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A Review of Nitric Acid Measurements by Tunable Diode Laser Absorption Spectroscopy (TDLAS)

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

A Review of Nitric Acid Measurements by Tunable Diode Laser Absorption Spectroscopy (TDLAS)

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Abstract

The nitric acid data obtained by tunable laser diode spectroscopy (TDLAS) in October 1993 in Azusa, CA were reviewed to evaluate their accuracy and hence suitability as a reference standard for the measurements made by CADMP, SCAQS-type, and two-week denuder samplers. The most consistent sets of HNO_3 data for comparison were those for the October 13 - October 24 period, which showed that the TDLAS results were about 30% higher than the SCAQS values and approximately 45% greater than the CADMP values (the latter were average of measurements by the primary and secondary CADMP samplers). The two-week sampler measurement was 30% higher than the TDLAS integrated value for the same two-week period.

Based on previous observations of the daytime nitric acid to ozone ratios in Azusa and other locations in the South Coast Air Basin, the TDLAS nitric acid measurements in Azusa during the 1993 study were significantly higher than expected. An HNO_3 : O_3 ratio of 0.1 with good correlation was shown by the secondary CADMP sampler, thus indicating a high probability that its measurements for the total period July - October 1993 were correct. However, the variability in performance by the CADMP design became a question due to the erratic measurements by the primary CADMP sampler during the same period.

The TDLAS HNO_3 time profiles, when examined with those of the concurrent O_3 and PAN profiles, showed no evidence of a nitric acid adsorption/desorption process occurring along the sampling train nor evidence of nitric acid vaporization from particulates on the Teflon front-filter. No errors in the overall TDLAS calibration was found. The possibility of interferences is raised by the presence of anomalous peaks on a number of the TDLAS HNO_3 time profiles and by measurements preceding the study period which found elevated levels of carbonyl group-bearing solvents (e.g., methyl ethyl ketone) which could be traced to one or more of several industrial operations surrounding the Azusa site.

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I. INTRODUCTION

Background

Tunable diode laser spectroscopy (TDLAS) is increasingly being employed to measure low-molecular weight gaseous constituents in the atmosphere. The TDLAS instrument configuration that is particularly suitable for air pollution studies evolved from a laboratory prototype in the early 1980's (Schiff *et al.*, 1983) to the present, fully transportable system (Mackay and Schiff, 1987) which has been employed in a number of atmospheric measurement studies in Southern California (see, for example, Hering *et al.*, 1988; Lawson *et al.*, 1990; Anlauf *et al.*, 1991). Briefly, the TDLAS system consists of a Pb salt diode laser as the infrared light source, a White cell with a total pathlength of $\sim$150 m which holds the air sample, a short-path cell containing the reference compound, infrared detectors, data system, and associated array of control electronics (Mackay and Schiff, 1987). The diode laser, which is tunable within a limited frequency range (e.g., 1680-1720 cm^{-1}) by precise temperature control, scans a very narrow range of frequencies over the selected absorption line while locked on the absorption line frequency of the species in the reference cell. The sample air continuously passes through the White cell under reduced pressure ($\sim$25 Torr) and this condition of low pressure significantly reduces line broadening and enhances absorption peak heights.

With the inherently high-resolution capability of the tunable diode, the absorption signal of the species of interest is analyzed at a resolution of 0.01 cm^{-1} or better, hence affording a high degree of specificity. In view of the specificity and low detection limit ($\leq$0.5 ppb) for HNO_3, a demonstrated good agreement with the open-path FTIR and other HNO_3-specific methods (see, for example, Anlauf *et al.*, 1991), as well as the capability for both temporal and integrated measurements, the TDLAS has been considered as a reference method for ambient HNO_3 measurement.

During the period September 30 - October 30, 1993 in Azusa, CA, a TDLAS system was operated by Unisearch Associates, Inc. to provide reference HNO_3 data for a test of specific samplers used by the California Air Resources Board (ARB) in the California Acid Deposition Monitoring Program (CADMP). A continuous sampler, developed by Aerosol Dynamics Inc., was also operated and provided one integrated HNO_3 measurement for a two-week period. In addition, a sampler of the type employed during the 1987 Southern California Air Quality Study

(SCAQS) was operated for fourteen 24-hr periods. A preliminary analysis of these 1993 Azusa data showed large differences among the samplers, and the extent and nature of the disparities in HNO_3 results prompted the ARB to initiate a review of the methods involved. Thus, for example, further experimental tests are currently being conducted on the CADMP sampler in another laboratory (Fitz, 1995). The present work focuses on the TDLAS method and the TDLAS HNO_3 data generated during the 1993 Azusa study.

Objectives

This work was undertaken to evaluate the accuracy of the TDLAS HNO_3 measurements during the 1993 Azusa study and to determine if there were temporal and/or systematic errors in the TDLAS method which contributed to the discrepancies between its results and those of the other HNO_3 samplers.

II. OVERVIEW

Data Coverage

The measurements were conducted at the South Coast Air Quality Management District's (SCAQMD) monitoring station in Azusa, CA. Three different types of denuder samplers for HNO_3 were employed with differing sampling periods. Data coverage by TDLAS overlapped those of the other methods.

- TDLAS: Measurements were made during the period 1200 PDT, September 30, 1993 through 2400 PDT, October 30, 1993. Data were obtained over 1 minute averaging periods. The instantaneous daily HNO_3 maxima ranged between 3 ppb to 30 ppb, with the maximum concentrations generally occurring between 1400 - 1600 PDT each day. Mackay (1994) reported the 1-hour average values and the daytime average (1000 - 1800 hr) values for comparison with the CADMP samplers. Fifteen-minute average values were also calculated for the present study. The TDLAS hourly average HNO_3 values are presented in Figure 1 and, along with the hourly average O_3 data, give an overview of the general levels of air pollution episodes which prevailed during the study period.

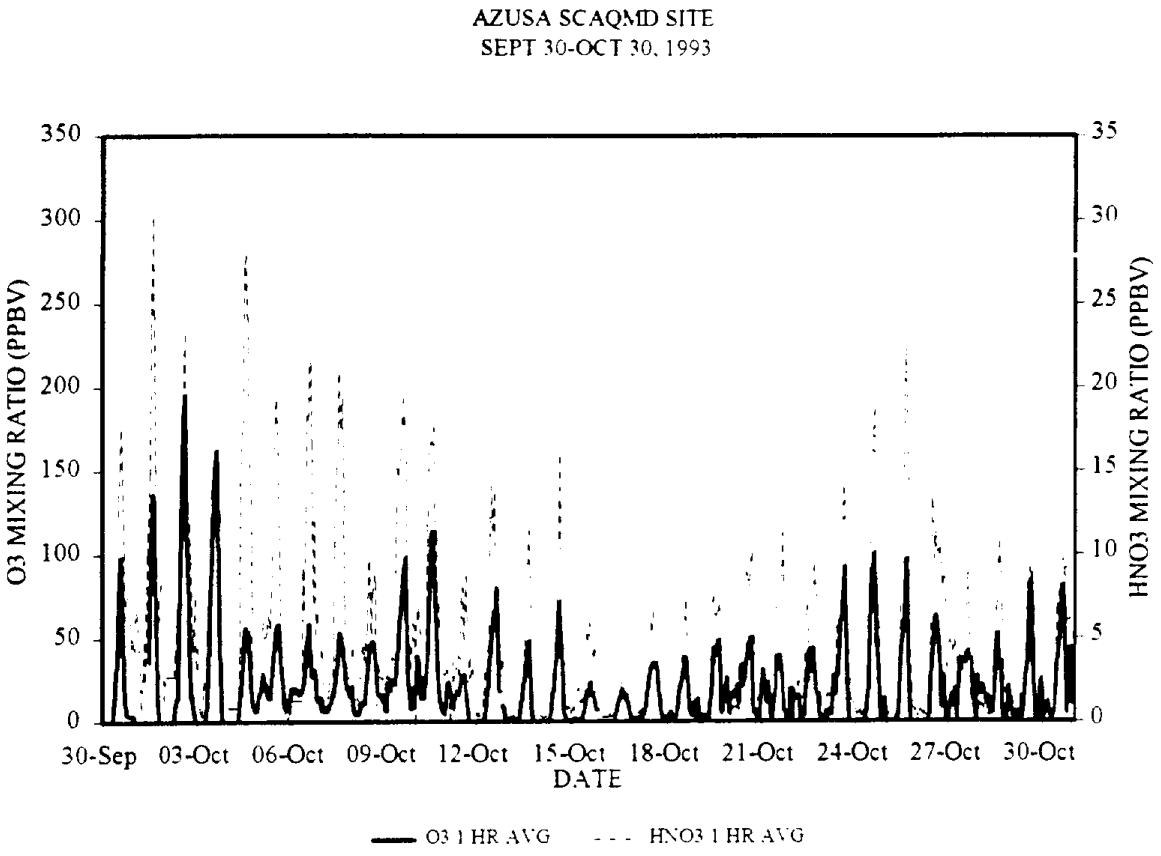

Figure 1. Time series plot of hourly average ozone and TDLAS nitric acid concentrations during the 1993 Azusa study.

• CADMP samplers: Two samplers, the primary sampler and a secondary (collocated) sampler, were operated on a daily basis during the 1000 - 1800 hr period between October 4 and October 31, 1993. Details of sampling by CADMP can be found in a draft report by Motallebi and Ashbaugh (1993).

• SCAQS sampler: One sampler was operated and collected 24-hr samples, starting at 1700 hr and ending at 1700 hr the following day, for 14 days during the period October 10 - 24, 1993 (Taylor, 1994).

• Two-week sampler: One unit was operated continuously with 8 sampling cartridges from 1700 hr, October 10, 1993 to 1700 hr, October 24, 1993 (Taylor, 1994). The mean of the HNO_3 measurements from the 8 cartridges constituted the single measurement value of 11.1 μg m^{-3} for the two-week period.

In addition, measurements of ozone and peroxyacetyl nitrate (PAN) were made by Unisearch during the entire period that the TDLAS was operated. Data on O_3, NO_x, other criteria pollutants, as well as temperature and relative humidity data were available from SCAQMD files.

Approach

This study compared the TDLAS HNO_3 data with concurrent data from the denuder samplers, examined the concentration-time profile with respect to those of the photochemically related products O_3 and PAN, and looked at the influence of temperature and relative humidity. Sampling and calibration of the TDLAS were reviewed and possible influence of emissions around the study site to the spectroscopic measurements of HNO_3 was investigated.

III. CADMP MEASUREMENTS

An examination of the data obtained by two CADMP samplers was necessary before a comparison with the HNO_3 measurements by TDLAS and other samplers could be made. The findings in this study are briefly described below.

Prior to the comparison study, during the period July 30 through September 28 (11 sampling days), the daytime (6:00 a.m. to 6:00 p.m.) denuded particulate nitrate measurements

from the CADMP primary sampler at Azusa exceeded those obtained from the secondary sampler by about 2 to 10 $\mu g\ m^{-3}$ (or 20 to 100 percent). The nighttime measurements, which ranged from about 2.5 to 5.5 $\mu g\ m^{-3}$, agreed to within 1 $\mu g\ m^{-3}$. *These results indicate that the denuder in the primary sampler, which had not been serviced in several years, was not removing nitric acid with 100 percent efficiency.* The meteorological data for that time period were examined but no obvious relationships of sampler replicability to either ambient temperature or relative humidity were found. Data from these earlier CADMP measurements in July - September 1993 are summarized in Appendix A, which include parallel plots of the particulate nitrate and nitric acid data from the two samplers.

During the 1993 comparison study, from October 4 through October 30 (23 sampling days), the daytime (10:00 a.m. to 6:00 p.m.) denuded particulate nitrate measurements from the primary and secondary CADMP samplers replicated well; the nondenuded particulate nitrate concentrations obtained from the Teflon filters also replicated well (Figure 2). Replicability of particulate nitrate measurements was unaffected by the cleaning of the primary sampler between October 19 and 23. *In brief, particulate nitrate measurements replicated well during October 1993. The data indicate that the efficiencies of the denuders in both samplers were equal under the ambient conditions occurring during that time (the 10:00 a.m. to 6:00 p.m. average temperature ranged from about 67 to 87 degrees Fahrenheit and the corresponding relative humidity ranged from about 10 to 65 percent). However, in the absence of calibration with known standards the possibility that both samplers lost some HNO_3 in the sampling train and operated at equal but less than 100% efficiency cannot be ruled out.* The specific cause of the improvement in replicability, which occurred with the primary and secondary sampler being operated "as is" from the prior measurements conducted in July 30 - September 28 but with a shortened period (by 4 hours) of sampling, was not investigated.

From October 4 through October 30, the HNO_3 concentrations from the primary and secondary CADMP samplers replicated well both before and after the primary sampler was cleaned (see Figure 3) (cleaning occurred October 19 through 21), except on two days (October 13 and October 22). On October 13, replication was probably within sampling error because the particulate and total nitrate concentrations were about 3 to 6 times greater than the HNO_3 concentrations (the HNO_3 would then be the difference of two large numbers). October 22 was

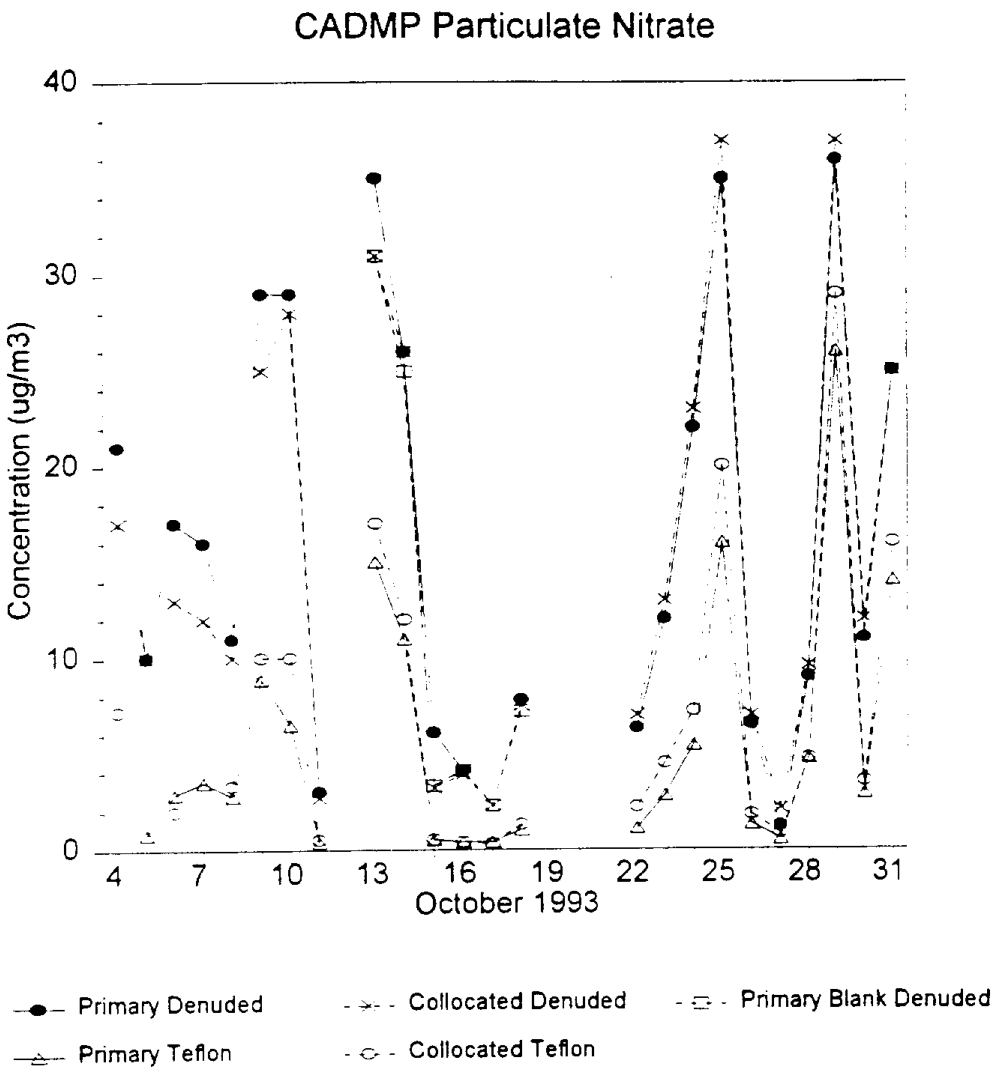

Figure 2. Denuded and nondenuded particulate nitrate concentrations from the primary and secondary CADMP samplers at Azusa versus date. (Note: primary blank refers to a second denuder channel of the primary sampler.) All samples were collected from 10:00 a.m. to 6:00 p.m.

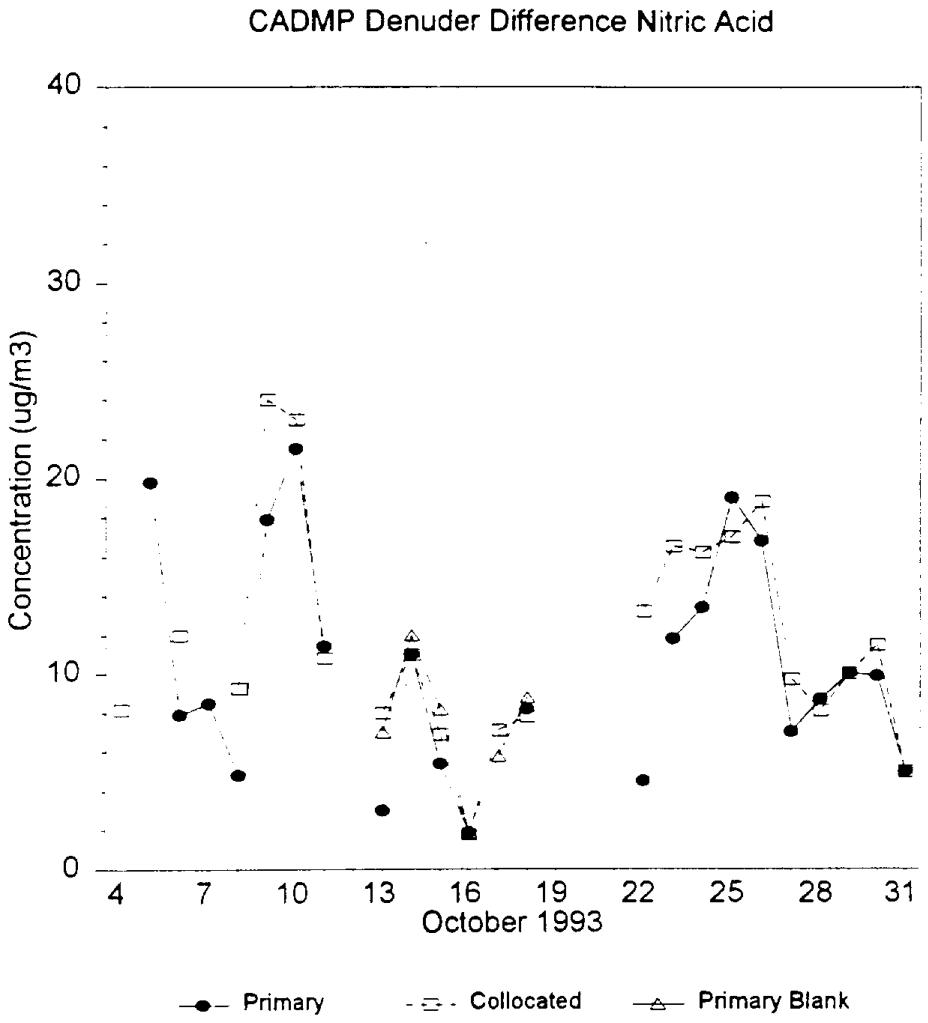

Figure 3. Denuder difference HNO_3 concentrations from the primary and secondary CADMP samplers at Azusa versus date. (Note: primary blank refers to a second denuder channel of the primary sampler.) All samples were collected from 10:00 a.m. to 6:00 p.m.

the first day of operation of the primary sampler following cleaning, so the validity of the value obtained from the primary sampler on that date may be open to question. *In general, the replicability of the CADMP HNO_3 measurements is considered here as acceptable.*

IV. OVERALL COMPARISON

Comparative data are plotted in Figure 4 for the time period when all samplers were operated. Reasonably good correlations exist among the measurements of HNO_3 obtained from the TDLAS, the CADMP samplers (average of primary and collocated), and the SCAQS-type sampler. *However, during the time period from October 13 through October 24, the ratio of the mean SCAQS HNO_3 to the mean TDLAS HNO_3 was 0.72 and the ratio of the mean CADMP HNO_3 to the mean TDLAS HNO_3 was 0.56 [this period of comparison was preceded by a spectral line change in the TDLAS on October 12 (Mackay, 1994)].* This suggests that the TDLAS HNO_3 concentrations are roughly 30 percent greater than those from the SCAQS sampler and 45 percent greater than those from the CADMP sampler, and while the concentrations from the SCAQS and CADMP samplers cannot be directly compared (the former collected 24-hr samples from 5:00 p.m. to 5:00 p.m. while the latter collected integrated samples from 10:00 a.m. to 6:00 p.m.), their respective comparisons with the TDLAS measurements indicate that the CADMP HNO_3 concentrations would average about 30 percent lower than those from the SCAQS sampler.

During the period October 10 - October 24, the two-week average HNO_3 concentrations from the SCAQS and TDLAS measurements were 5.5 $\mu g\ m^{-3}$ and 8.5 $\mu g\ m^{-3}$, respectively, compared to the value of 11.1 $\mu g\ m^{-3}$ which was obtained by the two-week sampler. Apart from the speculation that nitrous acid (HONO) was probably an interference in the HNO_3 measurement by the two-week sampler, no further discussion is offered in this report concerning the above comparative figures.

Poorer correlations are found in SCAQS vs. TDLAS and, more pronouncedly, with CADMP vs. TDLAS when data prior to October 13 are included. This is indicated by the linear regression results in Table 1. The more complete sets of TDLAS and CADMP data are further examined below.

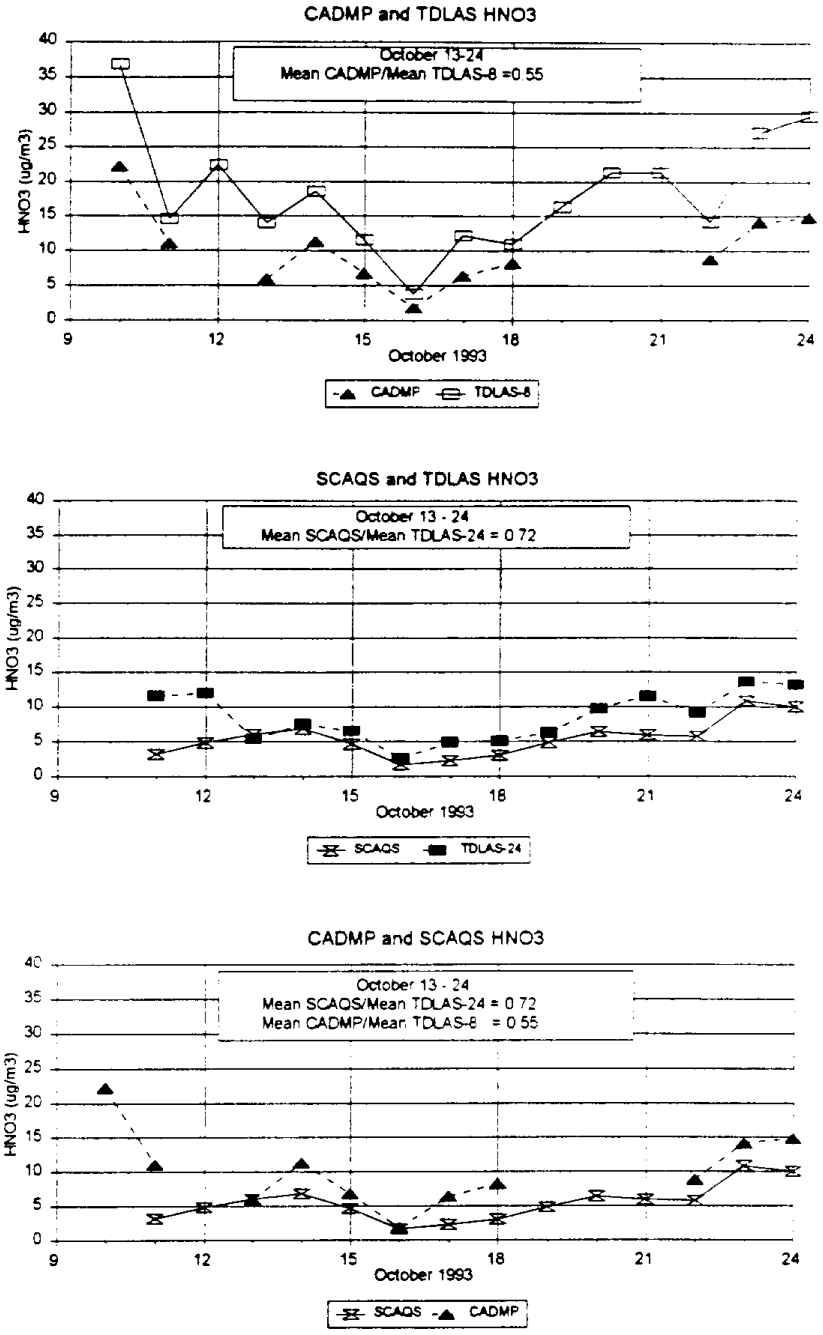

Figure 4. Plots of HNO_3 concentrations measured in Azusa vs. date compared among samplers. (Top) CADMP HNO_3 (average of primary and secondary samplers) and 10:00 a.m. to 6:00 p.m.TDLAS HNO_3 average. (Middle) SCAQS HNO_3 and 5:00 p.m.to 5:00 p.m.TDLAS HNO_3 average. (Bottom) 10:00 a.m. to 6:00 p.m.CADMP HNO_3 (average of primary and secondary samplers) and 5:00 p.m.to 5:00 p.m. SCAQS HNO_3.

