STUDIES OF DRY ACID DEPOSITION IN THE SOUTH COAST AIR BASIN: TUNABLE DIODE LASER ABSORPTION SPECTROMETER MEASUREMENTS OF HNO_3, HCHO AND NO_2 AND LUMINOL NO_2 MEASUREMENTS IN CLAREMONT CA., SEPTEMBER 1985

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by

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EXECUTIVE SUMMARY

The major components of acid deposition, nitric acid (HNO_3) and sulfuric acid (H_2SO_4) are formed by the oxidation of the primary pollutants NO_x and SO_x. In the South Coast Air Basin HNO_3 is particularly important because of the higher ratios of NO_x to SO_x emissions relative to those in central and eastern U.S.A. In addition, due to the relatively dry climate in the Basin, dry deposition is though to contribute the majority of the acid deposition. HNO_3 is also important because it is one of the final oxidation products in the formation of photochemical (urban) smog. Measurements of gas phase HNO_3 concentrations are therefore needed for understanding both of these problems but are largely lacking. In September, 1985, the Air Resources Board organized an inter-comparison of methods for measuring gas phase HNO_3 in ambient air.

Tunable diode laser absorption spectrometry (TDLAS) affords an attractive method for such measurements. It is a passive method applicable to virtually all gases of atmospheric interest. Because of its very high resolution the method provides unequivocal identification of the gas of interest with no interferences from other gases. It therefore can serve as a standard against which other, less definitive methods can be compared. It provides real time measurements with a time resolution of less than one minute and detection limits in the sub ppbv range.

Two TDLAS systems were used in the intercomparision study, one provided by Unisearch Associates and the other by the Atmospheric Environment Service of Canada (AES). Comparisons were made with methods using filter packs, denuders, chemiluminescence and Fourier Transform Infra Red (FTIR) spectroscopy.

The Unisearch TDLAS system was also used to measure formaldehyde (HCHO). Formaldehyde mixing ratio measurements provide information on the hydrocarbon oxidation level of the ambient atmosphere. Nitrogen dioxide (NO_2) was measured by the AES TDLAS system and by the LUMINOx, LMA-3 which is a new, small, simple and extremely sensitive instrument for NO_2 measurements. The importance of these measurements is the role that NO_2 plays as the direct

precursor to gas phase HNO_3.

The measurement period was between September 11- 19, 1985. Data was obtained over 5 minute averaging periods and also reduced to one hour averages. The data coverage of these one hour averages were better than 90% for HNO_3 over this period, 94% for NO_2 by the TDLAS method and 98% for the LUMINOx instrument. The coverage for HCHO by the Unisearch TDLAS was 89%. Virtually complete coverage was obtained for the 5 daily integration periods used for intercomparison with the other techniques.

Agreement between the HNO_3 measurements obtained by the 2 TDLAS systems were within the combined experimental errors with the largest deviations occurring when the ambient concentrations were changing rapidly.

The diurnal behavior of the HNO_3 concentrations were quite regular. The maximum concentrations occurred between 15:00 and 18:00 each day. Maximum concentrations were observed on September 14th when values as high as 18 ppbv were observed for 5 minute averages.

The measurements of NO_2 made by the TDLAS and the LUMINOx methods agreed within the combined uncertainties over most of the range of concentrations encountered. The LUMINOx instrument did, however give somewhat higher values at high NO_2 concentrations and somewhat lower values at low concentrations. The effect at low concentrations have subsequently been traced to a small non-linear response of the Luminol instrument at low concentrations. The instrument has now been modified to correct this difficulty.

The measurements made with the LUMINOx instrument were 35-50% higher than the TDLAS values at periods around 22:00 on two evenings when the concentrations were more than 120 ppbv. Since the LUMINOx instrument does not provide the same specificity as the TDLAS method, the most likely explanation is that the LUMINOx instrument is also responding to some other constituent(s) present in the highly polluted air at night.

Both instruments indicate the same diurnal behaviour with the NO_2 mixing ratio

exhibiting two maxima during each 24 hr period; one centered at about 10:00 and the other centered at 22:00.

The HCHO concentrations generally maximizes during periods of high pollution as indicated by maxima in the NO_2 mixing ratio. As with NO_2 and HNO_3 the maximum HCHO was observed during the period September 12th through 14th. After that time the HCHO levels were much lower and continued to decrease until the end of the measurement period. The mixing ratios do not show strong diurnal dependence but there is some indication for maxima near local noon.

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1. INTRODUCTION

The Kapiloff Acid Deposition Act of 1982 (California Health and Safety Code, Sections 39010.5, 39010.6, 39900 et seq.) requires the California Air Resources Board to design and operate a comprehensive research program to determine the nature, extent and potential effects of acid deposition in California. Furthermore, Senate Bill 55 requires the Air Resources Board to give priority in its research and monitoring program to the South Coast Air Basin. A monitoring programme to measure wet deposition throughout California has been established. However, some scientists estimate that dry deposition in California may be 5-15 times more important than wet deposition. In the South Coast Air Basin, with its dry climate and numerous sources of acid precursors, dry acid deposition is expected to be much more important than wet deposition. Despite these concerns, data documenting the nature and extent of dry acid deposition are scarce.

One of the most important parameters to be determined in assessing dry deposition is the concentration of the acidic species, H_2SO_4 and HNO_3 formed by the primary emissions of the precursor compounds SO_x and NO_x. Since the ratio of NO_x to SO_x emissions are probably higher in California than they are in eastern U.S.A. there is particular interest in measuring HNO_3 in the South Coast Air Basin.

In light of these concerns and the lack of adequate data, the Air Resources Board funded and co-ordinated a study in Claremont California during September 1985 to compare methods of sampling HNO_3 under ambient conditions. The methods included integrating samplers such as filter packs and denuder tubes as well as real time measurement techniques including a chemiluminescence technique, a Tunable Diode Laser Absorption Spectrometer (TDLAS) system and a long path Fourier Transport Infra Red (FTIR) instrument. The latter two, high resolution, spectroscopic methods provide direct, unequivocal identification of the measured species.

This report describes the results obtained by two Tunable Diode Laser Absorption spectrometer systems both of which measured HNO_3. One TDLAS system

also measured NO_2 and the other measured HCHO, which provides a measure of the oxidation state of the ambient air. This report also describes real time measurements of NO_2 obtained with a new Luminox chemiluminescence analyser.

2. THE TROPOSPHERIC AIR MONITORING SYSTEM (TAMS-2B)

2.1 Principal of the TDLAS System

Infrared absorption in the 2 to 15 micron region affords an attractive opportunity for measuring atmospheric trace gases. While virtually every gas of atmospheric interest absorbs in this spectral region the major gases, N_2 and O_2 do not. In fact, the absorption spectra for the trace gases are so rich that high resolution comparable to the line width, typically 2×10^{-3} cm^{-1}, is required to avoid mutual interferences.

The tunable diode laser absorption spectrometer (TDLAS) affords this high resolution and provides a number of additional advantages for atmospheric measurements. It is a passive technique with a response time of less than 1 minute, permitting "in situ", real time measurements. Because of its high resolution, it provides positive identification of the target species with no interferences from other atmospheric species. The resolution is sufficient to select one rotational-vibrational line of the target molecule. If an accidental resonance should happen to occur, it is readily identified by a change in line shape and another line can be chosen. Such interferences can also be checked by comparing absorptions for several lines. By utilizing a long path White cell, measurements can be made in the fractional ppbv level.

A mobile TDLAS system called TAMS (for Tropospheric Air Monitoring System) has been constructed and used for field measurements. The design and operation of an earlier system for the measurement of NO, NO_2 and HNO_3 has been described in detail in the literature (Hastie et al, Environmental Science and Technology 17, 352, 1984). The modified version of the system is briefly described below.

2.2 TAMS-2B: Optical and Electronic Sub-System

The present system, called TAMS-2B (Tropospheric Air Monitoring System-Dual Beam) was designed for simultaneous measuring of two species. Methods have been developed for the measurement of NO, NO_2, HNO_3, HCHO, NH_3 and H_2O_2 in the sub ppbv range.

A schematic of the optical system and a block diagram of the control and electronic systems of the TAMS-2B are shown in Figure 1. Up to four diode lasers are held in each laser source assembly (LSA-A and LSA-B). This allows any two of the target species to be monitored simultaneously as well as providing a back-up laser for each species in the event of failure in the field. During operation, the lasers are maintained to within $\pm$0.005 K of the operating temperature in the 20 to 60 K range. Temperature control is provided by the combination of a closed cycle helium cryocooler, a heater and a servo temperature control system. The current through the laser is supplied by a highly stabilized D.C. current control system. The current is modulated by a voltage from a multiple function generator and may be swept by voltages from either the function generator or the computer based data control system.

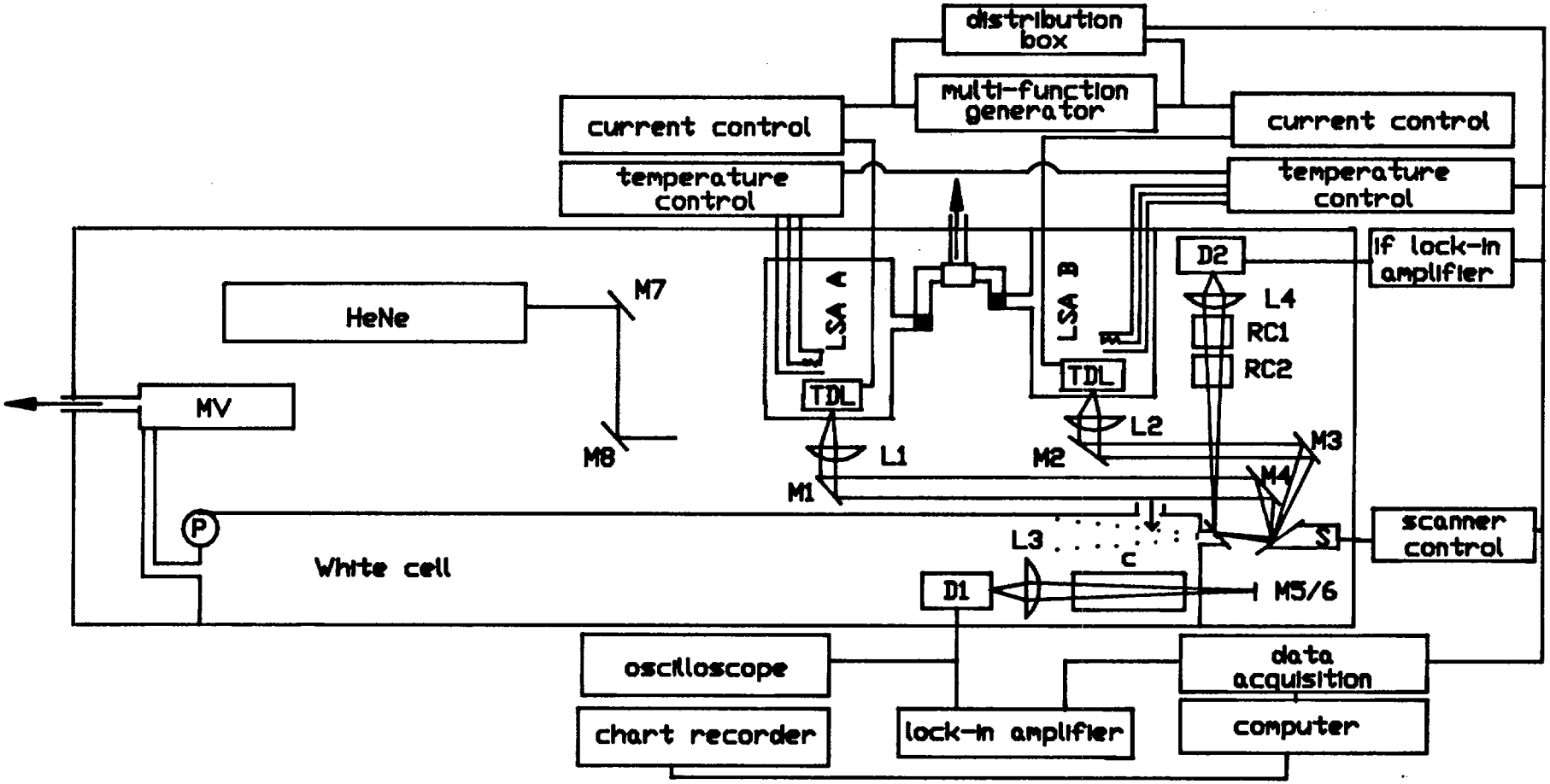
The laser radiation from each head is collected and focussed by the f/1.5 germanium meniscus lens, L1 and L2. A series of plane fold mirrors, M1 through M4, maneuver the beams onto scanning mirror S, which is switched to alternately permit the beam from each diode to enter the White cell.

The White cell is a Teflon lined 1 m long pyrex tube with an inside diameter of 11.5 cm. Sampled air enters through an inlet situated on the bottom of the tube 15 cm from one end and is exhausted from the cell through a 1 cm ID tube in the aluminum plate at the opposite end of the cell. The reflecting surfaces are gold, concave glass mirrors overcoated with MgF_2. The base path length of the White cell is 83.8 cm. The incident beam makes 40 passes of the White cell which provides an overall path length of 33.5 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

FIGURE 1

SCHEMATIC OF THE OPTICAL SYSTEM AND A BLOCK DIAGRAM OF THE CONTROL ELECTRONICS OF THE TAMS-2B


distribution box
multi-function generator
current control
current control
temperature control
temperature control
HeNe
M7
M8
MV
LSA A
LSA B
TDL
TDL
D2
L4
RC1
RC2
L2
L1
M2
M3
M4
M1
P
White cell
L3
C
D1
M5/6
S
scanner control
lf lock-in amplifier
oscilloscope
chart recorder
lock-in amplifier
data acquisition
computer

cell. However, about 5% of the beam is reflected. This reflected beam passes through cells, RC1 and RC2, containing high concentrations of the monitored species and then is focussed by lens L4 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.
The beam exiting the White cell is directed by two additional plane mirrors through a BaF_2 f/1.5 lens onto a liquid-nitrogen cooled, mercury cadmium telluride, infrared detector situated on top of the White cell. The output of the detector is fed into an oscilloscope for visual representation or to a lock-in amplifier and then to the data acquisition/computer control system for analysis and storage.

The spectrometer is operated in the frequency modulation, FM, mode which results in increased signal/noise ratio compared to the use of direct, amplitude modulated, absorption methods. Measurement of the detector output at the first harmonic of the modulation frequency, 2f, gives a signal related to the variation in power with frequency rather than the power incident on the detector itself. The amplitude of the 2f signal is proportional to the power absorbed by the target gas which can be measured to at least one part in 10^5. For HCHO, NO_2 and HNO_3, absorptions of this magnitude correspond to mixing ratios in the sub ppbv range for 33.5 m path lengths.

The optical system is mounted on a 225 lb., 2 ft. by 4 ft. stainless steel plate, shock mounted on top of a 30 in. high wheeled chassis which allows easy mobility in reasonably flat environments. The massive table top reduces the vibration produced by the cryocoolers in the two laser source assemblies. The shock mounting permits the unit to be transported intact from the laboratory to a field site and helps to reduce the magnitude of any vibrations passing through the table chassis due, for example, to the compressor and the vacuum pumps associated with the system. Such vibrations can cause the laser beam to oscillate both at the entrance of the White cell and over the surface of the detector resulting in an increase of the overall noise in the system. The cryocooler compressor, the calibration systems and the temperature and pressure control electronics are mounted under the optical table. The total

weight of the optical table is 750 lbs. and it occupies a space 29 in. deep, 48 in. long and 54 in. high.

The majority of the electronic components are mounted in a standard 6 ft. electronics rack which is on wheels to afford easy mobility. These include the current and temperature controls for the two LSA's, the multiple function generator, signal mixing electronics, lock-in amplifiers, oscilloscope, chart recorder and scanner control circuit. The computer system and the data acquisition system are located in a separate rack. The weight of the electronics rack and computer system is 400 lbs.

A typical configuration of the TAMS-2B is shown in Figure 2 and a photograph of the instrument is shown in Figure 3.

FIGURE 2

A SCHEMATIC OF THE OVERALL TAMS-2B SYSTEM CONFIGURATION

LEGEND	DESCRIPTION	LEGEND	DESCRIPTION
OSC	oscilloscope	LIA	lock-in amplifier
CTS-A	cryogenic temperature stabilizer	CTS-B	cryogenic temperature stabilizer
LCM-A	laser control module	LCM-B	laser control module
DB	distribution box	FG	function generator
CR	X-T strip chart	SC	scanner control
PS	power supply	TCR	refrigerator compressor
LSA-A	cold head A	LSA-B	cold head B
C-A	LSA-A control switch	C-B	LSA-B control switch
IP	ion pump	NO	NO calibration cylinder
E2M2	vacuum pump	IPC	ion pump control
TPDC	NO_2, HNO_3 calibration system	ICS	inlet calibration system
PC	pressure control	EC	electrical connections
I	inlet	D	infrared detector

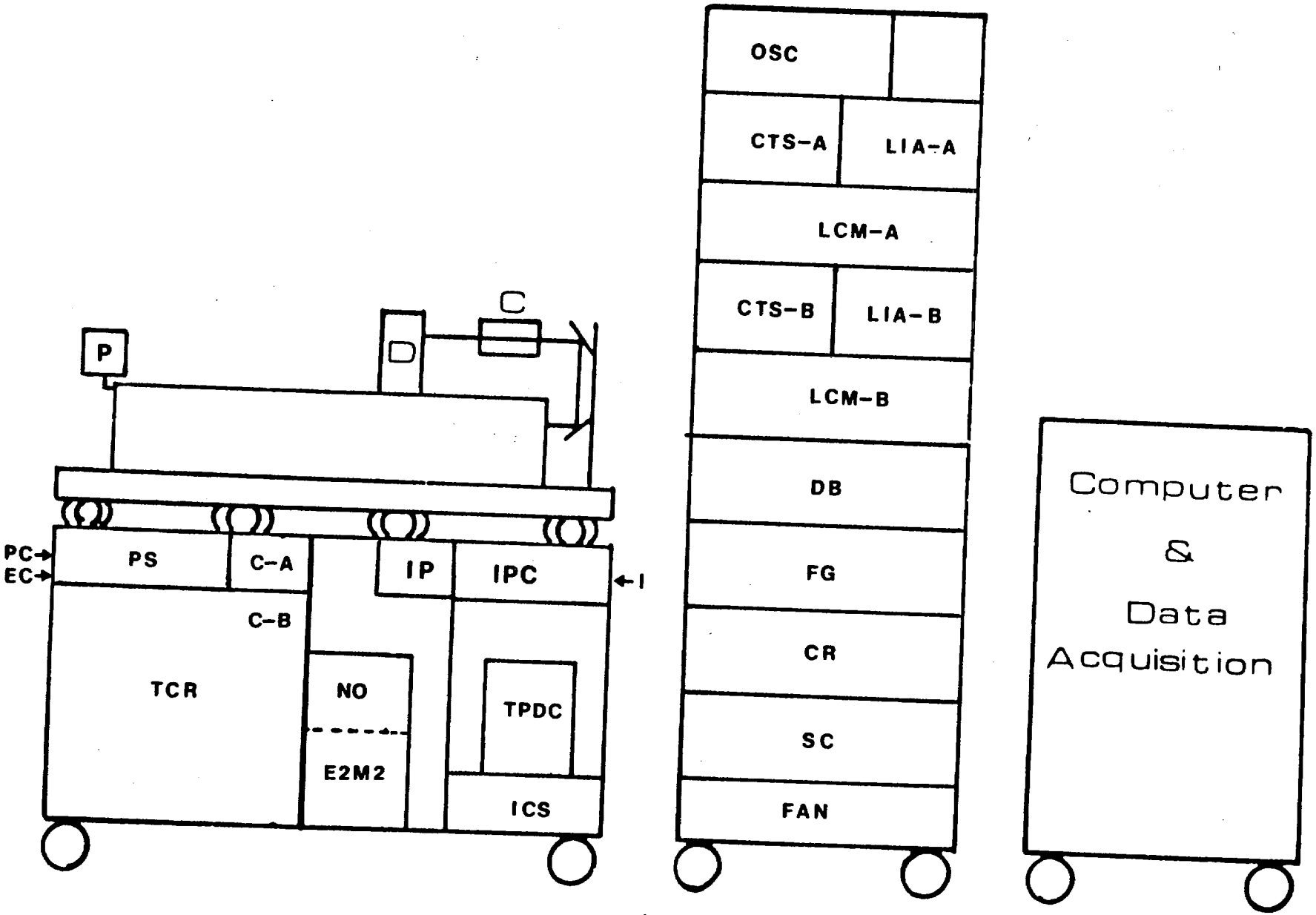
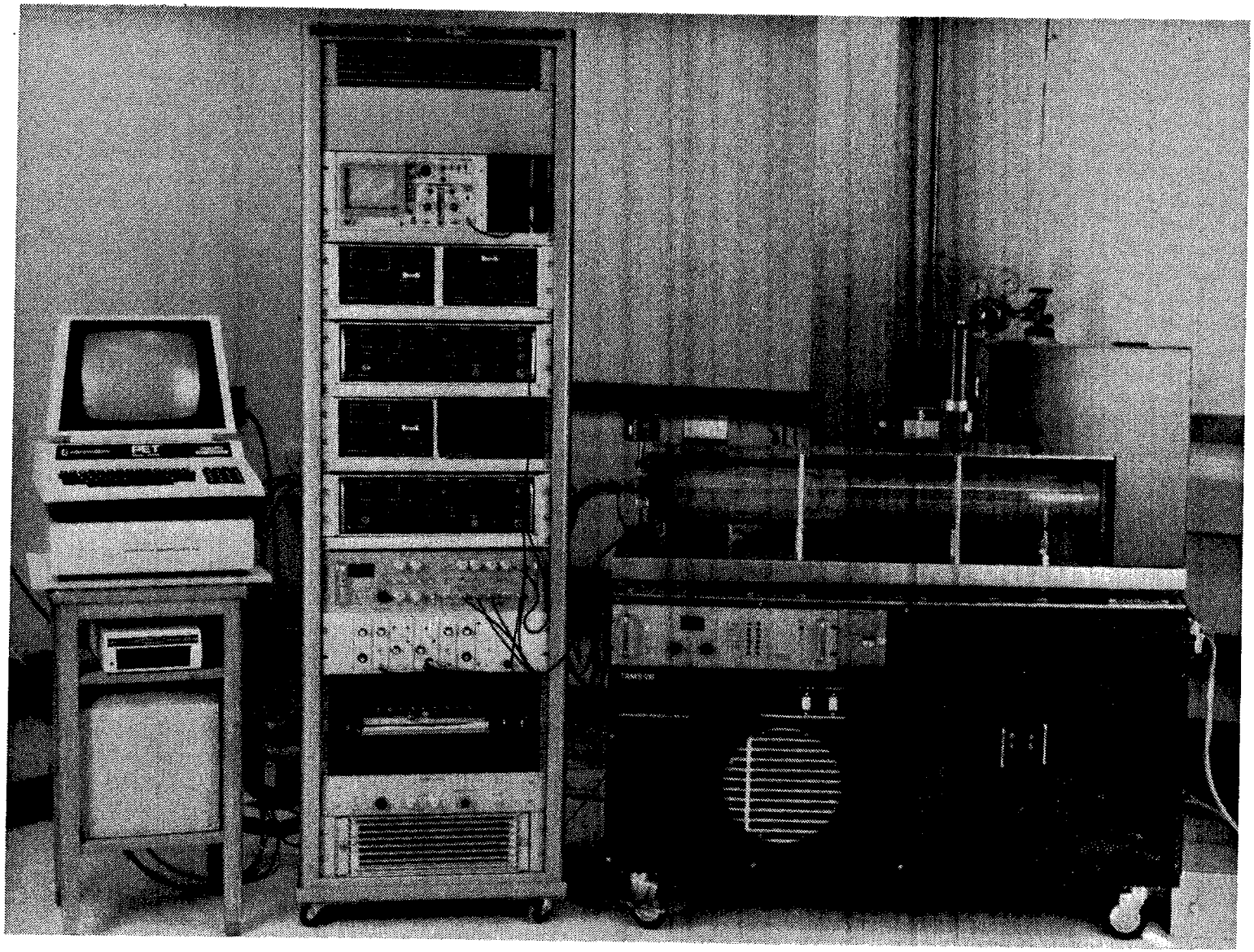

C
P
D
PC
EC
PS
C-A
C-B
IP
IPC
I
TCR
NO
E2M2
TPDC
ICS
OSC
CTS-A
LIA-A
LCM-A
CTS-B
LIA-B
LCM-B
DB
FG
CR
SC
FAN
Computer
&
Data
Acquisition

FIGURE 3

A PHOTOGRAPH OF THE TAMS-2B



2.3 Data Acquisition and Control

The data acquisition and control system, DAC, was designed in-house. An Analog Devices model AD364JD analog-to-digital converter with 12-bit accuracy permits the computer to read up to 16 different devices. Equipment control is obtained through the use of four Analog Devices model AD567JD digital-to-analog converters with 12-bit accuracy and four Analog Devices model AD558JD digital-to-analog converters with 8-bit accuracy. In addition, up to 8 on/off devices may be controlled through the use of two 4-bit SN74173 latches. The system also contains a calendar clock with battery backup for chronological data filing. Several auxiliary input and output channels are reserved for future expansion.

The computer chosen for the data analysis and system control is a Commodore model 4032 modified to allow 640 by 200 resolution graphics display, 80 by 24 text display and interfacing with the data acquisition system through the J4 and J9 memory expansion ports. The data acquisition system thus appears as computer memory located in the A000 block. This allows for extremely rapid data transmission. Data storage uses a Commodore 8252 dual floppy disk drive system providing 2 Mb of storage space, sufficient to store about 500 data sets or approximately 24 hours of continuous operation for the usual averaging time. Hard copy is obtained on an Epson MX-80 dot matrix printer, or on a strip chart recorder.

The interface between the data acquisition system and the instrumentation is through a signal mixer and distribution box (see Figure 1). All input signals (e.g. temperatures, pressures, lock-in amplifier etc.) first enter the mixer, are modified if necessary, and passed on to the data acquisition system for analog-to-digital conversion before being sent to the computer for analysis and storage.

Conditions of laser temperature and current are chosen for each species and are fed into the computer. The system is then switched to computer mode for essentially operator free running.

In operation, the computer signals the scanner, S, to position itself at a

preset angle so that the laser beam from LSA-A is directed into the White cell. The computer then produces a ramp voltage with 128 steps over a range just wide enough to encompass the absorption feature used for the measurement of species A. This ramp voltage is passed to the mixer where it is combined with a 5.7 kHz triangular wave modulation. The composite signal is then passed to the laser current control module. The line is scanned under computer control at a rate of approximately 10 Hz for two seconds and an accumulated 2f line shape is acquired.

On every scan, the computer also checks the signal on the reference channel, D2 in Figure 1. If the reference channel indicates that the line is not at the center of the 128 step ramp (i.e. channel 64) then the computer adjusts the laser temperature set point to bring the line back to the center. Such drifts are due to the very small changes in the temperature of the laser ($\sim 10^{-3}$ K) arising from large variations in the ambient temperature in the mobile laboratory($\sim$10 K) which shift the temperature set point of the stabilized temperature controller.

The computer then commands the scanner to move the angle which aligns the laser beam from LSA-B onto the entrance of the White cell and the measurement procedure is repeated for species B. In this way both species are monitored once within each five second period. Data is accumulated in this way for a period of, for example, one minute providing an average value of the 2f line shapes for the two species over that time frame. This data set, which provides one mixing ratio value for each species, is then stored on the disk, along with the data and time of the measurement. At the end of each data set all other input channels are monitored and the results are stored in the same file. The magnitude of the 2f signals is also passed to a chart recorder for backup data storage. Real time data analysis is also performed and the computer screen is updated with the most recent values.

2.4 Sampling and Calibration Procedures

Schematics of the sampling inlet and the inlet calibration system are shown in Figures 4 and 5 respectively. In operation, a sample of air is drawn through a 6 mm OD, 0.75 mm wall, Teflon tube. Particles are removed from the air by a 0.2 micron Teflon filter, F, located at the entrance of the tubing. A Teflon needle valve located downstream of the filter maintains the flow into the White cell at about 5 standard liters per minute (SLM). The air traverses the inlet line in a few tenths of a second while the residence time in the White cell is about 3 seconds. The flow of air entering the White cell is monitored with a calibrated mass flowmeter, FM1, as shown in Figure 5. The flow is measured just before each calibration and is adjusted by the needle valve as necessary. A motorized valve (MV in Figure 1), which is referenced to a MKS Baratron pressure gauge, controls the pressure in the White cell at 25 Torr.

The sensitivity of the TAMS-2B toward HCHO and NO_2 is determined by introducing a 'spike' of known concentration of the target gas to the air stream where it is sampled into the system. The concentration of the spike is chosen so as to provide mixing ratios similar to that of the constituent in the sampled air. In this way, any surface effects that may occur will be the same for the sampled and spiked air and should therefore cancel.

The sensitivity of the TAMS-2B toward HNO_3 is determined somewhat differently. Sampling integrity is checked periodically by adding a 'spike' to the sampled gas in the same manner as for HCHO and NO_2. However, due to the longer response time of the TAMS-2B toward HNO_3 (~5 minutes) than toward HCHO or NO_2 (~10 seconds) a different method is employed to calibrate the sensitivity during a standard measurement period. This calibration involves the use of a high concentration cell containing a known mixing ratio of HNO_3 which is interposed in the laser beam just in front of the infrared detector. This permits rapid calibration of the HNO_3 sensitivity without contamination of the White cell.

FIGURE 4

A SCHEMATIC OF THE TAMS-2B INLET SYSTEM

F: Teflon filter

SV3: 3-way stainless steel solenoid valve for HCHO flow

SV4: 3-way stainless Teflon solenoid valve for NO_2 flow

SV5/6: 3-way Teflon solenoid valve for HNO_3 flow

TV: Teflon needle valve

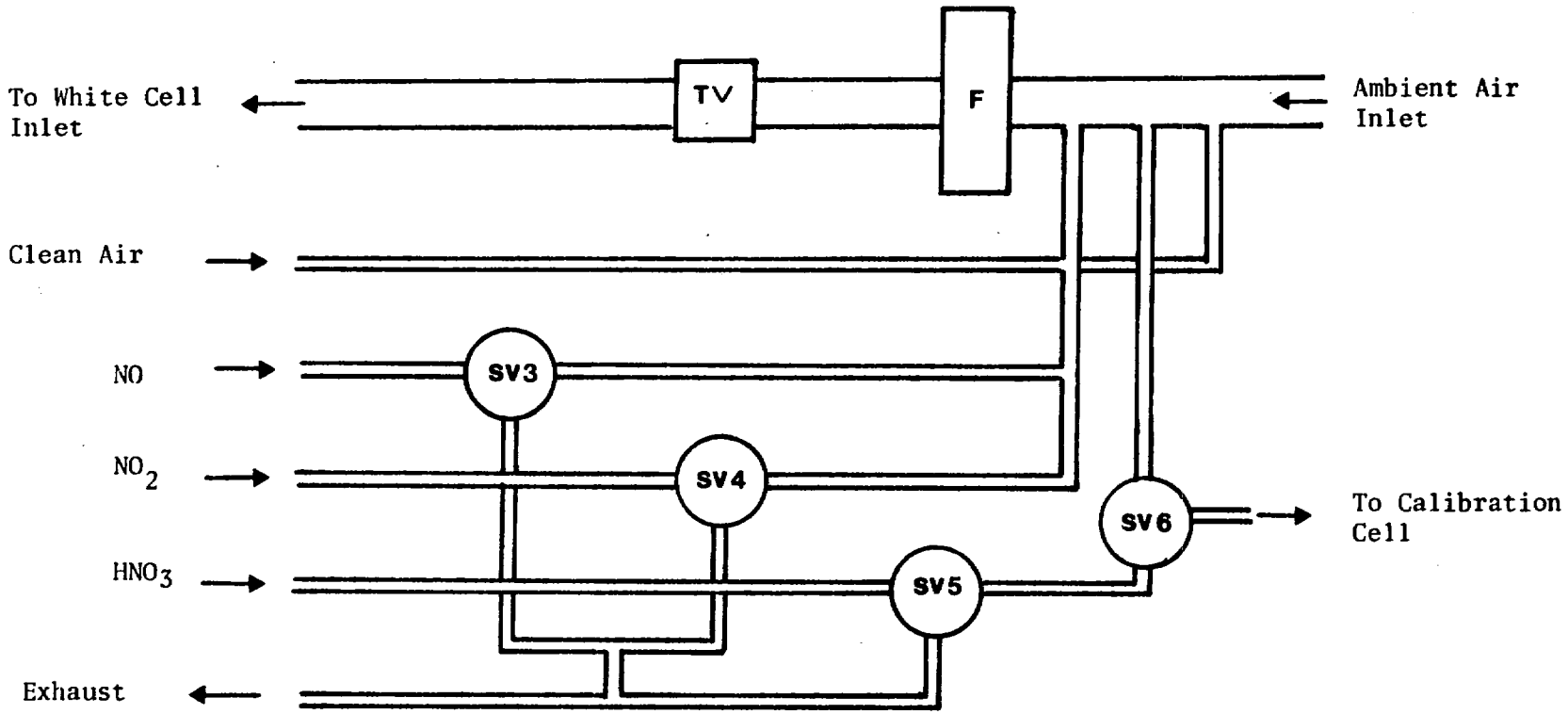

To White Cell Inlet
TV
F
Ambient Air Inlet
Clean Air
NO
SV3
NO_2
SV4
SV6
To Calibration Cell
HNO_3
SV5
Exhaust

FIGURE 5

A SCHEMATIC OF THE INLET CALIBRATION SYSTEM

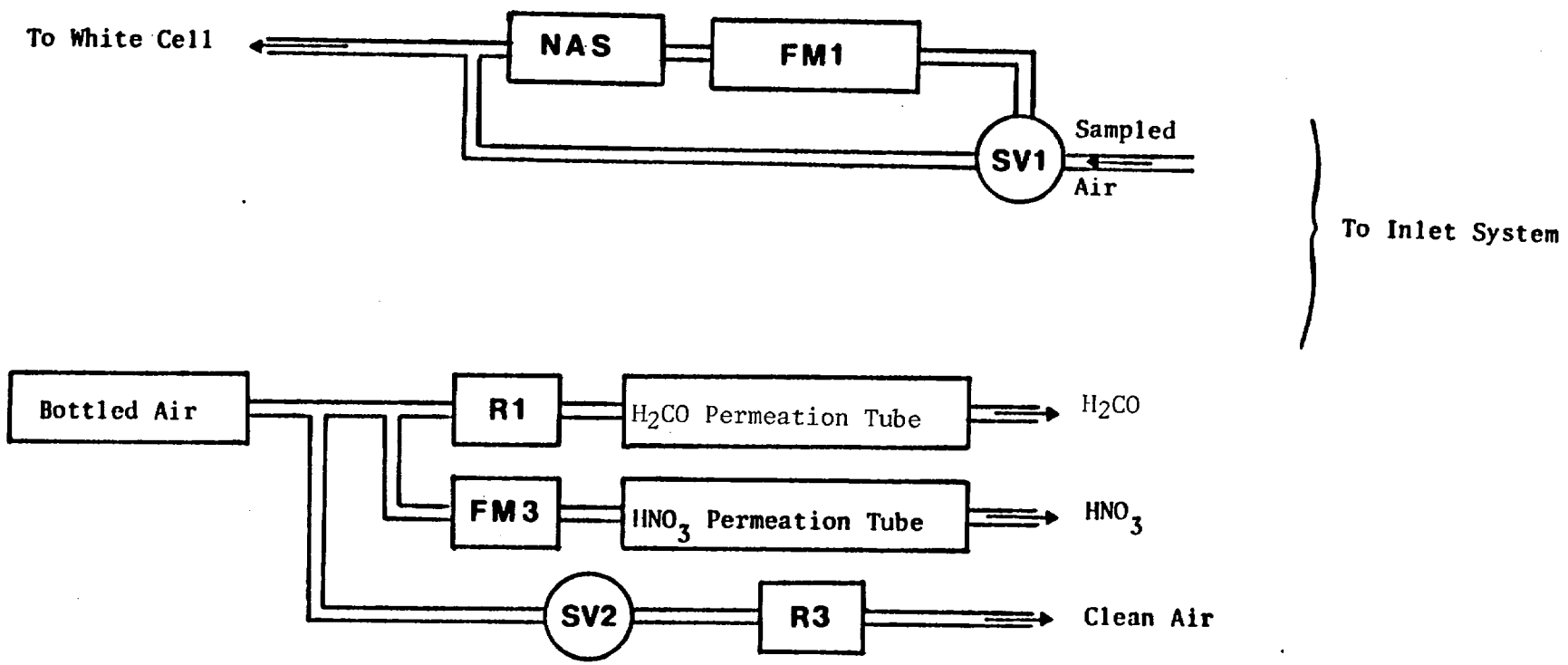
FM1: 0-10 SLM Flowmeter

FM3: 0-20 SCCM Flowcontroller

SV1: 3-way Teflon solenoid valve

SV2: 3-WAY stainless steel solenoid valve

NAS: Nitric Acid Scrubber


To White Cell
NAS
FM1
SV1
Sampled
Air
To Inlet System
Bottled Air
R1
H_2CO Permeation Tube
H_2CO
FM3
HNO_3 Permeation Tube
HNO_3
SV2
R3
Clean Air

The HCHO and HNO_3 standards used in this study were permeation devices of our own design. The two NO_2 sources were commercial wafer devices obtained from Metronics Ltd. The two NO_2 devices were calibrated by weighting at the end of the study. The permeation rates were 107±3 and 144±4 $ng.min^{-1}$ respectively. HCHO was calibrated colorimetrically using the chromotropic acid technique (see for example, Altshuller, Miller and Slera, Anal. Chem., 33, (1961) 621). The permeation rate was determined to be 105 $ng.min^{-1}$. HNO_3 was calibrated by titration against standard NaOH solutions. Three HNO_3 permeation tubes were available for use during this study. These tubes had permeation rates of 320, 560 and 1200 $ng.min^{-1}$.

