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THE SOUTHERN CALIFORNIA AIR QUALITY STUDY: TUNABLE DIODE LASER ABSORPTION SPECTROMETER MEASUREMENTS OF HNO_3 AT THE CLAREMONT "A" SITE

Submitted by

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Final Report to the

STATE OF CALIFORNIA
AIR RESOURCES BOARD

in

completion of research under
agreement number
A732-041

DISCLAIMER

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ACKNOWLEDGEMENTS

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We are thankful for the assistance of Ms. J. Green and Mr. J. Pisano during the field operation and with the subsequent data analysis.

EXECUTIVE SUMMARY

During June-July, 1987 the first part of the Southern California Air Quality Study was carried out in the greater Los Angeles area. Measurements were made to address the following issues: ozone (O_3), nitrogen dioxide (NO_2) and the roles of nitrogen oxides (NO_X), PM-10, fine particles, visibility, toxic air contaminants, and atmospheric acidity. Claremont college was chosen as one of the sites for in depth study of these issues.

The tunable diode laser absorption spectrometer (TDLAS) system was employed for the real time measurements of gas-phase HNO_3. TDLAS offers a number of advantages for making these measurements. Its high spectral resolution provides an unequivocal identification of the measured gaseous species free from interferences of other atmospheric constituents. This specificity makes it an ideal instrument to use as a standard against which other, less definitive methods, can be compared. In addition it has high sensitivity and rapid response time so that it can provide real time measurements with detection limits much better than those required for ambient concentrations of the majority of trace constituents under most atmospheric conditions.

The measurement were made with the TAMS-150 which had detection limits of better than 0.1 parts per billion (ppbv) for 1 minute averaging times. Measurements were made on 32 days during the period June 15th through July 24th 1986. The results have also been reduced to 1 hour average values for comparison with measurements made by other methods. Data coverage was better than 90%.

The diurnal behaviour of HNO_3 was quite regular. The maximum concentrations occurred between 12:00 and 18:00 each day. The daily maximum varied considerably during the study from a low of 5 ppbv on July 21th to a high of 24 ppbv on June 25. On average the daytime maxima were of the order of 10 ppbv. Nighttime minima occurred between 22:00 and 06:00 and were generally in the range 0.5 to 1 ppbv.

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1. INTRODUCTION

During June-July, 1987 the first part of the Southern California Air Quality Study was carried out in the greater Los Angeles area. Measurements were made to address the following issues: ozone (O_3), nitrogen dioxide (NO_2) and the roles of nitrogen oxides (NO_X), PM-10, fine particles, visibility, toxic air contaminants, and atmospheric acidity. Claremont college was chosen as one of the sites for in depth study of these issues.

The information obtained during SCAQS is expected to provide a better understanding of the relationships among the sources, receptors, and effects of the pollutants in question. The measurements at the intensive sites such as Claremont should be adequate for the development and testing of descriptive and prognostic models. This in turn will assist the development and evaluation of control strategies designed to ameliorate southern California's air quality.

Nitric acid is a major final product for "odd nitrogen" in the atmosphere and its measurement is important in evaluating nitrogen photochemistry. It is also a major component in acid deposition. It is particularly important in the South Coast Air Basin where the ratios of NO_X to SO_X emissions are higher than those in central and eastern U.S.A. In addition, the relatively dry climate in the Basin favors the formation of HNO_3 which occurs readily in the gas phase whereas much of the SO_2 oxidation in other regions is believed to occur in cloud droplets.

Tunable diode laser absorption spectroscopy (TDLAS) offers a number of advantages for making these measurements. Its high spectral resolution provides an unequivocal identification of the measured gaseous species free from interferences of other atmospheric constituents. This specificity makes it an ideal instrument to use as a standard against which other, less definitive methods, can be compared. In addition, its high sensitivity and rapid response provides real time measurements with detection limits much better than those required for the ambient concentrations of most trace constituents under most atmospheric conditions.

Unisearch Associates Inc. used the TAMS-150, its new, high sensitivity, tunable diode laser absorption spectrometer (TDLAS) designed for tropospheric air monitoring, to make real

time measurements of HNO_3. The detection limits of the TAMS-150 system (0.1 ppbv) were more than adequate for following the diurnal behaviour during the field study.

2. EXPERIMENTAL

2.1 Principle of the TDLAS System

The TDLAS method takes advantage of the high monochromaticity and rapid tunability of Pb salt diode lasers to measure absorptions arising from single rotational-vibrational lines in the mid-infrared spectrum of a molecule. In order to facilitate the measurement of very low optical densities ($<10^{-5}$) at line center and to reduce the chances of overlap between adjacent absorption lines, reduced pressures (~25 Torr) are used to minimize pressure broadening of the rotational lines. The atmospheric sample is pumped rapidly at the reduced pressure through a White cell which also provides the long optical path lengths (153 m) required to achieve the desired detection limits.

The technique of measuring NO, NO_2 and HNO_3 by TDLAS has been described in detail by Hastie et al. (Environmental Science and Technology 17, 352 (1984)) and a full description of the TAMS-150 field instrument may be found in the Unisearch Final Report to the State of California Air Resources Board (contract number A5-189-32, September 1987) and in a paper by Mackay et al. (Atmos. Environ. 22, xxx (1988) in press). A brief description of the system is provided below.

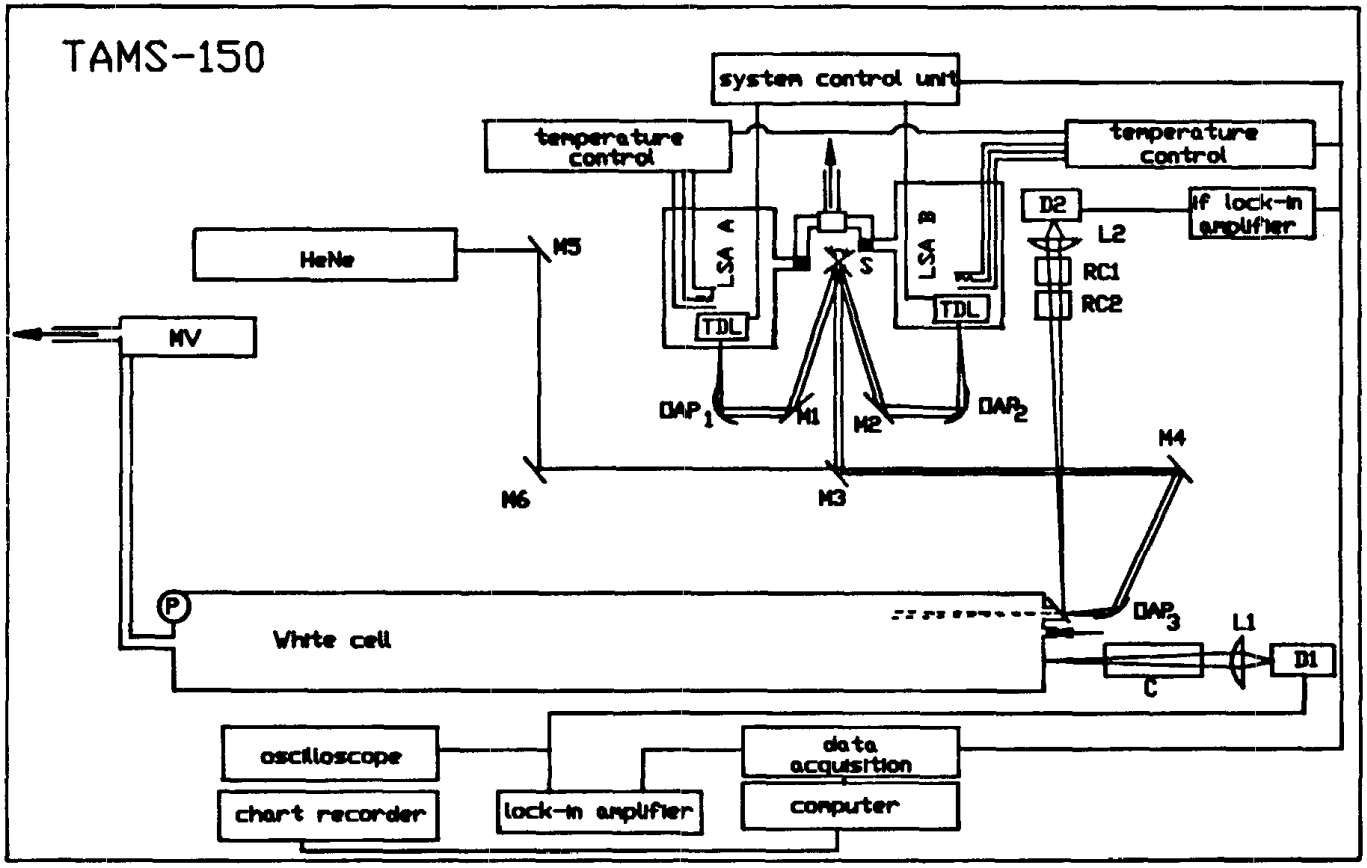
A schematic of the optical system and the electronic sub-assemblies is shown in figure 1. Two diode lasers, characterized for HNO_3 and H_2O_2 respectively, are housed in laser source assemblies LSA-A and LSA-B which maintain the temperature of the lasers in the 20 to 60°K range. The frequency of the emitted radiation from each laser is a function of its composition, the temperature and the current passing through the diode. The lasers operate in cw mode and the current may be modulated at kHz frequencies so that phase sensitive harmonic detection techniques may be employed (see for example Hastie et al, Environ. Sci. and Technol., 17, 352 (1984)).

The laser radiation from each head is collected and focussed by an f/2 off-axis parabolic mirror, OAP_1 or OAP_2, which produces a 15 mm OD parallel beam of light. Plane fold mirrors, M1 and M2, maneuver the beams onto a flip mirror, S, which is switched every three seconds to permit the beam from each diode to enter the White cell in turn. A second off axis-parabolic mirror OAP_3 focuses the beam into the White cell.

FIGURE 1

SCHEMATIC OF THE OPTICAL SYSTEM AND A BLOCK DIAGRAM OF THE CONTROL ELECTRONICS OF THE TAMS-150

Symbol	Description
MV	Pressure control valve
OAP1/2	f/2 off-axis parabolic mirrors
OAP3	Off-axis parabolic mirror with a 32 cm focal length
M1-2	Beam directing mirrors
LSA A/B	Laser source assembly
D1/2	Infrared detectors
L1/2	BaF_2 lenses
S	Flip mirror
RC1/2	Reference cells for line locking
HENE	HeNe alignment laser
TDL	Diode laser


TAMS-150
system control unit
temperature control
temperature control
HeNe
M5
MV
LSA A
LSA B
S
TDL
TDL
D2
if lock-in amplifier
L2
RC1
RC2
DAP1
M1
M2
DAP2
M4
M6
M3
P
White cell
DAP3
L1
D1
C
oscilloscope
chart recorder
lock-in amplifier
data acquisition
computer

The White cell is a Teflon lined 1.75 m long pyrex tube with an inside diameter of 15.2 cm. Sampled air enters through a 6 mm OD Teflon tube passing through one end plate and terminating just above, and in front of, the in-focus, White cell mirror. The gas is exhausted through a 2.5 cm OD tube in the aluminum plate at the opposite end of the cell. The reflecting surfaces are gold, concave Zerodur mirrors overcoated with MgF_2 and a surface quality of V16. The base path length of the White cell is 150 cm. A corner cube reflector at the point where the beam would normally exit, reflects the laser radiation back through the cell, retracing its path, but translated vertically about 1 cm from the original beam (Horn and Pimentel, Appl. Opt. 10, 1892 (1972)). In this way the beam can make twice as many passes at the minimum allowable spacing between reflections on the in-focus mirror, i.e. before interference from overlap of adjacent beams becomes an important source of optical noise. With this design the incident beam makes 102 passes of the White cell for an overall path length of 153 m.

The entrance window on the White cell is positioned at an angle of about 45° with respect to the laser beam and splits the beam into two parts. The majority of the laser radiation passes through the window and into the White cell. About 5% of the beam is reflected through cells, RC1 and RC2, which contain high concentrations of the monitored species and is then focussed by lens L2 onto detector D2. The output of this detector is passed to a specially designed lock-in amplifier which detects the center of the absorption line due to the trace gas being monitored and sends this information to the computer for line-locking.

The beam exiting the White cell is focussed by a BaF_2 f/1.5 lens, L1, onto a liquid-nitrogen cooled, mercury cadmium telluride, infrared detector, D1. The output of this detector is fed into an oscilloscope for visual representation and to a lock-in amplifier and data acquisition/computer control system for analysis and storage

2.2 Sampling and Calibration Procedures

Sample air is drawn through a 6 mm OD. 0.75 mm wall, FEP type Teflon tube. Particles are removed from the air by a 2 micron pore size Teflon filter located at the tubing entrance. A Teflon needle valve maintains the flow into the White cell at ~16 standard litres per minute (SLM). The high flow rate minimizes the response time of the TAMS-150. The section of the inlet line up to and including the needle valve is thermostated at 28°C. The low pressure portion of the line from the needle valve to the spectrometer is at ambient temperatures.

The air traverses the inlet line in a few tenths of a second while the residence time in the White cell is about 4 seconds. The flow of air entering the White cell is monitored with a calibrated mass flowmeter during each calibration and is adjusted by the needle valve as necessary to maintain the high flow rate. The flowmeter is removed from the sampling line during ambient monitoring since a knowledge of the air flow into the White cell is not necessary during ambient measurements and we have previously noted that it removes a significant fraction of HNO_3 from the sampled air. A motorized valve, which is referenced to a MKS Baratron pressure gauge, controls the pressure in the White cell at 25 Torr.

The sensitivity of the TAMS-150 toward HNO_3 is determined by an optical procedure due to the long response time of the spectrometer toward HNO_3 (~5 minutes). This procedure involves the use of a high concentration short cell containing a known mixing ratio of HNO_3 which is interposed in the laser beam just in front of the infrared detector. The sensitivity of the instrument is determined from the ratio of the optical paths (short calibration cell to total path in the White cell). This permits rapid calibration of the HNO_3 sensitivity without contamination of the White cell. The TAMS-150 sampling integrity is checked periodically by adding a 'spike' to the sampled gas at the inlet and measuring the ratio of the measured to the expected signals. During this study the ratio was approximately 1.

The minimum detectable limit, MDL, defined at a signal-to-noise ratio of 1, is determined experimentally at the selected laser operating conditions and absorption feature. Scrubbed ambient air or clean air from a compressed gas cylinder is introduced at the sampling inlet. The mixing ratio calculated by the spectrometer gives an estimate of the background noise level. The MDL measured for HNO_3 is about 0.1 ppbv for a 1 minute sampling interval.

The HNO_3 permeation tube was calibrated by titration against standard NaOH solutions before, during and after the field study. The average permeation rate was 570 ± 30 ng.min^{-1}.

The following description of the sequence of events during an automatic ambient air monitoring experiment illustrates how laser control, as well as data analysis, are achieved.

Information for the operating parameters selected for the HNO_3 measurements are input to the computer. The software then operates the system automatically. It first obtains a background spectrum by sampling scrubbed ambient air or clean air from a compressed gas cylinder at the inlet until the White cell is free of HNO_3. The background spectrum is obtained and archived. Next, calibration gas is added to the short cell and, after a suitable stabilization period, a calibration-reference spectrum is obtained. The reference spectrum is also archived in its untreated form as are all subsequent spectra of ambient air. The back-

ground spectrum is subtracted (channel by channel) from the reference spectrum. This procedure removes most of the frequency dependent structure present in the background from the reference spectra. The effective mixing ratio of the calibration gas in the White cell is calculated from the ratio of the optical paths as discussed above.

Once the calibration-background procedure has been completed the software resets the solenoid valves to admit ambient air and, after an appropriate delay to achieve steady conditions, an ambient air spectrum is acquired. The background structure is subtracted and the result digitally smoothed. The smoothing algorithm employs least squares fitting of the best quadratic or cubic function to a running window of seventeen channels and replaces the data in the central channel of the group with the value of the function at that point. This algorithm is very effective in suppressing high frequency noise without distorting line shapes if the number of channels per line width (i.e. the scan range) is appropriately chosen. The ambient air spectrum is then compared to the calibration spectrum using a least squares fitting procedure thus obtaining the intensity of the absorption line in the ambient air spectrum as a fraction of the calibration line intensity.

Since the detection limit was always well below the ambient HNO_3 levels, background and calibration measurements were usually made only once daily. This was done either in the early morning, or late at night while the ambient HNO_3 was low.

3. AMBIENT AIR MEASUREMENTS OF HNO_3

3.1 Experimental Configuration

On June 7, 1987 the Unisearch mobile laboratory containing the TAMS-150 arrived at the SCAQS Claremont 'A' intensive site. The mobile laboratory was positioned towards the south end of the sampling platform adjacent to a large playing field.

The inlet system used in this study was constructed entirely of Teflon fittings and tubing. The sampling port was positioned on the far side of the platform (the side opposite the location of all the mobile laboratories) 1.7 m (5 ft) above the platform and 3 m (10 ft) above the ground. The inlet tube consisted of 8 m of 6 mm OD, 0.75 mm wall FEP Teflon tubing.

A 2 micron pore size Teflon filter was installed in the sampling line about one metre down stream of the inlet to remove particles from the gas stream. This filter was replaced daily between 06:00 and 09:00 and the inlet line upstream of the filter was taken apart and thoroughly cleaned of particle matter.

3.2 Measurement Procedure

The TAMS-150 obtained data points every minute. The raw data were stored on floppy diskettes for future analysis in the laboratory and the real time measurements were printed out at 1 minute intervals. Calibrations and backgrounds were performed at least once a day usually between 06:00 and 08:00. The sensitivity of the instrument toward HNO_3 never varied by more than 10% and the changes were random in nature.

The accuracy of the measurements is estimated to be $\pm$ 20%. The pH titration has an uncertainty assessed at 5% and the use of the optical calibration introduces a further uncertainty of 5%. Additional uncertainties of $\pm$ 2% are caused by temperature variations of the permeation device, and $\pm$ 5% from the measurement of the carrier gas flow. The HNO_3 carrier gas flow controller (Tylan, model FC260-20SCCM) was checked against a bubble flowmeter prior to the study and found to agree within 2.5%.

Data coverage was ~95% with down times associated with the calibration periods for the most part. On a few occasions computer malfunction (due to power failures) gave rise to extended periods in which no data was recorded.

4. RESULTS AND DISCUSSION

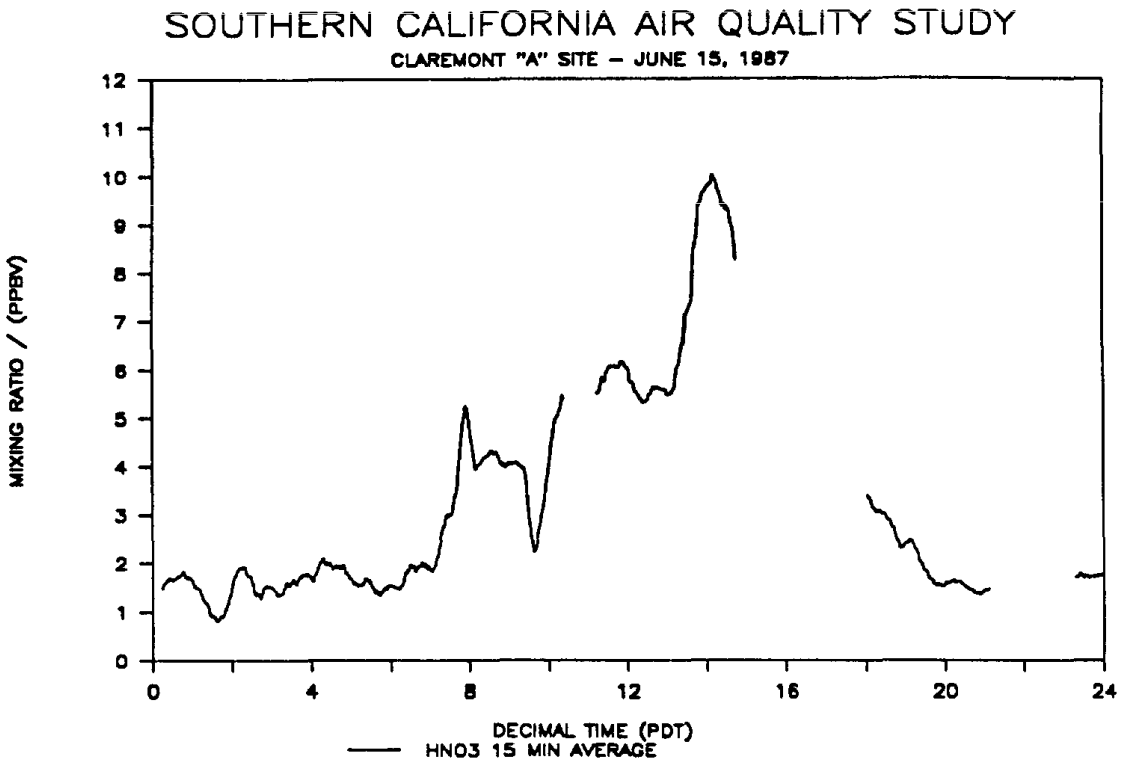
The measurement period was June 15th through July 24, 1987 during which HNO_3 measurements were made on 37 days. Three of these days were designated SCAQS intensive periods. Data points were obtained over 1 minute averaging periods. The results have been subsequently reduced to 1 hour average values. Data coverage was better than 95% on 32 of the days.

The results are presented in graphical form in Appendix A which includes representations of the signal variations for the 15 minute running average and 1 hour averages of the data.

The diurnal behaviour of HNO_3 was quite regular. The maximum concentrations occurred between 12:00 and 16:00 each day. The HNO_3 daily maximum showed considerable variation during the measurement period ranging from a high of 24 ppbv on June 25th to a low of 5 ppbv on July 21th. Generally the maximum was between 10 and 15 ppbv.

