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Field Test To Intercompare Carbon Monoxide, Nitric Oxide, and Hydroxyl Instrumentation at Wallops Island, Virginia

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ABBREVIATIONS AND SYMBOLS

A	intercept of linear regression analysis
AMES 1	NASA Ames Research Center carbon monoxide grab-sample technique
AMES 2	NASA Ames Research Center carbon monoxide direct sample injection gas-chromatograph technique
av	average
B	slope of linear regression analysis
chem	chemiluminescent
CI	confidence level
CITE	Chemical Instrumentation Test and Evaluation
CO	carbon monoxide
CPS	counts per second
D	average percent error
DACOM	differential absorption carbon monoxide measurement
<DIFF>	average difference
doc.	document
DP	dew point
EPA	Environmental Protection Agency
FORD	Ford Motor Company hydroxyl laser remote technique
GA TECH	Georgia Institute of Technology nitric oxide or hydroxyl laser technique
Ga Tech	Georgia Institute of Technology
GC	gas chromatograph
GSFC	NASA Goddard Space Flight Center
GTE	Global Tropospheric Experiment
ID	internal diameter
IIW	Instrument Intercomparison Workshop
inst.	instrument

LANGLEY	NASA Langley Research Center carbon monoxide laser technique
LIF	laser-induced fluorescent
MAPS	measurement of air pollution from satellites
max	maximum
min	minimum
met.	meteorological
N	number of samples
NASA	National Aeronautics and Space Administration
NBS	National Bureau of Standards
NMHC	nonmethane hydrocarbon
NO	nitric oxide
NOAA	National Oceanic and Atmospheric Administration
NOAA/NCAR	National Oceanic and Atmospheric Administration/National Center for Atmospheric Research nitric oxide chemiluminescent technique
OGC	Oregon Graduate Center
OH	hydroxyl
PI	principal investigator
ppbv	parts per billion by volume
ppmv	parts per million by volume
pptv	parts per trillion by volume
r	correlation coefficient from linear regression analysis
SRM	standard reference material
SNR	signal-to-noise ratio
T	temperature
TFE	tetrafluoroethylene
UMd	University of Maryland
UV	ultraviolet

WALLOPS	NASA Wallops Flight Facility nitric oxide chemiluminescent technique
WASH	Washington State University hydroxyl radiochemical technique
WSU	Washington State University
σ	standard deviation

SUMMARY

The report provides documentation of the first of three instrument intercomparison field missions conducted as part of the NASA Global Tropospheric Experiment/ Chemical Instrumentation Test and Evaluation (GTE/CITE-1). The first mission, a ground-based intercomparison, was conducted during July 1983 at NASA Wallops Flight Facility, Wallops Island, Virginia. The instruments being intercompared included one laser system and three grab-sample approaches for CO; two chemiluminescent systems and one laser-induced fluorescent (LIF) system for NO; and two different LIF systems and a radiochemical tracer technique for OH. The major objectives of this intercomparison was to intercompare ambient measurements of CO, NO, and OH at a common site by using techniques of fundamentally different detection principles. The ground-based intercomparison provided an opportunity to identify instrument procedural problems and major biases among the techniques prior to intercomparisons on an aircraft platform during the CITE-1 second and third missions. The ground-based intercomparison was particularly important because several of the techniques were "emerging" technologies with limited field experience. This report provides a comprehensive discussion of workshop requirements, philosophies, and operations. Previous publications have summarized the intercomparison results. For completeness, these results are also summarized herein to provide additional details for the analyses. Also summarized is the large body of nonintercomparison data incorporated into the workshop measurements for purposes of assisting the intercomparison investigators in the analysis of their instrument data. This report is an important source document for those interested in conducting similar large and complex intercomparisons tests as well as those interested in using the Wallops data base for purposes other than instrument intercomparison.

The workshop was successful in providing opportunities to intercompare the OH techniques. However, instrument operational problems resulted in few overlapping data periods. The overall conclusions for OH was that it was not possible to assess the capability of any of the three techniques for measuring global tropospheric levels of OH. For CO and NO, successful intercomparisons did result. An exchange of standards suggested a level of agreement of about 6 percent for standard measurements. For the CO intercomparisons a level of agreement of about 18 percent was determined for CO in ambient air and 12 percent for CO in nitrogen. These results were obtained at CO mixing ratios of 20 to 400 ppbv. An unexplained test-to-test variation was noted which at times approached 38 percent. The level of agreement was about 20 percent for the NO techniques for NO in ambient-air (10 to 200 pptv); the LIF results were consistently lower than the chemiluminescent techniques. However, this 20-percent level of agreement was within the range of the stated accuracy and precision for the techniques.

INTRODUCTION

For the past decade there has been considerable interest in the relative influence of natural versus anthropogenic activities on the chemical composition of the troposphere and ultimately the stratosphere. This interest has manifested itself in three major activities: (1) Laboratory studies of basic chemical reactions and proof of principles for instrument concepts, (2) theoretical modeling to predict concentration trends associated with the natural and disturbed atmosphere, and (3) field measurements of key atmospheric species. A measure of the success to which these three activities enhance our understanding of the chemical and physical processes occurring in the atmosphere is the degree to which observational data and theoretical predictions agree. Frequently such comparisons result in only limited success due, in part, to an uncertainty in our ability to measure some of the key tropospheric species coupled to an uncertainty in the accuracy and precision associated with many field measurements. In particular, questions concerning the relative accuracy of model predictions versus the quality of field measurement have been raised because of what appears to be excessive scatter in field measurements. In short, one of the limiting factors in further identifying the impact of anthropogenic activities on key atmospheric species is our inability to distinguish between true atmospheric variability and instrument errors.

A major research effort, the Global Tropospheric Experiment (GTE) (ref. 1), has been initiated by the National Aeronautics and Space Administration (NASA) to study the chemistry of the global troposphere and its interaction with the stratosphere, land, and oceans. GTE involves major field measurement programs to determine global atmospheric concentrations, distributions, and budgets of those trace species believed to be of key importance in global biogeochemical cycles. It is imperative that such a global measurement program have a well-established procedure, first, to aid in the assessment of the relative merits of current and future instrumentation, and second, to provide the mechanism for assessment of the validity of data obtained under a wide range of atmospheric conditions. NASA, along with others (refs. 2 through 4), has recognized that validation of measurement techniques for trace species is required to obtain credible data. Such validation requires not only laboratory testing of instrument concepts and performance characteristics but also intercomparison tests with other instruments, preferably in the field under realistic ambient environments.

One phase of GTE, Chemical Instrumentation Test and Evaluation (CITE), is aimed at developing and validating measurement techniques for trace species which play important roles in the tropospheric chemical cycles. CITE-1 focused on the intercomparison of instruments for the measurement of carbon monoxide (CO), nitric oxide (NO), and hydroxyl (OH). As a result of their participation in photochemical processes, these species have been identified as critical to advancing the understanding of homogeneous gas-phase chemistry in the troposphere. (See ref. 5.)

The purpose of this paper is to provide an in-depth documentation of the first of three instrument intercomparison field missions conducted as part of NASA GTE/CITE-1. The first mission, a ground-based intercomparison, was conducted during July 1983, at the Experimental Rocket Launch Facility at the Wallops Flight Facility on Wallops Island, Virginia. The ground-based intercomparison provided an opportunity to identify instrument procedural problems and major biases among the techniques prior to intercomparisons on an aircraft platform during the CITE-1 second and third missions. The ground-based workshop was particularly important considering that several of the techniques were emerging technologies with limited field experience. This report provides a comprehensive discussion of workshop requirements, philosophies, operations, and data analyses. Previous publications (refs. 6 to 9) have summarized the results from the workshop. This report also summarizes the large body of nonintercomparison data gathered at the workshop; thus, it is a source document for those interested in using the data base for other than intercomparison of instrumentation.