The HCHO, Luminox NO_2 source and the 320 ng HNO_3 permeation devices are housed in the Unisearch temperature controlled calibration system (Thermostated Permeation Device Calibrator or TPDC) at a temperature of 35°C. The TPDC provides an environment stabilized to ±0.2° C by the combination of a heating system with a thermoelectric cooler. The AES TAMS-2B NO_2 source and the 1200 ng HNO_3 permeation devices were housed in the AES TPDC and maintained at 30°C. The third HNO_3 (560 ng) source was maintained in its own TPDC at 40°C.

The standards were calibrated before and/or after the field study and the HNO_3 standard was calibrated both by titration against standard NaOH and by ion chromatography during the field mission. The latter results are presented in Table 1. During this period the standards were found to be stable to within ± 10% for HCHO ±5% for NO_2 and ±10% for HNO_3 except for those noted in Table 1 and discussed below.

The source of the high readings on September 14, 15 and 16 was identified as the excessively high temperature in the mobile laboratory, which exceeded 40°C in the area of the calibrators, on those days. The thermoelectric cooler used to maintain the tube envelope below ambient were unable to completely compensate for this heat load. The measurements taken during this period were corrected for the differing permeation rates. The uncertainties in the permeation rates of the calibration standards represent the major source of error in the measurements.

TABLE 1. HNO_3 PERMEATION RATE (NG/MIN) FROM THREE SOURCES NOMINALLY DELIVERING 320, 580, AND 1200 NG/MIN RESPECTIVELY[a].

DATE	SOURCE 1[b]	SOURCE 2[b]	SOURCE 3[b]
SEPT. 10	308	569	1163
	316	575	999*
	312	518	1219
	306	601	1231
			1220[c]*
SEPT. 11		614	1190
SEPT. 12		630	1224
SEPT. 13	389	602	1214
	360		
SEPT. 14		667*	1394*
SEPT. 15		777*	1348*
SEPT. 16		746*	1368*
SEPT. 17	378	589	
	318		
SEPT. 18	222*	561	1222
		632	1242
AVERAGE[d]	336 ±31	589 ±33	1213 ±24

a: Permeation rates determined in the laboratory by pH titration against standard NaOH solution prior to the field study.
b: Determined by ion chromatography on extract of KOH bubbler.
c: Determined by pH titration against standard NaOH solution.
d: Average not including the asterisked (*) values for reasons described in text

During the measurement periods the calibration gases flow continuously through the addition lines up to the 3-way solenoid valves situated near to the sample gas inlet as shown in Figure 4. When not required for calibration, these gas mixtures are exhausted far away from the inlet. When HCHO and NO_2 calibrations (or HNO_3 sampling integrity check) are performed the solenoid valve closes the exhaust line and opens the line to the inlet port just upstream of the particle filter (Figure 4). The lines are sufficiently short to ensure a negligible loss of the trace constituent in the line and little delay is observed before stabilization of the measured mixing ratio.

When HNO_3 is calibrated, solenoid valve SV6 (Figure 5) closes and redirects the calibration gas to a 15 cm cell situated in the laser beam in front of the infrared detector. The pressure in the cell is maintained at 25 Torr to match the conditions in the White cell and the flow is controlled at a level to provide an equivalent mixing ratio in the White cell of 80 ppbv.

The minimum detectable concentration, MDC, defined as a signal-to-noise ratio of 1, is determined experimentally for the three species at the selected laser operating conditions and absorption feature. For HCHO and NO_2, clean, bottled air is introduced at the sampling inlet and the laser current scanned over the range of the absorption feature to obtain a background noise level, S_n. For HNO_3 a scrubber is placed in the inlet gas line (see Figure 5) to remove HNO_3 from the ambient air and S_n is determined as above. A known mixing ratio, MR, in ppbv of trace constituent is then added and the signal, S_s measured. The ratio of S_n/S_s X MR provides the MDC in ppbv, which for HNO_3 and HCHO was about 0.3 ppbv and for NO_2 was about 0.15 ppbv.

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.

The software first sets up conditions and obtains a background (zero air or scrubbed ambient air) spectrum on one or both lasers which is then archived. Next, calibration gas is added to the zero/scrubbed air flow and, after a suitable stabilization period, a calibration/reference spectrum is obtained.

(Procedures vary in detail depending upon the target species; for simplicity this description will suppose single laser operation with HCHO as target gas.) The reference spectrum is archived in its untreated form as are all subsequent ambient spectra. Now the background spectrum is subtracted (channel by channel) from the reference spectrum and the result normalized to the mean value of the untreated reference spectrum. This procedure essentially removes the frequency dependent structure present in the background from the reference. (The extent to which this is true depends on the background stability on a time scale of one or two minutes or less.)

Valves are now reset under software control to admit ambient air, an appropriate delay is invoked and an ambient air spectrum acquired. The background structure is subtracted out 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. Since the mean values of the calibration spectrum and the ambient air spectrum may differ due to potentially varying broad band transmittance of ambient air outside the White cell and since the mean value of the ambient spectrum contains no useful information, the calibration spectrum is adjusted to have a zero mean value before fitting. Thus, the intensity of the absorption line in the ambient air spectrum is obtained as a fraction of the calibration line intensity.

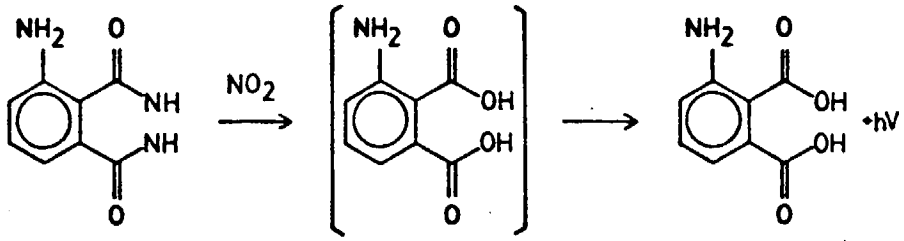
Shifting of the background data eventually reduces the integrity of the background spectrum and hence, new background (zero/scrubbed air) spectra are obtained at intervals determined by the operator.

This description of protocol for automatic control and data acquisition highlights the main software functions in the UNISYS programs. Other tasks include, as implied above, control and monitoring of gas flow rates and valves

as well as graphics display of spectra and provision of two hard copy versions (printer and strip chart recorder) of the concentration time behaviour of the target molecule(s).

2.5 The Luminol NO_2 Analyzer.

The instrument operates on the principle that gaseous NO_2 undergoes a surface reaction with an aqueous solution containing luminol. The luminol is oxidized and the product chemiluminesces according to the reaction scheme:

[1] 

The wavelength of the light emitted is in the 450 nm region.

The luminol solution is presented to the air stream on a wick which is replenished with solution from a 250 ml reservoir. The solution is introduced at the top of the wick and removed at the bottom to a 250 ml waste container by two channel peristaltic pump. The source reservoir holds sufficient solution for about 3 days (72 hours) of operation.

The light emitted by reaction 1 is detected by a photomultiplier tube, amplified and output to a chart recorder and a data logger. The output is a continuous DC voltage with a time constant of 0.3 seconds.

ALthough luminol can produce chemiluminescence with other oxidizers these reactions usually require the presence of metal ion catalysis. We have found that the use of carefully deionized water in the solution formulation prevents chemiluminescence from other oxidizers such as H_2O_2. Only O_3 and PAN was found to produce luminescence but additions of other substances to the solution, such as sodium sulfite reduced the response to O_3 to less than 1000 that of NO_2.

The instrument was calibrated manually several times a day. The calibration gas source was the Unisearch NO_2 permeation tube. The calibration gas was added to the ambient air stream at the inlet to the instrument.

4. AMBIENT AIR MEASUREMENTS OF NO_2, HNO_3 AND HCHO

4.1 Experimental Configuration

On September 5, 1985 the Atmospheric Environment Services (AES) Mobile Laboratory arrived at Pamona College, site of the ARB sponsored HNO_3 intercomparison study. In addition to the standard air monitoring systems operated by AES personnel, the mobile laboratory contained both the Unisearch and the AES TAMS-2B systems and the Unisearch model LMA-3 Luminox NO_2 monitor. Dr. Gervase Mackay and Ms. Laura K. Mayne from Unisearch operated the two TAMS-2B instruments and the LMA-3. The Unisearch TAMS-2B was configured for simultaneous measurements of HNO_3 and HCHO and the AES TAMS-2B measured HNO_3 and NO_2. The mobile laboratory was positioned in the middle of the east side of the sampling platform.

The inlet system used in the ambient studies was constructed entirely of Teflon fittings and tubing. The inlets to the Luminox NO_2 analyzer and the two TAMS-2b instruments were located on the inside of the platform (the side closest to the mobile laboratory) 5 ft above the platform and 8 ft above the ground. The inlets were protected from rain by an inverted cone. The inlet tube to the TAMS-2B instruments consisted of 8 ft of 1/4" O.D., .030" thick Teflon tubing. A 10 ft length of 1/4" Teflon tubing led directly to the Luminox NO_2 analyzer.

A 2 micron pore size Teflon filter was installed in the inlet tubing for TAMS-2B instrument to remove particles from the gas streams. This filter is located just inside the mobile laboratory and about 10 ft upstream of the entrance to the White cell. NO_2 and HCHO calibration gases were added to each of the TAMS inlet lines just upstream of the Teflon filter. A Teflon needle valve situated immediately downstream of the filter reduced the pressure in the inlets and maintained constant gas flow into each TAMS of ~5 standard liters per minute. The residence time of the gas in the inlet line under these conditions was a few tenths of a second. Each TAMS had a completely independent sampling lines. The two inlets were, however, adjacent to each other and to the Luminox inlet port.

The NO_2 calibration gas was added just upstream of the inlet to the Luminox NO_2 analyzer. A mass flow controller was periodically connected to the analyzer exhaust port to check the flow which was found to be constant throughout the field study at 1.75 standard liters per minute . The inlet line and the reaction chamber of the Luminol instrument are at atmospheric pressure. The residence time of the gas in the inlet line was several seconds.

4.2 Measurement Procedure

The two TAMS-2B instruments obtained data points every five minutes. The raw data was stored on floppy diskettes for future analysis in the laboratory and the real time measurements were printed out every five minutes. Calibrations were performed approximately every hour for HNO_3 and every two hours for NO_2 and HCHO. Sensitivities generally varied by less than 10% over this time frame. Data sets for which the sensitivity fluctuated by more than 15% are not included in the extended laboratory analysis. The accuracy of the measurements is estimated to be $\pm$15% for HNO_3 and HCHO and $\pm$10% for NO_2.

The Luminox NO_2 analyzer obtained data continuously and the results were displayed on a chart recorder. The signal was also passed to a data logger which provided an average value every 5 minutes. Calibrations were performed periodically at random intervals but at least twice a day. The sensitivity of the Luminox did not change by more than $\pm$15% over the entire field study except on two occasions, once when the instrument ran out of solution and once early in the study when the photomultiplier tube viewing window became coated. Neither of these problems resulted in a significant loss of data.

Data coverage was better than 98% for Luminox NO_2, 94% for AES TDLAS NO_2 and HNO_3, 89% for Unisearch TDLAS HCHO and 84% for Unisearch TDLAS HNO_3 based on the 1 hour average data sets. With respect to the 5 daily integrated sampling periods, 00:00-06:00, 08:00-12:00, 12:00-16:00, 16:00-20:00 and 20:00-24:00, significant values (more than 2 hours of data per period) were obtained in all 40 periods for Luminox NO_2, in 39 periods for the AES TDLAS NO_2 and HNO_3, 37 periods for Unisearch TDLAS HCHO and 32 periods for Unisearch HNO_3.

Most of the lost TAMS data could be attributed to periods when the cryogenic temperature stabilizers malfunctioned (probably due to an RF noise pulse from, for example, a mobile radio) and to loss of the absorption feature by the the line locking system. Some Unisearch HNO_3 data was also lost at the start of the study as the TAMS was not made completely operational until 16:00 on September 11th. Very minimal Luminol NO_2 data loss occurred. Every three days the solution needed to be replenished and no data was obtained during the 15 minutes required to refill the reservoir and for the instrument to restabilize. Calibration and zero tests accounted for the remaining lost data periods.

5. RESULTS

The TAMS HNO_3 data were re-analyzed when the instrument returned to the laboratory. When the measured HNO_3 signal was less than 2 ppbv or if the background measurements showed high variability, the following re-analysis procedure was used. Background and calibration data obtained during a standard sampling period (00:00-06:00 etc.) were co-added to provide average values for each species. Any calibration or background data that were considered to be in error were eliminated from the averages. The average calibration and background data were then applied to each 5 minute data file and new 5 minute values calculated. At large HNO_3 mixing ratios it was unnecessary to re-analyze the real time data.

Generally, there was little difference between the mixing ratios determined in real time from those calculated using the average calibration and background data. One hour average mixing ratios as well as standard deviations about the average value were calculated from the 5 minute data points, real time or re-analyzed data as appropriate.

The Luminox NO_2 5 minute averages obtained from the data logger were numerically averaged to provide 1 hour average values along with their standard deviations.

The results are presented in tabular form in Appendix A along with graphical representations of the signal variations for each of the species monitored.

Appendix B summarizes the 1 hour measurements for the 9 day period and presents graphical representations of the diurnal variation of each species over the entire measurement period. The average 1 hour HNO_3 values determined from the two individual measurements are also presented.

Appendix C provides tabulated values of the Luminox/TDLAS NO_2, HNO_3 and HCHO mixing ratios, and their respective standard deviations, for the 5 standard sampling periods, 00:00-06:00, 08:00-12:00, 12:00-16:00, 16:00-20:00 and 20:00-24:00 as well as for the two hour period 06:00-08:00 when most other

samplers were not operating. The average values and standard deviations are calculated from the 5 minute data points obtained during the respective sampling period. When less than 2 hours of data was obtained no average is calculated. Values calculated for periods in which more than 30 minutes but less than two hours of data are missing are marked with an asterisk.

6. DISCUSSION

6.1 NO_x

Figure B1 (Appendix B) shows the diurnal behaviour of 1 hour average NO_x as measured by the TDLAS (upper) and the Luminox (lower) instruments during the field study and Figure B2 shows the same data in mirror form. Both instruments indicate the same diurnal behaviour with the NO_x mixing ratio exhibiting two maxima during each 24 hr period; one centered at about 10:00 and the other centered at 22:00.

The agreement between the mixing ratios determined by the two techniques is generally good as demonstrated by Figure B3 which shows a plot of the NO_x mixing ratio measured by the TDLAS against that measured by the Luminox. The solid line is the correspondence line. Although there is generally good agreement between the two instruments the Luminox instrument appears to give higher values at high NO_x concentrations and somewhat lower values at low concentrations. The effect at low concentrations has subsequently been traced to a small non-linear response of the Luminol instrument at low concentrations. This difficulty has now been overcome. The deviations at high concentrations are all attributable to the periods around 22:00 hrs on September 12th and 13th, (Figs B2 and B3). The Luminox values were 35-50% higher than the TDLAS values although the agreement between the two instruments at times on either side of these peaks and also during the peaks at 10:00 on both days were within experimental errors.

The source of these differences has not been unequivocally determined. The sensitivities of the two instruments did not change significantly during this period so that instrumental errors can probably be ruled out. Since the Luminox instrument does not provide the same specificity as the TDLAS method, the most likely explanation is that the Luminox instrument is also responding to some other constituent(s) present in the highly polluted air at night.

Figure C1 displays the average NO_x data obtained by the TDLAS and the Luminox instruments during the 5 standard sampling periods and the 06:00-08:00 period.

The data points from the two instruments are plotted on the same graph for comparison purposes. Clearly the small differences between the two techniques evidenced at times in the 1 hour plots has been smoothed out by averaging. The agreement between the two methods appears to be very good except for the two periods (noted above) 20:00-24:00 on September 12th and 13th.

6.2 HNO_3

Figures B4 and B5 (Appendix B) show the diurnal behaviour of 1 hour averaged HNO_3 measurements obtained by the AES TDLAS (upper) and the Unisearch TDLAS (lower) instruments during the field study. The two graphs differ only in the way the results are presented. Both instruments indicate the same diurnal behaviour and the magnitude of the mixing ratios determined by the two techniques is generally in reasonable agreement. This is also demonstrated by Figure B6 which compares the HNO_3 mixing ratio measured by the two TDLAS instruments. The solid line is the correspondance line.

The behaviour of HNO_3 during the early part of the study was quite regular. The maximum HNO_3 mixing ratio was usually observed between 15:00 and 18:00 each day. The magnitude of this maximum was largest on September 14th when 5 minute averages reached values as high as 18 ppbv (AES) and 16 ppbv (Unisearch) at 15:45. It rained on the 16th and the HNO_3 mixing ratios decreased and remained low with little diurnal variation for the remainder of the study.

Differences between the two TDLAS instruments are almost always within the standard deviations of the two measurements with the most noticeable difference observed when the ambient mixing ratios were changing rapidly. This suggests that the response of the two instruments differed but, since there is no systematic difference between the two measurement sets, the response times of the instruments apparently varied independently throughout the study.

The Teflon inlet filters to the two instruments were changed once during the study, at 09:00 on September 16th and the Unisearch TAMS operated without a filter in the inlet line from 17:15 on September 18th until the end of the

study. When they were removed the filters were observed to be slightly discolored (grey) indicating the collection of some particulate material. Although the measured HNO_3 mixing ratios were initially lower immediately after a filter change the 5 minute real time measurement values recovered to those measured by each instrument prior to the change within about 10 minutes.

Figure B7 shows the diurnal variation of the average of the two TDLAS measurements.

Figure C2 displays the average HNO_3 data obtained by the two TDLAS instruments during the 5 standard sampling periods and the 06:00-08:00 period. The data points from the two instruments are plotted on the same graph for comparison purposes. The small differences between the two techniques evidenced at times in the 1 hour plots has been smoothed out by averaging. The agreement between the two methods is very good; the average difference is only -0.13 $\pm$0.84 ppbv (AES - Unisearch).

6.3 HCHO

Figures B8 and C3 show, respectively, the diurnal behaviour of the 1 hour and 4 hour HCHO mixing ratios for the study period. The HCHO generally maximizes during periods of high pollution as indicated by maxima in the NO_2 mixing ratio. As with NO_2 and HNO_3 the maximum HCHO was observed during the period September 12th through 14th. After that time the HCHO levels were much lower and continued to decrease until the end of the measurement period. The mixing ratios do not show strong diurnal dependence but there is some indication for maxima near local noon.

7. CONCLUSIONS

The two TDLAS systems and the Luminox NO_2 analyser operated very well during the measurement period with minimal loss of data. The agreement of the two TDLAS systems for HNO_3 measurements is very good with differences generally within the detection limits of the two instruments. Both the TDLAS and the Luminox describe essentially identical behaviour for NO_2 throughout the field study. The magnitude of the NO_2 mixing ratios measured by the two techniques are in good agreement except for two episodes during the evenings of September 12 and 13 when the Luminox indicated values almost 50% larger than the TDLAS. The source of this difference is not known but is probably caused by interfering substances present during the night under high pollution conditions.

APPENDIX A

Tabulated 1 hour averages for Luminox NO_2, AES TDLAS NO_2 and HNO_3, and Unisearch TDLAS HNO_3 and HCHO data obtained during the Claremont CA HNO_3 intercomparison study in September 1985. Results are presented for each day along with graphical representations of the diurnal variation of each species during the 24 hour period. Mixing ratios are given at STP (0°C and 760 Torr).

HNO3 INTERCOMPARISON CLAREMONT CA

DATE: SEPT. 11, 1985

TIME PERIOD	TIME AVERAGE	NO2 LUMINOX PPBV	STD DEV PPBV	NO2 TDL AES PPBV	STD DEV PPBV	HNO3 TDL AES PPBV	STD DEV PPBV	HNO3 TDL UNI PPBV	STD DEV PPBV	HCHO TDL UNI PPBV	STD DEV PPBV
00:00-01:00	0.5										
01:00-02:00	1.5										
02:00-03:00	2.5										
03:00-04:00	3.5										
04:00-05:00	4.5										
05:00-06:00	5.5										
06:00-07:00	6.5										
07:00-08:00	7.5										
08:00-09:00	8.5	22.86	17.78	22.65	4.02	-0.23	0.17			0.51	0.31
09:00-10:00	9.5	13.64	4.10	21.06	3.46	-0.05	0.22				
10:00-11:00	10.5	14.32	7.62	21.25	2.81	0.31	0.10				
11:00-12:00	11.5	8.09	5.57	15.16	5.43	0.54	0.28			1.75	0.47
12:00-13:00	12.5	9.87	3.91	16.94	3.65	1.41	0.63				
13:00-14:00	13.5	8.96	1.11	16.01	1.12	0.57	0.15			1.27	0.24
14:00:15:00	14.5	12.75	1.94	19.38	1.87	0.61	0.21			1.73	0.36
15:00-16:00	15.5	12.28	1.90	18.44	1.50	0.87	0.18			1.98	0.31
16:00-17:00	16.5	16.21	4.08	22.56	3.74	0.72	0.14	0.80	0.26	2.15	0.12
17:00-18:00	17.5	23.19	2.90	28.45	2.43	0.97	0.27	1.15	0.33	2.15	0.08
18:00-19:00	18.5	26.69	2.41	32.85	2.15	1.03	0.16	0.69	0.48	1.92	0.24
19:00-20:00	19.5	40.18	5.80	48.95	6.55	0.37	0.18	0.53	0.32	1.69	0.16
20:00-21:00	20.5	54.55	3.25	54.66	2.71	-0.29	0.40	0.50	0.49	1.18	0.13
21:00-22:00	21.5	50.31	3.16	50.64	3.09	0.22	0.13	0.60	0.18	1.26	0.32
22:00-23:00	22.5	49.15	2.11	51.95	1.97	0.33	0.15	0.69	0.50	1.37	0.22
23:00-24:00	23.5	39.58	2.59	44.18	2.43	0.06	0.34	0.95	0.51	1.04	0.12

FIGURE A-1.1

Diurnal variation in the 1 hour NO_2 mixing ratio measured by the TAMS and the Luminox on September 11, 1985.

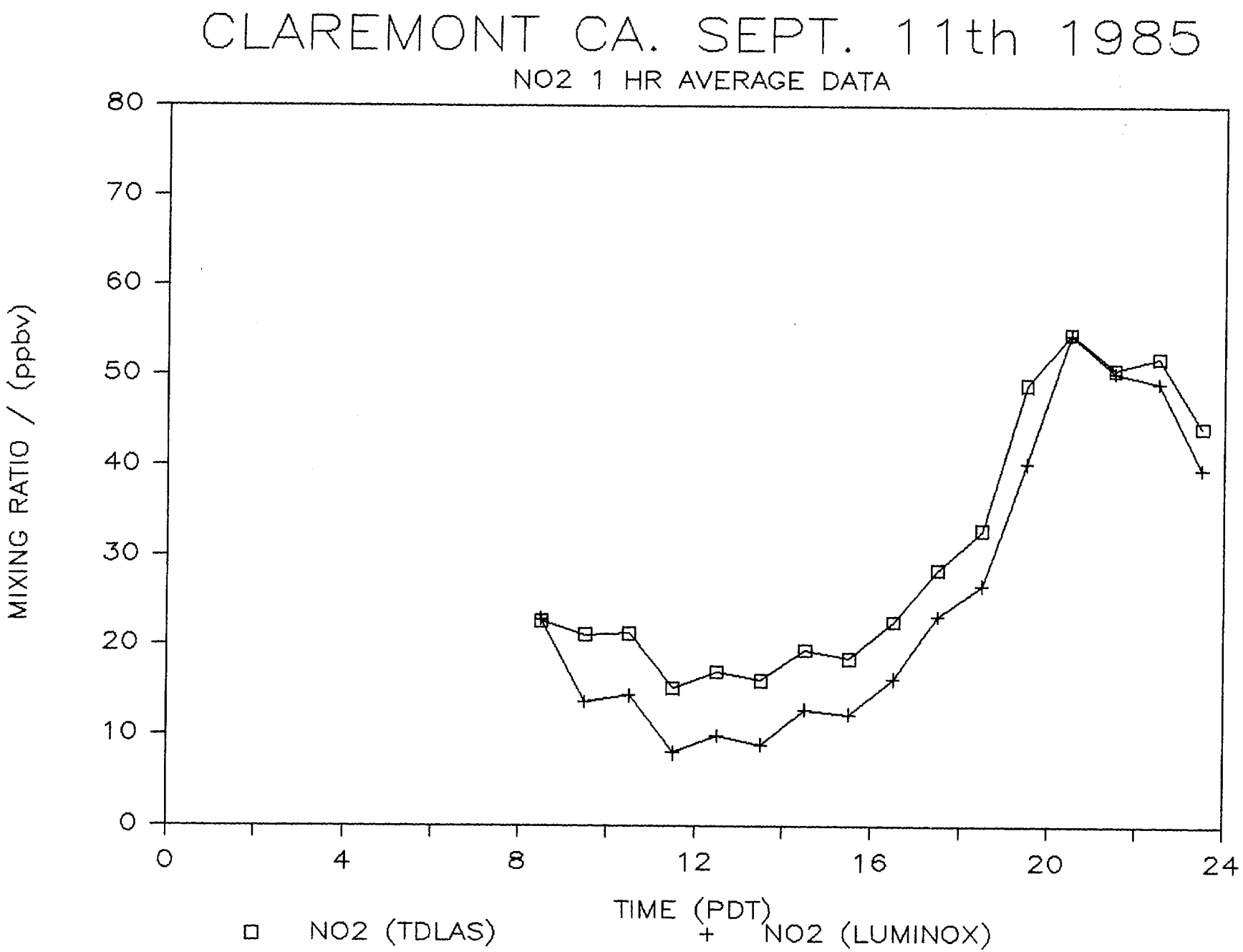

CLAREMONT CA. SEPT. 11th 1985
NO2 1 HR AVERAGE DATA
MIXING RATIO / (ppbv)
80
70
60
50
40
30
20
10
0
0
4
8
12
16
20
24
TIME (PDT)
NO2 (TDLAS)
NO2 (LUMINOX)

FIGURE A-1.2

Diurnal variation in the 1 hour HNO_3 mixing ratio measured by the Unisearch and AES TAMS on September 11, 1985.

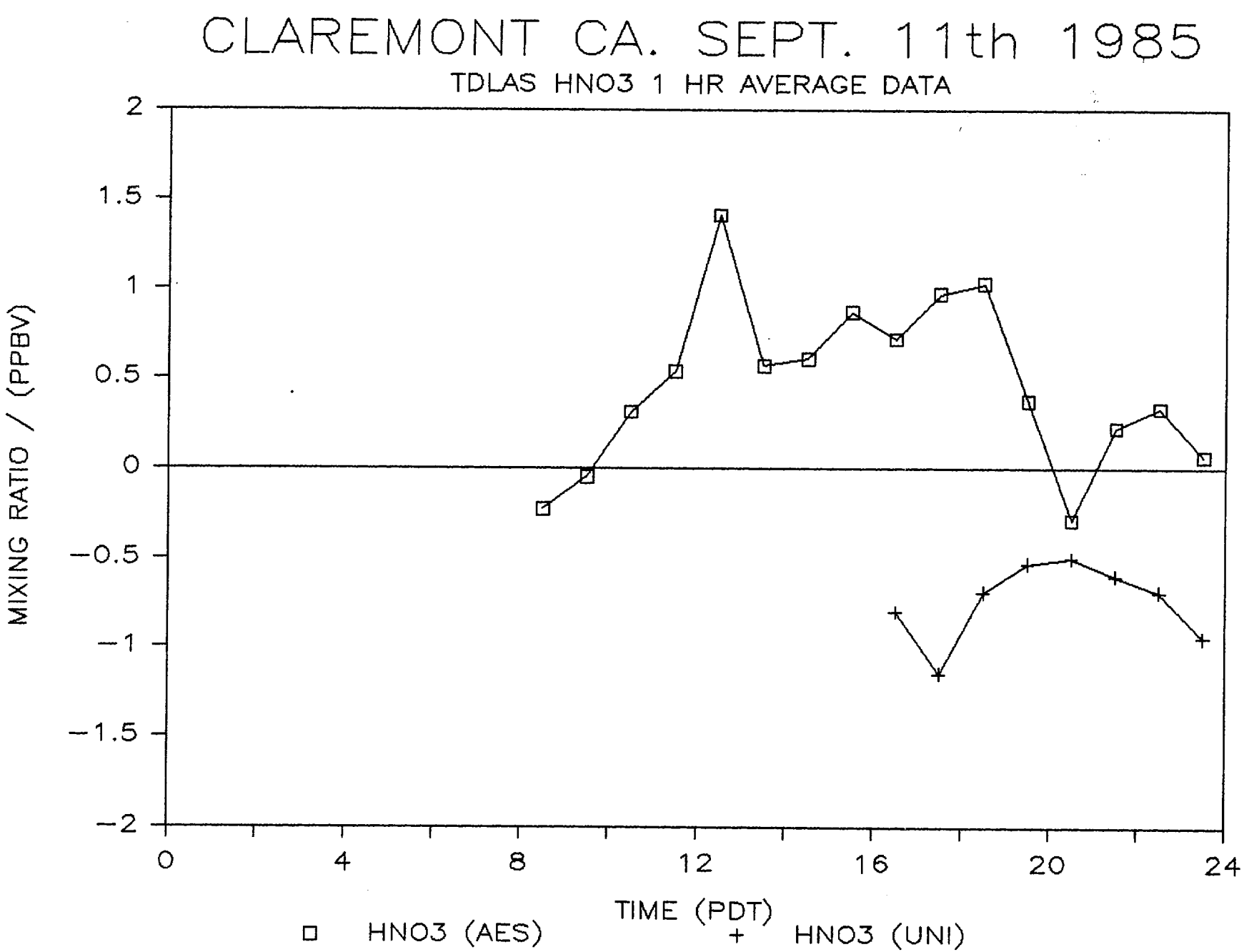
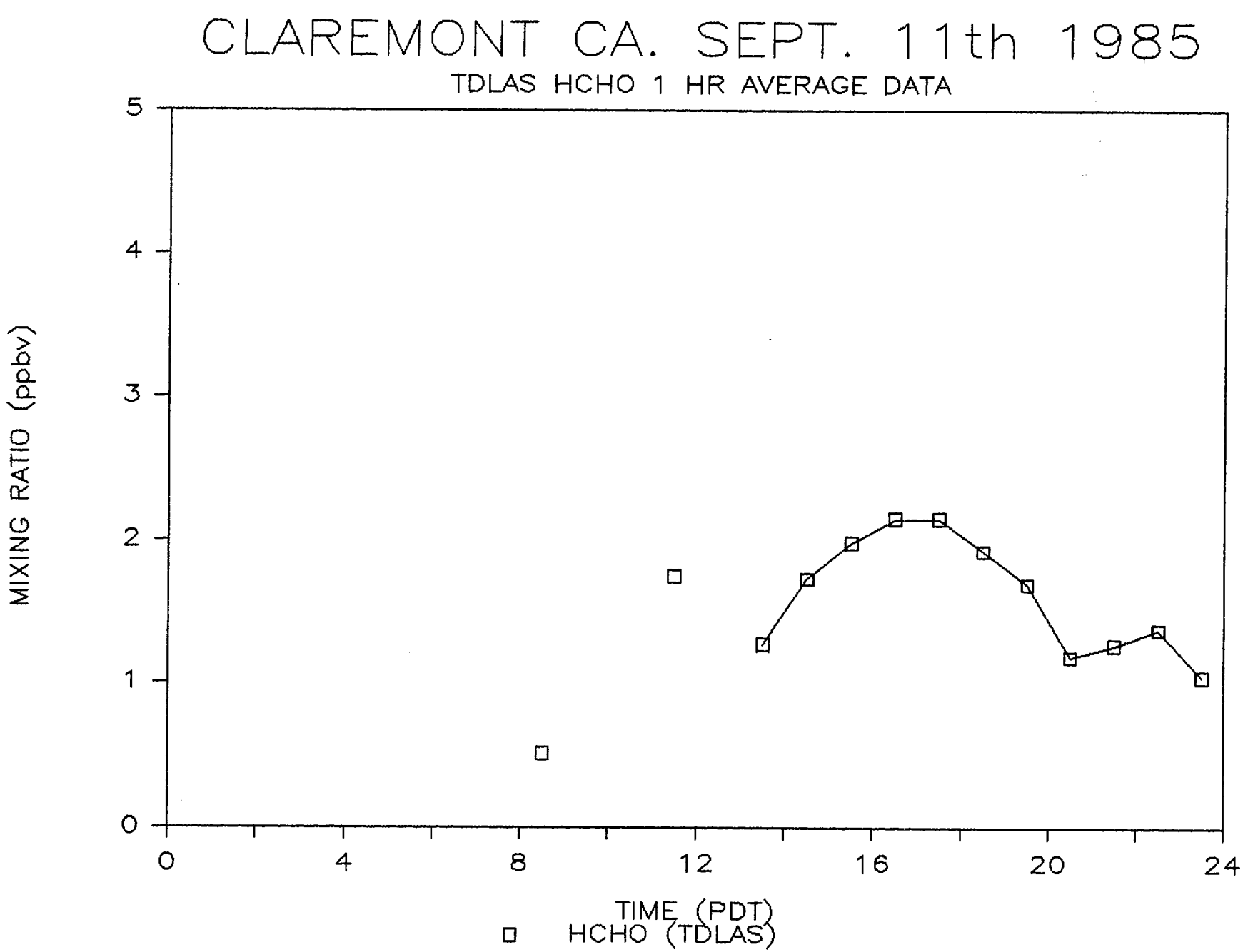

CLAREMONT CA. SEPT. 11th 1985
TDLAS HNO3 1 HR AVERAGE DATA
MIXING RATIO / (PPBV)
2
1.5
1
0.5
0
−0.5
−1
−1.5
−2
0
4
8
12
16
20
24
TIME (PDT)
HNO3 (AES)
HNO3 (UNI)

FIGURE A-1.3

Diurnal variation in the 1 hour HCHO mixing ratio measured by the Unisearch TAMS on September 11, 1985.