Table 1. Linear regression of SCAQS HNO_3 and CADMP HNO_3 versus TDLAS HNO_3

Sampler	*Period*	*Intercept*	*Slope*	r^2	*N*	*Mean Ratio (Method/TDLAS)*
SCAQS	10/13-10/24	0.062 ± 1.28	0.71 ± 0.11	0.80	12	0.72
SCAQS	10/11-10/24	0.97 ± 1.95	0.53 ± 0.16	0.50	14	0.66
CADMP	10/13-10/24	1.02 ± 1.25	0.49 ± 0.06	0.92	9	0.56
CADMP	10/13-10/30	0.75 ± 1.36	0.52 ± 0.05	0.91	15	0.57
CADMP	10/4-10/30	5.42 ± 4.41	0.25 ± 0.08	0.35	23	0.52

V. NITRIC ACID : OZONE RATIOS

Comparison with Previous Measurements

The curves of growth of ozone and nitric acid are known to closely track each other during the progress of photochemical smog. As seen in Figure 1, this is at least qualitatively true for the air pollution episodes encountered during the 1993 Azusa study. The range of HNO_3 : O_3 ratios which is associated with periods of photochemical activity can help evaluate the consistency of a set of daytime HNO_3 measurements. Hence, in this study HNO_3 : O_3 ratios were derived from the data of previous field studies conducted in southern California. The results are summarized in Table 2 and the individual plots of HNO_3 vs. O_3 for these previous measurements (from which the ranges of ozone and nitric acid concentrations can be seen) are presented in Appendix B.

Two sets of prior, extended HNO_3 measurements exist for Azusa, CA. One was conducted during the 1986 Carbon Species Methods Comparison Study (CSMCS) where the kilometer-path FTIR results were in very good agreement with those obtained by TDLAS and a filter pack method which sampled for 1-hr and 2-hr periods (Anlauf *et al.*, 1991). The CSMCS was held in August 1986 at Citrus College, approximately 2 miles east of the SCAQMD

Table 2. Daytime Nitric Acid to Ozone Ratios in Southern California

Method/Site	*Measurement Period & Data Blocks*	*Intercept*	*Slope*	r^2	*N*	*Mean* (HNO_3/O_3)
FTIR/AZUS	8/12/86 - 8/20/86 hourly ave 9 am - 6 pm	4.15 (± 2.19)	0.086 (± 0.004)	0.86	81	0.139
SCAQS/ANAH	6/19/87-9/387 11 days, 4-hr ave 9 am -1 pm and 1 pm - 5 pm	-2.07	0.103	0.65	20	0.066
SCAQS/AZUS	" "	2.42	0.062	0.41	19	0.086
SCAQS/BURK	" "	-3.40	0.139	0.56	20	0.105
SCAQS/CELA	" "	-6.35	0.202	0.66	18	0.116
SCAQS/CLAR	" "	0.39	0.079	0.79	20	0.082
SCAQS/HAWT	" "	-1.17	0.130	0.18	21	0.098
SCAQS/LBCC	" "	-2.94	0.122	0.63	22	0.070
SCAQS/RIVR	" "	0.13	0.021	0.48	20	0.023
TDLAS/CLAR	6/16/87 - 7/24/87 hourly ave 12 noon - 5 pm	1.91 (± 2.59)	0.068 (± 0.004)	0.56	195	0.088
TDLAS/AZUS	**9/30/93 -10/30/93** **hourly ave** **10 am - 6 pm** **10/13/93-10/30/93** **hourly ave** **10 am - 6 pm**	**3.86** **(± 4.58)** **0.97** **(±2.56)**	**0.122** **(± 0.010)** **0.159** **(±0.010)**	**0.39** **0.62**	**239** **142**	**0.226** **0.196**
CADMP/AZUS (Average of Primary and Collocated)	**10/4/93 - 10/30/93** **8-hr ave** **10 am - 6 pm**	**0.02** **(± 1.26)**	**0.107** **(± 0.017)**	**0.67**	**23**	**0.108**
CADMP/AZUS/ Primary	7/13/93-9/28/93 12-hr ave 6 am - 6 pm	0.26 (± 0.70)	0.046 (± 0.009)	0.69	13	0.049
CADMP/AZUS/ Collocated	7/30/93-9/28/93 12-hr ave 6 am - 6 pm	-0.12 (± 0.95)	0.100 (± 0.013)	0.88	10	0.097
CADMP/AZUS/ Collocated Total Data	7/30/93-10/30/93 8-hr and 12-hr averages	0.52 (± 1.13)	0.097 (± 0.01)	0.80	30	0.109

site in Azusa. The other was in 1987 during the South Coast Air Quality Study and employed the type of denuder unit which is designated as SCAQS sampler in this report. Several other HNO_3 measurements, concurrent with that made in Azusa (AZUS), were conducted in 1987 by SCAQS-type samplers at the other SCAQS stations: Anaheim (ANAH), Burbank (BURK), central (downtown) Los Angeles (CELA), Claremont (CLAR), Hawthorne (HAWT), Long Beach City College (LBCC), and Riverside-Rubidoux (RIVR). Extensive TDLAS measurements of HNO_3 were also conducted for the same general period in Claremont.

The results from SCAQS presented in Table 2 show both the regression slopes and the mean nitric acid to ozone ratios to vary among sites. Most of the slopes are in the range 0.06 to 0.14; Riverside has the smallest slope (0.02) and downtown Los Angeles has the highest (0.2). Because the regressions for five out of the eight sites have negative y-intercepts (ozone concentrations of 20 to 30 ppb were associated with near-zero concentrations of nitric acid) their mean HNO_3 : O_3 ratios are less than the regression slopes. The low HNO_3 : O_3 ratio for Riverside is associated with the conversion of HNO_3 to particulate NH_4NO_3 by prevailing high concentrations of NH_3 from agricultural sources. The high value for downtown Los Angeles is almost certainly due to a lowering of O_3 levels due to titration by NO being emitted from a heavier volume of vehicles.

The pre-1993 data for Azusa (SCAQS/AZUS and FTIR/AZUS) yielded intermediate values of the regression slopes and were similar to those for Claremont (SCAQS/CLAR and TDLAS/CLAR), both sites being sufficiently distanced from downtown Los Angeles but still out of the NH_3-rich region around Riverside.

The highest HNO_3 : O_3 correlation found in these earlier measurements is found in FTIR/AZUS which consisted of data from a period of well-defined smog episodes, with hourly average O_3 maxima between 160 ppb and 240 ppb. A time series plot of the hourly average HNO_3 and O_3 values corresponding to FTIR/AZUS is presented in Figure 5, where the 10X ordinate scale expansion for HNO_3 clearly depicts the consistency of the HNO_3 : O_3 ratios. This is in marked contrast to the plot of the 1993 Azusa TDLAS data (corresponding to TDLAS/AZUS) shown in Figure 1, which clearly corresponded to episodes of much lower O_3 levels, but where erratic HNO_3 : O_3 ratios are evident even for the episodes with peak O_3 concentrations near or above 100 ppb. [The value of the y-intercept for FTIR/AZUS (see Table 2) which translated the regression slope (0.086) to a comparatively higher value of the mean

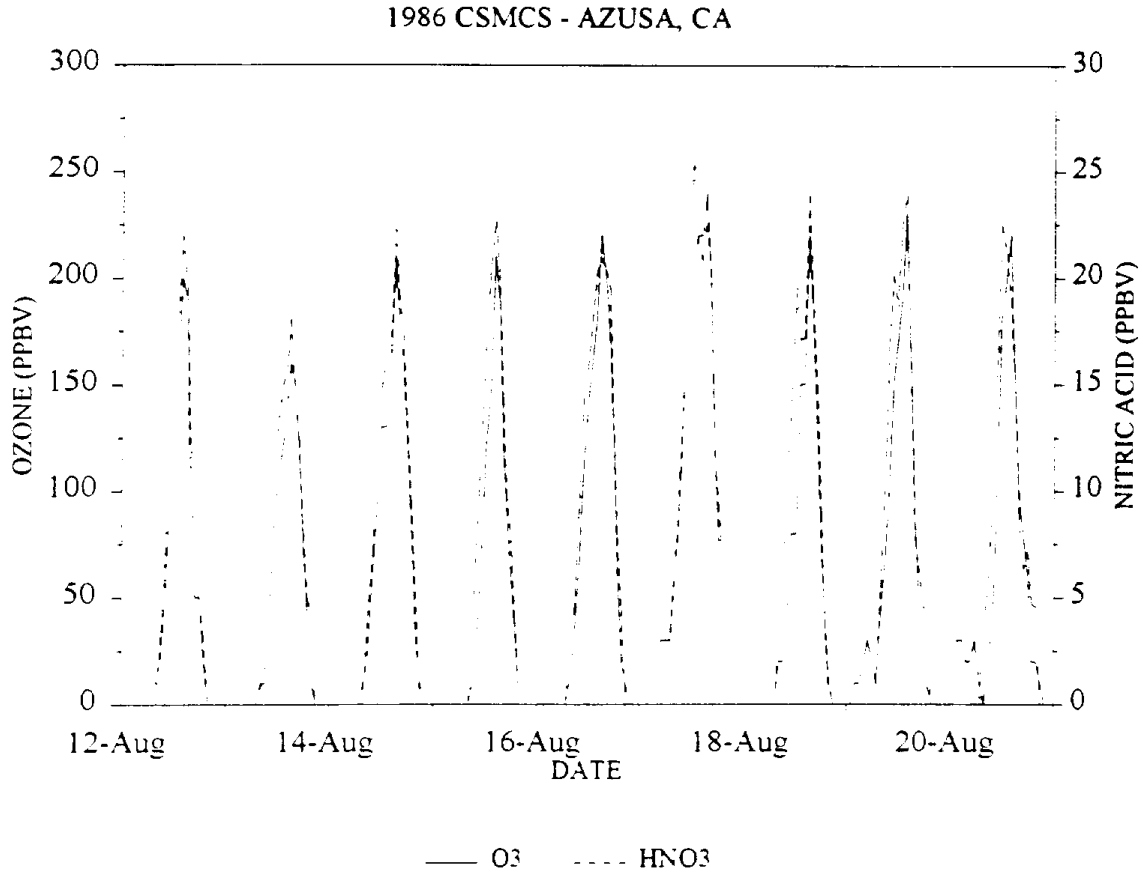

Figure 5. Time series plot of hourly average ozone and FTIR nitric acid concentrations for the 8:00 a.m. to 6:00 p.m. period during the 1986 CSMCS in Azusa.

HNO_3 : O_3 ratio (0.14) may largely be reflecting the relatively high detection limit (~4 ppb) of the FTIR method (Anlauf *et al.*, 1991).]

The results for the 1993 Azusa study, TDLAS/AZUS and CADMP/AZUS, are included in Table 2 (no daytime results can be extracted from the 24-hr integrated collection by the SCAQS sampler). From all the results shown in Table 2 for Azusa, it may be argued that an increase in HNO_3 : O_3 ratio in this locality occurred over the years. However, the argument is weakened by the poor correlation coefficients calculated for the 1987 SCAQS/AZUS (r^2 = 0.41) and the complete 1993 TDLAS/AZUS (r^2 = 0.39) data. A marked improvement in the correlation coefficient for TDLAS/AZUS is found when the TDLAS data prior to October 13 are excluded. *However, the overall results indicate that the daytime TDLAS HNO_3 : O_3 ratio for the 1993 Azusa comparison study is significantly higher than would be expected from this site and adjoining downwind locations.*

The entries CADMP/AZUS/Primary and CADMP/AZUS/Collocated in Table 2 correspond to data obtained for the months (July-September 1993) prior to the comparison study. It is noted that the HNO_3 : O_3 ratio for CADMP/AZUS (average of primary and collocated data during the study) is in agreement with that of CADMP/AZUS/Collocated (although only limited data was obtained with the latter). The collocated sampler is believed to have been more accurate than the primary sampler (by virtue of having a more efficient denuder, other factors being assumed equal), such that the improvement in replicability between these samplers during the October 1993 study must be attributed more to an improvement in the primary sampler's efficiency approaching that of the collocated sampler and less to a decrease of the latter's performance.

The CADMP/AZUS HNO_3 : O_3 ratio of 0.1 is seen in Table 2 to be closer to the "normal" range of HNO_3 : O_3 ratios for the Azusa area than the values obtained from the concurrent TDLAS measurements, but with both methods showing only fair to poor correlation of HNO_3 with O_3. As a separate entity, the secondary (collocated) sampler showed consistent and reasonably good HNO_3 : O_3 correlation for both the pre-intercomparison period (r^2 = 0.88 and slope = 0.10 for CADMP/AZUS/Collocated) and the study period (r^2 = 0.75, slope = 0.11, not shown in Table 2). The linear regression of the combined 8-hour average and 12-hour average HNO_3 concentrations by the secondary sampler with the corresponding O_3 data for the period July - October 1993 is shown in Table 2 as CADMP/AZUS/Collocated Total Data, with slope = 0.10 and r^2 = 0.80.

Influence of Temperature and Relative Humidity

The ratio of hourly-averaged TDLAS HNO_3 concentrations to O_3 concentrations during the 1993 Azusa study is plotted against date in Figure 6. The HNO_3 : O_3 ratios included in Figure 6 were computed only for O_3 exceeding 40 ppb, thereby excluding practically all of the nighttime data. Except for the period October 4 through October 7, the average HNO_3 : O_3 ratio is seen to be about 0.2 (as is also seen in Table 2). The higher ratios recorded during the October 4 - October 7 period were associated with relatively low temperature (Figure 7) and high relative humidity (Figure 8). The latter observation, though limited in extent, is somewhat surprising since higher losses of HNO_3 in sampling lines are normally associated with lower temperatures and higher relative humidity.

The ratio of 10:00 am to 6:00 pm CADMP HNO_3 concentrations to the corresponding 8-hr averaged O_3 concentrations during October 1993 plotted against data in Figure 9 gives a visual estimate of the average HNO_3 : O_3 ratio being about 0.1 (as also seen earlier in Table 2). As seen in Figures 10 and 11, the HNO_3 : O_3 ratio could be indicating the same effects of temperature and relative humidity as was observed with the TDLAS data but in a less pronounced manner because of the lower time resolution by CADMP sampling. Although the hypothesis that the CADMP sampler may lose HNO_3 along the inlet path under conditions of high relative humidity and low temperature merits consideration, the present sampling data provide no support for this hypothesis.

As mentioned earlier, there was a distinct improvement in the replicability of measurements between the primary and the secondary samplers at the start of the October 1993 study as the samplers were operated "as is" from the July - September 1993 measurements. It should be noted that the improvement coincided with generally wider ranges in temperature and relative humidity in October than occurred in the July - September period when the samplers did not replicate (see plots of hourly average temperature and relative humidity in Appendix A). The direction of improvement is contrary to the expectation that larger divergence would occur between the sampler results with wider variations in temperature and humidity.

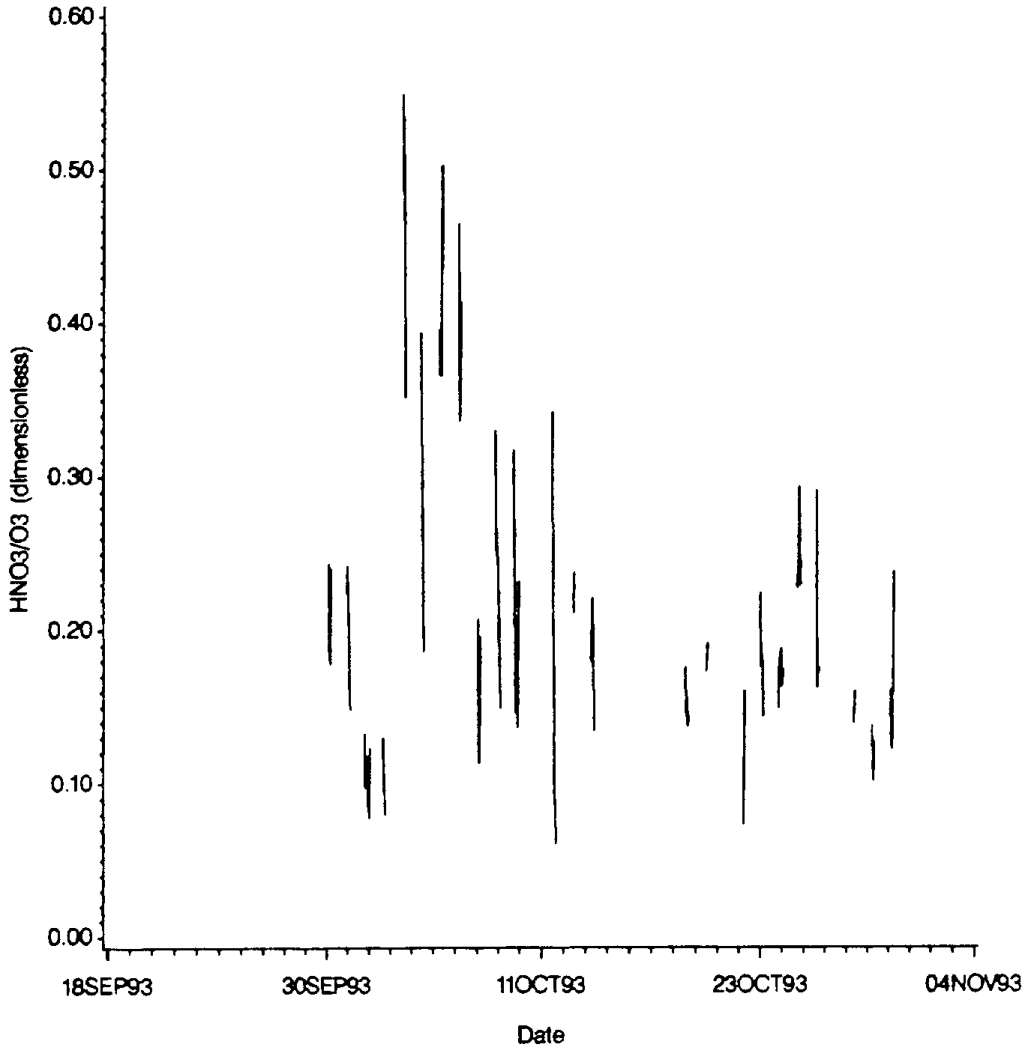

Figure 6. Ratio of hourly average TDLAS HNO_3 to ozone measured in Azusa versus date. Ratios were not calculated for ozone concentrations less than 40 ppb.

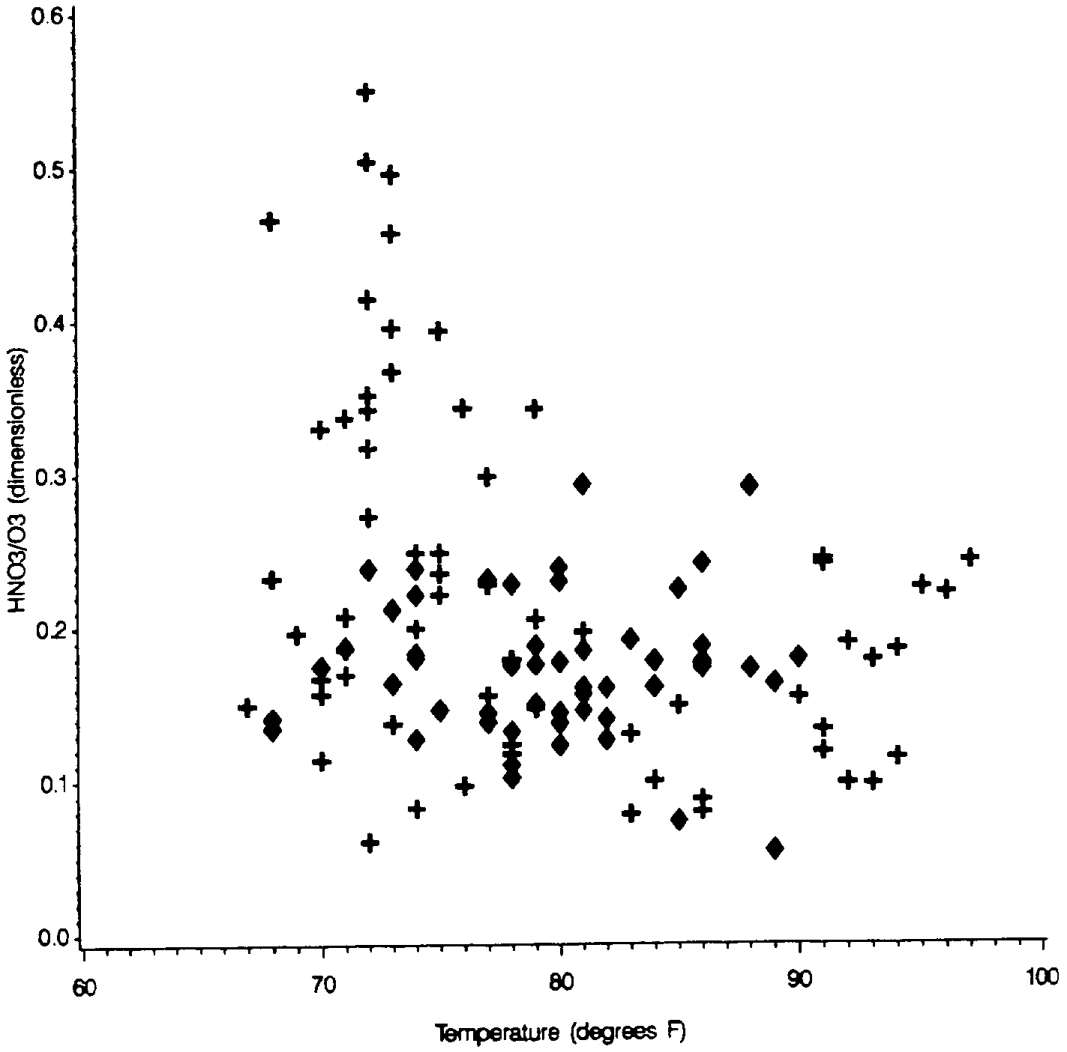

Figure 7. Ratio of hourly average TDLAS HNO_3 to ozone measured in Azusa versus temperature. Plus symbols denote measurements made on or before October 12, 1993; diamonds denote measurements made after October 12, 1993. Ratios were not calculated for ozone concentrations less than 40 ppb.

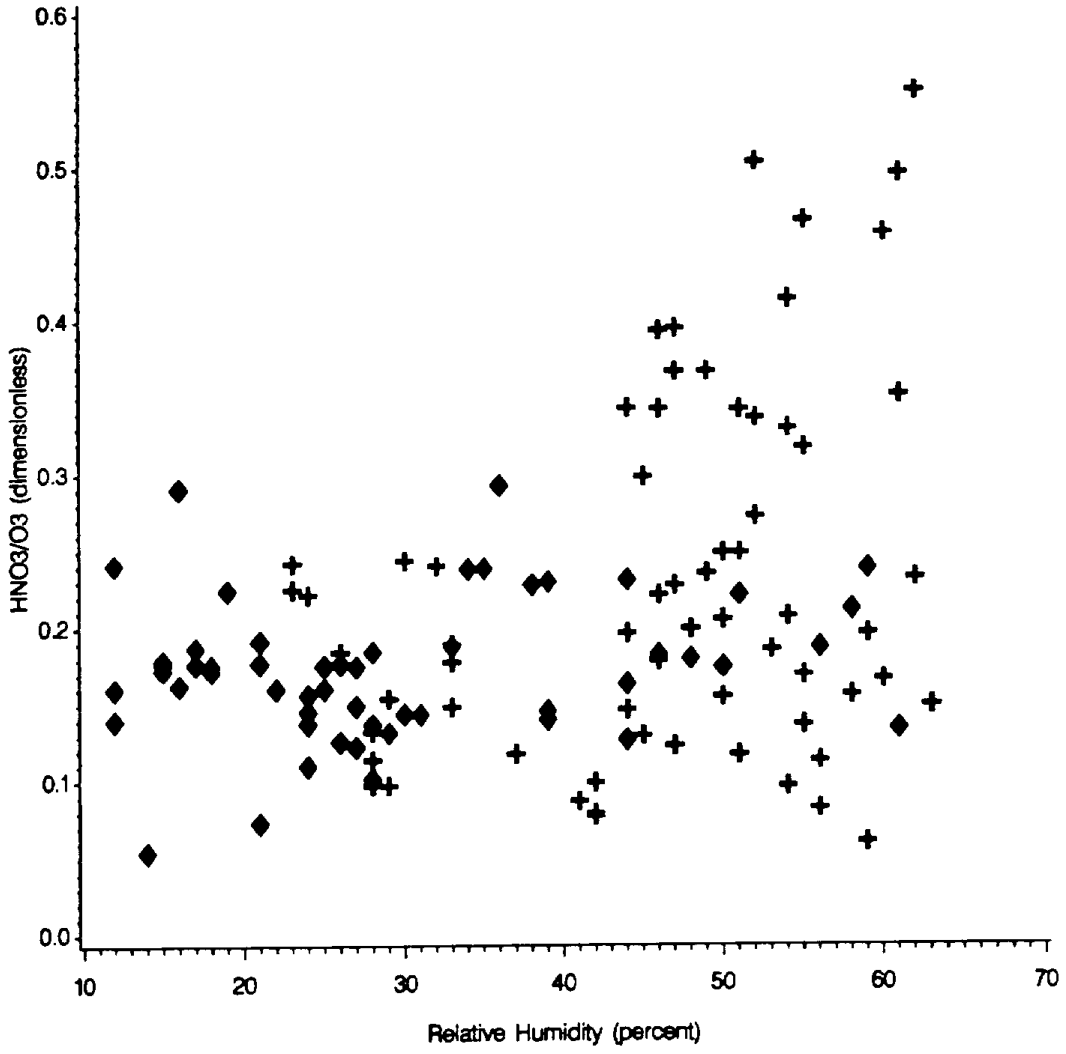

Figure 8. Ratio of hourly average TDLAS HNO_3 to ozone measured in Azusa versus relative humidity. Plus symbols denote measurements made on or before October 12, 1993; diamonds denote measurements made after October 12, 1993. Ratios were not calculated for ozone concentrations less than 40 ppb.