TEST OBJECTIVES

The basic question being addressed by GTE/CITE missions is different for each specie and, in general, reflects the difficulty of measuring the species. Tropospheric background concentrations of CO typically range from 50 to 200 ppbv. The grab-sample—gas-chromatograph and mercury oxide techniques have demonstrated the capability to routinely measure these levels of CO (refs. 10 through 12) with a time resolution of several minutes. The question addressed for the CO intercomparisons is, "Can we improve on the frequency response for measuring CO?" The background concentration of NO in the free troposphere can be lower than 10 pptv. (See refs. 13 and 14.) The question for NO is, "Can the current techniques measure background levels of tropospheric NO?" The OH radical, with an estimated tropospheric concentration of 10^6 OH/cm^3 (i.e., 0.1 pptv), has been most elusive, with at least 10 years of effort devoted to developing techniques for measuring tropospheric levels. (See refs. 15 through 19.) The question for OH is, "Do we now have a viable technique for measuring tropospheric OH?" The CO instruments included one laser absorption system (ref. 20) and three grab-sample approaches (refs. 10 and 11); the NO instrumentation included two chemiluminescent systems (refs. 13, 14, and 21) and one laser-induced fluorescent (LIF) system (ref. 22); and the OH instrumentation included two different LIF approaches (refs. 18 and 23) and a radiochemical tracer technique (ref. 24). Results from all three CITE-1 intercomparison missions are required in order to address these basic questions. The specific objectives for the Wallops intercomparisons were:

(1) To intercompare ambient measurements of CO, NO, and OH obtained at a common site by using techniques of fundamentally different detection principles

(2) To evaluate the extent to which each measurement system is susceptible to interference effects from other tropospheric species

(3) To evaluate the measurement accuracy and precision of each measurement system

WORKSHOP PARTICIPANTS

An integral part of the CITE-1 intercomparison strategy was to use specific ancillary measurements to facilitate interpretation of the intercomparison data and to aid in assessing the performance of specific techniques. For convenience in differentiating between the ancillary and intercomparison instruments, the specific CO, NO, and OH instrumentation was designated as "critical" whereas the remaining meteorological and chemical species measurements were designated as "supporting." The individuals and organizations responsible for the various critical and supporting measurements are given in table 1. It should be noted that only the CO laser differential absorption technique was characterized as critical to reflect the fact that this was an "unproven" approach, whereas the grab-sample—GC techniques were considered proven technologies. The single entry from NASA Ames Research Center in table 1 represents two separate CO measurement approaches, AMES 1 and AMES 2. The acronym for each CO, NO, and OH technique is given in brackets in table 1. These acronyms are used throughout this paper. A detailed description of each OH, NO, and CO measurement technique can be found in the references. References for other supporting measurements are not cited as most are standard and familiar measurement approaches.

DESCRIPTION OF TEST SITE, PROCEDURES, AND INSTRUMENTATION

Test Site Selection

Site selection was of utmost importance if the intercomparisons were to be successful. Not only must the site be a remote location in order to provide the air quality required by the objectives but also to provide the participants adequate work space and various support facilities to maintain and/or repair generally complex electronic or laser hardware. The workshop site (figs. 1(a) and (b)) was located at the north end of the Experimental Rocket Launch Facility at the Wallops Flight Facility approximately 1 km inland from the Atlantic coastline. The actual site (fig. 1(c)) was an open field surrounded by marshy or sandy soil with dense low brush and small pine trees. The actual facilities (fig. 1(d)) consisted of trailers set up in the open field. This arrangement provided a laboratory-type environment for the instrumentation in a relatively remote location. In addition, the trailer approach allowed the site to be set up to maximize desired instrument, procedural, and operational requirements.

During July the expected daytime surface winds are strongly influenced by a sea breeze and are predominantly southeasterly. Anticipating this surface wind direction, the site was set up to maximize the open areas on the eastern side of the facility and all air samples were obtained from the east side. Study of meteorological synoptic data, available air quality data (refs. 25 and 26) and photochemical modeling results suggested that in July the site could provide the air quality deemed necessary for the intercomparisons, that is, CO mixing ratios from about 100 to several hundred ppbv, NO mixing ratios in the range of 10 to 200 pptv, and OH in the mid to high 10^6 OH/cm^3 range.

Test Philosophy and Procedures

The workshop was conducted in three phases consisting of preworkshop, on-site, and postworkshop activities. The major thrust of the preworkshop activities was intercomparison of the primary calibration standards used by the individual CO and NO groups. The main thrust of the on-site activities was intercomparison of simultaneous ambient measurements for the CO, NO, and OH instruments. The postworkshop activities consisted of data analysis sessions conducted on an as-needs basis.

The preworkshop activities were initiated in May 1983 with round robin measurements of a primary CO and NO standard supplied by the GTE project. These measurements were followed by measurements on a blind CO or NO standard (separate standard each investigator) sent to each group. All standards were NBS standard reference materials or traceable to such. The mixing ratio for the GTE primary standards was given to each group along with the standard and instructions to measur its mixing ratio by the best means available. All investigators elected to measure the primary standard with the techniques employed at Wallops. The purpose of the GT primary standard was to normalize the primary standard of each group to a common GTE reference. Only an approximate range for the mixing ratio was provided with the blind standard sent to an investigator. Measurements of these standards were specified to be performed with the respective instrument, procedures, and calibration standards planned to be used during the workshop. During the workshop in July, the GTE primary and blind standards were made available to any investigator upon request The preworkshop standards as well as two additional CO standards implemented into th procedures while at Wallops are given in table 2. These two additional standards were supplied by Ames. The MAPS primary standard had been circulated in a previous intercomparison of standards (ref. 10). Oregon Graduate Center (OGC) was not requested to participate in the preworkshop exchange of standards.

The on-site activities were formally initiated on July 5, 1983, and were completed July 30, 1983. Test philosophies and procedures used on-site were influenced by several characteristics of both the particular species in question and the respective measurement technique. In particular, NO and CO are long lived species which can be mixed, by using standards and dynamic dilution, at mixing ratios comparable with expected tropospheric levels. Moreover, each of the NO and CO instruments are in situ point samplers which could share a common manifold for sampling of a common air mass. Thus the test philosophy for the CO and NO intercomparisons was to collocate each group of instruments (CO or NO) along a common manifold and to supply to that manifold the test gas mixture to be sampled. The test procedures for NO and CO consisted of performing a series of daytime and nighttime measurements on (1) ambient air drawn through a common manifold, (2) ambient air spiked with dynamically mixed levels of CO or NO, and (3) calibration levels of CO in dry nitrogen provided at each instrument by a common manifold. Figure 2 illustrates examples of typical spiked runs. In figure 2(a), the spike is added to or subtracted from the previous spike, whereas in figure 2(b), ambient (unspiked) or pure nitrogen (CO calibration runs) is sampled before and after each spike. For a given test sequence, the investigator groups were given the length of the test, the times at which the level of CO or NO would be changed, and the maximum mixing ratio that could be expected during the test sequence. The magnitude of the enhancement for each step was not announced. For ambient tests with no additions, only the start and stop time of the test was supplied.

The OH radical and instrumentation presented unique problems. Namely, the short lifetime of the species and the range of sample geometries (in situ point samplers and remote sensors) prevented the use of a common manifold. In addition, the lack of a well-defined source of OH prevented any consideration of calibration or spiked addition tests. The test philosophy for OH was to intercompare the instruments based on ambient air measurements only. A test area (≈20 m radius) was defined in the open field to the east of the facility and each investigator was required to simultaneously sample ambient air from that area. An elevation of ≈4 m above the ground was selected as the height for the OH measurements. For OH, the intercomparison tests were scheduled based on (1) the health of the instrumentation and (2) the general guidelines of measurement periods between 1000 and 1600 hours. In practice, however, OH measurements along with supporting data were obtained whenever any one of the three OH instruments was operational. Since both NO and OH are photochemically produced species, each should be at a minimum after sunset. Consequently, the nighttime measurements on OH and NO were particularly important for evaluating interference effects and determining minimum detectable levels for the various techniques.

Strict data handling protocol was established for those investigator groups intercomparing instruments. This protocol included (1) reporting of all data from the formal test periods, (2) real-time and on-site notification to the GTE workshop staff as to instrument problems and/or "suspect" data, (3) no interchange of data during or after the formal test periods, (4) submittal of preliminary data within 1 to 2 days after a test sequence, and (5) submittal of final results within 30 days after the completion of the on-site activities. Supporting measurements (i.e., all measurements except those of the species being intercompared) were made available on-site without restrictions. A supporting measurement data archive was supplied to each investigator group within 2 weeks of the completion of the on-site activities. While on-site, GTE staff personnel served as the focal point for discussion of the submitted data; they communicated with individual investigators to clarify submitted data and/or discuss procedural problems. This GTE staff analyzed preliminary data on a daily basis and used the analyzed results to plan additional test sequences. In instances where the results appeared inconsistent based on experience or earlier workshop data, the investigators were notified and asked to reexamine their data or instrument procedures. Even in these instances, communication was limited and actual results were not revealed.

After submittal of the final results (1 month after the workshop), the GTE staff performed an intercomparison analysis for each of the three species. The focus of this analysis was (1) to identify the level of agreement among the instruments, (2) to identify any consistent bias among the instruments, (3) to identify outlying data points, and (4) to identify any invalid or suspect test procedures. After completion of this initial data analysis, the GTE staff met with each group of PI's (CO, NO, or OH) to discuss the results and obtain explanations of selected observations. Additional data discussions were held until all investigators agreed to the methods of analysis being used for intercomparison of results. Editing of the data base occurred only after all investigators and the GTE staff were convinced that valid and consistent reasons did exist for such editing.

Facility Description

Based on the test objectives, philosophies, and procedures, various facilities and capabilities had to be established for the tests at Wallops. These are discussed in this section and include site design and construction, sampling manifolds, gas dilution system, and gas standards.

Site design and construction.- Figure 3 shows the completed site and a design layout for the site. Important in the design of the site were those items dictated by the nature of the planned intercomparisons and the participating instruments and included

(1) The need for air samples to be free from excessive variability and high levels associated with local sources, including on-site workshop activities, was the prime consideration. With the site location being a relatively remote area, the cooperation of Wallops management to allow the GTE staff to establish the site as a controlled access area, and the meteorology of frequent winds from northeast to south basically satisfied this requirement. The site was designed with sample inlets and test areas to the east of the site and instrument exhausts and on-site activities (trailers, parking, etc.) on the western side of the site.

