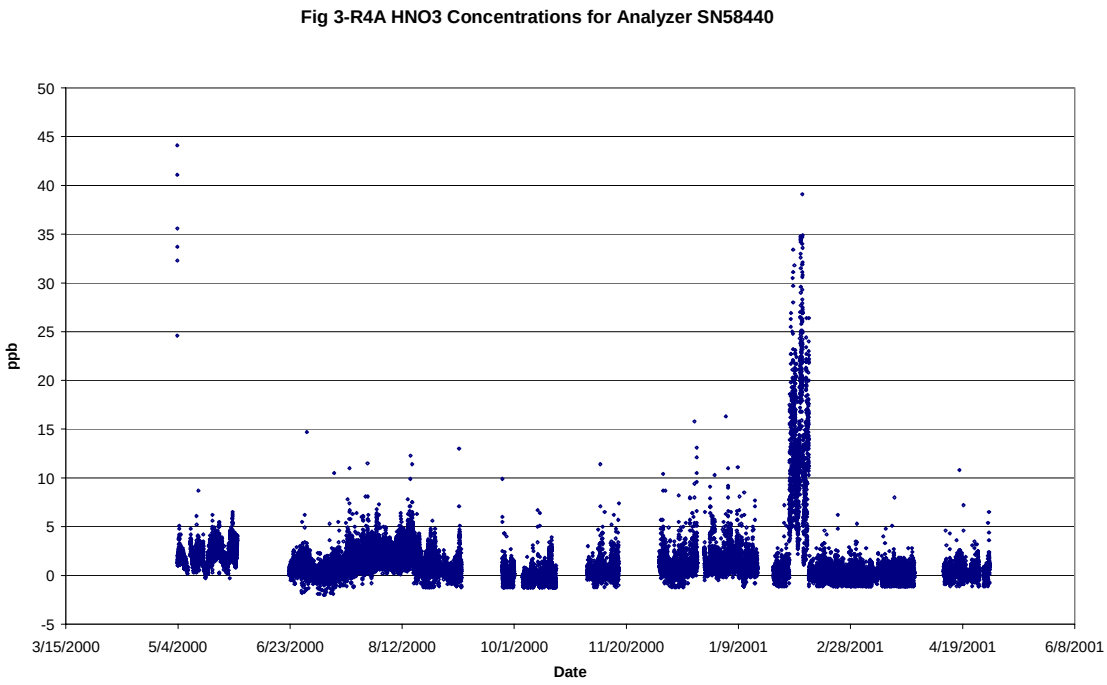


Figure 3-10. Comparison of NO_y between analyzers 58440 and 58441.

a



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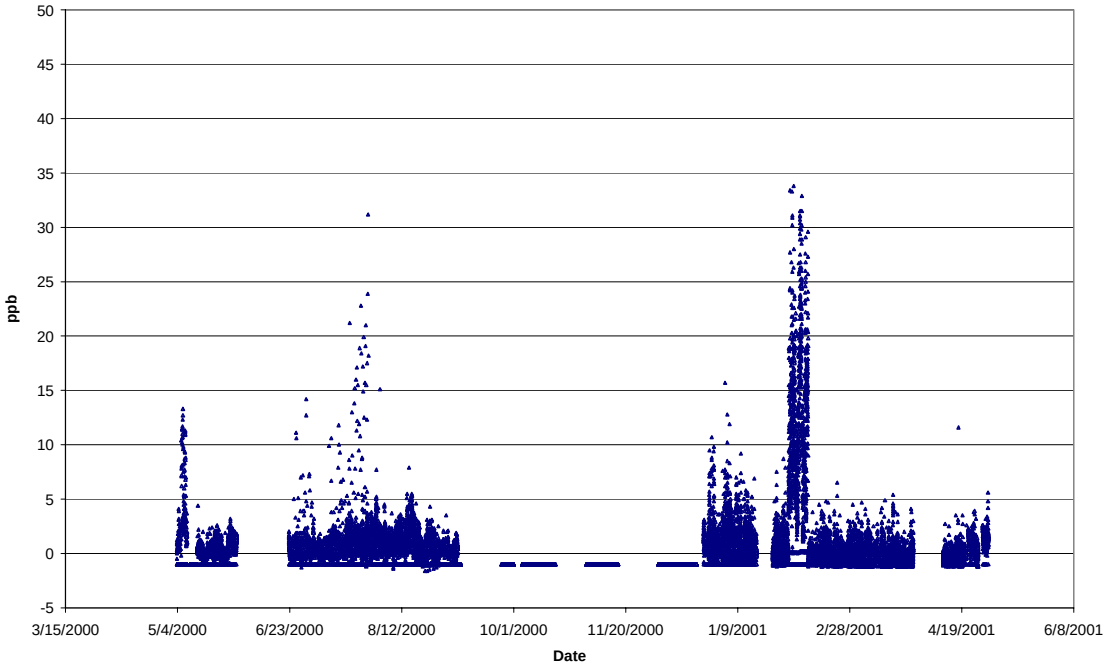
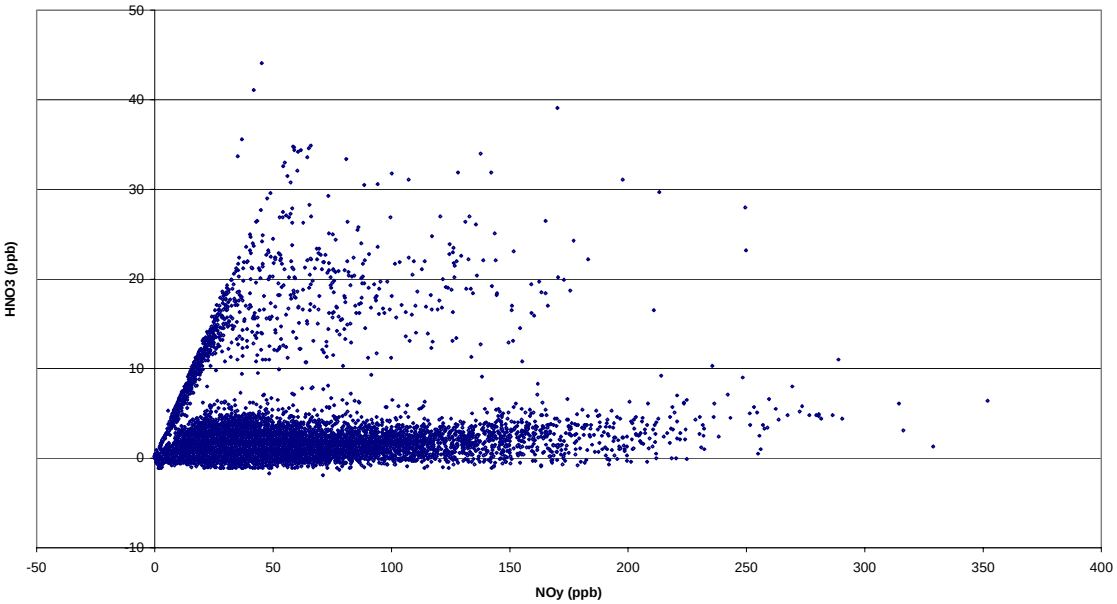


Figure 3-11. (a) HNO_3 concentrations for 58440. (b) HNO_3 concentrations for 58441.