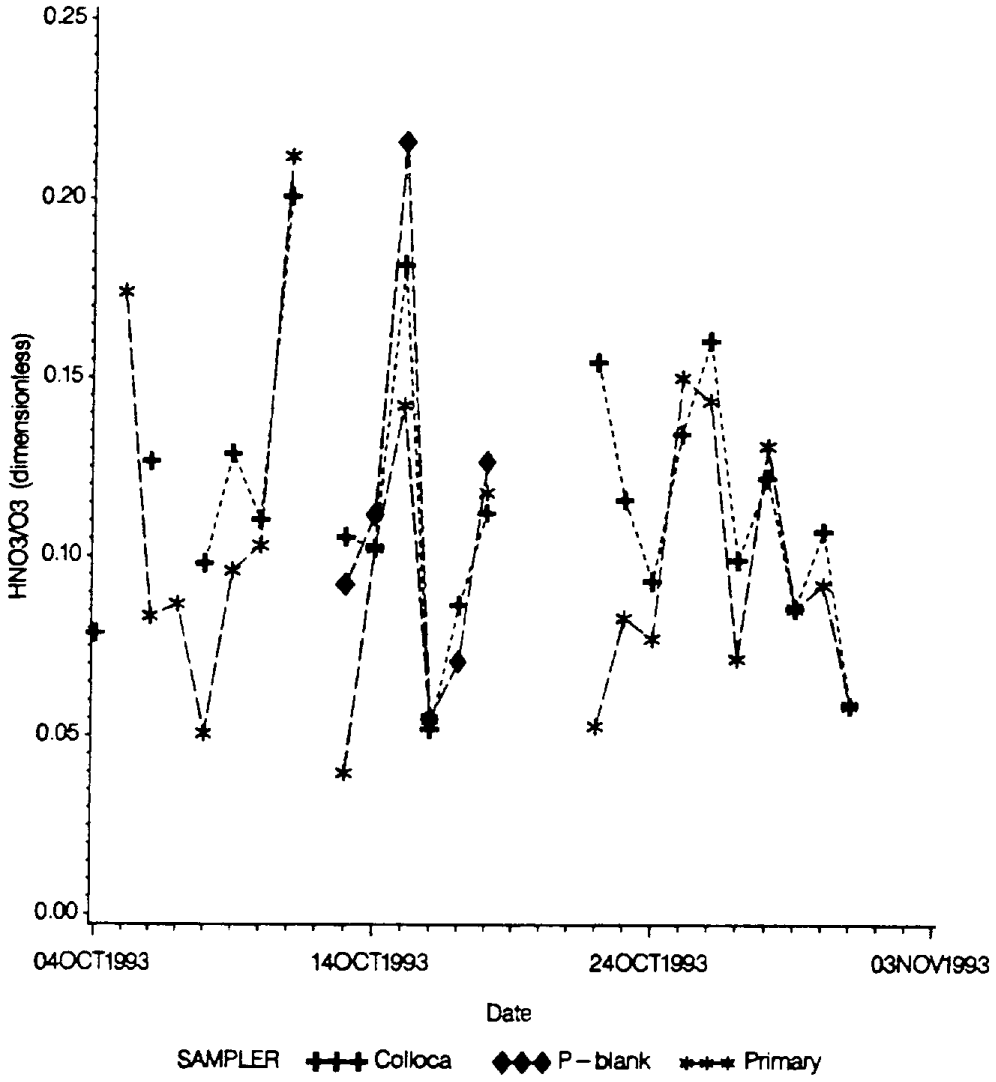

Figure 9. Ratio of CADMP HNO_3 to 10 am - 6 pm average O_3 at Azusa vs. date.

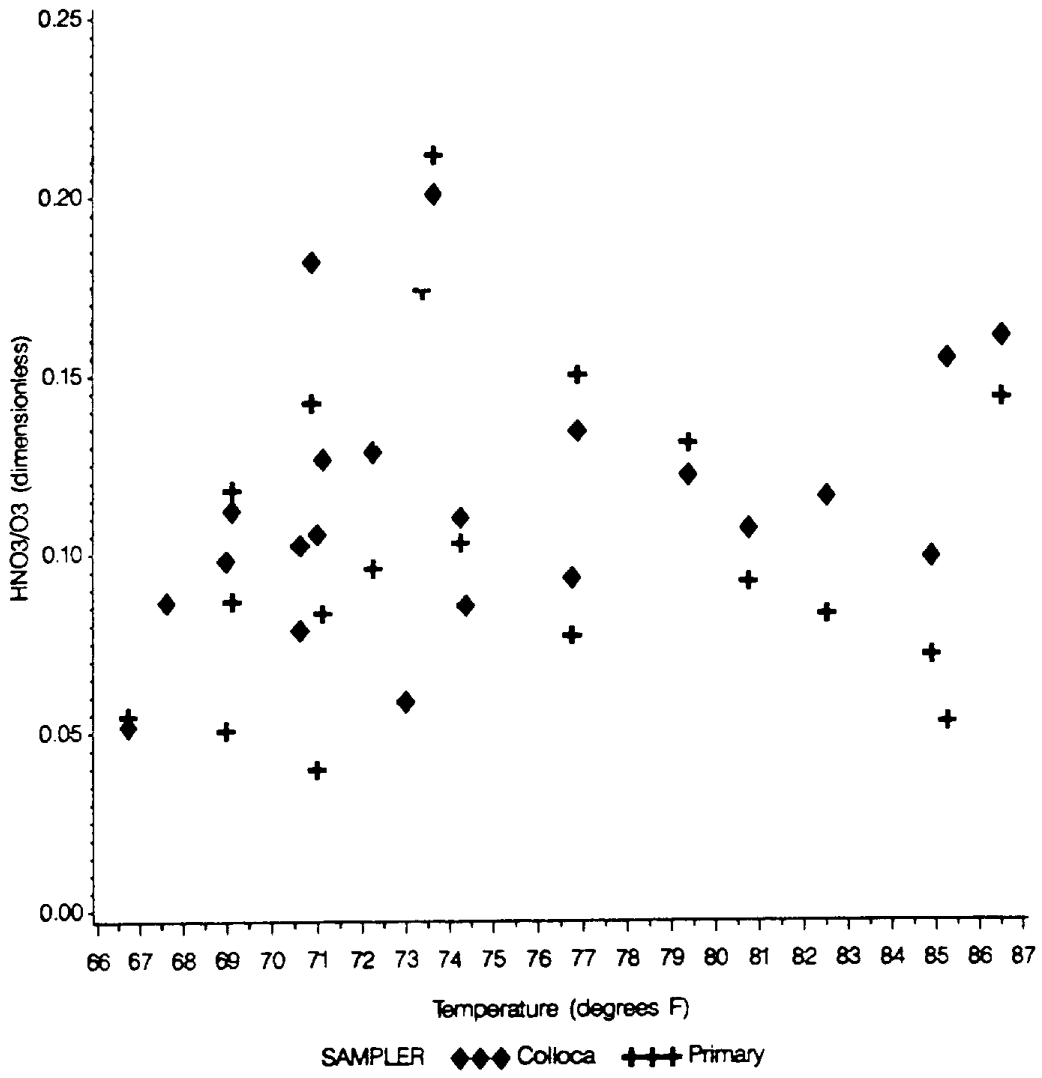

Figure 10. Ratio of CADMP HNO_3 to 10 am - 6 pm average O_3 at Azusa vs. 10 am - 6 pm average temperature.

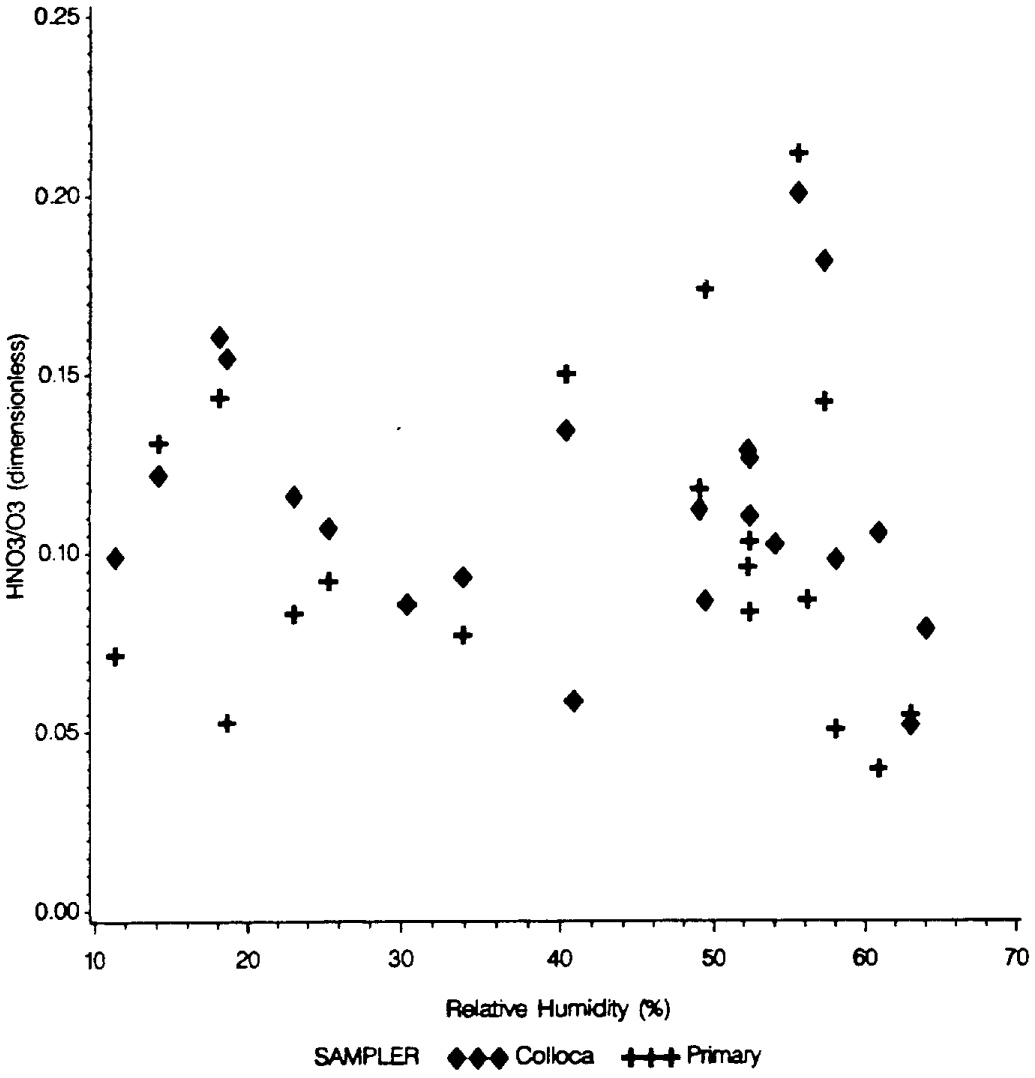

Figure 11. Ratio of CADMP HNO_3 to 10 am - 6 pm average O_3 at Azusa vs. 10 am - 6 pm average relative humidity.

VI. TDLAS METHODS

Sampling Configuration

For the 1993 Azusa study, sampling by TDLAS consisted of drawing air through a 6-mm O.D., 0.75-mm wall PFA Teflon tube approximately 4 m long. Particles were removed from the air by a 2-micron pore size Teflon filter located at the tubing entrance. A Teflon needle valve located 1 m upstream of the entrance to the White cell maintained the flow into the White cell at 10 liters per minute. The air traversed the inlet line in a few tenths of a second while the residence time in the White cell was about 4 seconds (Mackay, 1994).

The above sampling procedure was similar to that followed during the 1986 CSMCS, except for the use of a 5-m sampling line and a 1.2-micron pore size Teflon filter in the earlier study. As noted above, there was very good agreement among the measurements by TDLAS, FTIR, and short-duration (1-2 hr periods) filter-pack sampling during the 1986 CSMCS.

The known coincidence of the concentration-time profiles of HNO_3, O_3, and PAN during the progress of photochemical smog formation is used here to examine the time coherence of the sample analyzed in the TDLAS cell, i.e., whether or not significant amounts of HNO_3 adhered to the sampling line and then released into the air flow at a later time. For this purpose, the 15-min average concentrations of the three co-pollutants were employed. The time-series plots of these 15-min averages for the period 8:00 am - 8:00 pm each day are compiled in Appendix C. For some of the days, the 15-min values for HNO_3 were not processed from the voluminous 1-min TDLAS records, and for such days the plots of the more standard hourly average data are included in Appendix C.

The plots for October 2, 13, 24 and 29 are reproduced in Figures 12 - 15 and illustrate the close tracking of the concentration-time profiles of ozone, nitric acid and PAN. *The fact that in the majority of the days the TDLAS HNO_3 maximum coincided closely with the O_3 and PAN maxima indicates that the time distribution of HNO_3 was not significantly altered by the TDLAS sampling line. The general absence of HNO_3 "trailing" after the concentration maxima would also be consistent with insignificant bleeding of gaseous nitric acid from the particulates accumulated on the Teflon filter (which was replaced each morning) in front of the sampling line.*

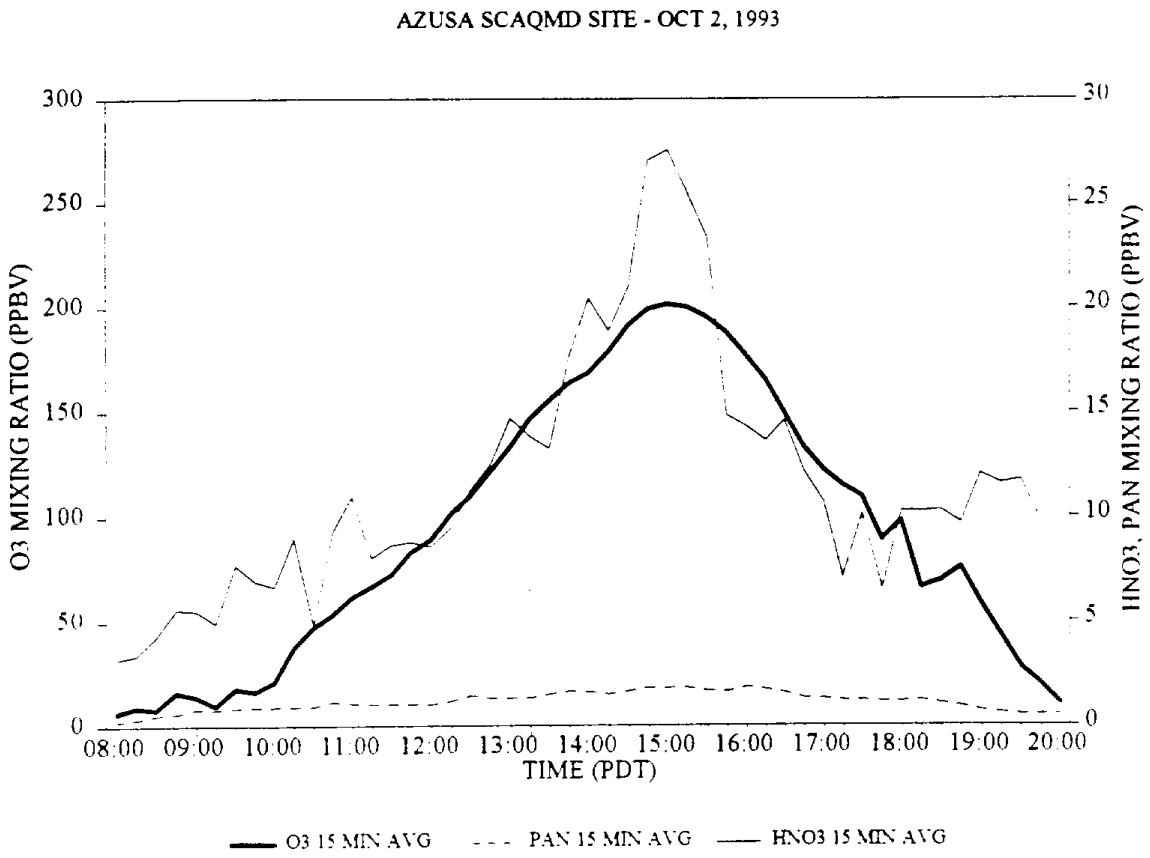

Figure 12. Daytime concentration profiles of ozone, PAN, and nitric acid by TDLAS on October 2, 1993 in Azusa.

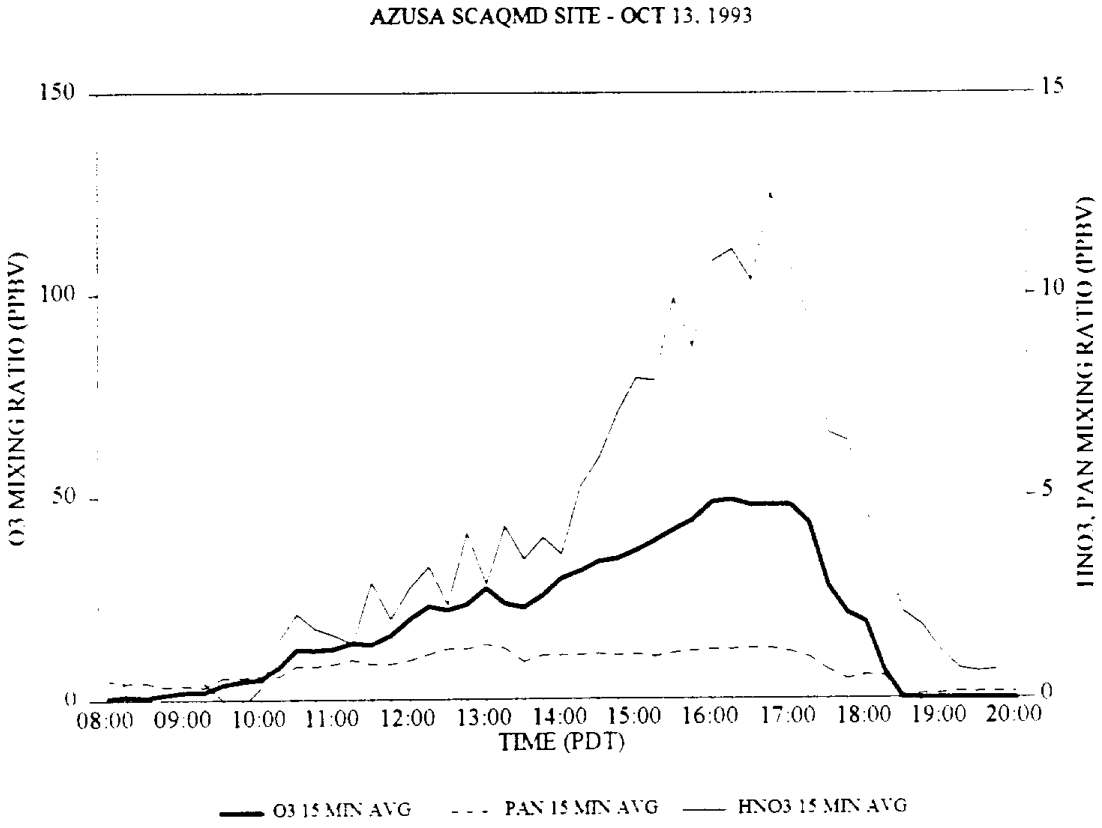

Figure 13. Daytime concentration profiles of ozone, PAN, and nitric acid by TDLAS on October 13, 1993 in Azusa.

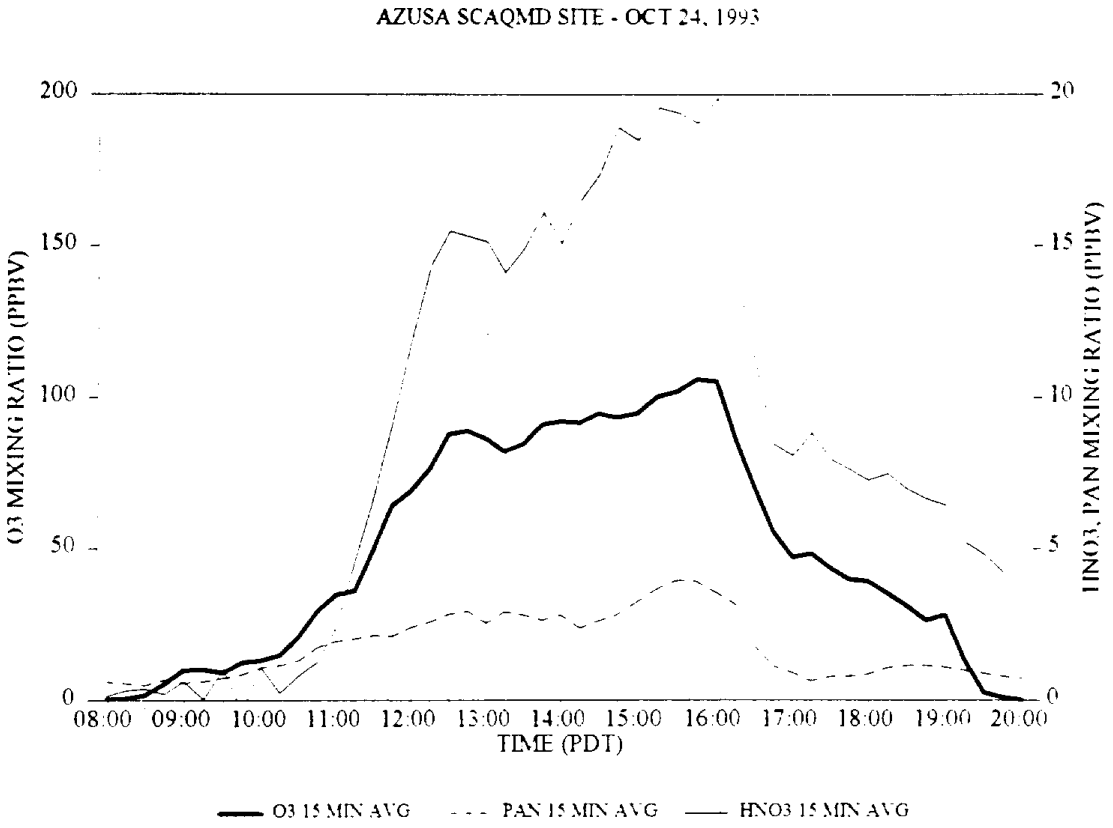

Figure 14. Daytime concentration profiles of ozone, PAN, and nitric acid by TDLAS on October 24, 1993 in Azusa.

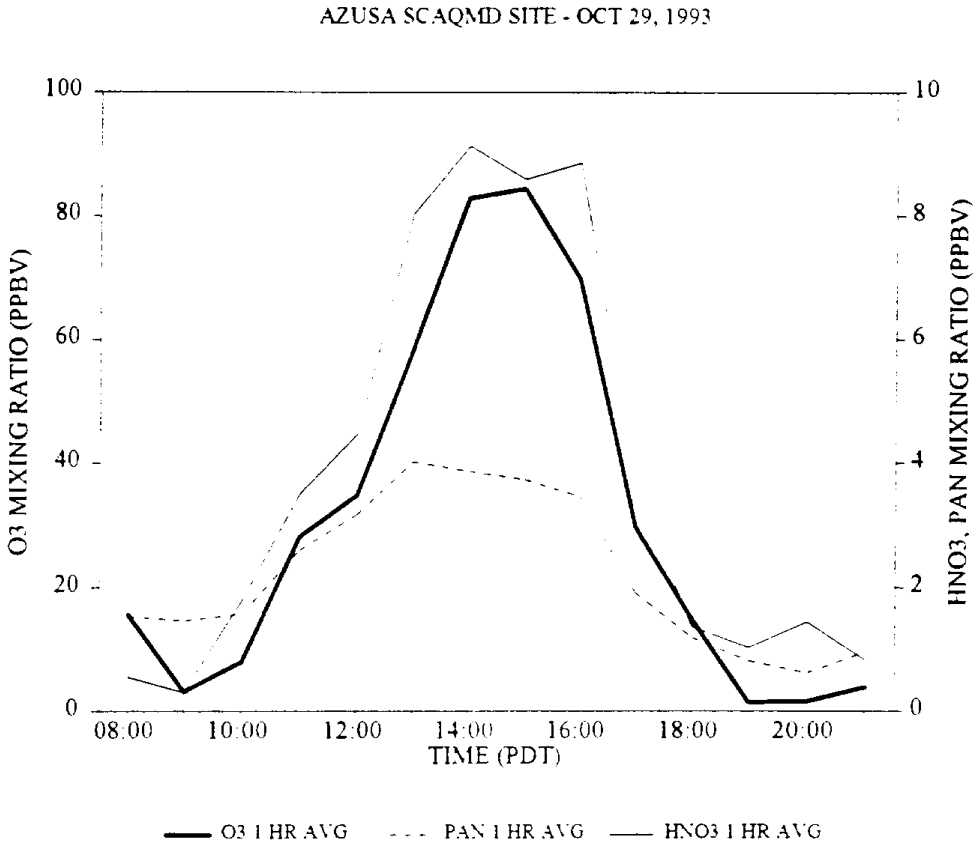

Figure 15. Daytime concentration profiles of ozone, PAN, and nitric acid by TDLAS on October 29, 1993 in Azusa.