(2) The need for the NO and CO instruments to sample a common ambient air sample and spiked-ambient samples forced to a large extent the basic layout of the trailers and the sampling manifolds. The positions of trailers 1, 3, and 4 with the sampling manifolds located adjacent to the trailers allowed the NO and CO inlets to be collocated on the manifolds; thus, sampling of the same air mass, ambient or spiked ambient, was assured. (It is noted as shown in fig. 3 that the OGC inlet for CO was located 6 m downstream of the other CO inlets; this will be addressed later.) The inlet to the main manifold (i.e., above trailer 5) permitted sampling of "clean" air for northeast to south winds. The location of trailer 5, the manifold inlet, and the injection port for spiked additions was, by design, some distance upstream from the NO and CO sample ports. Any chemical reactions induced by injection of a test gas into the manifold (e.g., NO + O_3) should have stabilized prior to reaching the sampling locations.

(3) The need to define an open-air sampling area to the east of the site for the OH investigators also influenced the location of trailer 4 (Ga Tech OH and NO instruments). Trailer 4 was located not only to allow Ga Tech to sample NO from the manifold but also to project its laser beam from the laboratory trailer to platform 1 which contained their OH sampling chamber. Platforms 1 and 2 were constructed on-site to permit Ga Tech and Washington State University an open-air ambient sampling area approximately 4 m above the ground and free of local sources and disturbances. Adjacent to the towers towards the east was the sample volume defined by the Ford remote LIF instrument. The location of the Ford van and backstop target were selected to collocate as close as practical the sampling volumes for all three instruments while ensuring noninterference among the investigators during the test periods.

(4) As a result of the remote location of the site, to minimize transit activities into and out of the site and to maximize available workshop time, the site was designed to provide the necessary logistical support. Additional trailers (2, 6, and 7) along with the aforementioned trailers provided laboratory space for instrument repair, office space, and meeting facilities as well as work space for a small secretarial staff.

Site construction started in April with installation of a septic tank field and siting of the trailers. In May and June, electrical, telephone, and various construction services were completed. Sampling manifolds and other GTE-supplied instrument systems were installed and tested in June. Workshop participants began assembling in late June with the workshop formally opened July 5. Workshop tests were completed by July 30 and the site dismantled by the end of August.

Sampling manifolds.- Three manifold systems were used for the NO and CO measurements. The primary manifold used for the ambient air (spiked and unspiked) was assembled from 3-m sections of 75-mm ID glass pipe and located as shown in figure 3. As already noted for northeast to south winds, the inlet was upwind of the site approximately 6 m above the ground level and 3 m above the surrounding roof line. The flow rate of ambient air drawn into the manifold was typically 35 standard L/sec and regulated by a mass-flow controller. A port for injecting known mixing ratios of CO or NO from a dynamic dilution mixing system was located approximately 5 m downstream of the inlet. Three separate sample ports for the NO instruments were collocated in a 20-cm section of pipe approximately 17 m downstream of the injection port. The sample ports for the Langley and Ames CO instruments were located approximately 25 m downstream of the injection port, whereas the OGC port was 6 m downstream of the Ames/Langley port. The total length of this manifold was about 38 m with its exhaust at ground level. The pumping source for the manifold was a synchronous-motor-driven roots blower located at the exhaust. The manifold and instrument locations were chosen so that the sample lines from each NO instrument to its manifold port were approximately equal with a similar arrangement for CO sample lines. A plan view and elevation sketch of the manifold is shown in figure 4. The main inlet and a typical 20-cm pipe section used for the investigator sample ports are illustrated in figure 5.

A second manifold (nitrogen manifold) was constructed with 25-mm ID glass pipe and was used to test mixtures of CO in dry nitrogen. The design and routing of this manifold was identical to that of the primary manifold. Ultra-zero nitrogen gas was pressure fed through the manifold at 0.5 standard L/sec from a gas cylinder supply. Gas mixtures of CO from the gas dilution system (in trailer 5) were injected into the manifold for spiked portions of the tests.

The third manifold system consisted of individual glass sampling canes located as shown in figure 3. These canes were constructed from 75-mm ID glass pipe identical to that used for the primary manifold. (See fig. 5.) A 20-cm section of pipe containing three sampling ports was located 4 m from the inlet. This 20-cm section then provided sampling ports similar to those used on the primary manifold. Separate manifolds of this type were provided for the CO and NO groups. Each inlet was approximately 6 m above the ground. A roots blower located on each cane at ground level provided continuous flow rates of 25 standard L/sec. These individual sampling canes provided two important functions: The capability to sample ambient air with significantly less residence time in a manifold than available from the longer primary manifold and the capability for comparison of measurements from the individual canes with those obtained from the longer primary manifold.

In addition, an exhaust manifold was provided and served as a "waste" line for all instrument exhausts including surplus gas flow from the gas dilution system. Its pumping source was a roots blower located at the exhaust and under trailer 2. (See fig. 3.)

Dynamic gas dilution system.- An important component of the supporting facilities was the dynamic gas dilution system. The dilution system was a two-stage mass-flow-controlled system similar to that of reference 27. It was designed to operate over a dilution range of 10^6. The system has been used in the laboratory for several years to provide gas standards for instrument calibration. At Wallops, the system was used to generate known levels of CO and NO, which were injected into the test manifolds. A final stage of dilution occurred within the manifolds at the point of gas injection. Figure 6 is a schematic of the system and shows those flow parameters required to generate at 10-pptv change in NO mixing ratio in the primary manifold.

Gas standards.- Gas standards served three functions in the CO and NO intercomparison tests: (1) "primary" GTE standards provided a means of normalizing intercomparison results based on the differences between the internal standards of the various investigator groups, (2) "blind" GTE standards provided the opportunity to identify major instrument biases which were not the result of differences in standards, and (3) "test" standards provided the gas supply to the dilution system from which the spiked-addition mixing ratios were determined. The primary and blind standard mixing ratios were selected after discussion with the investigators as to their instrument needs and limitations. However, in general, the main factor which influenced the selection of a given standard was its availability traceable to an NBS SRM. Test standards were selected based on the best operating conditions for the dilution system for the range of CO and NO mixing ratios used. All workshop CO or NO spiked samples were generated from a single CO or NO test gas cylinder supply to the dilution system. Diluent gas for the dilution system was ultra-zero grade nitrogen. The dilution system gases were purchased from a commercial gas vendor with a certified analysis. The CO and NO test standards were reanalyzed after the workshop by NBS. The specifications on the various gas standards are summarized in table 2.

Description of Intercomparison Instruments

A brief summary of the CO, NO, and OH instrumentation, focusing on those salient features influencing the intercomparison procedures and interpretation of the results, is presented in this section. A more detailed discussion can be obtained from the earlier cited references.

Carbon monoxide techniques.- Two fundamentally different measurement concepts were used. The tunable diode laser system measures energy change of monochromatic radiation (Pb-salt laser) transmitted through a multipass optical cell in which the sample is continuously flowing. Accordingly, real-time CO measurements are obtained. For the instrument as configured at Wallops, the temporal resolution was approximately 13 sec (time required to completely replenish the optical cell with a fresh sample), and the precision was stated as ±0.5 ppbv with an electronic integration of 4 sec. Three different grab-sample--GC approaches were used to provide intercomparison data for the laser instrument. Two approaches are represented by the single Ames entry in table 1, the third, by the OGC entry. The three techniques differ mainly in the method and duration of sample collection and the analysis times after collection. AMES 1 collected an ambient pressure sample in a container. Sample collection time was approximately 1 min with on-site GC analysis within 24 hours after collection. AMES 2 involved direct injection of an ambient air sample into the GC with immediate analysis. Sample injection time was only a few seconds; analysis required approximately 15 minutes. Generally, both Ames samples were collected every 15 to 20 min during a given intercomparison test sequence. OGC utilized cryogenic trapping of an ambient air sample in a container with a collection time of 6 min/sample. Analyses of these samples were performed at the OGC laboratories following shipment from Wallops. Analysis was generally completed within 36 to 48 hours after initial collection and included CO as well as other trace gas species. OGC samples were generally collected at a rate of one sample per given test condition.

Nitric oxide techniques.- The NO instrumentation with two chemiluminescent techniques and one two-photon laser-induced fluorescent technique also represent two fundamentally different measurement approaches. The two chemiluminescent systems differed primarily in the calibration and background suppression techniques. The most noteworthy difference was the injection of water vapor to the air stream entering the reaction chamber in the NOAA/NCAR instrument for purposes of (1) minimizing background variability due to ambient water vapor and (2) suppression of an O_3 related background. Both chemiluminescent systems employ photon-counting techniques to detect fluorescence from the decay of excited NO_2 molecules produced by the reaction of NO with O_3. The resulting fluorescent signal is related to ambient NO mixing ratio through a standard addition calibration. For the WALLOPS system, the basic integration period was 1 min with background and/or calibration measurements every 5 to 10 min. The basic measurement sequence for the NOAA/NCAR system consisted of a 30-min measurement period which included two 4-min calibration periods and four 2-min periods in the background fluorescent measurement mode. During each measurement or calibration period, the basic counting period (i.e., integration time) was either 4.6 or 10 sec. Measurements from these periods were processed by the NOAA/NCAR group and submitted as 1-min averages. The performance characteristics for the WALLOPS instrument were stated as follows: a precision of ±6 pptv (±2σ) for an individual 60-sec measurement, an accuracy of ±30 percent (±2σ) for long-term averages, and an artifact signal less than 6 pptv. The performance characteristics for the NOAA/NCAR instrument were stated as follows: a precision of ±8 pptv (±2σ) for an individual 10-sec measurement, an accuracy of ±20 percent (±2σ) for long-term averages, and an artifact signal of 5 pptv.