APPENDIX A

Graphical representations of the 15 minute running average point measurements and 1 Hour average HNO_3 mixing ratios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CLAREMONT "A" SITE – JUNE 15, 1987
MIXING RATIO / (PPBV)
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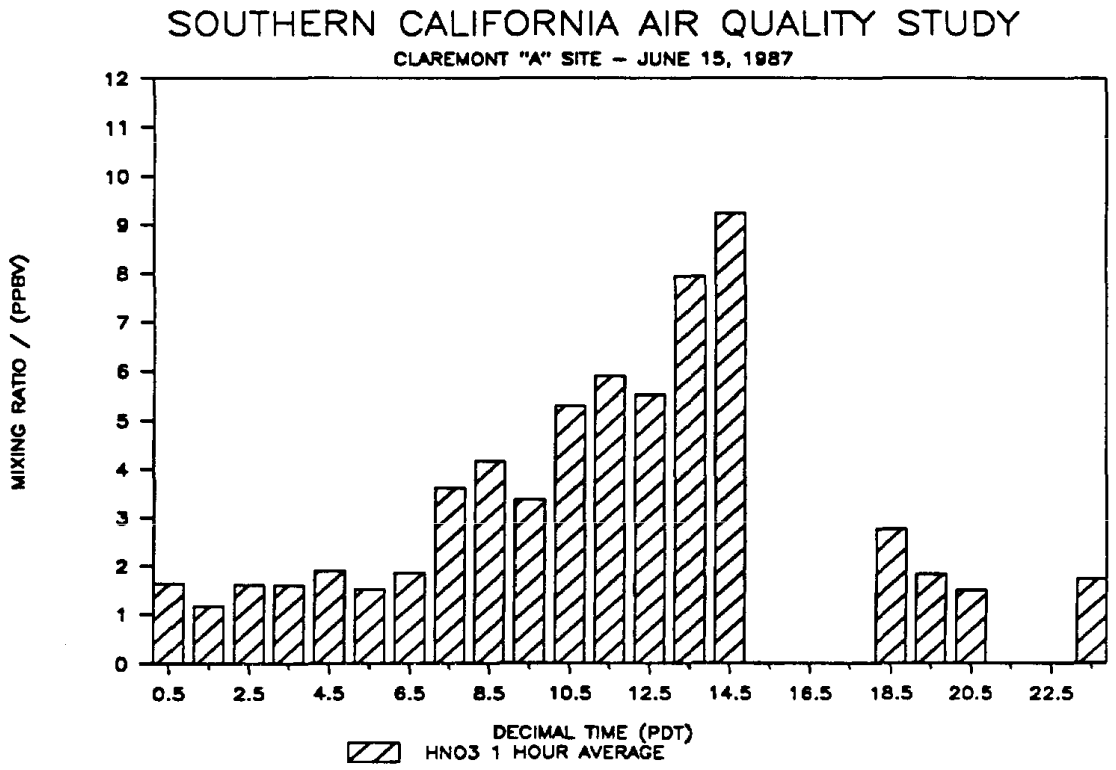
DECIMAL TIME (PDT)
HNO3 15 MIN AVERAGE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CLAREMONT "A" SITE – JUNE 15, 1987
MIXING RATIO / (PPBV)
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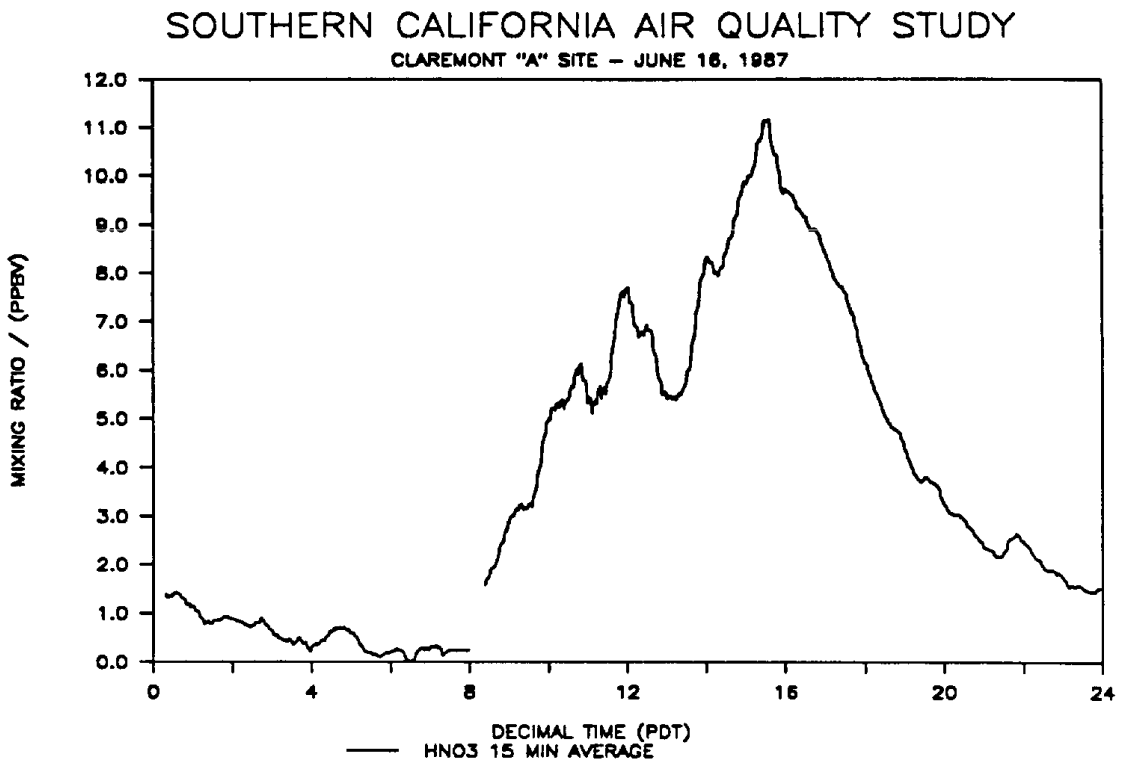
DECIMAL TIME (PDT)
HNO3 1 HOUR AVERAGE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MIXING RATIO / (PPBV)
12.0
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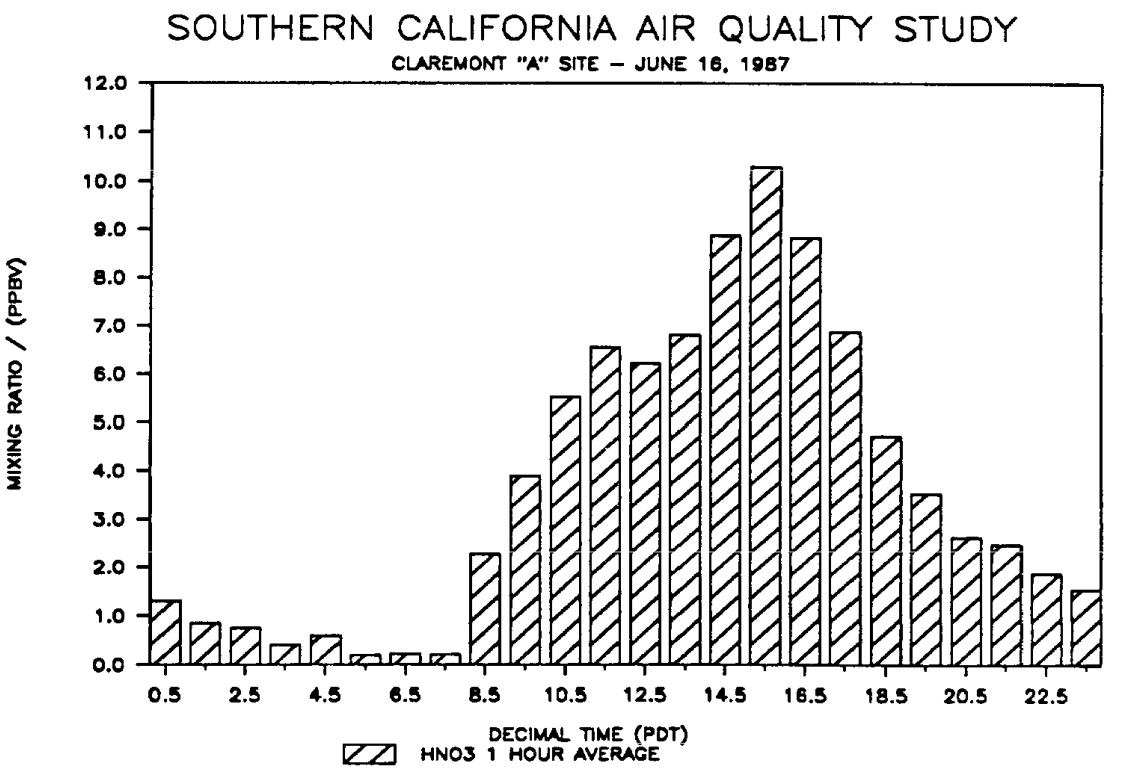
DECIMAL TIME (PDT)
HNO3 15 MIN AVERAGE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CLAREMONT "A" SITE – JUNE 16, 1987
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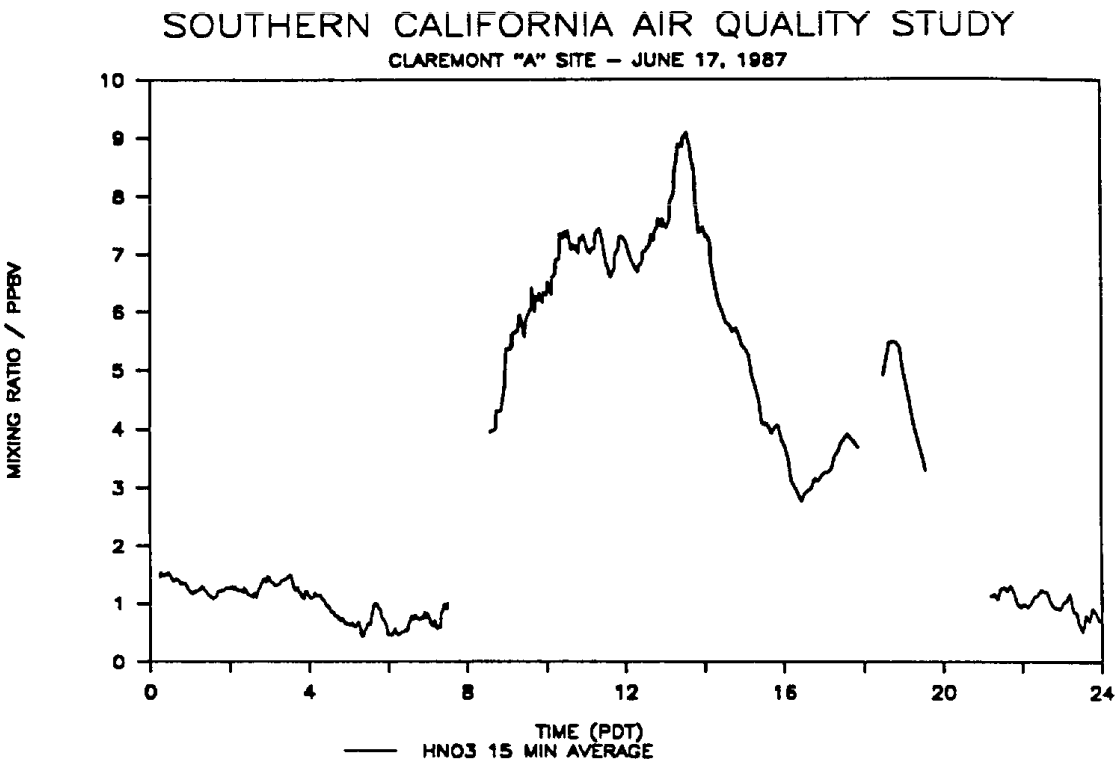
DECIMAL TIME (PDT)
HNO3 1 HOUR AVERAGE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CLAREMONT "A" SITE – JUNE 17, 1987
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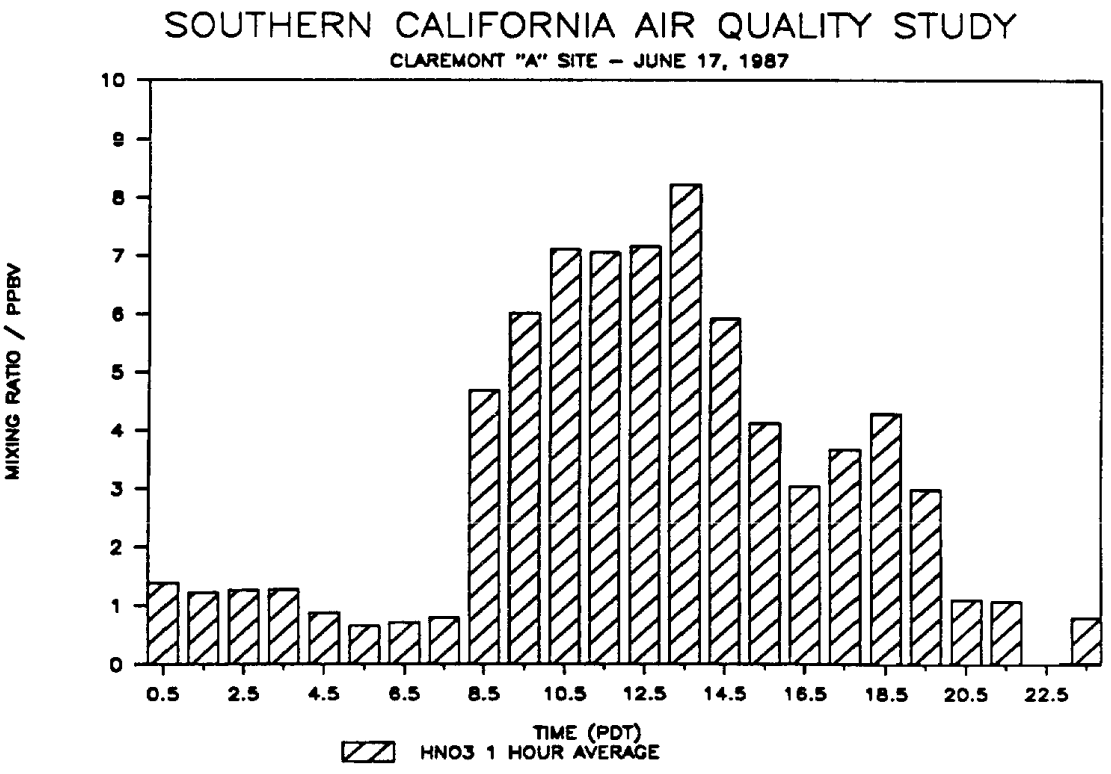
TIME (PDT)
HNO3 15 MIN AVERAGE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CLAREMONT "A" SITE – JUNE 17, 1987
MIXING RATIO / PPBV
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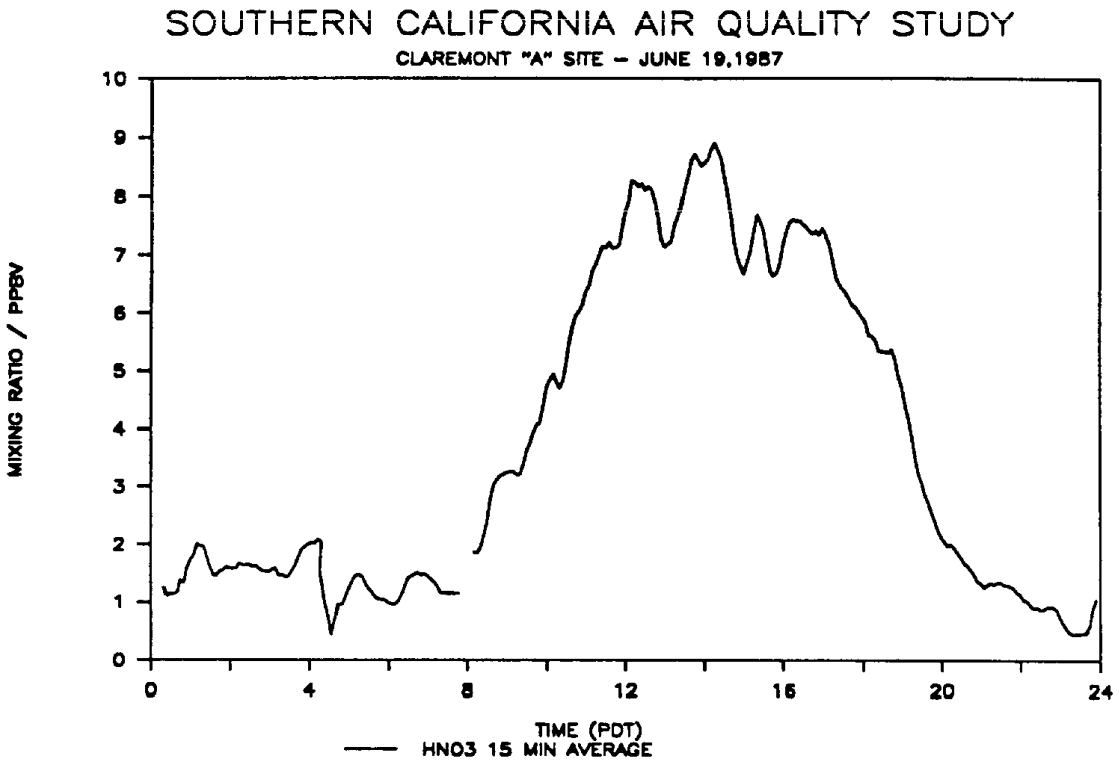
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 19,1987
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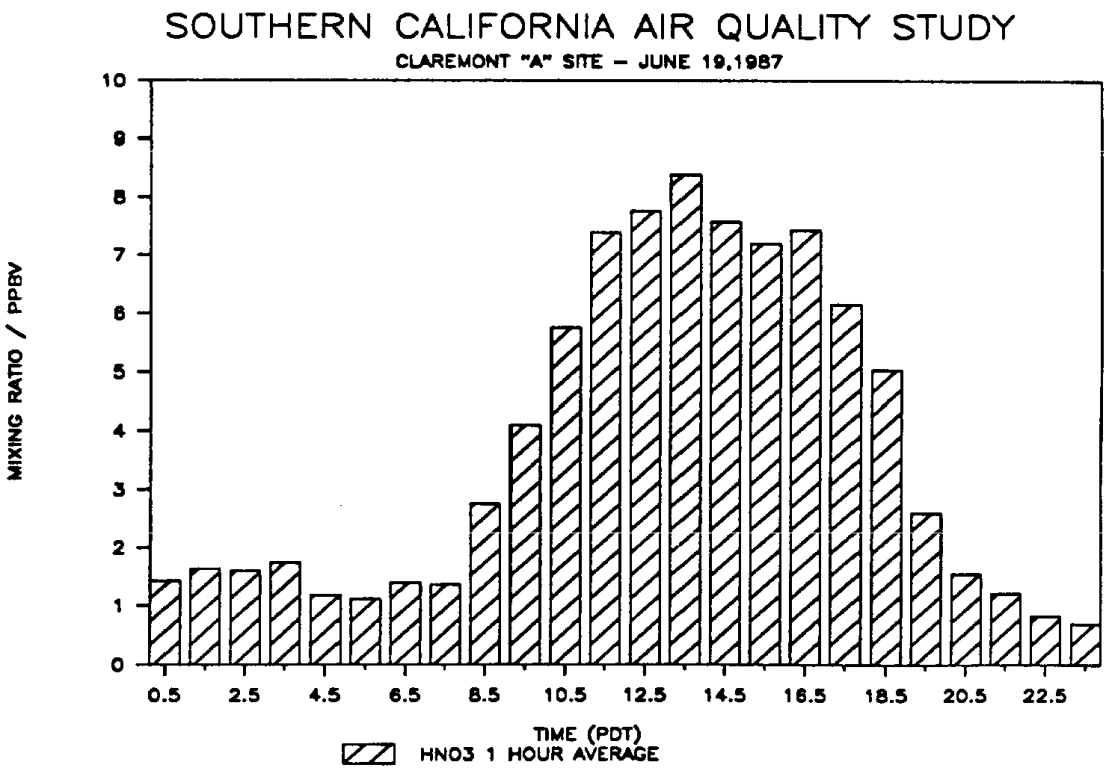
TIME (PDT)
HNO3 15 MIN AVERAGE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CLAREMONT "A" SITE – JUNE 19,1987
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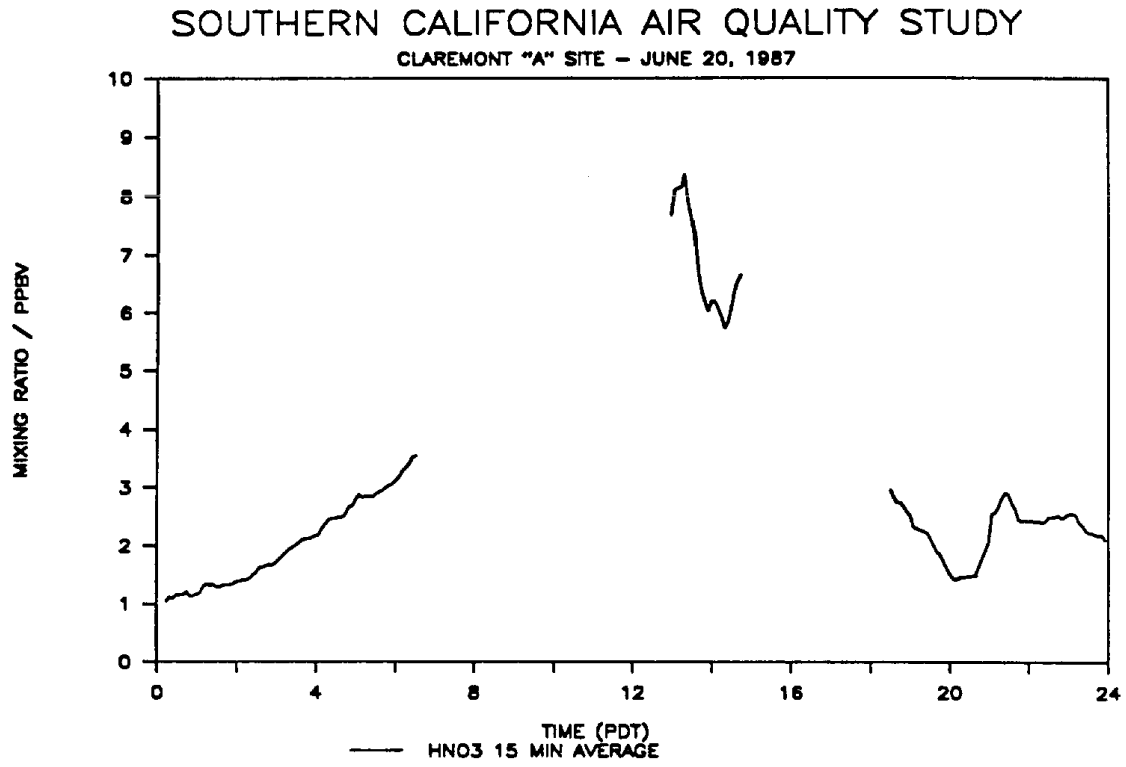
TIME (PDT)
HNO3 1 HOUR AVERAGE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CLAREMONT "A" SITE – JUNE 20, 1987
MIXING RATIO / PPBV
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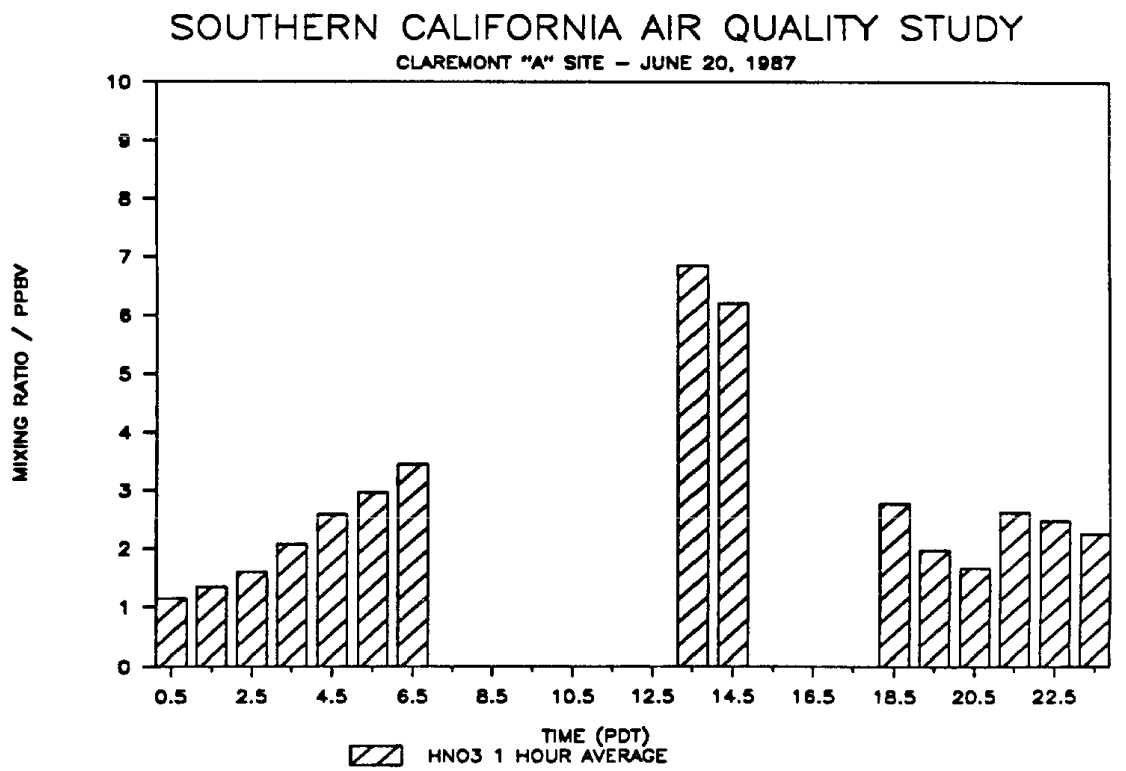
TIME (PDT)
HNO3 15 MIN AVERAGE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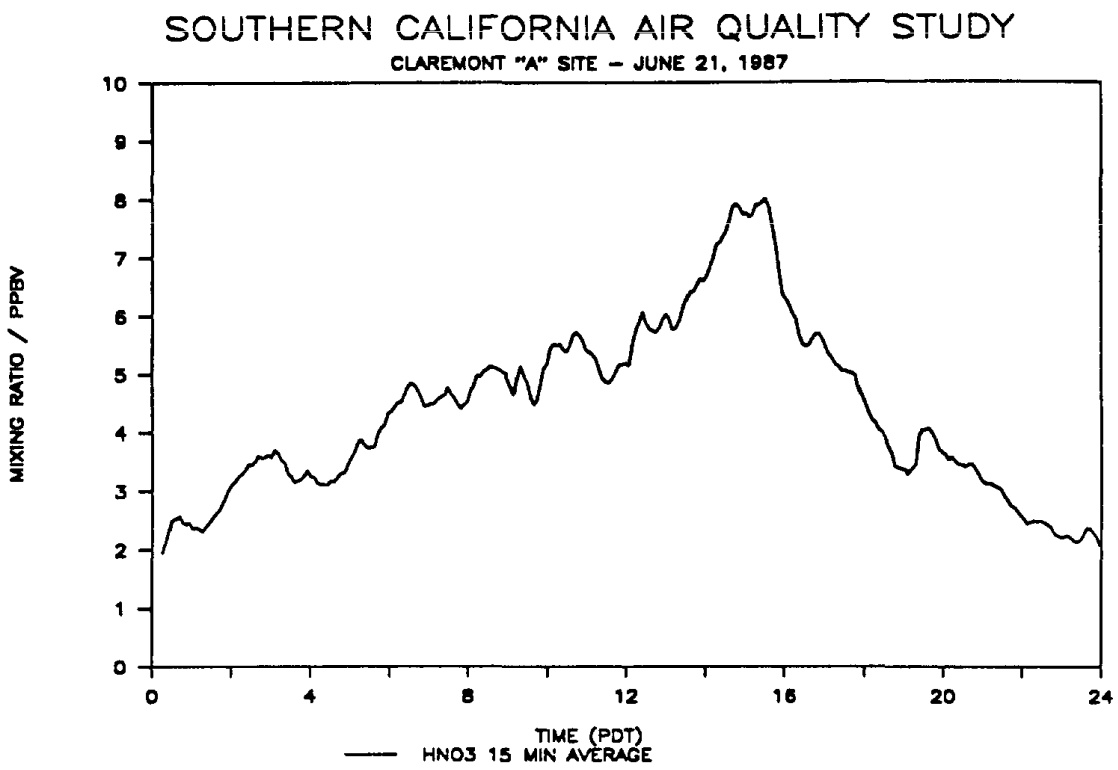
TIME (PDT)
HNO3 1 HOUR AVERAGE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CLAREMONT "A" SITE – JUNE 21, 1987
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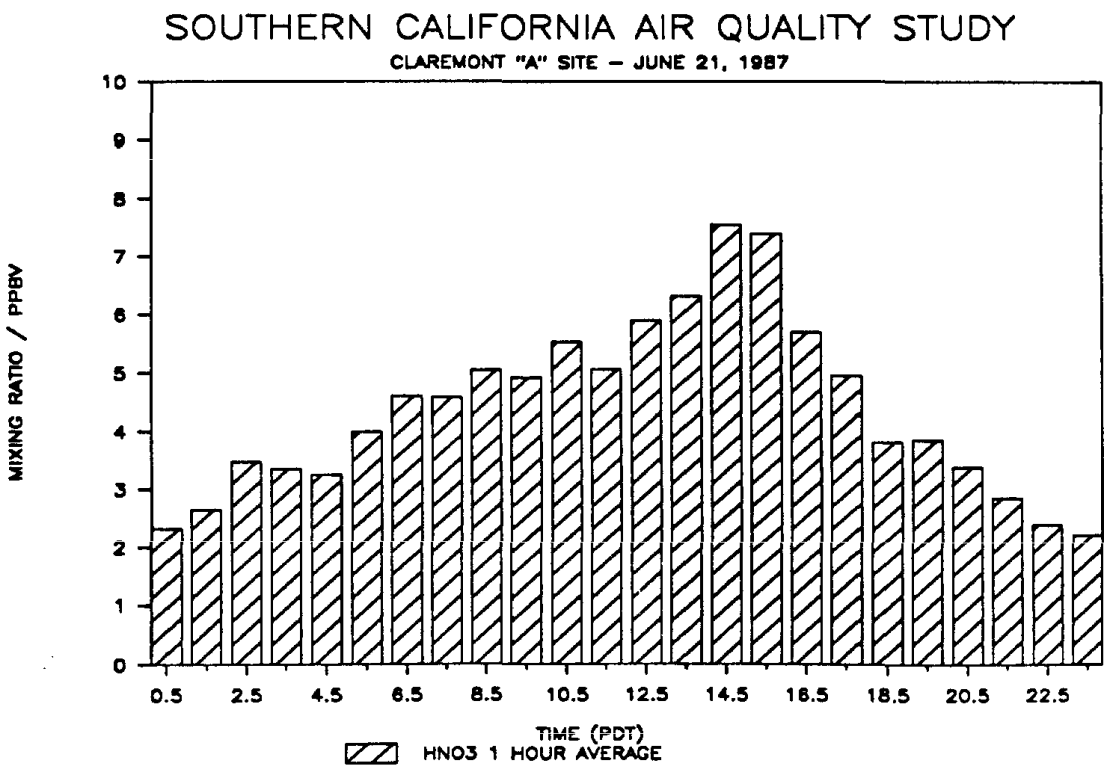
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 21, 1987
MIXING RATIO / PPBV
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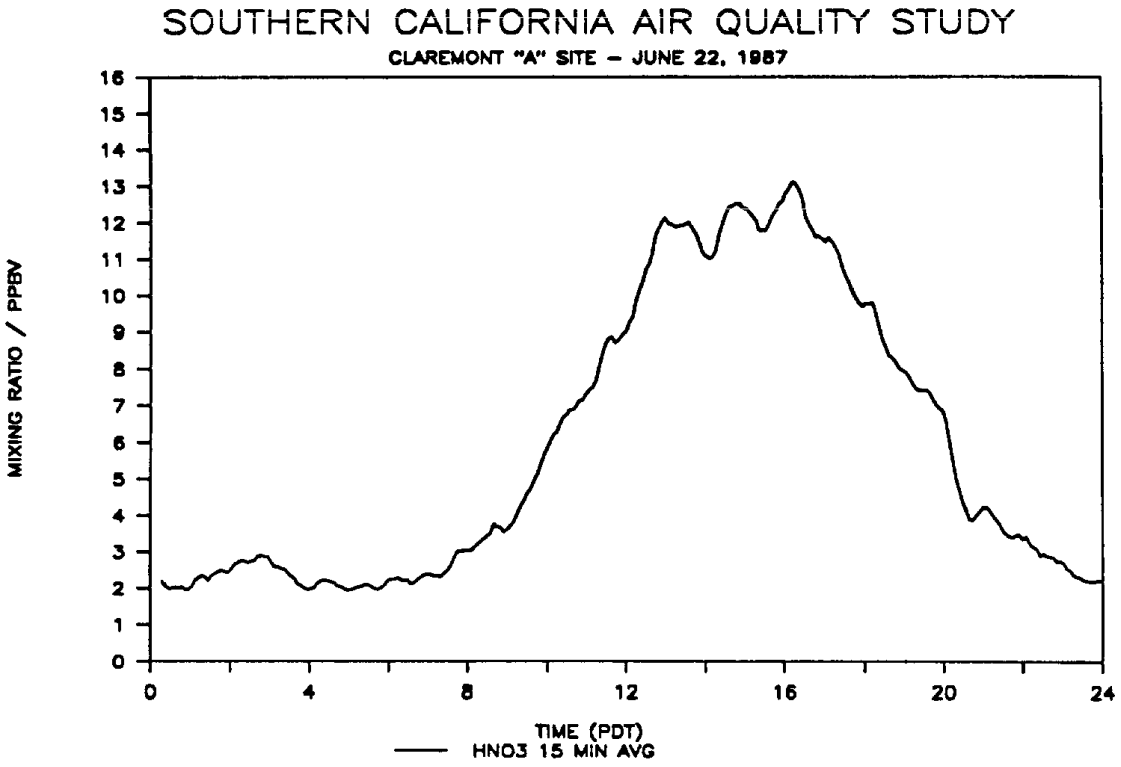
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 22, 1987
MIXING RATIO / PPBV
0
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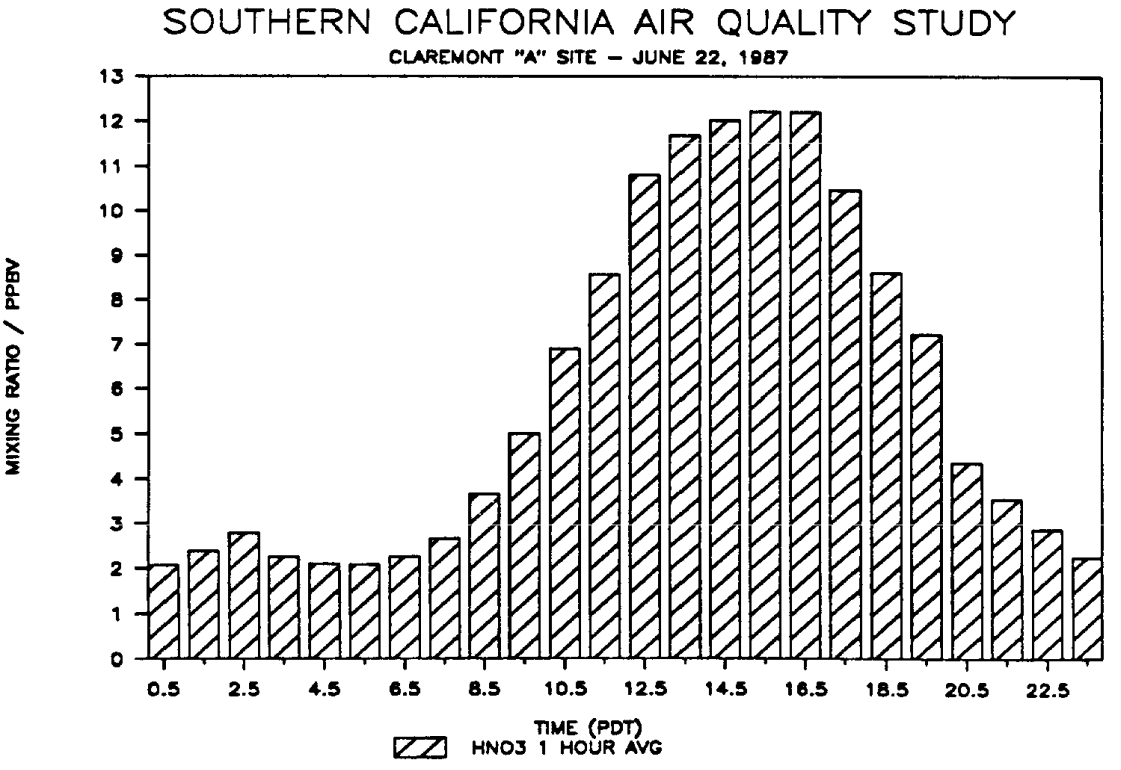
14
15
16
0
4
8
12
16
20
24
TIME (PDT)
HNO3 15 MIN AVG