a



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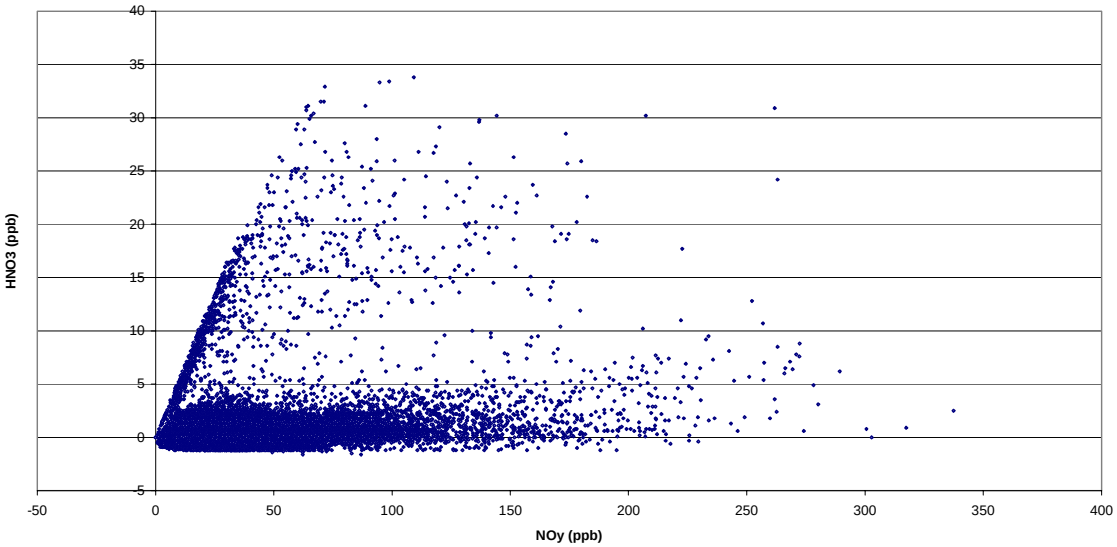
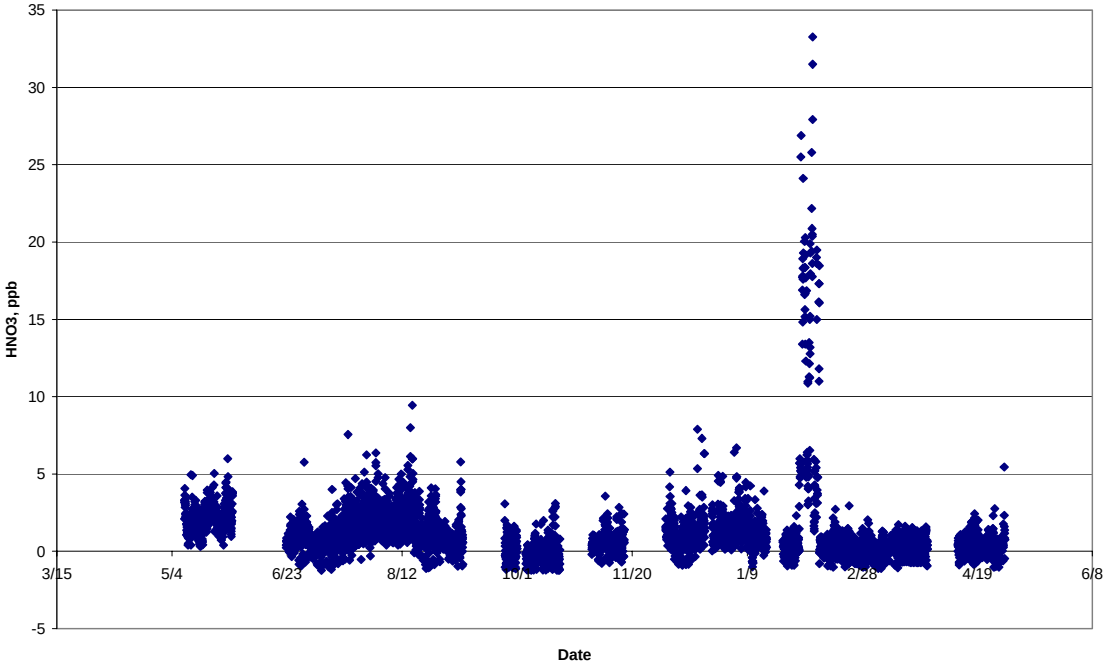


Figure 3-12. (a) HNO_3 vs NO_y Instrument 58440 (b) HNO_3 vs NO_y Instrument 58441.

a



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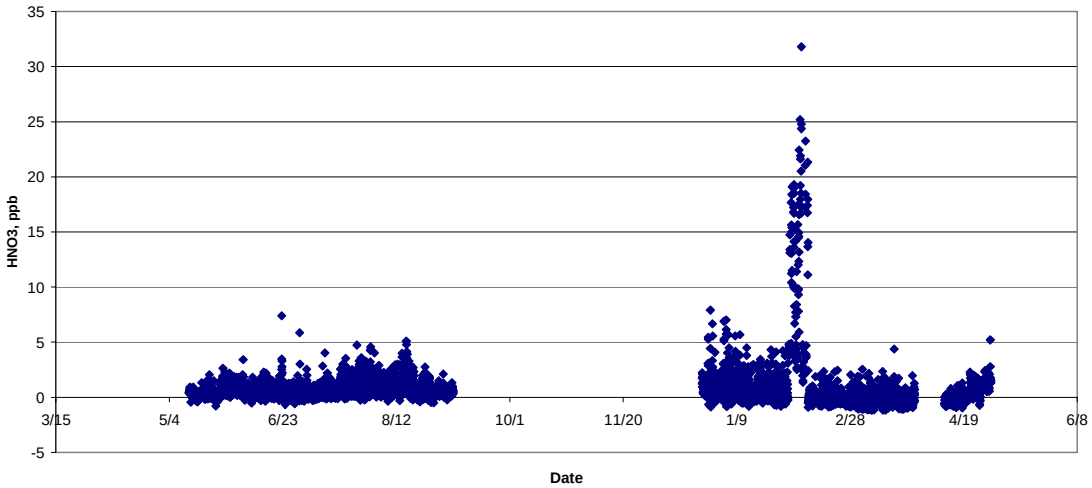


Figure 3-13. (a) Time series plot of HNO_3 for 58440. (b) Time series plot of HNO_3 for 58441.