The GA TECH LIF system utilized a detection scheme in which the NO molecule was excited in a two-step process resulting in fluorescent emission at UV wavelengths. Fluorescence from the excited NO molecule was measured by a photon-counting system and then related to the NO mixing ratio in the air sample through calibration. As configured for Wallops, the basic counting or integration interval was 5 min (some data were reported with 1- and 2-min counting intervals) with calibration periods before and after each test sequence. Unlike the chemiluminescent technique, the precision of the GA TECH technique depended upon the ambient level of NO as well as the integration period. For an ambient mixing ratio at Wallops Island of about 25 pptv, the precision of the GA TECH system was stated as approximately ±20 percent ($\pm 1\sigma$) for a 5-min integration period. Uncorrected photolytic interferences were believed to be less than 1 pptv and the accuracy was ±24 percent ($\pm 2\sigma$) for long-term integration.

Hydroxyl radical techniques.- The OH instruments covered a wider range of sample techniques, measurement approaches, and integration times than the CO or NO instruments. In particular, the radiochemical technique (WASH) and the Ga Tech LIF OH technique (GA TECH) were in situ samplers, whereas the Ford technique (FORD) was a remote sensor approach. The radiochemical technique, as configured at Wallops, relied upon natural advection of air into the instrument and was operated from an open platform constructed at the site. This technique was, in effect, a grab-sample approach in which a sample of radioactive $^{14}CO_2$ produced by the OH + ^{14}CO reaction is collected and analyzed at some later time. The time required to collect a sample was 100 sec and the sample frequency at Wallops was 1 sample every 15 to 30 min during a test sequence. Analyses of the samples were performed at Washington State University several days after acquiring the sample. The minimum detectable level for this system was quoted to be 1×10^4 OH/cm^3 with an accuracy of about ±30 percent.

The Ga Tech laser system was operated from a trailer-type laboratory that was set up at the site. The sample system employed by Ga Tech was originally designed for aircraft use and required a high-volume pump to continuously draw ambient air through a fluorescent chamber. The fluorescent chamber and associated photon-counting photomultiplier tubes were located on an open platform approximately 6 m from the trailer housing the laser system and adjacent to the platform used by the WSU group. This arrangement allowed the WASH and GA TECH inlets to be within 5 m and approximately 4 m above the ground while providing a laboratory environment for the Georgia Tech lasers. The minimum detectable level of the Ga Tech system, as configured, was quoted to be in the range of 2×10^6 to 5×10^6 OH/cm^3 for a 30-min integration period.

The Ford lidar system was operated from an environmentally controlled motorized van. The effective sample volume of this system was a conical section starting with a diameter of about 10 cm from 9 m downstream of the van and ending with a diameter of 30 cm at a backstop 35 m from the van. The van was located so that the effective volume was 4 m above ground level and 10 m to the side of but centered on the two sample platforms used by WSU and Ga Tech. The overall arrangement of the three OH systems permitted intercomparison measurements to be made with a radius of 20 m. The detection limit quoted for the FORD system was in the range of 5×10^6 to 7×10^6 OH/cm^3.

Supporting Measurements

As stated earlier the instrument intercomparison tests included a comprehensive set of ancillary or supporting measurements. The purposes of these measurements were threefold: (1) to define the characteristics of the various air masses occurring at Wallops during the July time frame, (2) to provide concurrent measurements of certain species which were determined a priori as potential interferences for the instruments being intercompared, and (3) to assess any contamination or sample modification which might be induced in the ambient samples as a result of the sampling manifolds. As such, the location of the supporting measurements on-site were determined based on the primary objective of that particular measurement. In general in terms of instrument siting, intercomparison PI's requirements overshadowed supporting measurements when conflicts or competing requirements surfaced. In addition, some supporting measurements were located such that the same systems could sample free ambient as well as manifold air, the choice being dependent on the particular test. The supporting measurements are summarized in table 3 where the location of each instrument, its measurement capabilities, and the type of environment sampled are given. The reader is referred to figures 3 and 4 to assist in locating each measurement location in relation to the site layout and to table 1 for the responsible investigator. All supporting measurements were made by proven techniques and investigators with demonstrated capabilities. These investigators were approved by the GTE Science Team including the CO, NO, and OH investigators.

In addition to the supporting measurements of table 3, meteorological summaries were continually being supplied to the on-site workshop staff. Weather briefings were held twice daily with pertinent information being forwarded to the workshop participants throughout the day.

OPERATIONAL SUMMARY

Test Site and Equipment Verification

In order to ensure that the test procedures and test measurements were to constitute a valid set of intercomparison data, certain test equipment and procedures required verification. These included (1) gas dilution system, (2) air-sampling manifolds, and (3) the spiked-ambient test procedures. Prior to site selection, available meteorological and air quality data (refs. 25 and 26) were studied to ensure that the site could supply the required air quality. In addition, the available data on air quality was compared with existing photochemical modeling results in terms of potential OH production. These data will not be reviewed in this document. The concensus among the GTE Science Team and the CO, NO, and OH investigators was that the site with its high frequency of northeast to south winds would provide sufficiently low NO and CO and high OH concentrations to result in a meaningful instrument intercomparison.

Gas dilution system.- As discussed earlier, the gas dilution system was an existing facility which had been used in numerous laboratory studies. The system had a history of successful operation (ref. 27) for dilution of test gases to the ppbv level and for dilution ratios of 10^5 to 10^6. Since the last stage of dilution occurred in the manifold, only dilution ratios of about 200 were required within the dilution system. The larger dilution ratios were typically required for the NO tests (N-series). For the CO tests (C- and X-series), dilution ratios ranged from no dilution (i.e., mixing system provided gas from the cylinder supply directly into the manifold, only diluted by manifold flow) to about a dilution factor of 25.

Verification of the dilution system was initiated approximately 3 months prior to the on-site activities. The system was disassembled and each flowmeter was calibrated in air and N_2 throughout its operational range. Results were compared with the 2-percent specification of the manufacturer and any out-of-specification flowmeters were replaced. The dilution system was reassembled and sent to NBS for characterization, which was to include the following work tasks:

(1) Recalibration of flowmeters (without disassembly from the system)

(2) Characterization of mixing accuracy for NO in the mixing-ratio range of 10 000 ppmv to 10 ppbv with dilution factors up to 10^6

(3) Characterization of mixing accuracy for CO in the mixing-ratio range of 10 000 ppmv to 1 ppmv with dilution factors of 10^4

Characterization tests at NBS included preparation of gas mixtures with the dilution system and comparison of calculated mixing ratios with those measured with NBS-supplied analysis equipment.

Upon receipt of the system, NBS performed a series of preliminary system checks in preparation for the NO characterization tests. Several problems including leaks and potential sources of contamination were identified. At the recommendation of NBS, the system was refurbished by them, with the incorporation of new TFE tubing and fittings and two new flowmeters. As a result of this effort and the Wallops time schedule, work task 3 was deleted and remaining tests focused on work tasks 1 and 2, as task 2 was the more stringent requirement for the dilution system. Work task 1 included a thorough leak check of the rebuilt system including static-pressure checks and mass-balance-flow checks before and after various system components. Flowmeter calibrations were performed that agreed with earlier calibrations or, in the case of the new flowmeters, with manufacturer's specifications. For work task 2, over 60 NO mixing ratios were dynamically mixed and analyzed by NBS with a chemiluminescent NO detector. Various combinations of dilution factors and NO mixing ratios were investigated. The results of these tests for the dilution factors (maximum of about 200) and mixing ratios (minimum of 0.5 ppmv) employed within the dilution system at Wallops are summarized in the following paragraph.

In the 10- to 1000-ppmv mixing-ratio range, the agreement (measured versus calculated) was generally better than 2 percent. The dilution factors employed were in the range of 10 to 1000. For NO mixing ratios around 1 ppmv, the agreement fell within 0.1 to 3.5 percent, with most values better than 2 percent. The dilution factors employed were 10 to 10 000. Mixing ratios of 0.1 ppmv were generated by using dilution factors of 100, 1000, and 100 000. Agreement was in the 1- to 3-percent range.

Based on the NBS results and the dilution factors and mixing ratios used at Wallops, output mixing ratios from the dilution system were accurate to better than 3 percent.