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 22, 1987
MIXING RATIO / PPBV
0
1
2
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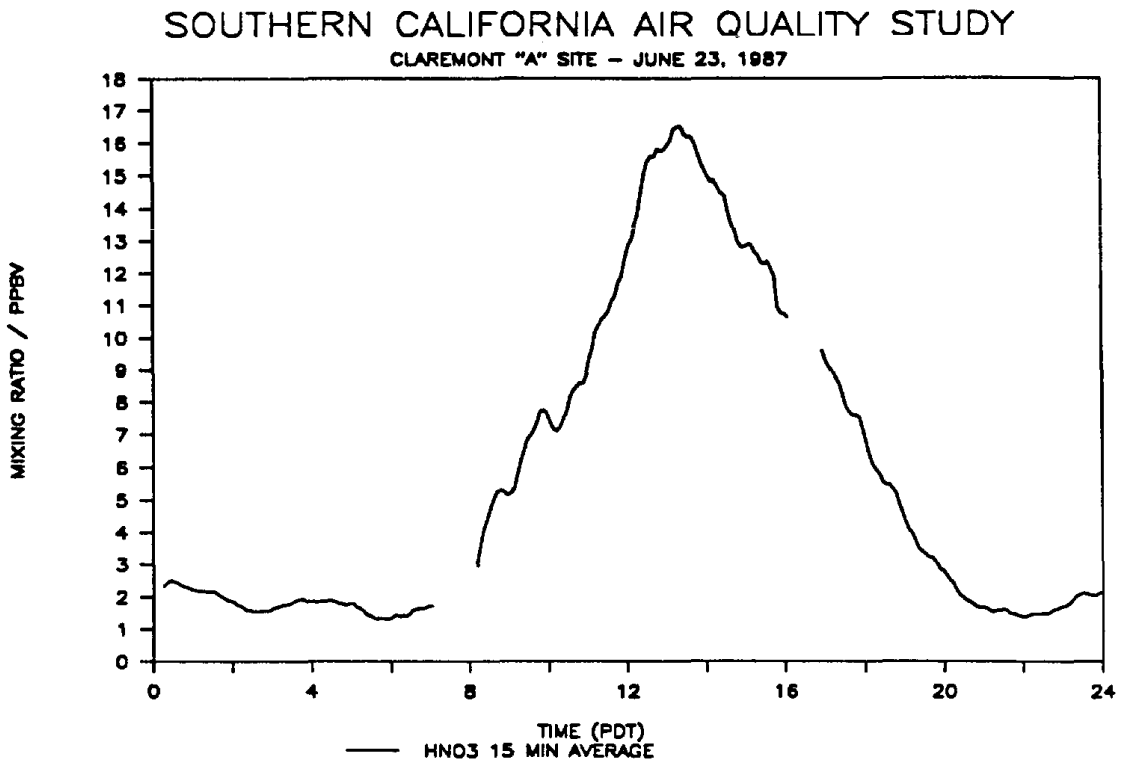
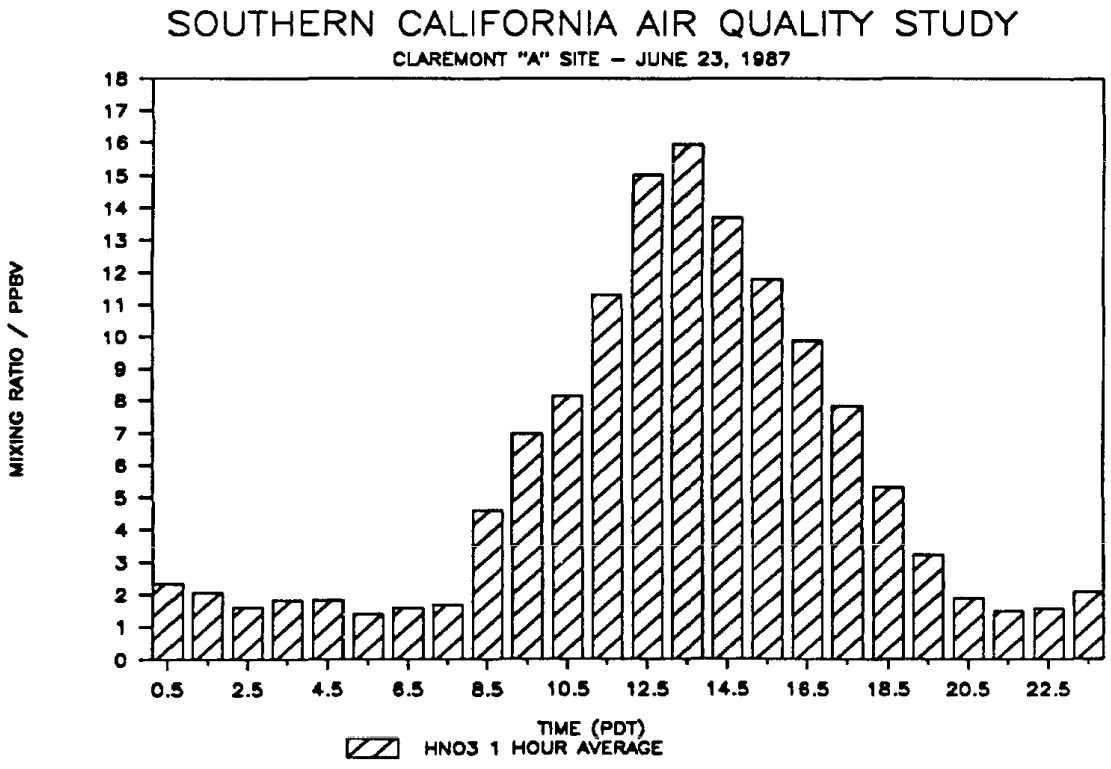
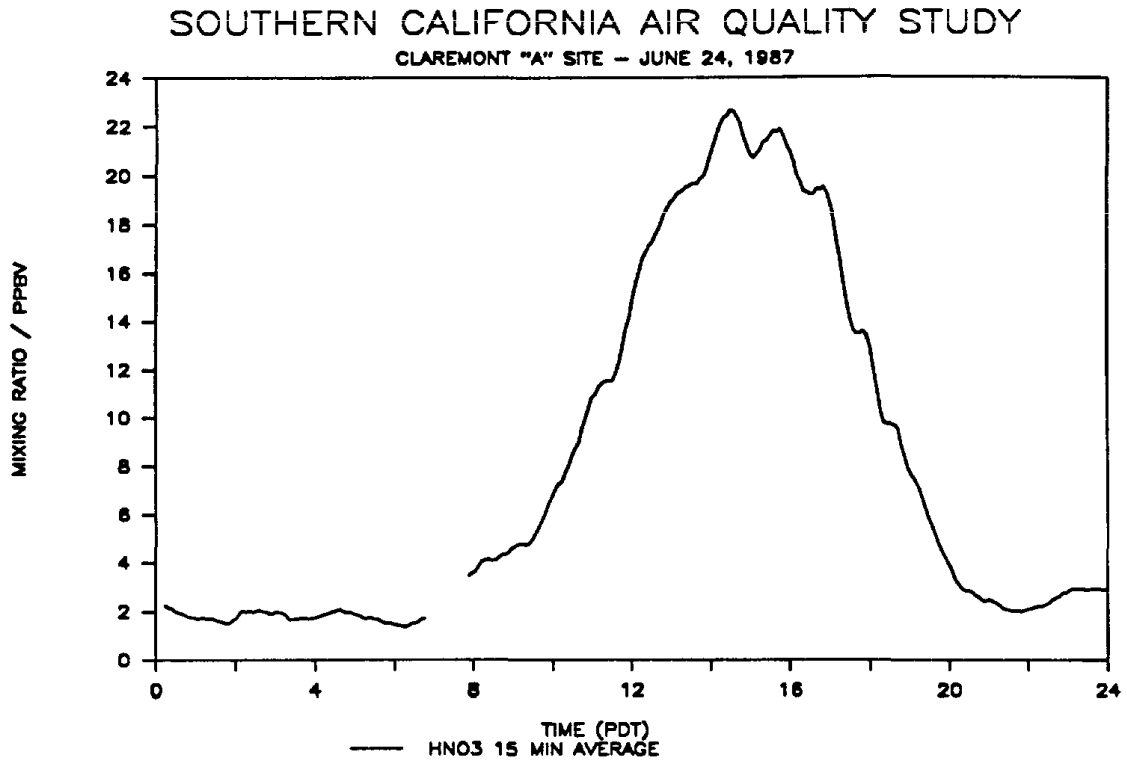
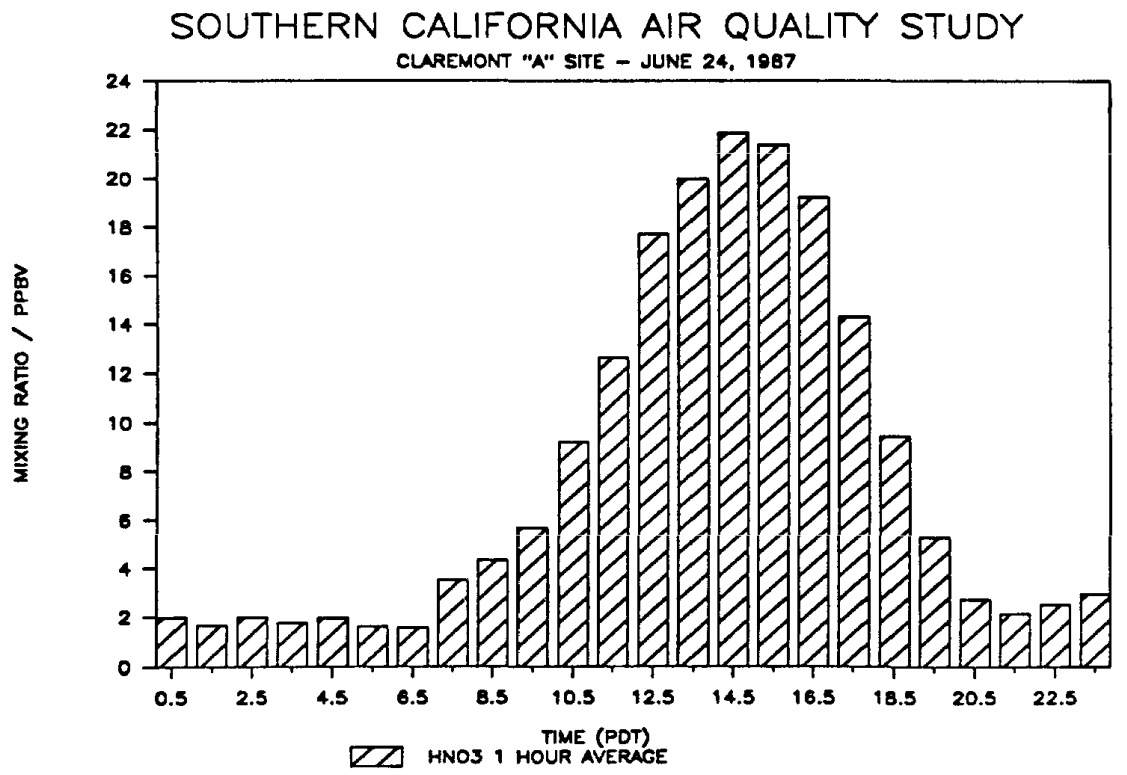
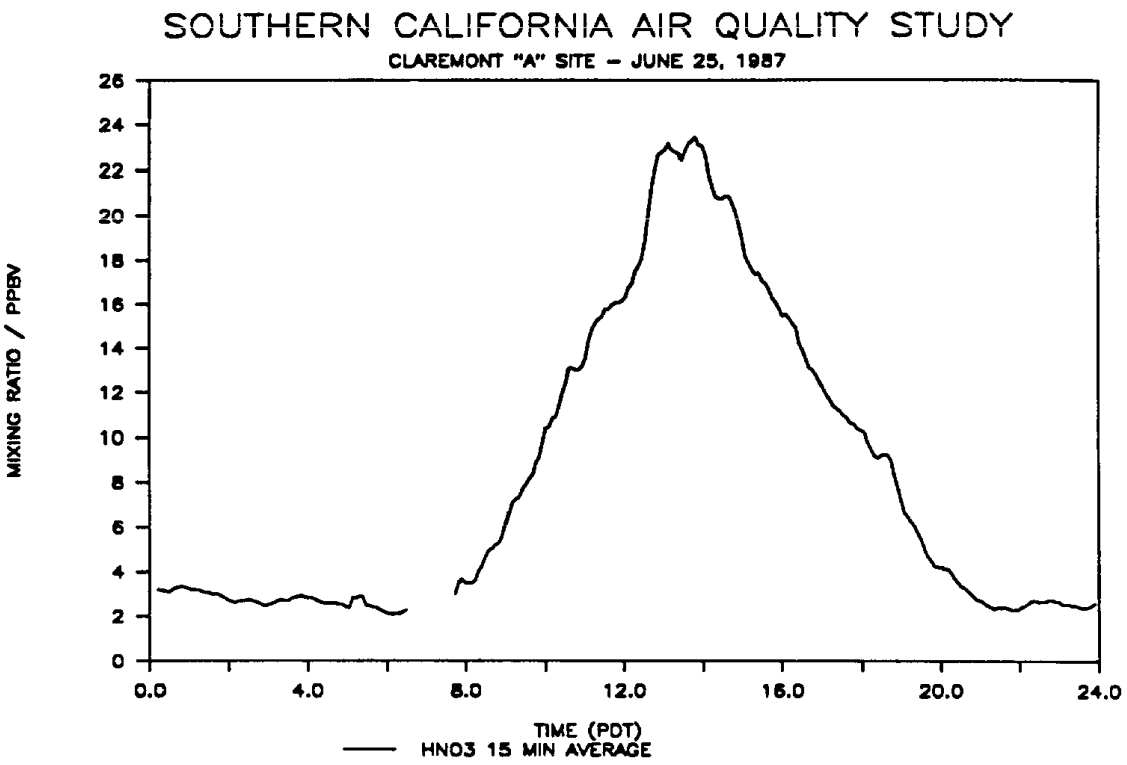
12
13
0.5
2.5
4.5
6.5
8.5
10.5
12.5
14.5
16.5
18.5
20.5
22.5
TIME (PDT)
HNO3 1 HOUR AVG