CLAREMONT CA. SEPT. 11th 1985
TDLAS HCHO 1 HR AVERAGE DATA
MIXING RATIO (ppbv)
0
1
2
3
4
5
0
4
8
12
16
20
24
TIME (PDT)
HCHO (TDLAS)

HNO3 INTERCOMPARISON CLAREMONT CA

DATE: SEPT. 12, 1985

TIME PERIOD	TIME AVERAGE	NO2 LUMINOX PPBV	STD DEV PPBV	NO2 TDL AES PPBV	STD DEV PPBV	HNO3 TDL AES PPBV	STD DEV PPBV	HNO3 TDL UNI PPBV	STD DEV PPBV	HCHO TDL UNI PPBV	STD DEV PPBV
00:00-01:00	0.5	41.48	1.38	45.77	3.09	-0.20	0.19	0.46	0.26	1.41	0.09
01:00-02:00	1.5	41.83	2.19	45.77	1.59	-0.08	0.21	0.60	0.36	1.02	0.12
02:00-03:00	2.5	31.66	2.33	37.07	1.22	0.36	0.18	0.01	0.28	0.92	0.09
03:00-04:00	3.5	25.75	2.33	33.13	2.15	0.40	0.16	0.42	0.24	0.91	0.28
04:00-05:00	4.5	33.56	4.01	39.50	3.37	0.08	0.10	-0.51	0.21	0.96	0.05
05:00-06:00	5.5	34.50	1.58	41.09	1.59	0.00	0.15	0.41	0.58	1.04	0.13
06:00-07:00	6.5	41.99	3.68	47.74	3.28	0.31	0.18	0.82	0.48	0.93	0.25
07:00-08:00	7.5	44.12	2.07			0.28	0.20	0.54	0.30	1.50	0.10
08:00-09:00	8.5	52.00	9.50					0.79	0.46	1.46	0.42
09:00-10:00	9.5	58.93	2.48	56.53	2.06	1.96	0.48	0.94	0.63	2.50	0.33
10:00-11:00	10.5	54.99	8.37	51.01	5.52	1.60	0.40	1.55	0.57	2.05	0.83
11:00-12:00	11.5	58.03	8.08	49.42	5.80	2.82	0.39	2.43	0.88	2.26	0.18
12:00-13:00	12.5	26.79	7.75	26.40	5.43	1.63	1.02	2.37	1.85	1.73	0.28
13:00-14:00	13.5	8.64	4.12	11.42	3.37	1.02	0.70	0.78	0.43	0.84	0.12
14:00:15:00	14.5	8.85	8.85	10.11	4.68	2.76	0.92	1.39	0.70	0.93	0.06
15:00-16:00	15.5	38.09	3.22	29.30	1.31	6.52	0.67	3.03	0.58	1.59	0.25
16:00-17:00	16.5	37.15	2.19					4.00	0.98	1.68	0.18
17:00-18:00	17.5	47.52	10.55	44.18	2.90	9.00	0.72				
18:00-19:00	18.5	43.88	4.37	50.36	4.49	8.67	1.40	7.95	2.74	5.71	1.08
19:00-20:00	19.5	98.39	25.46	86.39	25.27	8.57	4.00				
20:00-21:00	20.5	166.29	18.49	136.75	14.23	4.97	2.79				
21:00-22:00	21.5	178.46	6.77	139.18	6.65	2.48	1.31				
22:00-23:00	22.5	143.69	24.49	99.50	20.87	0.80	0.46				
23:00-24:00	23.5	136.59	7.89	98.28	19.77			1.53	0.47	6.19	0.60

FIGURE A-2.1

Diurnal variation in the 1 hour NO_z mixing ratio measured by the TAMS and the Luminox on September 12, 1985.

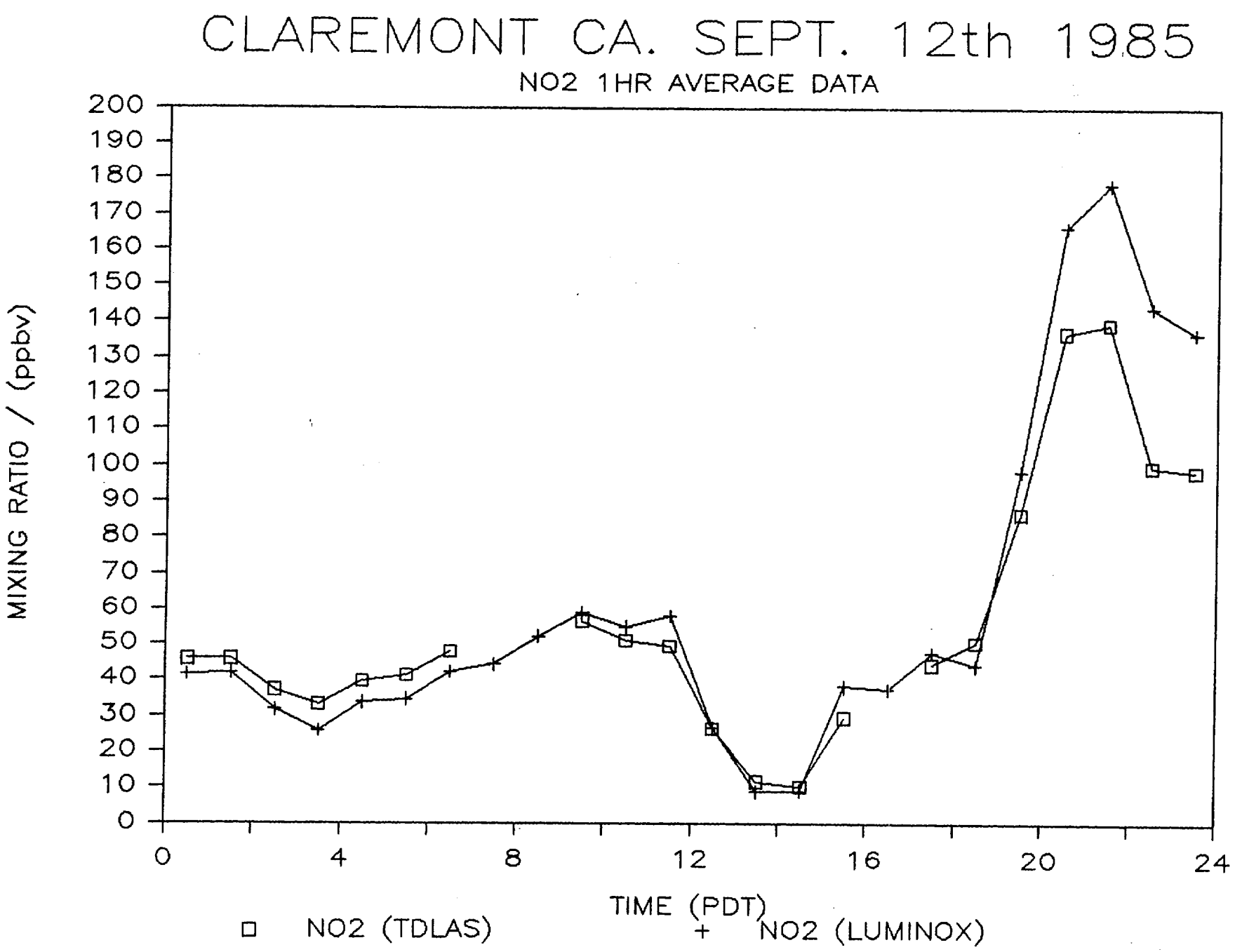

CLAREMONT CA. SEPT. 12th 1985
NO2 1HR AVERAGE DATA
MIXING RATIO / (ppbv)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
4
8
12
16
20
24
TIME (PDT)
NO2 (TDLAS)
NO2 (LUMINOX)

FIGURE A-2.2

Diurnal variation in the 1 hour HNO_3 mixing ratio measured by the Unisearch and AES TAMS on September 12, 1985.

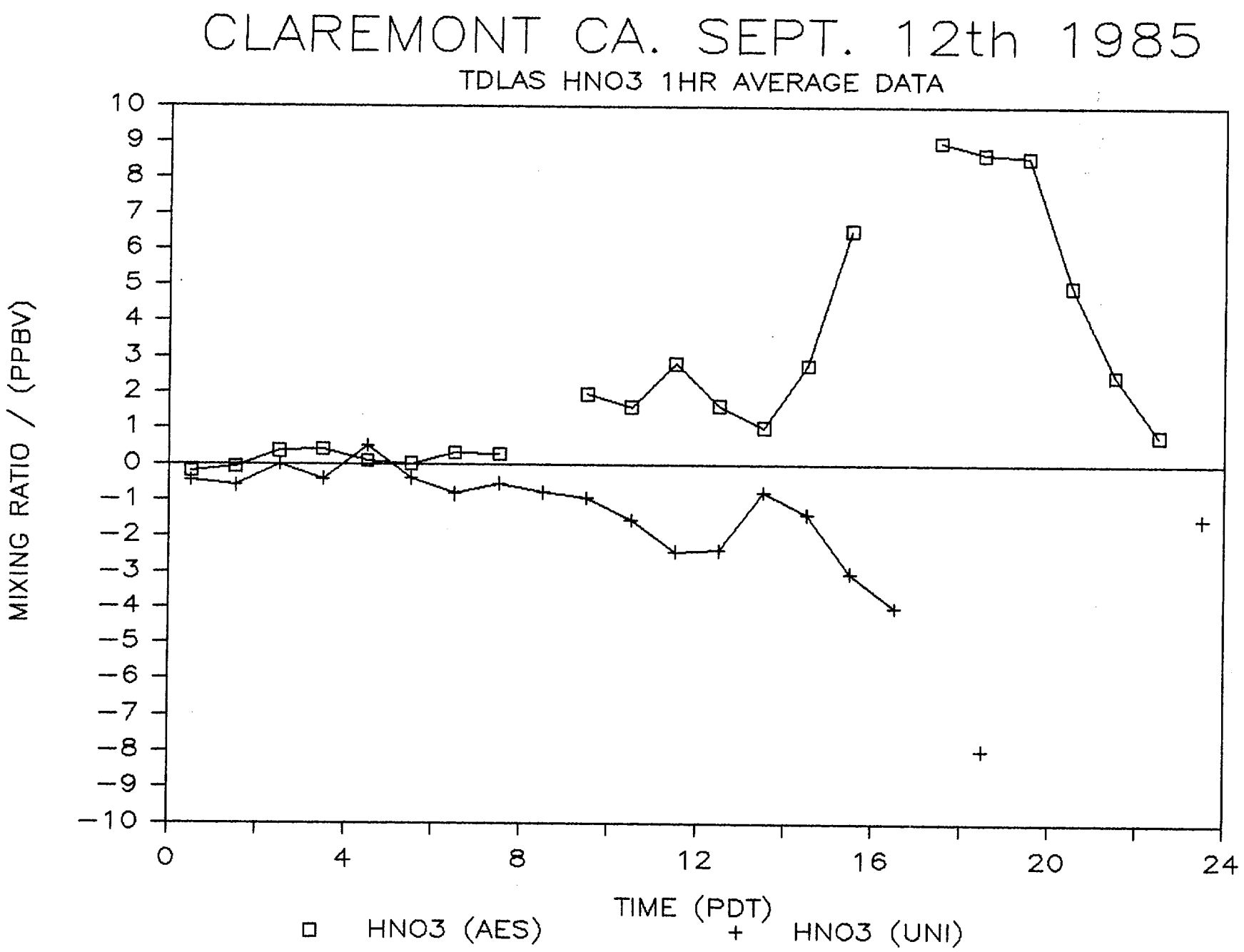
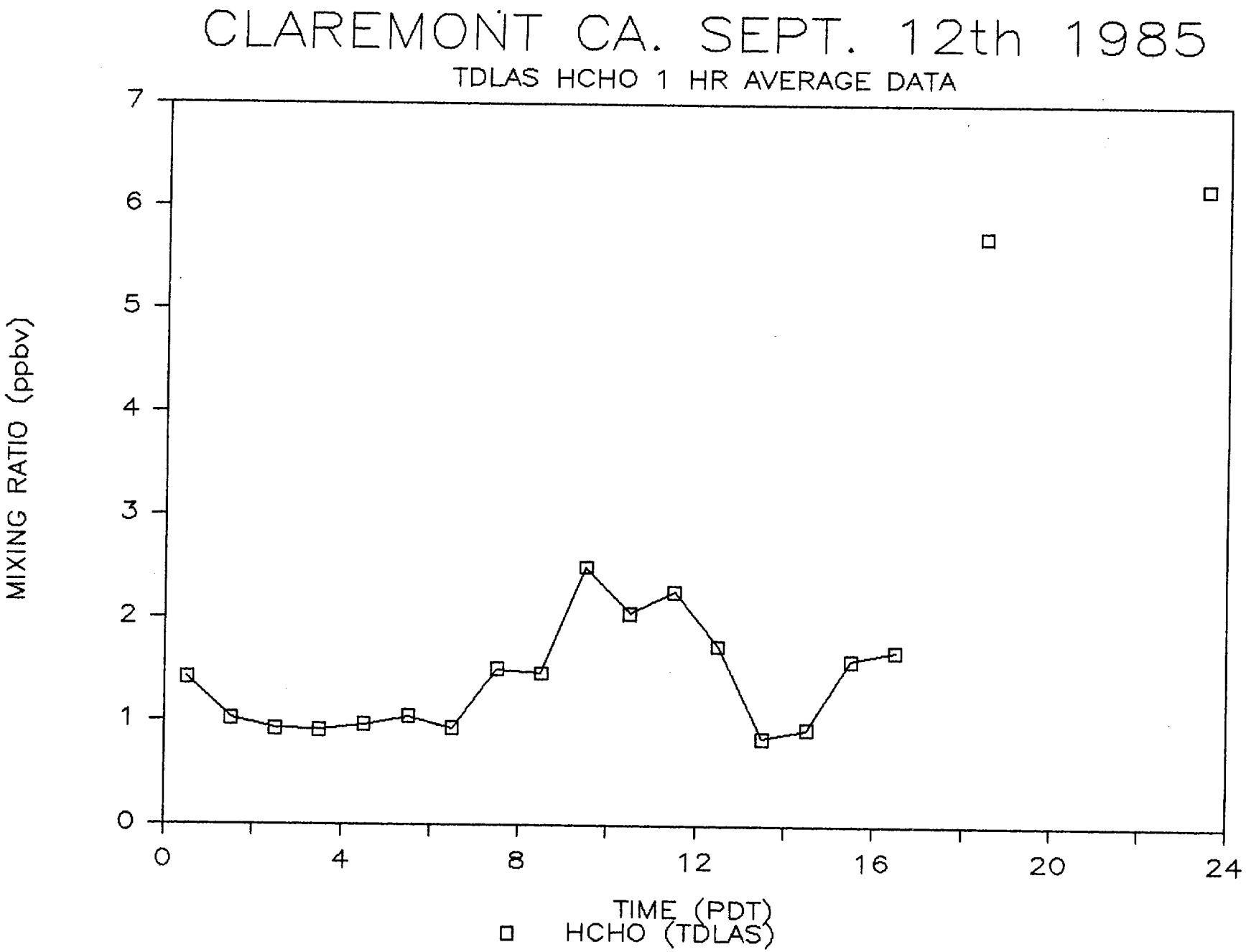

CLAREMONT CA. SEPT. 12th 1985
TDLAS HNO3 1HR AVERAGE DATA
MIXING RATIO / (PPBV)
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
−5
−6
−7
−8
−9
−10
0
4
8
12
16
20
24
TIME (PDT)
HNO3 (AES)
HNO3 (UNI)

FIGURE A-2.3

Diurnal variation in the 1 hour HCHO mixing ratio measured by the Unisearch TAMS on September 12, 1985.


CLAREMONT CA. SEPT. 12th 1985
TDLAS HCHO 1 HR AVERAGE DATA
MIXING RATIO (ppbv)
0
1
2
3
4
5
6
7
0
4
8
12
16
20
24
TIME (PDT)
HCHO (TDLAS)

HNO3 INTERCOMPARISON CLAREMONT CA

DATE: SEPT. 13, 1985

TIME PERIOD	TIME AVERAGE	NO2 LUMINOX PPBV	STD DEV PPBV	NO2 TDL AES PPBV	STD DEV PPBV	HNO3 TDL AES PPBV	STD DEV PPBV	HNO3 TDL UNI PPBV	STD DEV PPBV	HCHO TDL UNI PPBV	STD DEV PPBV
00:00-01:00	0.5	99.25	24.84	84.71	19.28	0.69	0.38	1.31	0.34	4.16	0.98
01:00-02:00	1.5	38.68	9.64	39.78	5.80	1.15	0.27	1.20	0.48	2.50	0.35
02:00-03:00	2.5	30.69	5.23	21.81	8.61	1.78	0.25	1.57	0.57	2.70	0.26
03:00-04:00	3.5	18.08	2.92	10.95	4.49	1.58	0.15	1.60	0.44	2.11	0.31
04:00-05:00	4.5	14.79	1.40	4.02	2.71	1.47	0.20	1.46	0.43	1.90	0.30
05:00-06:00	5.5	20.26	4.29	5.34	1.22	1.63	0.20	1.67	0.49	1.92	0.23
06:00-07:00	6.5	57.79	8.97	60.00	5.34	0.60	0.33	1.38	0.63	2.03	0.23
07:00-08:00	7.5	85.23	6.54	79.37	5.52	0.47	0.17	1.19	0.54	3.80	2.12
08:00-09:00	8.5	85.00	13.53	73.20	10.30	1.37	0.21	1.03	0.59	3.40	1.08
09:00-10:00	9.5	68.88	13.89	63.09	11.14	1.83	0.41	1.10	0.88	3.10	0.43
10:00-11:00	10.5	63.52	7.39	61.50	8.33	2.27	0.40	1.92	0.68	4.20	0.55
11:00-12:00	11.5	42.85	26.28	43.52	18.91	1.68	0.56	0.89	0.54	2.87	0.85
12:00-13:00	12.5	8.02	4.59	13.95	4.21	2.04	0.61	1.86	1.17	1.83	0.44
13:00-14:00	13.5	35.64	12.20	34.16	9.55	6.68	1.87	4.97	1.28	3.96	1.53
14:00:15:00	14.5	24.18	3.29	24.52	2.81	8.94	0.78	7.90	0.95	7.59	1.80
15:00-16:00	15.5	28.76	3.69	28.27	3.09	8.93	0.48	8.01	1.55	11.52	2.10
16:00-17:00	16.5	44.00	11.91	34.63	4.21	9.06	1.00	8.58	0.78	8.08	2.67
17:00-18:00	17.5	57.94	3.49	37.35	3.18	8.42	1.23	8.65	0.95	6.97	1.06
18:00-19:00	18.5	68.61	12.59	40.62	8.61	7.02	2.23	5.46	0.71	9.59	0.95
19:00-20:00	19.5	100.46	8.97	66.18	3.74	2.94	0.56	3.53	0.58	8.53	0.71
20:00-21:00	20.5	131.28	14.56	91.35	12.36	5.23	0.48	3.35	1.64	5.72	0.72
21:00-22:00	21.5	150.98	5.06	111.48	3.46	4.34	0.78	5.84	1.05	5.69	0.59
22:00-23:00	22.5	133.26	3.60	97.34	3.84	2.02	0.50	6.03	1.25	6.53	0.63
23:00-24:00	23.5	126.99	11.70	80.78	7.96	1.39	0.21	2.56	1.80	4.00	0.71

FIGURE A-3.1

Diurnal variation in the 1 hour NO_2 mixing ratio measured by the TAMS and the Luminox on September 13, 1985.

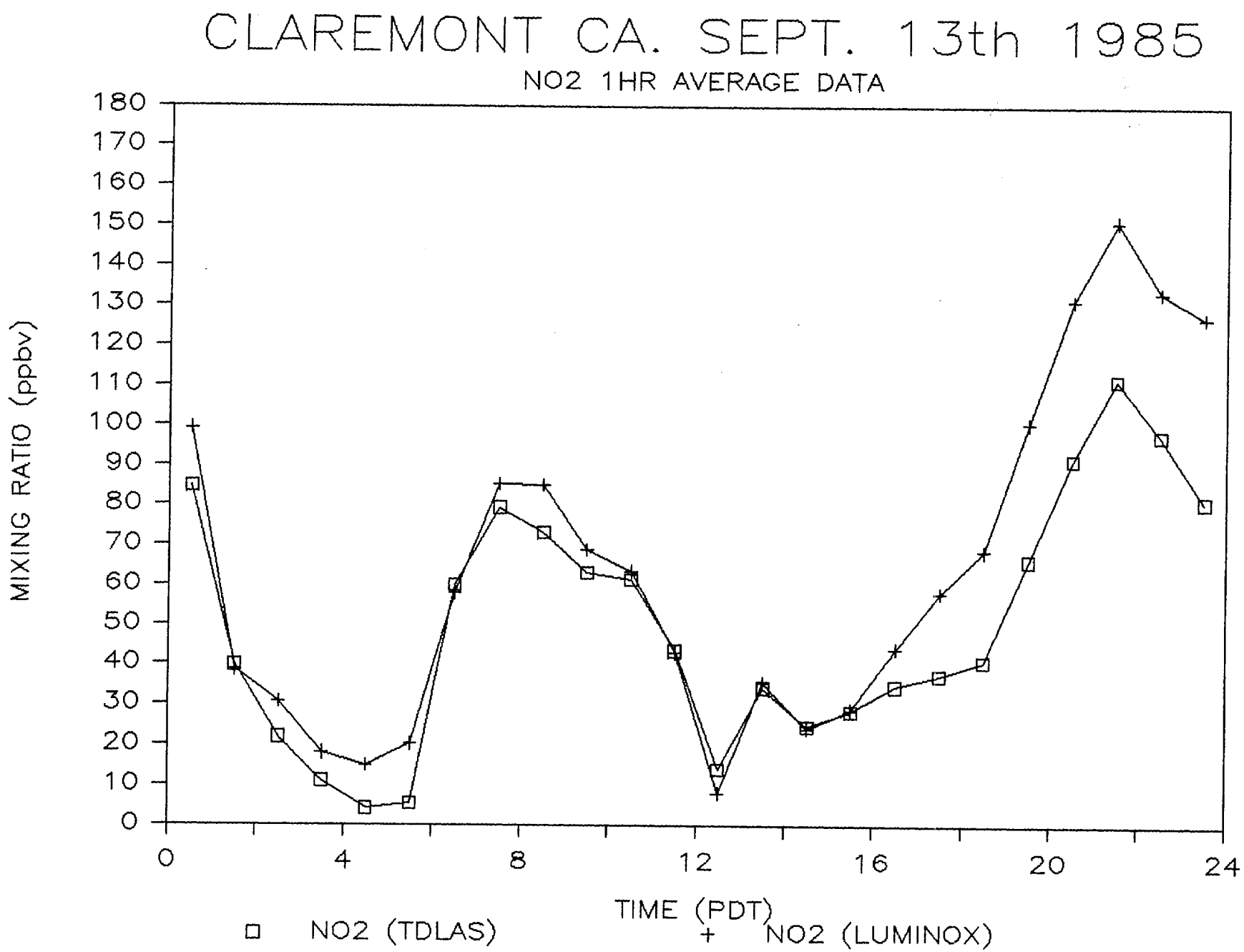

CLAREMONT CA. SEPT. 13th 1985
NO2 1HR AVERAGE DATA
MIXING RATIO (ppbv)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
4
8
12
16
20
24
TIME (PDT)
NO2 (TDLAS)
NO2 (LUMINOX)

FIGURE A-3.2

Diurnal variation in the 1 hour HNO_3 mixing ratio measured by the Unisearch and AES TAMS on September 13, 1985.

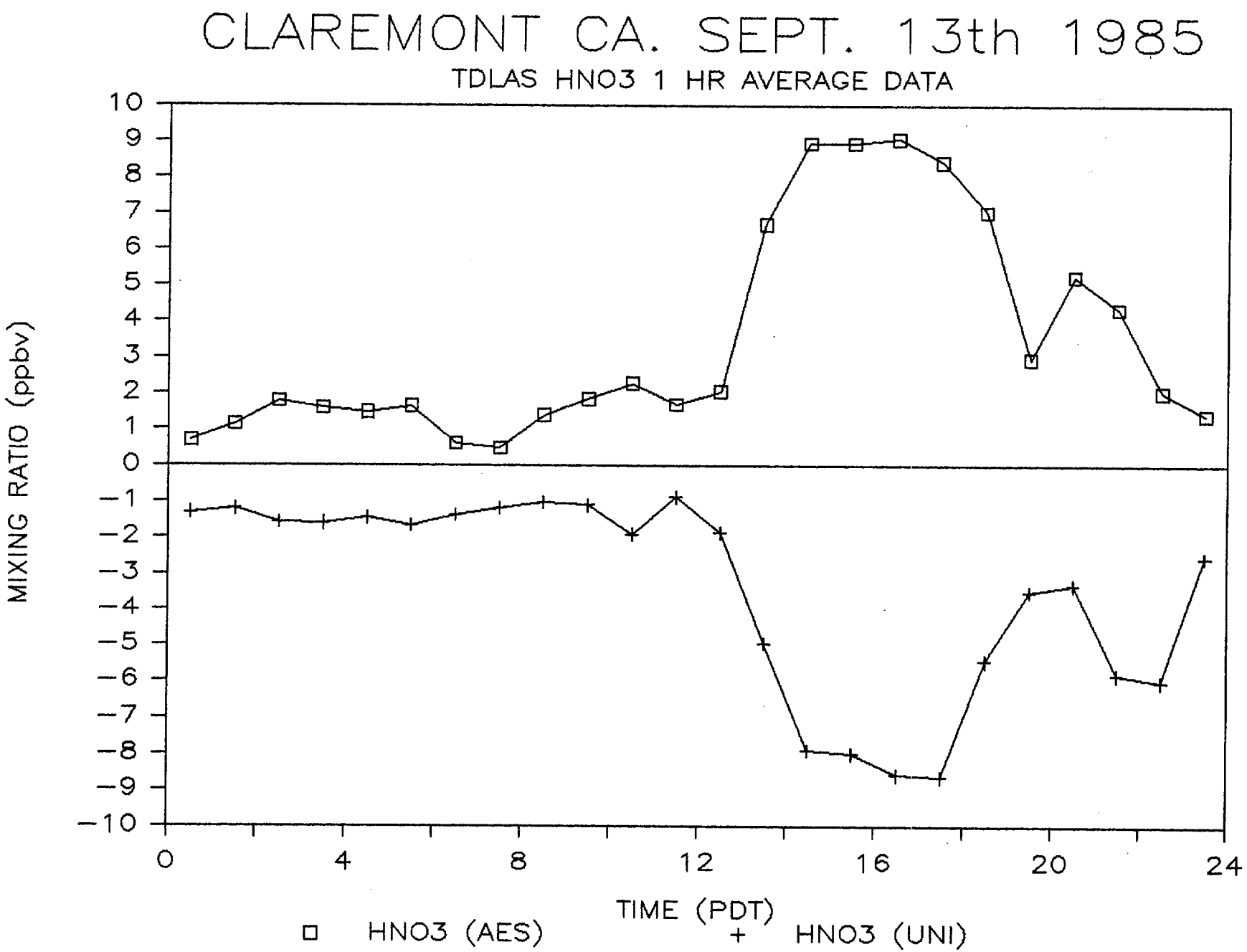
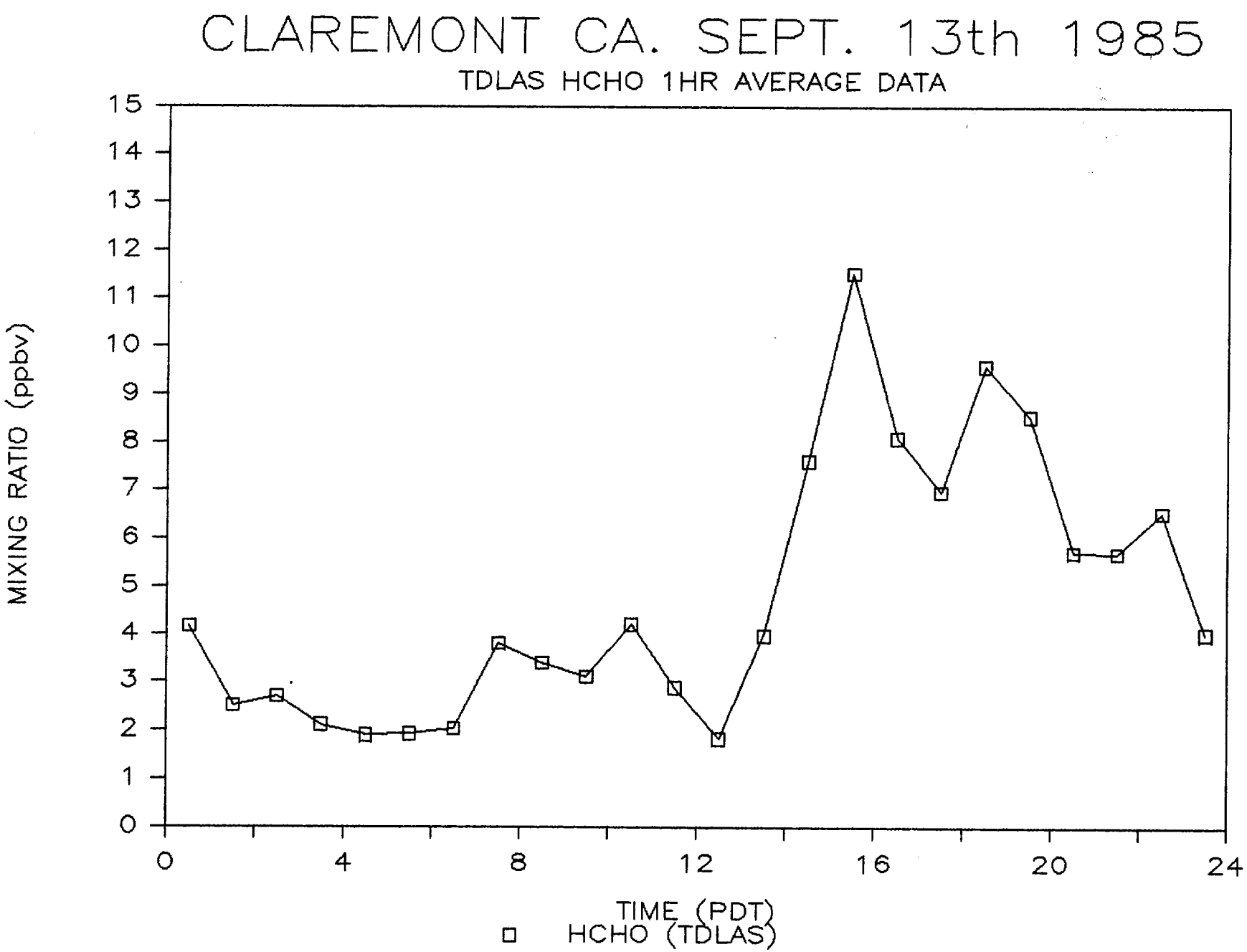

CLAREMONT CA. SEPT. 13th 1985
TDLAS HNO3 1 HR AVERAGE DATA
MIXING RATIO (ppbv)
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
−5
−6
−7
−8
−9
−10
0
4
8
12
16
20
24
TIME (PDT)
HNO3 (AES)
HNO3 (UNI)

FIGURE A-3.3

Diurnal variation in the 1 hour HCHO mixing ratio measured by the Unisearch TAMS on September 13, 1985.