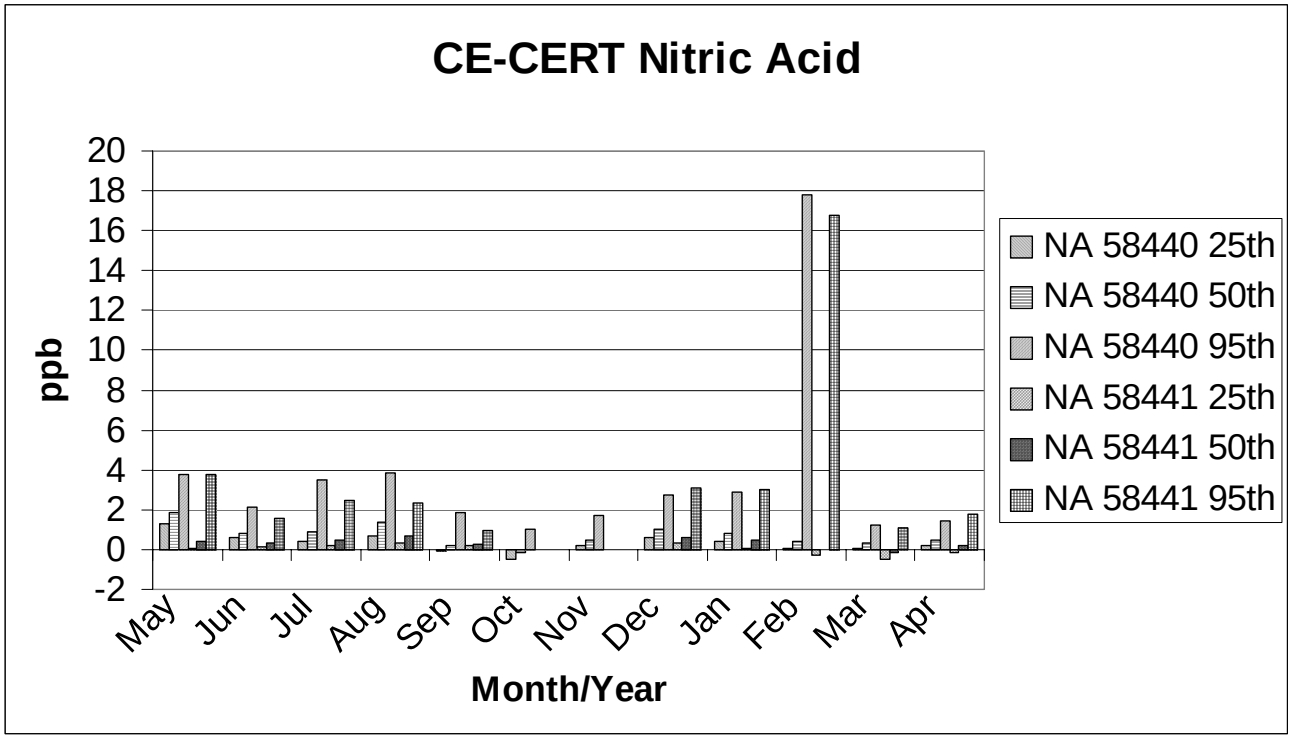
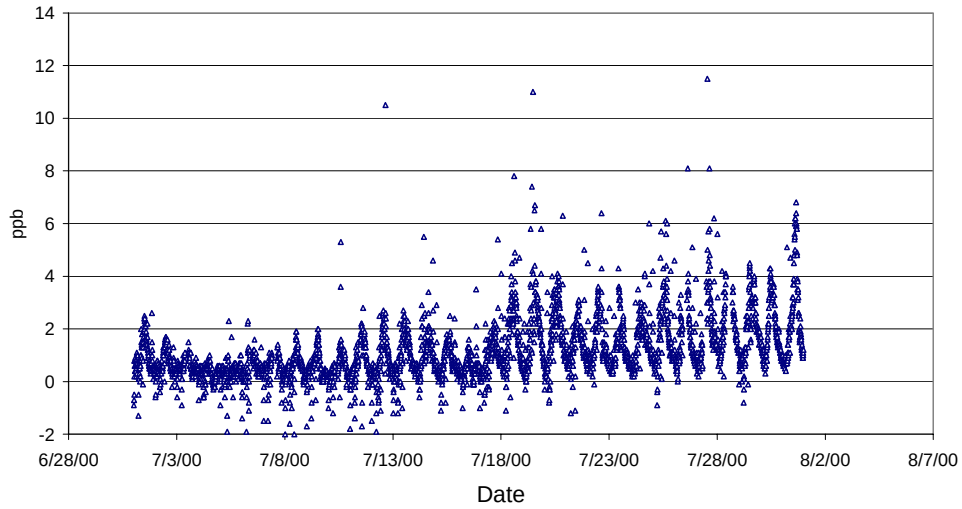


Figure 3-14. Percentile distribution of nitric acid concentrations by month.

a



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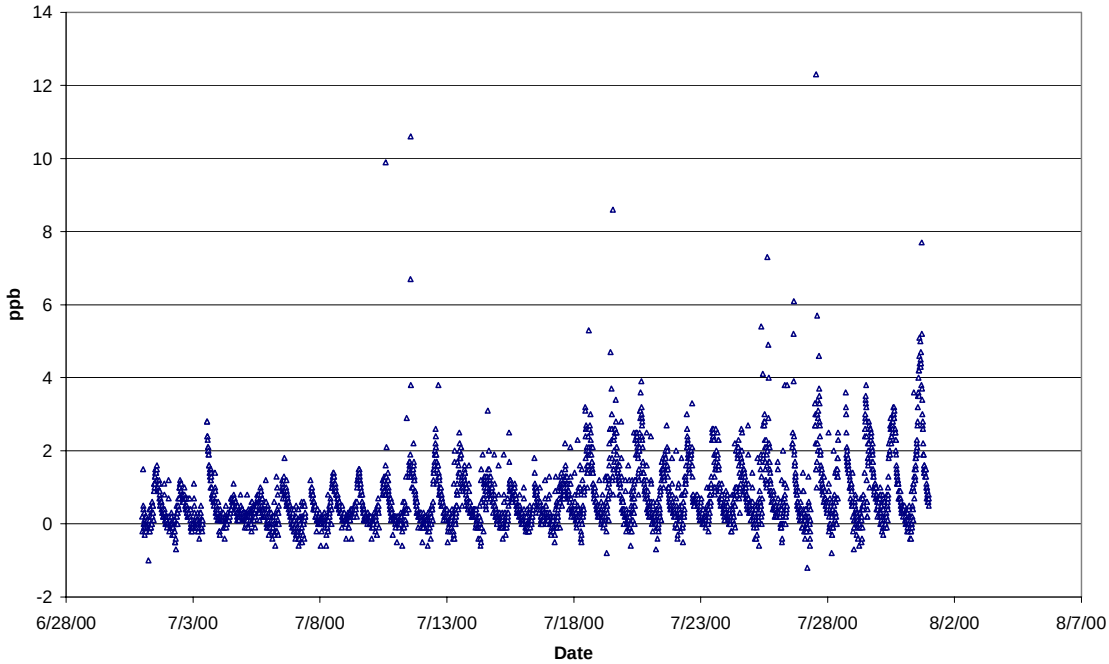
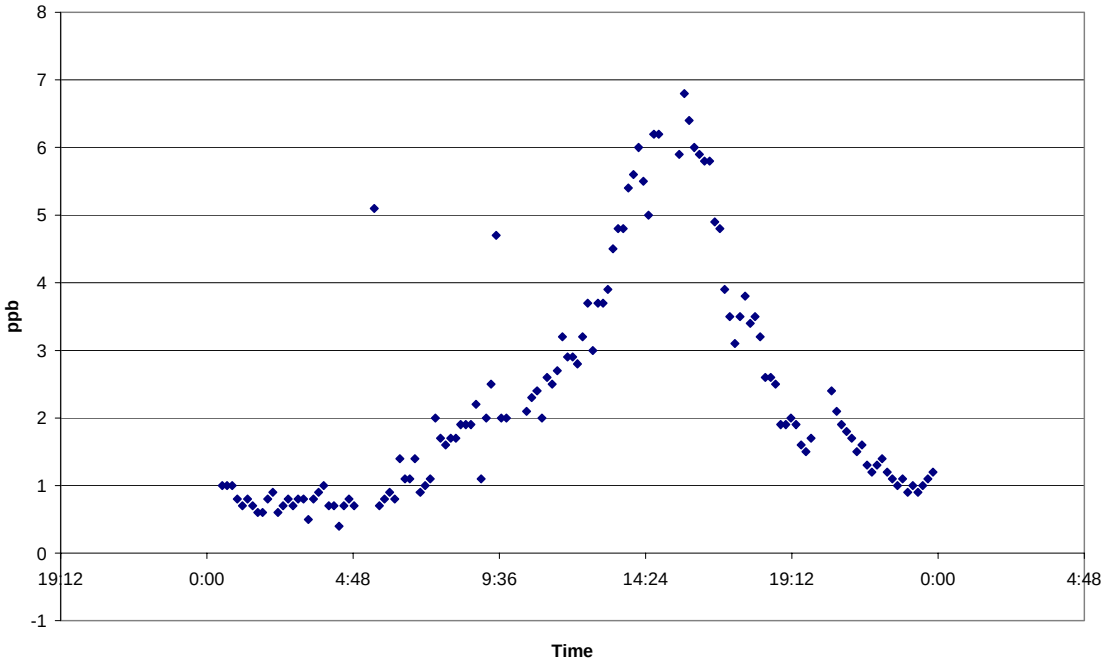