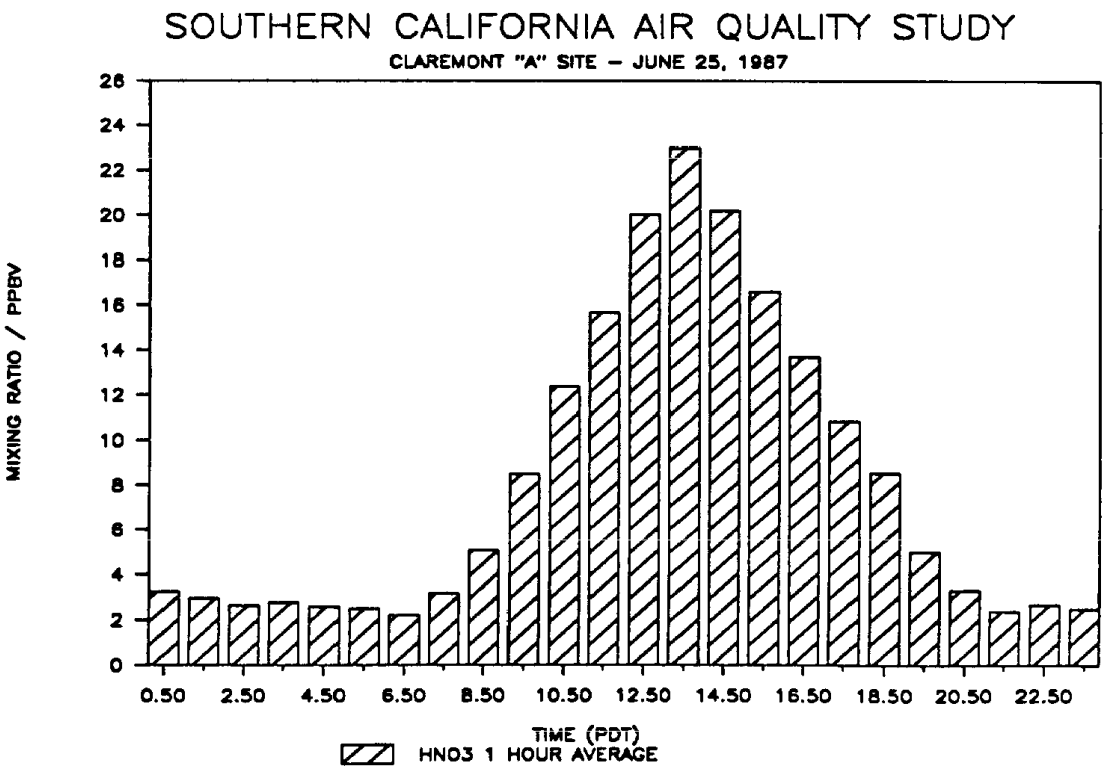

SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 23, 1987
MIXING RATIO / PPBV
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
0 4 8 12 16 20 24
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 23, 1987
MIXING RATIO / PPBV
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
0.5 2.5 4.5 6.5 8.5 10.5 12.5 14.5 16.5 18.5 20.5 22.5
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 24, 1987
MIXING RATIO / PPBV
0
2
4
6
8
10
12
14
16
18
20
22
24
0
4
8
12
16
20
24
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 24, 1987
MIXING RATIO / PPBV
0
2
4
6
8
10
12
14
16
18
20
22
24
0.5
2.5
4.5
6.5
8.5
10.5
12.5
14.5
16.5
18.5
20.5
22.5
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 25, 1987
MIXING RATIO / PPBV
0
2
4
6
8
10
12
14
16
18
20
22
24
26
0.0
4.0
8.0
12.0
16.0
20.0
24.0
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 25, 1987
MIXING RATIO / PPBV
0
2
4
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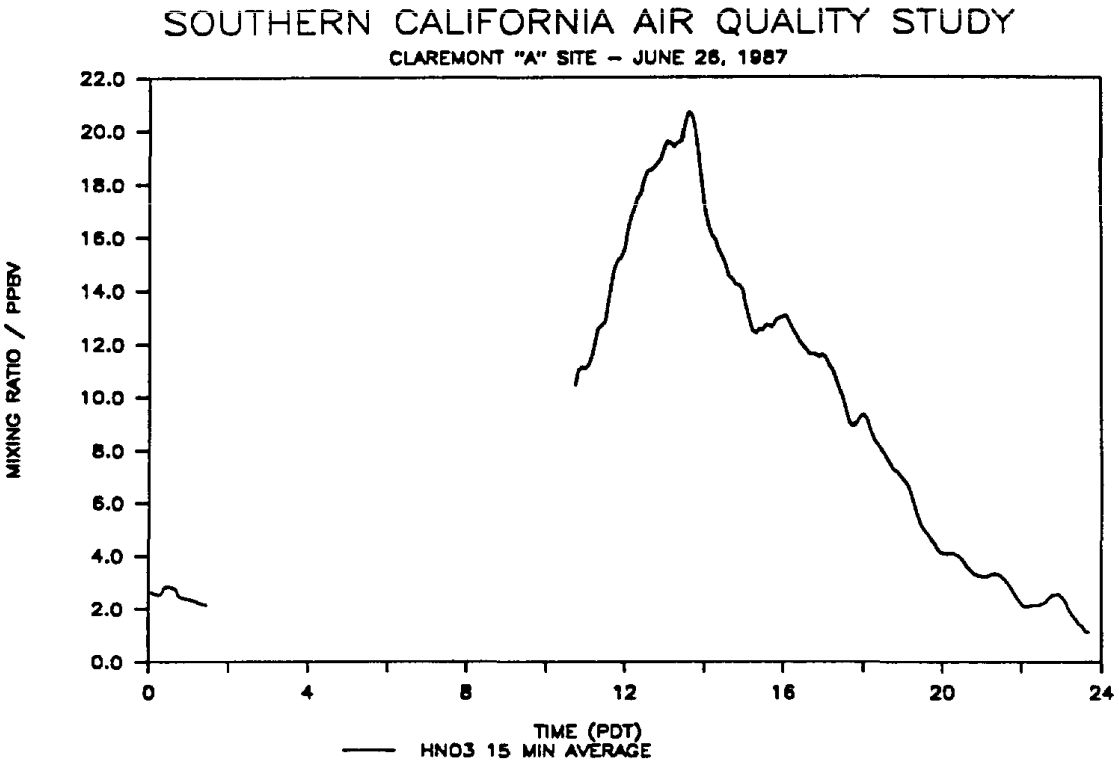
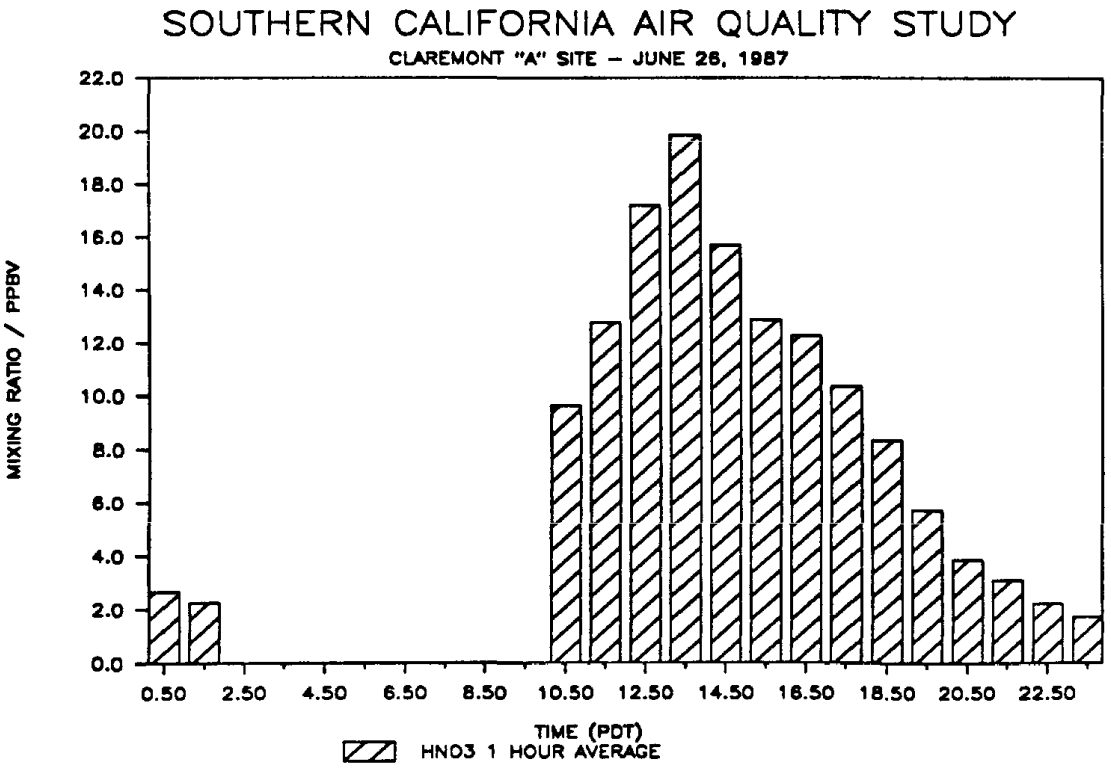
8
10
12
14
16
18
20
22
24
26
0.50
2.50
4.50
6.50
8.50
10.50
12.50
14.50
16.50
18.50
20.50
22.50
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 26, 1987
MIXING RATIO / PPBV
22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0
4
8
12
16
20
24
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 26, 1987
MIXING RATIO / PPBV
22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0.50
2.50
4.50
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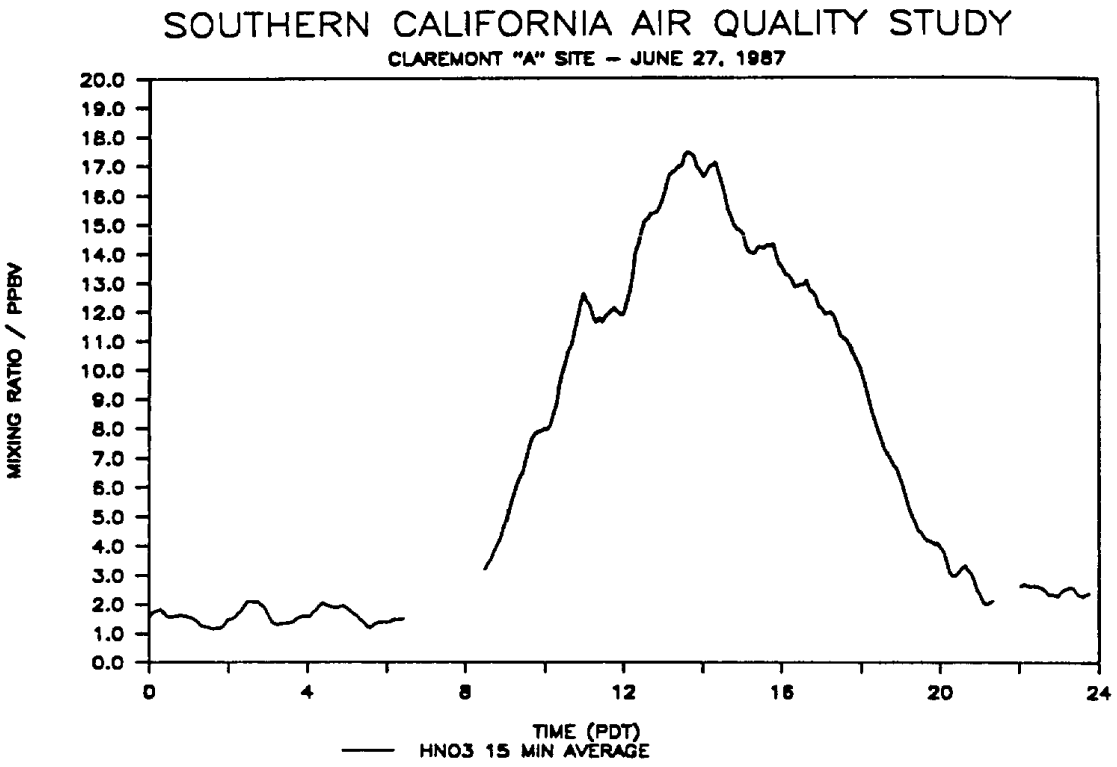
10.50
12.50
14.50
16.50
18.50
20.50
22.50
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 27, 1987
MIXING RATIO / PPBV
20.0
19.0
18.0
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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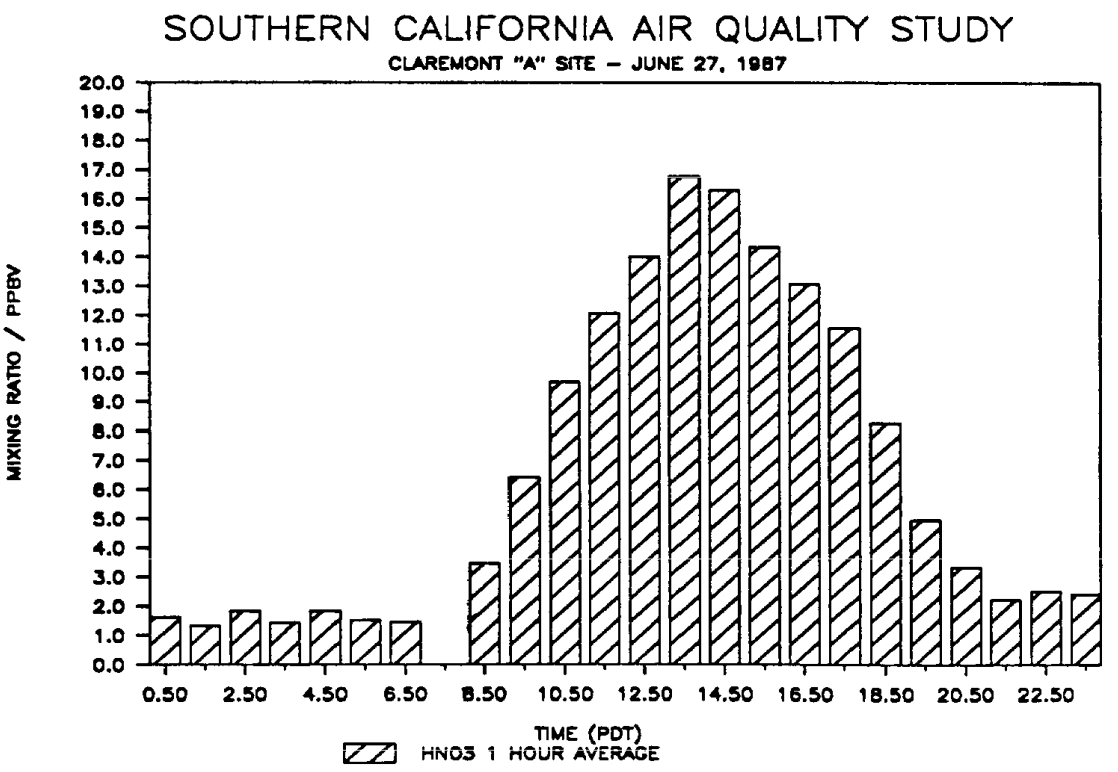
8
12
16
20
24
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 27, 1987
MIXING RATIO / PPBV
20.0
19.0
18.0
17.0
16.0
15.0
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12.0
11.0
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8.0
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0.0
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4.50
6.50
8.50
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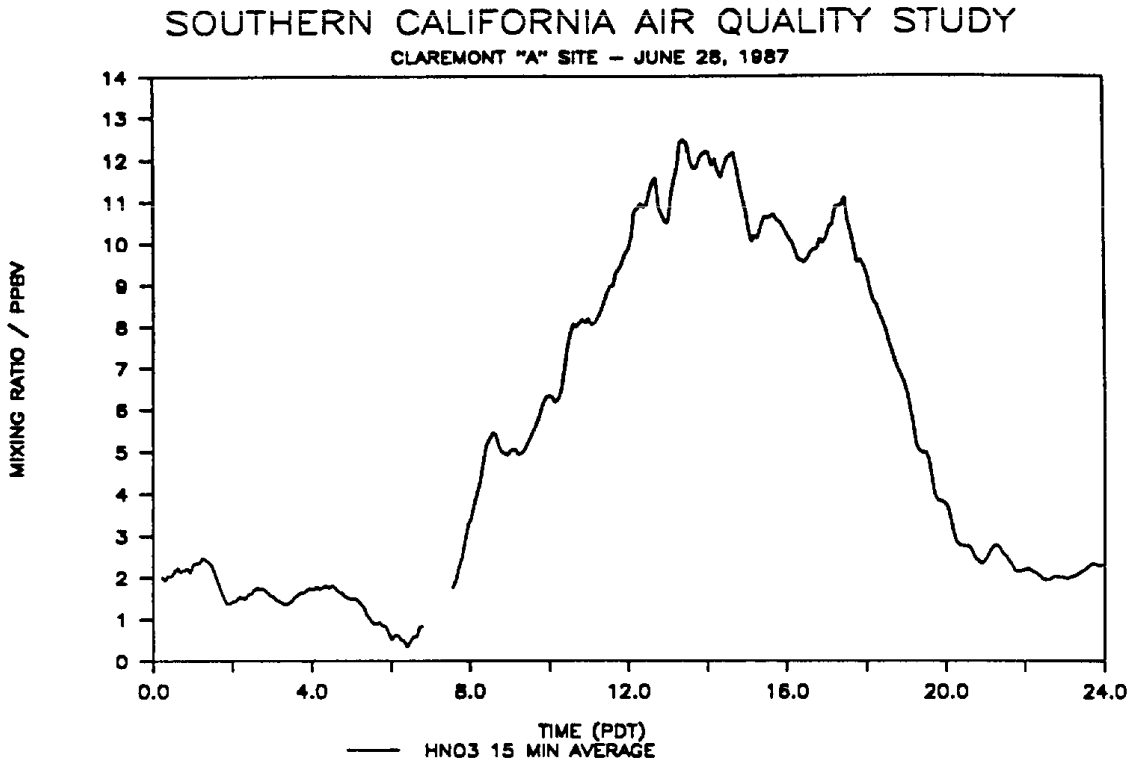
12.50
14.50
16.50
18.50
20.50
22.50
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 28, 1987
MIXING RATIO / PPBV
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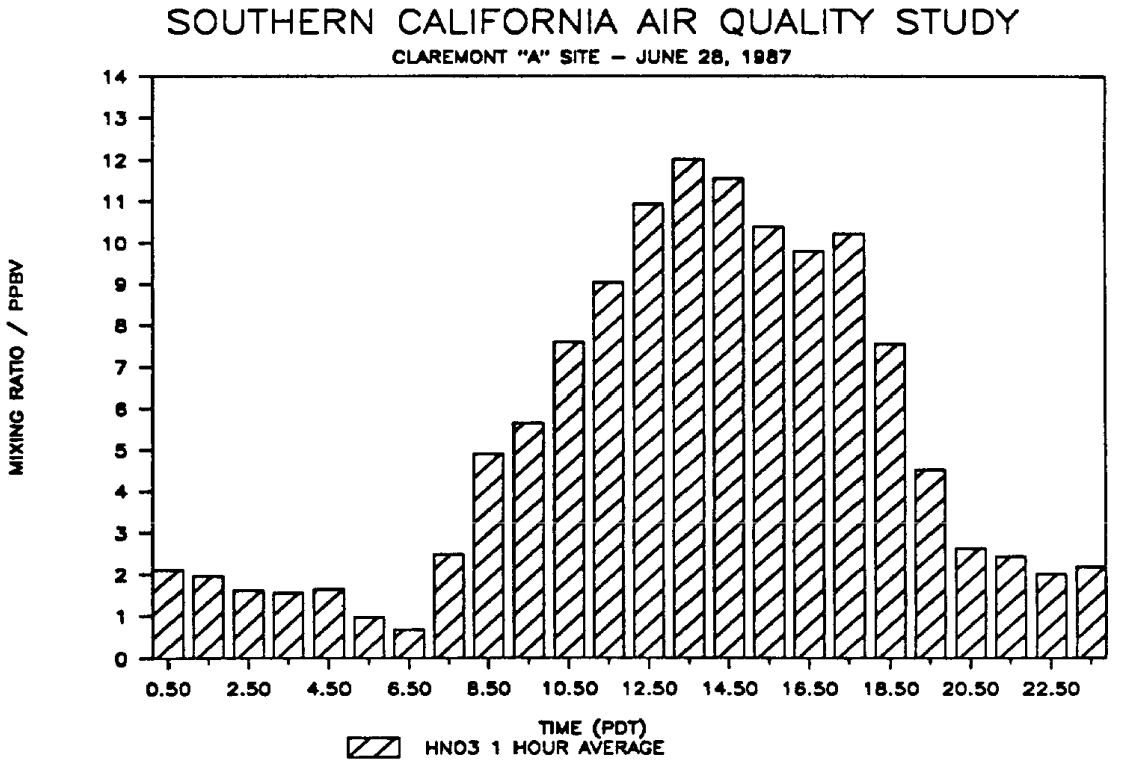
4.0
8.0
12.0
16.0
20.0
24.0
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 28, 1987
MIXING RATIO / PPBV
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0.50
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6.50
8.50
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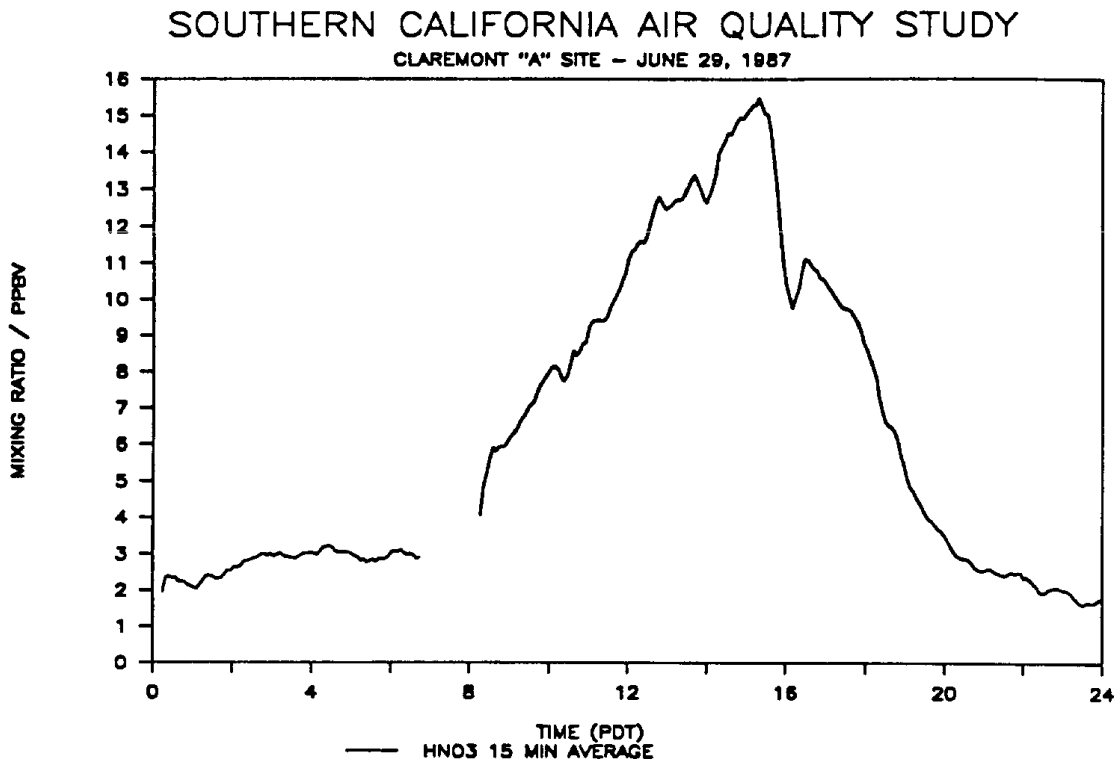
12.50
14.50
16.50
18.50
20.50
22.50
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE - JUNE 29, 1987
MIXING RATIO / PPBV