Air sampling manifolds.- As previously discussed, the sampling manifolds were constructed of glass (75 or 25 mm ID). Prior to construction of the manifolds at Wallops, studies were conducted to evaluate CO or NO losses or contamination by the manifold. These studies were performed by Research Triangle Institute at their North Carolina facilities. Tests were performed on a 10-m length of the 75-mm ID manifold (with 90° and 180° bends) and at CO and NO mixing ratios of 3 to 100 ppmv and 9 to 400 ppbv, respectively. Ambient air was drawn into the manifold at 35 standard L/sec to which mixes of CO or NO were added. Measurements of CO or NO were made at various sampling stations downstream of the test gas injection port to evaluate manifold-induced sample losses or contamination. The gas injection port was 1.4 m downstream of the ambient inlet with sampling stations 1.4, 3.3, 4.8, 5.6, and 8.3 m downstream of the injection port. The test results are summarized in table 4. Analyses of CO and NO were by nondispersive infrared and chemiluminescent techniques, respectively. Results showed that within the 5-percent precision of the tests, no significant sample loss or contamination occurred within the manifold. It must be emphasized that because of the detection limits of the analysis instruments, these studies were limited to mixing ratios 100 to 1000 times greater than the minimum mixing ratios used at Wallops and, as such, cannot be conclusive proof of an absence of losses or contamination along the primary manifold.

During construction of the manifolds at Wallops, each manifold section was cleaned with distilled water and dried prior to installation. TFE screens were used on each ambient inlet cane to minimize bugs and debris being drawn into the manifold, and collection bottles were installed at the bottom of vertical runs to capture debris and water. The manifolds and collection bottles were inspected daily during the workshop tests. During these inspections, rarely was any debris or water found in these collection bottles. After final construction of the manifolds, the manifolds were sealed (TFE caps) and pressure tested for leaks.

The sample flow for the primary manifold was controlled by a roots blower driven by a synchronous motor. The unit was located at the exhaust of the primary manifold. Flow-rate control was obtained by using the output of a mass flowmeter (located near the inlet of the primary manifold) to control the speed of the synchronous motor and hence the flow through the blower. The performance of this system was critical to the CO and NO intercomparison tests because the final stage of gas dilution occurred automatically within the primary manifold. Absolute accuracy of the primary manifold flow rate was better than 2 percent as determined by calibration. Flow stability tests were performed on the primary manifold flow, and flow control was found to be better than 1 percent (24-hour period) for flow rates ranging from 3 to 35 standard L/sec.

The nitrogen manifold flow was controlled by a mass flowmeter located at the gas cylinder supply. Flow stability was better than 2 percent. Postworkshop calibration of the flowmeter showed it to have a calibration factor 20 percent higher than recommended by the manufacturer. (Time schedules did not permit a preworkshop calibration of this flowmeter.) All workshop results for the nitrogen tests are based on the postworkshop calibration (2 percent accuracy).

During the on-site intercomparison tests, an attempt was made to continually verify the operation and performance of the air sampling manifolds. In addition to routine visual and operational checks, a series of supplementary measurement scenarios were instituted which focused on ascertaining the representativeness of air samples from the primary manifold compared with free ambient air samples or samples from the shorter individual sampling canes. These measurements included

(1) Ozone, temperature, and dew-point measurements at the primary manifold inlet; in the manifold, 5 m from the inlet; and in the manifold, just prior to the manifold blower

(2) Trace gas samples (OGC measurements) taken in the free air, from one of the shorter individual sampling canes, and from the primary manifold, just in front of the manifold blower

(3) Methane and nonmethane hydrocarbon measurements (on-line gas chromatograph) from one of the individual shorter sampling canes and from the primary manifold just in front of the primary manifold blower

The investigators responsible for these measurements stated that no differences were observed between samples taken at the various locations. Typical results from some of these tests are shown in table 5.

Spiked-ambient procedures.- Once the main sampling manifold, gas dilution system, and other facility instrumentation were installed and certified as operational, the test procedures planned for the spiked-addition tests for CO and NO were verified and modified as required. Flow rates for the gas dilution system and main manifold were recorded continuously on the central data acquisition system used for the workshop. Flow records were analyzed and procedures modified until the workshop staff became experienced in producing sharp square-wave mixing-ratio changes with minimal fluctuations. A final test of the procedures included a simulated test run by using the LANGLEY CO instrument. This test was performed blind to the LANGLEY investigator. A comparison of LANGLEY records with the computer records of flow rates showed that the test procedure was valid and required no further modification.

Scheduled Tests

Figure 7 is the calendar of events for the Wallops workshop with the arrival times of the various investigator groups, dates of the various tests, and major instrument problems. The sequence of tests was influenced by the state of readiness of the various instrumentation systems, the expected difficulty of obtaining an intercomparison for the various species, and the fact that Ga Tech was participating in both the NO and OH intercomparisons and was using systems common to both species. Initial plans called for the first week to be dedicated to CO; the second week, to OH; the third week, to NO; and the fourth week, to retests for CO or NO as dictated by earlier workshop results. Project rationale influencing this test plan is briefly summarized as follows:

(1) The CO tests were believed to be the most straightforward when considering the ambient air requirements, the desired range of test mixing ratios, and the degree of instrument readiness. All CO techniques had previously been used in the field. In addition, by completing CO first, any gained procedural experience could be applied to the NO tests. Having CO first also provided the OH and NO investigators with more on-site time to set up and verify their more generally complex instrumentation.

(2) The OH tests were expected to be the most difficult and time-consuming part of the workshop. Based on the different instrument configurations, the complexity of the instruments (principle of detection and operation), and the more stringent meteorological requirements, 1 week was thought to be a minimal test period. It was decided that the workshop staff could more readily extend the OH test period if CO tests had already been completed and remaining tests (NO) were procedurally similar to the completed CO tests. Because of the importance of the OH intercomparisons, it was not deemed advisable to schedule OH last. In addition, Ga Tech recommended that from their instrumentation viewpoint a switch from OH to NO was more advisable than from NO to OH. It was necessary to complete OH tests before switching to NO as time was only available (3 days required) for Ga Tech to change detection configuration once.

(3) For CO and NO, if the intercomparison results were successful in the initial tests, then during the last week of intercomparison, additional tests could be defined to refine levels of agreement or disagreement among the instruments.

Eight formal CO tests were conducted, six during the CO test week (July 8 to 14), and two tests later in the workshop. Seven OH tests were conducted during the second week (July 15 to 22). Washington State [WASH] did not arrive on-site until July 21 and participated in only the last 4 OH tests. The NO tests were delayed several days to allow Ga Tech to switch to NO and replace a damaged laser. Eight NO tests were conducted (July 26 to 29). GA TECH was not operational for the first three tests as the damaged laser had not been replaced and aligned. The formal tests and pertinent test conditions are summarized in table 6. The test sequences for CO and NO are described in detail in appendix A. Instrument and procedural problems experienced during the formal test periods are discussed in appendix B along with their effects on the reported data. Appendix B is useful in identifying those data which have been omitted from consideration in the formal comparisons as the result of problems. Also included in appendix B is the project test log records during the official OH test periods.

DISCUSSION OF ERRORS

This section summarizes and/or discusses those errors and inaccuracies associated with the intercomparison test procedures. Various instrument characteristics (e.g., detection limits and precision) for the CO, NO, and OH instruments intercompared were cited earlier. These characteristics were supplied to the GTE project by the investigators and are not discussed. The reader is referred to the earlier cited instrument references for documentation of these values. Precision and accuracy of the CO and NO techniques as applicable to the preworkshop exchange of standards are discussed in appendix C.

Gas Standards

Based on the data of table 2 and at a 90-percent confidence level, gas standard accuracies were within the following specifications:

(1) GTE primary and blind CO standards, 1 percent

(2) GTE primary and blind NO standards, 2 percent

(3) Gas dilution system standards, 1 percent

These accuracies were the ones supplied by the gas suppliers. As indicated in table 2, the gas dilution system standards were recertified after the workshop and found to be in the 1- to 2-percent accuracy range.

Ambient Variability

Although it is difficult to perform an analysis to quantitatively define the magnitude of error introduced into the intercomparisons as the result of ambient variations of the test species, some discussion of these variations and related effects is justified. The intercomparison tests were set up (site selection, site layout and construction, and test procedures) based on guidelines of minimizing ambient variability of the test species during intercomparison periods. Desirable test conditions for ambient-only tests were a range of mixing ratios over the 4-week period but minimal or slowly changing ambient mixing ratios during any specific test. For the spiked-ambient tests, ideal conditions were defined as no-ambient fluctuation during a test or fluctuations 10 percent or less when compared with the spiked mixing ratios being measured. Generally these test conditions were met for most of the formal tests.