Figure 3-15. (a) Time series of nitric acid at Riverside during July 2000, Instrument 58440. (b) Time series of nitric acid at Riverside during July 2000, Instrument 58441.

a



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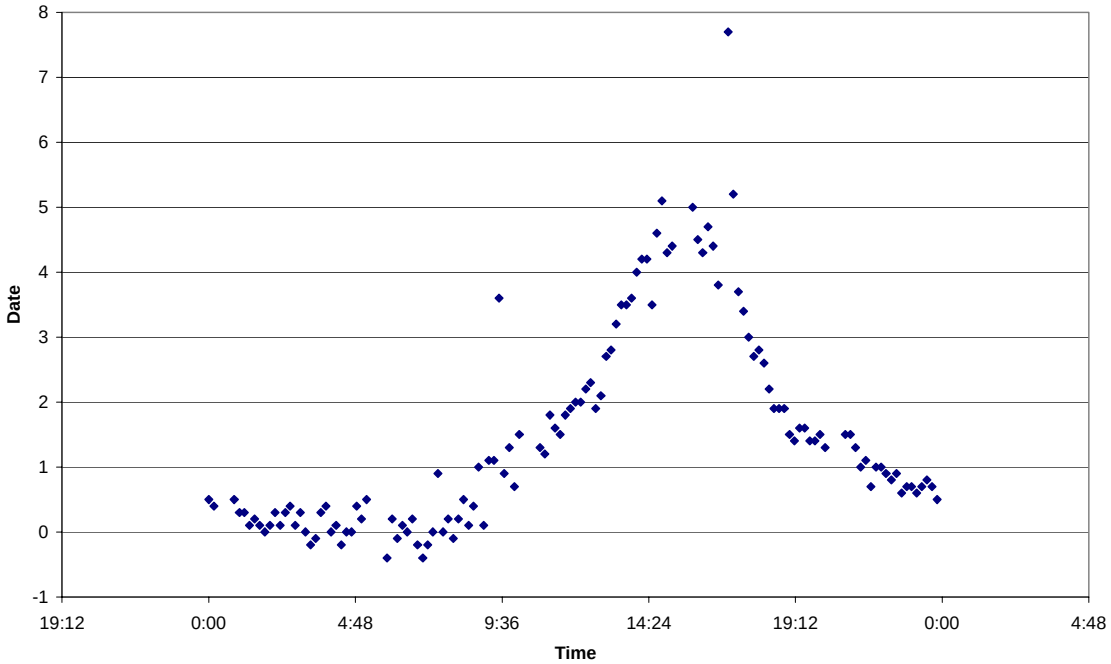

Figure 3-16. (a) Time series of nitric acid at Riverside during July 31, 2000, Instrument 58440. (b) Time series of nitric acid at Riverside during July 31, 2000, Instrument 58440.

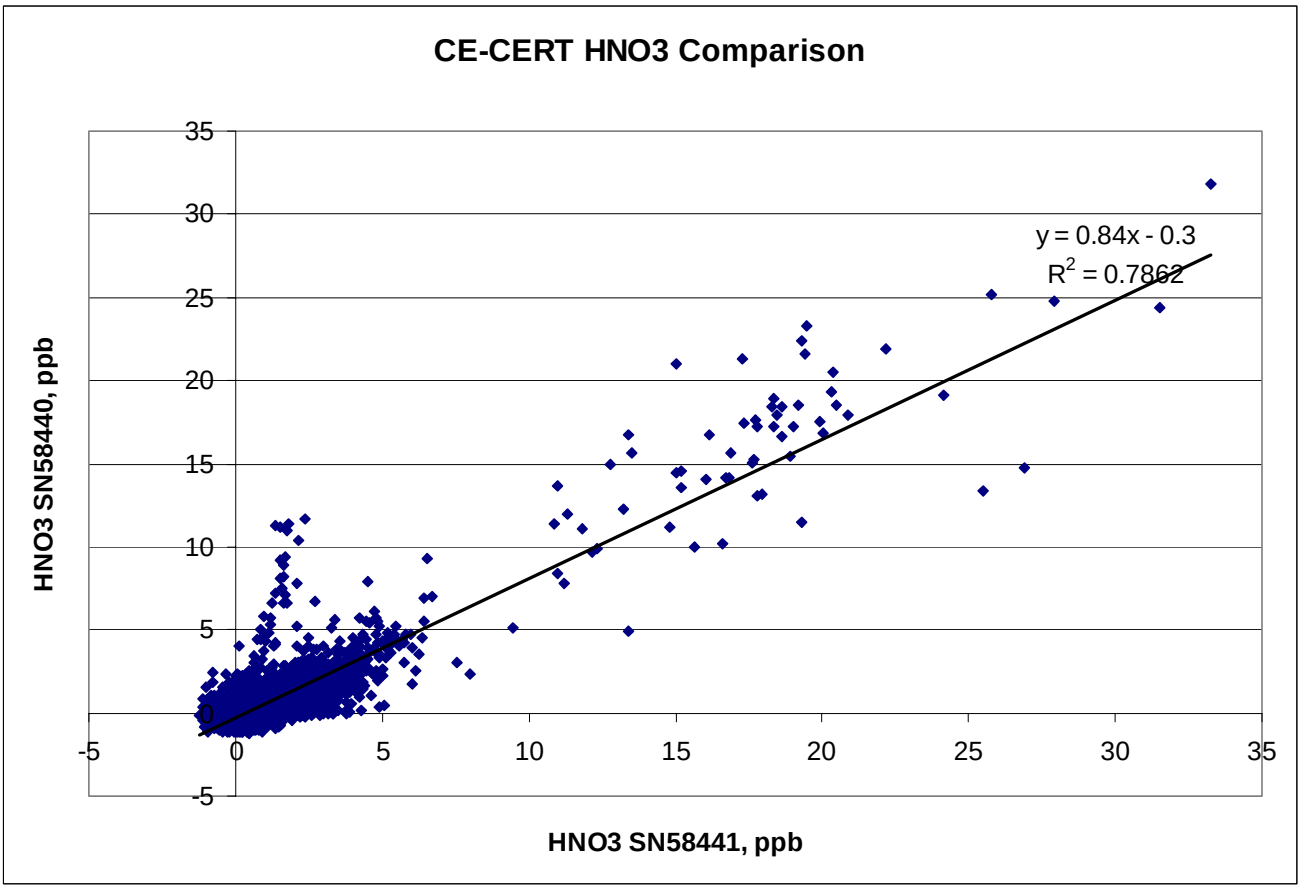

Figure 3-17. Comparison of HNO_3 measured by both analyzers at Riverside.

3.4.2 Azusa

Automated Zero Checks

Figure 3-18 shows the automated zero checks that were performed during the entire period reported. Note that during the period from November 18 to 27 that the zero responses were very high. This was due to the failure of the air compressor that supplied the zero air. It resulted in ambient room air being inducted into the sample inlet instead of the zero air. Note also that during this period the zero response is invariably higher for the NO_y than the NO_y^-. This is due to the memory effect that is almost always observed when sampling ambient air, especially in more highly polluted areas.