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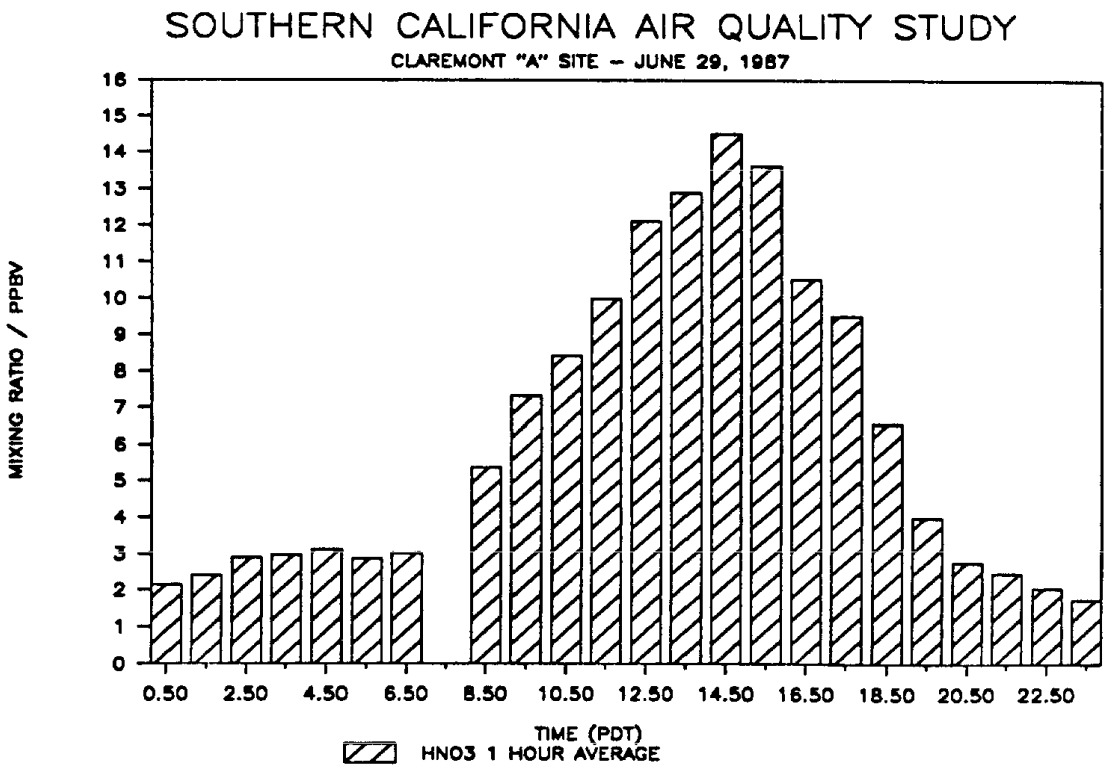
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE - JUNE 29, 1987
MIXING RATIO / PPBV
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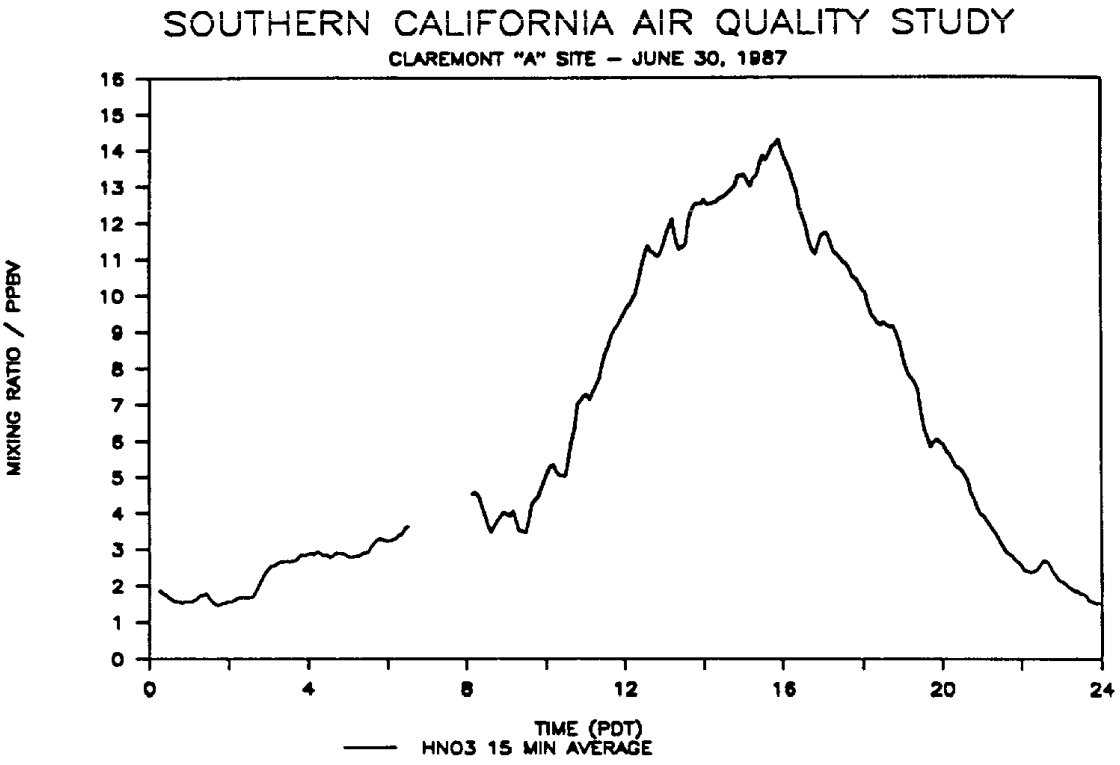
16
0.50
2.50
4.50
6.50
8.50
10.50
12.50
14.50
16.50
18.50
20.50
22.50
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 30, 1987
MIXING RATIO / PPBV
0
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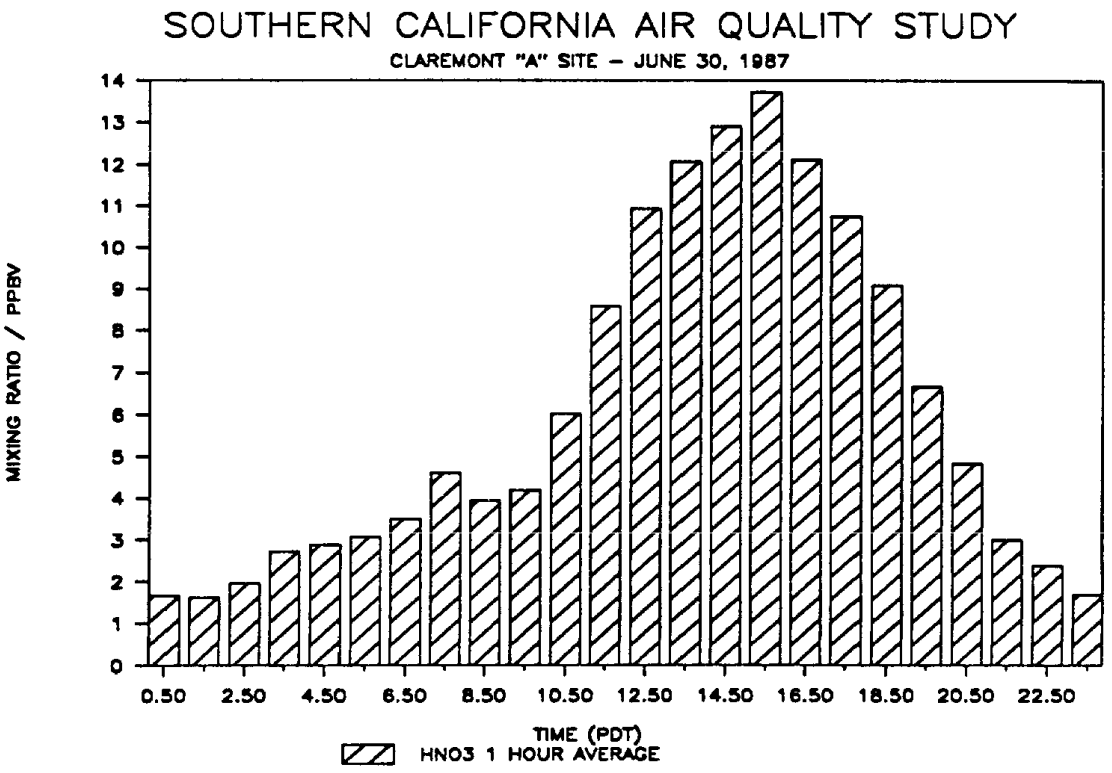
24
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JUNE 30, 1987
MIXING RATIO / PPBV
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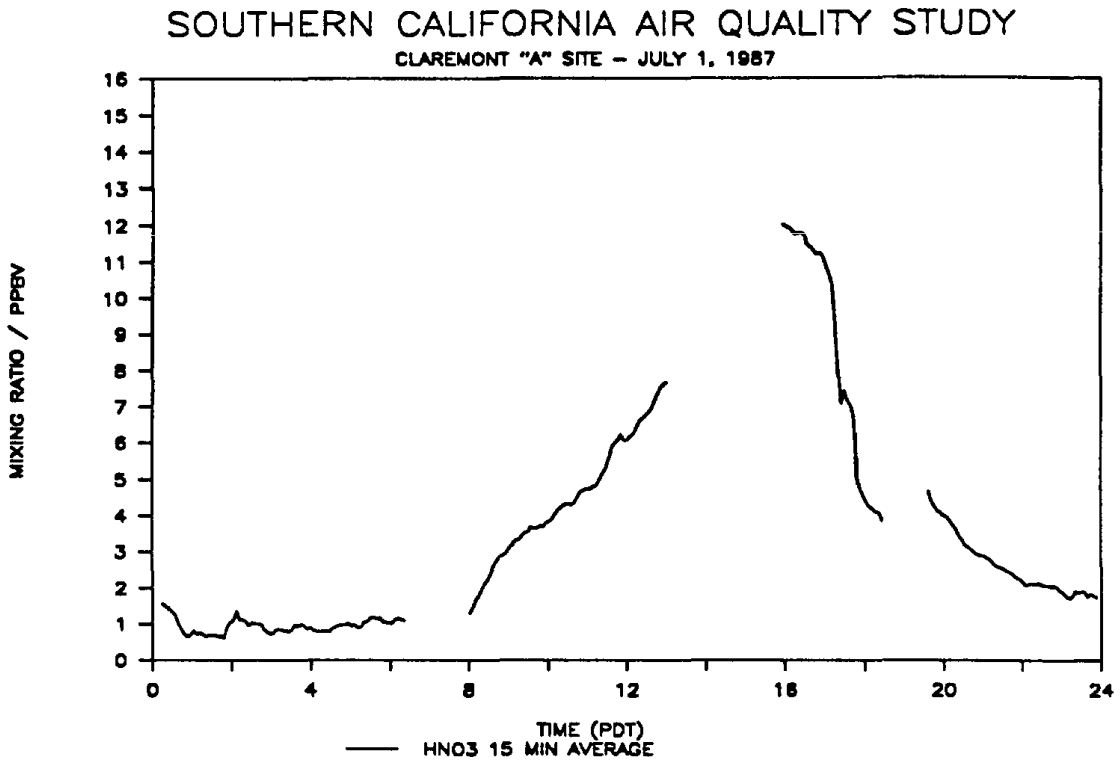
0.50
2.50
4.50
6.50
8.50
10.50
12.50
14.50
16.50
18.50
20.50
22.50
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 1, 1987
MIXING RATIO / PPBV
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0
4
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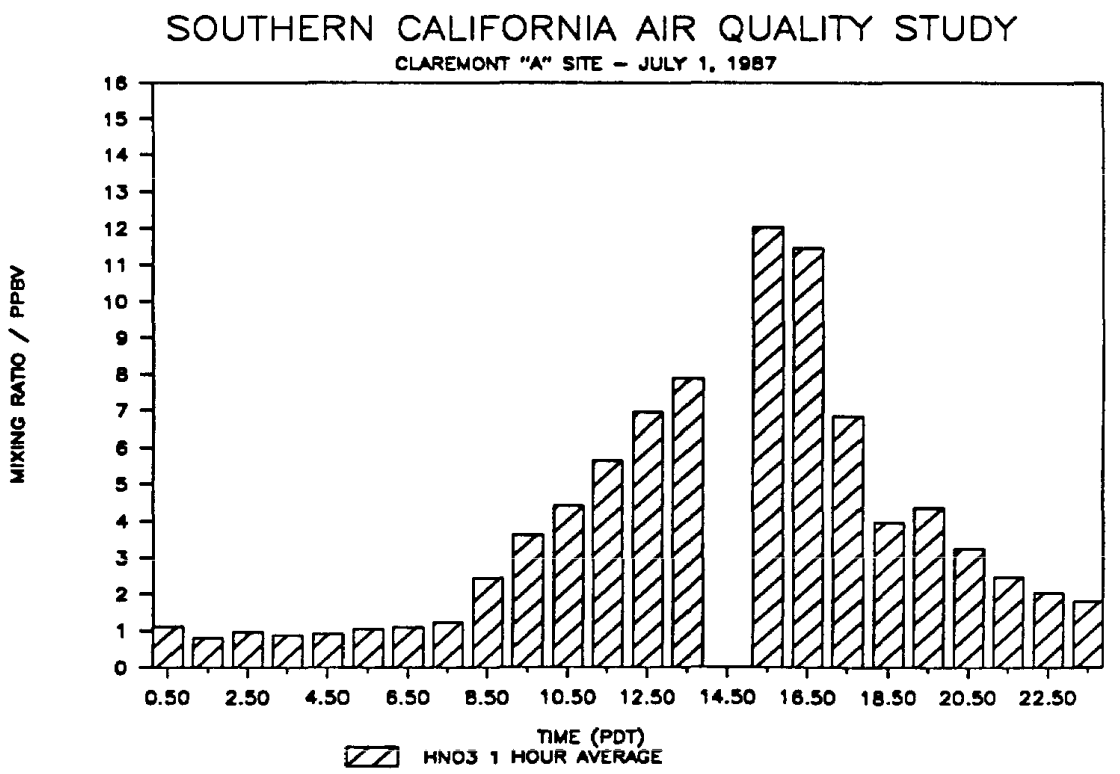
16
20
24
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 1, 1987
MIXING RATIO / PPBV
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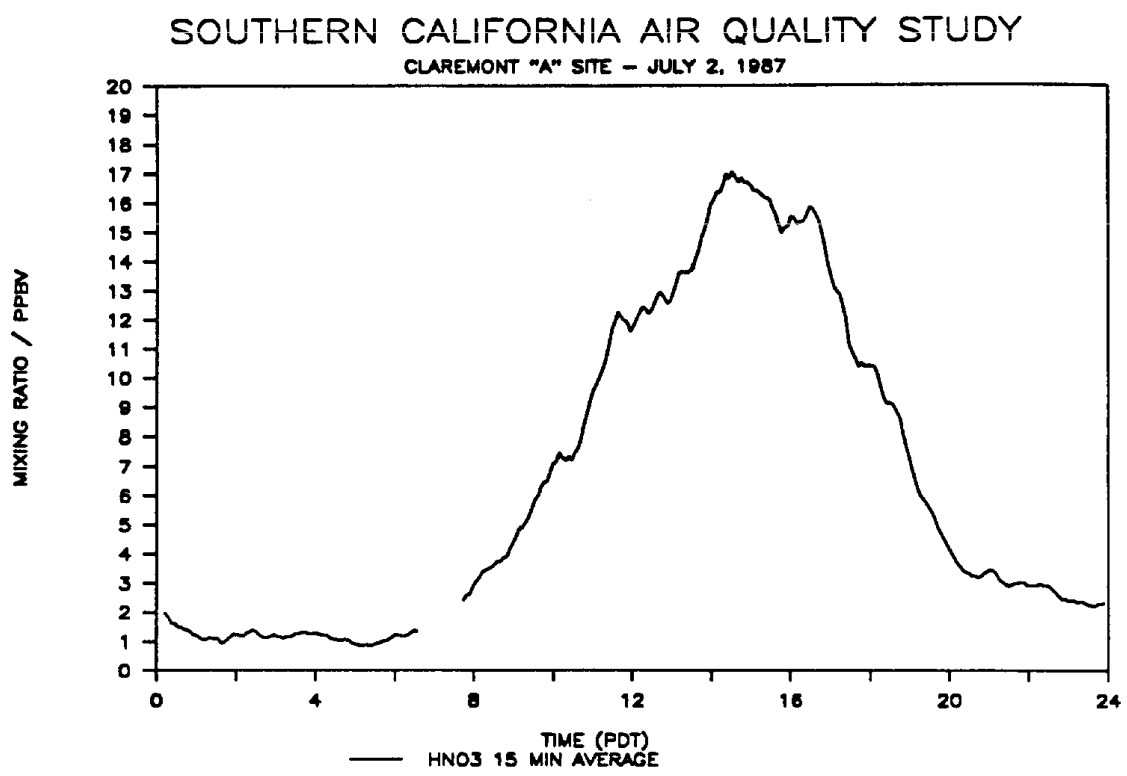
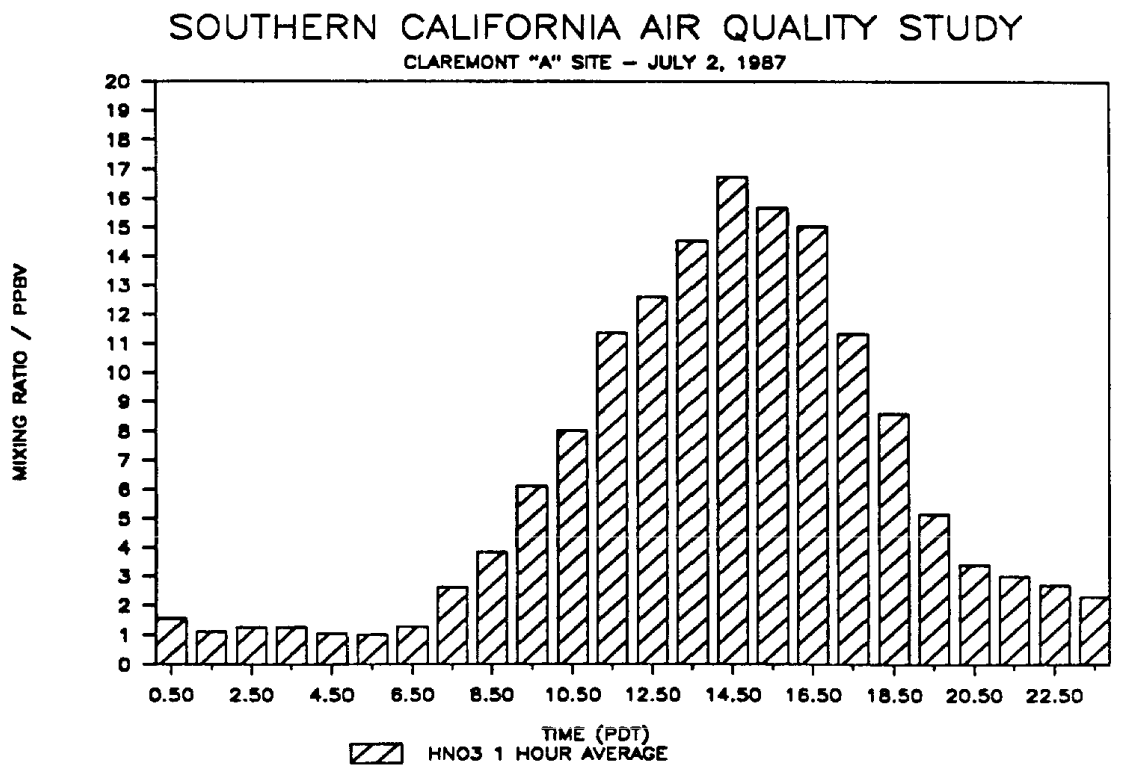
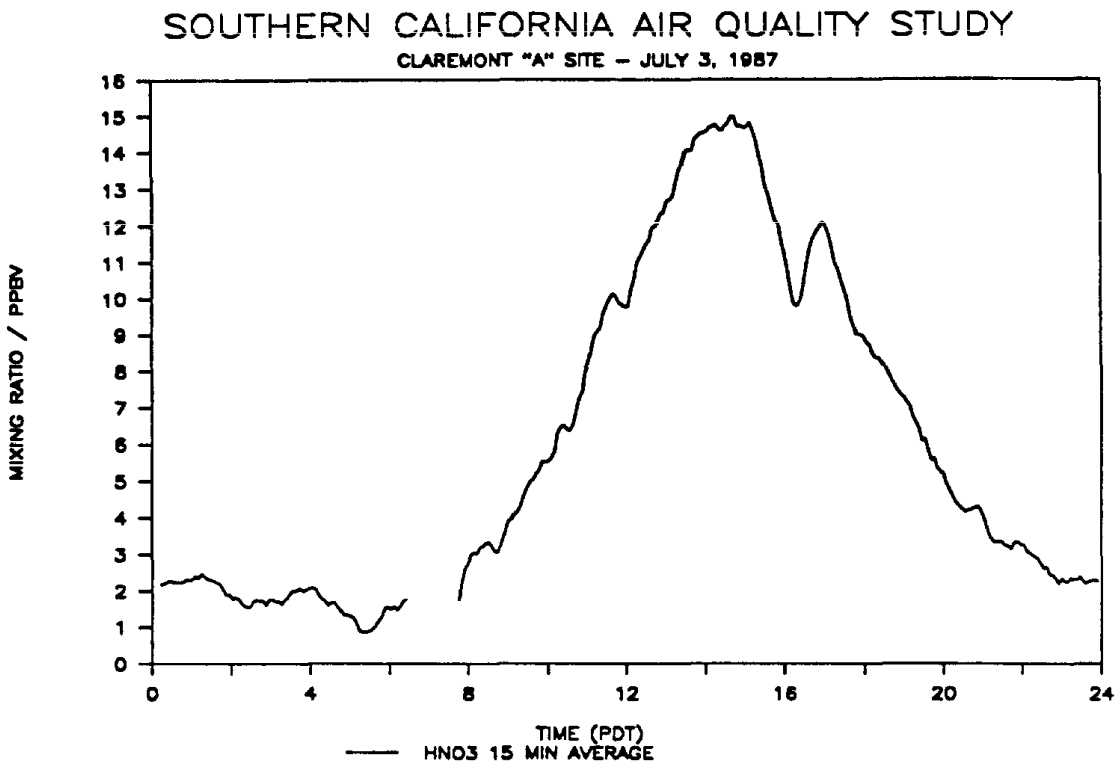
0.50
2.50
4.50
6.50
8.50
10.50
12.50
14.50
16.50
18.50
20.50
22.50
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 2, 1987
MIXING RATIO / PPBV
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
0 4 8 12 16 20 24
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 2, 1987
MIXING RATIO / PPBV
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
0.50 2.50 4.50 6.50 8.50 10.50 12.50 14.50 16.50 18.50 20.50 22.50
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 3, 1987
MIXING RATIO / PPBV
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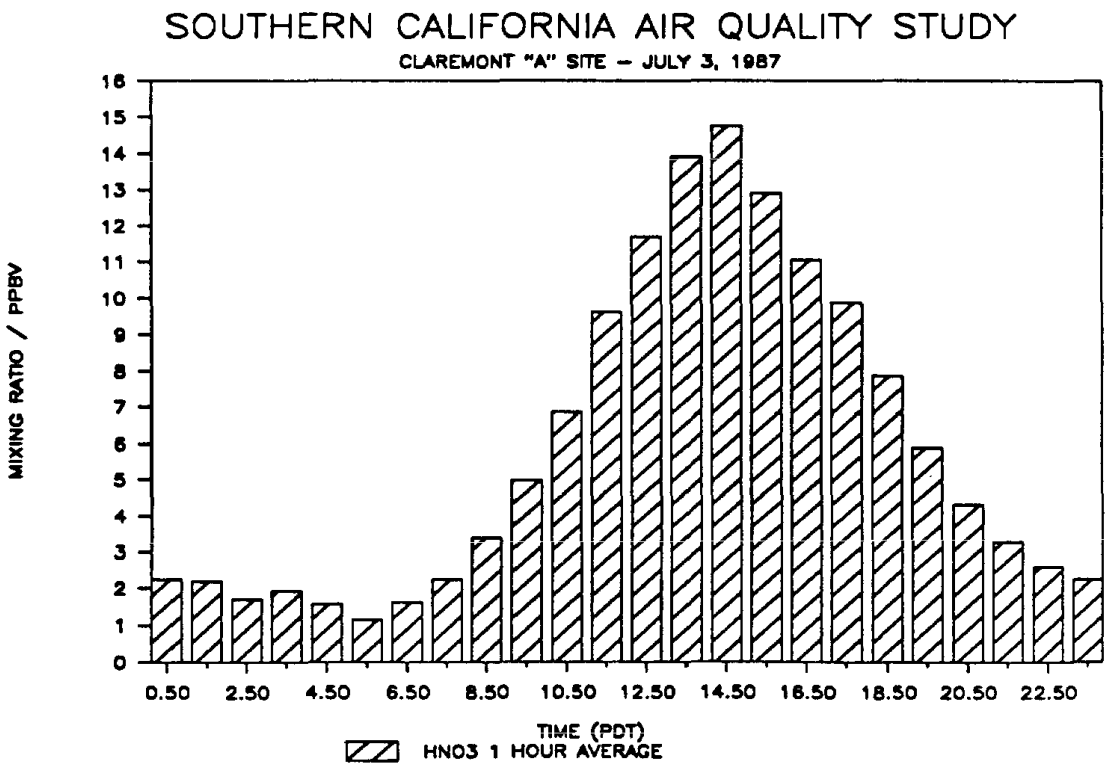
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 3, 1987
MIXING RATIO / PPBV
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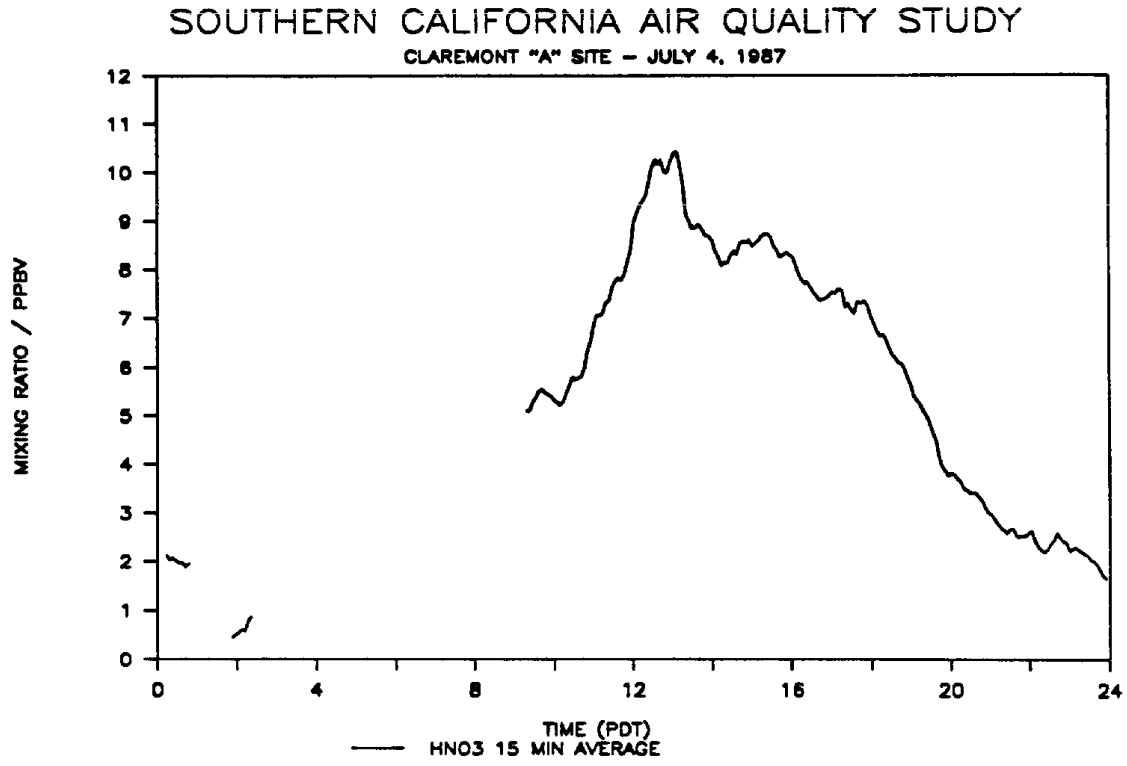
0.50
2.50
4.50
6.50
8.50
10.50
12.50
14.50
16.50
18.50
20.50
22.50
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 4, 1987
MIXING RATIO / PPBV
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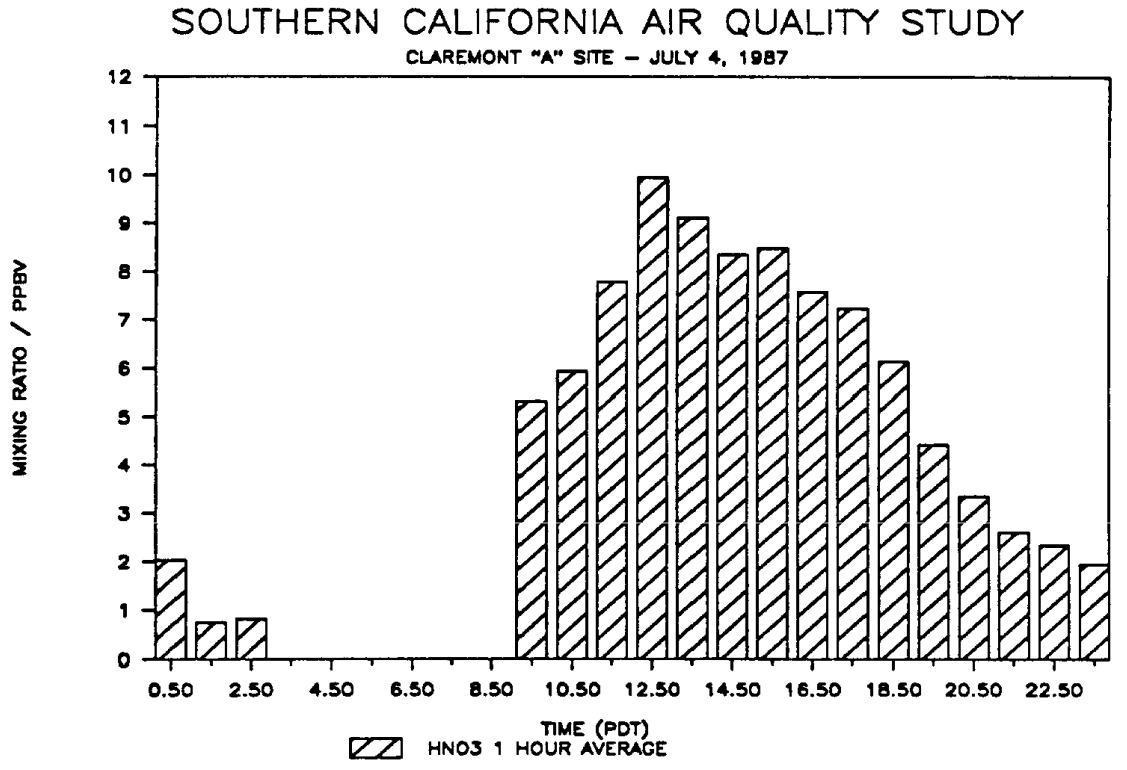
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 4, 1987
MIXING RATIO / PPBV
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0.50
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4.50
6.50
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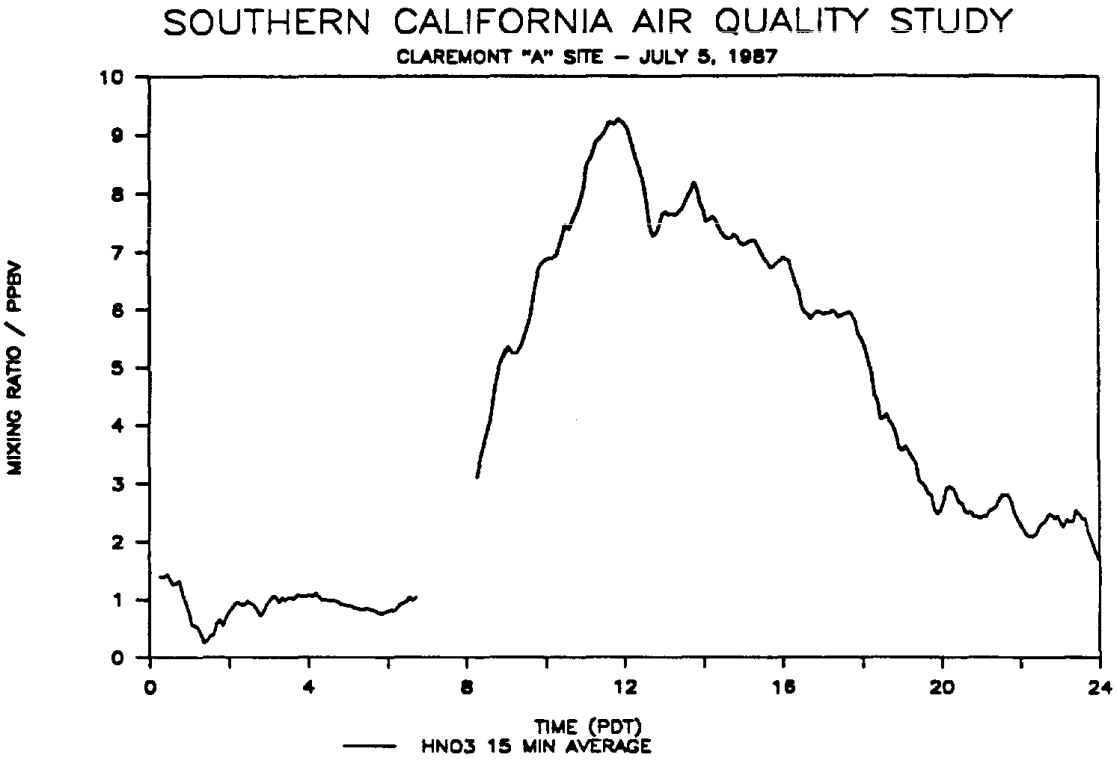
10.50
12.50
14.50
16.50
18.50
20.50
22.50
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 5, 1987
MIXING RATIO / PPBV
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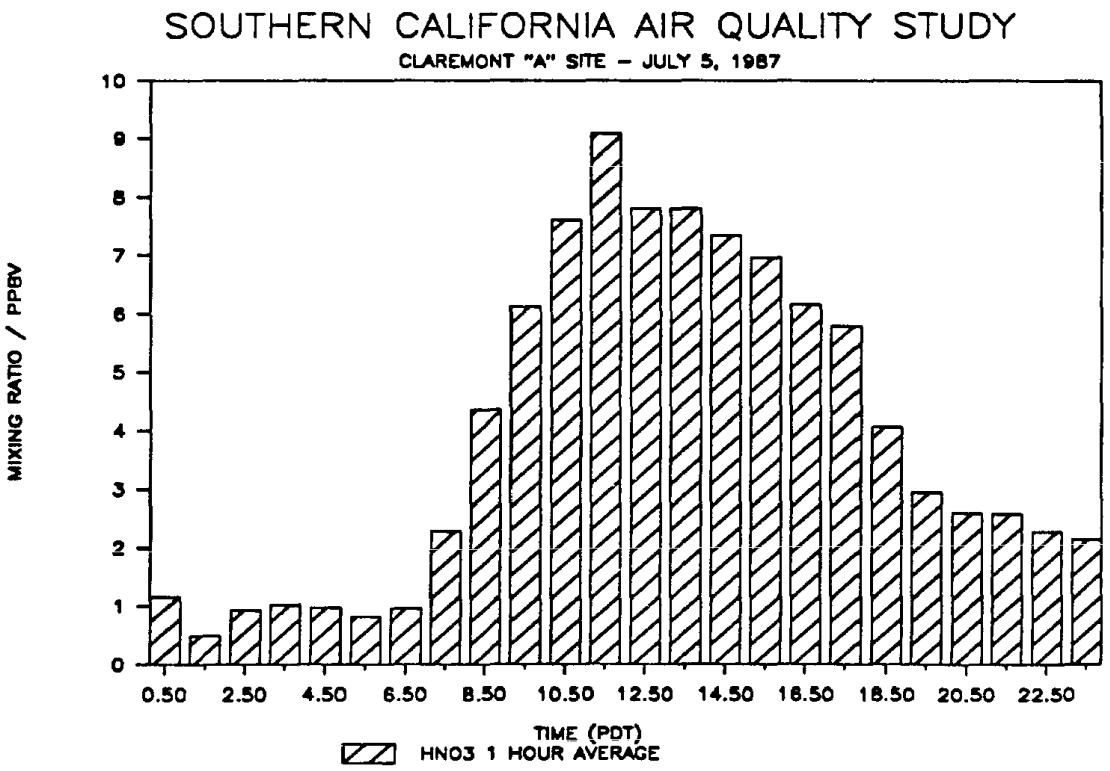
8
9
10
0
4
8
12
16
20
24
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 5, 1987
MIXING RATIO / PPBV
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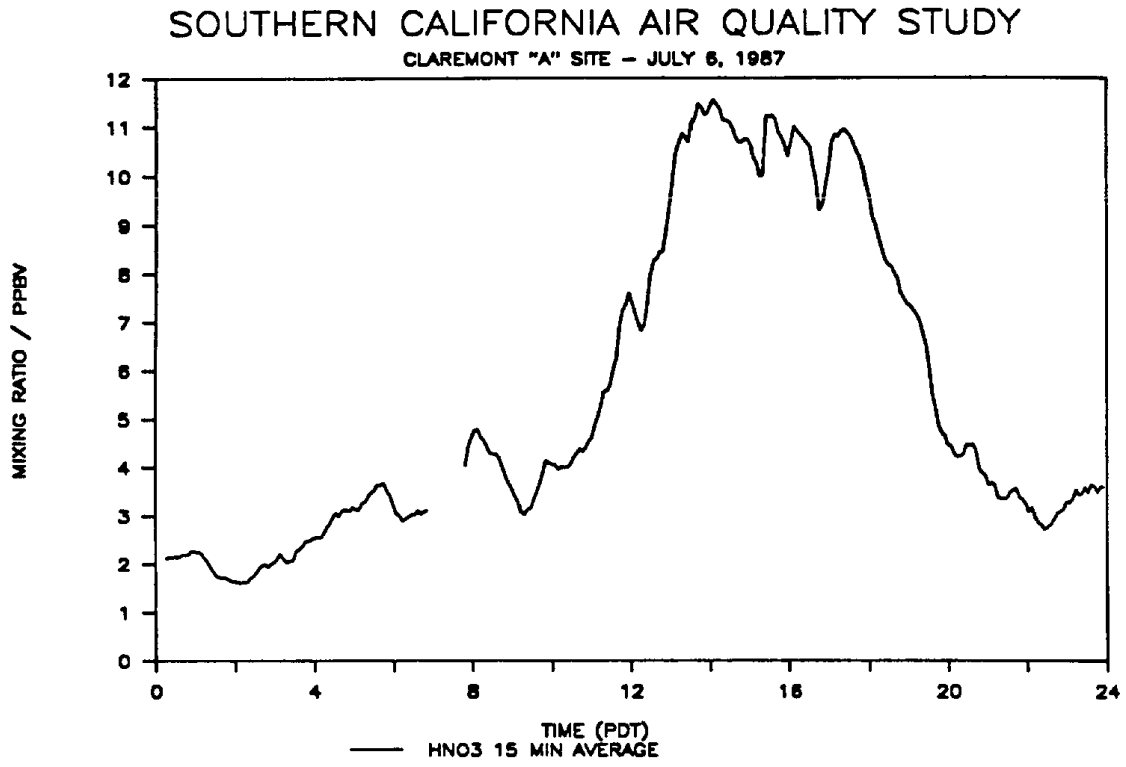