CLAREMONT CA. SEPT. 13th 1985
TDLAS HCHO 1HR AVERAGE DATA
MIXING RATIO (ppbv)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0
4
8
12
16
20
24
TIME (PDT)
HCHO (TDLAS)

HNO3 INTERCOMPARISON CLAREMONT CA

SEPT. 14, 1985

TIME PERIOD	TIME AVERAGE	NO2 LUMINOX PPBV	STD DEV PPBV	NO2 TDL AES PPBV	STD DEV PPBV	HNO3 TDL AES PPBV	STD DEV PPBV	HNO3 TDL UNI PPBV	STD DEV PPBV	HCHO TDL UNI PPBV	STD DEV PPBV
00:00-01:00	0.5	97.73	23.07	78.72	12.36	1.38	0.27			3.21	1.58
01:00-02:00	1.5	53.95	3.97	55.88	3.28	1.87	0.24			3.26	1.10
02:00-03:00	2.5	57.76	6.79	60.75	5.15	2.20	0.30				
03:00-04:00	3.5	47.42	7.54	55.60	8.05	2.28	0.20				
04:00-05:00	4.5	34.16	6.87	44.37	7.21	2.49	0.28				
05:00-06:00	5.5	38.29	8.67	45.49	7.68	2.48	0.31				
06:00-07:00	6.5	34.39	19.83	37.07	14.13	2.77	0.18				
07:00-08:00	7.5	34.89	10.05	46.05	8.14	2.53	0.35				
08:00-09:00	8.5	50.62	2.14	89.48	27.52	2.35	0.31	4.39	1.20	6.06	0.13
09:00-10:00	9.5			111.20	7.02	2.72	0.43	3.74	1.13	7.00	0.83
10:00-11:00	10.5	54.92	5.09	72.26	22.37	4.66	1.14	5.65	1.75	6.23	1.21
11:00-12:00	11.5	33.57	5.45	41.56	4.49	8.21	0.58	8.92	1.71	4.85	0.37
12:00-13:00	12.5	38.68	10.99	40.62	11.70	10.37	1.64	10.90	1.12	4.52	0.43
13:00-14:00	13.5	18.54	5.27	22.65	4.68	12.23	0.94	11.80	1.83	3.02	0.42
14:00:15:00	14.5	12.80	3.14	16.66	2.90	11.14	0.73	13.73	0.90	2.89	0.43
15:00-16:00	15.5	20.38	6.77	19.66	3.93	16.52	2.55	14.98	1.50	4.04	0.52
16:00-17:00	16.5	22.36	2.00	24.62	1.68	15.04	0.53	14.28	0.89	2.21	0.43
17:00-18:00	17.5	16.94	3.20	23.68	2.15	10.52	2.30	13.33	2.27	1.03	0.46
18:00-19:00	18.5	23.94	5.57	31.64	4.68	7.97	0.88	11.62	1.62	2.42	0.32
19:00-20:00	19.5	46.96	4.89	54.01	5.62	5.72	0.64	10.54	3.05	2.53	0.43
20:00-21:00	20.5	53.78	4.68	56.82	5.24	3.14	0.79	1.55	1.21	1.18	0.27
21:00-22:00	21.5	81.29	9.30	83.96	8.52	2.44	0.65	1.33	1.53	1.56	0.30
22:00-23:00	22.5	86.67	2.68	87.89	1.59	0.30	0.36	-0.11	1.28	2.10	0.08
23:00-24:00	23.5	91.13	2.73	91.17	1.87	-0.02	0.34	2.51	0.33	2.12	0.06

FIGURE A-4.1

Diurnal variation in the 1 hour NO_2 mixing ratio measured by the TAMS and the Luminox on September 14, 1985.

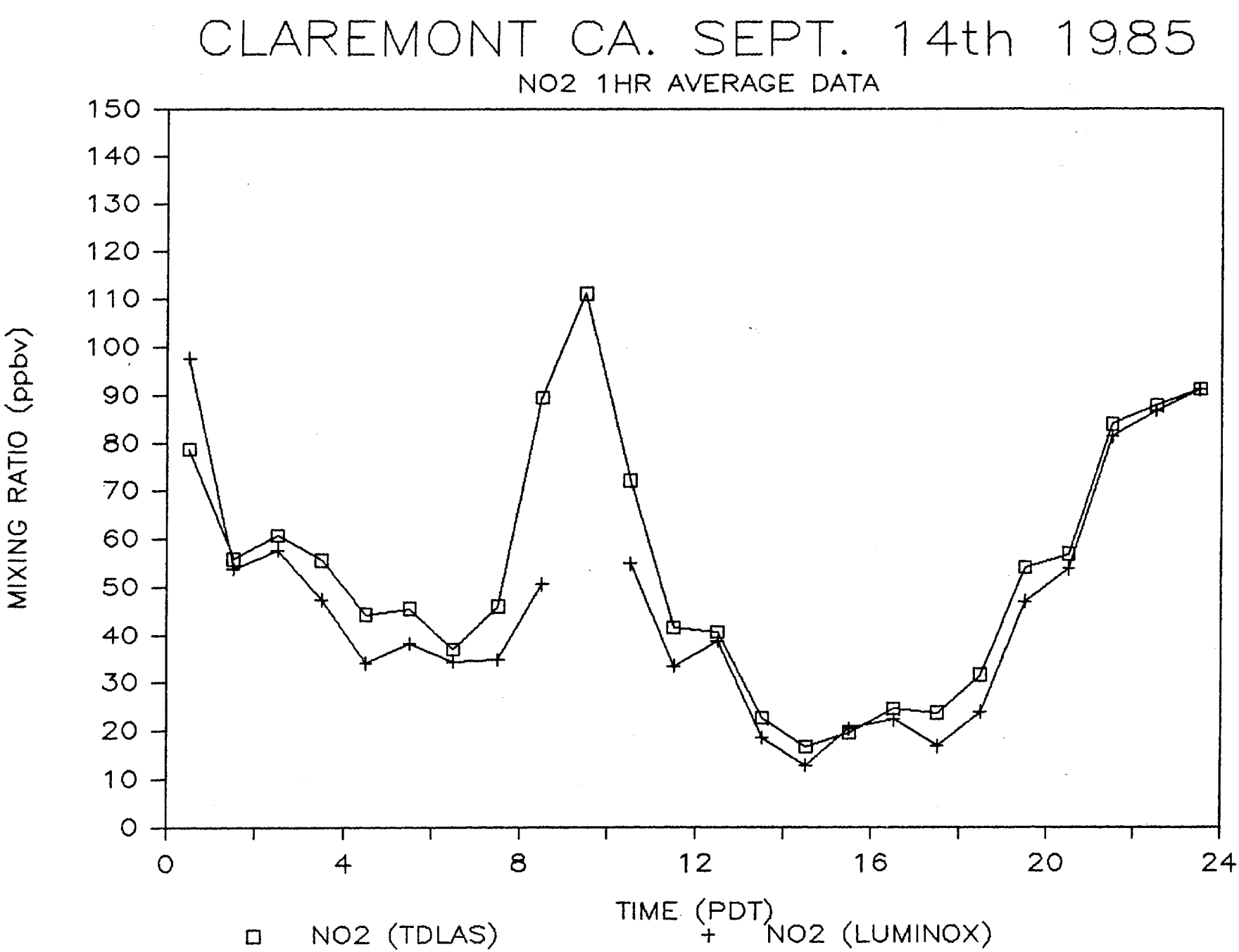

CLAREMONT CA. SEPT. 14th 1985
NO2 1HR AVERAGE DATA
MIXING RATIO (ppbv)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
4
8
12
16
20
24
TIME (PDT)
NO2 (TDLAS)
NO2 (LUMINOX)

FIGURE A-4.2

Diurnal variation in the 1 hour HNO_3 mixing ratio measured by the Unisearch and AES TAMS on September 14, 1985.

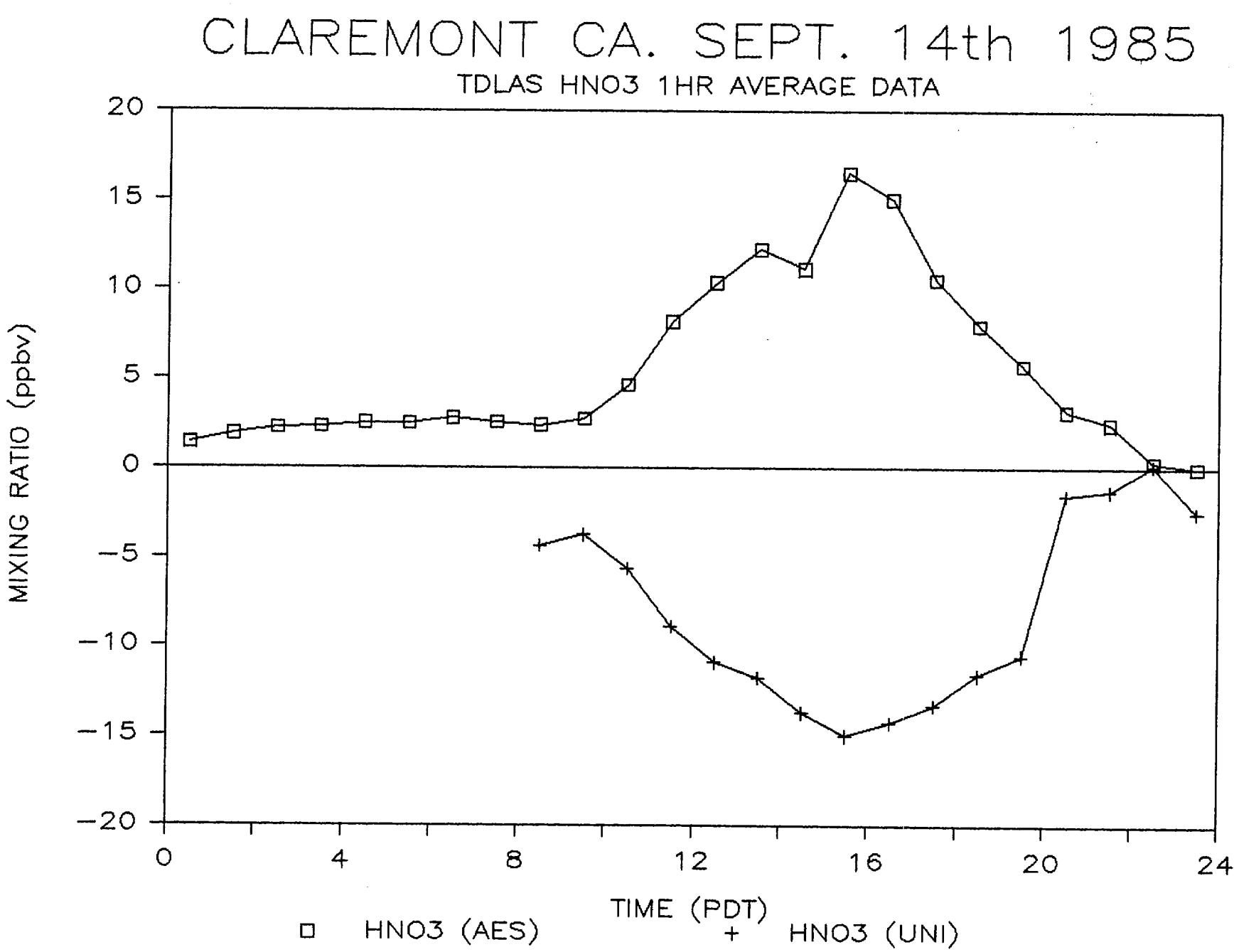
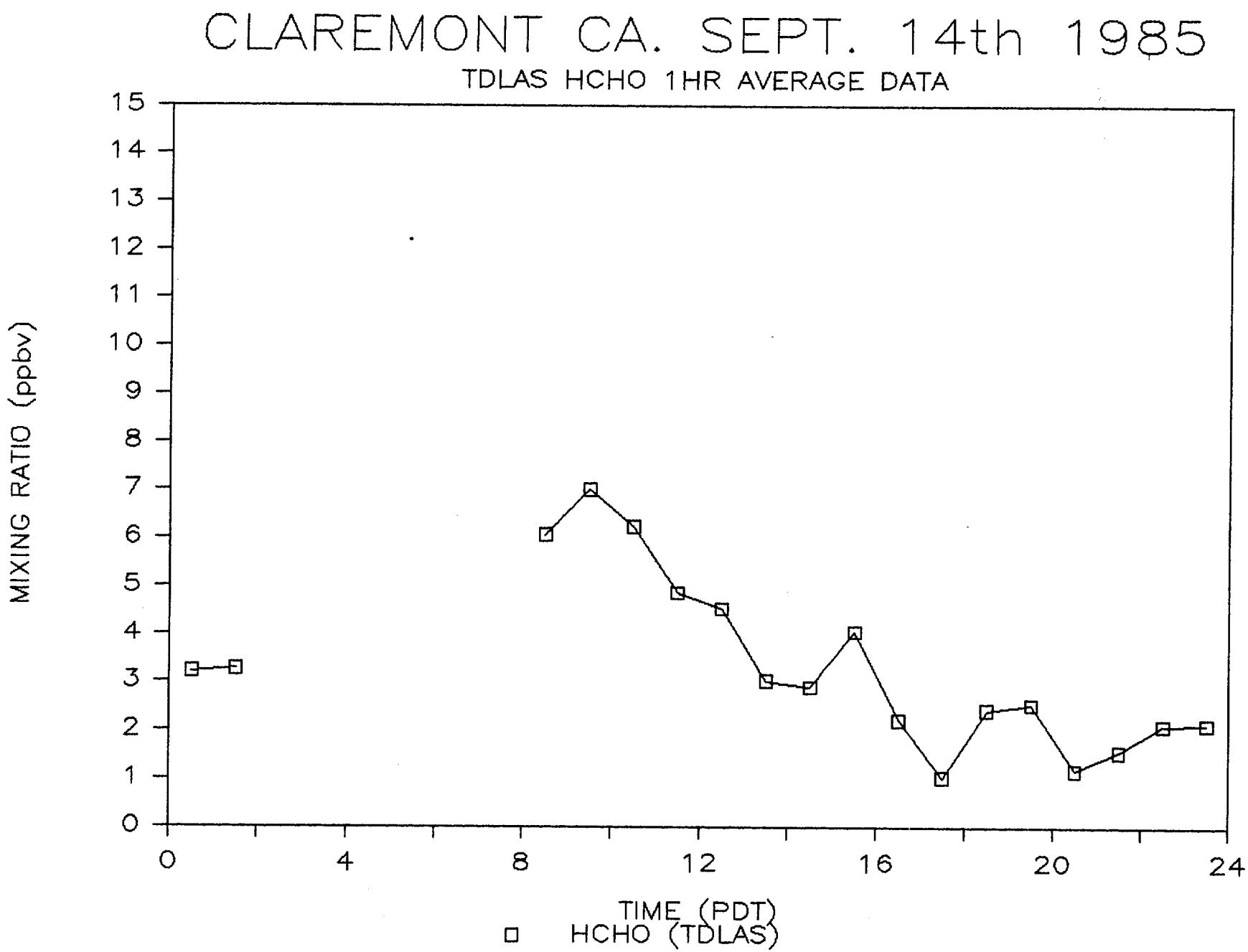

CLAREMONT CA. SEPT. 14th 1985
TDLAS HNO3 1HR AVERAGE DATA
MIXING RATIO (ppbv)
20
15
10
5
0
−5
−10
−15
−20
0
4
8
12
16
20
24
TIME (PDT)
HNO3 (AES)
HNO3 (UNI)

FIGURE A-4.3

Diurnal variation in the 1 hour HCHO mixing ratio measured by the Unisearch TAMS on September 14, 1985.


CLAREMONT CA. SEPT. 14th 1985
TDLAS HCHO 1HR AVERAGE DATA
MIXING RATIO (ppbv)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0
4
8
12
16
20
24
TIME (PDT)
HCHO (TDLAS)

HNO3 INTERCOMPARISON CLAREMONT CA

DATE: SEPT. 15, 1985

TIME PERIOD	TIME AVERAGE	NO2 LUMINOX PPBV	STD DEV PPBV	NO2 TDL AES PPBV	STD DEV PPBV	HNO3 TDL AES PPBV	STD DEV PPBV	HNO3 TDL UNI PPBV	STD DEV PPBV	HCHO TDL UNI PPBV	STD DEV PPBV
00:00-01:00	0.5	81.89	11.54	80.12	9.45	-0.13	0.22	2.03	0.95	2.26	0.21
01:00-02:00	1.5	29.57	11.64	33.32	8.42	-0.08	0.34	1.48	0.37	1.91	0.14
02:00-03:00	2.5	43.41	14.86	49.89	13.95	0.61	0.40	1.12	0.60	1.74	0.08
03:00-04:00	3.5	22.65	15.04	29.67	8.52	0.72	0.24	2.35	0.96	1.64	0.12
04:00-05:00	4.5	35.40	11.40	44.09	10.76	0.94	0.23	1.06	0.85	1.50	0.13
05:00-06:00	5.5	15.84	10.48					1.39	0.45	1.34	0.09
06:00-07:00	6.5	8.20	2.44					1.14	0.51	1.52	0.16
07:00-08:00	7.5	32.21	7.83					1.73	0.72	1.77	0.16
08:00-09:00	8.5	37.63	21.13					2.16	1.10	2.59	0.49
09:00-10:00	9.5	58.63	11.20	58.69	7.49	2.49	0.61	2.40	1.01	3.69	0.25
10:00-11:00	10.5	38.22	12.50	42.78	16.38	4.14	0.48	4.04	2.63	3.95	0.44
11:00-12:00	11.5	16.61	2.98	23.87	2.90	4.56	0.58	4.57	1.00	2.44	0.51
12:00-13:00	12.5	5.00	3.16	11.70	3.37	2.25	0.40			2.73	0.36
13:00-14:00	13.5	6.28	1.55	11.42	1.50	4.78	0.86	2.96	1.33	2.14	0.64
14:00:15:00	14.5	4.35	0.96	8.61	1.12	8.61	1.15	8.18	1.76	1.96	0.44
15:00-16:00	15.5	4.28	0.83	10.67	3.09	9.07	0.31	7.98	1.50	1.50	0.10
16:00-17:00	16.5	5.30	2.49	15.07	2.90	6.93	1.12	6.75	1.18	1.36	0.17
17:00-18:00	17.5	7.83	3.64	16.85	3.65	3.32	0.47	5.38	1.12	1.39	0.08
18:00-19:00	18.5	23.15	6.05	34.73	5.99	3.63	0.59	6.73	0.94	2.27	0.37
19:00-20:00	19.5	34.95	1.82	50.17	3.09	1.51	1.16	2.55	2.42	1.49	0.26
20:00-21:00	20.5	57.45	10.02	69.73	5.90	1.76	0.59	2.00	3.51	1.26	0.27
21:00-22:00	21.5	75.30	4.41	76.85	3.74	0.95	0.26	1.78	1.03	1.40	0.19
22:00-23:00	22.5	67.26	2.92	70.57	2.81	1.66	0.28	3.08	0.56	1.23	0.13
23:00-24:00	23.5	57.52	4.71	61.03	3.65	1.18	0.28	1.37	0.62	1.61	0.14

FIGURE A-5.1

Diurnal variation in the 1 hour NO_e mixing ratio measured by the TAMS and the Luminox on September 15, 1985.

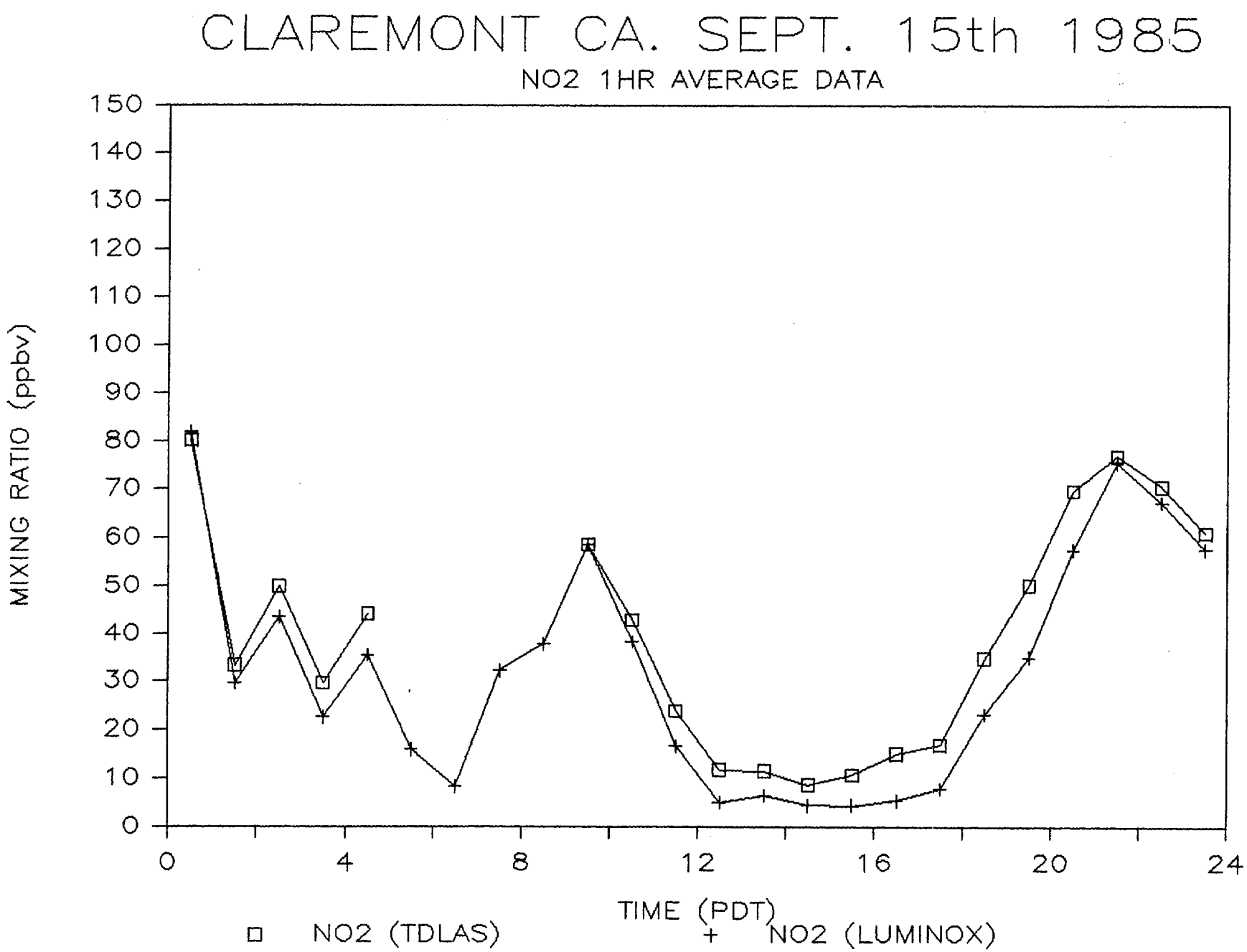

CLAREMONT CA. SEPT. 15th 1985
NO2 1HR AVERAGE DATA
MIXING RATIO (ppbv)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
4
8
12
16
20
24
TIME (PDT)
NO2 (TDLAS)
NO2 (LUMINOX)

FIGURE A-5.2

Diurnal variation in the 1 hour HNO_3 mixing ratio measured by the Unisearch and AES TAMS on September 15, 1985.

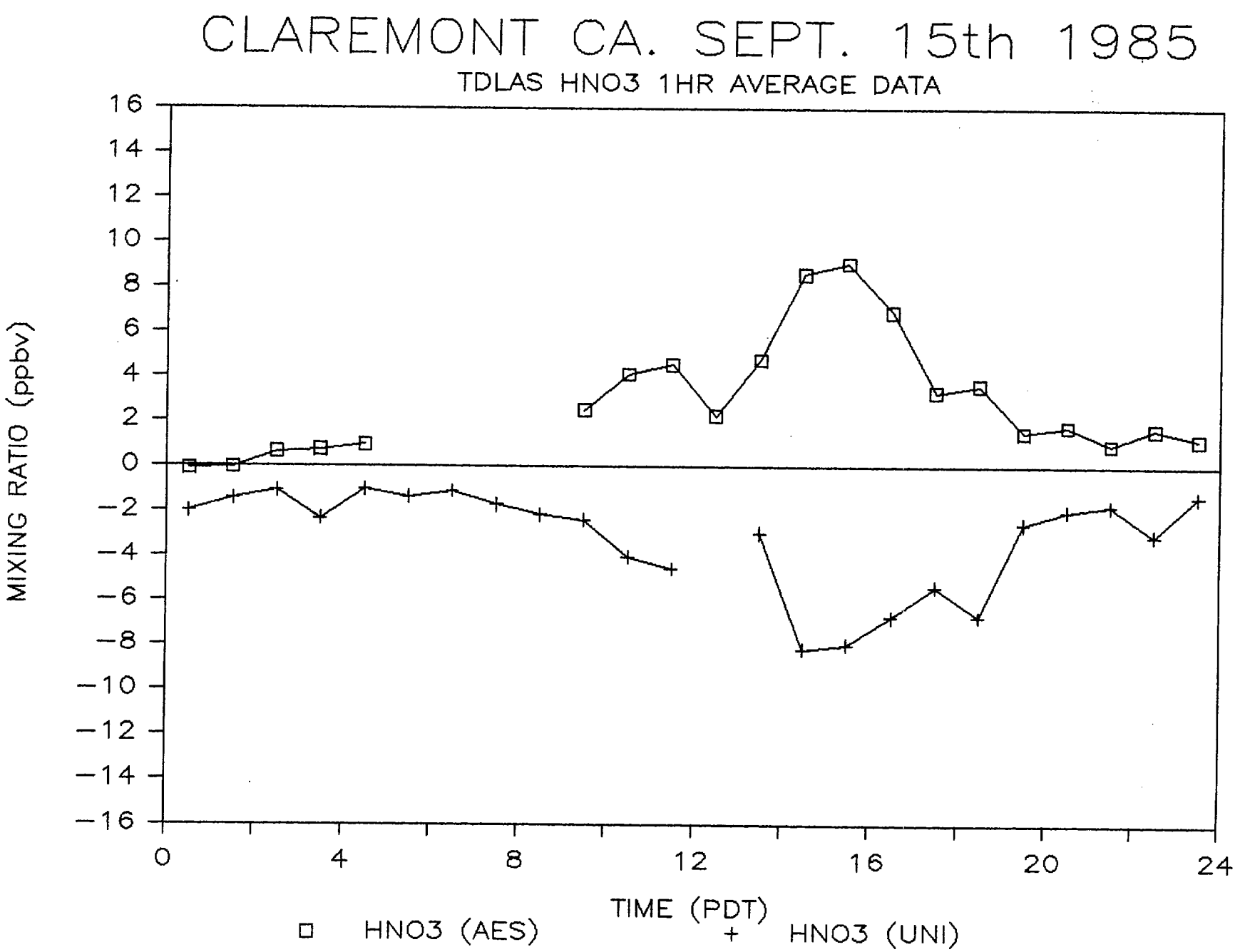
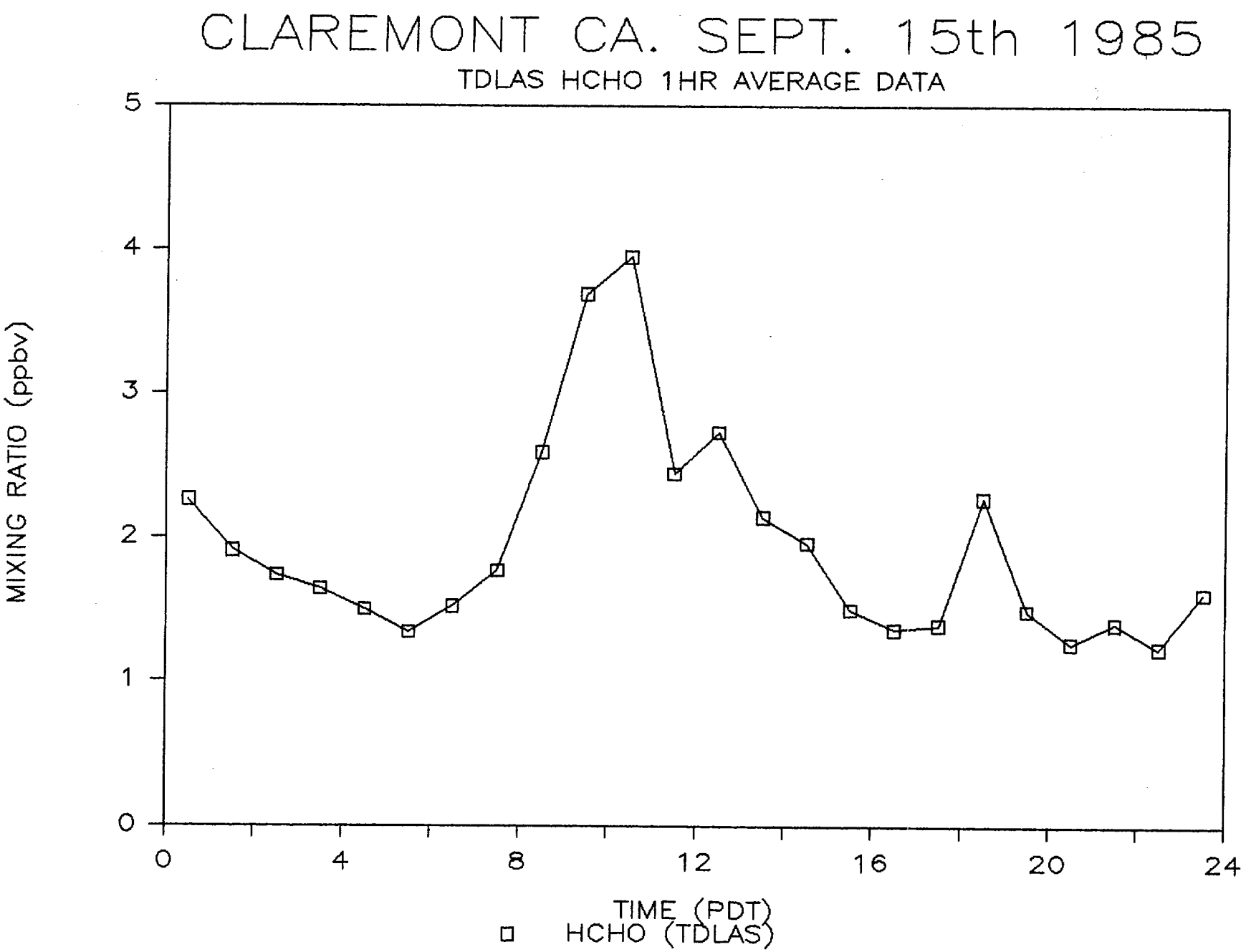

CLAREMONT CA. SEPT. 15th 1985
TDLAS HNO3 1HR AVERAGE DATA
MIXING RATIO (ppbv)
16
14
12
10
8
6
4
2
0
−2
−4
−6
−8
−10
−12
−14
−16
0
4
8
12
16
20
24
TIME (PDT)
HNO3 (AES)
HNO3 (UNI)

FIGURE A-5.3

Diurnal variation in the 1 hour HCHO mixing ratio measured by the Unisearch TAMS on September 15, 1985.


CLAREMONT CA. SEPT. 15th 1985
TDLAS HCHO 1HR AVERAGE DATA
MIXING RATIO (ppbv)
0
1
2
3
4
5
0
4
8
12
16
20
24
TIME (PDT)
HCHO (TDLAS)

HNO3 INTERCOMPARISON CLAREMONT CA

DATE: SEPT. 16, 1985

TIME PERIOD	TIME AVERAGE	NO2 LUMINOX PPBV	STD DEV PPBV	NO2 TDL AES PPBV	STD DEV PPBV	HNO3 TDL AES PPBV	STD DEV PPBV	HNO3 TDL UNI PPBV	STD DEV PPBV	HCHO TDL UNI PPBV	STD DEV PPBV
00:00-01:00	0.5	57.52	7.33	54.76	5.52	0.92	0.21	0.53	0.68	1.51	0.11
01:00-02:00	1.5	20.99	11.14	28.92	7.96	1.42	0.34	0.55	0.64	1.18	0.11
02:00-03:00	2.5	9.77	2.14	18.81	2.25	1.76	0.33	1.20	0.72	0.93	0.12
03:00-04:00	3.5	27.72	9.36	39.69	7.02	1.57	0.22	2.50	0.94	1.30	0.08
04:00-05:00	4.5	27.39	5.27	36.78	3.93	1.39	0.41	2.14	0.44	1.27	0.20
05:00-06:00	5.5	26.88	5.37	36.32	4.77	1.13	0.27	1.30	0.75	0.93	0.13
06:00-07:00	6.5	19.51	2.96	30.98	1.87	1.31	0.27	1.41	1.01	0.88	0.25
07:00-08:00	7.5	12.83	3.42	24.34	2.43	1.44	0.32	1.91	0.91	1.19	0.24
08:00-09:00	8.5	31.23	12.57	46.89	10.67	1.21	0.35	2.50	1.22	2.19	0.30
09:00-10:00	9.5	62.52	3.02	58.50	3.18	0.36	0.16	0.71	0.47	2.03	0.42
10:00-11:00	10.5	47.76	8.21	50.36	5.52	0.69	0.20	0.50	0.85	2.19	0.23
11:00-12:00	11.5	23.43	9.17	29.58	7.02	0.28	0.21	1.30	1.50	2.06	0.19
12:00-13:00	12.5	12.92	5.57	21.53	5.15	0.33	0.16	1.93	1.23	1.83	0.26
13:00-14:00	13.5	10.20	3.48	18.06	3.74	0.81	0.30	-0.50	1.85	1.82	0.20
14:00:15:00	14.5	8.11	2.84	16.38	3.18	1.27	0.23	0.66	1.29	2.05	0.18
15:00-16:00	15.5	8.28	1.60	16.29	1.80	1.76	0.15	1.82	1.09	1.83	0.20
16:00-17:00	16.5	10.35	2.30	19.19	2.90	1.82	0.74	1.86	1.29	1.82	0.08
17:00-18:00	17.5	16.78	1.54					1.12	1.33	2.05	0.18
18:00-19:00	18.5	24.88	3.96							2.02	0.20
19:00-20:00	19.5	27.51	2.52	39.41	1.97	0.42	0.18			1.51	0.08
20:00-21:00	20.5	26.83	5.23	41.18	5.43	0.29	0.47			1.31	0.18
21:00-22:00	21.5	55.89	7.84	66.46	5.52	0.91	0.21				
22:00-23:00	22.5	63.04	1.44	72.26	1.87	0.82	0.17				
23:00-24:00	23.5	52.49	5.17	55.88	2.06	1.03	0.23				

FIGURE A-6.1

Diurnal variation in the 1 hour NO_2 mixing ratio measured by the TAMS and the Luminox on September 16, 1985.