During the on-site tests, steps were taken to minimize any effect of ambient variability. For example, as part of each spiked-ambient tests, the first sampling period was of ambient air only. During this time period, the GTE workshop staff observed the ambient mixing ratios as recorded by the intercomparison instruments and then selected step-change (delta) values for the test based on these observations. In addition during data analysis of the workshop results, efforts were taken to minimize any effects of ambient variability. Although the effects of ambient variability were somewhat magnified by the instruments having different temporal resolution (i.e., continuous to finite grab samples), intercomparisons were generally restricted to those times over which all instruments provided overlapping data. For the CO tests, the grab-sample data provided the key to the selection of overlapping data periods, and the LANGLEY continuous data were averaged over the grab-sample periods. Where the two grab-sample techniques did not provide overlapping data, LANGLEY results were used to normalize any significant ambient variation which occurred between the times of the grab samples. Such normalization was required only once (fig. 8(a)) and was the result of an instantaneous change in ambient CO concentration which occurred during a morning test. As shown in figure 8(a), this change occurred at approximately 1100 hours and CO ambient concentrations jumped approximately 20 ppbv. The cause of the change was a wind shift from off the ocean to off the land. Temperature, dew point, and aerosol data also showed the effects of this wind shift. For the CO formal test periods, the maximum observed ambient variability is shown in figure 8. Figure 8(a) is for the previously discussed spiked-ambient test, whereas figure 8(b) is for an ambient-only test.

For the NO tests, the key to the selection of overlapping data periods was the sampling period of the LIF technique, generally a 5-min average. Each chemiluminescent measurement (approximately 1-min average) was averaged over the LIF data period for intercomparison purposes. When sufficient overlap did not occur between one or more of the chemiluminescent measurements and the LIF measurement, a judgment was made that was based on the chemiluminescent measurements before and after the LIF data period, and the data (either before or after) showing the lesser ambient variability were used for intercomparison. When this judgment was questionable, the data have been marked as "invalid" for intercomparison purposes.

Spiked Mixing Ratios

For the CO tests, 24 spiked additions were introduced into the instruments. Ten additions required the use of the gas dilution system, and all ten were mixed by using a dilution factor of approximately 25 and an output (from the dilution system) mixing ratio of approximately 4 ppmv. The remaining dilution occurred within the sampling manifold by varying the amount of test gas supplied from the dilution system to the manifold in order to obtain the desired test condition. The 14 remaining spiked additions were obtained by direct injection from the gas cylinder standard (approximately 100 ppmv) into the sampling manifold. For NO 14 spiked additions were tested, all requiring use of the gas dilution system. All but two additions required dilution factors within the dilution system of <100 and output mixing ratios >100 ppbv. The two remaining mixing ratios required a dilution factor of approximately 150 and an output mixing ratio of approximately 60 ppbv.

For the GTE-generated CO and NO ambient-spiked mixing ratios, the mixing-ratio accuracies at exit from the dilution system (i.e., just prior to injection into the manifold) were better than 3 percent with a variability of less than 2 percent. Primary manifold flow was accurate to 2 percent with a variability of less than 1 percent. The accuracies of CO or NO mixing ratios in the manifold at the point of injection but after final dilution by the manifold flow were of the order of 5 percent with a variability of better than 2 percent. As the result of potential and undefined wall effects within the manifold, it was difficult to determine mixing-ratio accuracies at the CO or NO sampling locations along the manifold. When the manifold studies conducted by Research Triangle Institute and all other factors pertaining to the use of the primary manifold were considered, the GTE mixing ratios (i.e., GTE-generated steps) were believed to be accurate to at least 10 percent with a variability of less than 2 or 3 percent.

Accuracies for the CO/N_2 gas mixtures were similar to those given, namely, better than 10 percent accuracy and 3 percent variability at the respective sampling locations along the nitrogen manifold. The 20-percent higher calibration factor for the nitrogen manifold flowmeter (discussed earlier) was not believed to have affected the accuracy of the test gas mixtures.

During each spiked test, the output from the flow controllers was continually recorded on the GTE central data system. From these records, the precision of the various mixing ratios was calculated. These results including the average, maximum, and minimum mixing ratios during each step change are shown in table 7. Transient data, the first and last 30 sec associated with each step, are not included in table 7. Precision of the mixing ratios were quite good, generally less than 2 ppbv (CO) or 2 pptv (NO) maximum to minimum.

INTERCOMPARISON ANALYSES

Methodology

The analyses generally followed a three-phase approach. Phase 1 focused on dentifying the general level of agreement among the techniques. The results were hen used to judge whether the level of disagreement and any indicated biases waranted more detail analyses, that is, phases 2 and 3. Phase 2 analyzed and then dentified the nature of the bias (offset, proportional, etc.) and to which techiques they applied. Phase 3 focused on quantifying the biases and level of greement among the techniques at a statistical level of confidence. Several interomparison methods, statistical treatments, and data groupings were used in the nalyses. These are discussed and are referred to in the section "Discussion of esults".

General Intercomparison Methods

An important aspect of any intercomparison is the choice of a comparison ethod. This choice is particularly important in the consideration of potential rrors and inaccuracies. Since none of the techniques used in the CO, NO, or OH ests could be regarded as a standard, three methods were adopted for intercomparson of the test results.

Method 1.- For method 1 a "comparison reference" was defined as the average f the observations reported by the PI's (e.g., 3 NO PI's) during a given sampling eriod. The level of agreement among the instruments was obtained by comparing each nstrument measurement with this average. An advantage of this approach was that ffects of ambient variability on the intercomparison were reduced if the time period an be made sufficiently short. In addition, the accuracy of the GTE delta mixing atios had no effect. A general guideline for the application of this method was that all instruments must report valid measurements for the given sampling periods. This method, however, was susceptible to at least two potential biases. First, it was susceptible to erratic or extreme values by any one technique, which could act to skew the results. Second, since the number of systems utilizing each measurement approach was different (e.g., for NO, two chemiluminescent techniques and one LIF technique), a proportional bias affecting only one technique could be effectively weighted by the number of instruments of that type included in creating the comparison reference.

Method 2.- For method 2, the comparison reference was taken to be the magnitude of the GTE delta mixing ratio, and the delta measured by each instrument was compared with the calculated GTE delta. This approach possessed the advantages of providing a means of distinguishing between effects of offset errors and errors which were proportional to mixing ratio, and the results were traceable to an NBS SRM subjected to those inaccuracies associated with the dilution system, manifolds, and gas standards. This method allowed for intercomparison of instrument results when measurements from one or more of the other instruments were not available.

Method 3.- Method 3 involved a linear regression analysis of results between instruments (e.g., for NO, WALLOPS with NOAA/NCAR, WALLOPS with GA TECH, and NOAA/NCAR with GA TECH). All measurements obtained from the pairs of instruments (for a data grouping) were used in the regression analyses, with the guidelines that individual measurements should be overlapping. Method 3 has the same advantages of method 2, but the results were not traceable to NBS and were not subject to the inaccuracies associated with generating the GTE delta mixing ratios.

Statistical Treatments

Two statistical treatments were considered. The first used the average percent error D and the standard deviation associated with D, σ_D. The values of D for each technique were calculated, in percent, from

$$D = \frac{1}{N}\sum \frac{Y_i - X_i}{X_i} \tag{1}$$

where Y_i is the technique measurement value for a given intercomparison period and X_i is the corresponding value of the comparison reference. The number of valid intercomparison periods for the techniques (based on method guidelines and data category) is N. For each technique, D is a measure of overall bias relative to the comparison reference, and the range of D within a data category is representative of a level of agreement among the techniques. The terms σ_D were indicative of the variability of D for each technique observed during the various (N) intercomparison periods. In the summation function of equation (1), the positive and negative differences could tend to cancel and force a low value for D. However, such occurrences were easily identified from the value of σ_D associated with each value of D. This statistical treatment was most representative of an average level of agreement among the techniques but provided no information as to the nature of biases, that is, proportional or offset bias.

The second statistical treatment was based on a linear regression analysis over a range of mixing ratios of measurements from a given technique to those of the associated comparison reference (methods 1 and 2) or to those of a second technique (method 3). In each data category, all valid intercomparison periods (i.e., N periods) were included in a weighted analysis in which the intercept A and slope B of the best-fit straight line were determined. (The weighting factor used in the regression fit was obtained from the calculated standard deviation determined for each average measurement for an intercomparison period.) Also obtained from the regression analysis was the correlation coefficient r and the standard deviations, on the intercept and slope, σ_A and σ_B, respectively. The intercept A provided a measure of any constant bias between the respective data sets, whereas the slope provided a measure of any proportional bias. A constant bias would indicate a systematic offset that was independent of the magnitude of the mixing ratio and could be associated with instrument artifacts or interference effects that were independent of mixing ratio. A proportional bias would indicate an offset that was dependent upon the magnitude of mixing ratio and would be associated with calibration differences, sample line losses, or interference effects that were dependent upon mixing ratio. The standard deviations σ_A and σ_B were used to calculate the 95-percent confidence intervals on A and B, respectively. Using these confidence intervals, a 95-percent confidence level criterion was used to determine if the biases were statistically significant. For example, if A ± 95-percent confidence interval includes 0, then it is concluded that at the 95-percent level, no statistically significant bias exists. Likewise, if B ± 95-percent confidence interval includes 1, then no statistically significant bias exists.

Data Categories

Data from one or more of the following categories were used in the analyses:

Category 1 - ambient-only data periods

Category 2 - spiked-ambient data periods

Category 3 - ambient and spiked-ambient data periods, that is, category 1 and 2 data

Category 4 - spiked-nitrogen data periods

As discussed earlier, intercomparison intervals for ambient data were selected based on overlapping data periods among the instruments. For the spiked data category, the intercomparison interval was defined to start 30 sec after initiating a delta mixing ratio and end 30 sec prior to the end of the delta. This interval minimized any transient effects at the beginning and end of a delta step. During each intercomparison interval, the data reported for a technique were averaged to yield a single "measurement" for that time period and a standard deviation calculated for that observation which in turn became the weighting factor for the linear regression analyses. When some of the reported data included the first or last 30 sec of a delta, the flow records of the dilution system were inspected to insure that any transients were negligible.