Calibration

Although errors were made in the calibration of the HNO_3 permeation tube output prior to the study, by the use of an ill-prepared NaOH standard solution for titration, and during the study, by the use of "de-ionized" water from the local supermarket, the errors were fully recoverable. This was made possible by the documented constant output of the HNO_3 permeation tube.

Possibility of Interferences

Despite the generally good coincidences among the concentration-time profiles of HNO_3, PAN, and O_3, there were several days during the 1993 Azusa study when the TDLAS HNO_3 values were much higher than could be reconciled with the totality of prior data represented in Table 2. *The most acute examples are the HNO_3 levels during the October 4 - 7 period when $HNO_3 : O_3$ ratios were typically 0.3 - 0.5 near peak ozone levels of ≤ 60 ppb (see Figure 1 and Appendix C).* Even on these days the HNO_3 profile coincided well with the O_3 profile. However, there were other low-ozone days such as October 8, 11, and 22 when the HNO_3 growth curves displayed "bumps" that appeared extraneous (see corresponding plots in Appendix B), and there are other cases where the appearance of "unexpected" peaks could be argued. These observations raise the question of possible interferences to the TDLAS measurements.

The site where the study was conducted is the AQMD monitoring station located at 803 N. Loren Avenue, Azusa, CA, approximately 300 feet north from the intersection of N. Loren Avenue with Foothill Boulevard. N. Loren Avenue is a short street bound by Foothill Boulevard to the south, by Todd Avenue approximately 300 feet to the west, by 10th Street to the north at a distance of about 0.4 mile from Azusa Avenue, and by Coney Avenue which is approximately 600 feet to the east. *A number of industrial operations exist around the site which could be potential sources of organic chemical releases into the air.* Located along Foothill Boulevard between Coney and Todd Avenues are at least two automotive body repair shops which most likely employ solvents and paint formulations. Situated along Todd Avenue and almost in a direct west to east trajectory with the SCAQMD station is an aluminum extrusion plant, a sizable welding operation, and a plant with a metal storage tank but whose activity could not be immediately determined from the exterior. On 10th Street, sizable manufacturing operations by a paint company (Valspar Corporation) and a plastics company (Bokof Plastic Materials) are in existence. In addition, a distribution terminal for an even larger paint company (Reichold

Corporation) is located at 237 S. Motor Ave., approximately 1.5 mi southeast (south of Freeway 210) of the AQMD monitoring station.

The manufacturing operations noted above could have released organic compounds during the 1993 field study, in particular solvents with carbonyl moieties that could present interferences in the narrow region around 1720 cm^{-1} where an absorption line of nitric acid was employed by the TDLAS method for measurement. Such compounds would not affect nitric acid measurements by collection on filter media.

Elevated levels of acetone and methyl ethyl ketone (MEK) were, in fact, measured at the Azusa AQMD station prior to October 1993. Grosjean et al. (1995) reported 4-hr average concentrations of 0.2 - 6.4 ppb for acetone and 0.6 - 8.4 ppb for MEK, by the DNPH collection method, during two 24-hr periods on September 8 and September 9, 1993. (Interestingly, the highest concentrations were measured during the late night and early morning periods.) From April 1993 to September 1993, a series of 24-hr sampling conducted every two weeks with a passive charcoal badge (and subsequent GC analysis), measured average concentrations of 6 - 43 ppb of MEK and 0.6 - 5.2 ppb of methyl isobutyl ketone (MIBK), with an estimated uncertainty of $\pm 50\%$ for the badge method which was still at an experimental stage (Fung, 1995).

The extent of interference to the TDLAS measurement would depend upon the resolvability of the vibration-rotation band structure of the carbonyl compound such as MEK. The high resolution capability of the TDLAS method allows a single vibration-rotation line structure of HNO_3 to be chosen in between the numerous lines of the low-molecular weight species such as H_2O, HCHO and even relatively heavier molecules such as CH_3CHO. A further check on the presence of interference is the correlation coefficient for the fit of the measured line to that of the calibration gas. However, it can be more difficult to avoid the potential interferences of compounds of "intermediate" molecular weights such as $(CH_3)_2CO$ or MEK if they possess resolvable absorption bands, since the spacings between line structures are smaller. The absorption band of $(CH_3)_2CO$ in the 1720 cm^{-1} region was shown by experiment to be structureless in terms of the TDLAS resolution (perhaps due to the additional complex energy sub-levels introduced by the CH_3 group internal rotations) and hence would not present an interference to the derivative method of analysis by TDLAS. The observation that the C=O stretch band of acetone is structureless diminishes the likelihood that MEK, being a heavier molecule, has resolvable fine structures. The potential interferences by the common industrial

solvents such as MEK and MIBK, as well as carbonyl products in photochemical smog including glyoxal and methylglyoxal, have yet to be experimentally investigated. It will generally be quite difficult to apply corrections to an interfered TDLAS signal, since the degree of overlap with the HNO_3 line, the interfering line's intrinsic strength (absorption coefficient), and the concentration of the interfering species must be known. Hence, a catalog of neighboring lines from potentially interfering compounds is implicitly required for the proper selection of an isolated HNO_3 absorption line for TDLAS analysis.

VII. SUMMARY AND CONCLUSIONS

A review of the nitric acid data during the 1993 Azusa comparison study was conducted to evaluate the consistency and accuracy of the measurements by the TDLAS method, and in particular with respect to the suggested use of the TDLAS data as the reference standard for the other HNO_3 samplers employed during the study.

During the two-week period of October 11 - October 24, 1993, the daytime measurements between 10:00 a.m. to 6:00 p.m. indicated that the ratio of the mean CADMP HNO_3 to TDLAS HNO_3 was 0.56, while the 24-hr measurements showed that the ratio of the mean SCAQS HNO_3 to TDLAS HNO_3 was 0.72. During the same period, the continuous two-week HNO_3 sampler by Aerosol Dynamics Inc. obtained an integrated measurement which was 30% higher than the corresponding TDLAS HNO_3 average.

The nitric acid data from prior field studies in 1986 and 1987, which consisted mostly of measurements by SCAQS-type samplers but also included limited measurements by the TDLAS and FTIR methods, were examined to form a wider base of comparison for the 1993 Azusa study. The regression slopes of the plot of daytime HNO_3 vs daytime O_3 for eight southern California locations were calculated to be in the range 0.02 to 0.2, with the lowest value found in the NH_3-rich Riverside area and the highest value in the NO-rich location of downtown Los Angeles. The slopes for the mid-basin locations of Azusa and Claremont were in the range 0.06 to 0.09 and the corresponding mean HNO_3 : O_3 ratios were in the range 0.08-0.14. Hence, the regression slope of 0.12 and mean HNO_3 : O_3 ratio of 0.2 derived from the daytime TDLAS measurements during the 1993 study indicate TDLAS HNO_3 values which are significantly higher than expected for Azusa and adjoining downwind locations.

The generally good correspondence of the TDLAS HNO_3 concentration-time profile with those of its photochemical co-products O_3 and PAN is consistent with little or no HNO_3 lag caused by an adsorption/desorption process in the TDLAS sampling train and is also consistent with insignificant HNO_3 vaporization from particulates on the Teflon front-filter. No errors were found in the overall TDLAS calibration during the 1993 Azusa study. The correlation being made for each sample measurement with the HNO_3 reference in terms of line shape and line position remains the strongest self-check feature of the TDLAS method for the presence of interferences. Despite the latter, the possibility of positive interference on the TDLAS HNO_3 measurement is being suggested by unusual peaks in the observed HNO_3 concentration-time profiles on particular days, by the presence of a number of industrial operations around the study site, and by the detection of elevated levels of carbonyl-group containing solvents by two research groups (Grosjean et al., 1995; Fung, 1995; see above) during the weeks preceding the 1993 study in Azusa.

The data from the secondary (collocated) CADMP sampler showed an average HNO_3 : O_3 ratio of 0.1 (the linear regression slope is also 0.1) with good HNO_3 to O_3 correlation, which indicates a high probability that its 1993 daytime HNO_3 measurements in Azusa were correct. A more robust compilation of data depicting trends in HNO_3 : O_3 ratios will be helpful, but further controlled experimentation is required to arrive at a definitive conclusion. No explanation could be found for the observed erratic performance of the primary CADMP sampler. Given the fact that the samplers are of equal design and construction, the observed divergence in their performance should be a concern with respect to their interchangability and should be investigated further.

VIII. RECOMMENDATIONS

It is clear from the foregoing that a satisfactory explanation and absolute accounting of the large discrepancies among the HNO_3 measurements by the various samplers, particularly those between CADMP and TDLAS, will require controlled experimentation that will directly measure the losses that could occur in the sampling trains of the different samplers. The laboratory comparison should employ a common, "standard" calibration source, such as a flow of an accurately diluted output from a permeation tube, and should be conducted over adequate ranges of temperature and relative humidity. This type of test is, in fact, already being carried

out for the CADMP sampler (Fitz, 1994). It should also be conducted for the TDLAS apparatus as well as for the SCAQS-type sampler, ideally under a parallel sampling arrangement for all modules. Such tests may actually extend to the development of a common, practical HNO_3 calibration device in the field for the different types of sampler.

In order that interferences can be more confidently excluded, the compilation of TDLAS spectra of volatile, carbonyl-group bearing organic compounds over the frequency region for HNO_3 measurement should be a continuing effort. They should be recorded for the common solvents such as methyl ethyl ketone, as well as for other known photooxidation products such as glyoxal and methyl glyoxal. The TDLAS itself is the most practical instrument to use for this compilation which requires very high resolution but in only a very narrow region of the infrared spectrum.

IX. REFERENCES

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Taylor, C. (1994): Private communication.

APPENDIX A

This appendix summarizes the data from the primary and secondary (collocated) CADMP samplers obtained during several days in July - September 1993 in Azusa, CA, prior to the methods comparison conducted in October 1993. Parallel time series plots of the two samplers' results are presented for daytime and nighttime denuded particulate nitrate and denuder difference nitric acid, as well as for nitric acid measurements from filter packs upstream of the samplers' denuders. The plot of nitric acid against the corresponding block-averaged ozone for the entire period July - October 1993 are illustrated for each sampler. The hourly temperature and relative humidity for the 10:00 a.m. - 6:00 p.m. period are also plotted for July - October 1993.

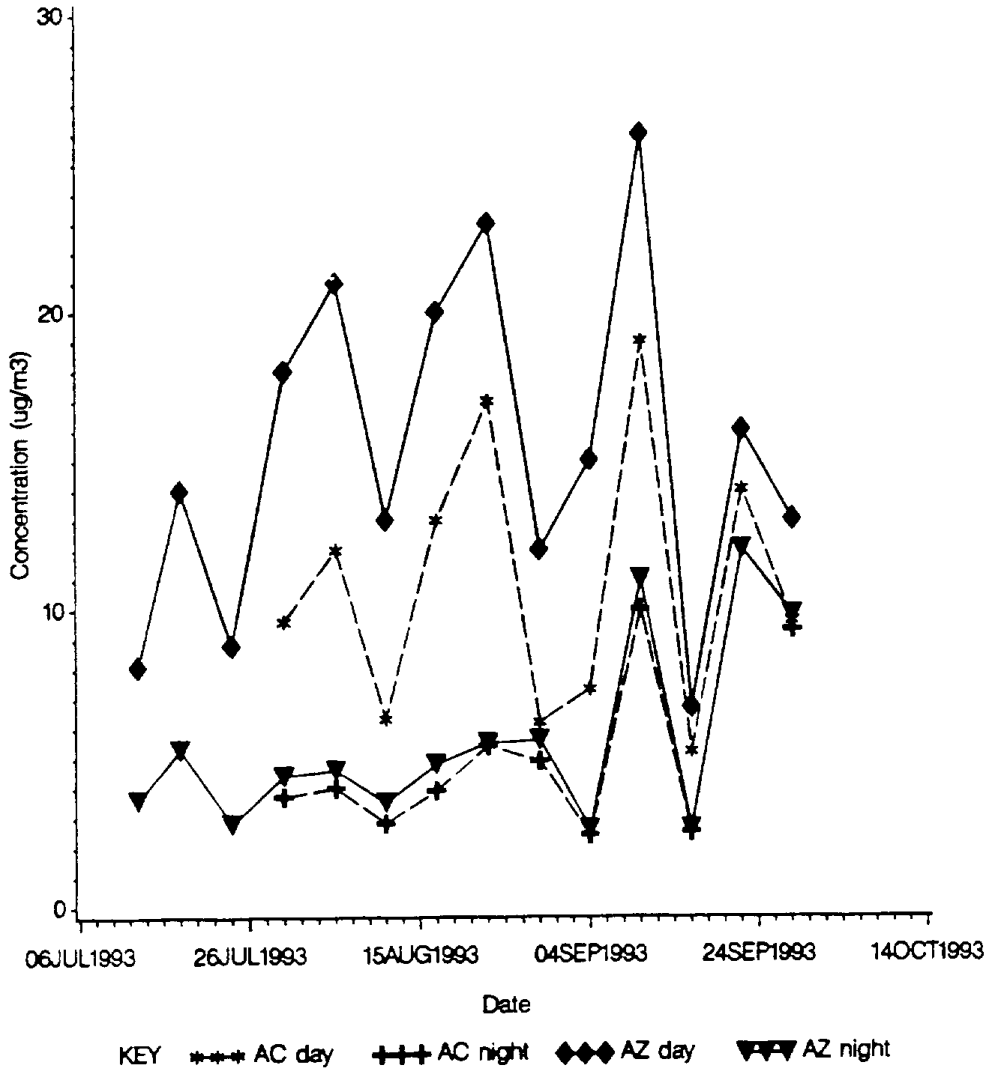


Figure A-1. Denuded particulate nitrate vs. date for CADMP Azusa primary (AZ) and collocated (AC) samplers. Sampling periods were 6:00 a.m. - 6:00 p.m. and 6:00 p.m. - 6:00 a.m.

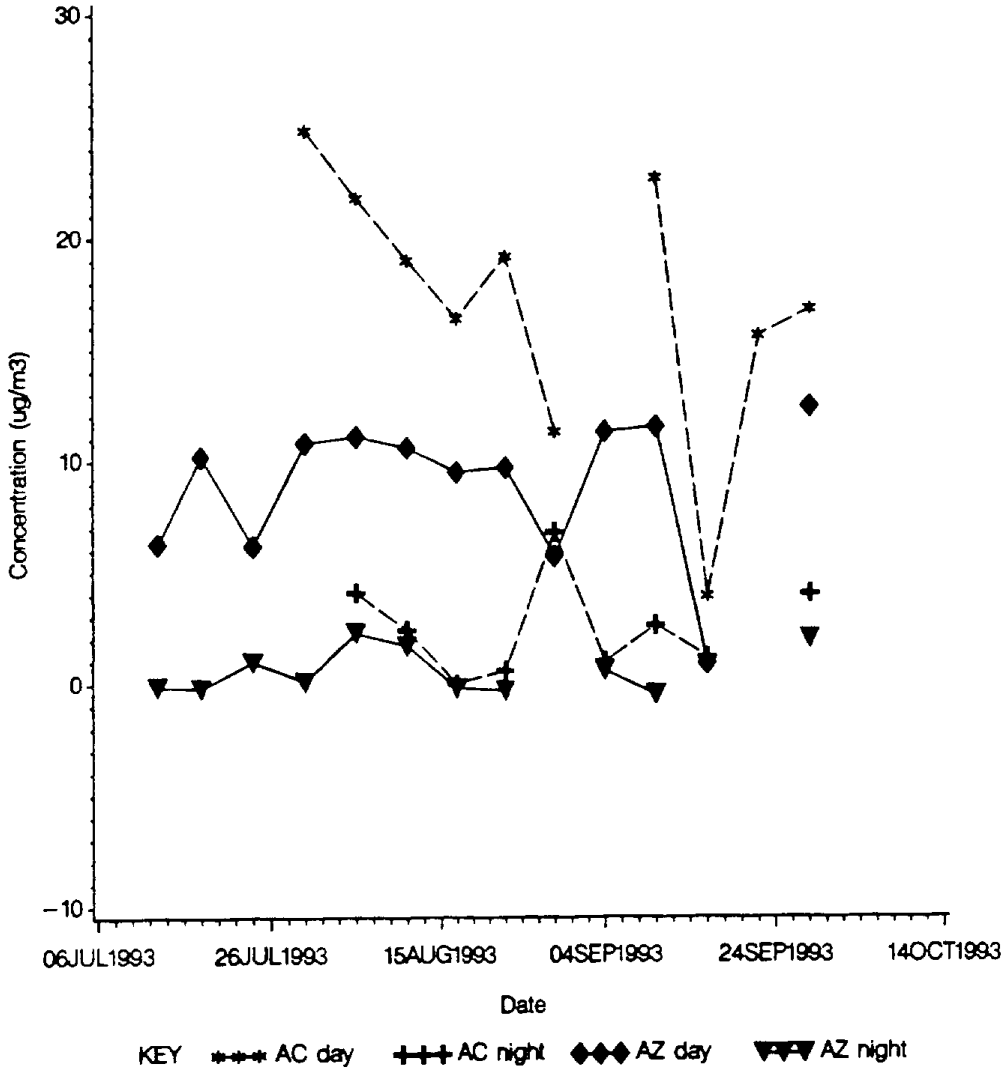


Figure A-2. Denuder difference nitric acid vs. date for CADMP Azusa primary (AZ) and collocated (AC) samplers. Sampling periods were 6:00 a.m. - 6:00 p.m. and 6:00 p.m. - 6:00 a.m.

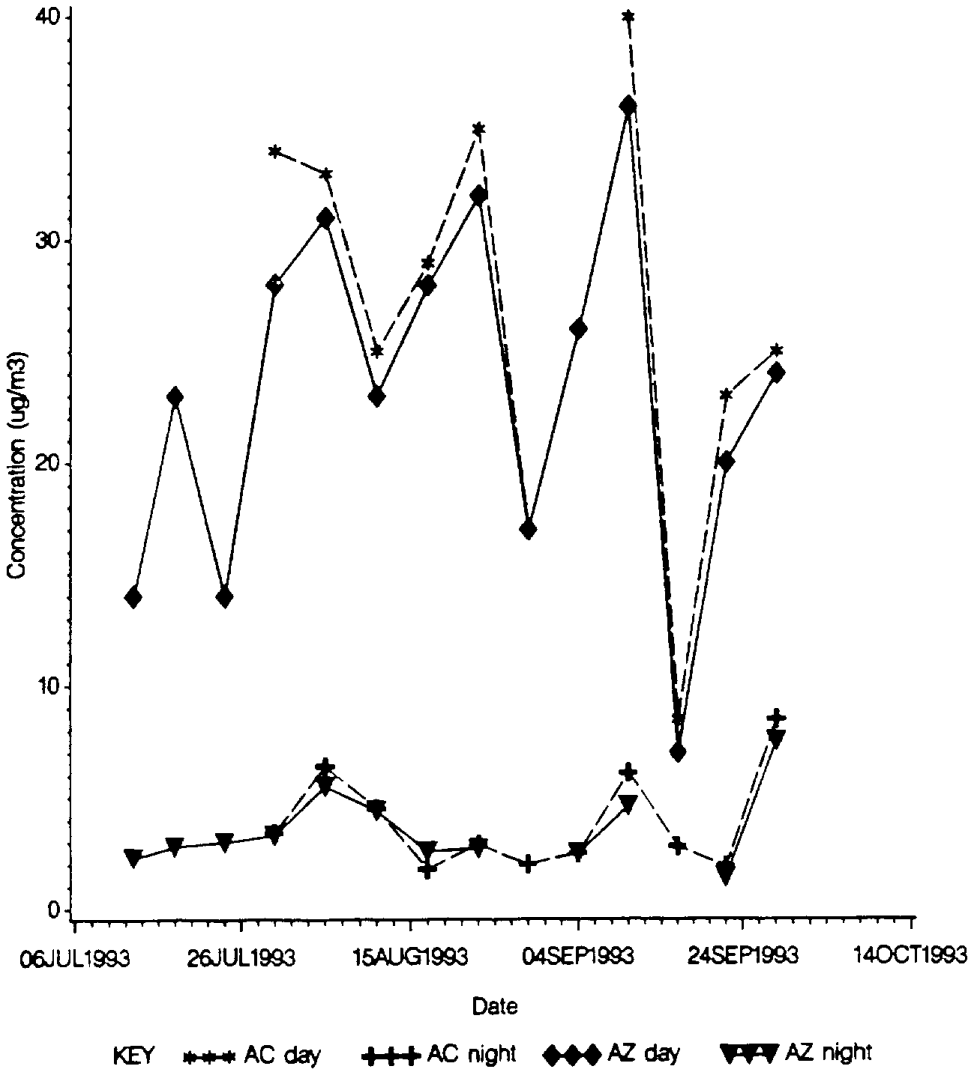


Figure A-3. Filter-pack nitric acid vs. date for CADMP Azusa primary (AZ) and collocated (AC) samplers. Sampling periods were 6:00 a.m. - 6:00 p.m. and 6:00 p.m. - 6:00 a.m.

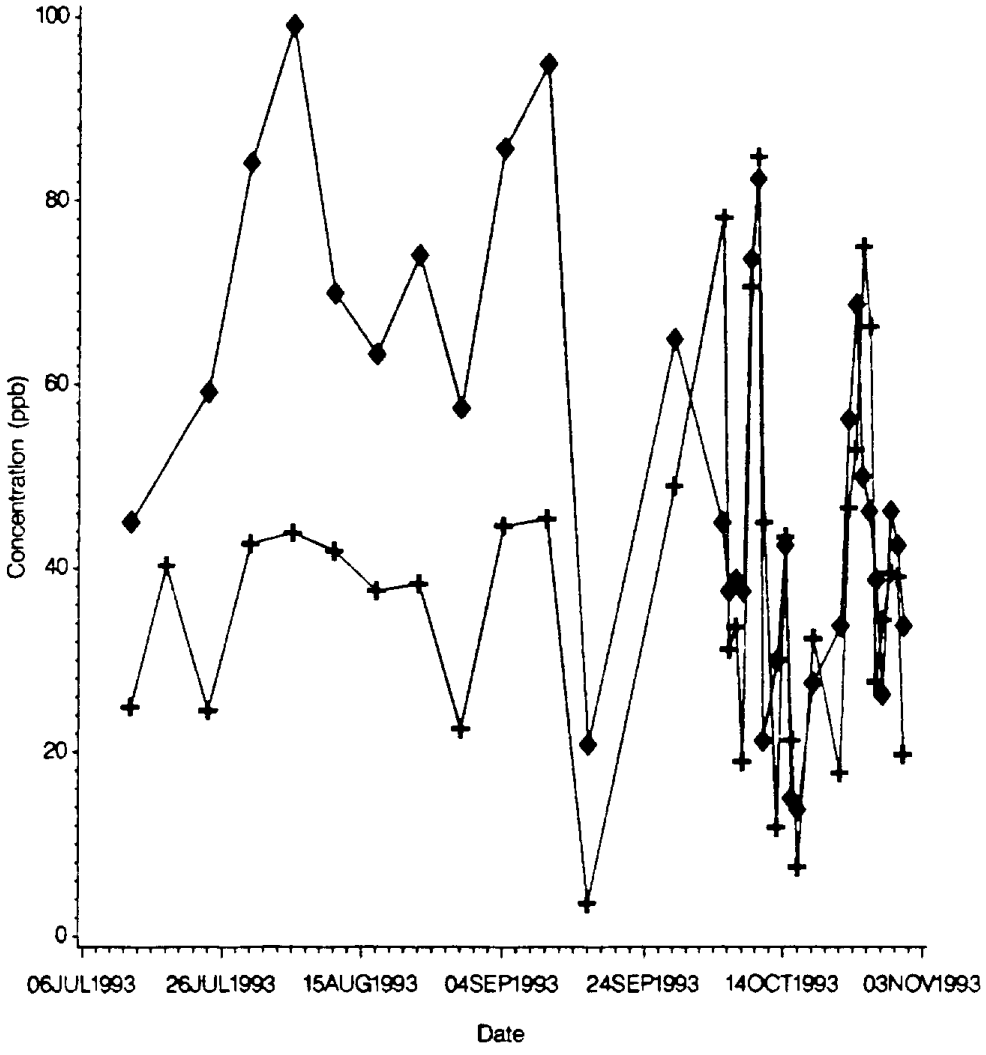


Figure A-4. Nitric acid (x10) (plus symbols) by CADMP primary sampler plotted with the corresponding block-averaged ozone (diamonds) for the period July - October 1993.