Data and Data Analysis

Figure 3-19 summarizes the NO_y data for the analyzer at Azusa for the entire measurement period. Each data point represents a 10-minute average. The peak concentrations were in the 500ppb range, significantly higher than the peak values in Riverside. Figure 3-20 shows the percentile distribution by month for the NO_y and Figure 3-21 gives the percentile distribution of ozone concentrations. Figure 3-22 summarizes the nitric acid data for the measurement period. As in Riverside, there appear to be periods when the nitric acid concentrations were unrealistically high. Figure 3-23 shows a plot of nitric acid versus the NO_y concentration. The results are very similar to those obtained in Riverside, showing two distinct relationships with a sharp demarcation line. We again corrected the nitric acid data by eliminating values that were above 5 ppb and were more than 30% of the concurrent NO_y value. This again effectively removed the values corresponding to the points forming the relationship of high nitric acid to NO_y ratio. Figure 3-24 is a time series plot of the corrected nitric acid concentration and Figure 3-25 is the percentile distribution by month. As in the Riverside data, there does not appear to be any seasonal variation, rather a general spread of values from 0-10 ppb. Figure 3-26 is a time series plot of corrected nitric acid for April 25, 2001. This is the month during the limited measurement period for this analyzer when the highest nitric acid concentrations might be

expected. While there are some outliers, the diurnal profile follows the expected curve, peaking at approximately 8 ppb. These results are consistent with those observed in Riverside.

Figure 3-27 compares the NOx measured at the Azusa site with that from the NO_y analyzer that we operated at the same site. This plot appears similar in nature to the NO_y vs. nitric acid plot before erroneous data were removed and therefore the question arises that perhaps the NO_y measurement is the problem. There are several reasons why this is unlikely:

- The data from the periods with the NO_y being close in value to the nitric acid had already been removed from this data set as suspect.
- Unlike the NO_y/HNO_3 comparison, the NO_y was lower than NO_x for one discrete period of time after which the instrument was repaired.
- For the NO_y/HNO3 comparison the HNO3 concentrations were unrealistically high and therefore suspect.

The similarities between the plots are therefore due to a similar underlying reason (periods of calibration mismatch) but they do not appear to be related in any other way.

If the data between February 17, 2001 (when the NO_y analyzer instrument suddenly had a low response relative to NO_x) and March 10, 2001 (when it was repaired) is excluded the slope of the linear regression is 0.85, the intercept is 0.5ppb and the correlation coefficient squared is 0.96. Although this is a significant bias, it should be noted that these instruments never were allowed to sample the same calibration gas. If this had been done, we would have had a more accurate comparison of the differences between the concentrations of these two parameters.

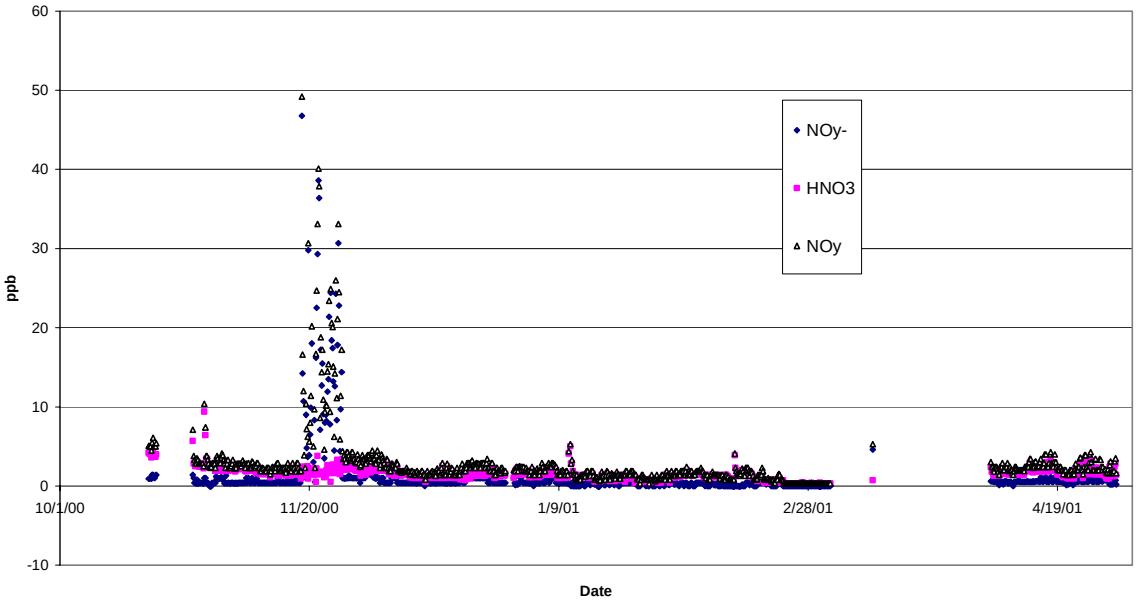

Figure 3-18. Auto-zero at Azusa.

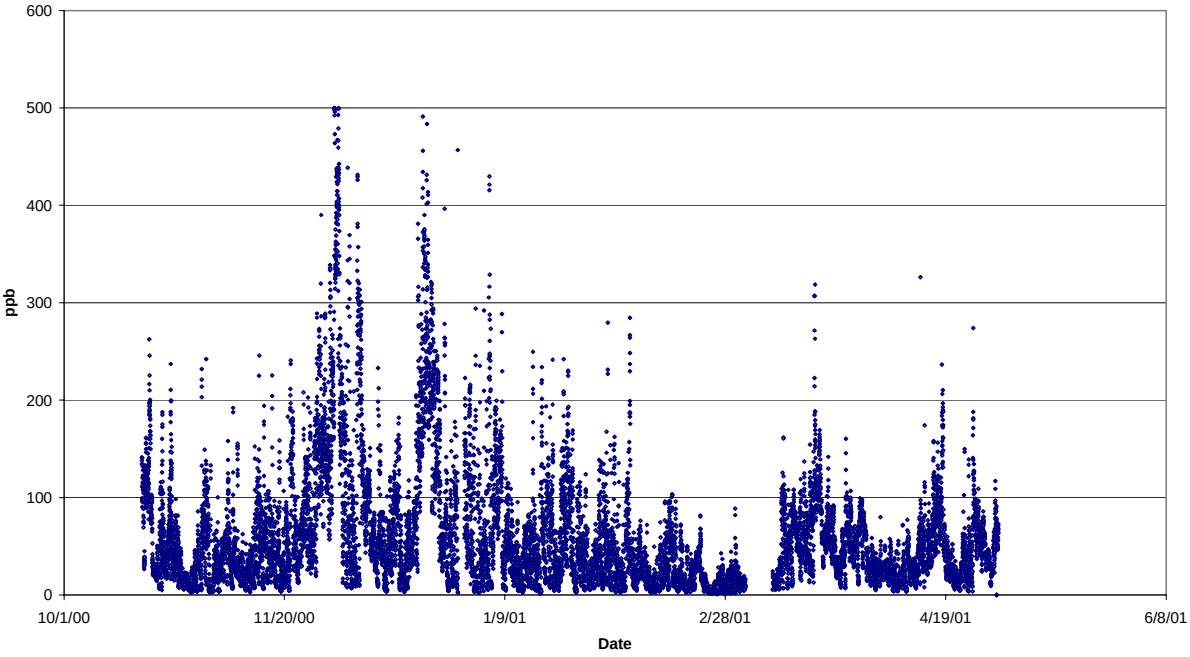

Figure 3-19. NO_y concentrations at Azusa.