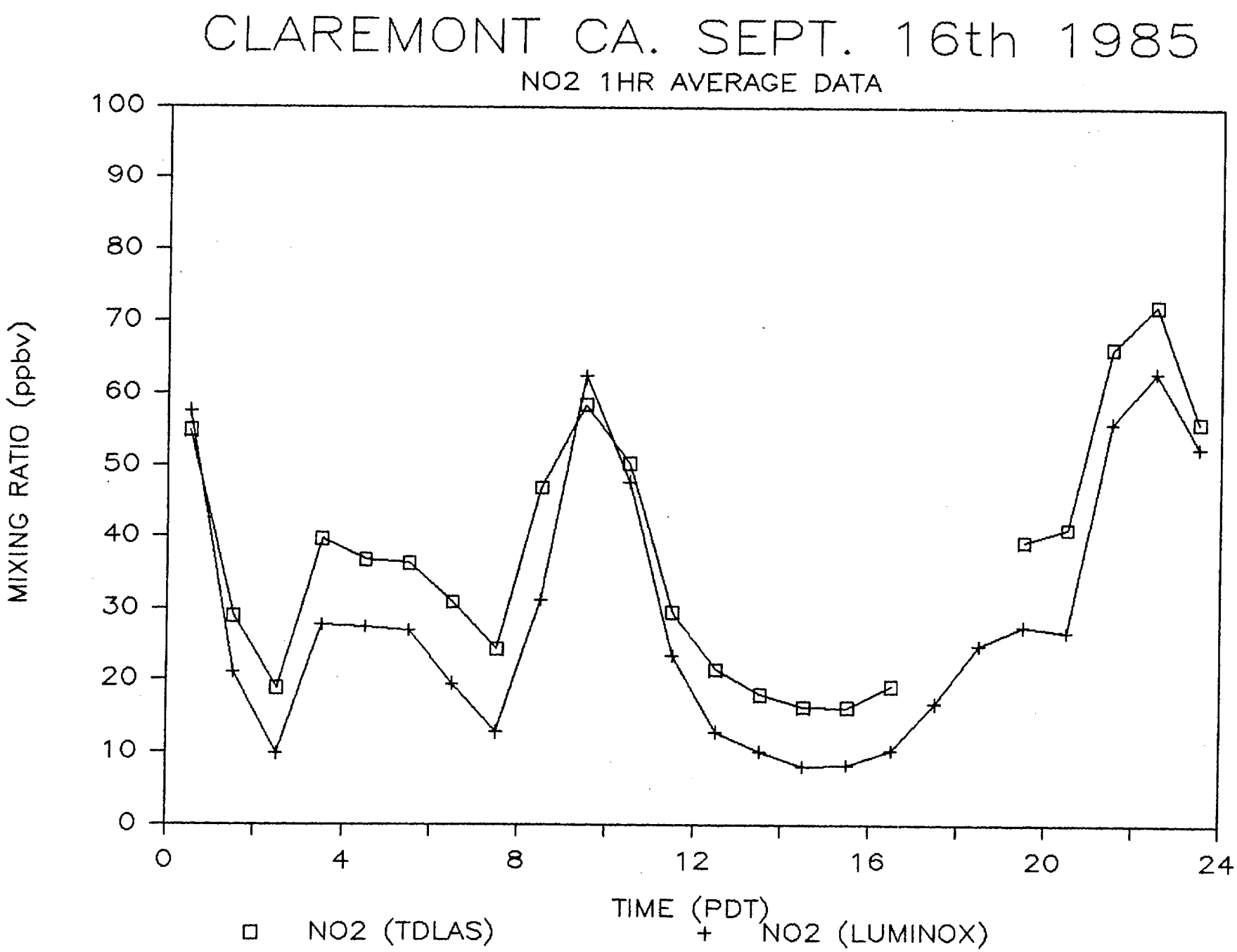

CLAREMONT CA. SEPT. 16th 1985
NO2 1HR AVERAGE DATA
MIXING RATIO (ppbv)
100
90
80
70
60
50
40
30
20
10
0
0
4
8
12
16
20
24
TIME (PDT)
NO2 (TDLAS)
NO2 (LUMINOX)

FIGURE A-6.2

Diurnal variation in the 1 hour HNO_3 mixing ratio measured by the Unisearch and AES TAMS on September 16, 1985.

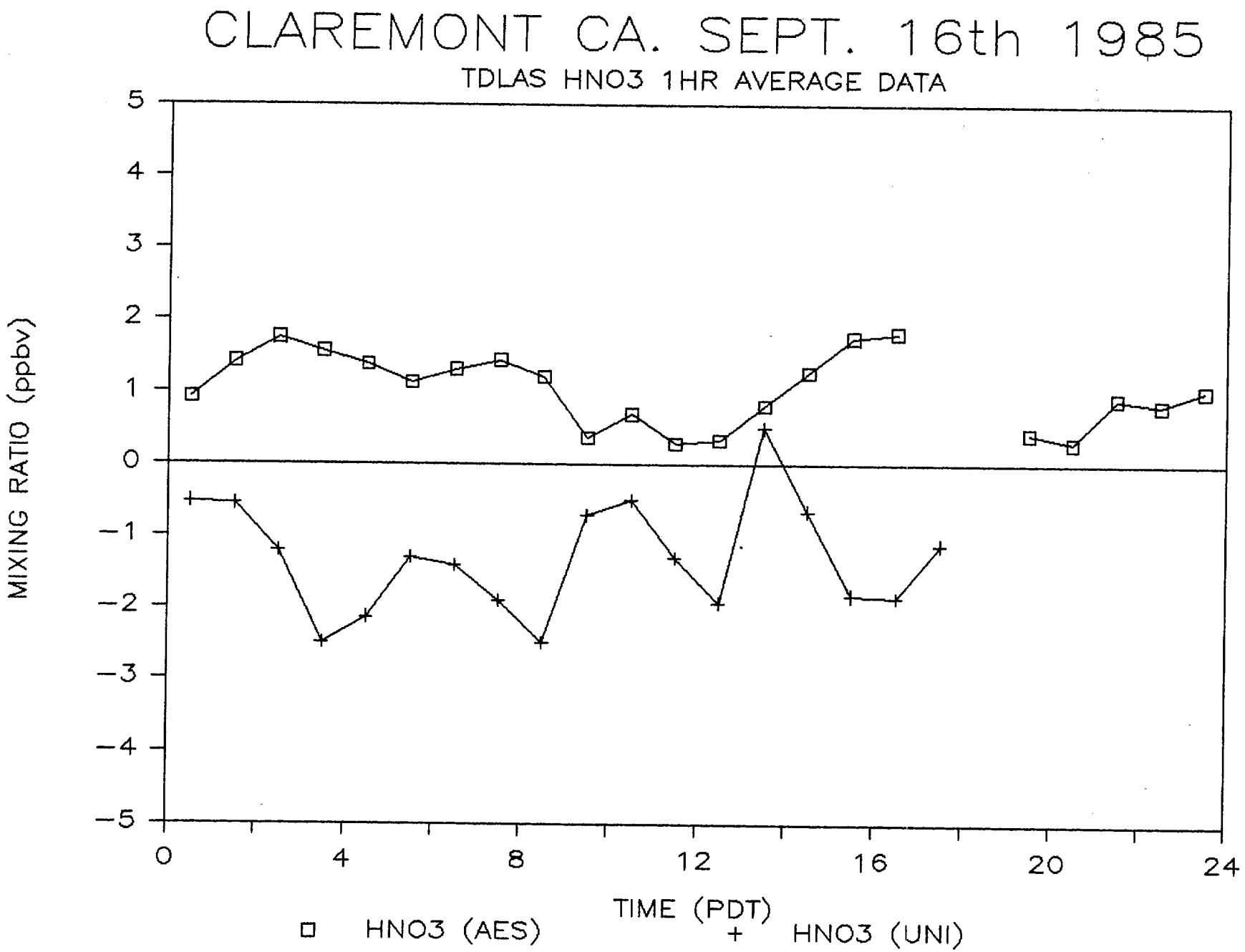
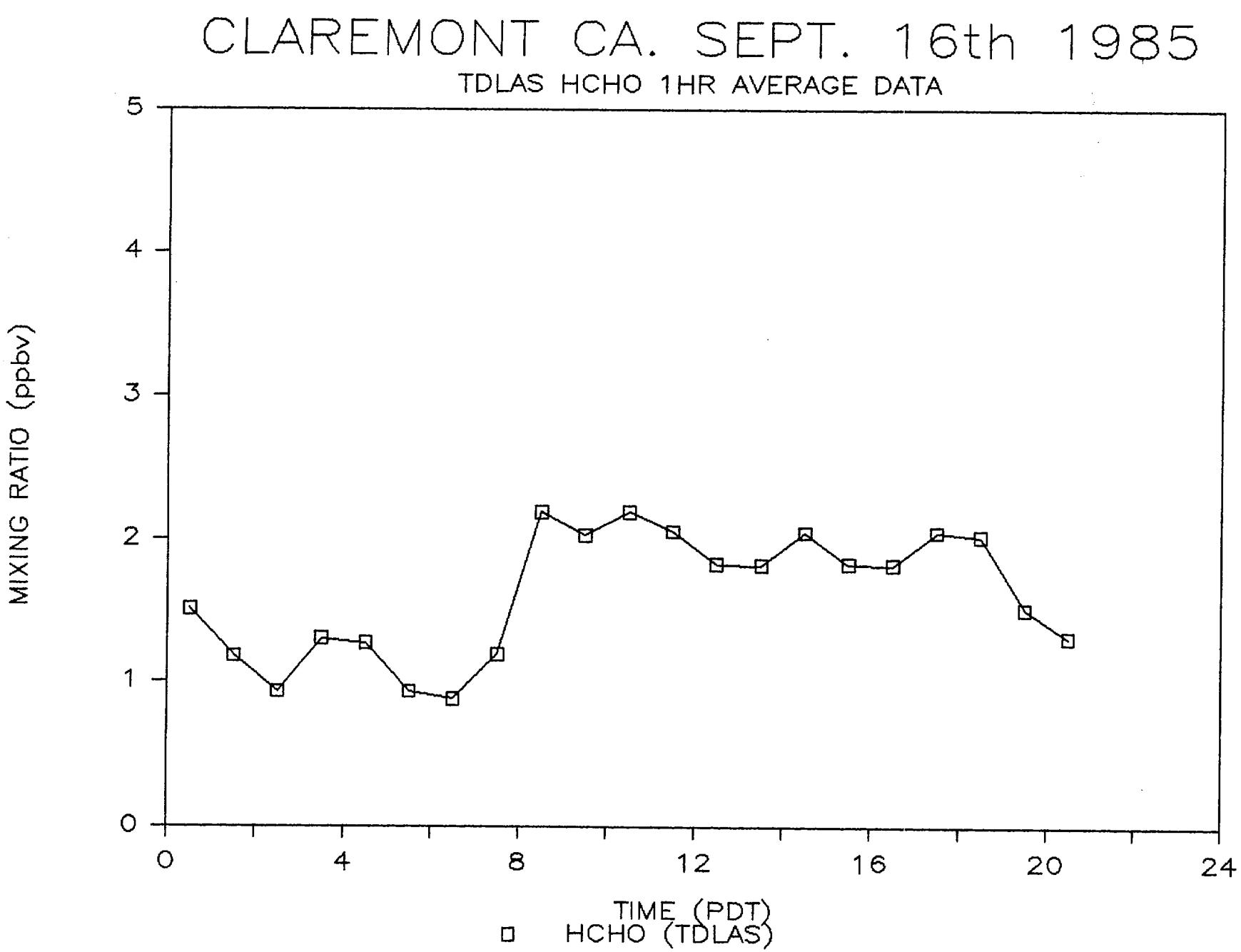

CLAREMONT CA. SEPT. 16th 1985
TDLAS HNO3 1HR AVERAGE DATA
MIXING RATIO (ppbv)
5
4
3
2
1
0
−1
−2
−3
−4
−5
0
4
8
12
16
20
24
TIME (PDT)
HNO3 (AES)
HNO3 (UNI)

FIGURE A-6.3

Diurnal variation in the 1 hour HCHO mixing ratio measured by the Unisearch TAMS on September 16, 1985.


CLAREMONT CA. SEPT. 16th 1985
TDLAS HCHO 1HR AVERAGE DATA
MIXING RATIO (ppbv)
0
1
2
3
4
5
0
4
8
12
16
20
24
TIME (PDT)
HCHO (TDLAS)

HNO3 INTERCOMPARISON CLAREMONT CA

DATE: SEPT. 17, 1985

TIME PERIOD	TIME AVERAGE	NO2 LUMINOX PPBV	STD DEV PPBV	NO2 TDL AES PPBV	STD DEV PPBV	HNO3 TDL AES PPBV	STD DEV PPBV	HNO3 TDL UNI PPBV	STD DEV PPBV	HCHO TDL UNI PPBV	STD DEV PPBV
00:00-01:00	0.5	50.10	7.03	46.81	4.04	0.64	0.52	2.01	1.12		
01:00-02:00	1.5	47.88	3.47	45.50	2.73	2.03	0.33	2.46	0.76	1.12	0.24
02:00-03:00	2.5	17.09	8.58	24.91	6.39	2.46	0.31	2.61	0.43	0.88	0.13
03:00-04:00	3.5	4.34	0.58	13.63	1.03	2.47	0.18	2.37	0.47	0.86	0.08
04:00-05:00	4.5	6.16	2.12	16.54	2.63	2.73	0.09	2.86	0.67	0.74	0.15
05:00-06:00	5.5	3.08	1.27	11.47	2.16	2.96	0.14	2.51	0.91	0.87	0.06
06:00-07:00	6.5	7.72	3.93	17.67	4.32	2.22	0.20	3.64	1.02	0.80	0.11
07:00-08:00	7.5	10.00	2.26	20.68	1.88	2.69	0.18	2.58	0.74	0.71	0.11
08:00-09:00	8.5	9.79	3.32	22.56	2.54	0.89	0.45			1.06	0.02
09:00-10:00	9.5	21.59	6.03	33.93	2.91	0.34	0.12	0.80	0.64	1.34	0.12
10:00-11:00	10.5	28.12	2.05	36.10	1.50			1.25	0.83	2.01	0.17
11:00-12:00	11.5	21.81	3.61	25.94	2.82	1.01	0.05	2.49	1.68	2.23	0.26
12:00-13:00	12.5	17.12	6.15	23.12	4.51	1.38	0.26	1.95	1.26	2.13	0.36
13:00-14:00	13.5	16.67	1.05	23.50	1.13	2.13	0.54	1.64	1.58	2.00	0.34
14:00:15:00	14.5	12.14	2.04	18.71	1.79	4.90	0.79	3.22	2.04	1.58	0.12
15:00-16:00	15.5	13.57	2.05	21.62	3.38	5.37	0.38	4.88	1.67	1.51	0.18
16:00-17:00	16.5	26.17	2.00	29.80	1.41	4.02	0.42	4.47	1.81	1.82	0.17
17:00-18:00	17.5	31.85	4.96	34.40	3.20	2.86	0.38	2.46	0.60	1.68	0.11
18:00-19:00	18.5	48.31	9.86	45.50	6.11	2.80	0.70	4.07	3.73	1.63	0.13
19:00-20:00	19.5	44.90	3.25	44.56	2.44	2.22	0.38	2.34	1.73	1.69	0.28
20:00-21:00	20.5	76.37	10.22					2.26	1.41		
21:00-22:00	21.5	67.74	1.86	62.70	7.43	1.35	0.58	3.13	0.95	1.20	0.20
22:00-23:00	22.5	60.18	3.64	58.94	1.97	1.80	0.25	2.48	1.87	1.14	0.19
23:00-24:00	23.5	45.39	8.77	49.26	5.45	1.70	0.38	2.75	0.48	0.80	0.18

FIGURE A-7.1

Diurnal variation in the 1 hour NO_2 mixing ratio measured by the TAMS and the Luminox on September 17, 1985.

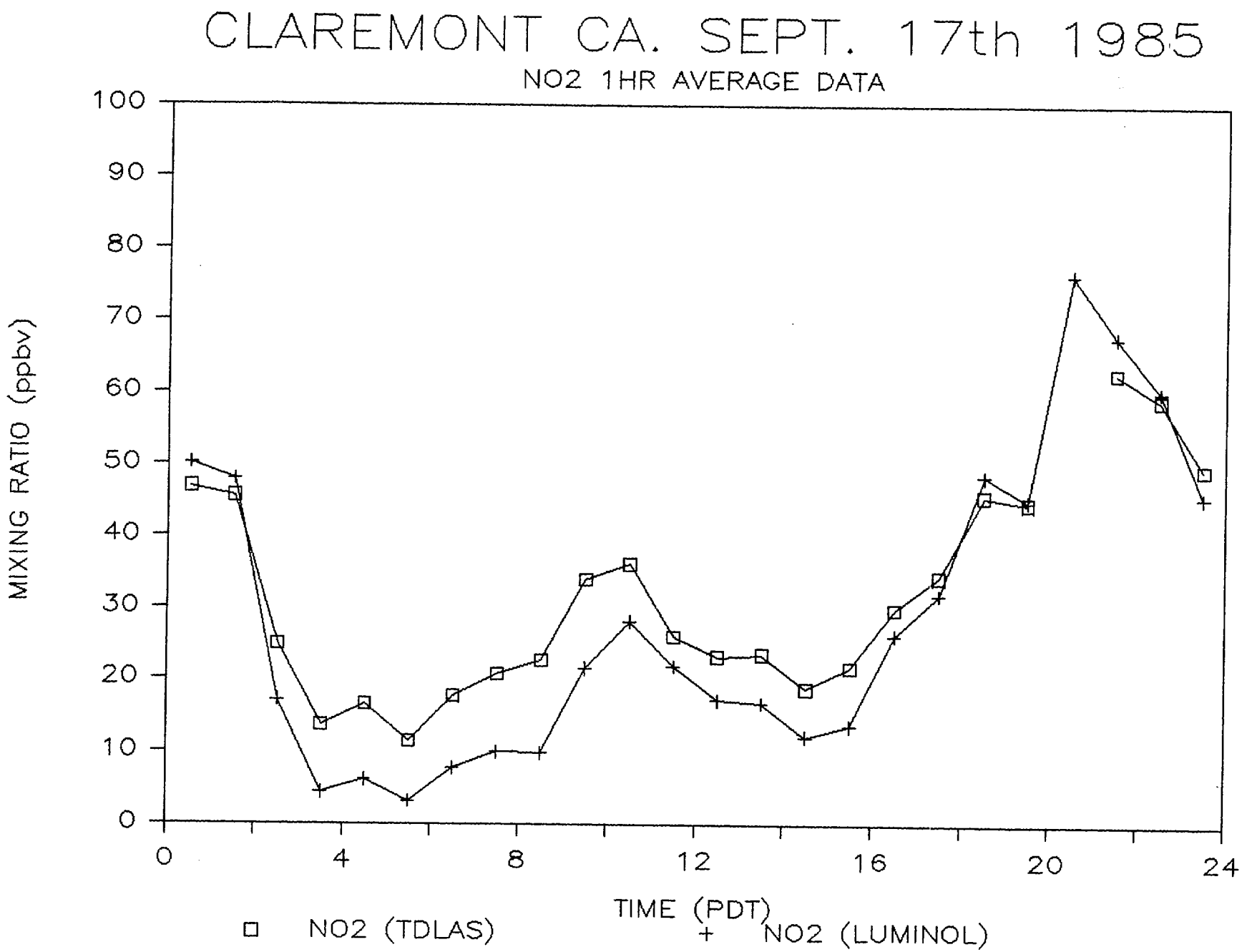

CLAREMONT CA. SEPT. 17th 1985
NO2 1HR AVERAGE DATA
MIXING RATIO (ppbv)
100
90
80
70
60
50
40
30
20
10
0
0
4
8
12
16
20
24
TIME (PDT)
NO2 (TDLAS)
NO2 (LUMINOL)

FIGURE A-7.2

Diurnal variation in the 1 hour HNO_3 mixing ratio measured by the Unisearch and AES TAMS on September 17, 1985.

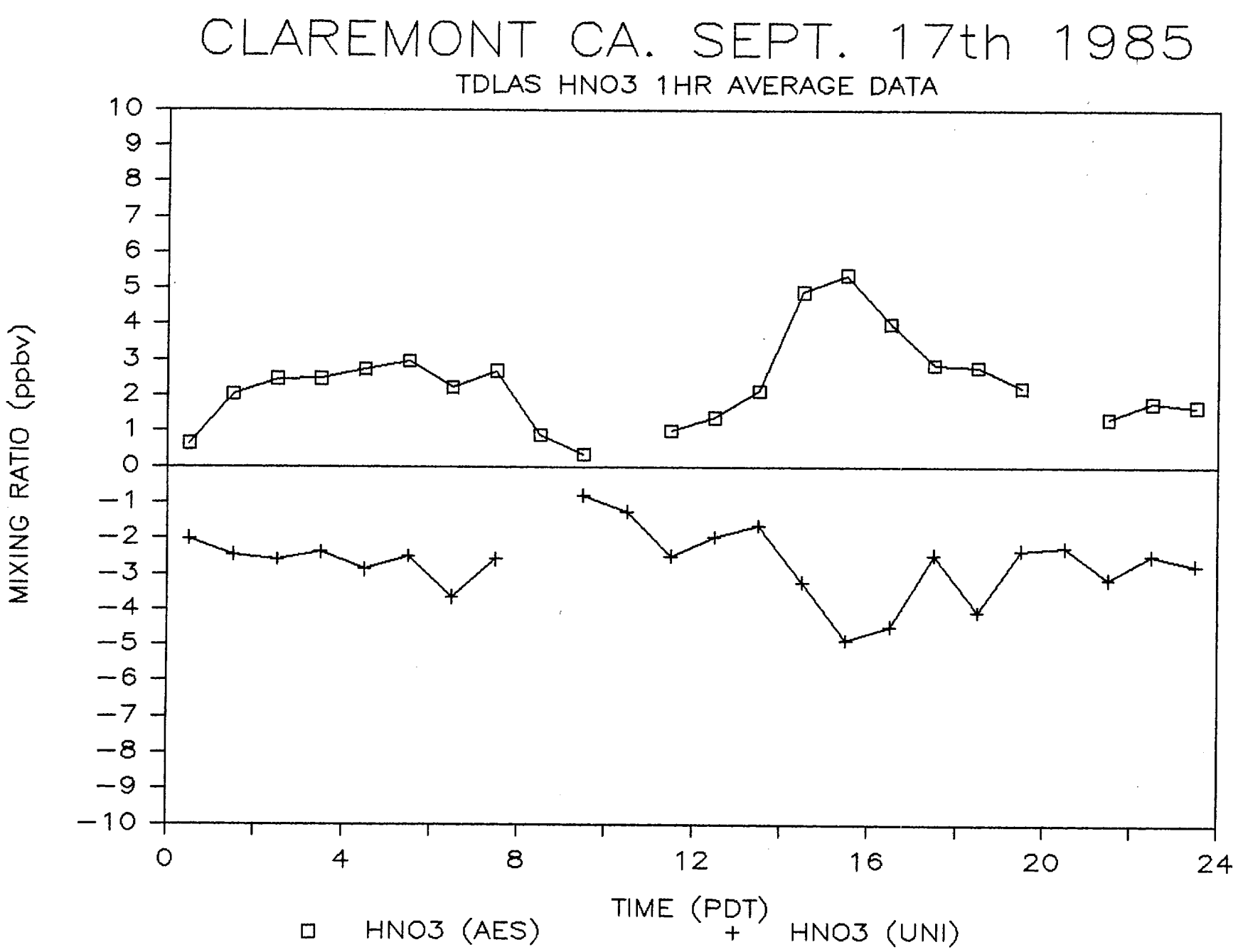
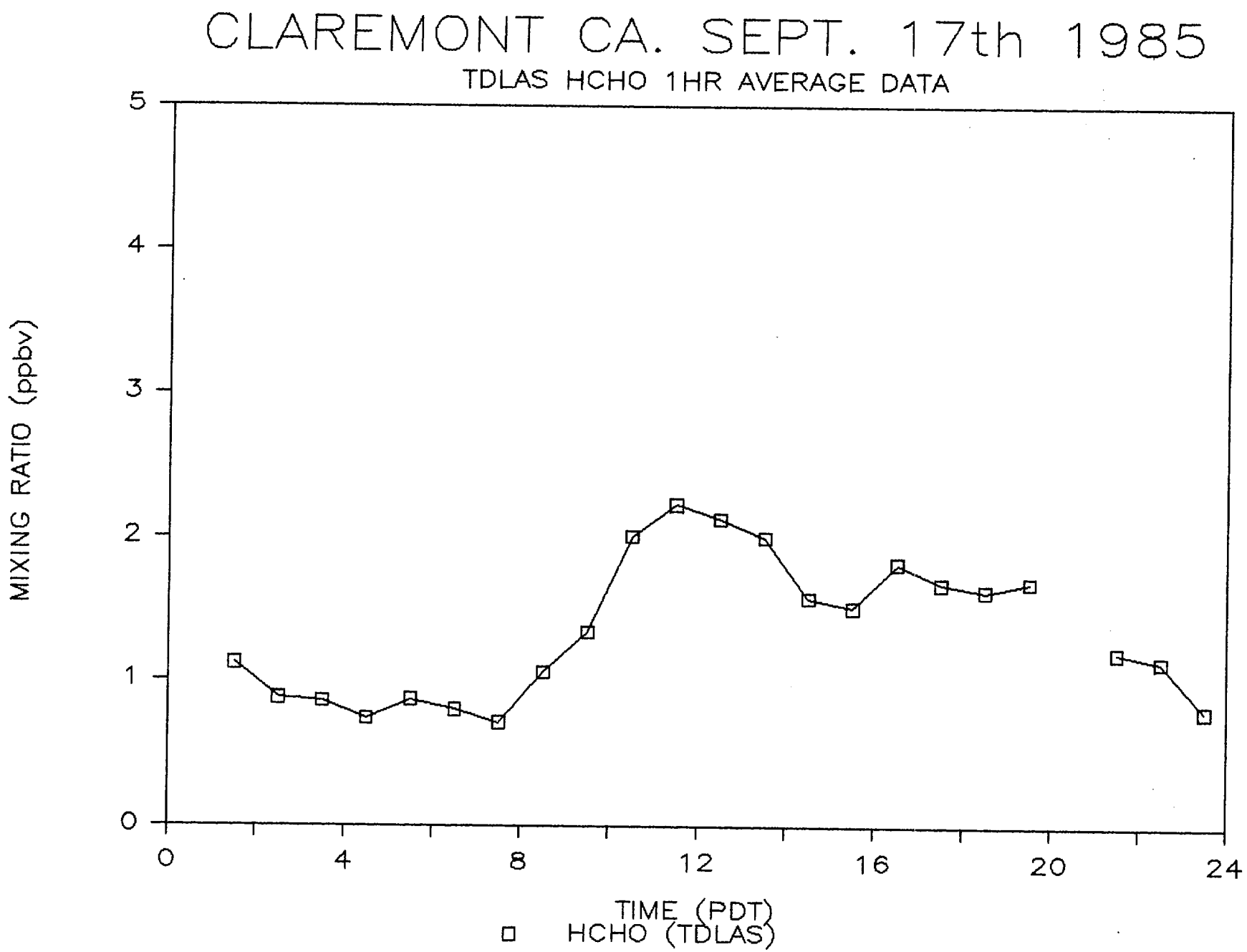

CLAREMONT CA. SEPT. 17th 1985
TDLAS HNO3 1HR AVERAGE DATA
MIXING RATIO (ppbv)
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
−5
−6
−7
−8
−9
−10
0
4
8
12
16
20
24
TIME (PDT)
HNO3 (AES)
HNO3 (UNI)

FIGURE A-7.3

Diurnal variation in the 1 hour HCHO mixing ratio measured by the Unisearch TAMS on September 17, 1985.


CLAREMONT CA. SEPT. 17th 1985
TDLAS HCHO 1HR AVERAGE DATA
MIXING RATIO (ppbv)
0
1
2
3
4
5
0
4
8
12
16
20
24
TIME (PDT)
HCHO (TDLAS)

HNO3 INTERCOMPARISON CLAREMONT CA

DATE: SEPT. 18, 1985

TIME PERIOD	TIME AVERAGE	NO2 LUMINOX PPBV	STD DEV PPBV	NO2 TDL AES PPBV	STD DEV PPBV	HNO3 TDL AES PPBV	STD DEV PPBV	HNO3 TDL UNI PPBV	STD DEV PPBV	HCHO TDL UNI PPBV	STD DEV PPBV
00:00-01:00	0.5	48.40	7.38	44.18	3.57	1.89	0.16	2.09	0.54	0.70	0.17
01:00-02:00	1.5	41.47	5.04	40.61	2.63	1.97	0.20	2.20	0.50	0.95	0.44
02:00-03:00	2.5	47.60	2.95	44.56	1.60	2.07	0.26	2.30	1.17	1.02	0.14
03:00-04:00	3.5	49.57	2.75	44.93	1.60	2.00	0.18	2.20	0.66	0.92	0.13
04:00-05:00	4.5	34.35	12.20	39.48	3.38	1.93	0.24	2.16	0.73	0.73	0.17
05:00-06:00	5.5			41.74	1.41	2.21	0.16	3.21	0.74	0.43	0.11
06:00-07:00	6.5			41.08	1.88	1.76	0.60	2.07	0.81	0.53	0.18
07:00-08:00	7.5	35.44	4.43	35.25	1.88	0.32	0.32	1.24	1.05	1.31	0.05
08:00-09:00	8.5	34.53	2.61	34.22	1.32	0.63	0.34	0.42	1.64		
09:00-10:00	9.5	36.45	3.42	31.96	2.63	1.40	0.34	0.71	1.34	0.81	0.09
10:00-11:00	10.5	43.34	7.63	35.81	5.92	2.08	0.76	1.73	1.68	0.94	0.23
11:00-12:00	11.5	23.41	16.86	21.71	8.18	1.38	0.61	2.29	1.32	0.62	0.16
12:00-13:00	12.5	23.05	13.87	26.70	6.86	2.55	0.79	0.84	1.21	0.48	0.16
13:00-14:00	13.5	46.75	19.88	46.62	2.14	3.48	0.25	1.71	0.39	0.75	0.15
14:00:15:00	14.5	16.47	2.01	23.50	2.16	2.88	1.30	3.24	0.82	0.61	0.20
15:00-16:00	15.5	14.90	1.72	34.31	6.86	2.95	0.19			0.69	0.12
16:00-17:00	16.5	46.04	7.03	42.49	3.10	2.05	0.19	2.02	1.06	0.43	0.23
17:00-18:00	17.5	43.82	9.75	39.67	5.26	2.05	0.33	0.93	1.64	0.39	0.33
18:00-19:00	18.5	29.79	10.40	34.12	6.49	2.22	0.10	0.29	0.72	0.32	0.64
19:00-20:00	19.5	57.31	5.73	49.63	2.73	1.89	0.24	0.36	0.81	0.50	0.54
20:00-21:00	20.5	51.97	2.05					3.23	1.14	0.22	0.20
21:00-22:00	21.5	43.63	7.15	41.27	2.07	0.38	0.63	0.53	0.92		
22:00-23:00	22.5	26.31	3.19	32.99	1.97	1.18	0.45			0.42	0.41
23:00-24:00	23.5	16.34	4.60	26.32	3.38	1.66	0.26			0.52	0.25

FIGURE A-8.1

Diurnal variation in the 1 hour NO_2 mixing ratio measured by the TAMS and the Luminox on September 18, 1985.

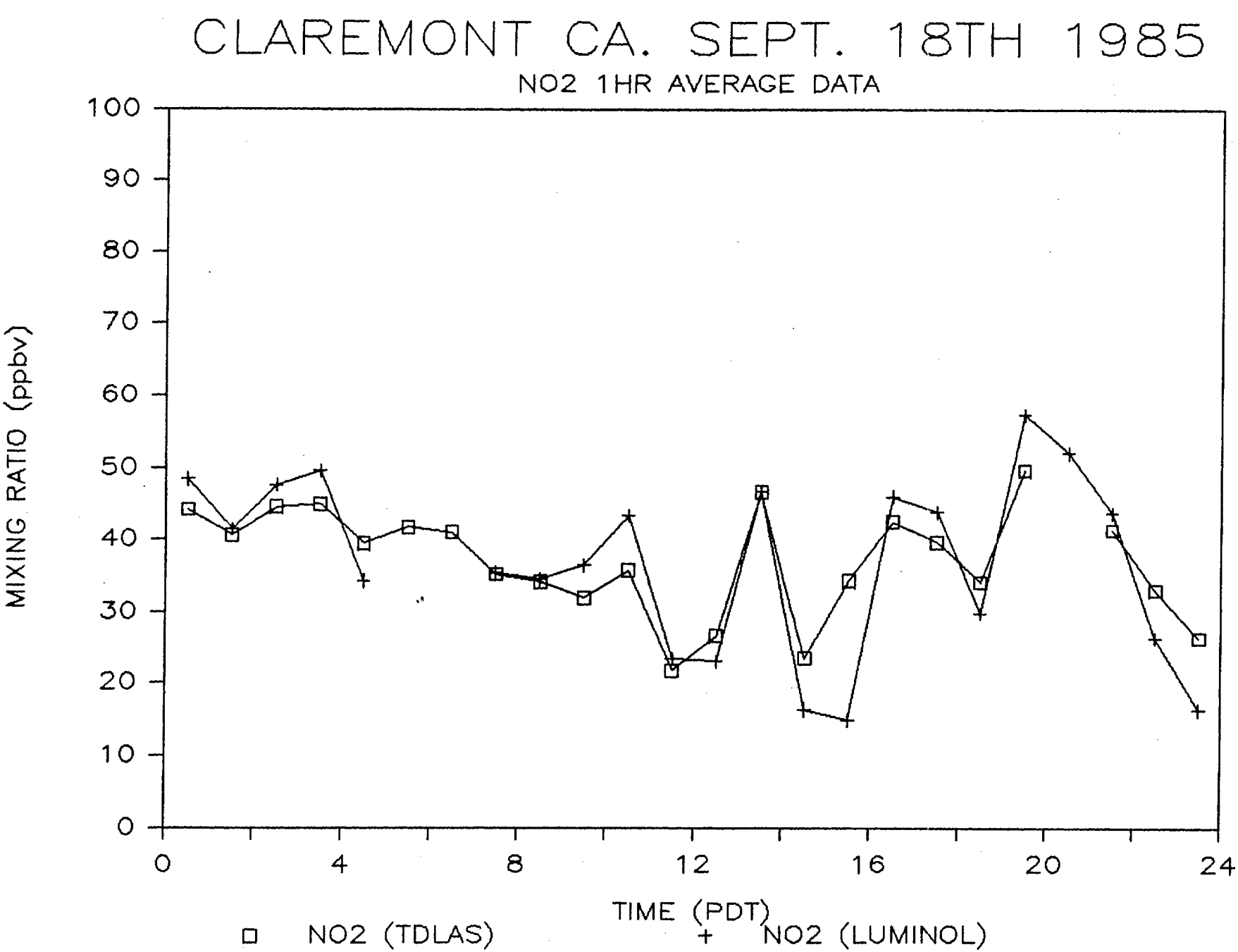

CLAREMONT CA. SEPT. 18TH 1985
NO2 1HR AVERAGE DATA
MIXING RATIO (ppbv)
100
90
80
70
60
50
40
30
20
10
0
0
4
8
12
16
20
24
TIME (PDT)
NO2 (TDLAS)
NO2 (LUMINOL)

FIGURE A-8.2

Diurnal variation in the 1 hour HNO_3 mixing ratio measured by the Unisearch and AES TAMS on September 18, 1985.