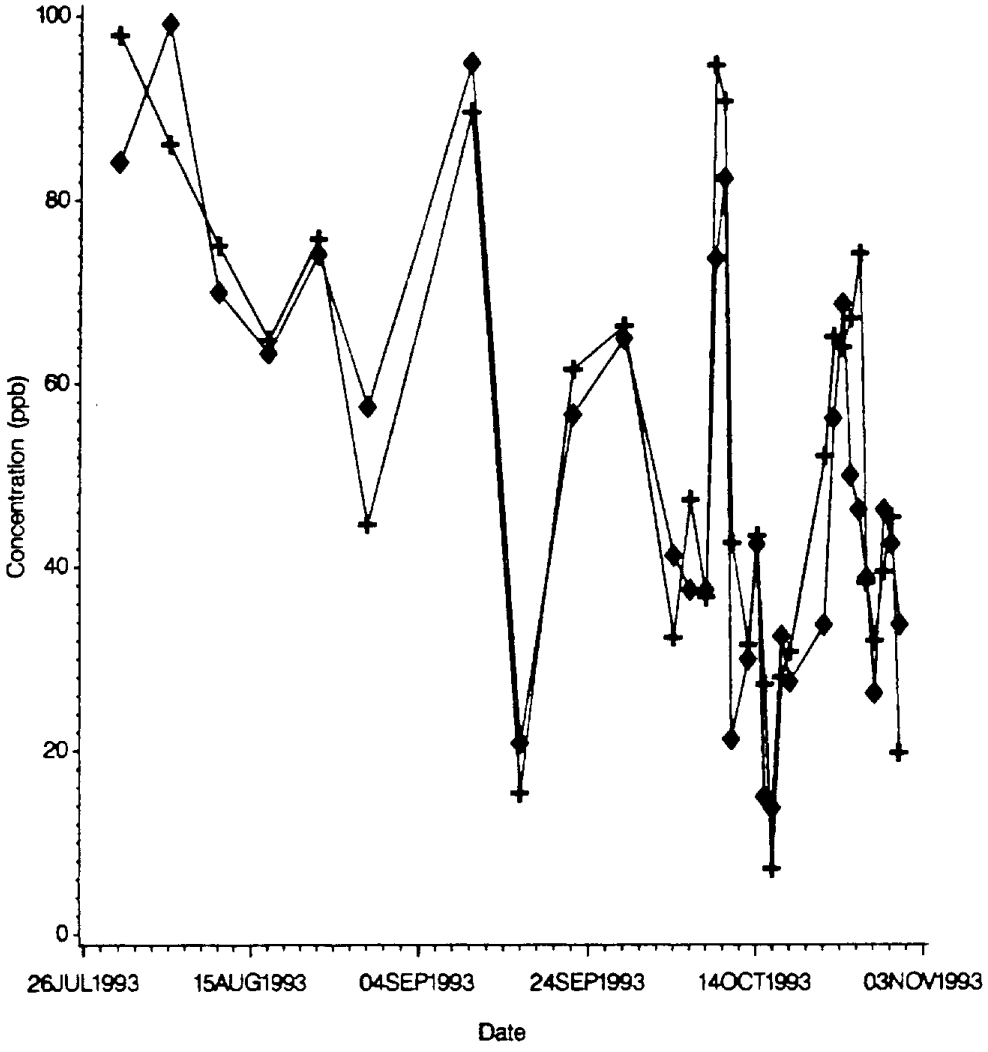


Figure A-5. Nitric acid (x10) (plus symbols) by CADMP secondary sampler plotted with the corresponding block-averaged ozone (diamonds) for the period July - October 1993.

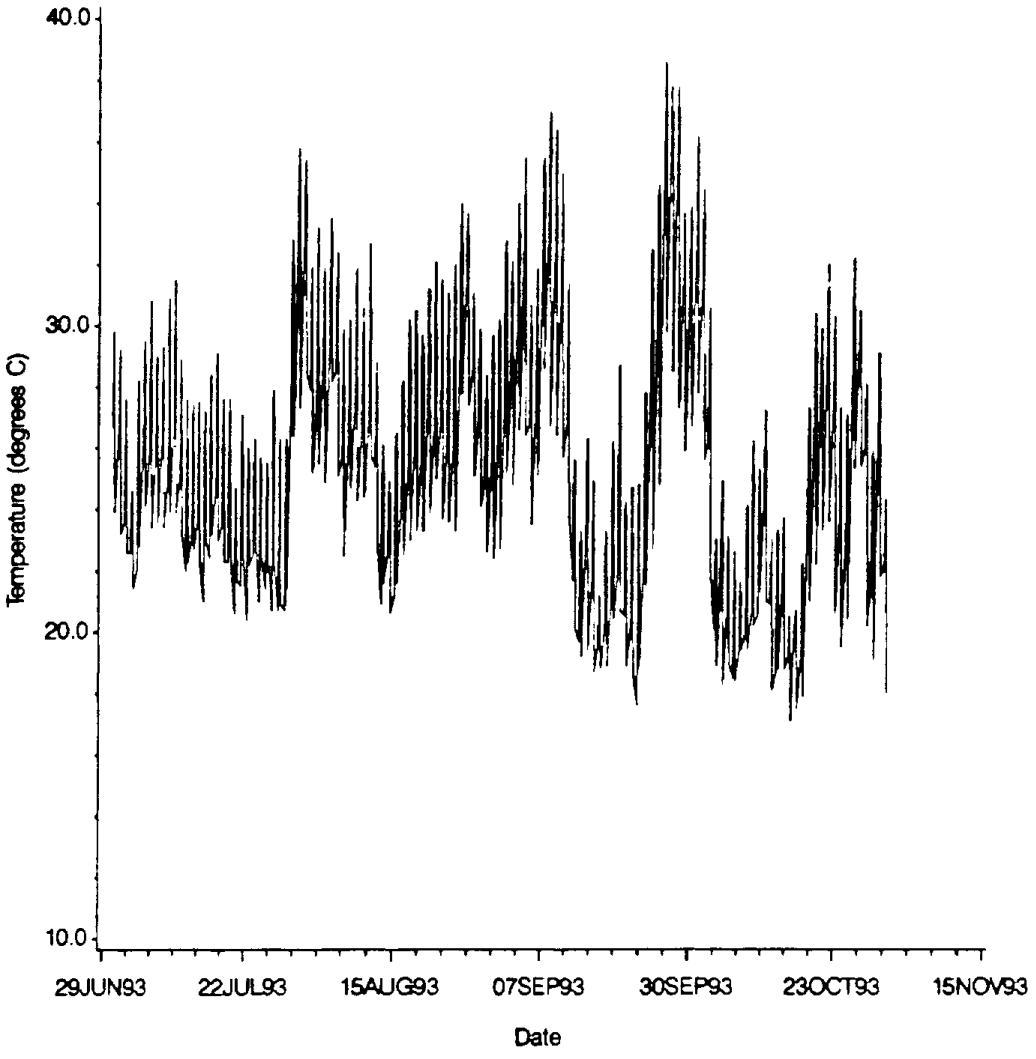


Figure A-6. Hourly average temperatures during the 10:00 a.m. - 6:00 p.m. period plotted versus date for July - October 1993.

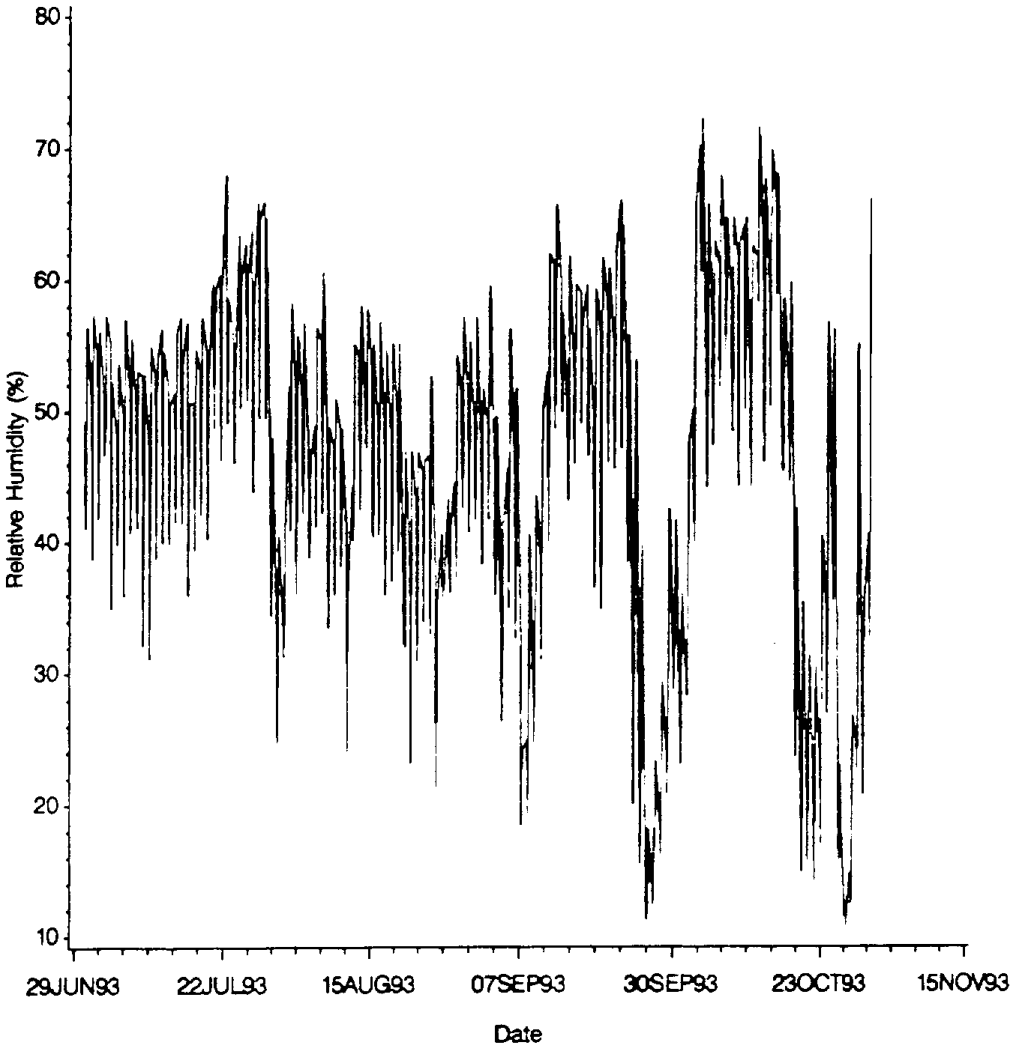


Figure A-7. Hourly average relative humidity values during the 10:00 a.m. - 6:00 p.m. period plotted versus date for July - October 1993.

APPENDIX B

This appendix contains plots of summer daytime nitric acid concentrations versus ozone concentrations at different locations in southern California. These comprise the pre-1993 data sets used for the linear regression analysis presented in Table 2 of the main text.

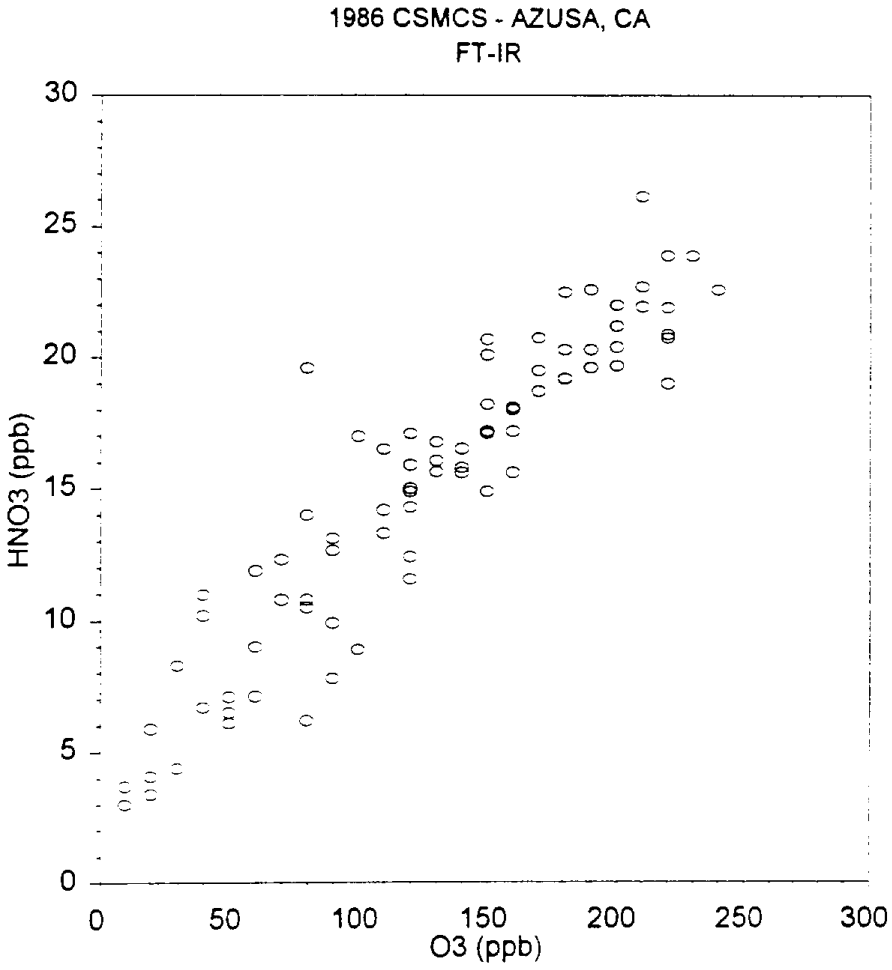


Figure B-1. Hourly average HNO_3 by FT-IR vs. hourly average O_3 for the 9 a.m. - 6 p.m. period, August 12 - August 20, 1986 in Azusa, CA. The data correspond to FTIR/AZUS in Table 2 of the text.

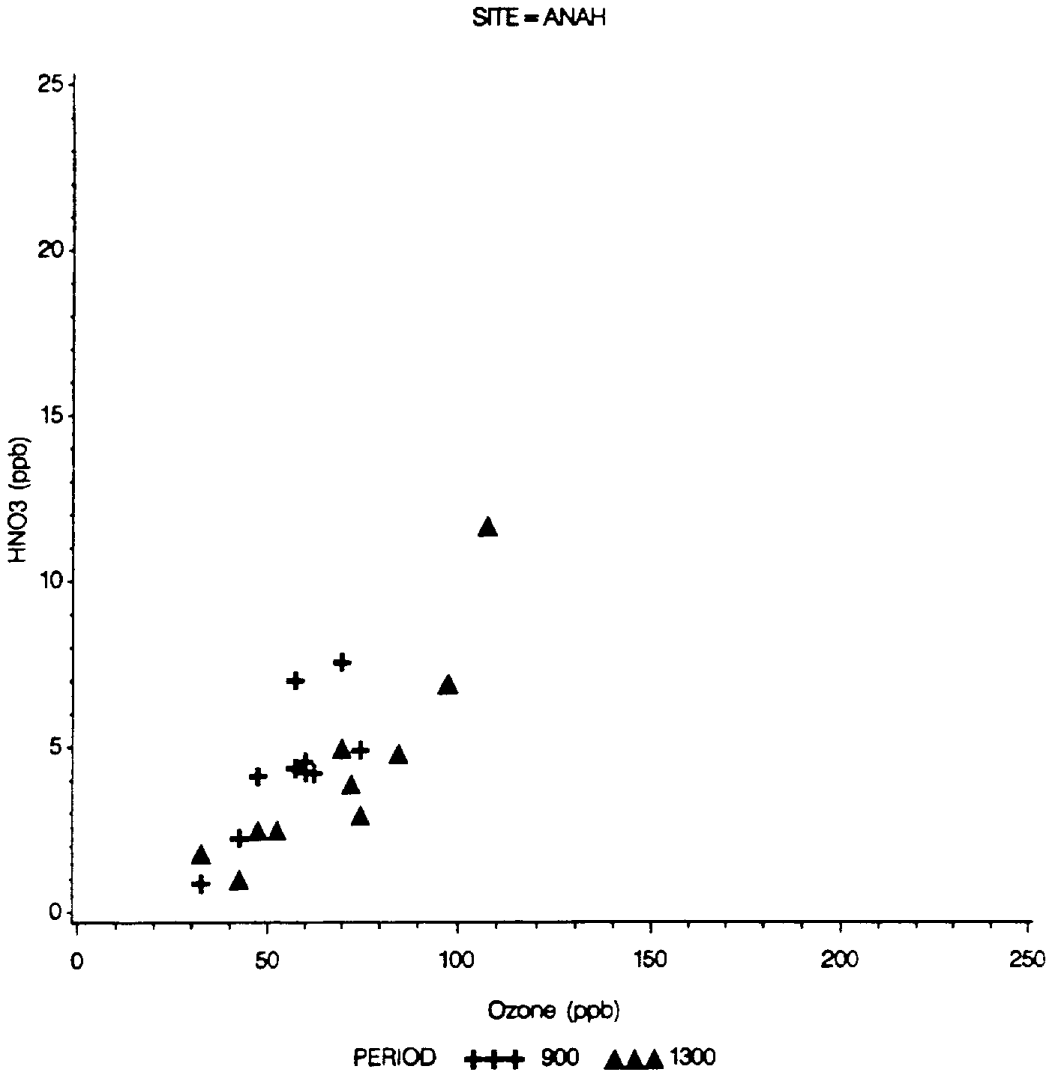


Figure B-2. HNO_3 by a SCAQS sampler vs. average O_3 for the 9 a.m. - 1 p.m. and 1 p.m. - 5 p.m. periods during 11 days in June 19 - September 3, 1987 in Anaheim, CA. The data correspond to SCAQS/ANAH in Table 2 of the text.

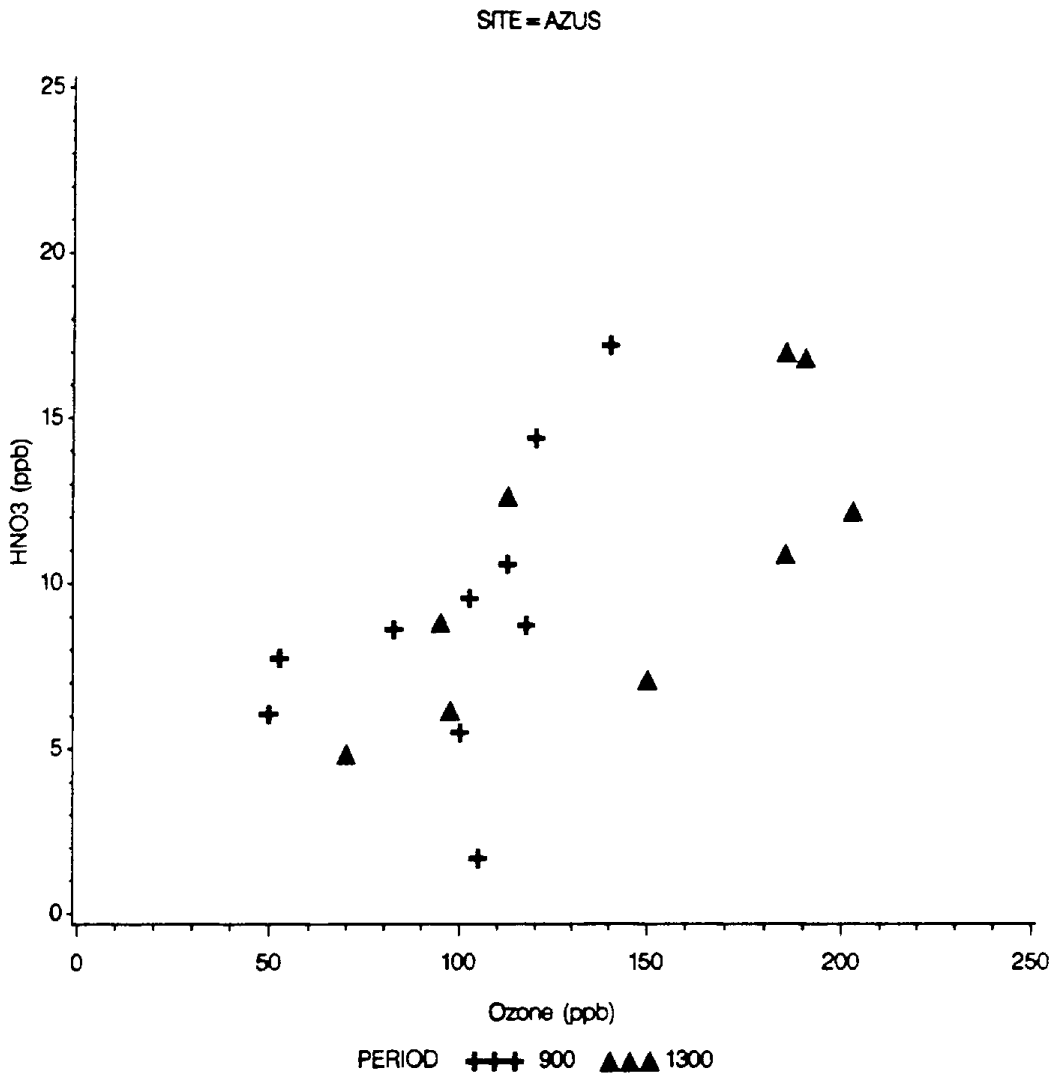


Figure B-3. HNO_3 by a SCAQS sampler vs. average O_3 for the 9 a.m. - 1 p.m. and 1 p.m. - 5 p.m. periods during 11 days in June 19 - September 3, 1987 in Azusa, CA. The data correspond to SCAQS/AZUS in Table 2 of the text.

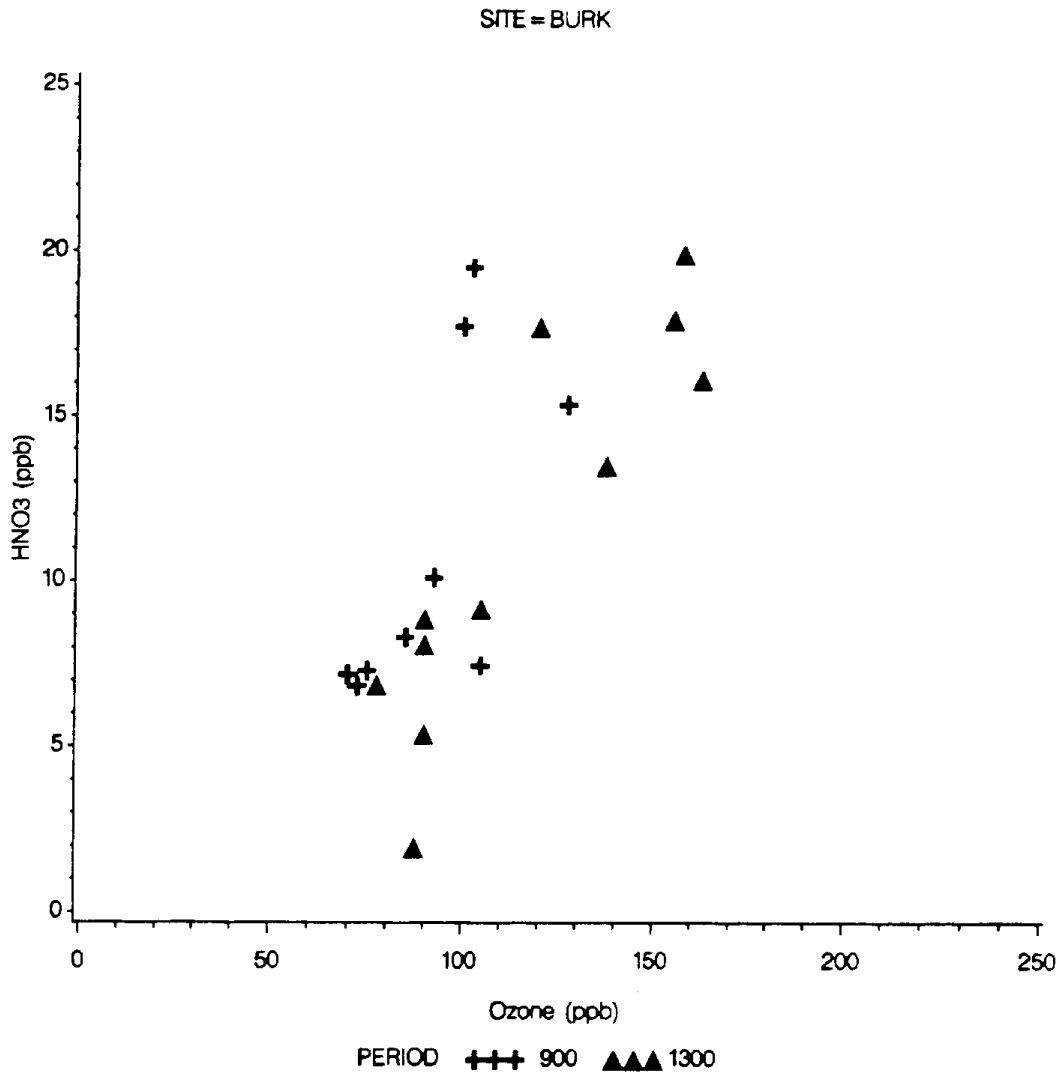


Figure B-4. HNO_3 by a SCAQS sampler vs. average O_3 for the 9 a.m. - 1 p.m. and 1 p.m. - 5 p.m. periods during 11 days in June 19 - September 3, 1987 in Burbank, CA. The data correspond to SCAQS/BURK in Table 2 of the text.