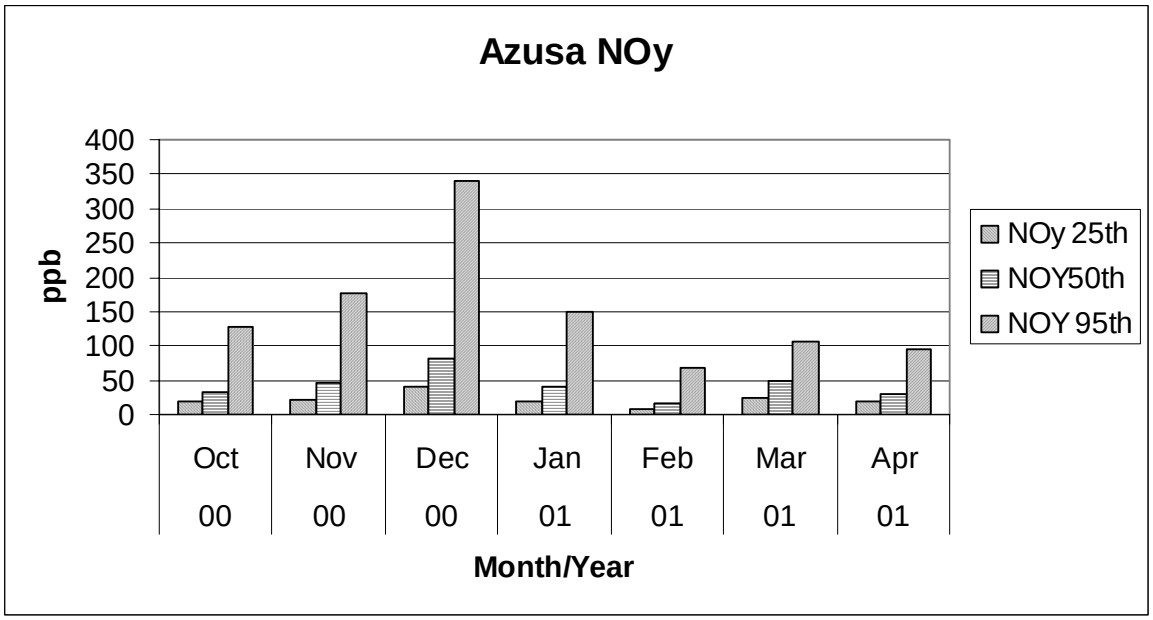

Figure 3-20. Percentile distribution of NO_y concentrations at Azusa by month.

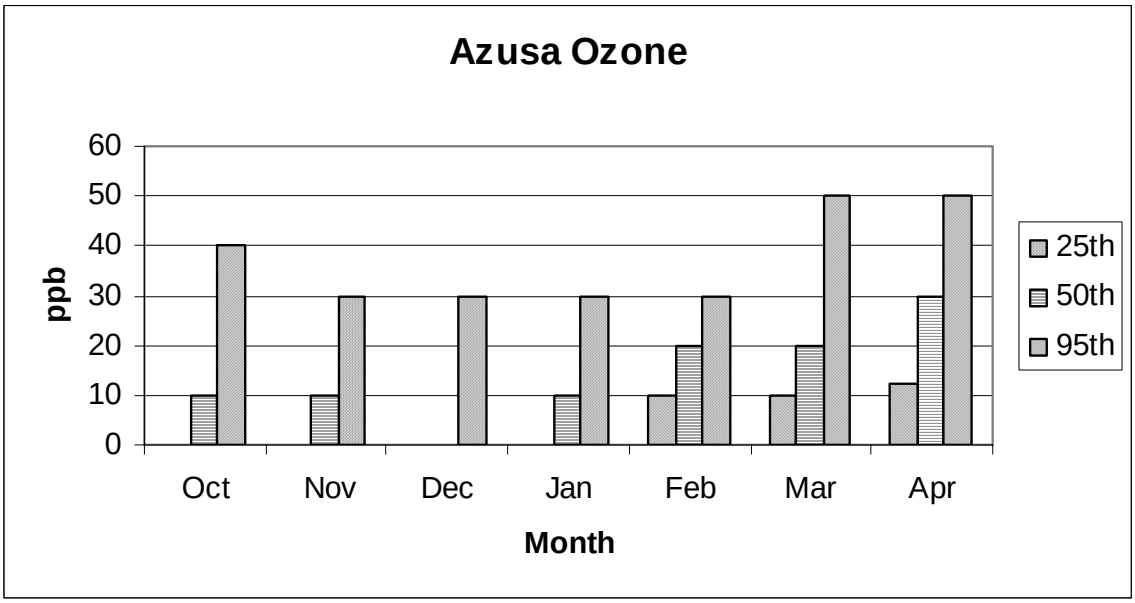

Figure 3-21. Percentile distribution of ozone concentrations by month.

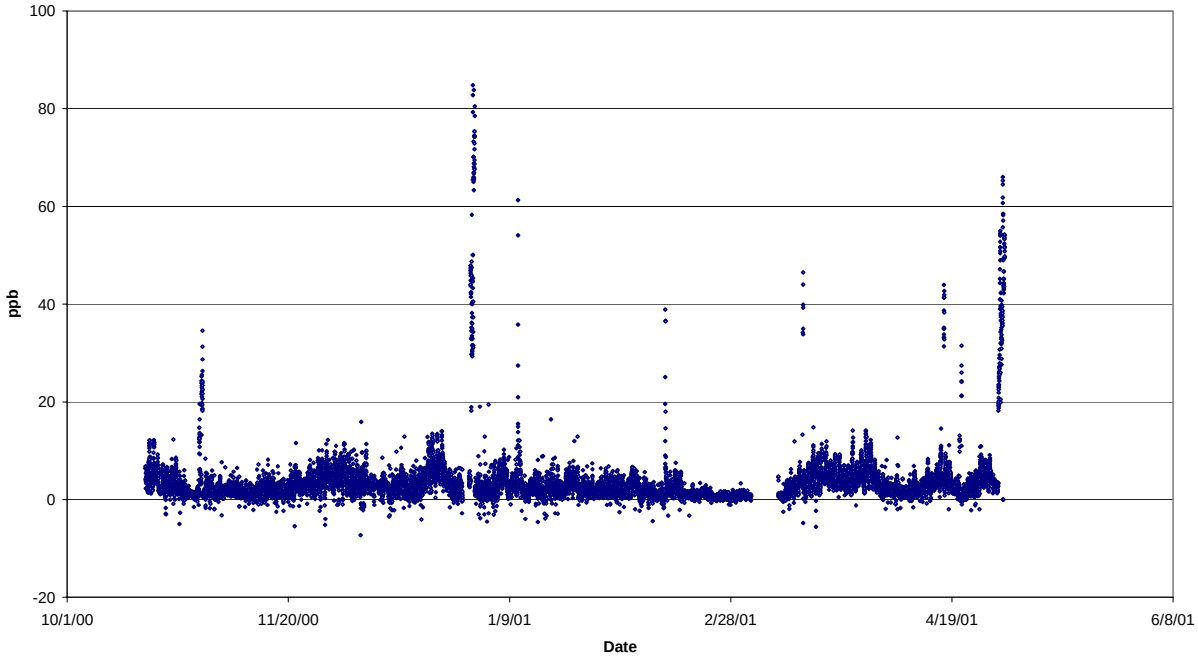

Figure 3-22. HNO_3 concentrations at Azusa.