0.50
2.50
4.50
6.50
8.50
10.50
12.50
14.50
16.50
18.50
20.50
22.50
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 6, 1987
MIXING RATIO / PPBV
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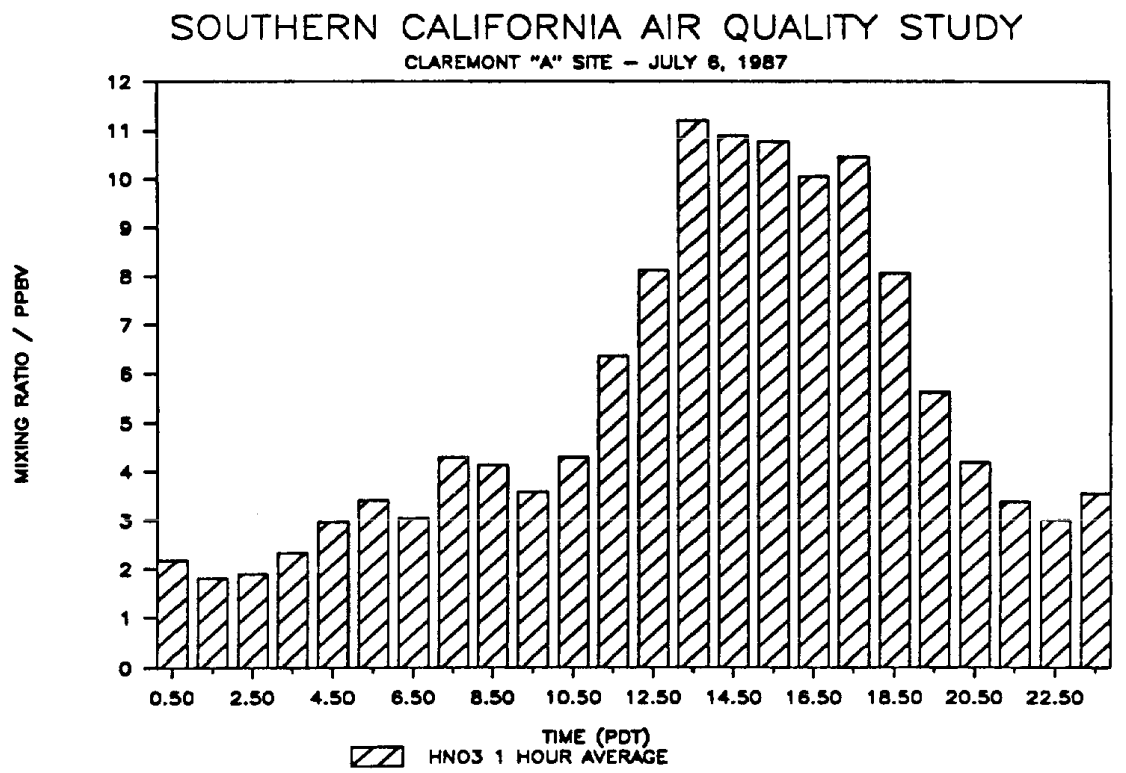
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 6, 1987
MIXING RATIO / PPBV
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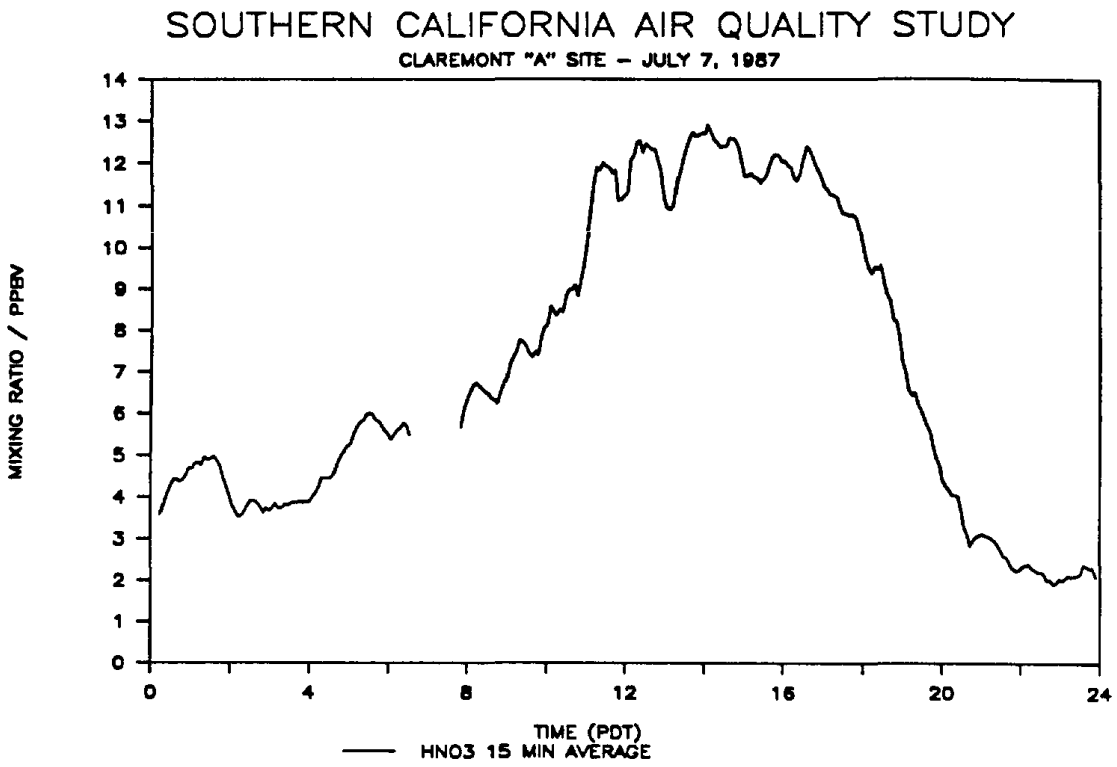
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 7, 1987
MIXING RATIO / PPBV
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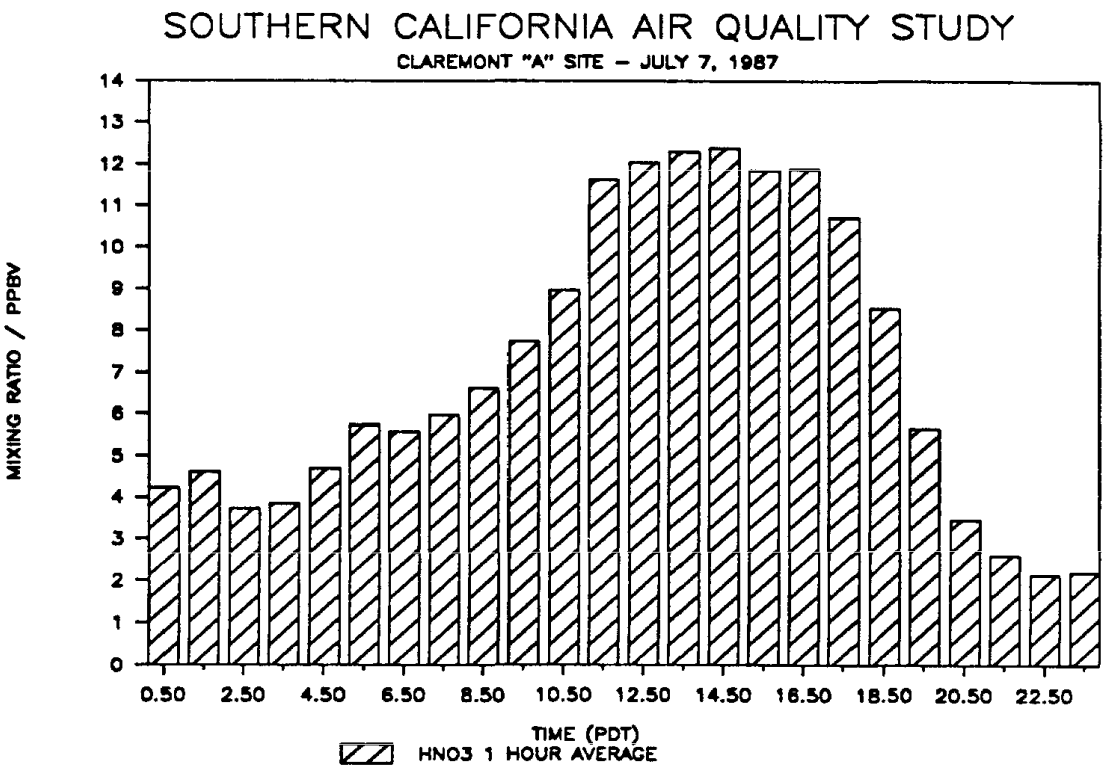
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 7, 1987
MIXING RATIO / PPBV
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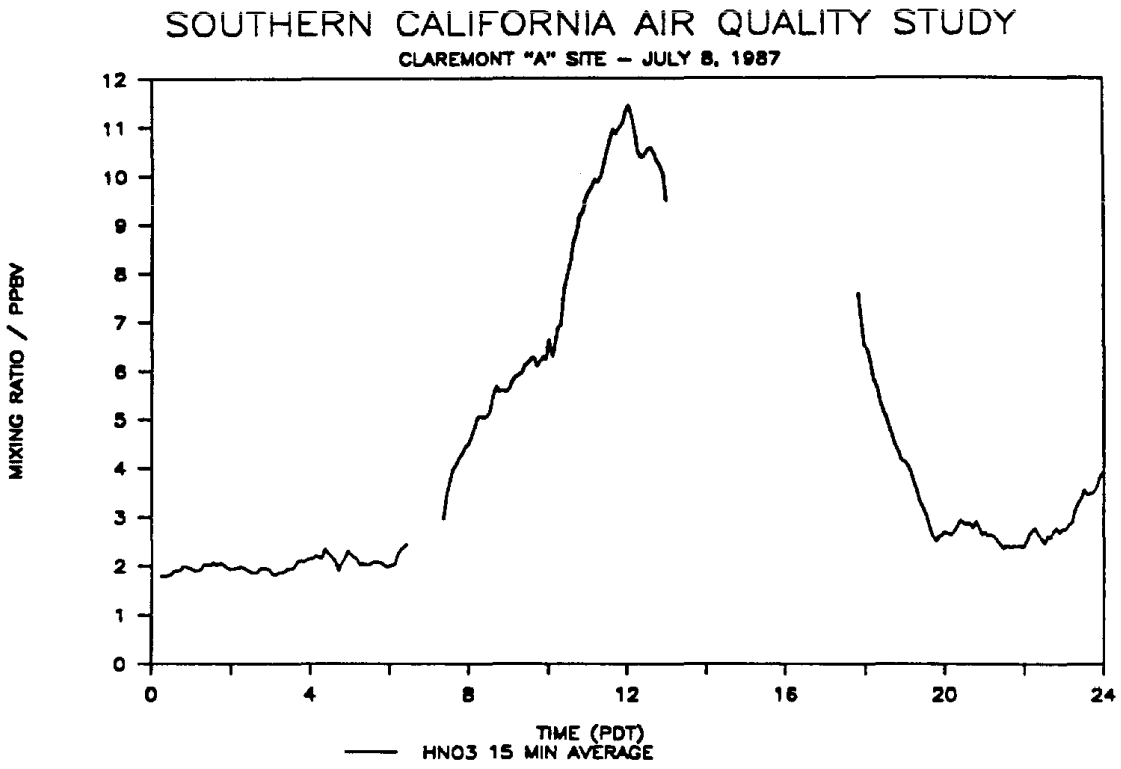
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 8, 1987
MIXING RATIO / PPBV
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TIME (PDT)
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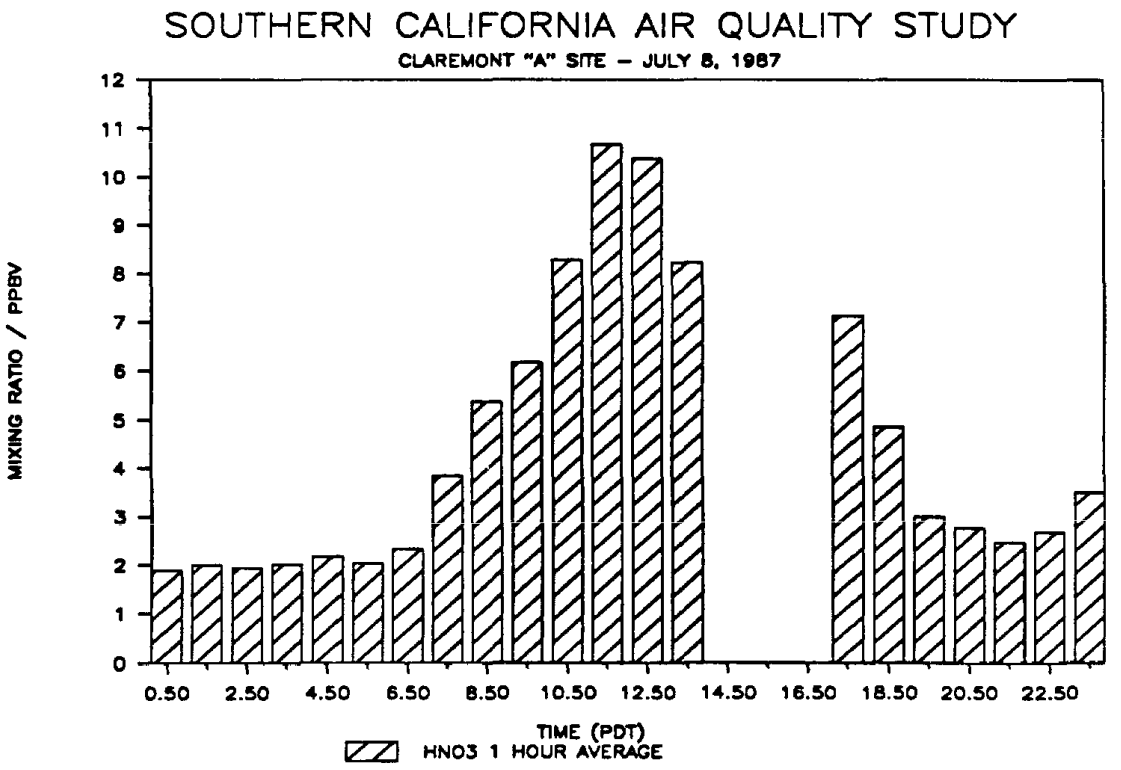
SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 8, 1987
MIXING RATIO / PPBV
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TIME (PDT)
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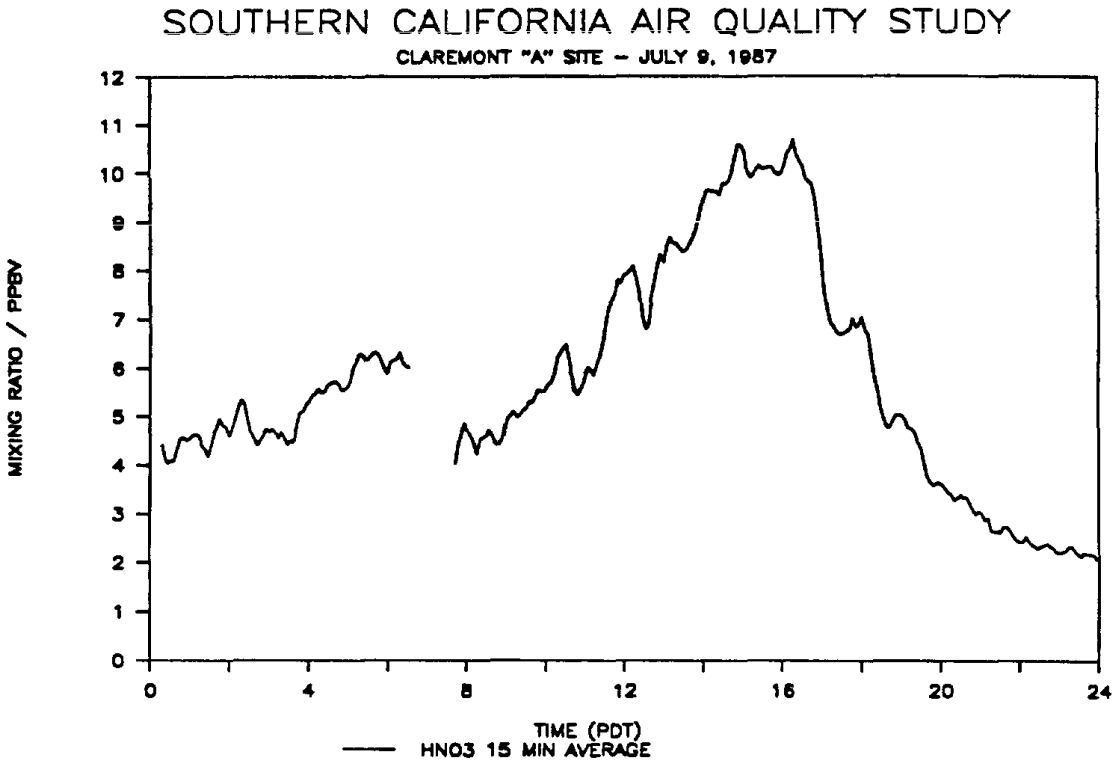
SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 9, 1987
MIXING RATIO / PPBV
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TIME (PDT)
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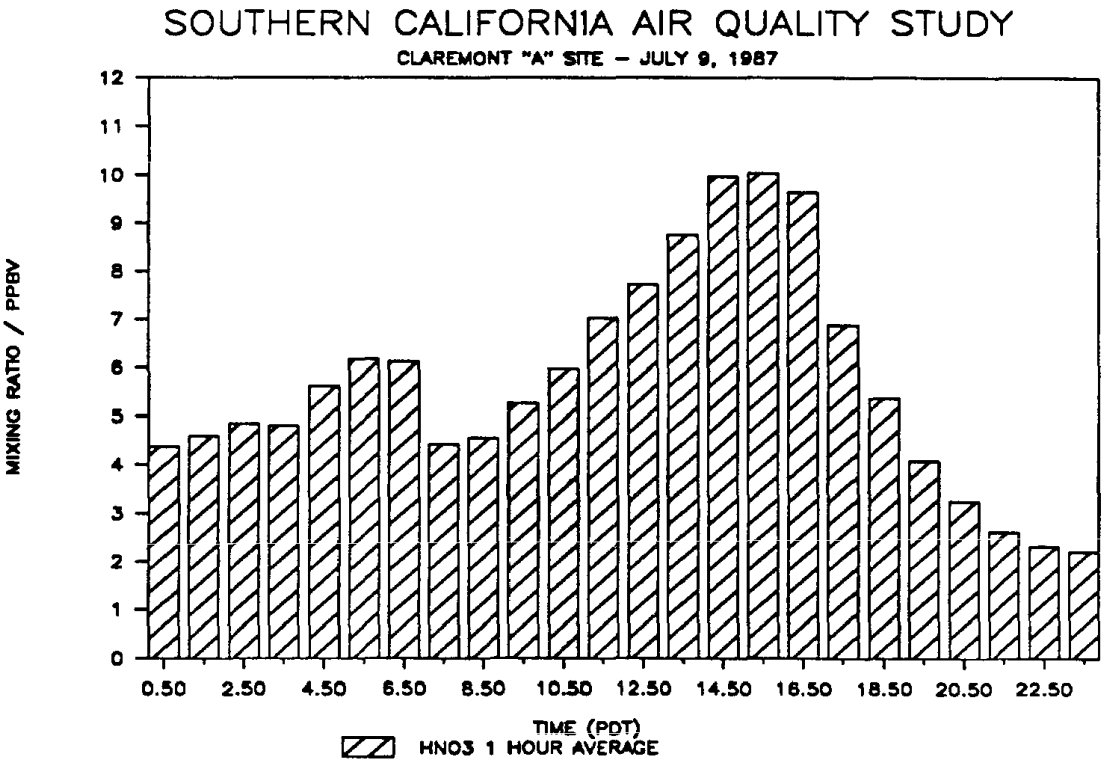
SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 9, 1987
MIXING RATIO / PPBV
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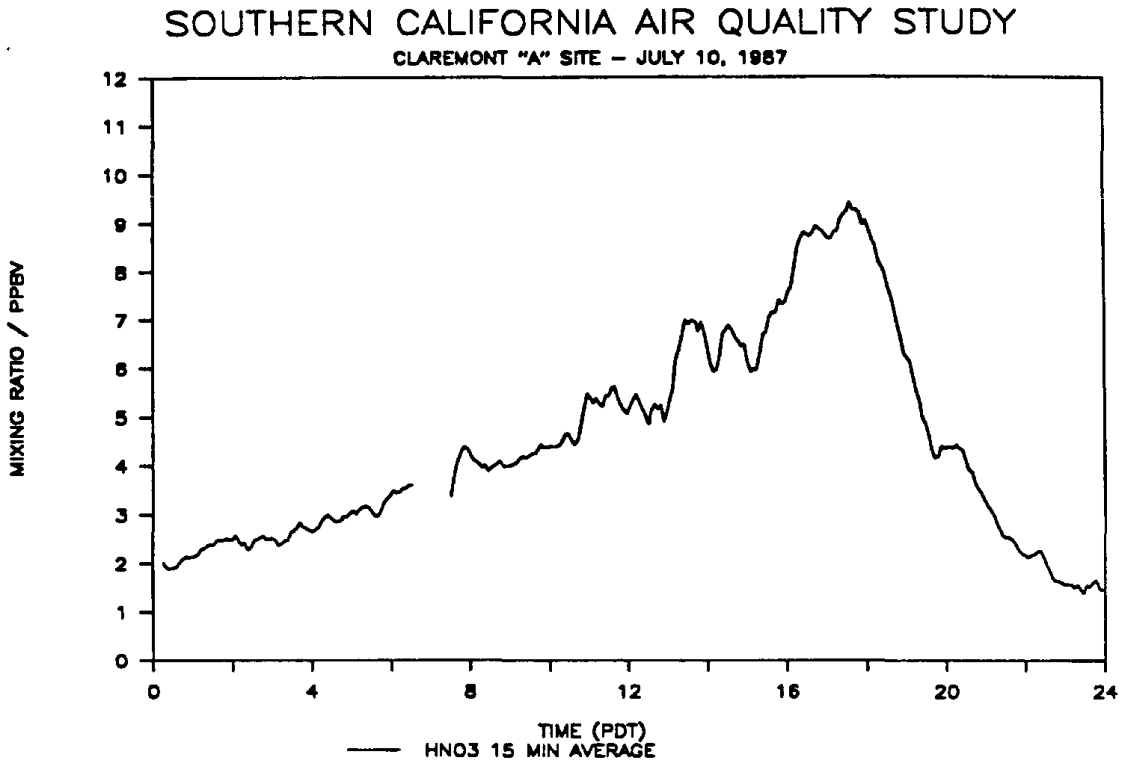
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 10, 1987
MIXING RATIO / PPBV
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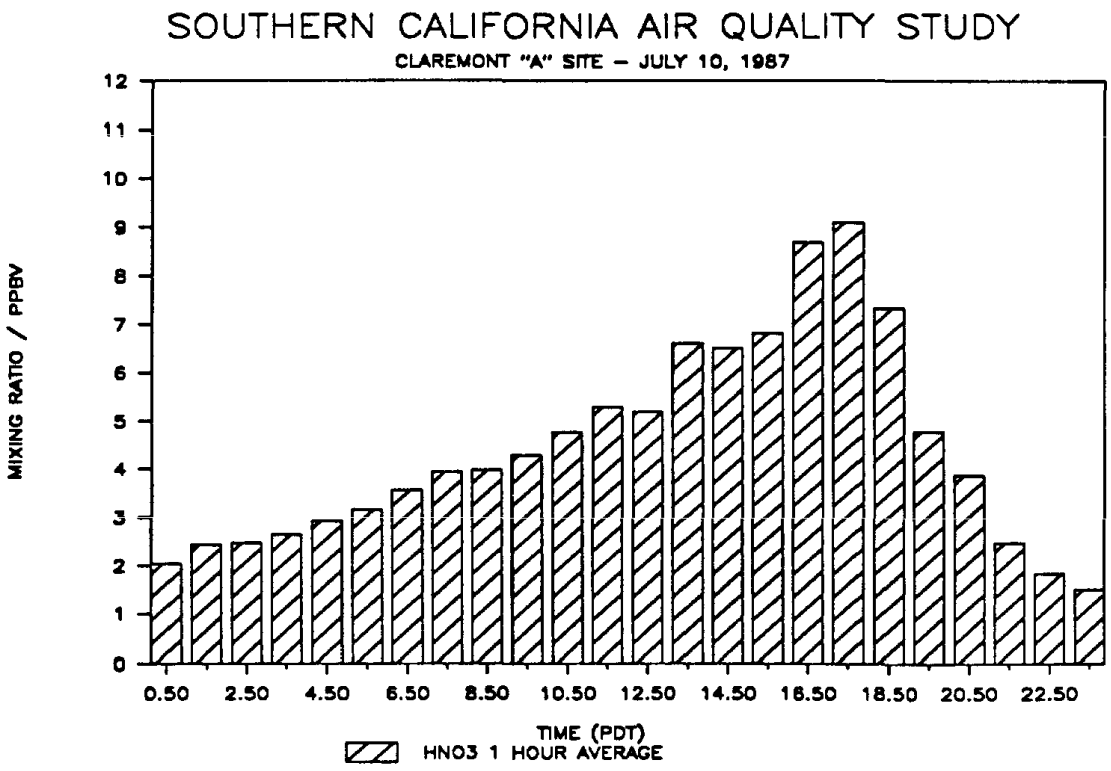
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 10, 1987
MIXING RATIO / PPBV
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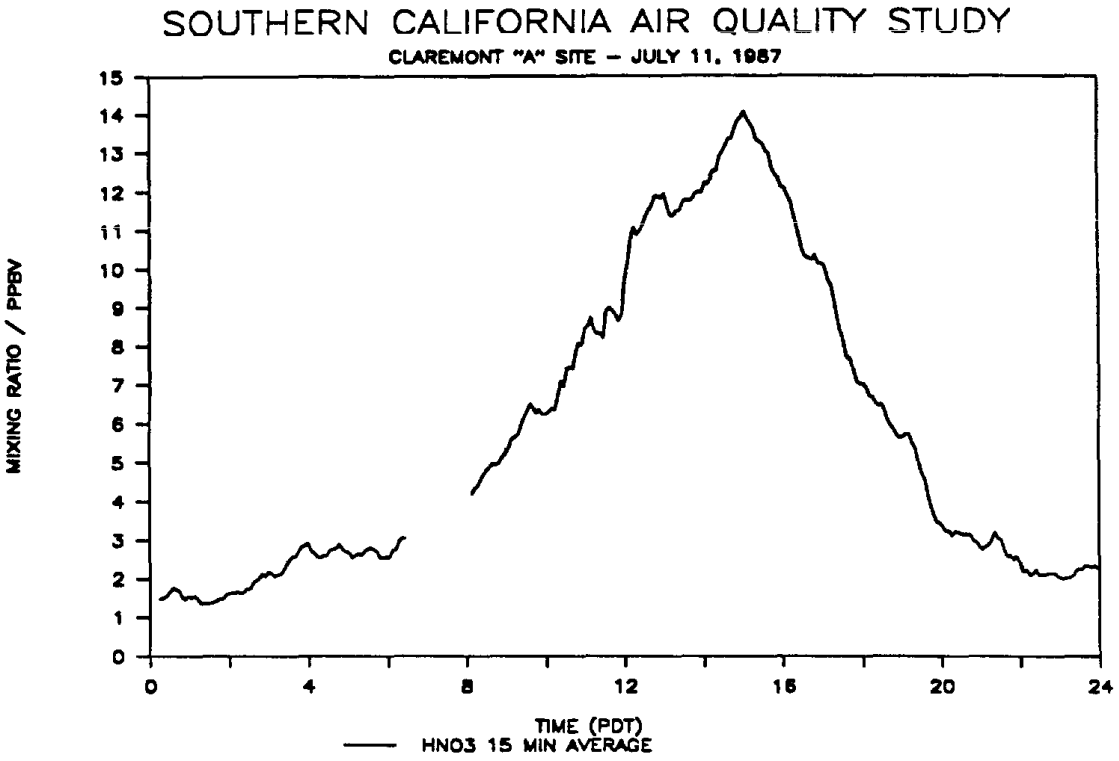
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 11, 1987
MIXING RATIO / PPBV
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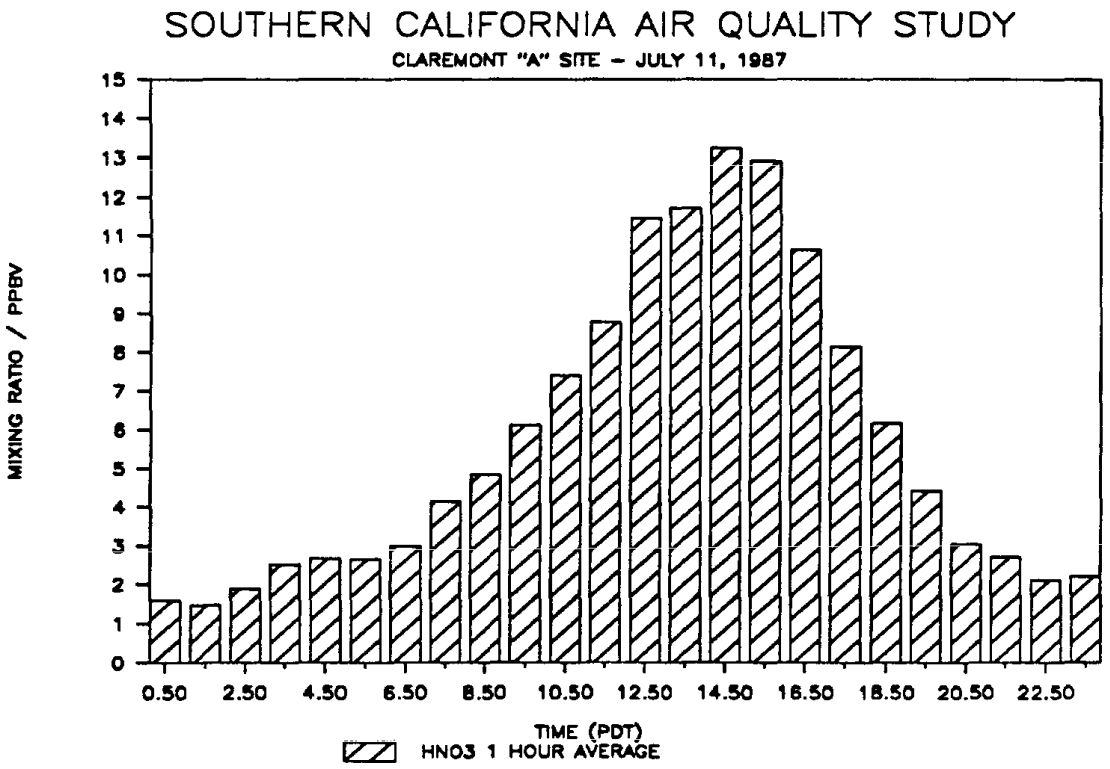
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 11, 1987
MIXING RATIO / PPBV
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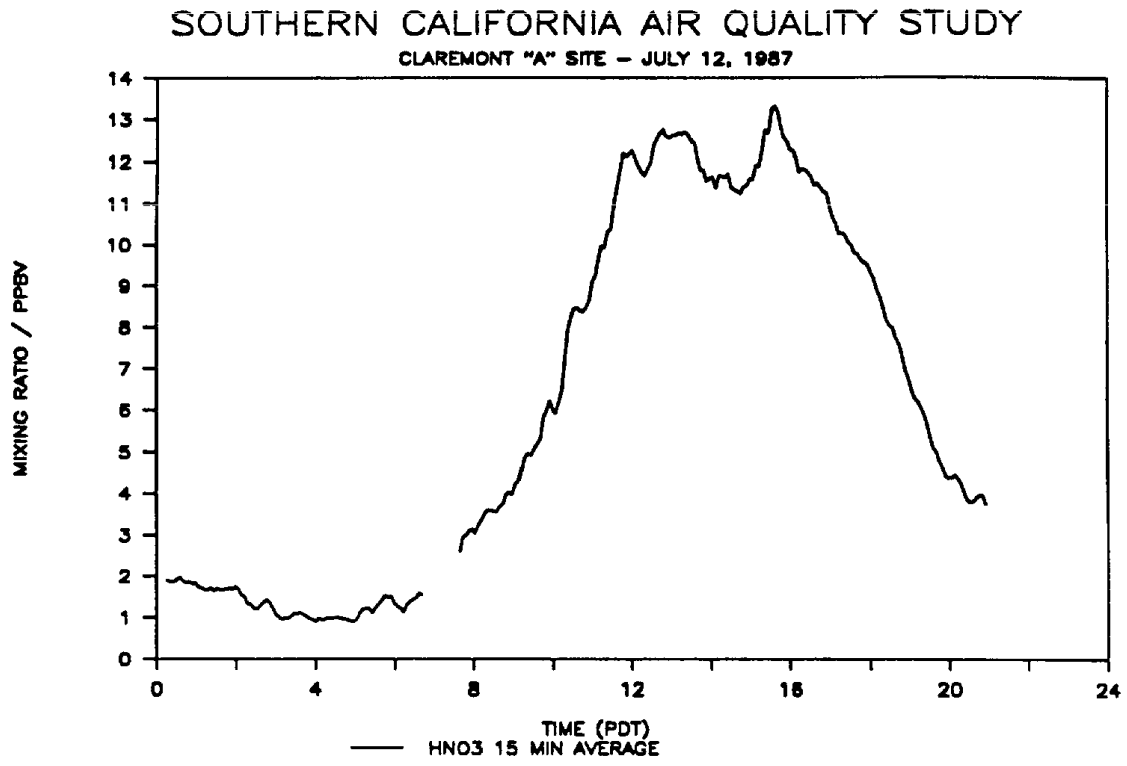
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 12, 1987
MIXING RATIO / PPBV
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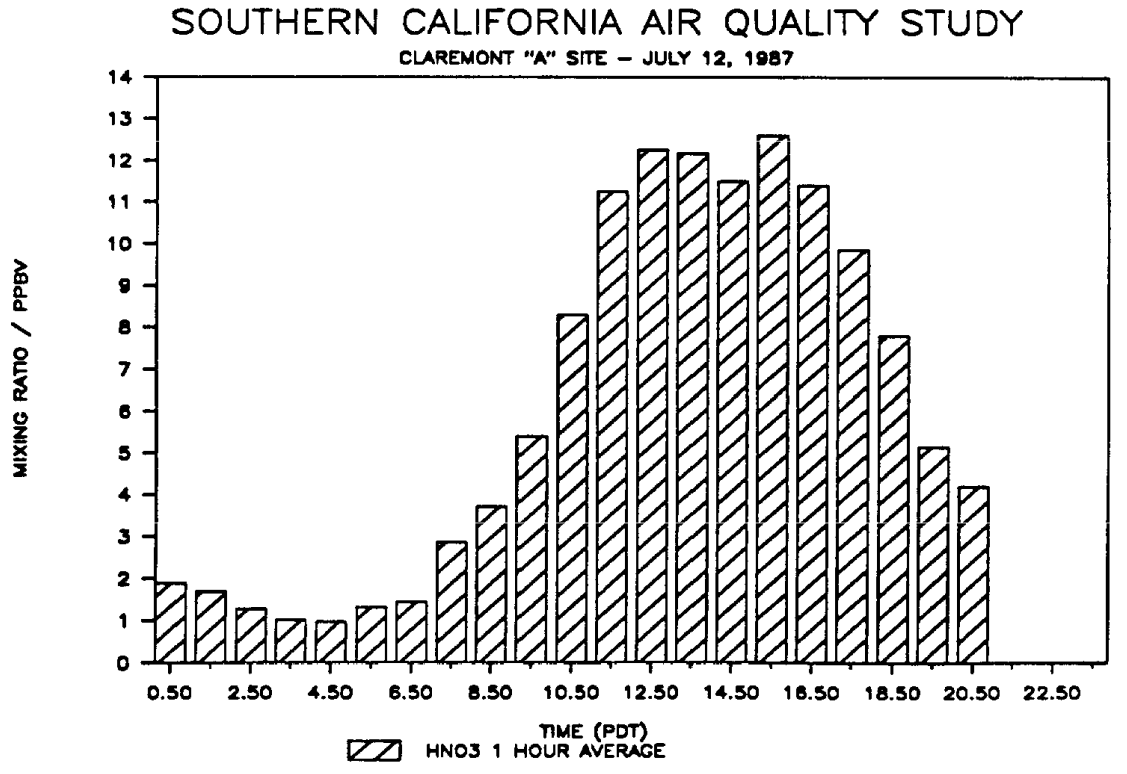
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 12, 1987
MIXING RATIO / PPBV
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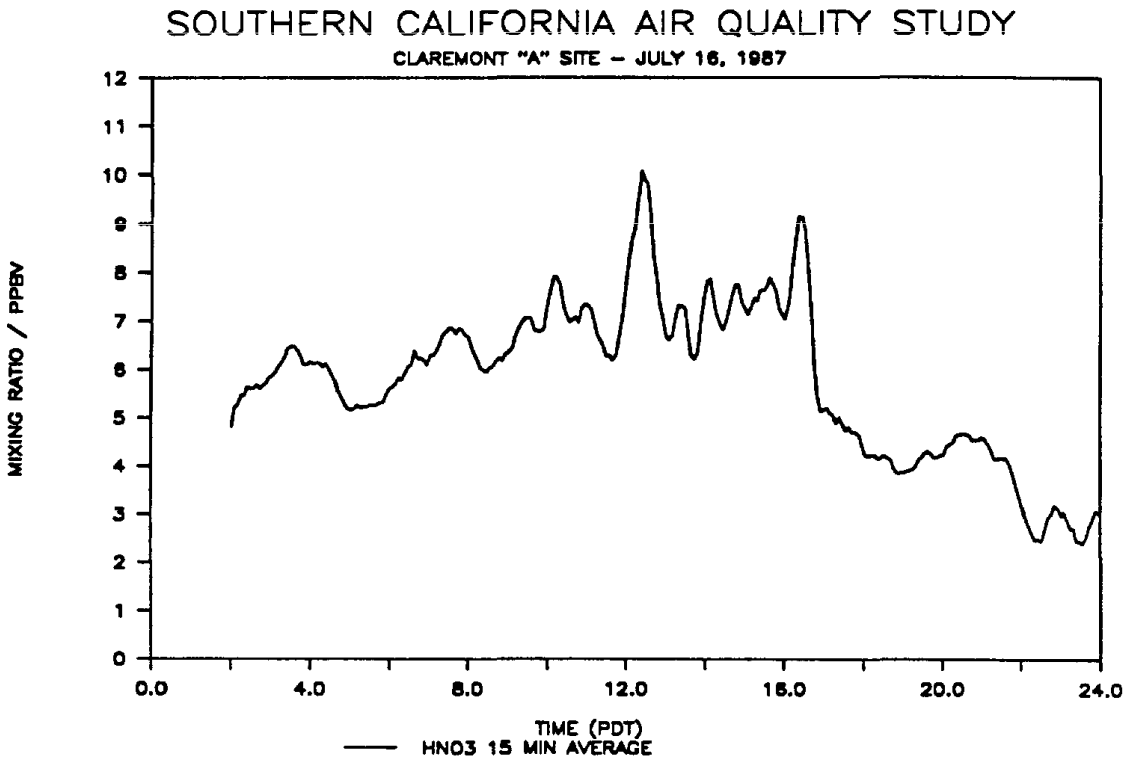
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 16, 1987
MIXING RATIO / PPBV
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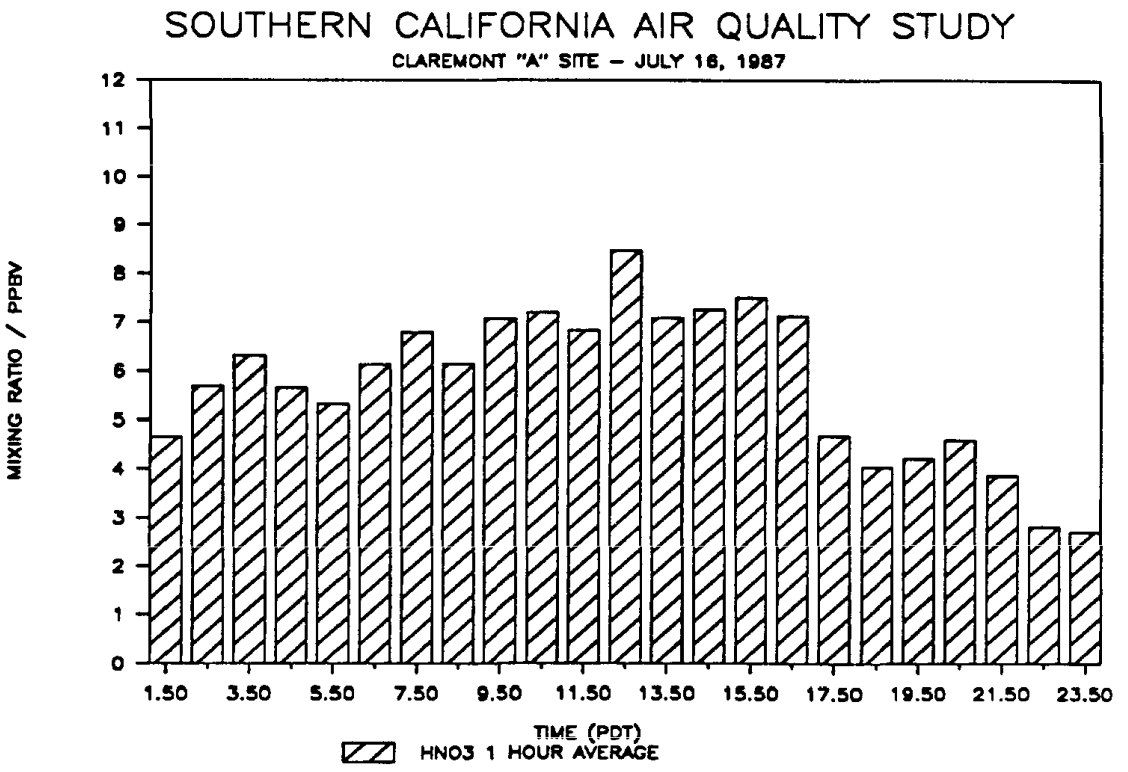
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 16, 1987