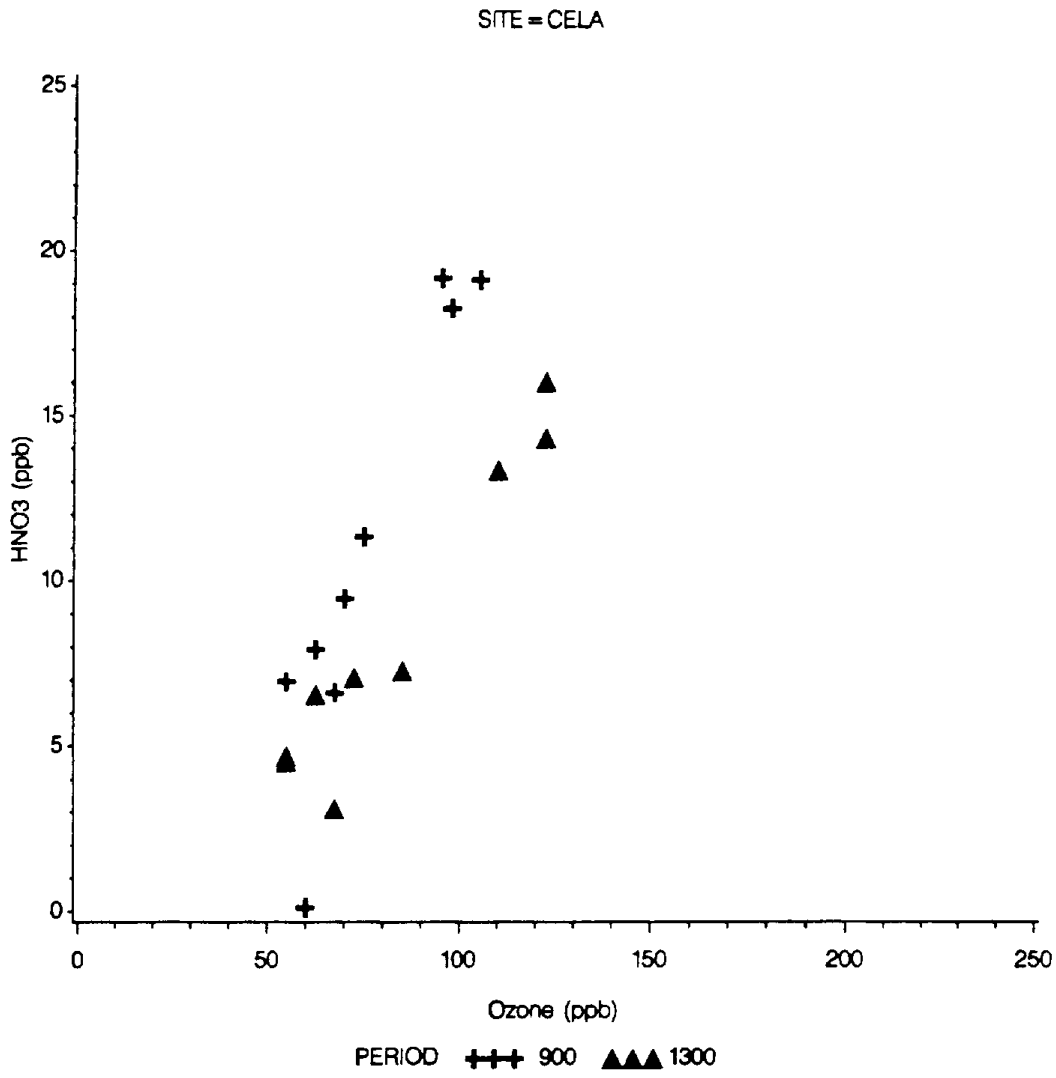


Figure B-5. HNO_3 by a SCAQS sampler vs. average O_3 for the 9 a.m. - 1 p.m. and 1 p.m. - 5 p.m. periods during 11 days in June 19 - September 3, 1987 in central Los Angeles. The data correspond to SCAQS/CELA in Table 2 of the text.

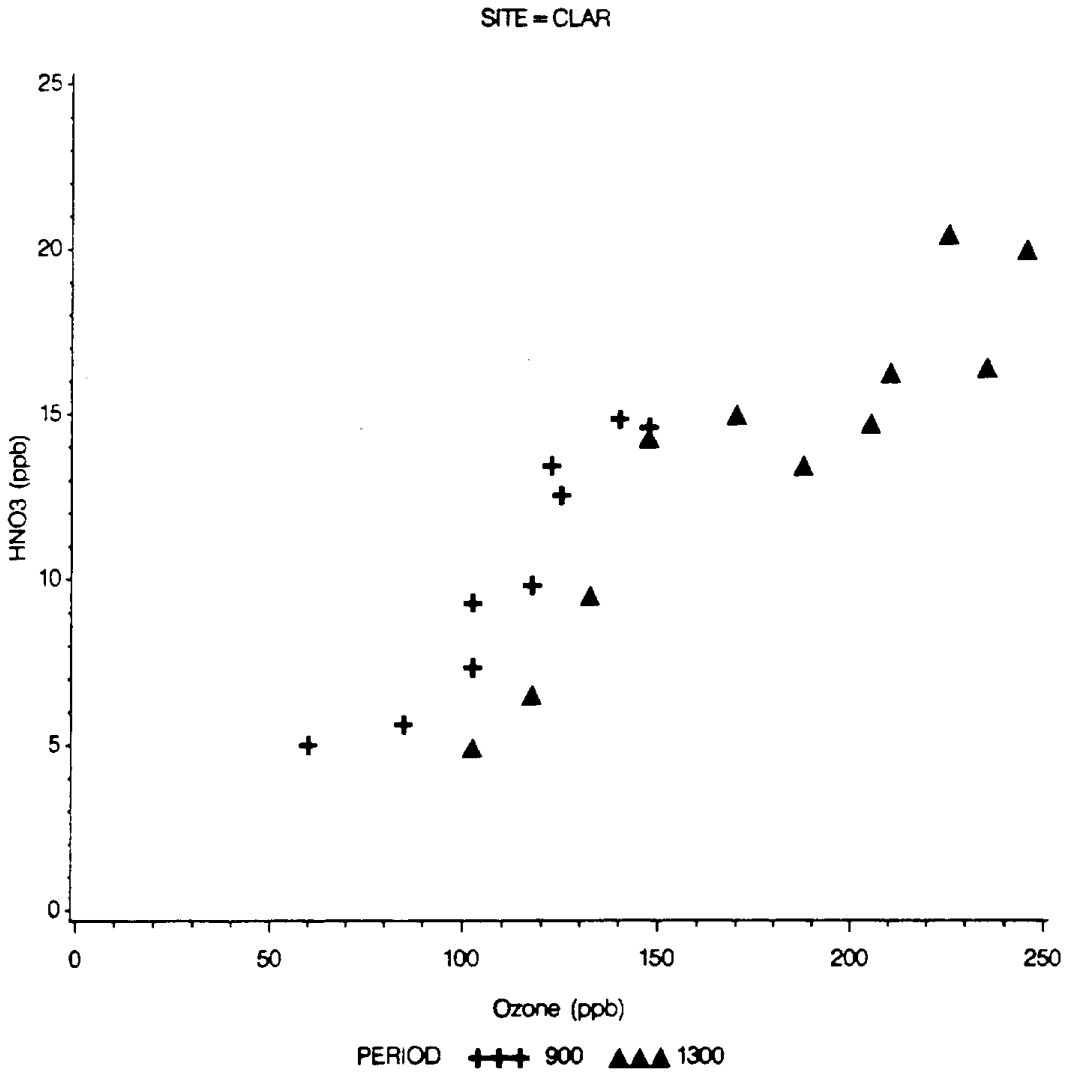


Figure B-6. HNO_3 by a SCAQS sampler vs. average O_3 for the 9 a.m. - 1 p.m. and 1 p.m. - 5 p.m. periods during 11 days in June 19 - September 3, 1987 in Claremont, CA. The data correspond to SCAQS/CLAR in Table 2 of the text.

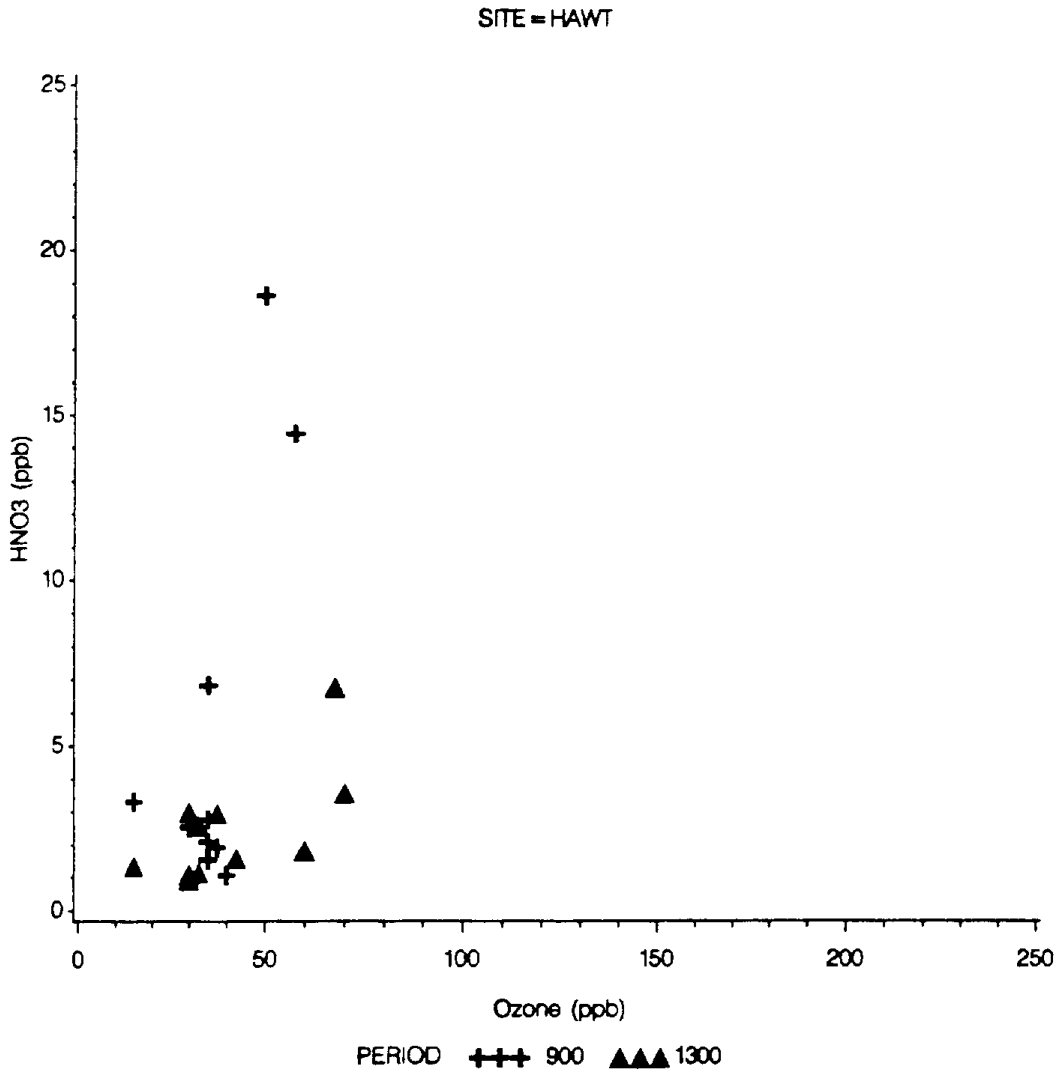


Figure B-7. HNO_3 by a SCAQS sampler vs. average O_3 for the 9 a.m. - 1 p.m. and 1 p.m. - 5 p.m. periods during 11 days in June 19 - September 3, 1987 in Hawthorne, CA. The data correspond to SCAQS/HAWT in Table 2 of the text.

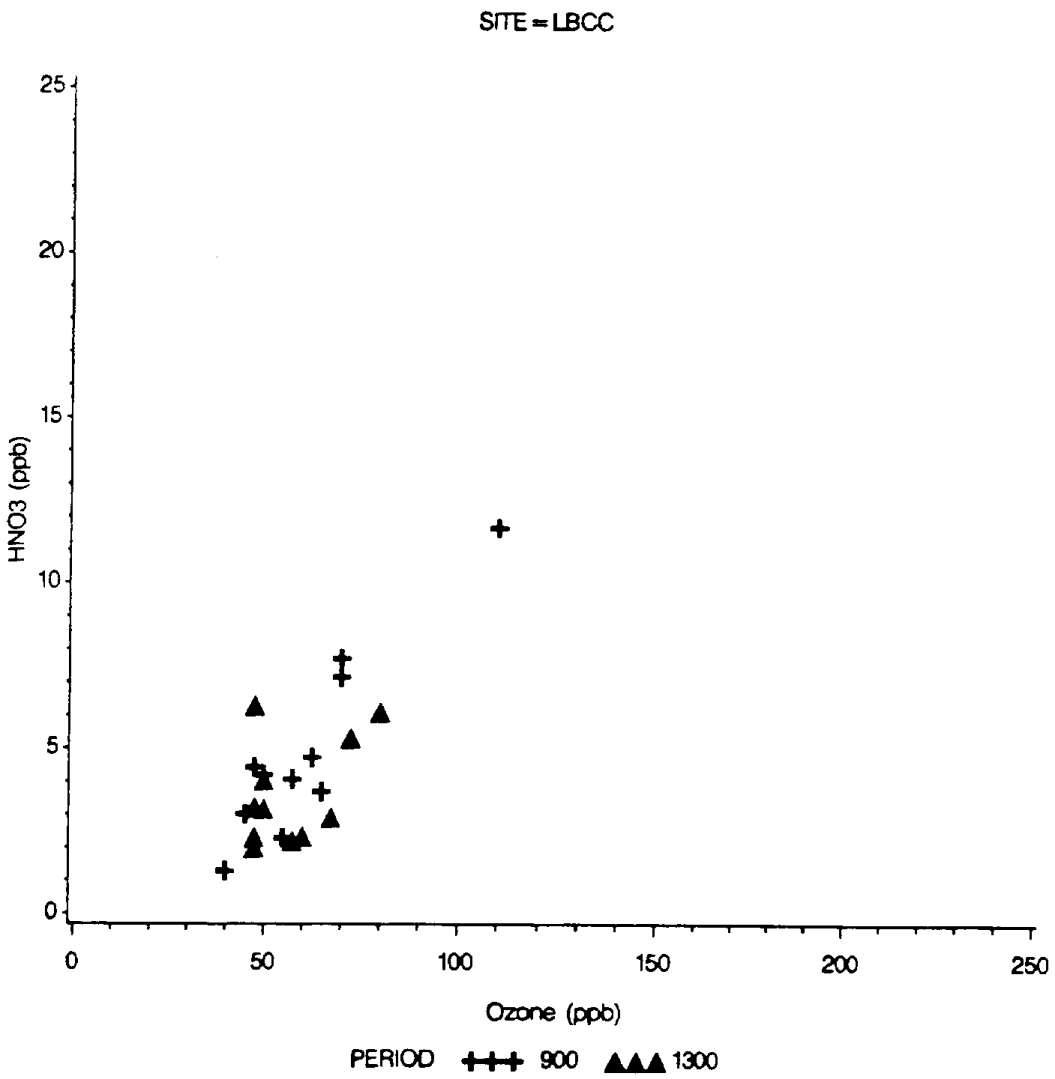


Figure B-8. HNO_3 by a SCAQS sampler vs. average O_3 for the 9 a.m. - 1 p.m. and 1 p.m. - 5 p.m. periods during 11 days in June 19 - September 3, 1987 in Long Beach, CA. The data correspond to SCAQS/LBCC in Table 2 of the text.

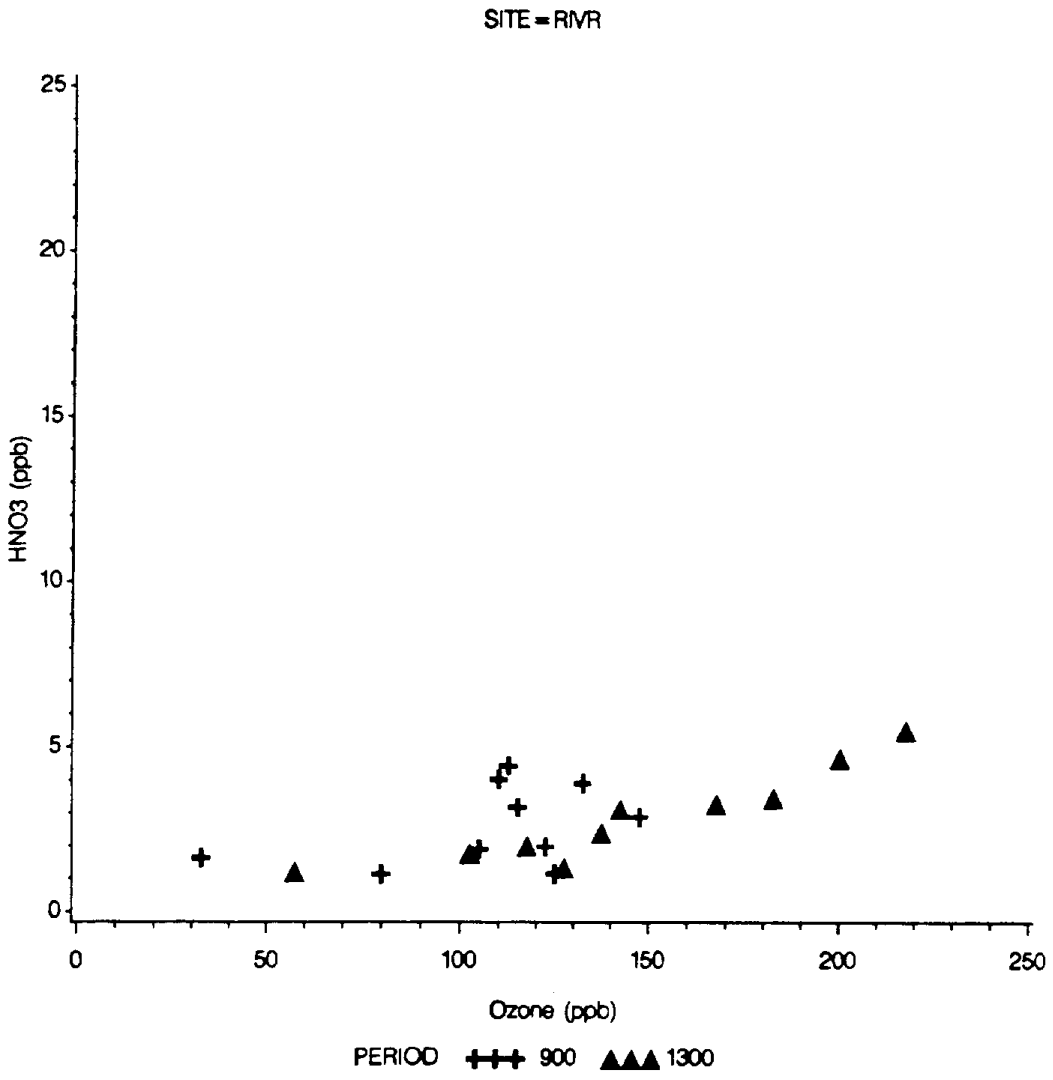


Figure B-9. HNO_3 by a SCAQS sampler vs. average O_3 for the 9 a.m. - 1 p.m. and 1 p.m. - 5 p.m. periods during 11 days in June 19 - September 3, 1987 in Riverside, CA. The data correspond to SCAQS/RIVR in Table 2 of the text.

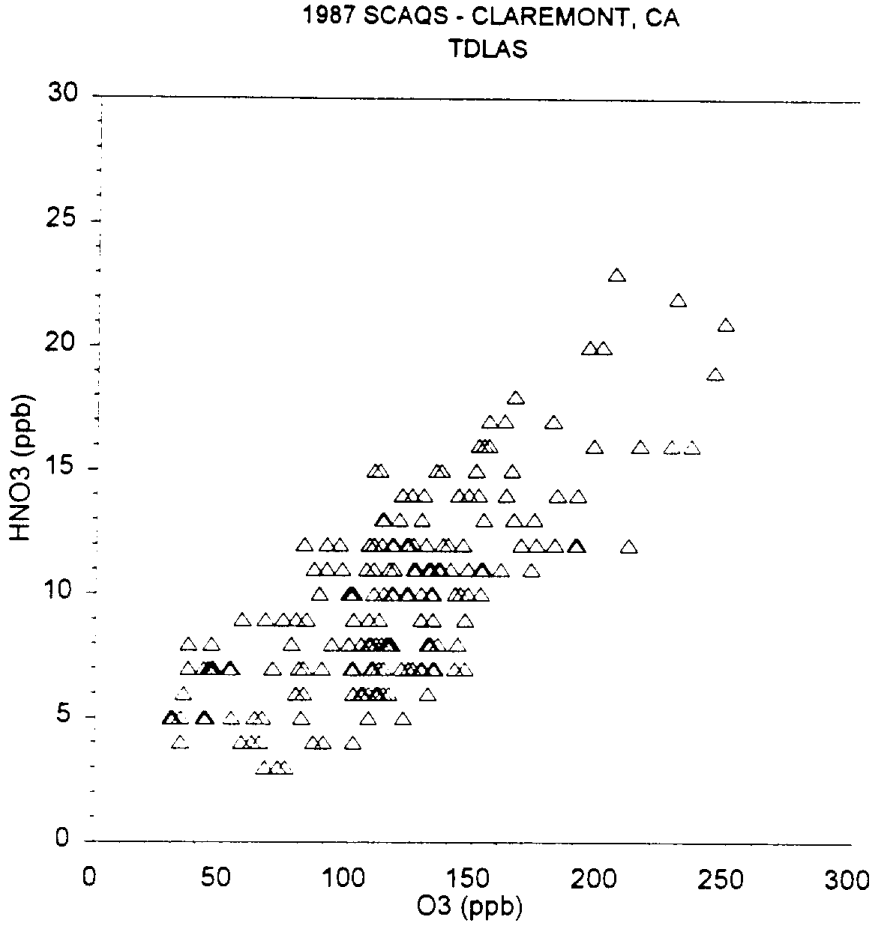
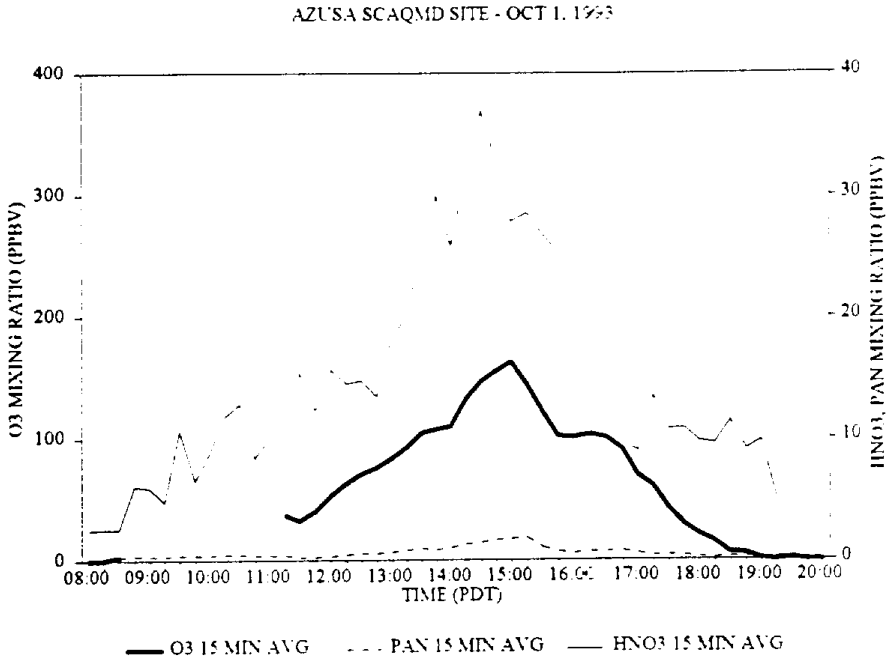


Figure B-10. Hourly average HNO_3 by TDLAS vs. hourly average O_3 for the 12 noon - 5 p.m. period, June 16- July 24, 1987 in Claremont, CA. The data correspond to TDLAS/CLAR in Table 2 of the text.

APPENDIX C

This appendix presents the daytime concentration profiles of O_3, PAN, and TDLAS HNO_3 for the October 1 - October 30, 1993 period in Azusa, CA (plotted from data recorded by Unisearch Associates, Inc.).



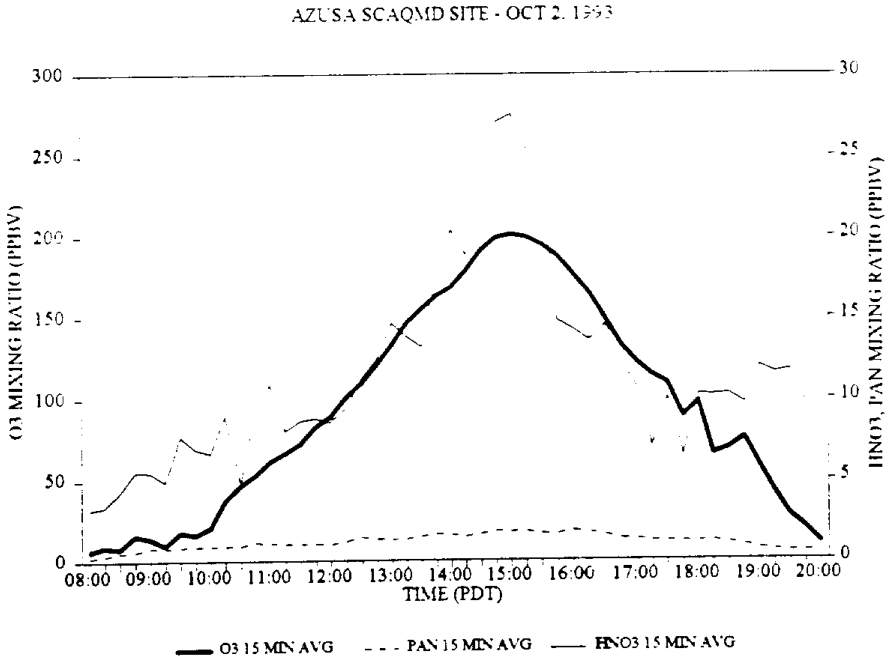
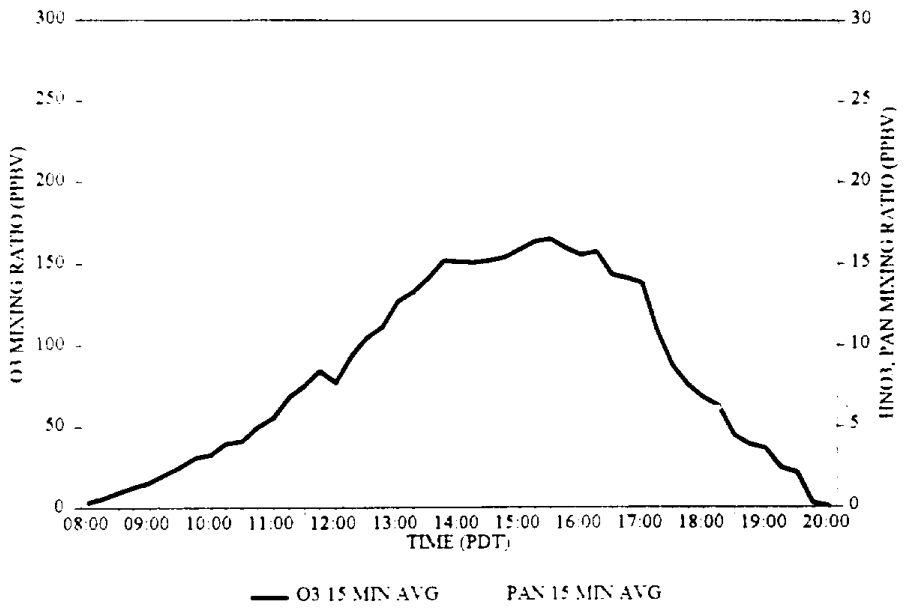


Figure C-1
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 1 and 2, 1993 in Azusa, CA.