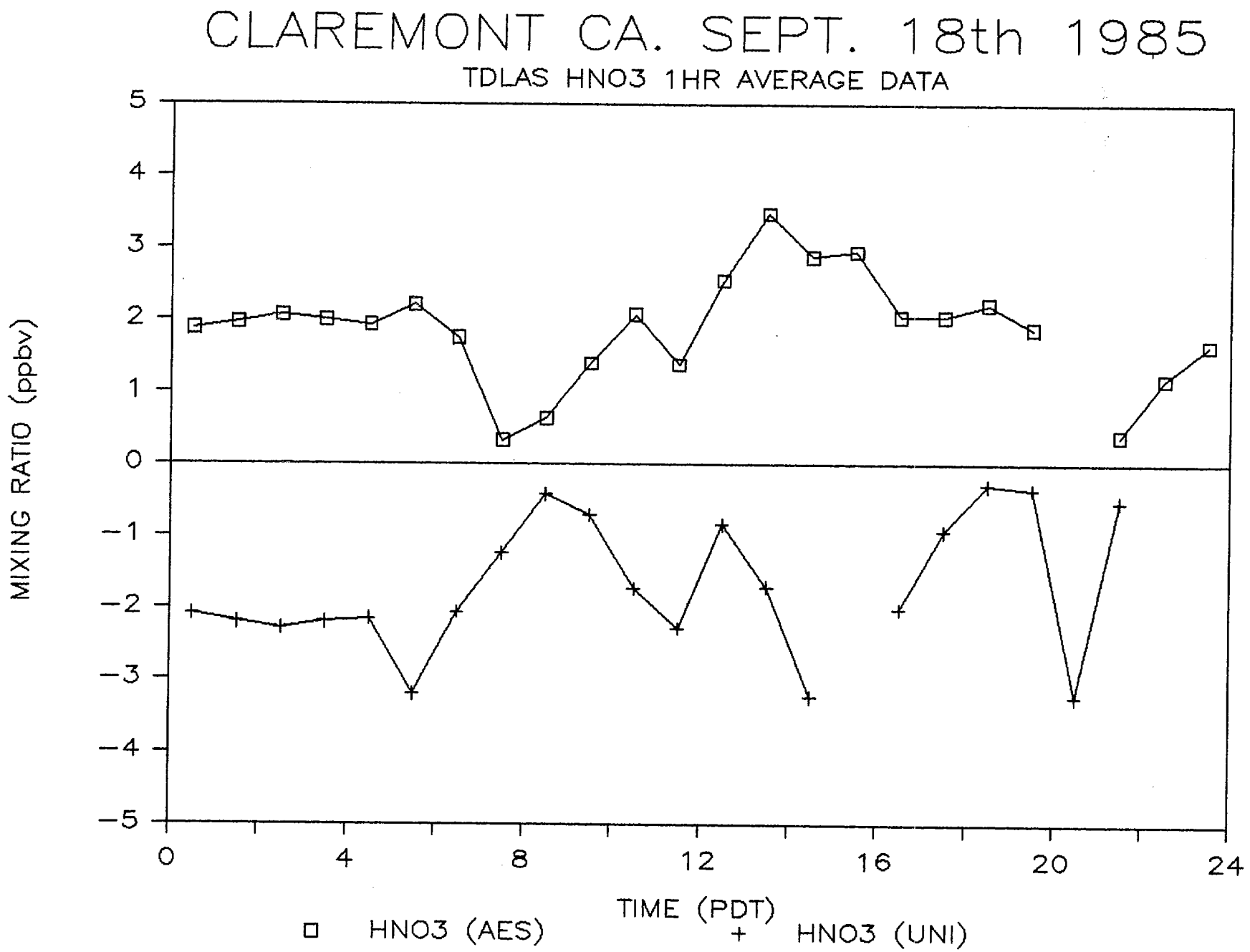
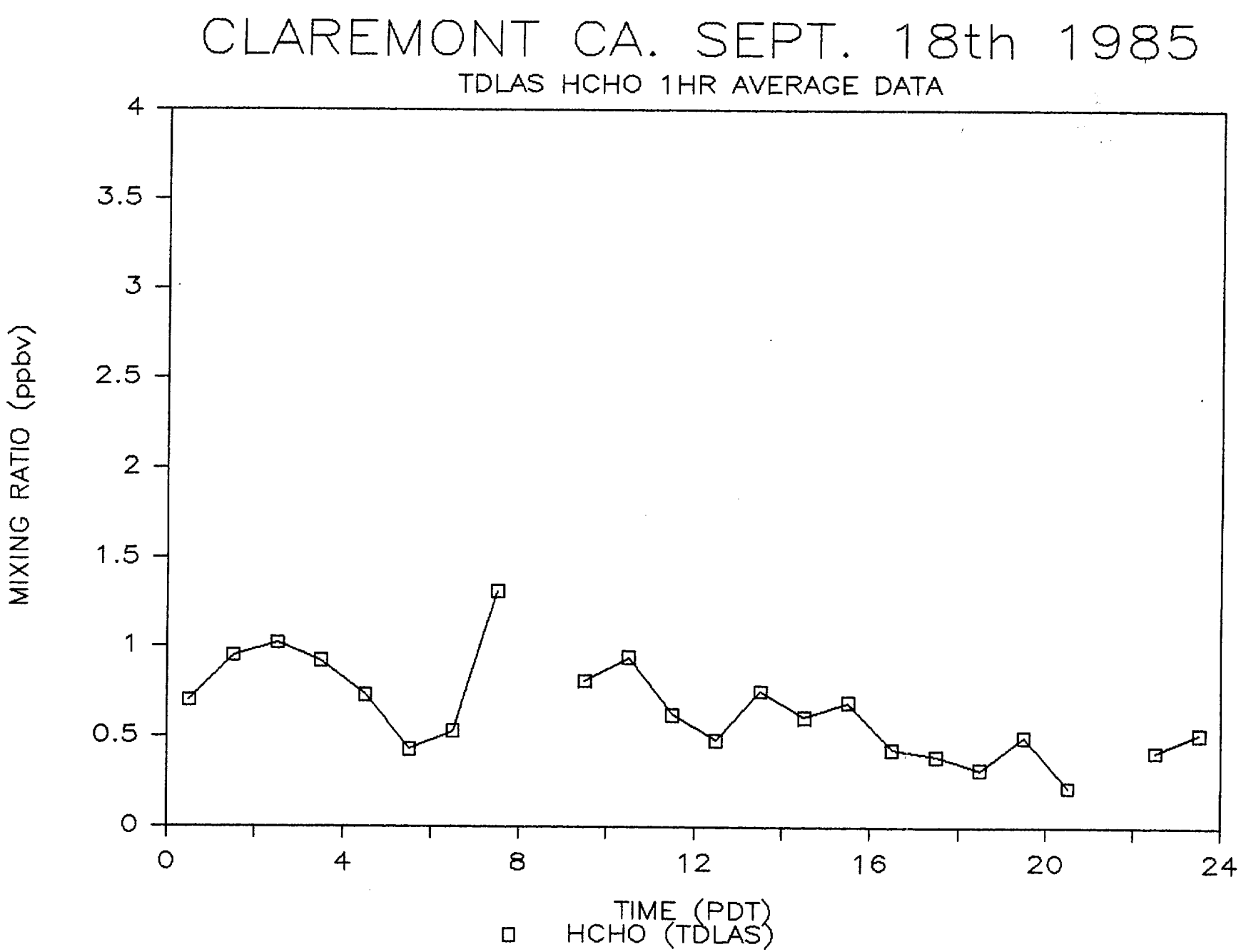

CLAREMONT CA. SEPT. 18th 1985
TDLAS HNO3 1HR AVERAGE DATA
MIXING RATIO (ppbv)
5
4
3
2
1
0
−1
−2
−3
−4
−5
0
4
8
12
16
20
24
TIME (PDT)
HNO3 (AES)
HNO3 (UNI)

FIGURE A-8.3

Diurnal variation in the 1 hour HCHO mixing ratio measured by the Unisearch TAMS on September 18, 1985.


CLAREMONT CA. SEPT. 18th 1985
TDLAS HCHO 1HR AVERAGE DATA
MIXING RATIO (ppbv)
4
3.5
3
2.5
2
1.5
1
0.5
0
0
4
8
12
16
20
24
TIME (PDT)
HCHO (TDLAS)

HNO3 INTERCOMPARISON CLAREMONT CA

DATE: SEPT. 19, 1985

TIME PERIOD	TIME AVERAGE	NO2 LUMINOX PPBV	STD DEV PPBV	NO2 TDL AES PPBV	STD DEV PPBV	HNO3 TDL AES PPBV	STD DEV PPBV	HNO3 TDL UNI PPBV	STD DEV PPBV	HCHO TDL UNI PPBV	STD DEV PPBV
00:00-01:00	0.5	4.63	1.17	20.21	2.16	0.30	0.81	0.84	0.58	0.46	0.12
01:00-02:00	1.5	3.49	0.51	18.42	1.03	-0.70	0.27	0.74	0.78	0.28	0.20
02:00-03:00	2.5	2.42	0.39	14.48	4.14	-0.50	0.27	-0.65	1.19	0.14	0.10
03:00-04:00	3.5	1.49	0.18	12.97	0.56	0.14	0.24	-0.62	0.98	0.29	0.20
04:00-05:00	4.5	5.55	3.68	22.18	6.30	0.55	0.20	0.83	0.32	0.54	0.10
05:00-06:00	5.5	10.98	1.17	30.93	1.50	0.76	0.12	1.64	1.51	0.48	0.18
06:00-07:00	6.5			31.02	1.13	1.04	0.24	2.52	1.74	1.11	0.09
07:00-08:00	7.5			31.68	1.32	1.17	0.19	1.25	1.60	0.94	0.13
08:00-09:00	8.5										
09:00-10:00	9.5										
10:00-11:00	10.5										
11:00-12:00	11.5										
12:00-13:00	12.5										
13:00-14:00	13.5										
14:00:15:00	14.5										
15:00-16:00	15.5										
16:00-17:00	16.5										
17:00-18:00	17.5										
18:00-19:00	18.5										
19:00-20:00	19.5										
20:00-21:00	20.5										
21:00-22:00	21.5										
22:00-23:00	22.5										
23:00-24:00	23.5										

FIGURE A-9.1

Diurnal variation in the 1 hour NO_z mixing ratio measured by the TAMS and the Luminox on September 19, 1985.

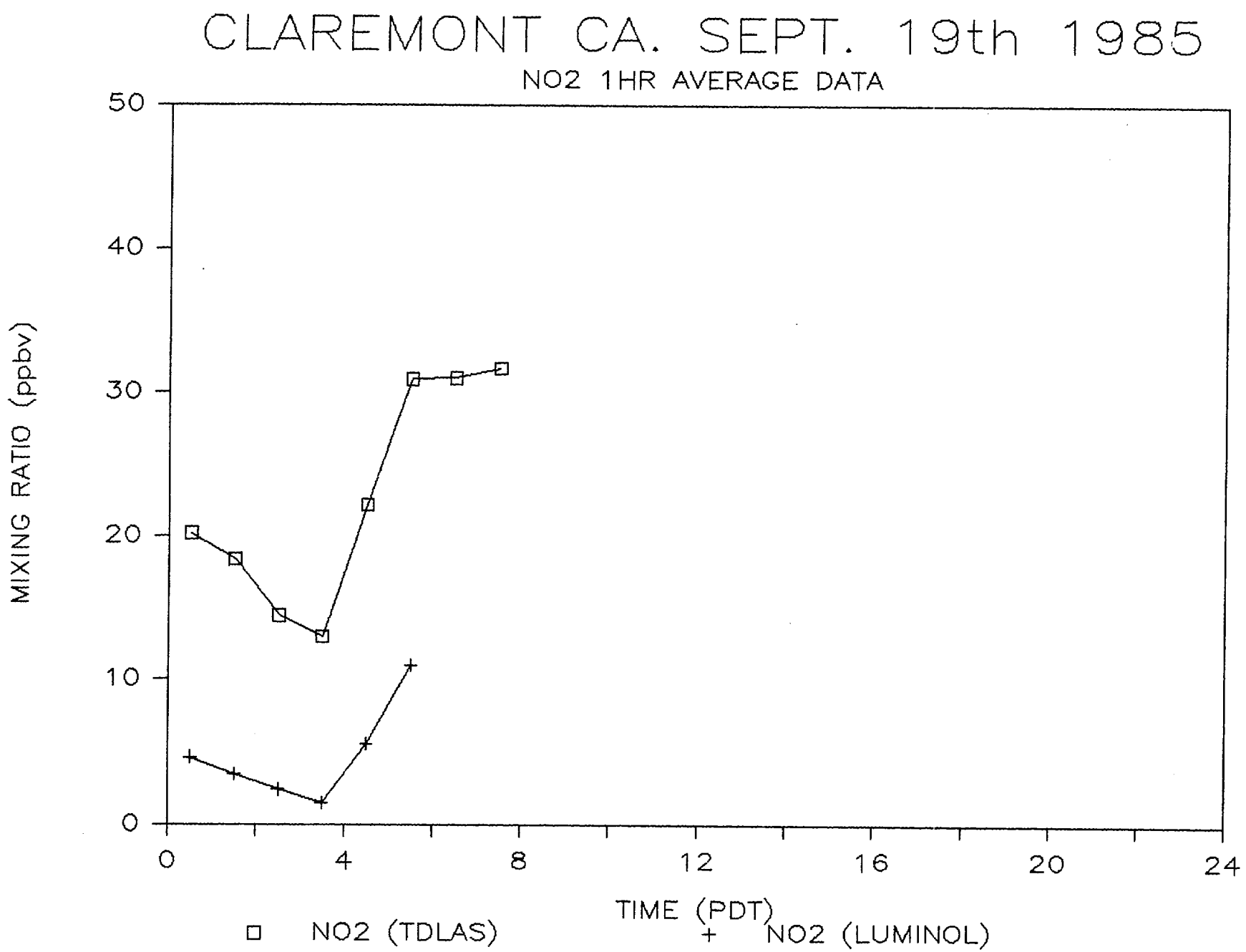

CLAREMONT CA. SEPT. 19th 1985
NO2 1HR AVERAGE DATA
MIXING RATIO (ppbv)
50
40
30
20
10
0
0
4
8
12
16
20
24
TIME (PDT)
NO2 (TDLAS)
NO2 (LUMINOL)

FIGURE A-9.2

Diurnal variation in the 1 hour HNO_3 mixing ratio measured by the Unisearch and AES TAMS on September 19, 1985.

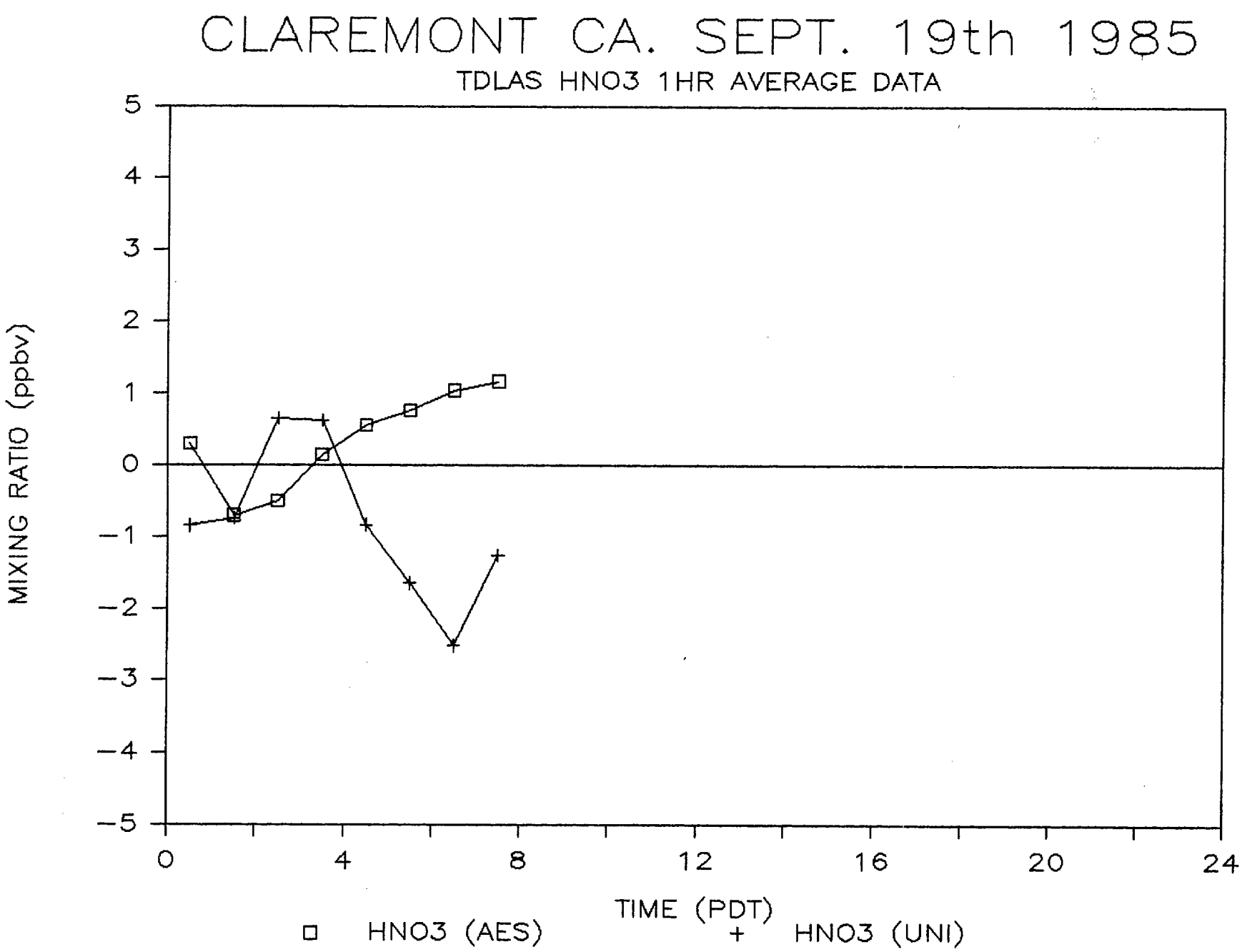
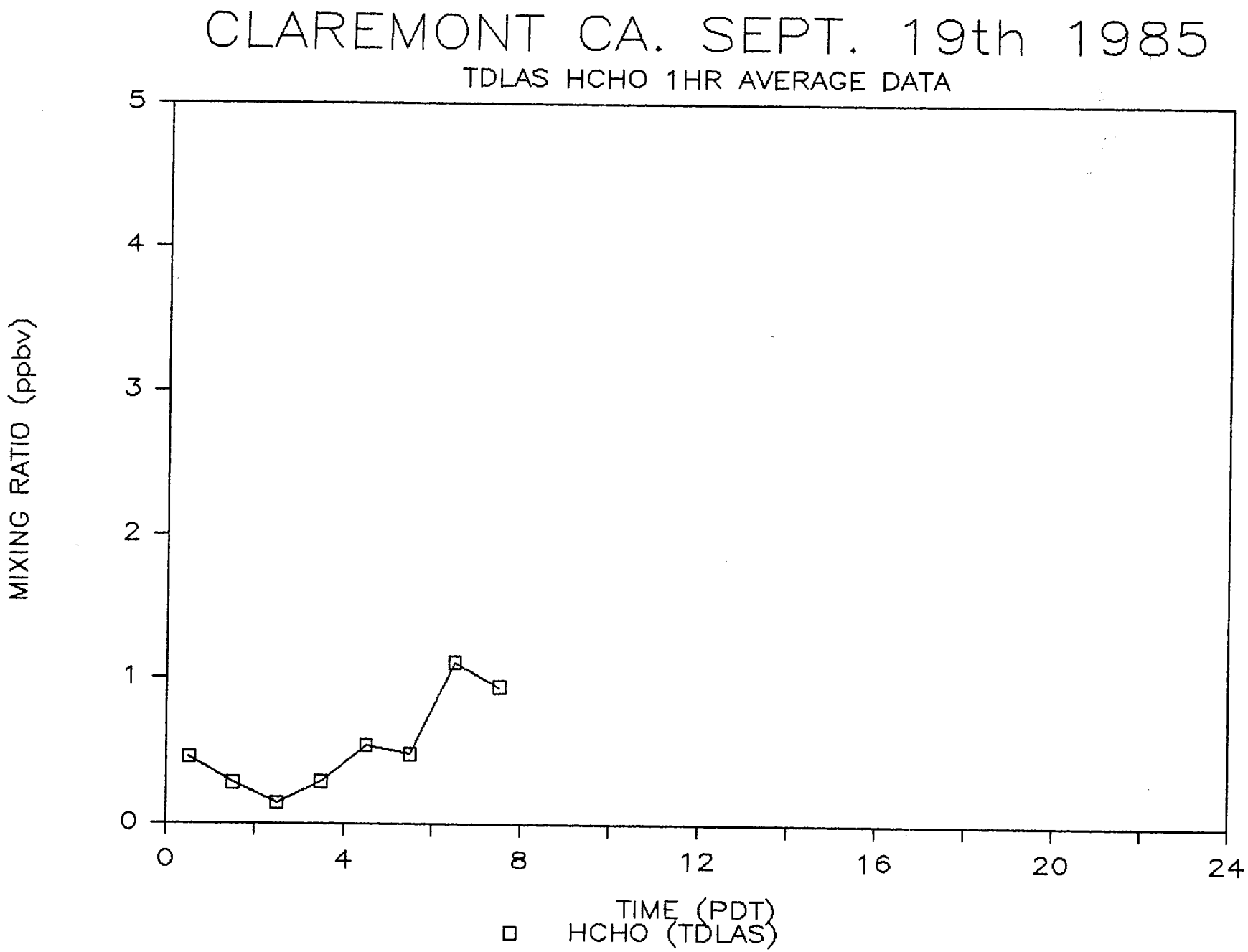

CLAREMONT CA. SEPT. 19th 1985
TDLAS HNO3 1HR AVERAGE DATA
MIXING RATIO (ppbv)
5
4
3
2
1
0
−1
−2
−3
−4
−5
0
4
8
12
16
20
24
TIME (PDT)
HNO3 (AES)
HNO3 (UNI)

FIGURE A-9.3

Diurnal variation in the 1 hour HCHO mixing ratio measured by the Unisearch TAMS on September 19, 1985.


CLAREMONT CA. SEPT. 19th 1985
TDLAS HCHO 1HR AVERAGE DATA
MIXING RATIO (ppbv)
0
1
2
3
4
5
0
4
8
12
16
20
24
TIME (PDT)
HCHO (TDLAS)

APPENDIX B

Summary tabulation of TDLAS NO_2, HNO_3 and HCHO, and Luminox NO_2 1 hour average data obtained during the Claremont CA HNO_3 intercomparison study September 11 - 19, 1985 and graphical representations of the diurnal variation of each species over the 9 day measurement period. Average HNO_3 represents the average of the two TDLAS measurements. For continuity, where HNO_3 data is not available from one TDLAS the average is assumed to be equal to the single measurement. Mixing ratios are given at STP (0°C and 760 Torr).

TDLAS/LUMINOX 1HR AVERAGE DATA CLAREMONT CA. SEPT. 11-19, 1985

DATE	TIME DECIMAL DAY	NO2 LUMINOX PPBV	NO2 TDL AES PPBV	HNO3 TDL AES PPBV	HNO3 TDL UNI PPBV	AVERAGE HNO3 PPBV	HCHO TDL UNI PPBV
SEPT 11	11.02						
	11.06						
	11.10						
	11.15						
	11.19						
	11.23						
	11.27						
	11.31						
	11.35	23.00	22.75	-0.23		-0.23	0.51
	11.40	13.70	21.15	-0.05		-0.05	
	11.44	14.38	21.34	0.31		0.31	
	11.48	8.13	15.23	0.54		0.54	1.75
	11.52	9.91	17.01	1.41		1.41	
	11.56	9.00	16.07	0.57		0.57	1.27
	11.60	12.81	19.46	0.61		0.61	1.73
	11.65	12.34	18.52	0.87		0.87	1.98
	11.69	16.28	22.65	0.72	0.80	0.76	2.15
	11.73	23.29	28.58	0.97	1.15	1.06	2.15
	11.77	26.81	32.99	1.03	0.69	0.86	1.92
	11.81	40.36	49.16	0.37	0.53	0.45	1.69
	11.85	54.79	54.90	-0.29	0.50	0.11	1.18
	11.90	50.53	50.85	0.22	0.60	0.41	1.26
	11.94	49.36	52.17	0.33	0.69	0.51	1.37
	11.98	39.75	44.37	0.06	0.95	0.51	1.04
SEPT 12	12.02	41.66	45.97	-0.20	0.46	0.13	1.41
	12.06	42.01	45.97	-0.08	0.60	0.26	1.02
	12.10	31.79	37.22	0.36	0.01	0.19	0.92
	12.15	25.86	33.28	0.40	0.42	0.41	0.91
	12.19	33.71	39.67	0.08	-0.51	-0.22	0.96
	12.23	34.65	41.27	0.00	0.41	0.21	1.04
	12.27	42.17	47.94	0.31	0.82	0.57	0.93
	12.31	44.30		0.28	0.54	0.41	1.50
	12.35	52.22			0.79	0.79	1.46
	12.40	59.18	56.78	1.96	0.94	1.45	2.50
	12.44	55.22	51.23	1.60	1.55	1.58	2.05
	12.48	58.28	49.63	2.82	2.43	2.63	2.26
	12.52	26.91	26.51	1.63	2.37	2.00	1.73
	12.56	8.67	11.47	1.02	0.78	0.90	0.84
	12.60	8.89	10.15	2.76	1.39	2.08	0.93
	12.65	38.25	29.42	6.52	3.03	4.78	1.59
	12.69	37.31			4.00	4.00	1.68
	12.73	47.73	44.37	9.00		9.00	
	12.77	44.06	50.57	8.67	7.95	8.31	5.71
	12.81	98.81	86.76	8.57		8.57	
	12.85	167.00	137.33	4.97		4.97	
	12.90	179.22	139.78	2.48		2.48	
	12.94	144.30	99.92	0.80		0.80	
	12.98	137.17	98.70		1.53	1.53	6.19

TDLAS/LUMINOX 1HR AVERAGE DATA CLAREMONT CA. SEPT. 11-19, 1985

DATE	TIME DECIMAL DAY	NO2 LUMINOX PPBV	NO2 TDL AES PPBV	HNO3 TDL AES PPBV	HNO3 TDL UNI PPBV	AVERAGE HNO3 PPBV	HCHO TDL UNI PPBV
SEPT 13	13.02	99.68	85.07	0.69	1.31	1.00	4.16
	13.06	38.46	39.95	1.15	1.20	1.18	2.50
	13.10	30.22	21.90	1.78	1.57	1.68	2.70
	13.15	17.64	11.00	1.58	1.60	1.59	2.11
	13.19	14.29	4.04	1.47	1.46	1.47	1.90
	13.23	19.39	5.36	1.63	1.67	1.65	1.92
	13.27	54.81	60.25	0.60	1.38	0.99	2.03
	13.31	80.11	79.71	0.47	1.19	0.83	3.80
	13.35	79.19	73.51	1.37	1.03	1.20	3.40
	13.40	63.61	63.36	1.83	1.10	1.47	3.10
	13.44	58.17	61.76	2.27	1.92	2.10	4.20
	13.48	38.90	43.71	1.68	0.89	1.29	2.87
	13.52	7.22	14.01	2.04	1.86	1.95	1.83
	13.56	31.83	34.31	6.68	4.97	5.83	3.96
	13.60	21.42	24.63	8.94	7.90	8.42	7.59
	13.65	25.28	28.39	8.93	8.01	8.47	11.52
	13.69	38.38	34.78	9.06	8.58	8.82	8.08
	13.73	50.14	37.51	8.42	8.65	8.54	6.97
	13.77	58.92	40.80	7.02	5.46	6.24	9.59
	13.81	85.63	66.46	2.94	3.53	3.24	8.53
	13.85	131.84	91.74	5.23	3.35	4.29	5.72
	13.90	151.63	111.95	4.34	5.84	5.09	5.69
	13.94	133.83	97.76	2.02	6.03	4.03	6.53
	13.98	127.53	81.12	1.39	2.56	1.98	4.00
SEPT14	14.02	98.15	79.05	1.38		1.38	3.21
	14.06	54.18	56.12	1.87		1.87	3.26
	14.10	58.01	61.01	2.20		2.20	
	14.15	47.62	55.84	2.28		2.28	
	14.19	34.31	44.56	2.49		2.49	
	14.23	38.45	45.68	2.48		2.48	
	14.27	34.54	37.22	2.77		2.77	
	14.31	35.04	46.25	2.53		2.53	
	14.35	50.84	89.86	2.35	4.39	3.37	6.06
	14.40		111.67	2.72	3.74	3.23	7.00
	14.44	55.15	72.57	4.66	5.65	5.16	6.23
	14.48	33.71	41.74	8.21	8.92	8.57	4.85
	14.52	38.85	40.80	10.37	10.90	10.64	4.52
	14.56	18.61	22.75	12.23	11.80	12.02	3.02
	14.60	12.86	16.73	11.14	13.73	12.44	2.89
	14.65	20.47	19.74	16.52	14.98	15.75	4.04
	14.69	22.45	24.72	15.04	14.28	14.66	2.21
	14.73	17.01	23.78	10.52	13.33	11.93	1.03
	14.77	24.04	31.77	7.97	11.62	9.80	2.42
	14.81	47.16	54.24	5.72	10.54	8.13	2.53
	14.85	54.01	57.06	3.14	1.55	2.35	1.18
	14.90	81.64	84.32	2.44	1.33	1.89	1.56
	14.94	87.04	88.27	0.30	-0.11	0.10	2.10
	14.98	91.52	91.56	-0.02	2.51	1.25	2.12

TDLAS/LUMINOX 1HR AVERAGE DATA CLAREMONT CA. SEPT. 11-19, 1985

DATE	TIME DECIMAL DAY	NO2 LUMINOX PPBV	NO2 TDL AES PPBV	HNO3 TDL AES PPBV	HNO3 TDL UNI PPBV	AVERAGE HNO3 PPBV	HCHO TDL UNI PPBV
SEPT 15	15.02	82.24	80.46	-0.13	2.03	0.95	2.26
	15.06	29.70	33.46	-0.08	1.48	0.70	1.91
	15.10	43.60	50.10	0.61	1.12	0.87	1.74
	15.15	22.75	29.80	0.72	2.35	1.54	1.64
	15.19	35.55	44.27	0.94	1.06	1.06	1.50
	15.23	15.90			1.39	1.39	1.34
	15.27	8.23			1.14	1.14	1.52
	15.31	32.35			1.73	1.73	1.77
	15.35	37.79			2.16	2.16	2.59
	15.40	58.88	58.94	2.49	2.40	2.45	3.69
	15.44	38.39	42.96	4.14	4.04	4.09	3.95
	15.48	16.68	23.97	4.56	4.57	4.57	2.44
	15.52	5.02	11.75	2.25		2.25	2.73
	15.56	6.31	11.47	4.78	2.96	3.87	2.14
	15.60	4.37	8.65	8.61	8.18	8.40	1.96
	15.65	4.30	10.72	9.07	7.98	8.53	1.50
	15.69	5.32	15.13	6.93	6.75	6.84	1.36
	15.73	7.87	16.92	3.32	5.38	4.35	1.39
	15.77	23.25	34.87	3.63	6.73	5.18	2.27
	15.81	35.10	50.38	1.51	2.55	2.03	1.49
	15.85	57.69	70.03	1.76	2.00	1.88	1.26
	15.90	75.63	77.17	0.95	1.78	1.37	1.40
	15.94	67.55	70.88	1.66	3.08	2.37	1.23
	15.98	57.76	61.29	1.18	1.37	1.28	1.61
SEPT 16	16.02	57.77	54.99	0.92	0.53	0.73	1.51
	16.06	21.08	29.05	1.42	0.55	0.99	1.18
	16.10	9.81	18.89	1.76	1.20	1.48	0.93
	16.15	27.84	39.86	1.57	2.50	2.04	1.30
	16.19	27.51	36.94	1.39	2.14	1.77	1.27
	16.23	27.00	36.47	1.13	1.30	1.22	0.93
	16.27	19.59	31.11	1.31	1.41	1.36	0.88
	16.31	12.89	24.44	1.44	1.91	1.68	1.19
	16.35	31.36	47.09	1.21	2.50	1.86	2.19
	16.40	62.79	58.75	0.36	0.71	0.54	2.03
	16.44	47.97	50.57	0.69	0.50	0.60	2.19
	16.48	23.53	29.70	0.28	1.30	0.79	2.06
	16.52	12.97	21.62	0.33	1.93	1.13	1.83
	16.56	10.24	18.14	0.81	-0.50	0.16	1.82
	16.60	8.14	16.45	1.27	0.66	0.97	2.05
	16.65	8.32	16.36	1.76	1.82	1.79	1.83
	16.69	10.39	19.27	1.82	1.86	1.84	1.82
	16.73	16.85			1.12	0.56	2.05
	16.77	24.99					2.02
	16.81	27.63	39.57	0.42		0.42	1.51
	16.85	26.94	41.36	0.29		0.29	1.31
	16.90	56.13	66.74	0.91		0.91	
	16.94	63.31	72.57	0.82		0.82	
	16.98	52.71	56.12	1.03		1.03	