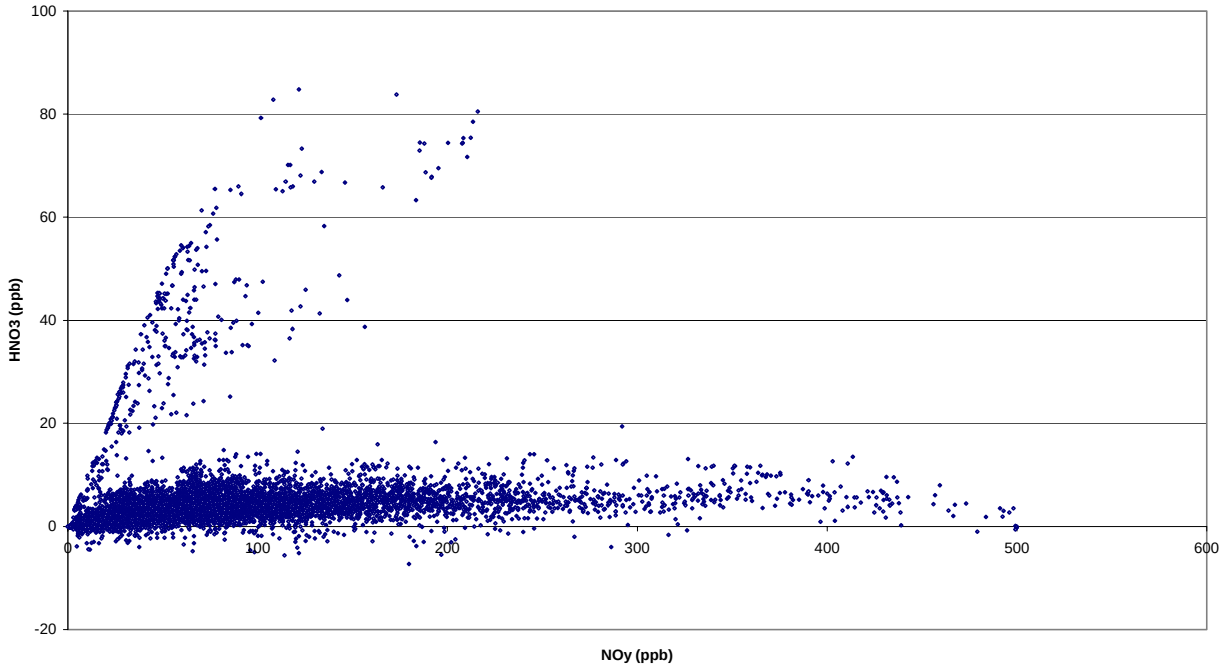

Figure 3-23. Comparison of NO_y and HNO_3 measurements at Azusa.

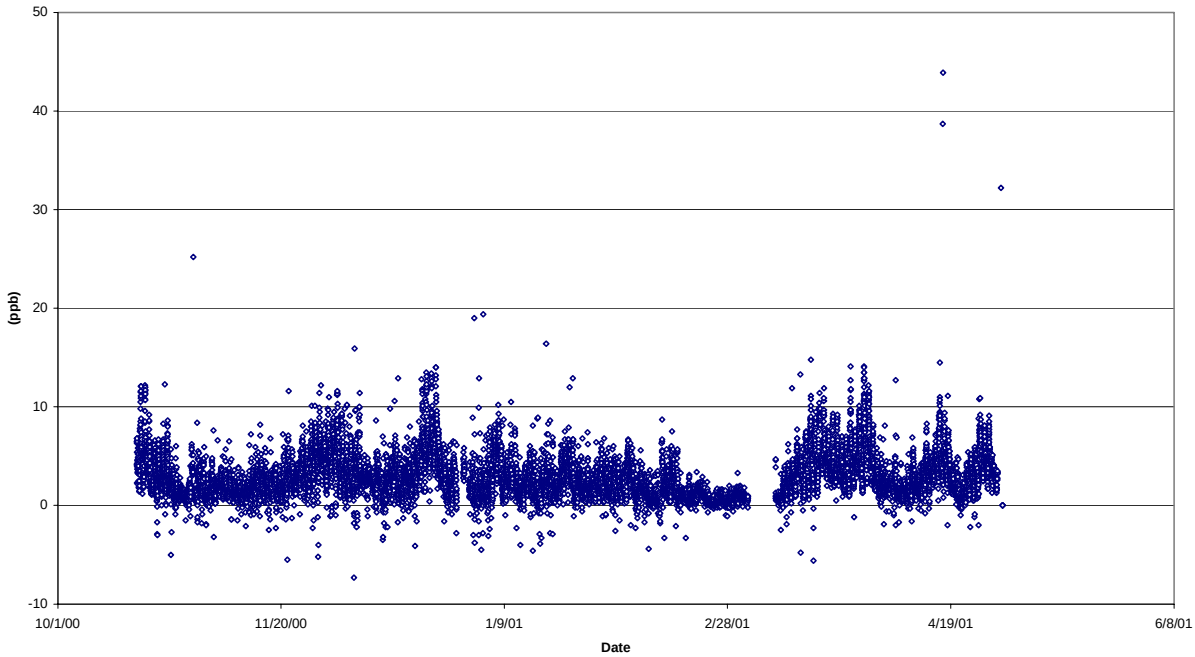

Figure 3-24. Corrected HNO_3 concentrations at Azusa.

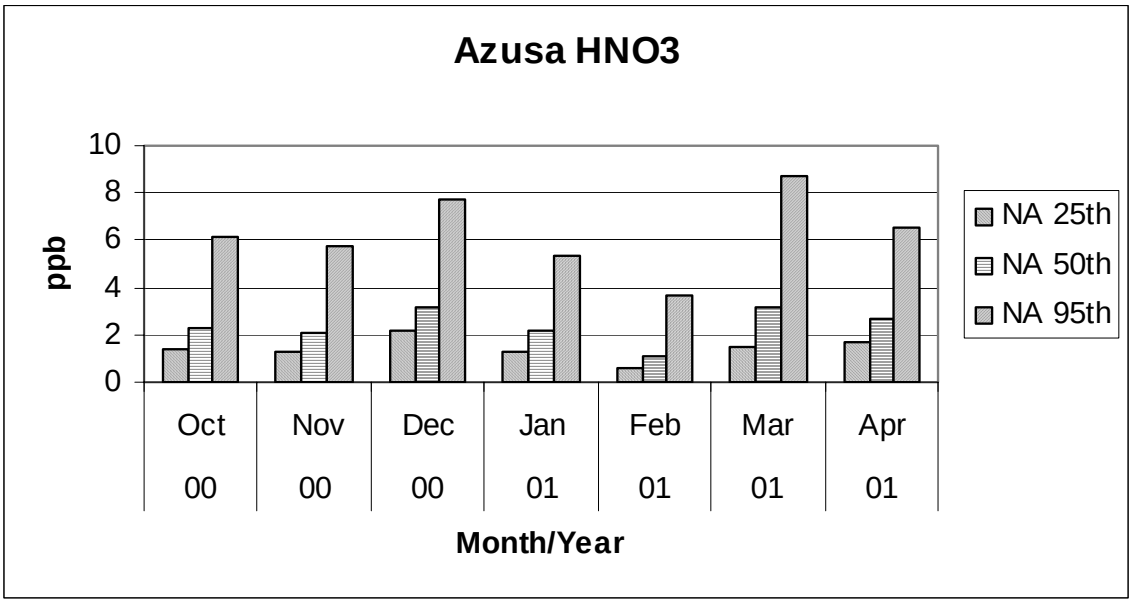

Figure 3-25. Percentile distribution of nitric acid concentrations at Azusa.