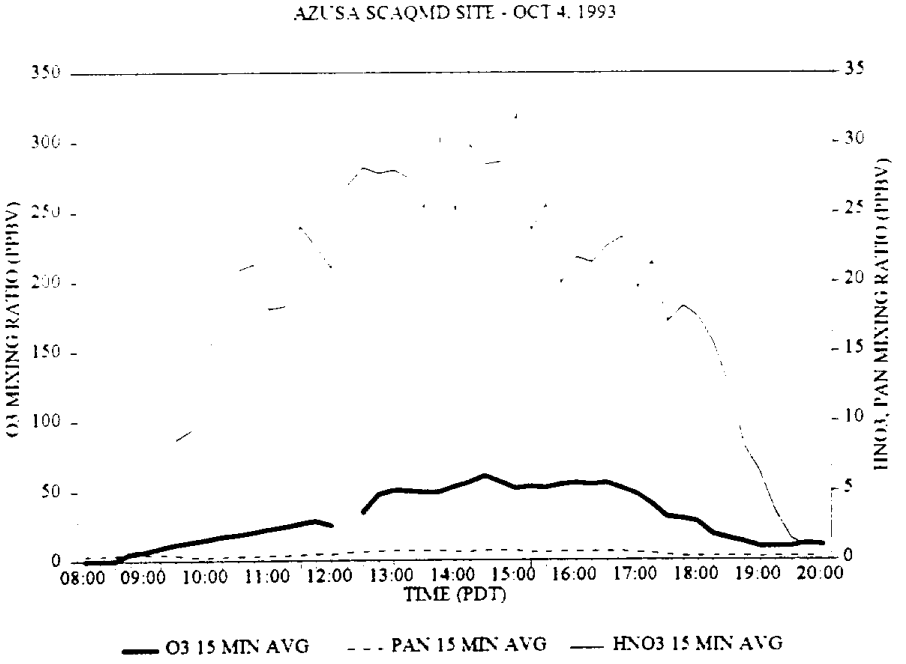
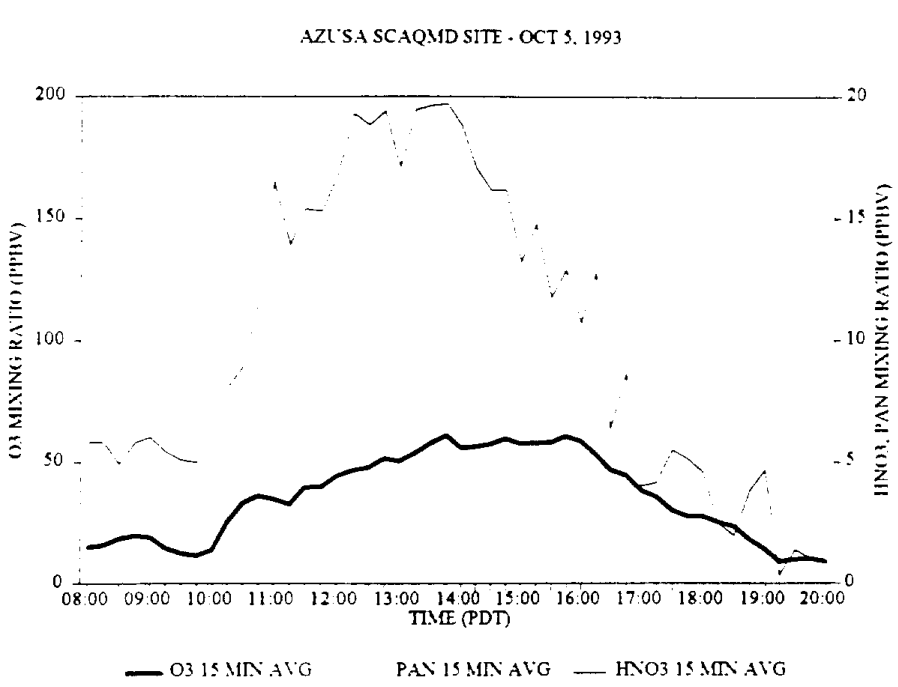


Figure C-2
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 3 and 4, 1993 in Azusa, CA.



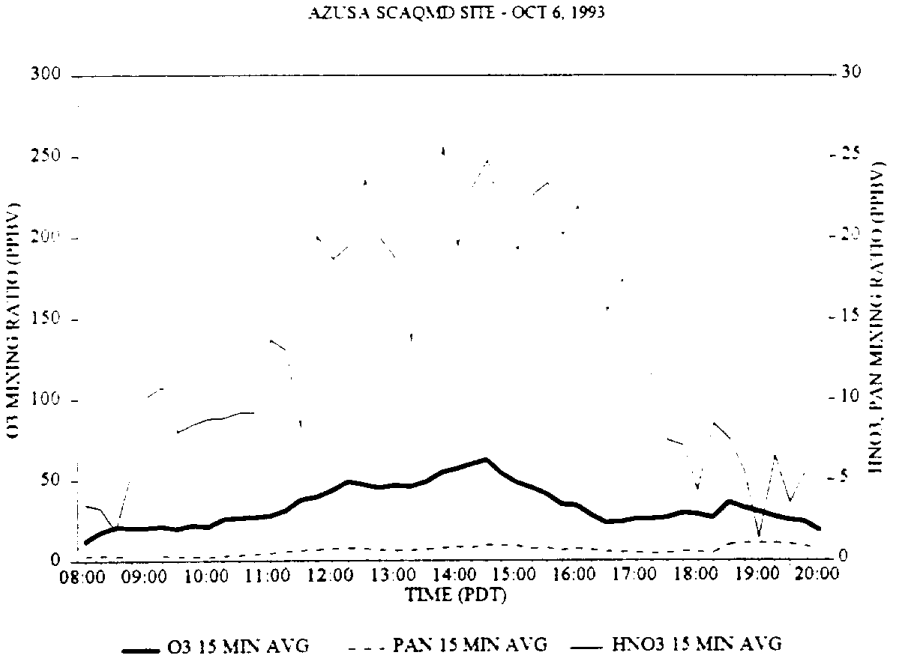
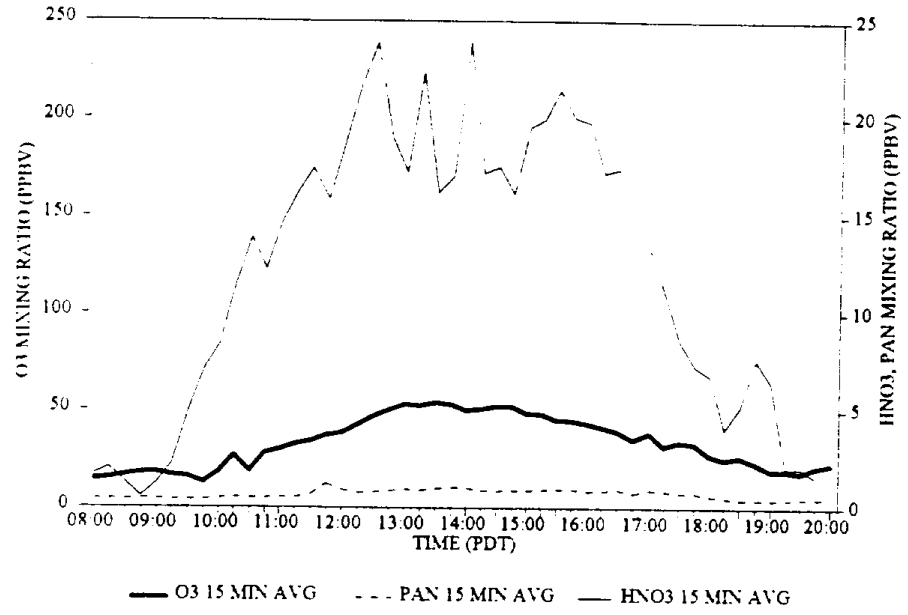


Figure C-3
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 5 and 6, 1993 in Azusa, CA.



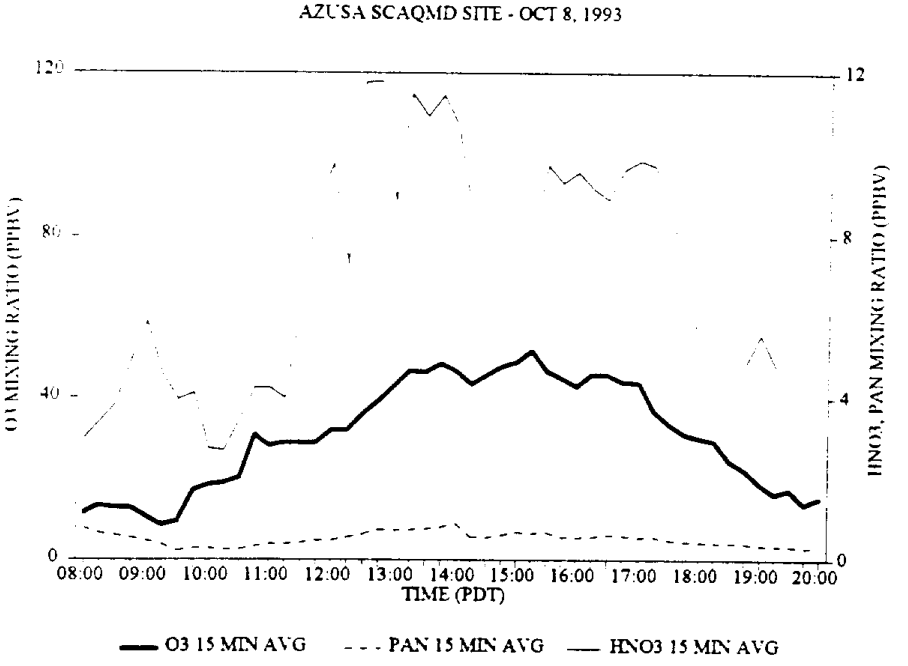
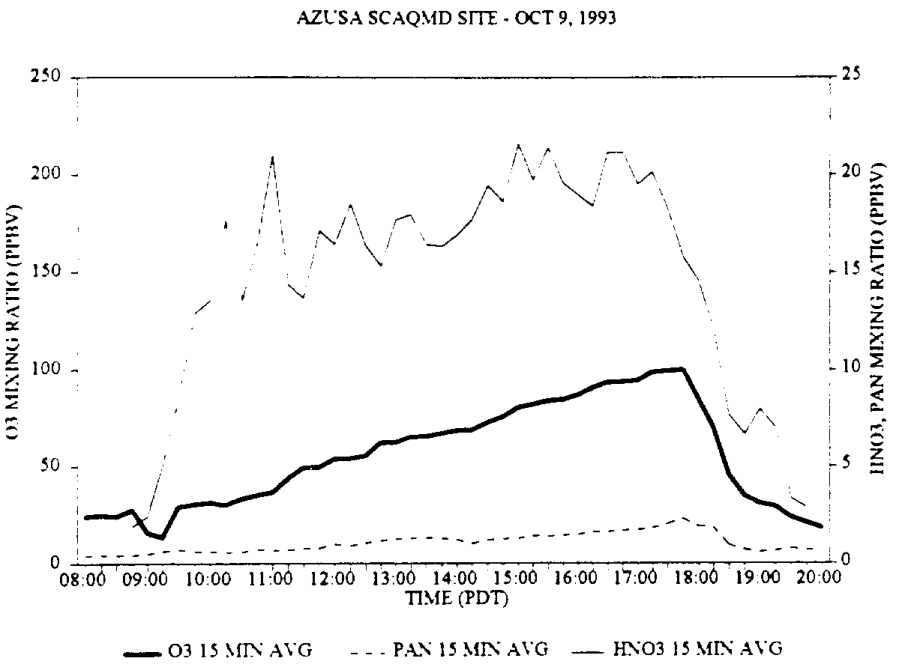


Figure C-4
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 7 and 8, 1993 in Azusa, CA.



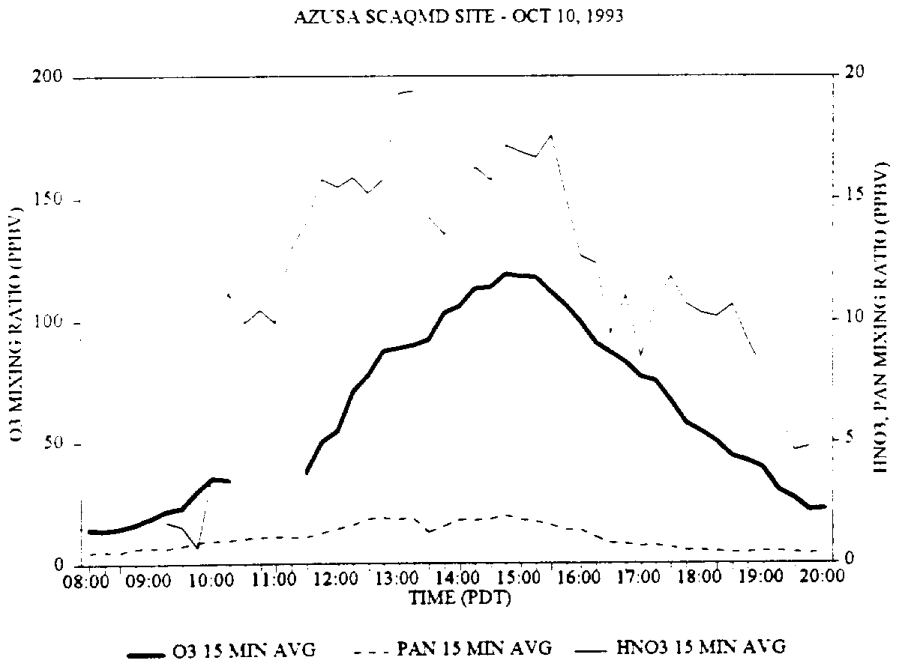
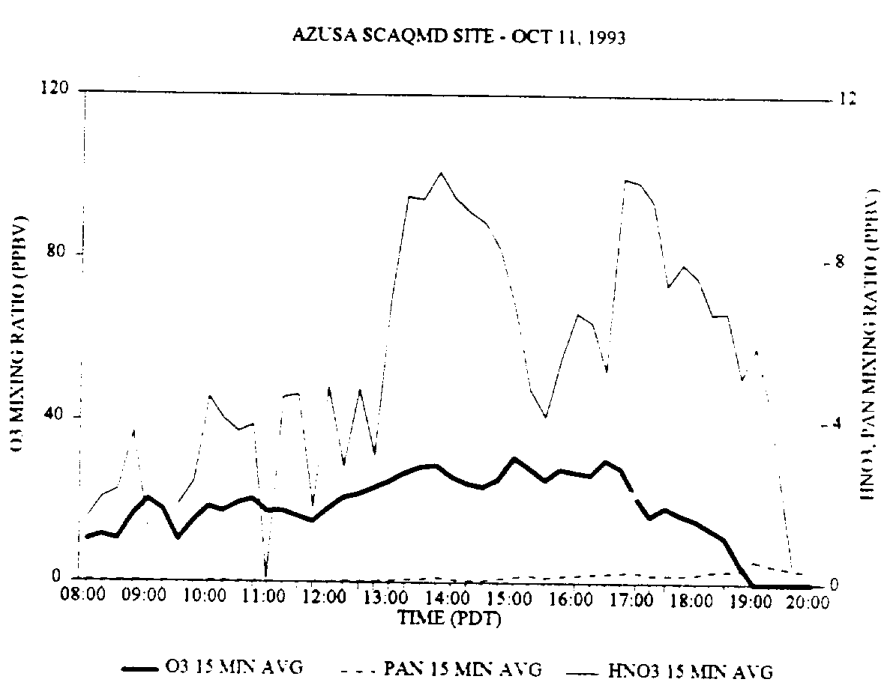


Figure C-5
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 9 and 10, 1993 in Azusa, CA.



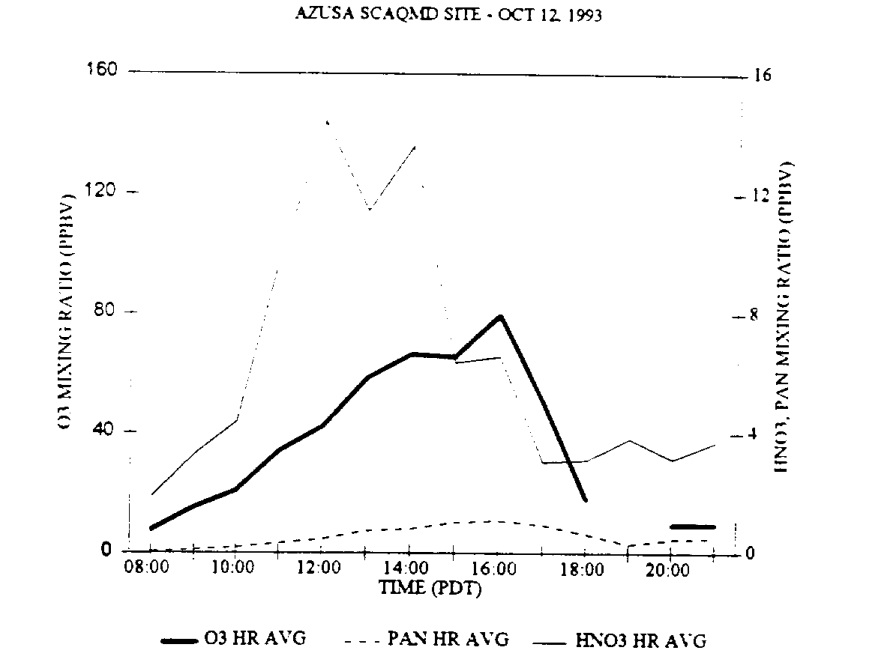


Figure C-6
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 11 and 12, 1993 in Azusa, CA.

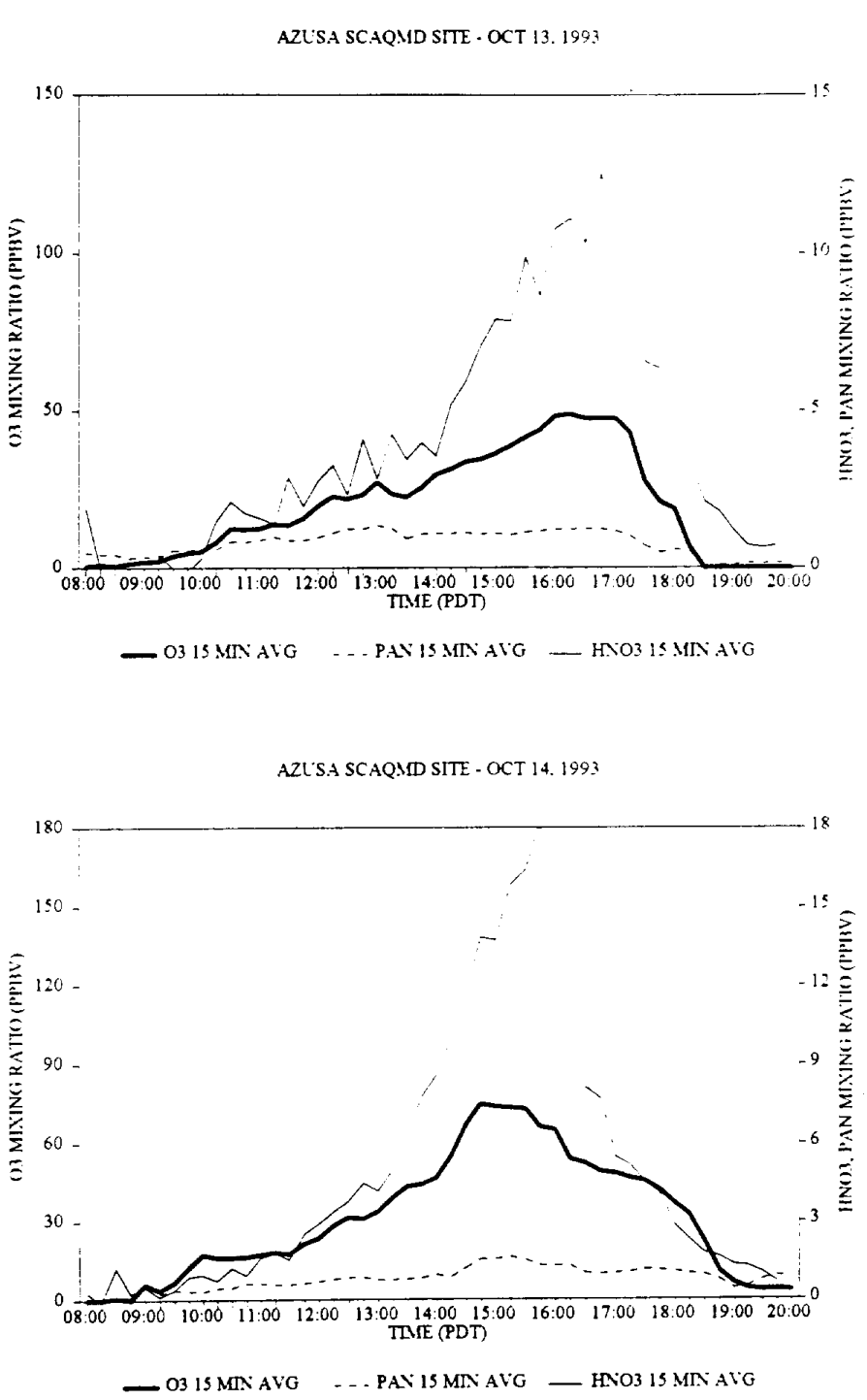
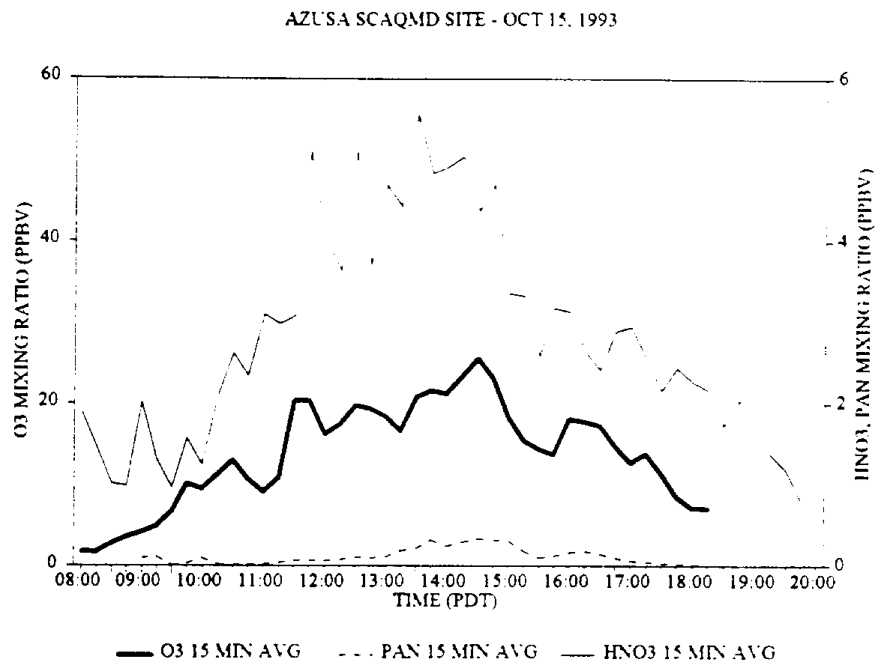


Figure C-7
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 13 and 14, 1993 in Azusa, CA.