MIXING RATIO / PPBV
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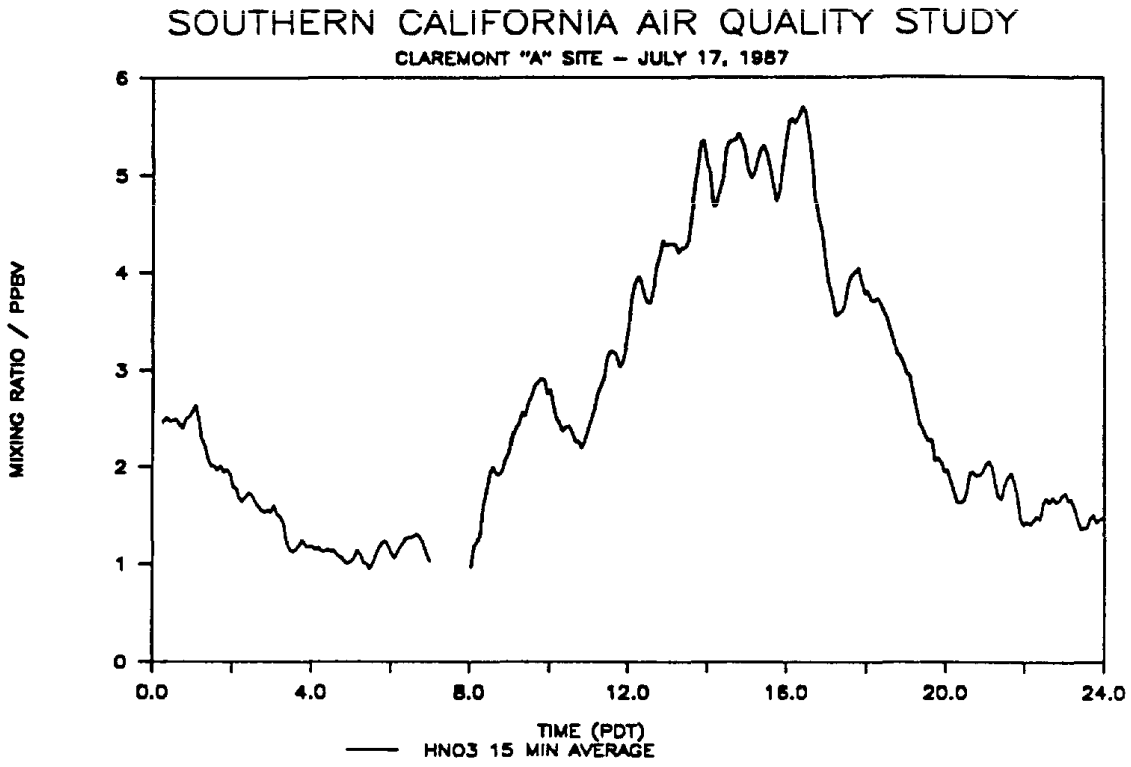
TIME (PDT)
HNO3 1 HOUR AVERAGE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MIXING RATIO / PPBV
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TIME (PDT)
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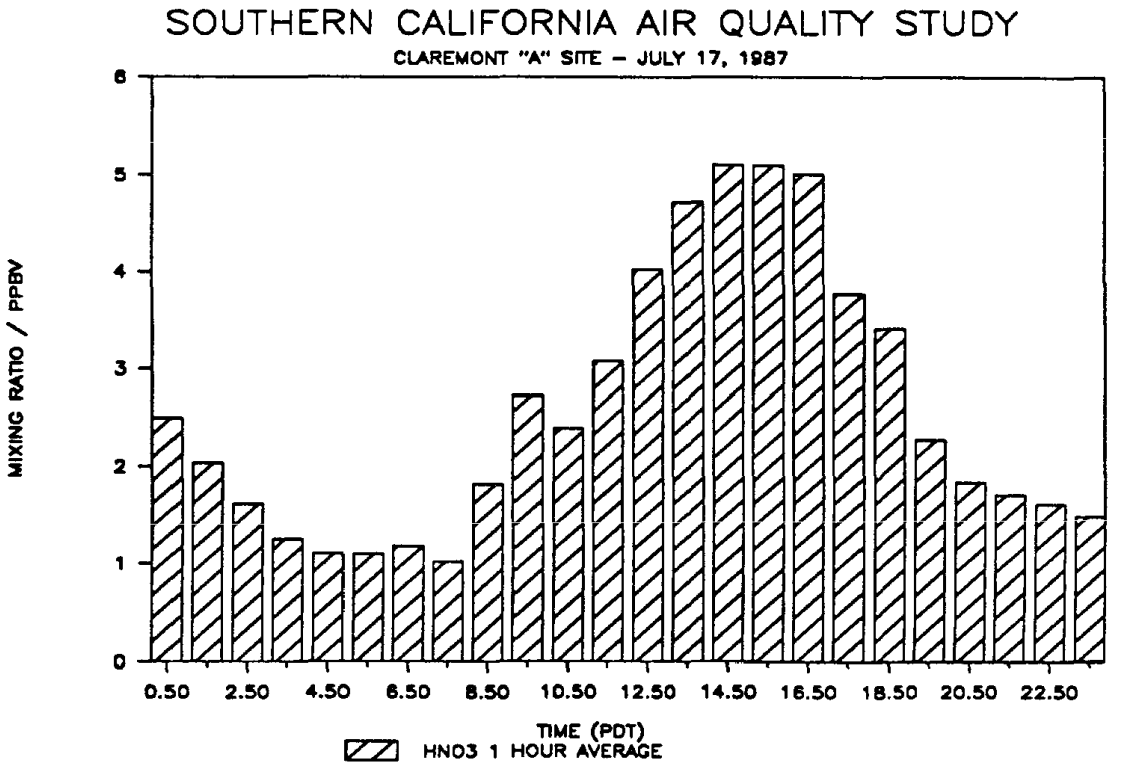
SOUTHERN CALIFORNIA AIR QUALITY STUDY
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MIXING RATIO / PPBV
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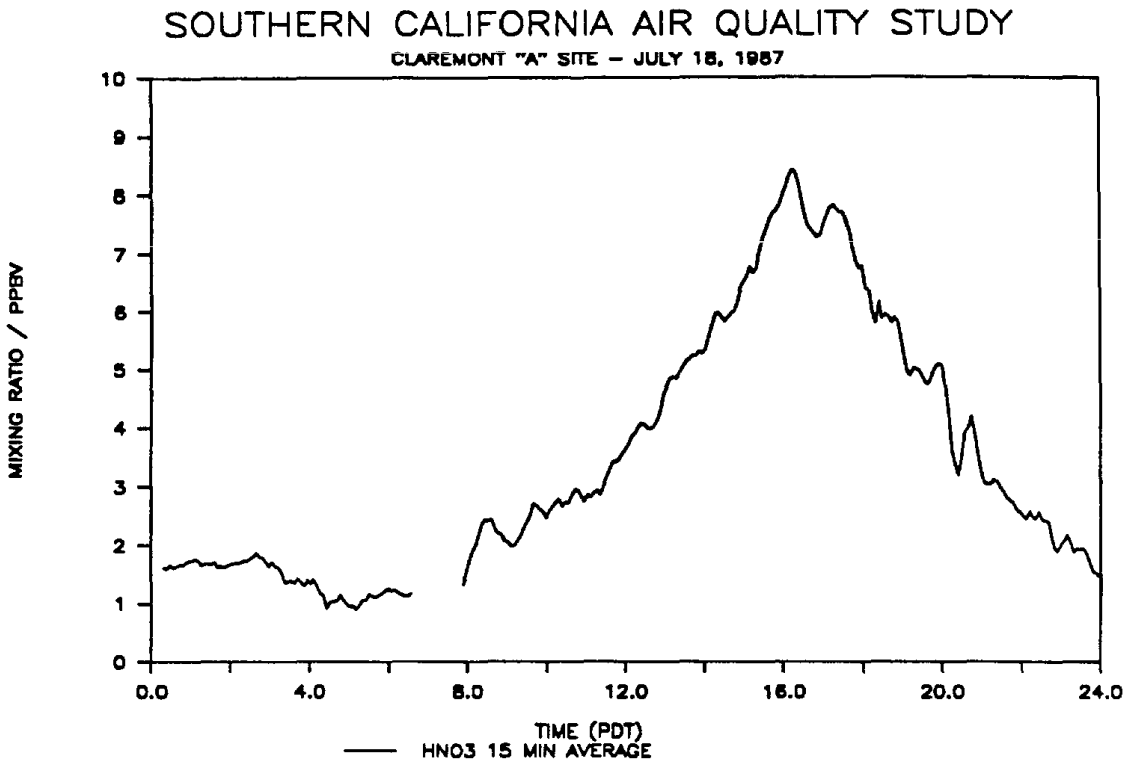
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 18, 1987
MIXING RATIO / PPBV
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TIME (PDT)
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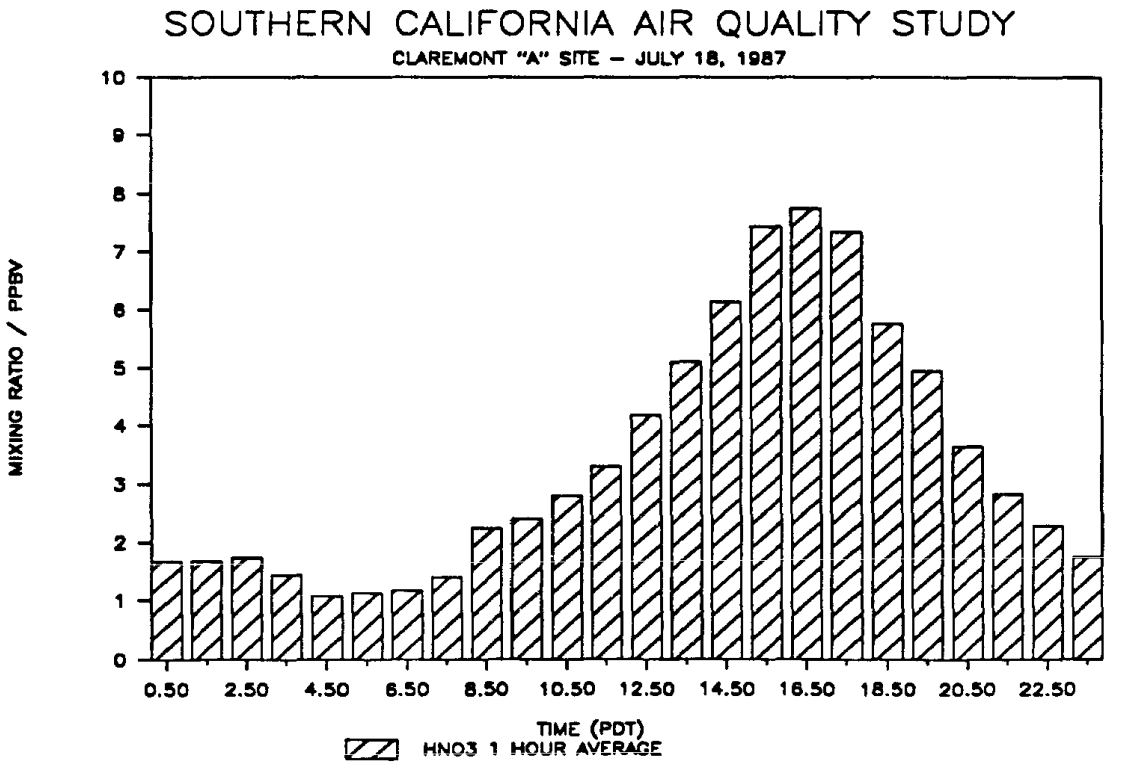
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CLAREMONT "A" SITE – JULY 18, 1987
MIXING RATIO / PPBV
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TIME (PDT)
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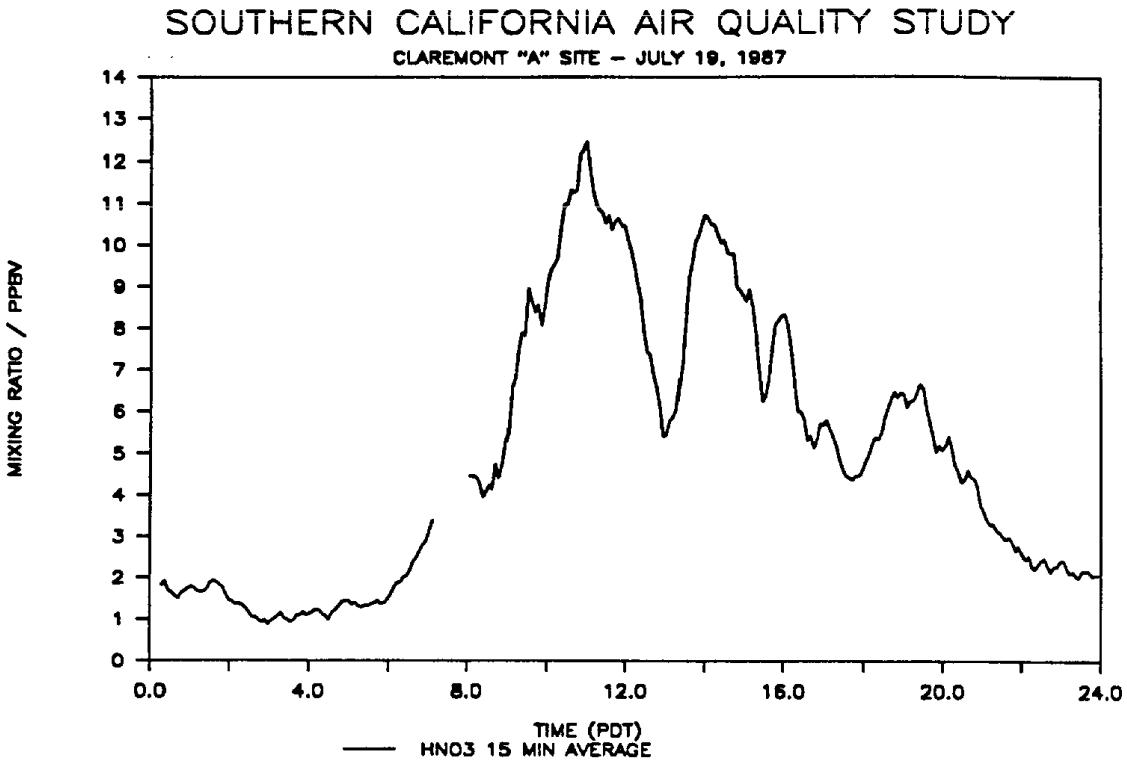
SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 19, 1987
MIXING RATIO / PPBV
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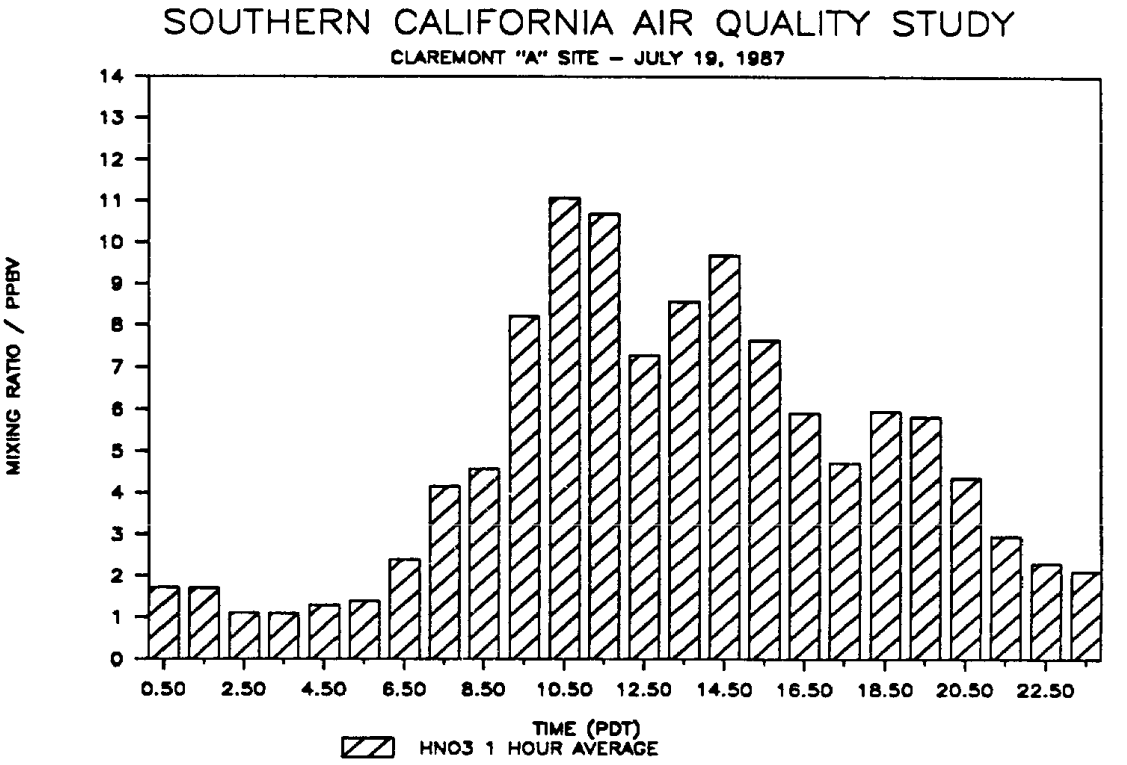
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 19, 1987
MIXING RATIO / PPBV
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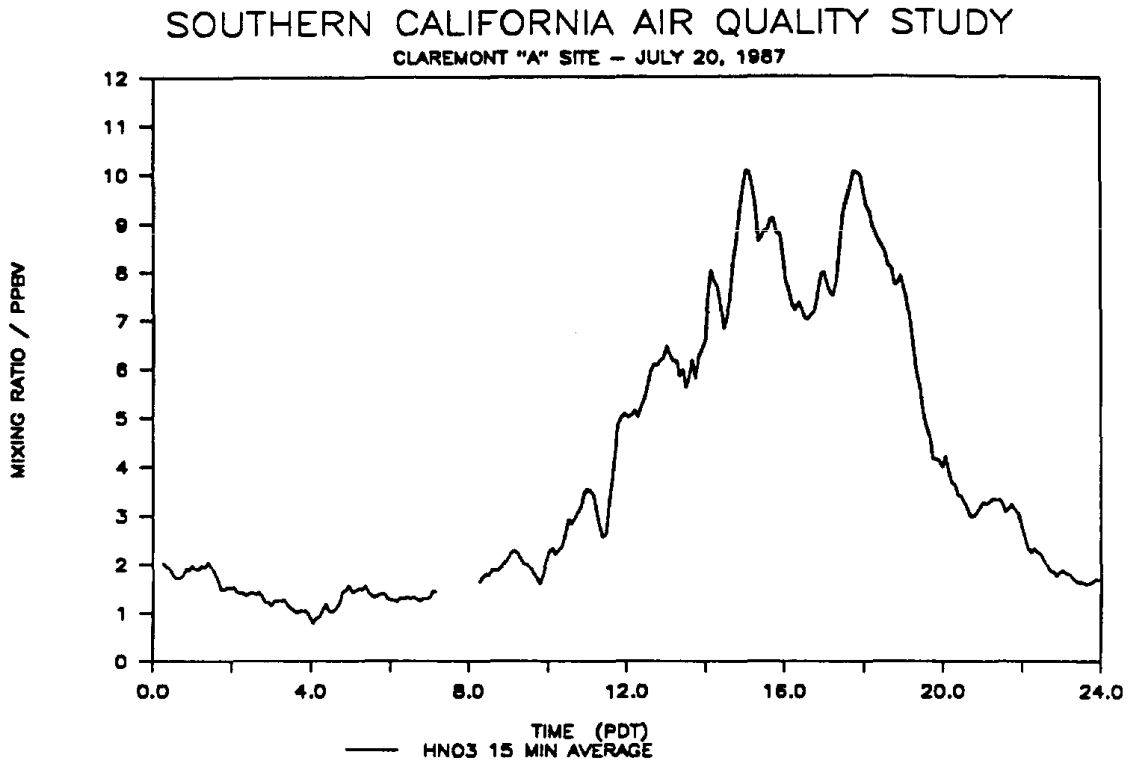
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 20, 1987
MIXING RATIO / PPBV
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TIME (PDT)
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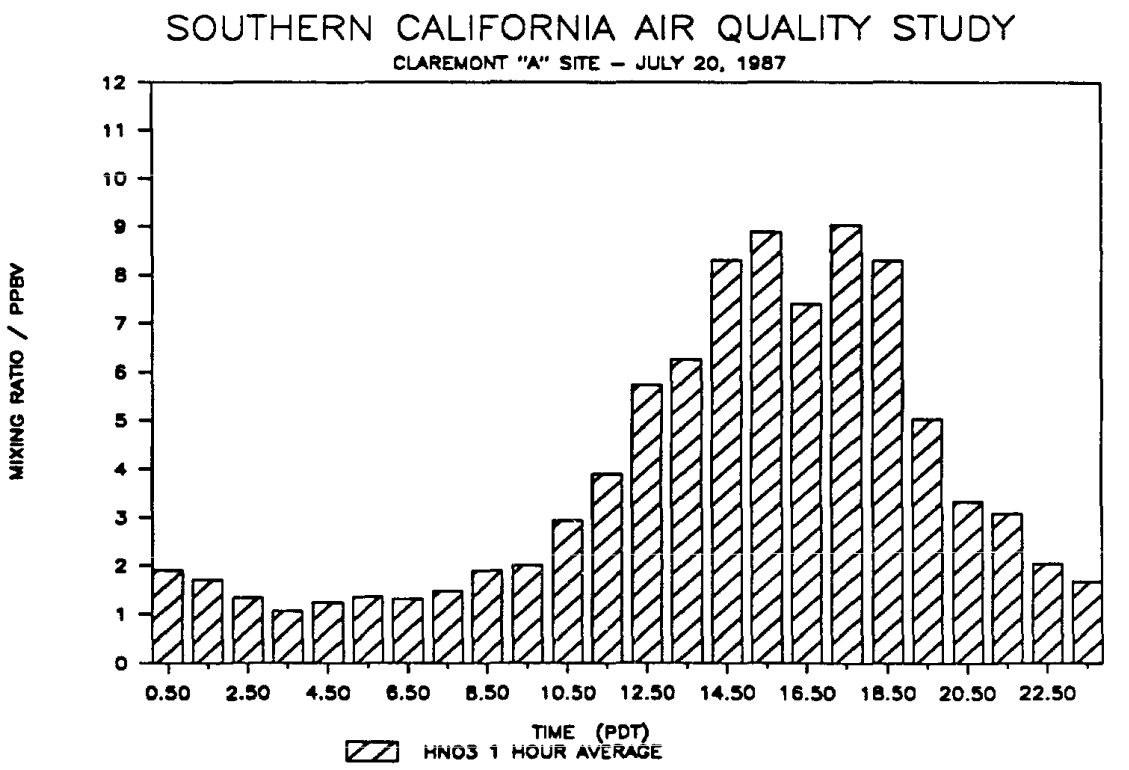
SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 20, 1987
MIXING RATIO / PPBV
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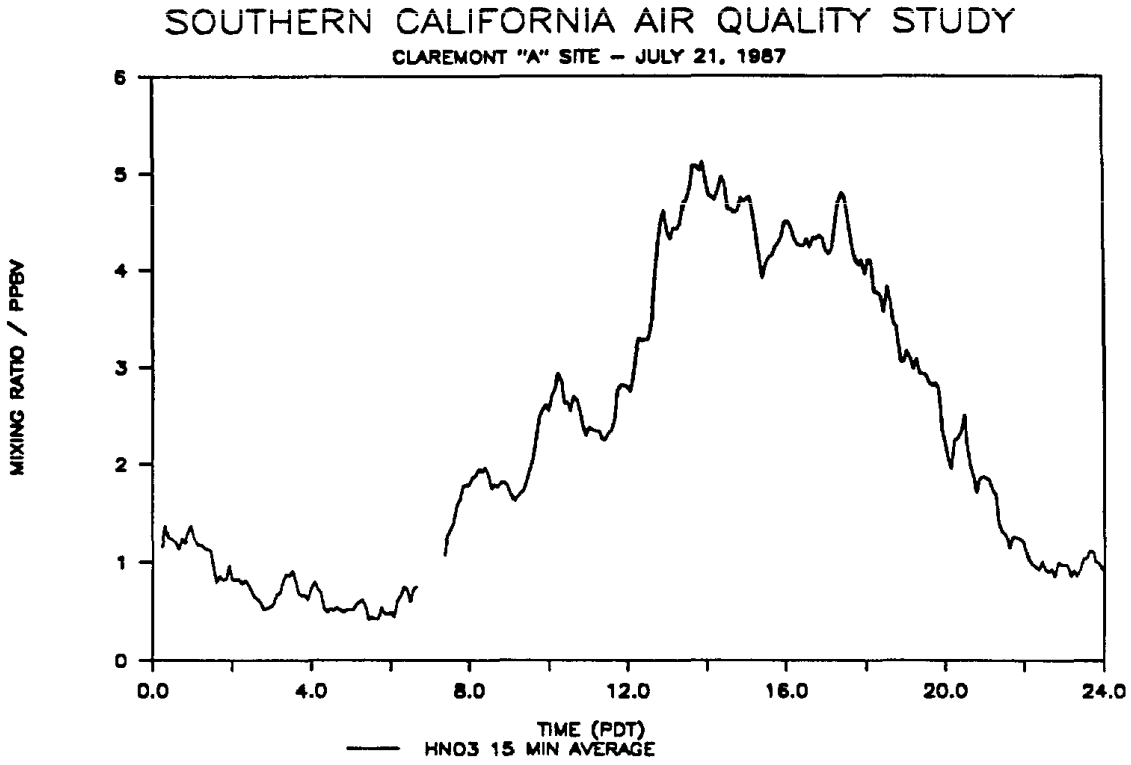
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE - JULY 21, 1987
MIXING RATIO / PPBV
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TIME (PDT)
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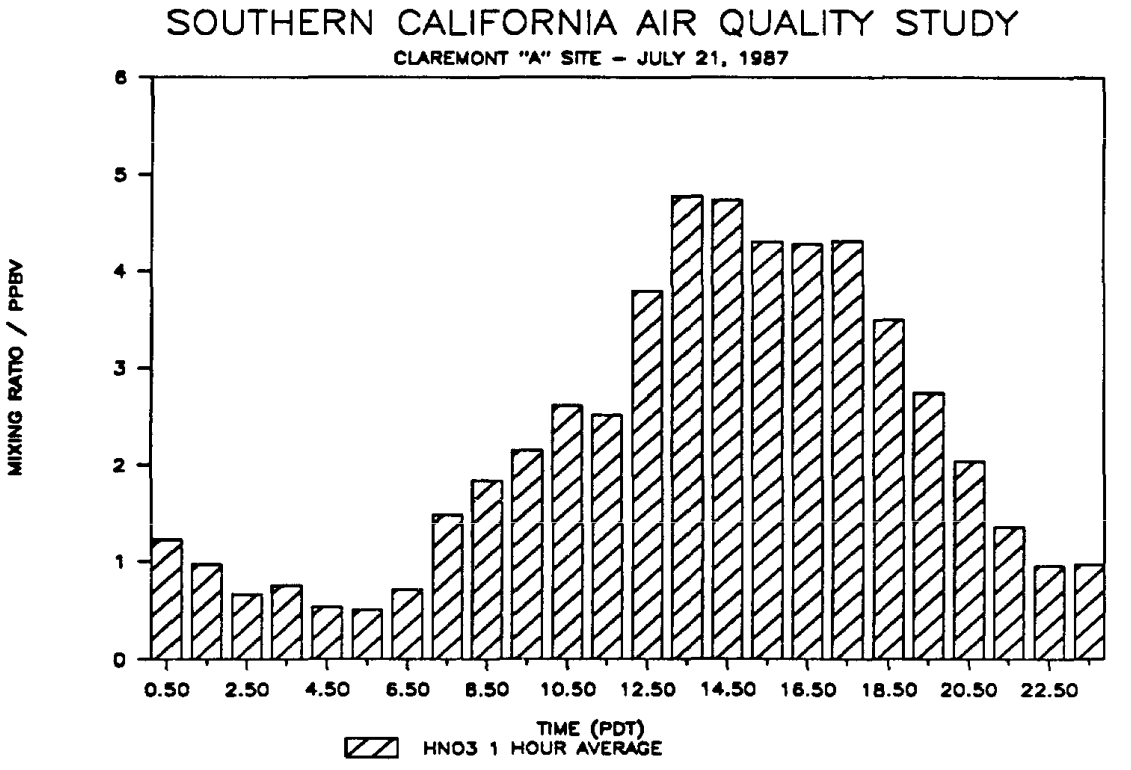
SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE - JULY 21, 1987
MIXING RATIO / PPBV
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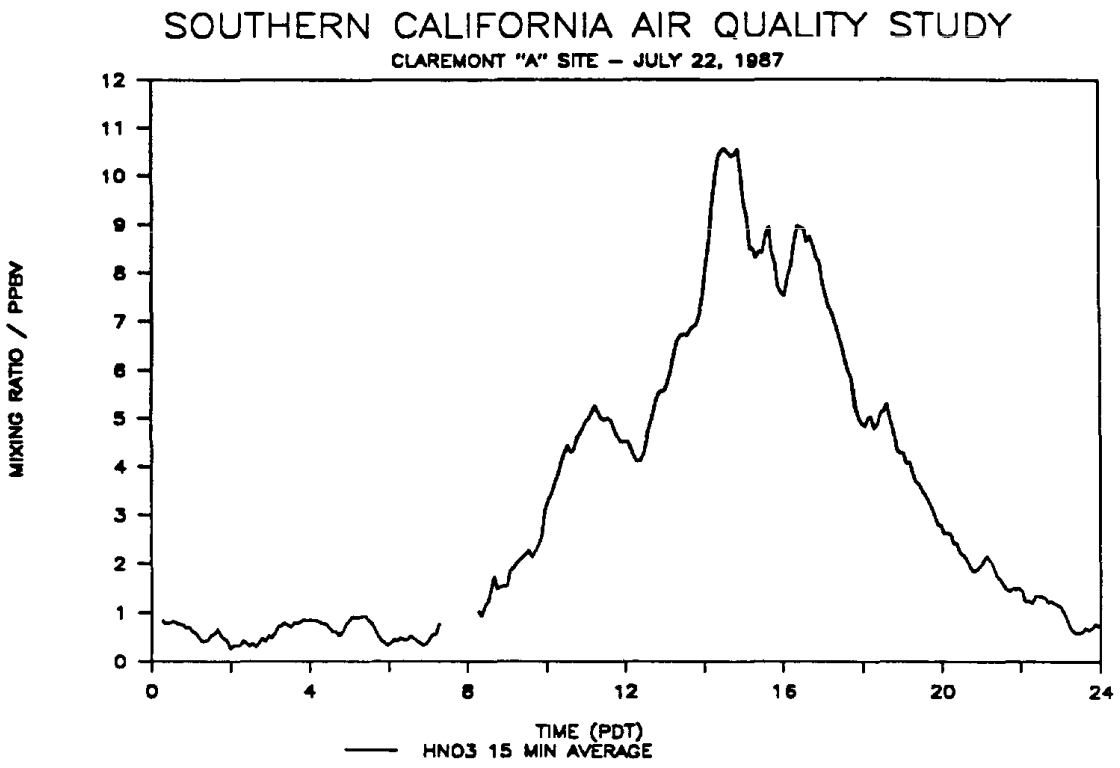
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 22, 1987
MIXING RATIO / PPBV
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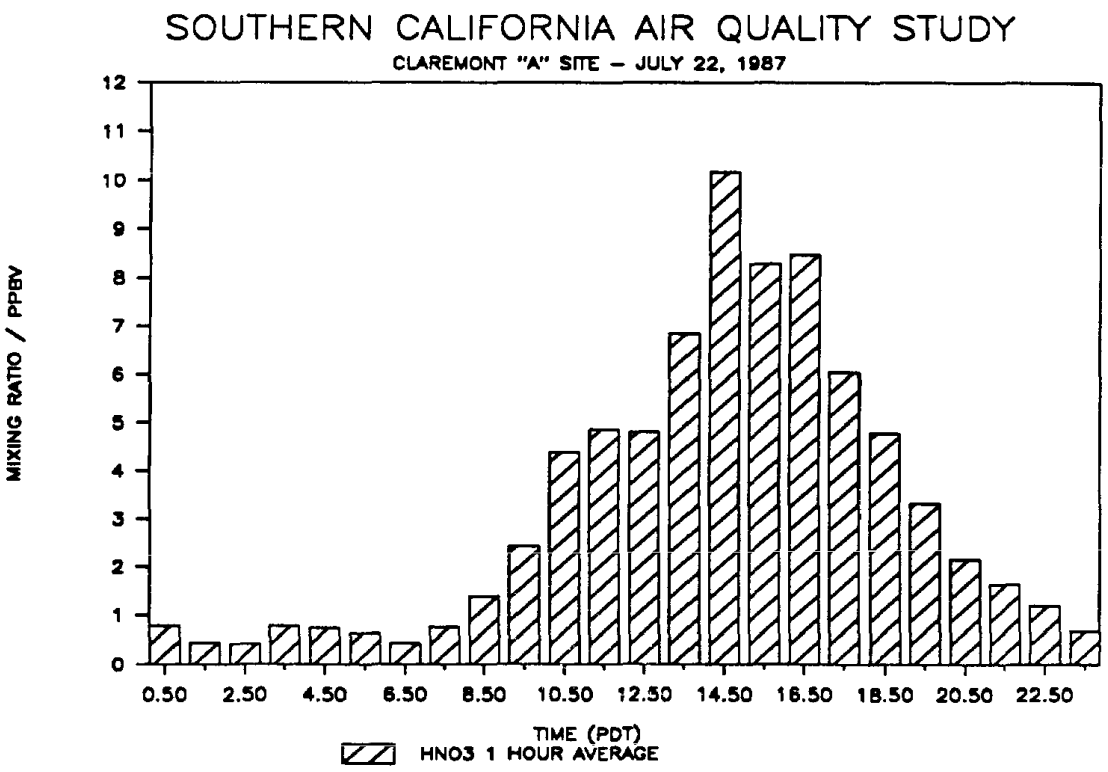
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 22, 1987
MIXING RATIO / PPBV
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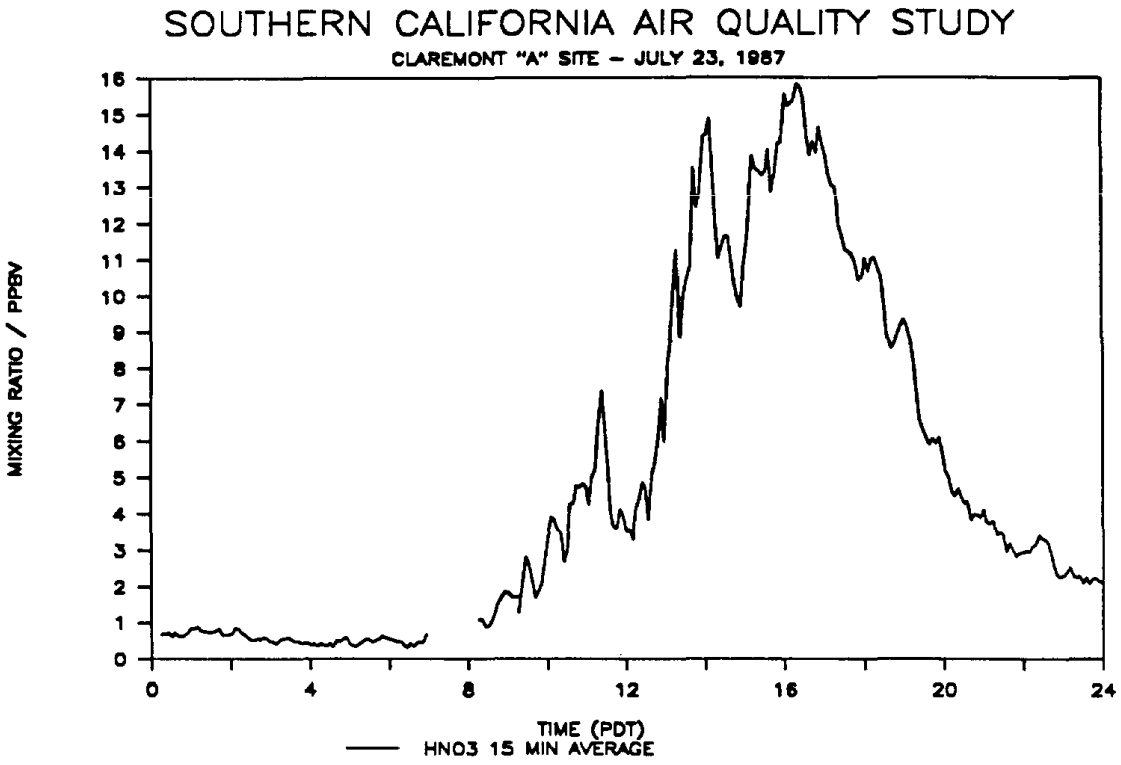
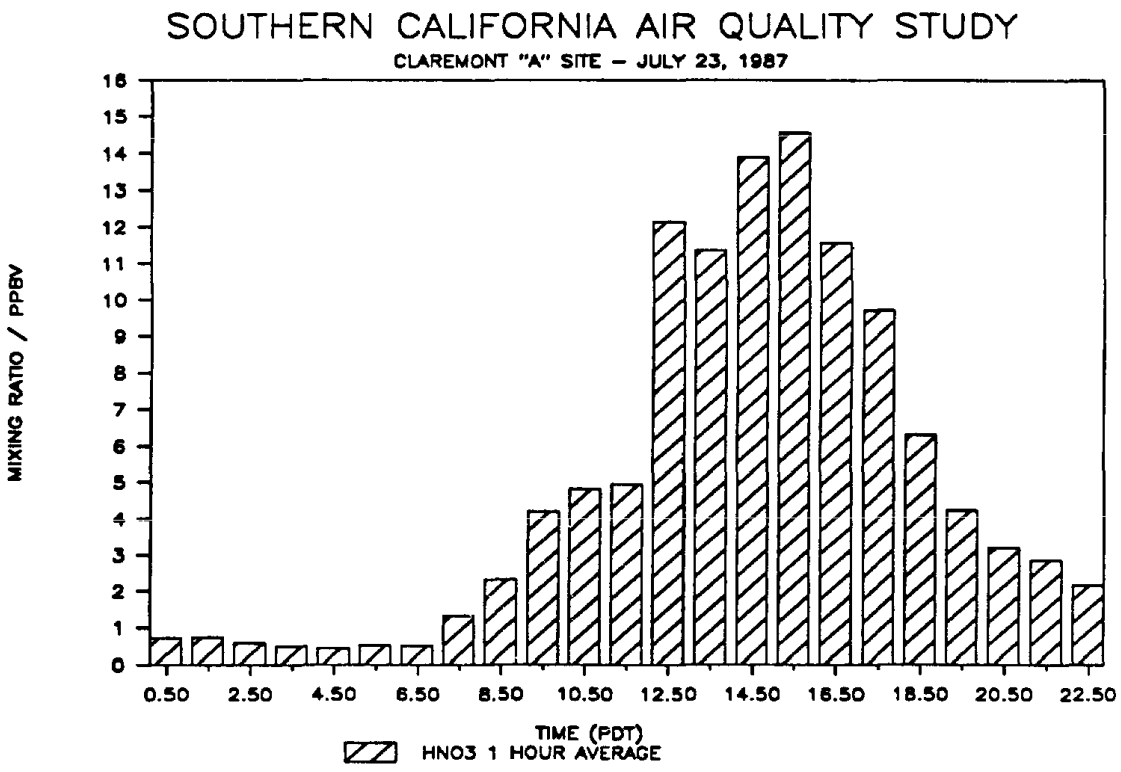
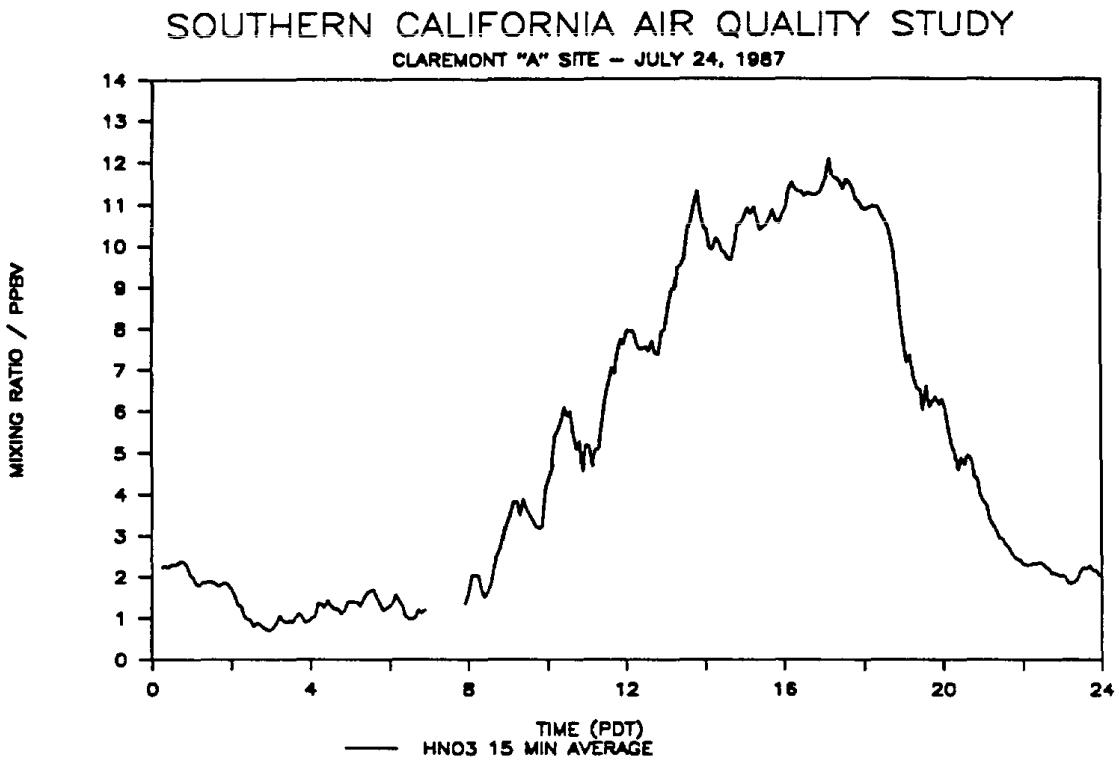
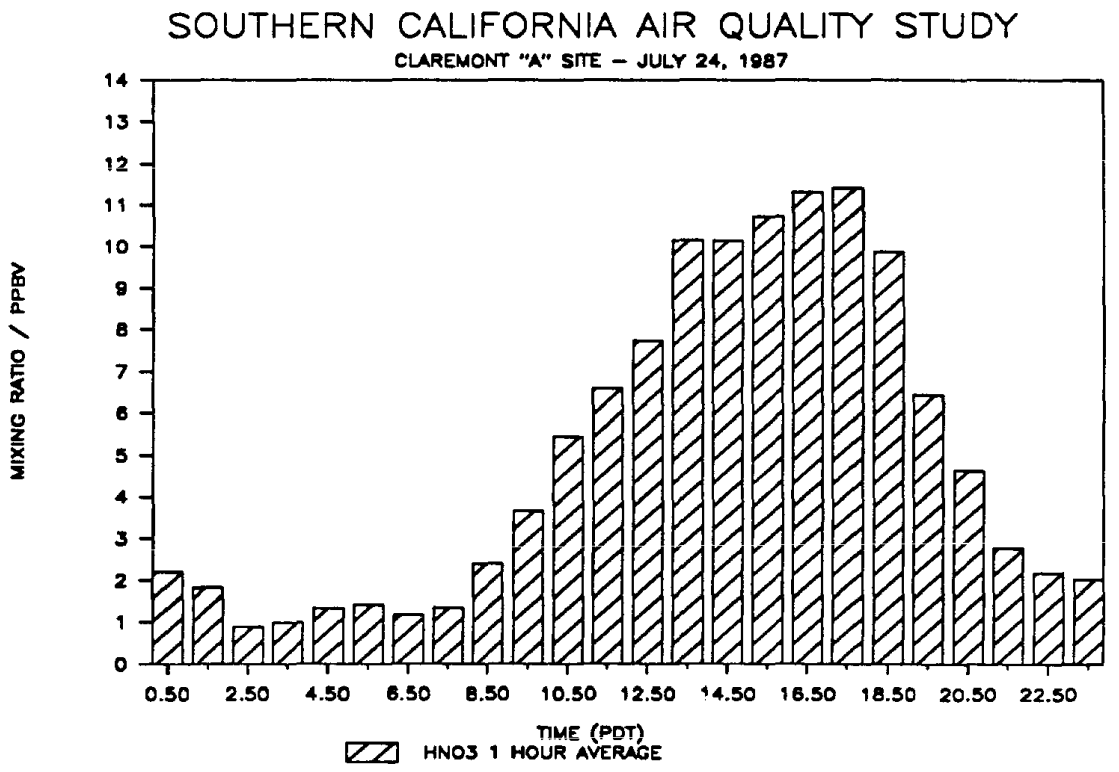
TIME (PDT)
HNO3 1 HOUR AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 23, 1987
MIXING RATIO / PPBV
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
0
4
8
12
16
20
24
TIME (PDT)
HNO3 15 MIN AVERAGE