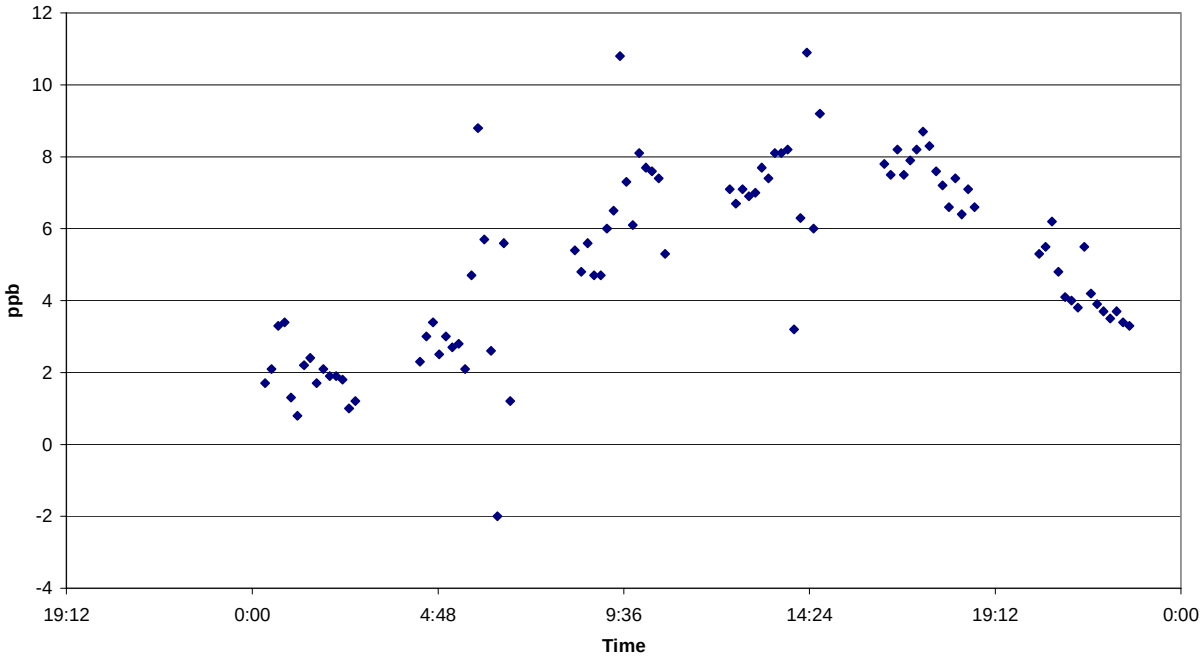

Figure 3-26. Time series of nitric acid concentrations in Azusa during April 25, 2001.

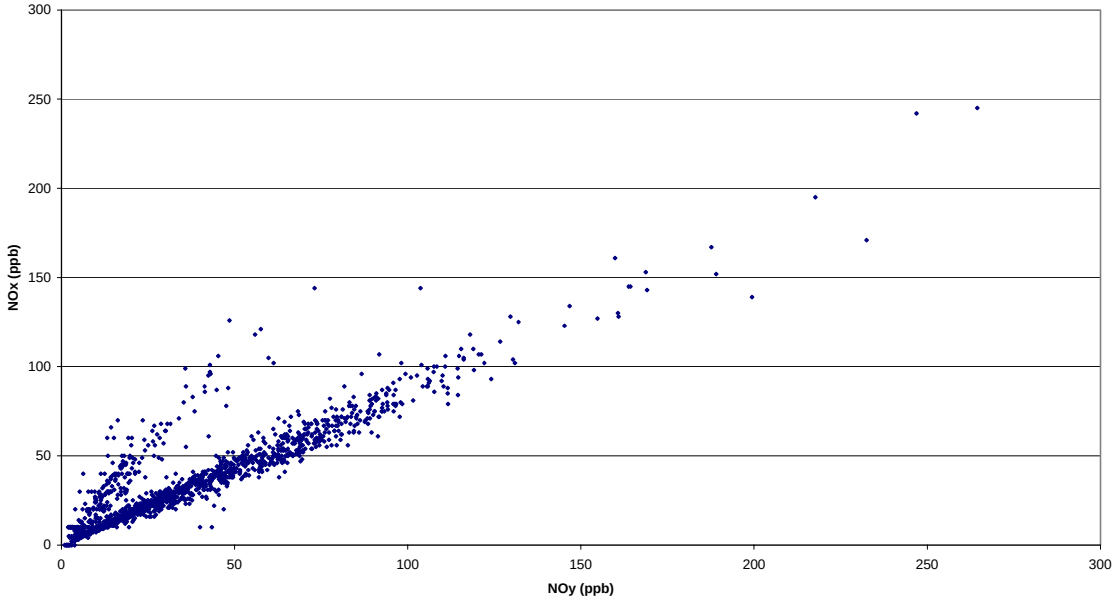

Figure 3-27. Comparison of NO_x and NO_y concentrations at Azusa.

4.0 Conclusions

The thermal evolution denuder was developed to the point where it could detect nitric acid, but the thermal decomposition yield was so low that reproducible measurements could not be made. The basic feasibility of the approach still appears to have potential to be a reliable measurement method through further research.

The dual converter approach appears to be a viable method for measuring nitric acid. Concentrations and their diurnal profiles are those expected for the measurement sites. The NO_y measurements in Azusa agreed quite closely with NO_x measurements reported at the site by the South Coast Air Quality Management District.

Except during special studies such as the 1997 Southern California Ozone Study and the 1987 Southern California Air Quality Study, California's measurement network consist only of standard chemiluminescent NO_x analyzers. In areas of high concentrations of nitrogenous species these instruments will under-measure NO_y (nitric acid lost to the sampling lines) and over-measure NO_2 (by including all other NO_y components). Under these conditions the NO_y-NO_y* analyzer will provide an important complement to the standard instrumentation. For example, it is likely that higher weekend ozone concentrations have in part been explained by hydrocarbon to NO_x ratios that have overstated the amount of NO_x. Likewise, NO_2 concentrations may be biased high because of the inclusion of nitric acid. Photochemically aged smog may well have a higher fraction of nitric acid and organic nitrate than fresh emissions, although this will not be reflected by the current measurement approach.

It is therefore critical to develop a network to accurately and specifically measure nitrogenous species. It is also important to measure organic nitrates, particularly their primary constituents, peroxyacetyl nitrate (PAN) and peroxyprionyl nitrate (PPN), since concentration of these species may be useful in understanding the impact of oxygenated fuel additives (methyl tertiary butyl ether and ethanol) . Fundamental advances in modeling ozone and aerosol formation would also require continuous and routine measurement of nitrogenous species.

5.0 Recommendations and Future Research Needs

Although reproducible results could not be obtained with the TED approach, this method could produce more acceptable results through further research. The primary current problems are that decomposition yield is low and that considerable time is needed to cool the detection assembly prior to collecting the next sample. The use of a microwave oven specifically designed for this purpose is likely to more effectively thermalize the sodium nitrite by applying more even heating. This should require less microwave exposure and therefore will avoid overheating of some portions of the denuder. This would eliminate the problem of requiring long cooling periods. The system could also be automated to allow zero air to be flushed through the system to cool the collection assembly prior to the next sampling period.

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. Through a second period of funding we will continue to operate the dual-channel NO_y analyzers and NO_2/PAN GCs until October 2002. Due to the limited amount of funding, the focus will be on operating the Riverside monitoring site. To verify that the nitric acid measured by the dual-channel analyzers indeed reflects the ambient nitric acid concentrations, we will operate the TDLAS on ambient air in Riverside during periods of expected high nitric acid concentrations. This TDLAS has been thoroughly refurbished under other funding and is currently being used to make measurements in our smog chamber.

While not possible in the scope of the second period of funding, it would be useful to operate collocated NO_y and NO_x analyzers that daily receive the same span gas to their respective inlets. This is necessary since the differences between NO_x and NO_y concentrations are apparently small. It is currently not possible to do this at the existing monitoring site at Azusa because of the SCAQMD policy of not risking losing data by participating in studies where their sampling inlets are either challenged to span gases produced by others or inlets of analyzers not operated by SCAQMD personnel. Thus it would be necessary to separately operate another analyzer in the NO_x mode. While this could be done, we feel that it is currently more important for two

instruments to make collocated nitric acid measurements so that the precision and accuracy of the method can be evaluated.

It also 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 again require that the calibration of both instruments be traced to the same span gas. This also was not possible at Azusa as the SCAQMD would not allow us to connect the NO_2/PAN gas chromatograph to the sampling line used by the NO_x analyzer.

6.0 References

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