TDLAS/LUMINOX 1HR AVERAGE DATA CLAREMONT CA. SEPT. 11-19, 1985

DATE	TIME DECIMAL DAY	NO2 LUMINOX PPBV	NO2 TDL AES PPBV	HNO3 TDL AES PPBV	HNO3 TDL UNI PPBV	AVERAGE HNO3 PPBV	HCHO TDL UNI PPBV
SEPT 17	17.02	50.10	46.81	0.64	2.01	1.33	
	17.06	47.88	45.50	2.03	2.46	2.25	1.12
	17.10	17.09	24.91	2.46	2.61	2.54	0.88
	17.15	4.34	13.63	2.47	2.37	2.42	0.86
	17.19	6.16	16.54	2.73	2.86	2.80	0.74
	17.23	3.08	11.47	2.96	2.51	2.74	0.87
	17.27	7.72	17.67	2.22	3.64	2.93	0.80
	17.31	10.00	20.68	2.69	2.58	2.64	0.71
	17.35	9.79	22.56	0.89		0.89	1.06
	17.40	21.59	33.93	0.34	0.80	0.57	1.34
	17.44	28.12	36.10		1.25	1.25	2.01
	17.48	21.81	25.94	1.01	2.49	1.75	2.23
	17.52	17.12	23.12	1.38	1.95	1.67	2.13
	17.56	16.67	23.50	2.13	1.64	1.89	2.00
	17.60	12.14	18.71	4.90	3.22	4.06	1.58
	17.65	13.57	21.62	5.37	4.88	5.13	1.51
	17.69	26.17	29.80	4.02	4.47	4.25	1.82
	17.73	31.85	34.40	2.86	2.46	2.66	1.68
	17.77	48.31	45.50	2.80	4.07	3.44	1.63
	17.81	44.90	44.56	2.22	2.34	2.28	1.69
	17.85	76.37			2.26	1.13	
	17.90	67.74	62.70	1.35	3.13	2.24	1.20
	17.94	60.18	58.94	1.80	2.48	2.14	1.14
	17.98	45.39	49.26	1.70	2.75	2.23	0.80
SEPT 18	18.02	48.40	44.18	1.89	2.09	1.99	0.70
	18.06	41.47	40.61	1.97	2.20	2.09	0.95
	18.10	47.60	44.56	2.07	2.30	2.19	1.02
	18.15	49.57	44.93	2.00	2.20	2.10	0.92
	18.19	34.35	39.48	1.93	2.16	2.05	0.73
	18.23		41.74	2.21	3.21	2.71	0.43
	18.27		41.08	1.76	2.07	1.92	0.53
	18.31	35.44	35.25	0.32	1.24	0.78	1.31
	18.35	34.53	34.22	0.63	0.42	0.53	
	18.40	36.45	31.96	1.40	0.71	1.06	0.81
	18.44	43.34	35.81	2.08	1.73	1.91	0.94
	18.48	23.41	21.71	1.38	2.29	1.84	0.62
	18.52	23.05	26.70	2.55	0.84	1.70	0.48
	18.56	46.75	46.62	3.48	1.71	2.60	0.75
	18.60	16.47	23.50	2.88	3.24	3.06	0.61
	18.65	14.90	34.31	2.95		2.95	0.69
	18.69	46.04	42.49	2.05	2.02	2.04	0.43
	18.73	43.82	39.67	2.05	0.93	1.49	0.39
	18.77	29.79	34.12	2.22	0.29	1.26	0.32
	18.81	57.31	49.63	1.89	0.36	1.13	0.50
	18.85	51.97			3.23	1.62	0.22
	18.90	43.63	41.27	0.38	0.53	0.46	
	18.94	26.31	32.99	1.18		1.18	0.42
	18.98	16.34	26.32	1.66		1.66	0.52

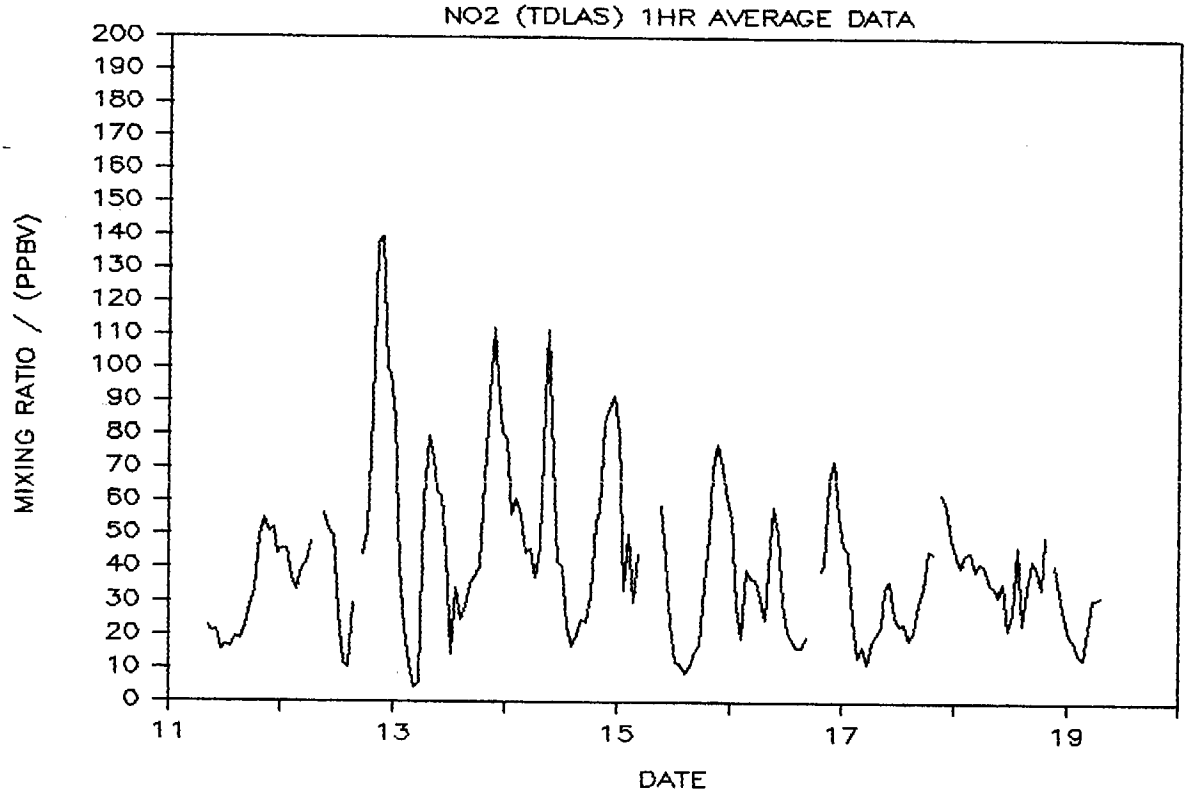
TDLAS/LUMINOX 1HR AVERAGE DATA CLAREMONT CA. SEPT. 11-19, 1985

DATE	TIME DECIMAL DAY	NO2 LUMINOX PPBV	NO2 TDL AES PPBV	HNO3 TDL AES PPBV	HNO3 TDL UNI PPBV	AVERAGE HNO3 PPBV	HCHO TDL UNI PPBV
SEPT 19	19.02	4.63	20.21	0.30	0.84	0.57	0.46
	19.06	3.49	18.42	-0.70	0.74	0.02	0.28
	19.10	2.42	14.48	-0.50	-0.65	-0.58	0.14
	19.15	1.49	12.97	0.14	-0.62	-0.24	0.29
	19.19	5.55	22.18	0.55	0.83	0.69	0.54
	19.23	10.98	30.93	0.76	1.64	1.20	0.48
	19.27		31.02	1.04	2.52	1.78	1.11
	19.31		31.68	1.17	1.25	1.21	0.94

FIGURE B-1.1

Diurnal variation in the 1 hour NO_e mixing ratio measured by the TAMS (upper) and the Luminox (lower) during September 11-19, 1985.

CLAREMONT CA. SEPT. 11—19, 1985



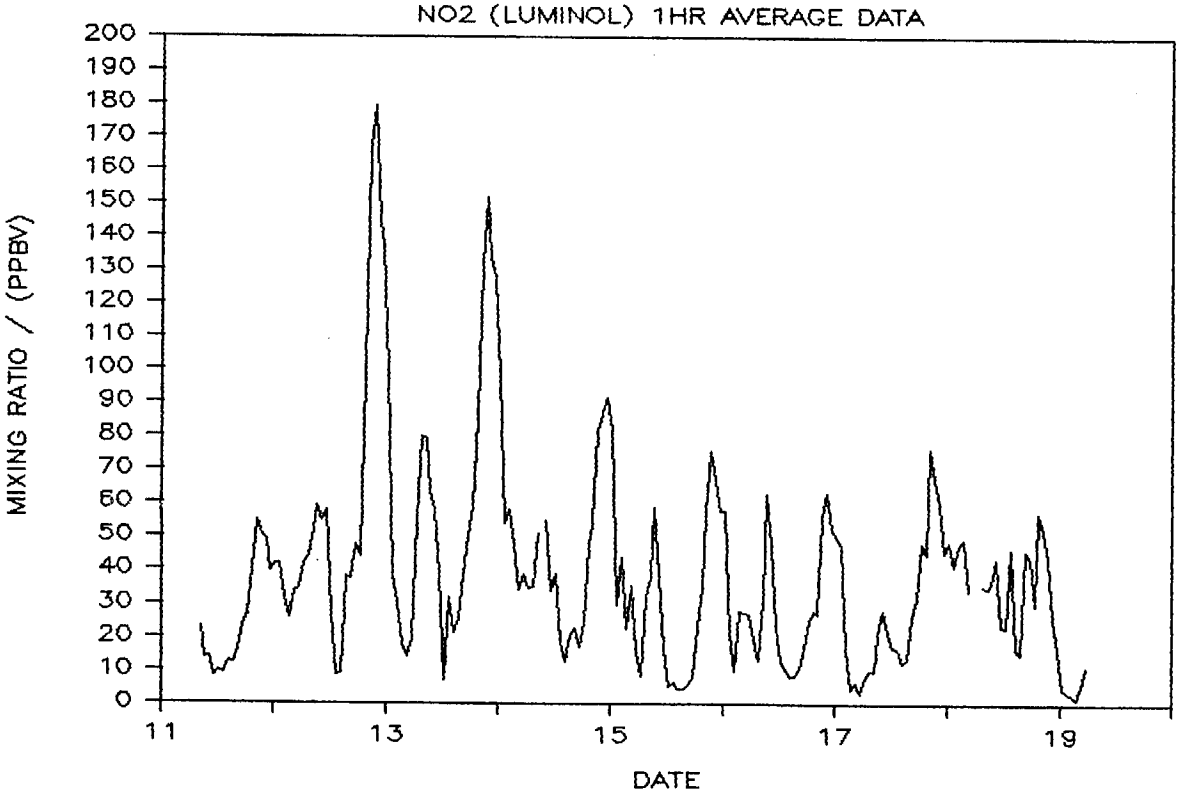


FIGURE B-1.2

Diurnal variation in the 1 hour NO_2 mixing ratio measured by the TAMS (upper) and the Luminox (lower) during September 11-19, 1985.

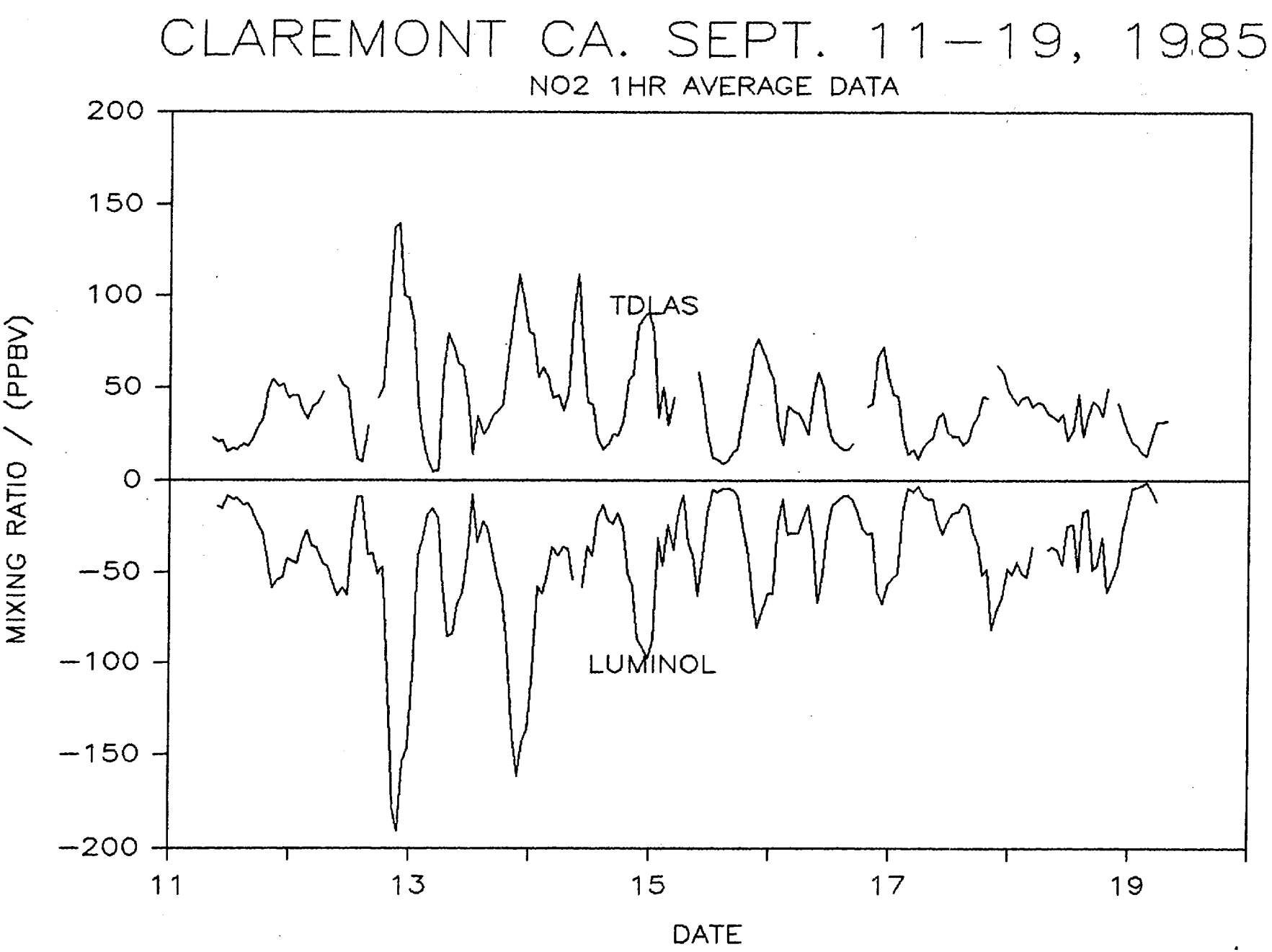

CLAREMONT CA. SEPT. 11–19, 1985
NO2 1HR AVERAGE DATA
200
150
100
50
0
−50
−100
−150
−200
MIXING RATIO / (PPBV)
TDLAS
LUMINOL
11
13
15
17
19
DATE

FIGURE B-1.3

Comparison of the 1 hour NO_2 mixing ratios measured by the TAMS and the Luminox during September 11-19, 1985. The solid line is the correspondance line.

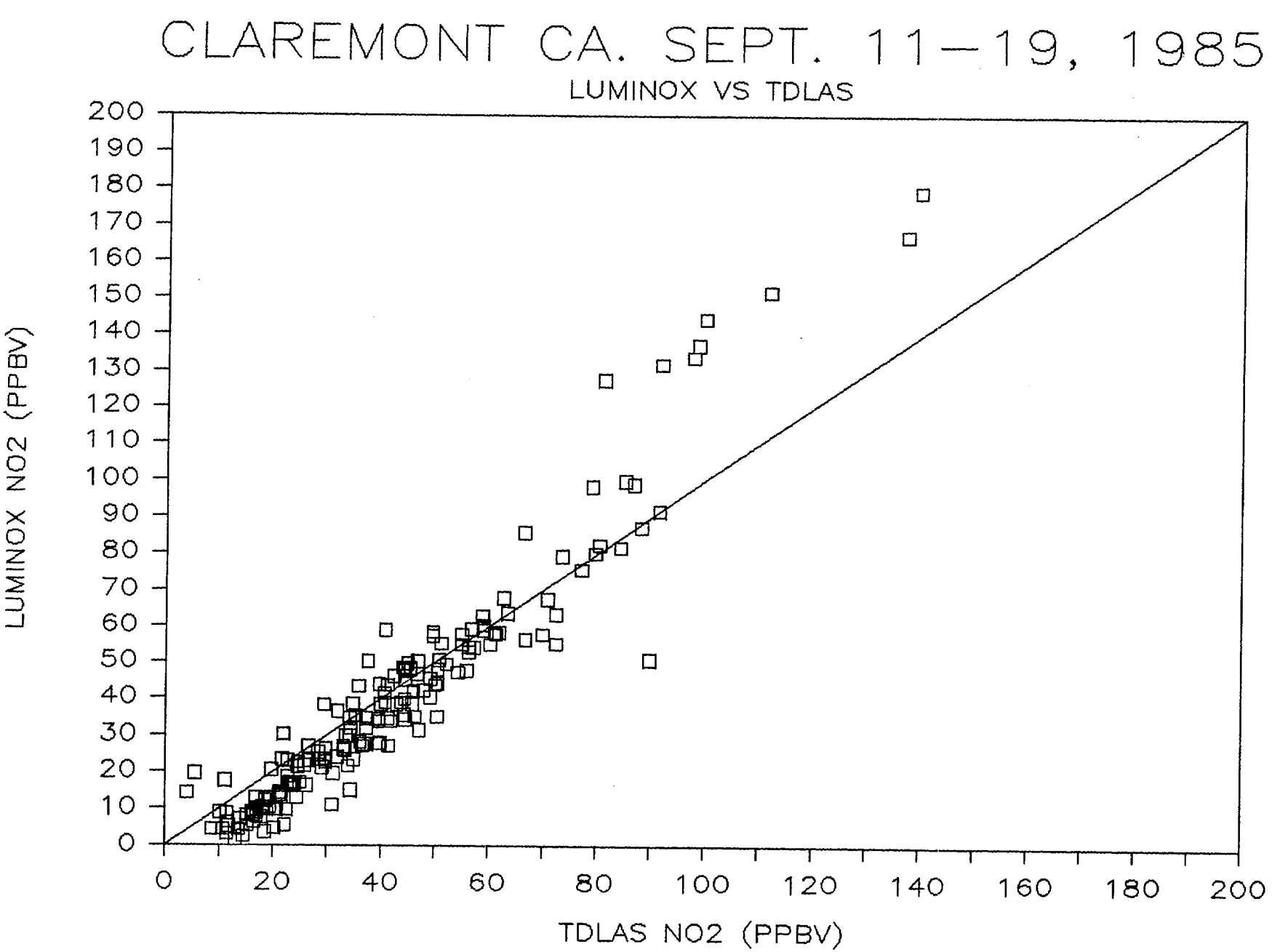
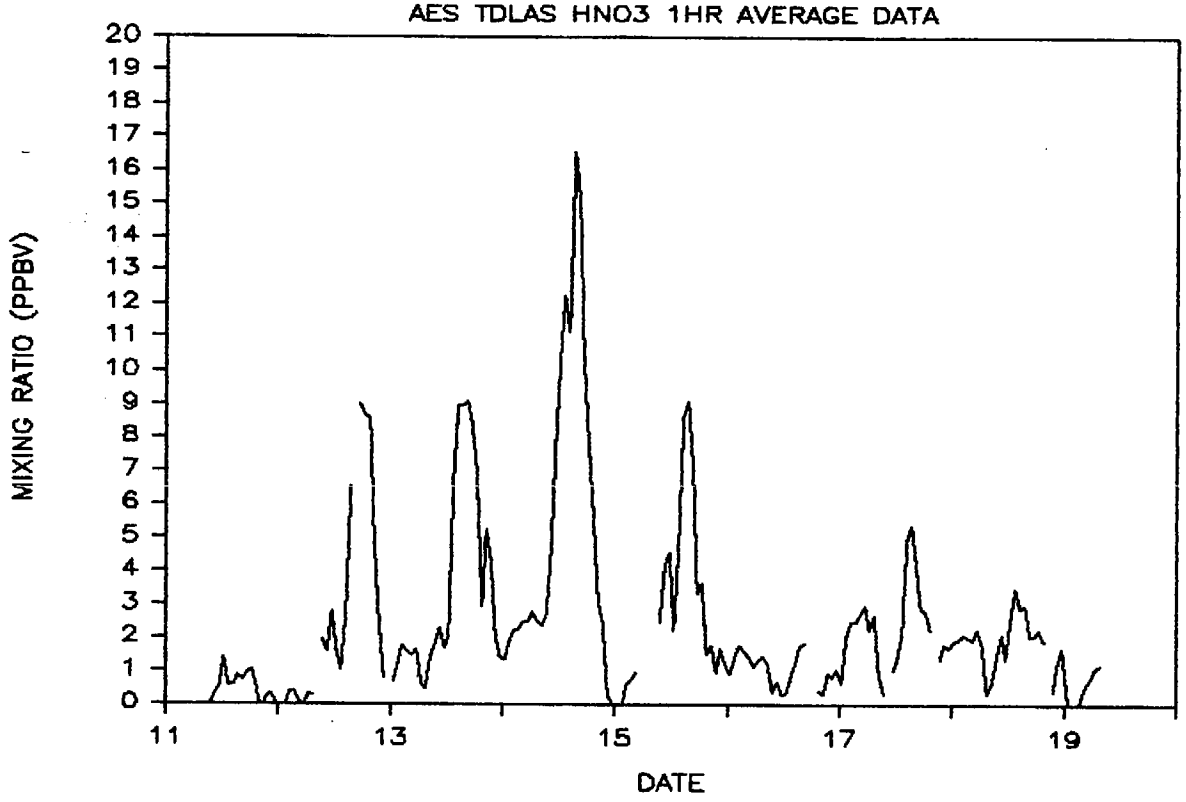

CLAREMONT CA. SEPT. 11–19, 1985
LUMINOX VS TDLAS
LUMINOX NO2 (PPBV)
TDLAS NO2 (PPBV)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
0
20
40
60
80
100
120
140
160
180
200

FIGURE B-2.1

Diurnal variation in the 1 hour HNO_3 mixing ratio measured by the AES (upper) and Unisearch (lower) TAMS during September 11-19, 1985.

CLAREMONT CA. SEPT. 11—19, 1985



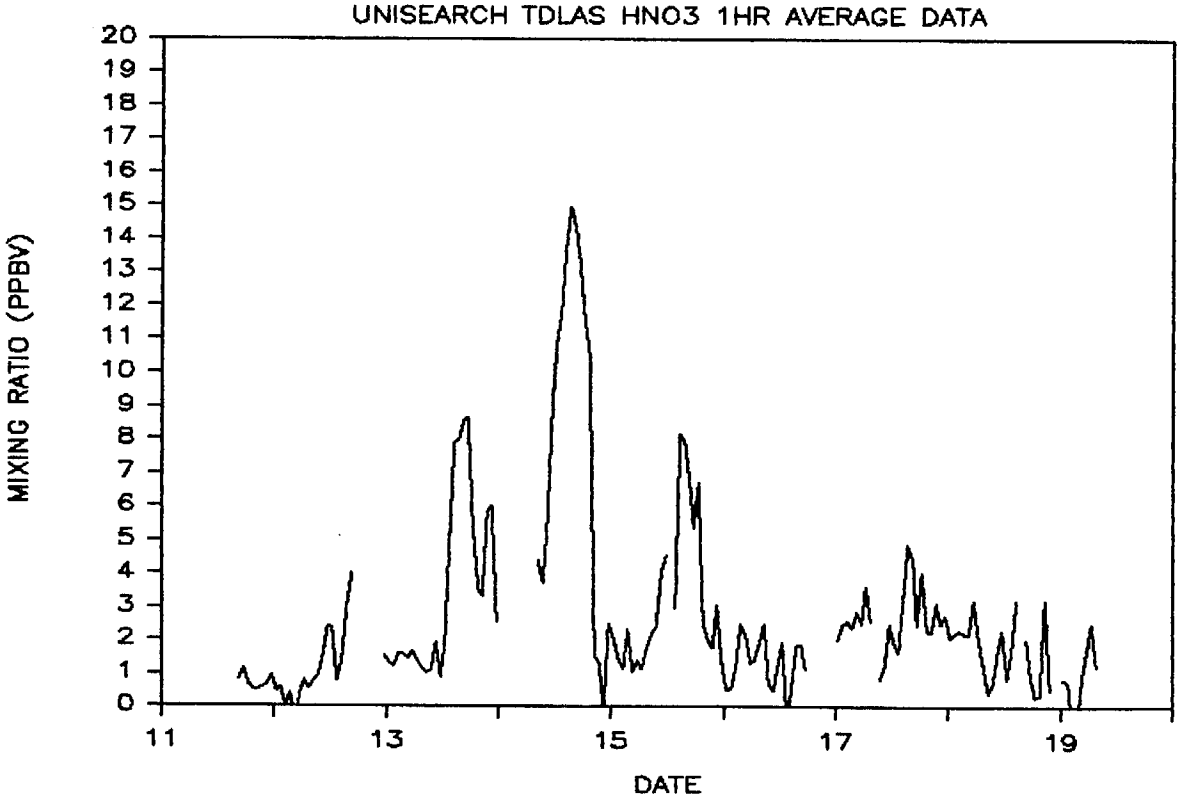


FIGURE B-2.2

Diurnal variation in the 1 hour HNO_3 mixing ratio measured by the AES (upper) and Unisearch (lower) TAMS during September 11-19, 1985.

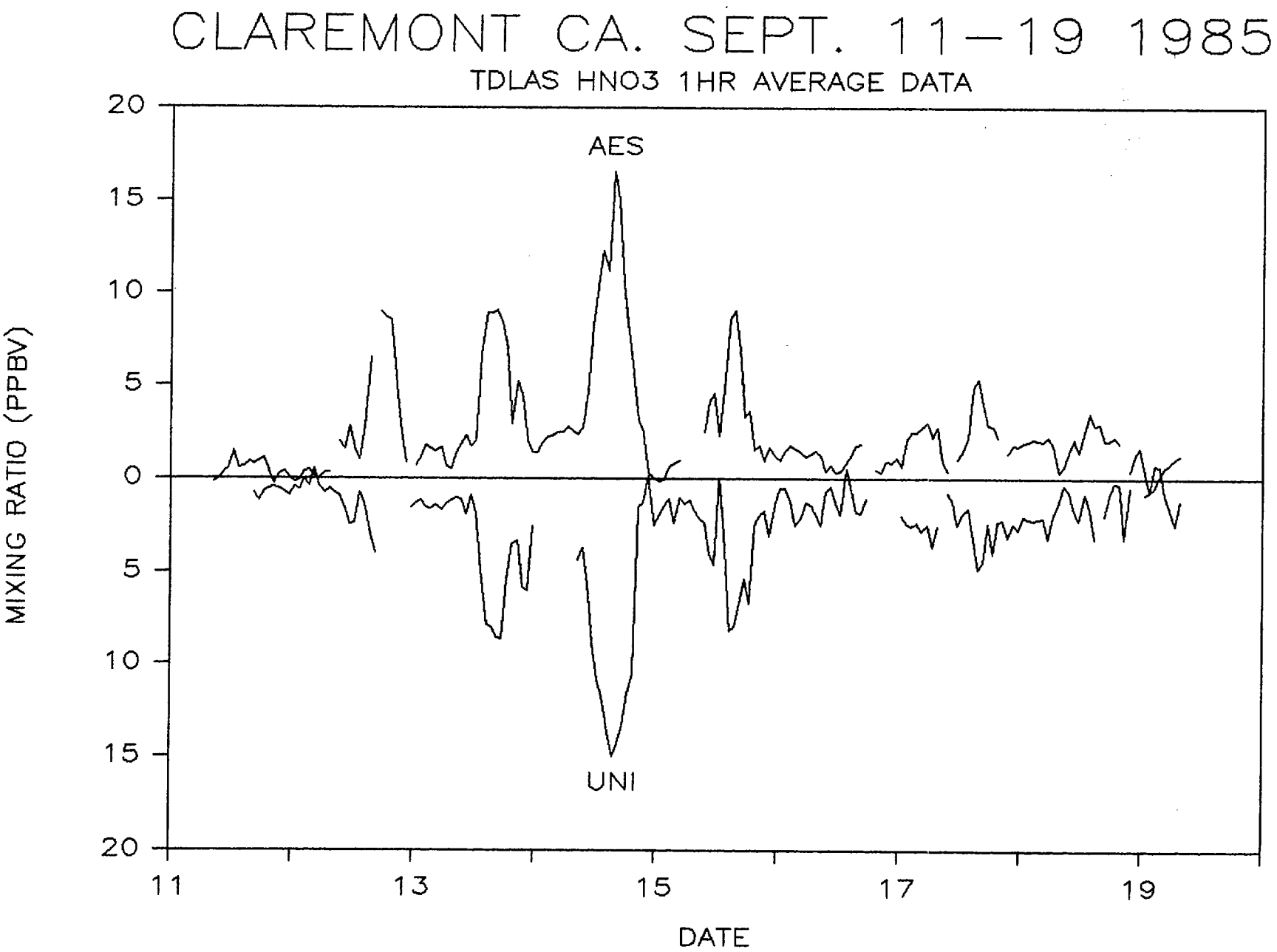

CLAREMONT CA. SEPT. 11–19 1985
TDLAS HNO3 1HR AVERAGE DATA
AES
UNI
MIXING RATIO (PPBV)
20
15
10
5
0
5
10
15
20
11
13
15
17
19
DATE

FIGURE B-2.3

Comparison of the 1 hour HNO_3 mixing ratios measured by the Unisearch and AES TAMS during September 11-19, 1985. The solid line is the correspondance line.

CLAREMONT CA. SEPT. 11–19, 1985

TDLAS HNO3 1HR AVERAGE DATA

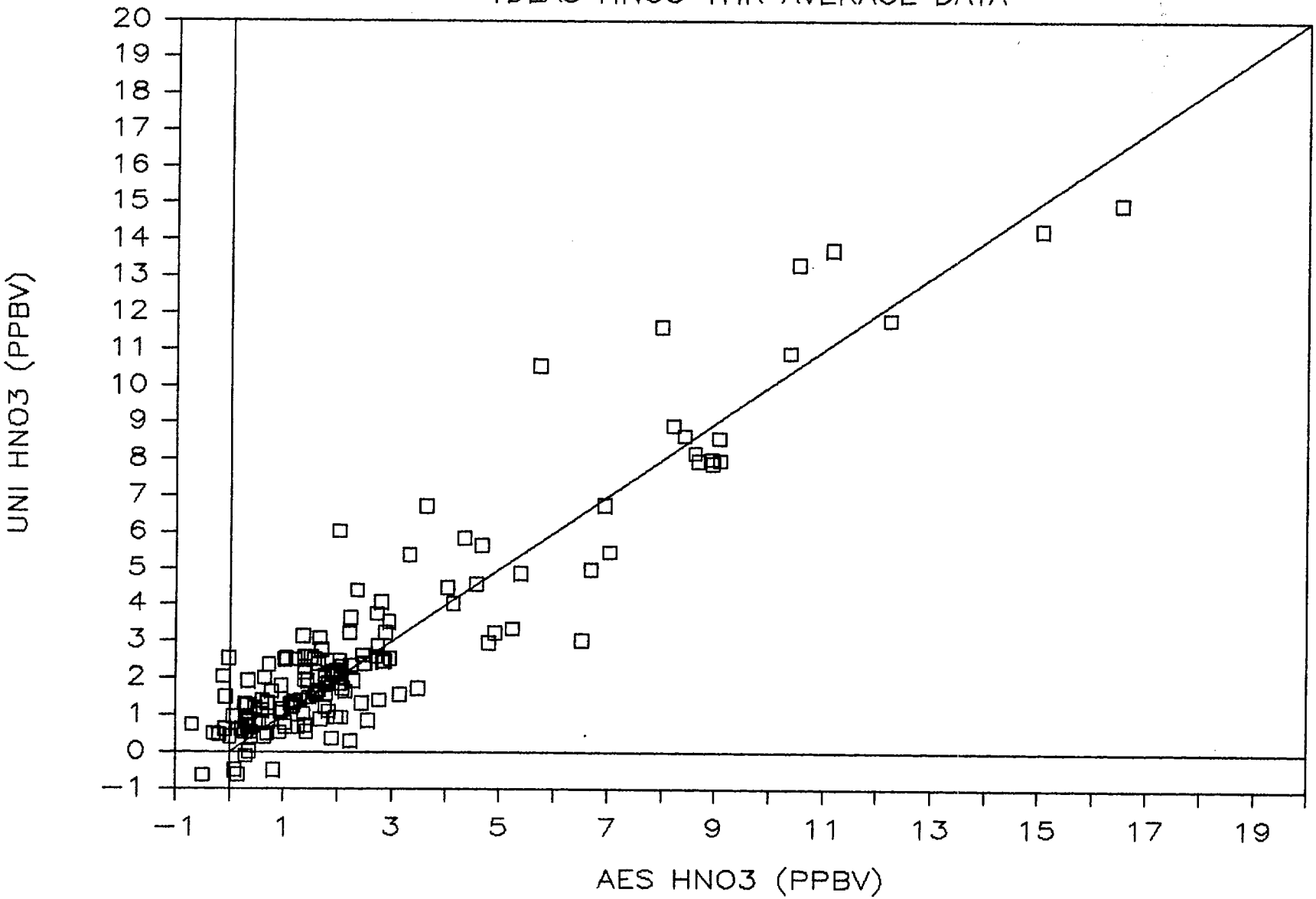


FIGURE B-2.4

Diurnal variation in the average 1 hour HNO_3 mixing ratio measured by the Unisearch and AES TAMS during September 11-19, 1985.