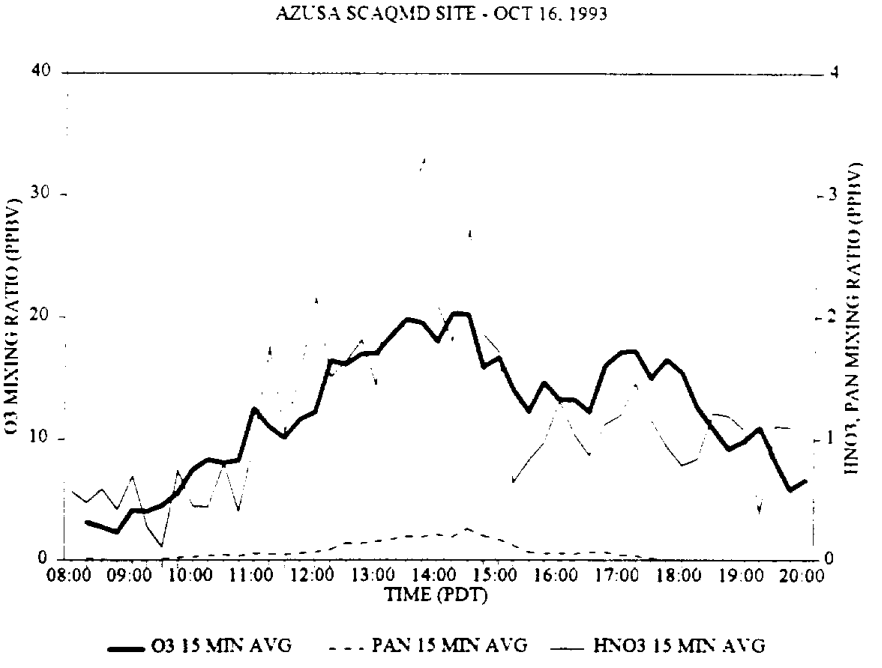
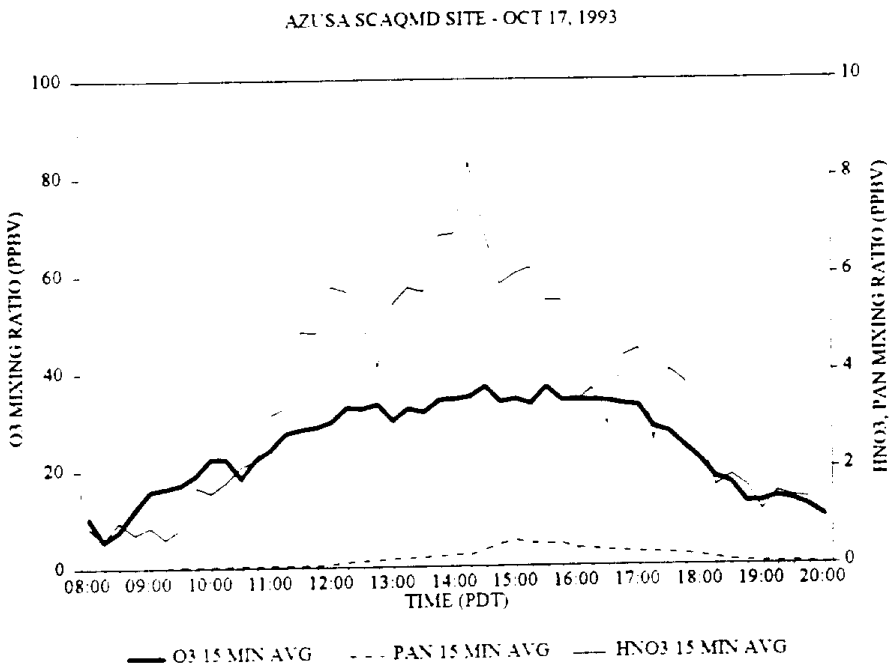


Figure C-8
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 15 and 16, 1993 in Azusa, CA.



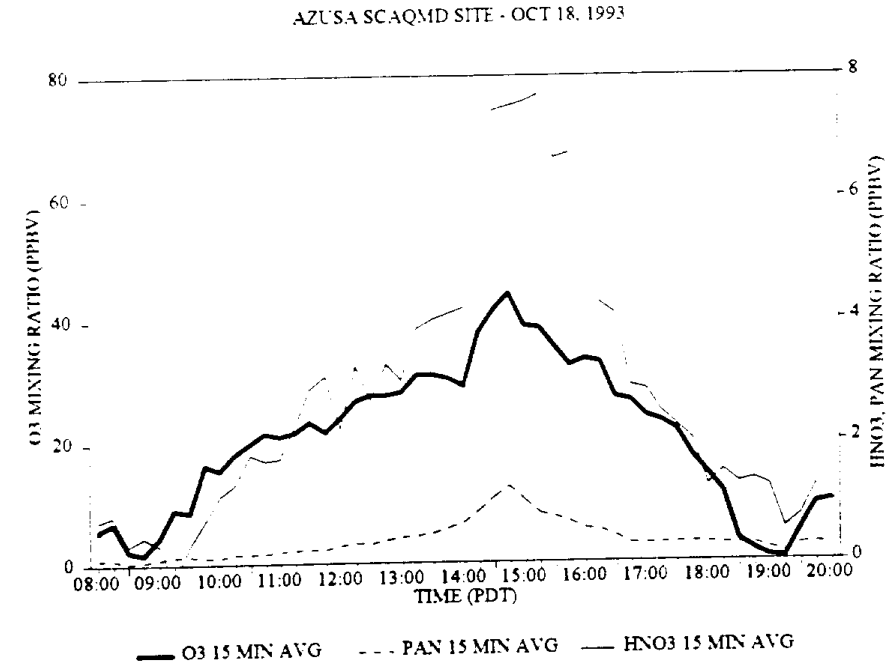
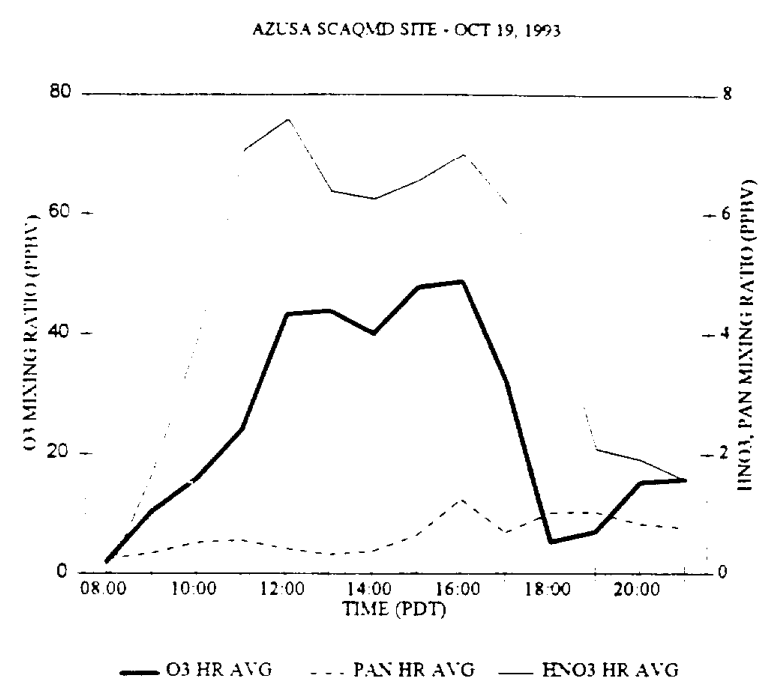


Figure C-9
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 17 and 18, 1993 in Azusa, CA.



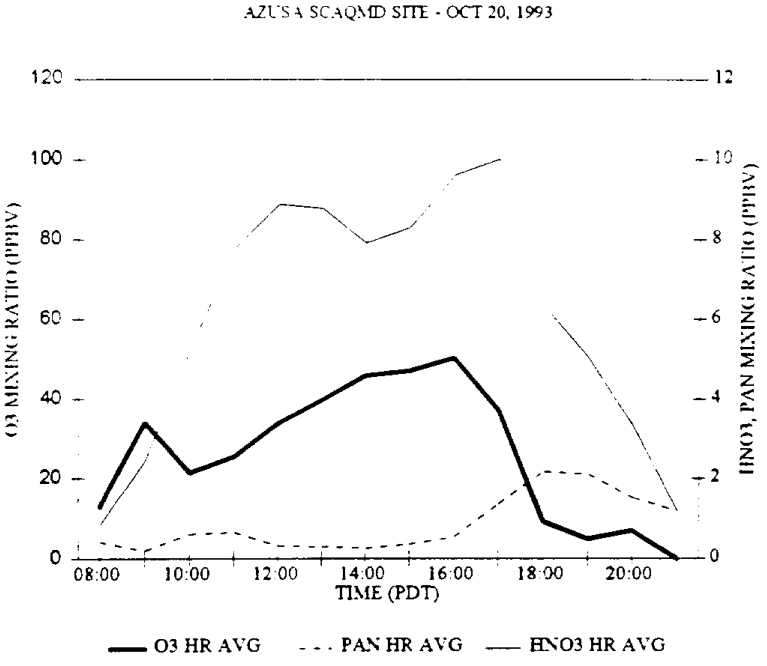
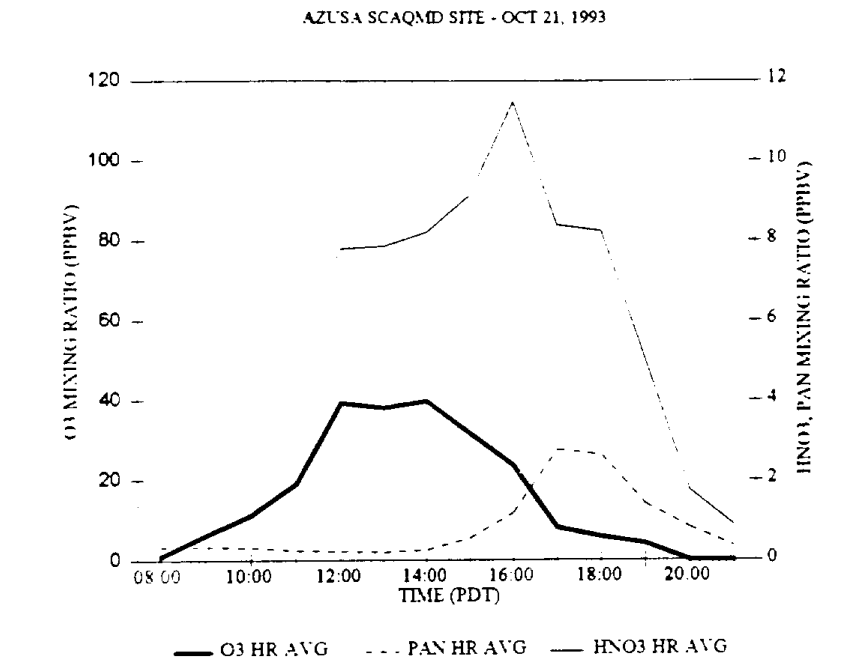


Figure C-10
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 19 and 20, 1993 in Azusa, CA.



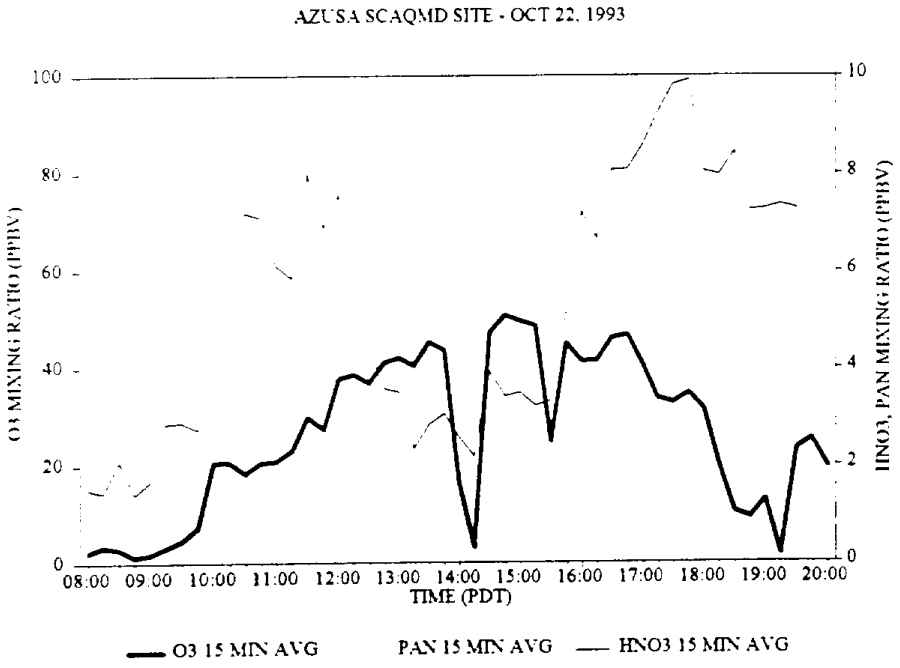
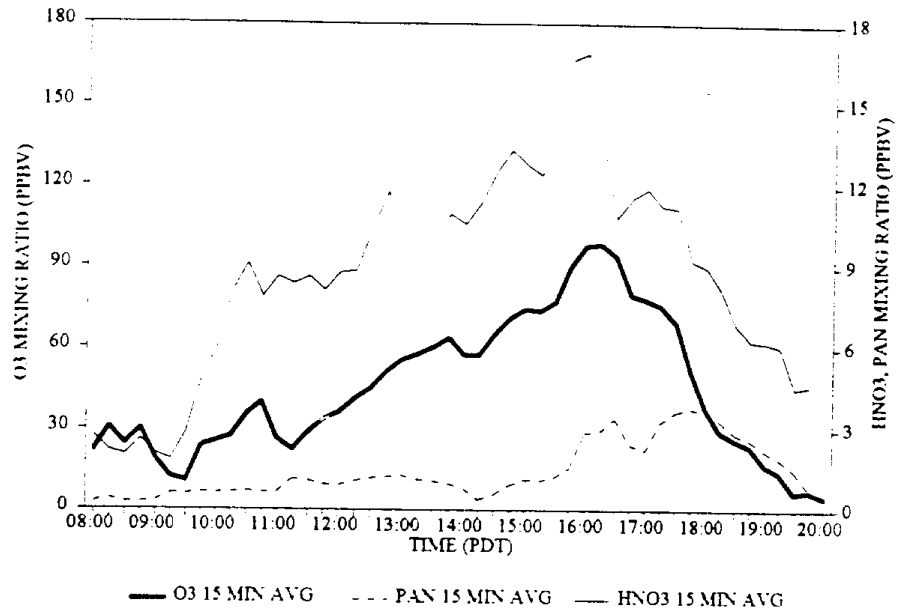


Figure C-11
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 21 and 22, 1993 in Azusa, CA.



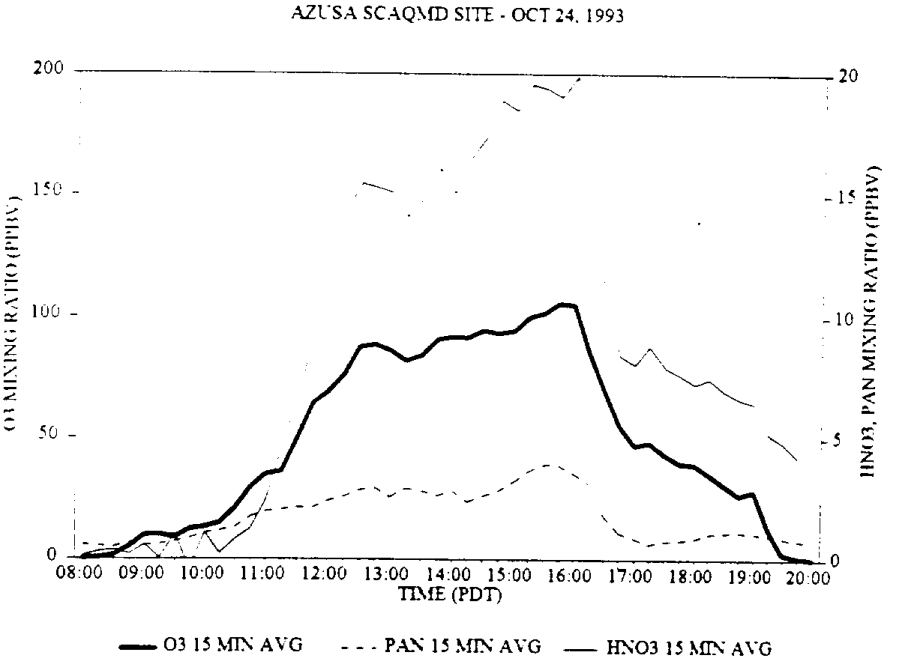
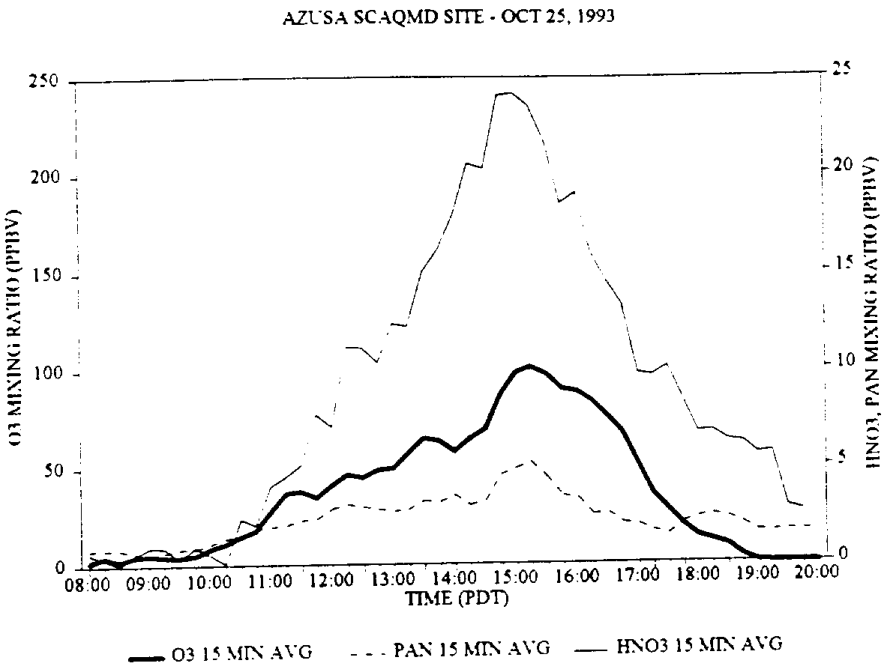


Figure C-12
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 23 and 24, 1993 in Azusa, CA.



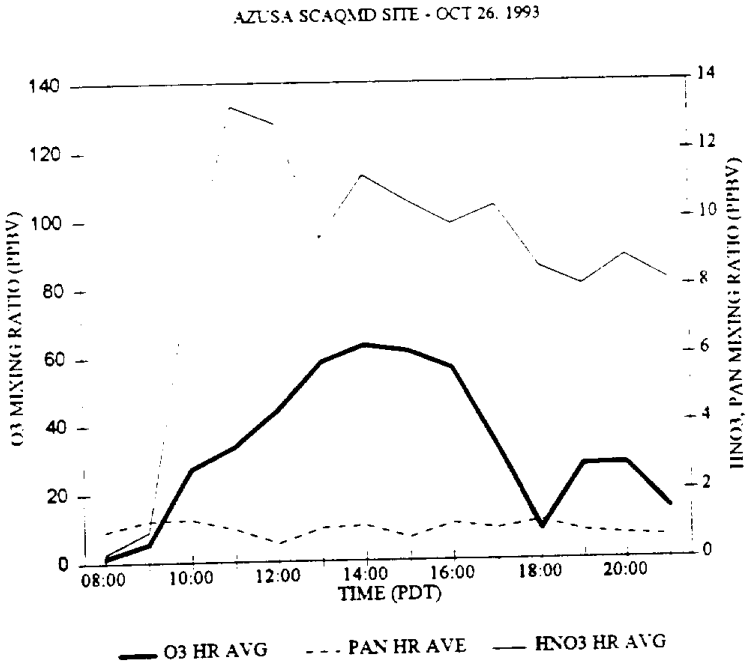
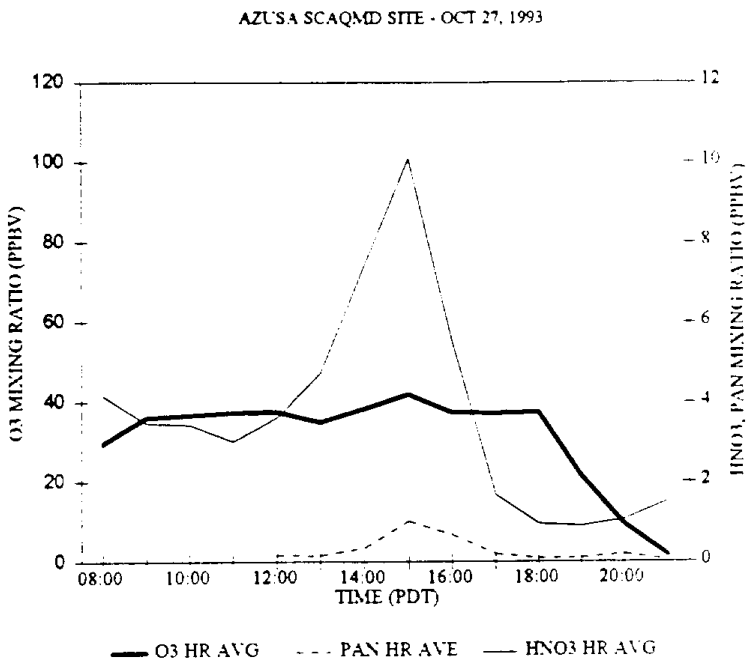


Figure C-13
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 25 and 26, 1993 in Azusa, CA.



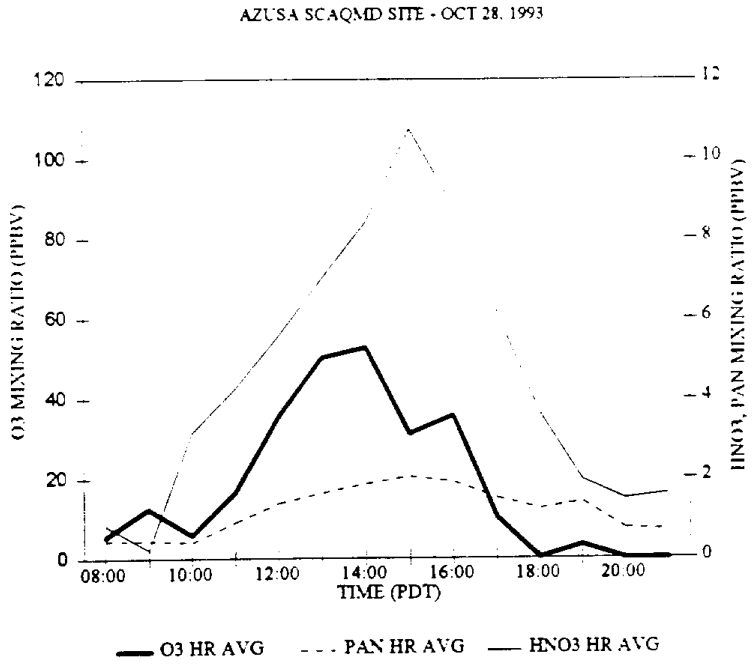
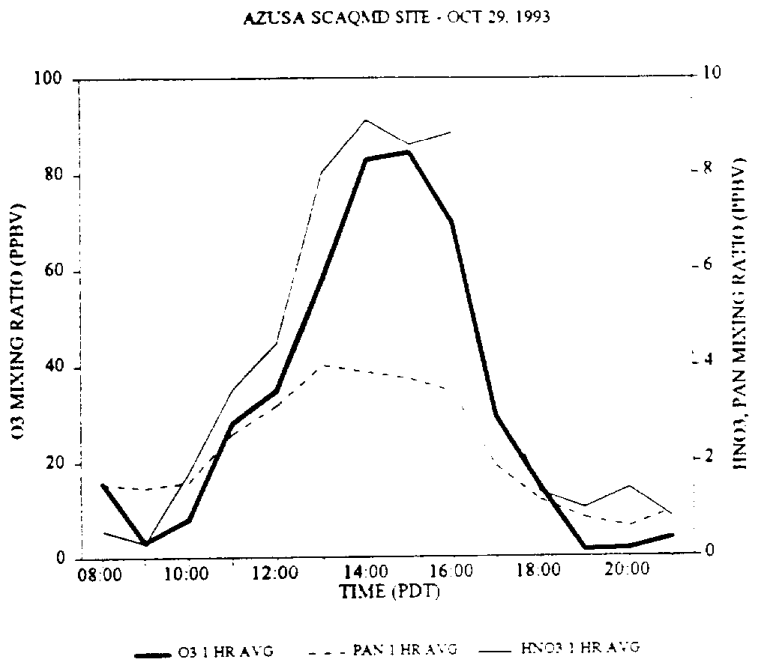


Figure C-14
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 27 and 28, 1993 in Azusa, CA.



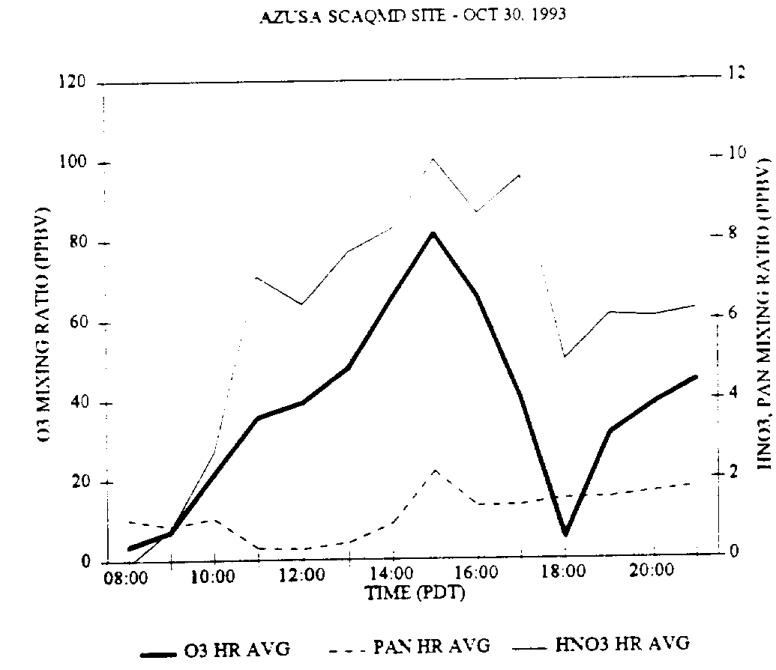


Figure C-15
Time-concentration profiles of nitric acid, ozone, and peroxyacetyl nitrate on October 29 and 30, 1993 in Azusa, CA.