SOUTHERN CALIFORNIA AIR QUALITY STUDY
CLAREMONT "A" SITE – JULY 23, 1987
MIXING RATIO / PPBV
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
0.50
2.50
4.50
6.50
8.50
10.50
12.50
14.50
16.50
18.50
20.50
22.50
TIME (PDT)
HNO3 1 HOUR AVERAGE





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15. Supplementary Notes

16. Abstract (Limit: 200 words)

The tunable diode laser absorption spectrometer was used during the Southern California Air Quality Study to continuously measure the concentration of gas-phase nitric acid at Claremont, California. The measurements were made from June 15 through July 24, 1987. The detection limit was less than 0.1 ppbv for 1 minute averaging times. The data are presented in 1-minute, 15-minute, and 1-hour averages. Data recovery was better than 90%.

The diurnal behavior of nitric acid was quite regular. The maximum concentrations occurred between 1200 and 1800 each day. The daily maximum varied considerably during the study from a low of 5 ppbv on July 21 to a high of 24 ppbv on June 25. Nighttime minima occured between 2200 and 0600 and were generally in the range 0.5 to 1 ppbv.

17. Document Analysis a. Descriptors

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Spectrometers

b. Identifiers/Open-Ended Terms

Southern California Air Quality Study

c. COSATI Field/Group 0402, 0702, 2005

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