RESULTS

Meteorology

During the period July 5 to 29, 1983, the meteorology for the test site was affected synoptically by four major weather systems and locally by a midmorning to early-evening sea breeze. The sea breeze, which occurred about 30 percent of the time, was characterized by a sudden wind shift to 180° (southerly flow), a 2° to 4°C temperature drop, and a 2° to 4°C dew-point increase. A description of the four weather systems and their synoptic affect on the test site is discussed as follows. The numbers given in parentheses reflect the date of the various events; that is, 6 means July 6, 1983.

The first system was a western cold front which moved through the test area on July 5 as the leading edge of a continental polar high-pressure system. The center of the high moved to Michigan (6), Ohio (7), West Virginia (8), and stalled over the Tennessee Valley (9). Synoptic winds at the test site during this period were from the north with cool, dry temperatures. On July 10, a northern cold front moved south through the area and then north through the area again later in the day. The northerly flow was cool and dry. The center of the stalled high-pressure system, now more representative of a continental subtropical high, moved over Pennsylvania (11) and Virginia (12). The winds at Wallops were northwesterly with warmer and moderately humid temperatures. On July 13, the high was off the southeast coast with southwesterly winds and hot and humid temperatures at Wallops.

The second system was a northern cold front which moved rapidly through the area late on July 13. The continental polar high was centered over the Appalachian states (14) but stalled over the Tennessee Valley (15, 16, 17, and 18). During this period, the high became characterized as a continental subtropical high. The stalled high broadened in extent, with the central portion located over Mississippi (19), Texas (20), and the Mississippi Valley (21). Throughout this period, a weak low-pressure trough persisted either over or just off the test area. Consequently, the winds during this 8-day period were northwesterly with hot and humid conditions.

The third system, a northern cold front, moved through the area with the center of the continental polar high located over Ontario (22) and Pennsylvania (23). The winds were northwest and the temperatures were cool and dry. The cold front moved back north on July 24, and a low-pressure trough was located over the test area. The winds were northwesterly and conditions were hot and humid.

The fourth system was initiated when the cold front moved back south on July 25. A new continental polar high was centered over Minnesota (25). The high moved to Lake Superior (26), Pennsylvania (27), just off the Virginia coast (28), and then closer to the Virginia coast (29). The winds varied from northwesterly (24), northeasterly (26), variable (27), and southwesterly (28 and 29). The air temperatures slowly increased from a daily high of 78° (25) to 84° (29). During the last 2 days (28 and 29), the air had passed over the Atlantic ocean for 24 to 48 hours before intersecting the test area.

Synoptic conditions at the Wallops site are summarized in table 8. The July synoptic weather charts are given in appendix D.

Supporting Measurements

The supporting measurements, described in table 3, have been assembled into a data archive for the use of the investigators during data analysis and evaluation of instrument performance. These data have been archived and are available upon

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request.[1] Supporting measurements are summarized in table 9 and figures 9 through 12. The range of variation of the measured parameters are given in the table. The data of the figures are from analysis of the particulate filters collected on-site. Particulate loadings are grouped into four classes: crustal dust, sea salt, sulfates, and nitrates. These samples were typically 12-hour integrated samples with daytime samples (D) from 0800 to 2000 hours and nighttime samples (N) from 2000 to 0800. A detailed elemental analysis of each sample is a part of the archive.

Exchange of CO/NO Standards

As previously discussed and as shown by table 2, various standards were analyzed as part of the preworkshop and on-site activities. The results of the exchange of standards are summarized in table 10. The procedures used by the investigators in the preworkshop analyses are documented in appendix C.

Intercomparison Data

The results from the intercomparison tests are presented in this section (figs. 13 through 17) as a means of identifying those data from which the various analyses and conclusions were drawn. The results are presented without discussion and include only those data considered as representing valid intercomparison opportunities. Those data determined during the workshop or postworkshop discussions and analyses as being invalid are omitted. The omitted data and reasons therefor are defined in appendix B. These data are given in tabular format in appendix B. The reader is referred to earlier sections of the report for a description of facilities, procedures, and test conditions. The data shown in the figures are basically the raw results reported by the investigators. Horizontal bars on the data indicate the time interval over which an individual sample or measurement was made.

The CO results for ambient, spiked-ambient, and spiked-nitrogen tests are presented in figures 13 through 15, respectively. Figures 16 and 17 show the NO results for ambient and spiked-ambient tests. The data of figures 13 through 17 are the data on which the intercomparisons are based. The times of valid OH measurements in which SNR > 1 are given in table 11.

DISCUSSION OF RESULTS

Exchange of Standards for CO and NO

The data of table 10 can be used in various statistical treatments to determine any bias among the techniques as applied to the measurement of standards. One such treatment is presented. The difference between the technique measured value and the NBS value is given for each gas standard in table 12. This difference is stated in percent as referenced to the NBS value for each standard. The Average entry is the

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[1] Requests for this data archive should be addressed to
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calculated average difference for each technique based on the number of values reported in the table. The standard deviation for each average is given as well as the number of data points (in parentheses) used in each calculation. These average percent differences and the associated 2σ bands for each of the techniques are shown in figure 18. Also shown as the shaded areas is the $\pm 2\sigma$ uncertainty for the NBS values of the gas standards. Note that for each investigator group (CO or NO), the instrument 2σ bands overlap the 2σ gas standard band and overlap each others' band. Therefore, it was concluded from this analysis that at the 2σ confidence level, there was no statistically significant bias between the instrument measurements of the standards and the NBS values for the gas standards or among the instrument measurements themselves.

Table 12 can also be used to estimate a "figure of merit" for the CO and NO techniques, which is representative of the level of agreement that can be expected during laboratory intercomparisons with standards. For CO, the figure of merit is obtained by calculating the average range of percent difference among the techniques for each of the four standards measured by all three techniques (table 12). For example, for the GTE primary standard this range is 2.3 percent (-1.6 percent (Ames) to +0.7 percent (Langley)). Averaging these ranges for the four standards results in a figure of merit for CO of 6.2 ± 2.3 percent. Similarly, for NO, a figure of merit of 6.0 ± 3.4 percent is obtained. For NO, only the primary standard was measured by all the investigators. The results for the blind standards were normalized to the NBS value for each standard to obtain the range of percent difference for the blind standards.

Intercomparisons of OH Techniques

For OH, definitive intercomparison results were not obtained at Wallops. A total of five daytime and two nighttime tests (see table 6), scheduled over approximately a 1-week period produced only a few "potentially" valid measurements of OH with $SNR > 1$. Moreover, the OH techniques experienced operational difficulties to such an extent that few overlapping data periods were available. Accordingly, it was not possible to determine the level of agreement or disagreement among the techniques. Based on the Wallops experience, it was impossible to assess the capabilities of any single OH technique for measuring global tropospheric levels of OH.

Intercomparisons of CO Techniques

Phase 1 analyses for the CO data used the average percentage error statistical treatment with data category 3. The analysis was by method 1. Combining data category 3 with analysis method 1 produced results independent of the accuracy of the GTE delta mixing ratios and represented "in-air" measurements only. Any technique bias for measurement of CO in a pure N_2 background was thus eliminated. The results of the analyses are given in table 13. Important observations are a level of agreement among the techniques of about 14 percent (-8.7 to +5.1 percent) and the relative magnitude of D and σ_D for each technique. AMES 1 data were not included in the analyses. (See appendix B.) A 95-percent confidence interval test on the D values suggested statistically significant biases may exist between one or more of the techniques, and as such, phase 2 and 3 analyses were performed. Since a bias was indicated among the techniques, method 1 (average of all technique measurements as a comparison reference) was not used for phase 2 or 3 analyses.

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The linear regression treatment, method 3, and data category 3 were used for phase 2 analyses. The results are shown in figure 19 and table 14. As for phase 1, AMES 1 data were not included. It must be noted at this point, that the correlation coefficient r of table 14 (as well as those for all the linear regression analyses presented) are sufficiently high to suggest a strong correlation between respective data sets. For example, the probability of obtaining a correlation coefficient that exceeds 0.9 for 10 samples from an uncorrelated parent population (i.e., r = 0) is less than 10 percent. The data of table 14 clearly indicate biases (offset and proportional) between pairs of techniques. Applying the 95-percent confidence level criterion discussed earlier suggests that all biases were statistically significant. Since the phase 2 analyses show biases in all comparisons, it was not possible to isolate the biases to any one or more of the techniques.