CLAREMONT CA. SEPT. 11–19, 1985

AVERAGE TDLAS HNO3 1HR AVERAGE DATA

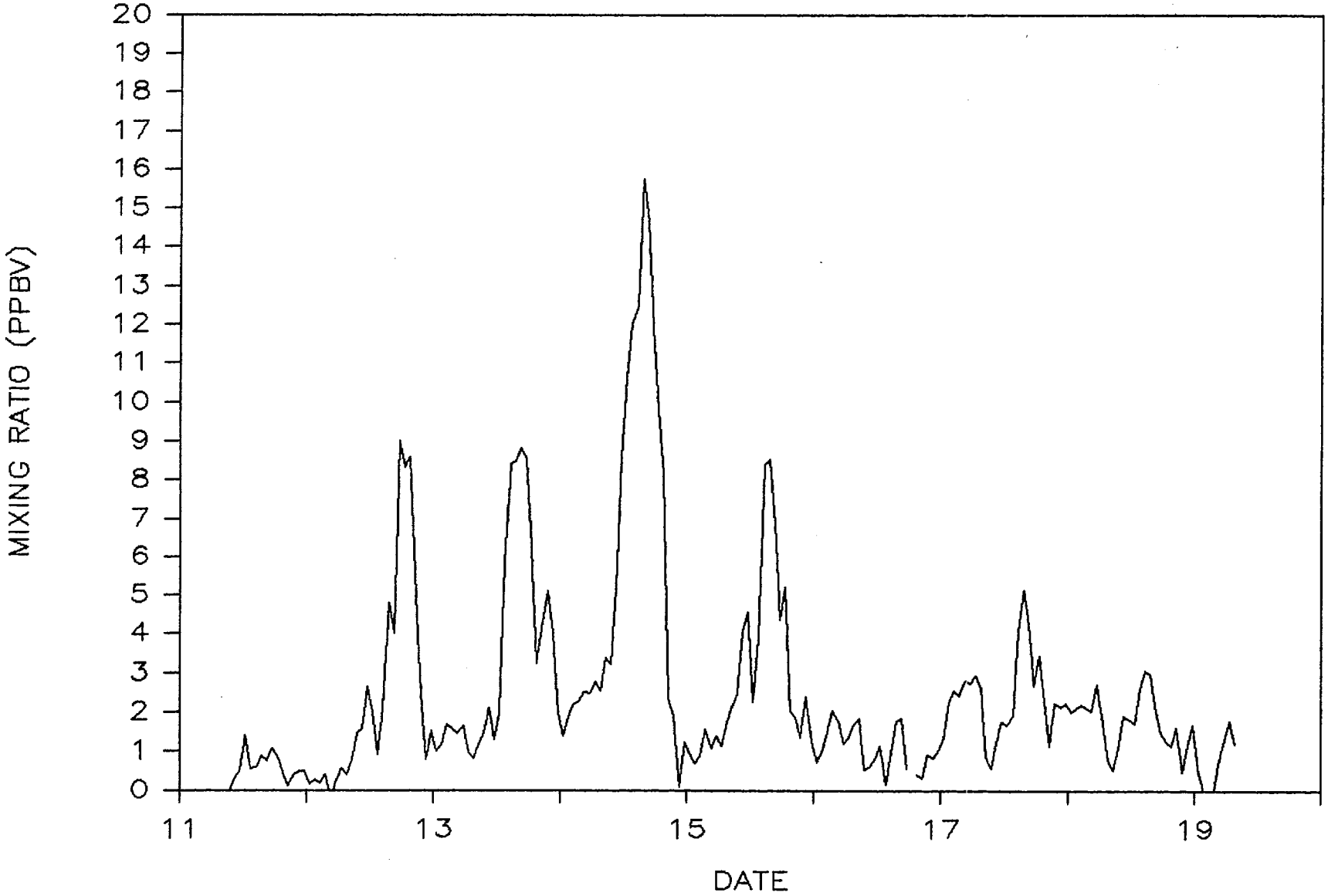
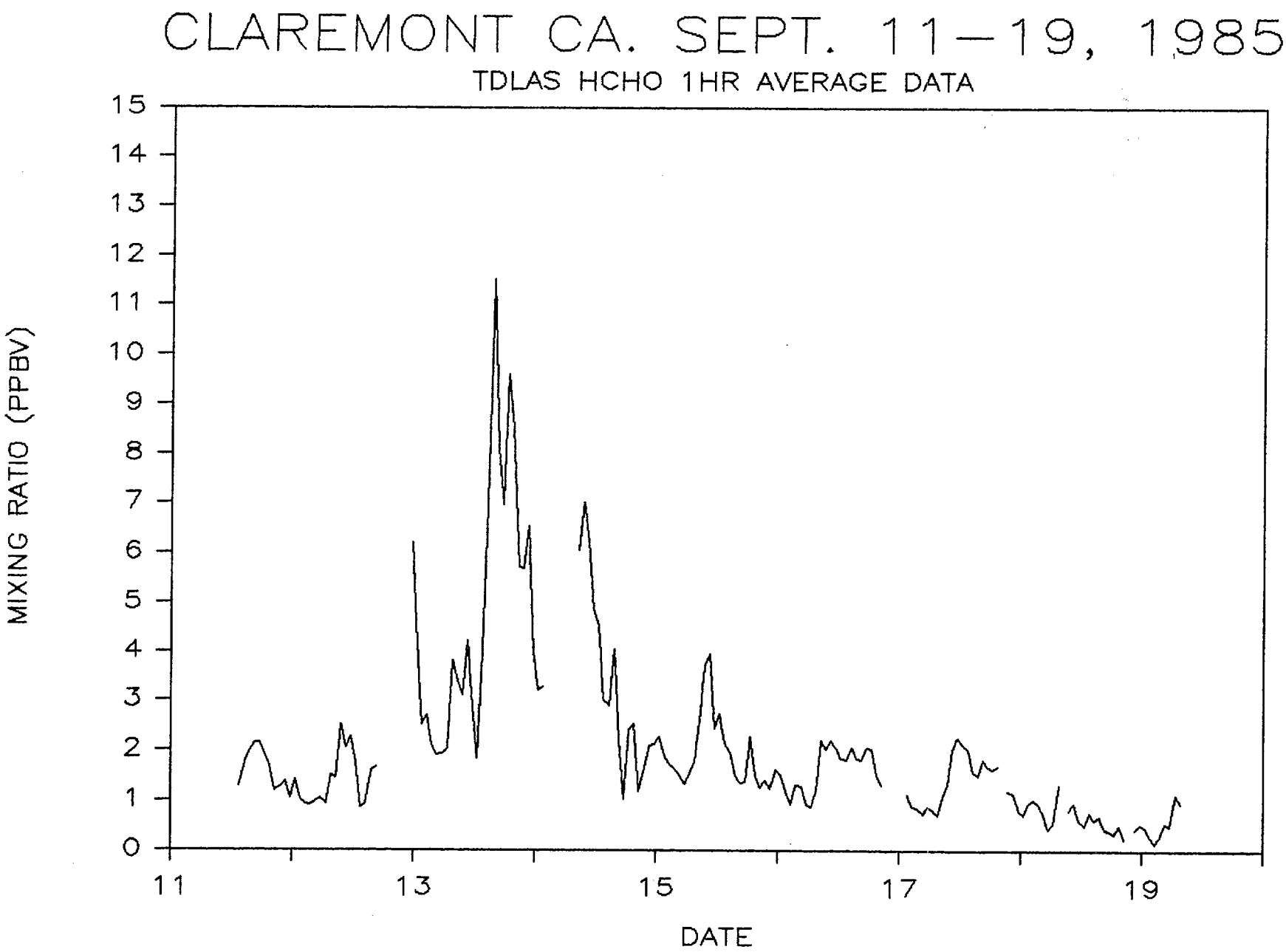


FIGURE B-3.1

Diurnal variation in the 1 hour HCHO mixing ratio measured by the Unisearch TAMS during September 11-19, 1985.


CLAREMONT CA. SEPT. 11—19, 1985
TDLAS HCHO 1HR AVERAGE DATA
MIXING RATIO (PPBV)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
11
13
15
17
19
DATE

APPENDIX C

Tabulated Luminox NO_2 and TDLAS NO_2, HNO_3 and HCHO for the six sampling periods 00:00-06:00, 06:00-08:00, 08:00-12:00, 12:00-16:00, 16:00-20:00 and 20:00-24:00 obtained during the Claremont CA HNO_3 intercomparison study, September 11-19, 1985 along with graphical representations of the diurnal behaviour of each species throughout the 9 day period. Mixing ratios are given at STP (0°C and 760 Torr).

HNO3 INTERCOMPARISON CLAREMONT CA
4 HOUR AVERAGE DATA

TIME - PERIOD	NO2 LUMINOX PPBV	STD DEV PPBV	NO2 TDL AES PPBV	STD DEV PPBV	HNO3 TDL AES PPBV	STD DEV PPBV	HNO3 TDL UNI PPBV	STD DEV PPBV	HCHO TDL UNI PPBV	STD DEV PPBV	LOST* DATA PERIOD
SEPT. 11											
08:00-12:00	14.78	11.56	20.12	5.83	0.18	0.36	-		1.13	0.74	
12:00-16:00	11.00	2.91	18.05	2.07	0.87	0.49	-		1.66	0.43	
16:00-20:00	27.63	9.68	33.37	10.72	0.77	0.32	0.79	0.42	1.98	0.25	
20:00-24:00	48.60	6.20	50.57	4.70	0.08	0.37	0.69	0.47	1.21	0.24	
SEPT. 12											
00:00-06:00	34.97	6.11	40.61	5.08	0.09	0.28	0.23	0.51	1.05	0.22	
06:00-08:00	46.25	7.43	47.94*	3.29	0.30	0.19	0.62	0.48	1.22	0.35	7
08:00-12:00	57.53	7.14	52.55*	5.73	2.13 *	0.67	1.43	0.92	2.07	0.63	8
12:00-16:00	20.68	14.10	19.36	9.59	2.98	2.30	1.89	1.36	1.27	0.44	
16:00-20:00	56.96	28.20	60.50*	23.88	8.75 *	2.49	5.98	2.85	3.70	2.16	16,17
20:00-24:00	156.70	23.69	118.91	25.66	2.75 *	2.48	-		-		23
SEPT. 13											
00:00-06:00	36.57	31.49	27.92	29.80	1.38	0.44	1.47	0.49	2.55	0.91	
06:00-08:00	67.49	14.66	70.03	11.19	0.54	0.27	1.29	0.59	2.92	1.75	
08:00-12:00	57.62	21.43	60.63	16.73	1.79	0.53	1.24	0.80	3.39	0.92	
12:00-16:00	21.43	11.00	25.38	9.31	6.65	3.03	5.69	2.83	6.23	4.02	
16:00-20:00	58.28	19.36	44.93	13.72	6.86	2.76	6.56	2.30	7.34	2.30	
20:00-24:00	136.21	13.54	95.69	13.63	3.25	1.67	4.44	2.11	5.49	1.14	
SEPT. 14											
00:00-06:00	55.08	23.88	57.06	13.91	2.12	0.47	-		3.24	1.36	
06:00-08:00	41.74	12.41	34.78	15.79	2.65	0.30	-		-		
08:00-12:00	-		78.96	31.49	4.49	2.42	5.68	2.48	6.04	1.08	
12:00-16:00	22.65	12.13	25.00	11.56	12.57	2.88	12.85	2.11	3.62	0.82	
16:00-20:00	27.66	12.31	33.65	12.88	11.18	3.27	12.95	2.60	2.05	0.73	
20:00-24:00	78.58	15.60	80.28	14.57	1.47	1.47	1.32	1.51	1.74	0.45	
SEPT. 15											
00:00-06:00	38.26	25.00	47.66*	20.77	0.41*	0.53	1.57	0.87	1.73	0.33	5
06:00-08:00	20.30	13.35	-		-		1.44	0.69	1.65	0.20	
08:00-12:00	37.98	20.21	41.92*	17.77	3.45*	0.93	3.29	1.90	3.20	0.84	8
12:00-16:00	4.98	2.07	10.62	2.73	6.18	2.91	6.37*	2.86	2.16	0.62	12
16:00-20:00	17.86	12.69	29.70	15.42	3.85	2.15	5.35	2.30	1.61	0.48	
20:00-24:00	64.67	9.68	69.84	7.05	1.38	0.54	2.06	1.98	1.36	0.25	

HNO3 INTERCOMPARISON CLAREMONT CA
4 HOUR AVERAGE DATA

TIME PERIOD	NO2 LUMINOX PPBV	STD DEV PPBV	NO2 TDL AES PPBV	STD DEV PPBV	HNO3 TDL AES PPBV	STD DEV PPBV	HNO3 TDL UNI PPBV	STD DEV PPBV	HCHO TDL UNI PPBV	STD DEV PPBV	LOST[a] DATA PERIOD
SEPT. 16											
00:00-06:00	28.48	16.26	30.46	17.30	1.37	0.41	1.37	1.03	1.19	0.24	
06:00-08:00	16.26	4.61	28.39	3.20	1.38	0.30	1.66	0.99	1.04	0.29	
08:00-12:00	41.45	17.58	46.53	12.78	0.64	0.44	1.25	1.33	2.12	0.31	
12:00-16:00	9.96	4.14	18.14	4.23	1.04	0.57	0.98	1.71	1.88	0.23	
16:00-20:00	19.93	7.33	IC		IC		IC		1.85	0.26	
20:00-24:00	49.82	14.76	59.22	12.50	0.76	0.41	-		IC		
SEPT. 17											
00:00-06:00	21.43	20.59	26.51	14.95	2.22	0.82	2.47	0.81	0.89*	0.19	0
06:00-08:00	8.84	3.38	19.18	3.67	2.46	0.30	3.11	1.04	0.76	0.12	
08:00-12:00	20.30	7.71	29.61	6.11	0.75*	0.40	1.51*	1.35	1.54	0.68	10,8
12:00-16:00	14.48	4.14	21.71	3.57	3.49*	1.84	2.92	2.09	1.81	0.38	
16:00-20:00	37.79	10.81	38.54	7.61	2.98	0.81	3.34	2.46	1.71	0.20	
20:00-24:00	62.42	13.35	56.96	7.90	1.62*	0.47	2.67	1.33	1.05*	0.26	20
SEPT. 18											
00:00-06:00	42.96*	9.59	42.58	3.29	2.03	0.22	2.36	0.85	0.79	0.30	5
06:00-08:00	IC		38.16	3.48	1.04	0.87	1.63	1.04	0.92	0.41	6
08:00-12:00	34.40	11.94	30.93	7.61	1.37	0.75	0.97	1.68	0.79*	0.21	8
12:00-16:00	25.29	17.58	32.71	10.25	2.97	0.84	1.93*	1.32	0.63	0.19	15
16:00-20:00	44.18	12.88	41.45	7.24	2.05	0.26	0.90	1.31	0.41	0.47	
20:00-24:00	34.59	14.76	33.56*	6.58	1.07*	0.71	IC		0.39 *	0.32	20,20,21
SEPT. 19											
00:00-06:00	4.79	3.48	19.83	6.77	0.09	0.66	0.46	1.28	0.37	0.21	

a: START OF ONE HOUR PERIOD DURING WHICH THE SAMPLE COVERED LESS THAN 30 MINUTES AND THEREFORE NOT INCLUDED IN THE 4 HOUR AVERAGE.

LEGEND: (-) LESS THAN ONE HOUR OF DATA COVERAGE IN THE 4 HOUR PERIOD; (IC) DATA MISSING IN TWO OR THREE 1-HOUR PERIODS; (*) DATA MISSING DURING ONE 1-HOUR PERIOD.

FIGURE C-1.1

Diurnal variation in the 4 hour NO_2 mixing ratio measured by the TAMS and the Luminox during September 11-19, 1985.

CLAREMONT CA. SEPT 11—19, 1985.

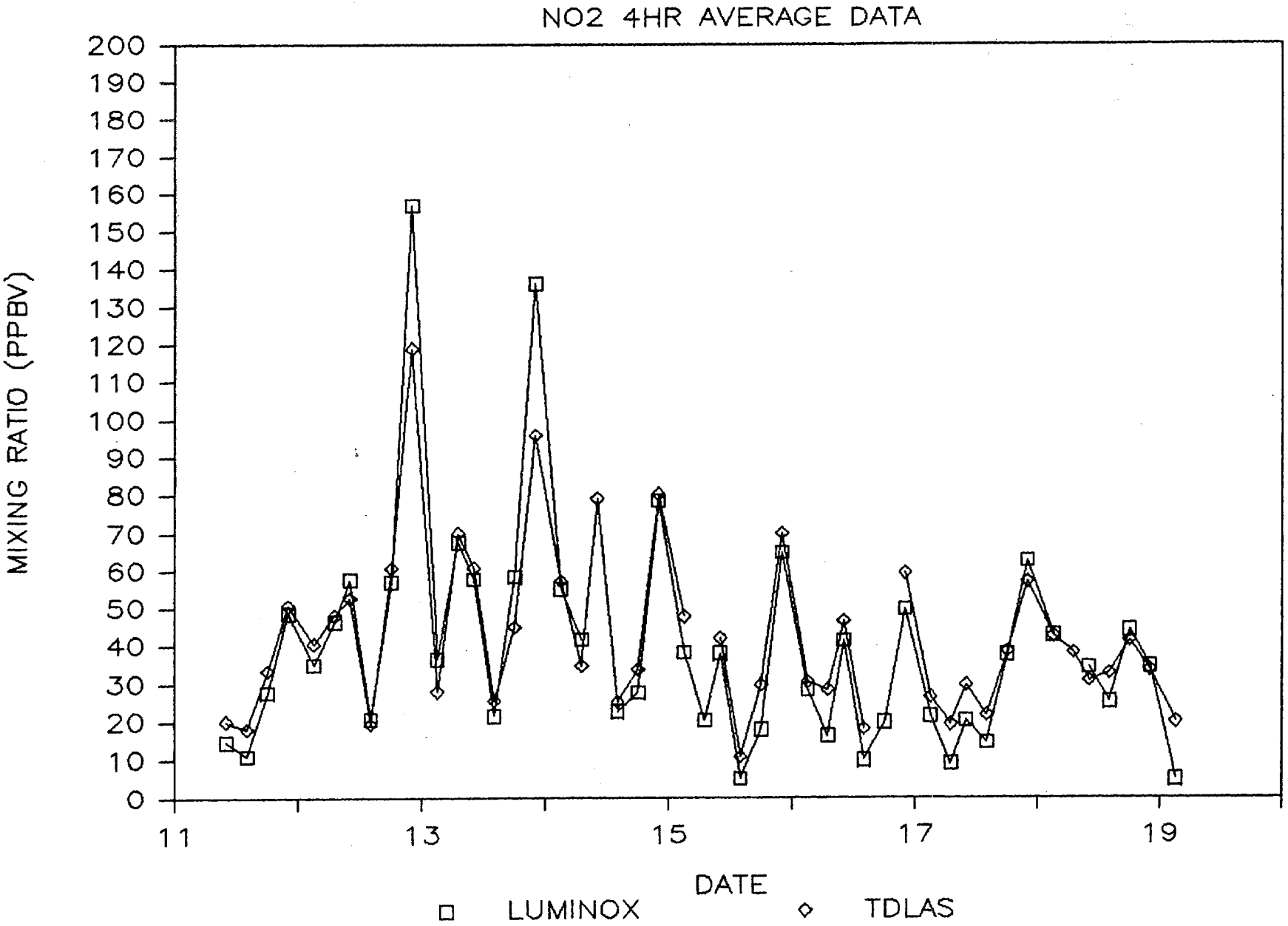


FIGURE C-1.2

Comparison of the 4 hour NO_e mixing ratios measured by the TAMS and the Luminox during September 11-19, 1985. The solid line is the correspondance line.

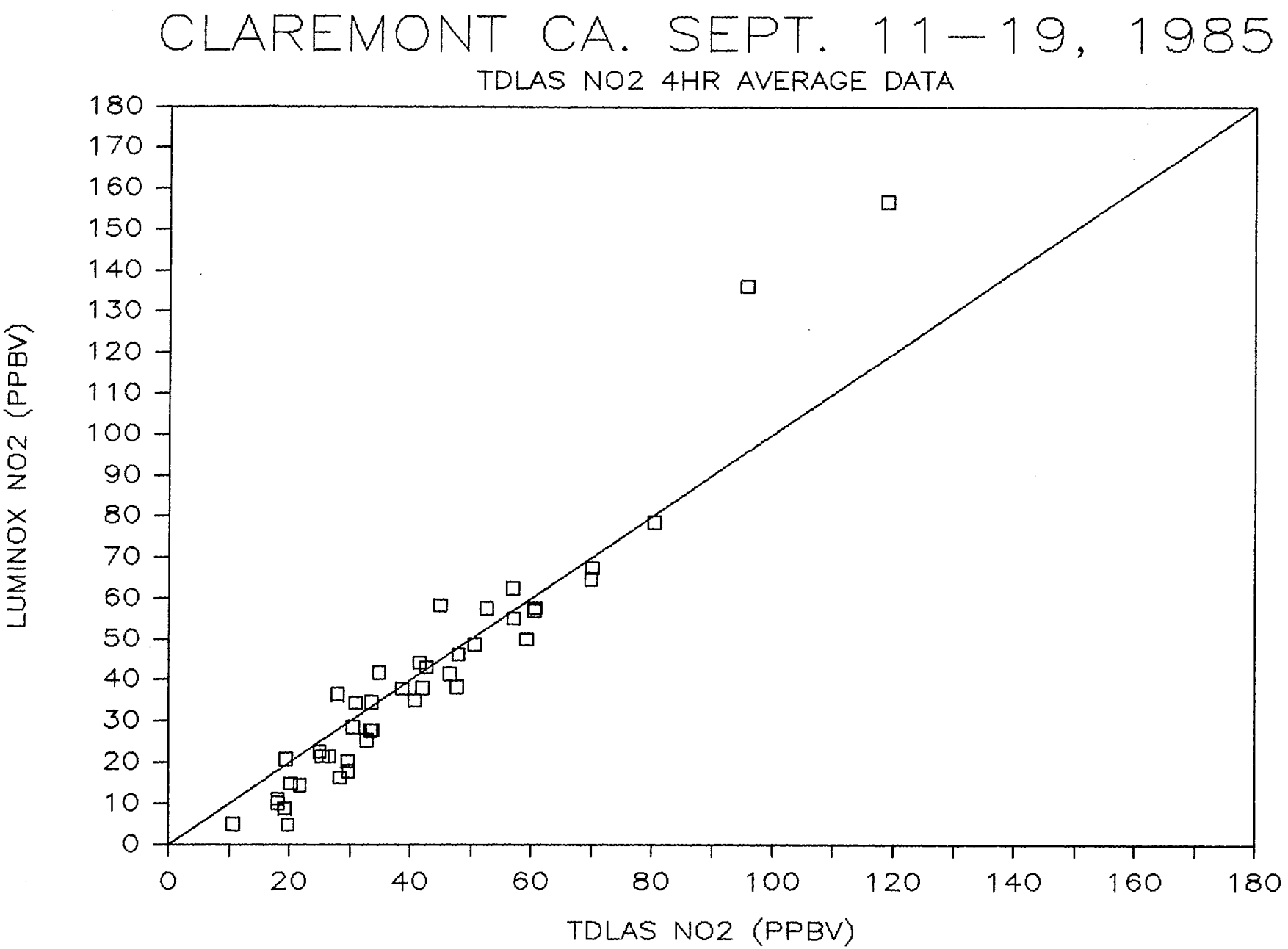

CLAREMONT CA. SEPT. 11–19, 1985
TDLAS NO2 4HR AVERAGE DATA
LUMINOX NO2 (PPBV)
TDLAS NO2 (PPBV)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
0
20
40
60
80
100
120
140
160
180

FIGURE C-2.1

Diurnal variation in the 4 hour HNO_3 mixing ratio measured by the Unisearch and AES TAMS during September 11-19, 1985.

CLAREMONT CA. SEPT 11–19, 1985.

TDLAS HNO3 4HR AVERAGE DATA

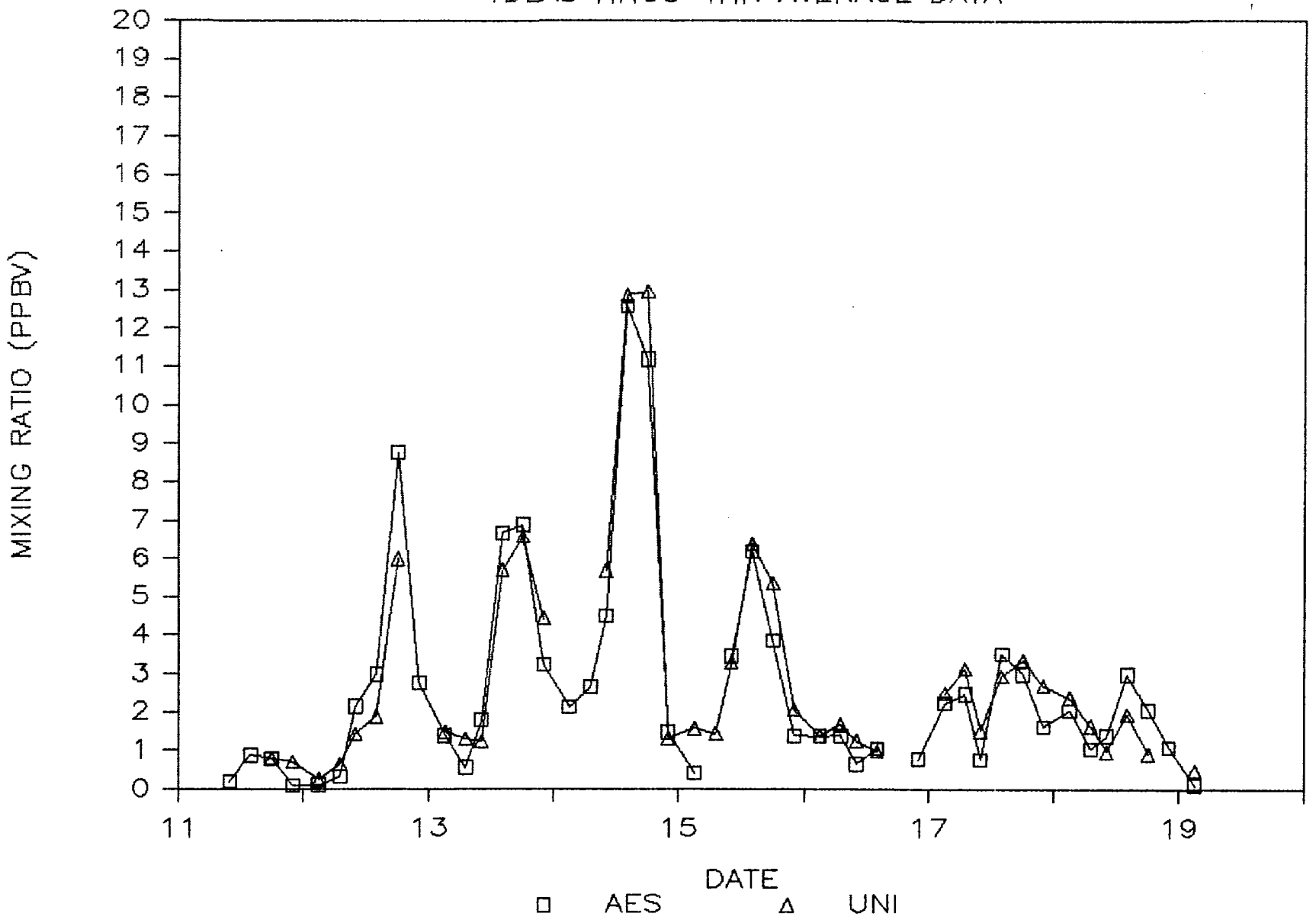


FIGURE C-2.2

Comparison of the 4 hour HNO_3 mixing ratios measured by the Unisearch and AES TAMS during September 11-19, 1985. The solid line is the correspondance line.

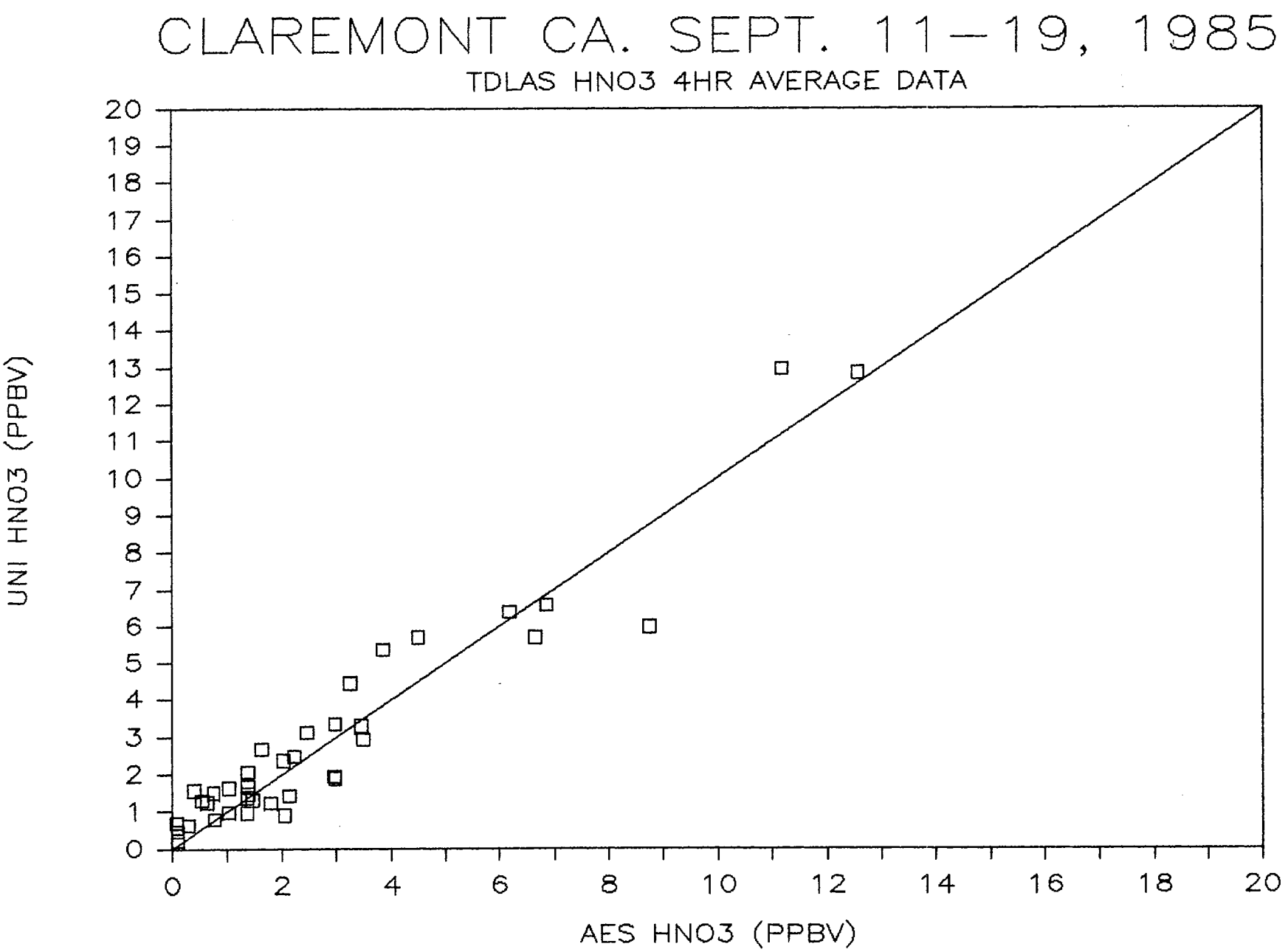
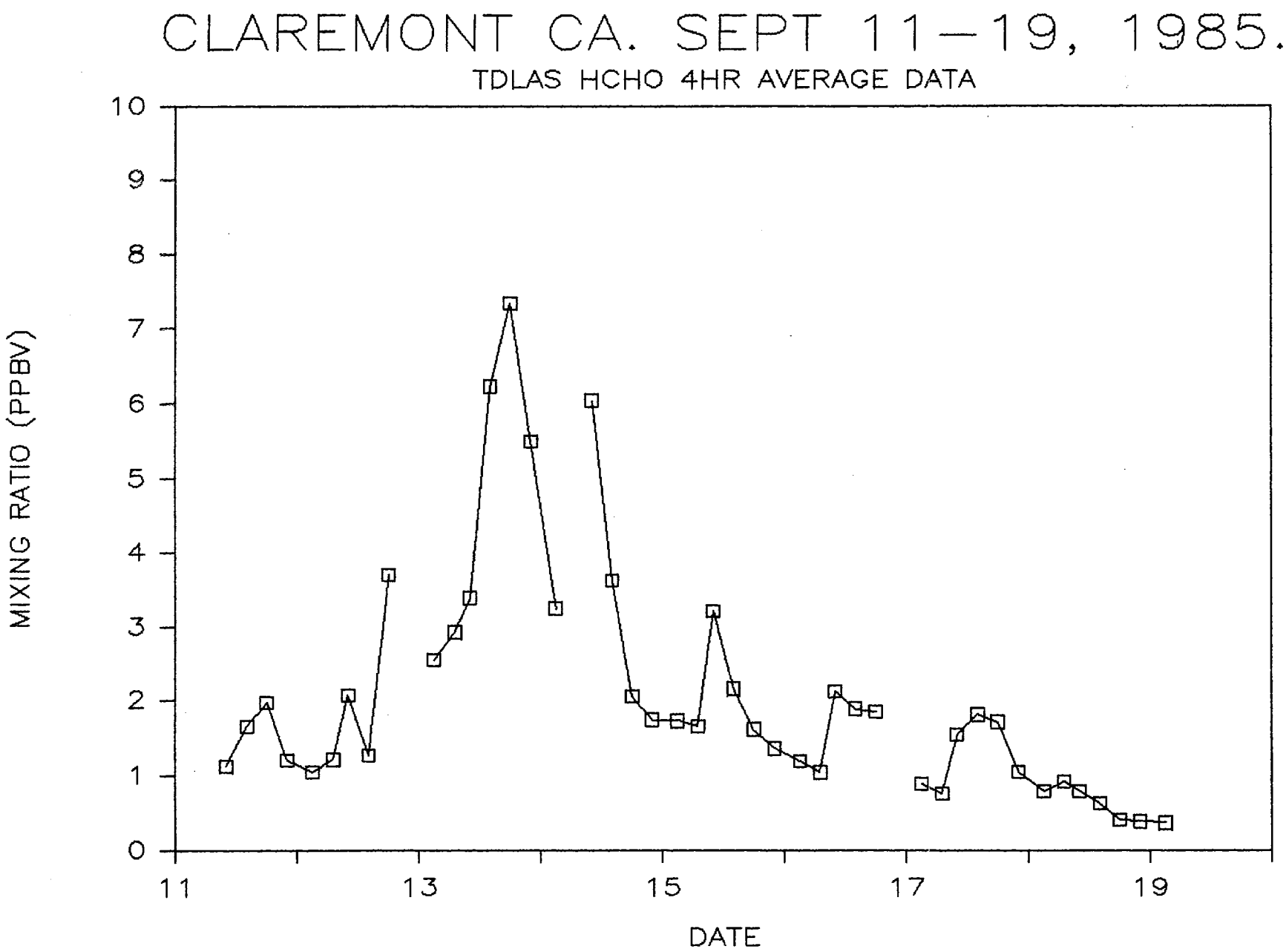

CLAREMONT CA. SEPT. 11–19, 1985
TDLAS HNO3 4HR AVERAGE DATA
UNI HNO3 (PPBV)
AES HNO3 (PPBV)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

FIGURE C-3.1

Diurnal variation in the 4 hour HCHO mixing ratio measured by the Unisearch TAMS during September 11-19, 1985.


CLAREMONT CA. SEPT 11—19, 1985.
TDLAS HCHO 4HR AVERAGE DATA
MIXING RATIO (PPBV)
0
1
2
3
4
5
6
7
8
9
10
11
13
15
17
19
DATE