Phase 3 focused on defining the magnitude and nature of these biases as well as establishing a level of agreement among the techniques. Method 2 was used for the analyses; thus, each technique measurement can be compared with the same reference (i.e., GTE deltas), but a reference independent of results from any one technique. The results of the linear regression analyses for data category 2 (spiked ambient) are shown in table 15 and figure 20. Included in the table are the parameters from the regression analyses as well as results from applying the 95-percent confidence level criterion to the intercepts and slopes. Although two of the techniques sta-tistically show an intercept bias (offset type) based on the GTE deltas, these biases are only a few ppbv (perhaps as small as 1 or 2 ppbv when considering the confidence ntervals) and are considered negligible in terms of measuring ambient CO of 50 to everal hundred ppbv. In terms of the slopes (table 15(c)), two techniques show iases (proportional type) which are statistically significant, but it should be oted that the 95-percent confidence interval for one (LANGLEY) is only 1.01 to .03. Since the offset biases are considered negligible in terms of the application f the techniques to measuring ambient mixing ratios, the slope values from the re-ression analyses (table 15(a)) can be used to arrive at a level of agreement among he instruments for measuring CO mixing-ratio changes in ambient air. This level of greement is approximately 18 percent (1.19 (AMES 2) minus 1.01 (OGC)). Again it is oted that AMES 1 was not included in the results.

The results from similar analyses on category 4 data (spiked nitrogen) are shown n table 16 and figure 21. These analyses include AMES 1 data but not OGC (invalid ata, see appendix B). The conclusions are similar to the ones for category 2 data; amely, that offset biases are negligible and the slopes indicate a level of agree-ent among the instruments for measuring CO in nitrogen changes of approximately 2 percent (0.91 (LANGLEY) minus 0.79 (AMES 1)). The lower 12-percent level of greement as compared with the 18 percent for the spiked-ambient test is reasonable, ince any effects of any ambient variation during the tests are eliminated from the esults in a category 4 data analyses.

It must be cautioned at this point that the results from the analyses should not used to conclude which technique is the best or most accurate. The workshop pro-dures focused on providing high precision (2 to 3 percent) GTE mixing ratio deltas, d as mentioned earlier, absolute accuracy of the GTE deltas are at the 10-percent vel. In the authors' opinion, absolute accuracies should be better than a few rcent before attempting to use the data to make judgments as to which technique is e best. A closer look at the data of table 16 helps to reinforce this caution. ese data suggest that the GTE CO in nitrogen deltas may in themselves be biased in at all techniques show a proportional bias at least 10 percent lower than GTE. examination of the data for the gas dilution system (flow records, calibrations, c.) has resulted in no cause for a correction to the GTE deltas for these tests.

The CO investigators have also reexamined their results and likewise report no source of error to account for such a bias. Whether the deltas are, in fact, biased does not affect the relative agreement among the techniques since all CO instruments sampled from a common manifold and accordingly see the same mixing ratios. However, such a bias would affect a judgment as to which technique is the most accurate.

To obtain additional insight into the agreement among the techniques, the average percentage error was calculated on the same data (categories 2 and 4) by using method 2. The results are given in table 17. Although the D values from the table can be used to arrive at a level of agreement, an inspection of the σ_D values shows that any level of agreement would be statistically insignificant as a result of the large σ_D values relative to the D values; for example, AMES 1 σ_D of 26.6 percent compared with its D value of -0.43 percent. However, the large σ_D values are useful for indicating another important feature of the CO intercomparisons, namely, an observed test-by-test variation in the agreement among the instruments. The relative agreement between the techniques is summarized on a test-by-test basis in table 18. Shown are the average differences, <DIFF>, in ppbv and in percent between the absolute CO mixing ratios reported by any two techniques for data category 3 (all the in-air results). The uncertainty given for each entry is the standard deviation on the average and is indicative of the effects of ambient variability and instrument uncertainties. The data of the table clearly show a test-by-test variation among the instruments. In most cases, differences are significant when compared with the associated standard deviations and the earlier stated accuracy of the techniques. The maximum difference between the techniques occurred on July 11, with OGC reporting values 18 percent above LANGLEY and AMES 2 reporting values 20 percent below LANGLEY. The resulting difference is 38 percent among techniques for that test. The test-by-test differences do not appear to be related to any ambient variables such as temperature, dew point, and ozone and cannot be explained based upon the results from the preworkshop or workshop exchange of standards results.

In summary, the CO techniques showed on the average for the workshop a level of agreement of the order of 12 to 18 percent as determined from a linear regression analysis of the results. The 12-percent level of agreement was observed during spiked-nitrogen tests in which any effect of ambient variability in CO mixing ratio was eliminated. The workshop data suggested that any major biases were of the proportional type such as those that might occur as the result of calibration differences, sample line losses, or interferences or artifacts which are proportional to the CO mixing ratio. The workshop results did not identify the causes of the observed biases. Small offset biases of several ppbv were noted but considered negligible in terms of measuring ambient CO mixing-ratio levels. Although the average level of agreement was noted to be in the 12- to 18-percent range, a sizable and unexplained daily or test-to-test variation was noted among the techniques. For one test this variation resulted in a level of agreement among the instruments of only 38 percent.

Intercomparisons of NO Techniques

The NO intercomparison analyses were similar in sequence and format to those performed for CO. Category 4 data were not available as spiked-nitrogen tests were not conducted for NO. In addition, since the workshop goals were to intercompare all three techniques, the analyses focused on the last four NO tests (table 4). Data from tests in which only the chemiluminescent techniques participated were omitted from the analyses. Phase 1 analyses focused on data category 3 (ambient and spiked ambient) by using the average percentage error treatment. The comparison reference was the average mixing ratio reported from all three techniques (method 1). The results are shown in table 19. Important observations are a level of agreement among the techniques of about 17 percent (-9.6 to +6.9 percent) and the relative magnitude of D and σ_D for each technique. A 95-percent confidence interval test on the D values showed that as a result of the high σ_D values (relative to D values), statistically no biases were indicated. Phase 2 and 3 analyses were performed to gain additional insight into the data set.

For phase 2, linear regression analyses were applied to data category 1 and 2 by using method 3 (pairs of techniques). Since the NO intercomparisons were to evaluate the techniques for measuring low levels of NO, category 1 and 2 data were considered independently rather than combining the data into a category 3 analysis. Results from category 1 (mixing ratios <50 pptv) were directly amenable to low levels of NO, whereas category 2 covers the higher levels of NO. The results are given in figures 22 and 23 and table 20. Applying the 95-percent level criterion associated with the linear regression concept to the results from both data categories suggested that biases did exist between the techniques. From the category 1 analyses, only the WALLOPS vs NOAA/NCAR intercept bias of -6 pptv is statistically significant. Two of the slope biases are also statistically significant (GA TECH vs WALLOPS is not); however, the large values of σ_B of 20 to 26 percent tend to overshadow this observation. It is speculated that the high values of σ_B are a result of ambient variability and different temporal resolution of the techniques, the effects of which are magnified in the analyses by limiting the data to mixing ratios <50 pptv. This speculation is supported by noting the low values of σ_B for the category 2 results. Data category 2 extends the NO mixing ratio (GTE deltas) to about 170 pptv. All the indicated slope biases in the category 2 analyses are statistically significant. The intercept results are similar to these results, and indicate a potential offset bias but no more than 6 pptv.

Phase 3 focused on defining the level of agreement among the techniques. Since biases were noted in phase 2, method 2 (GTE deltas) was used and the linear regression analyses applied to data category 3. The results are shown in table 21 and figure 24. Since the intercept biases were small compared with the mixing ratios of data category 3, the slopes could be used to estimate the level of agreement among the instruments. The indicated level of agreement is about 20 percent (1.04 (NOAA/NCAR) minus 0.84 (GA TECH)). As was true for CO, an average percentage error analysis was also performed as part of phase 3 (method 2 and data category 3). The results are given in table 22 and, considering the range of D values, indicate a level of agreement of about 23 percent.

In terms of test-by-test variations, the NO techniques showed more consistency than observed for the CO techniques. The LIF technique consistently measured lower than the chemiluminescent techniques, and generally NOAA/NCAR was higher than WALLOPS.

In summary, the NO techniques showed on the average for the workshop a level of agreement of about 20 percent as determined from a linear regression analysis of the results. The workshop data suggested that any major biases among the techniques were of the proportional type such as those that might occur as the result of calibration differences, sample line losses, or artifact and interferences which were proportional to mixing ratio. The data also suggested the potential of a small offset bias among the techniques, but if present it was no larger than about 6 pptv.

CONCLUDING REMARKS

This report has discussed (1) the anticipated measurement capabilities of the techniques as supplied to the GTE (Global Tropospheric Experiment) project by the respective investigators, (2) the accuracy and precision of the various test procedures used at Wallops, (3) the results from the exchange-of-standards portion of the workshop, and (4) the intercomparison results during ambient and spiked addition intercomparison testing. The pertinent conclusions are summarized as follows.

OH Techniques

The detection limits of the OH techniques as operated at Wallops ranged from 1×10^4 OH/cm^3 for the radiochemical technique to the mid 10^6 range for the two LIF (laser-induced fluorescent) techniques. In terms of the GTE project goals, the workshop was successful in providing approximately 1 week of experimental test opportunity to intercompare the techniques. Seven formal tests were conducted and included over 32 hours of concentrated data taking in which supporting measurements were made available to the investigators for interpretation of instrument performance. However, OH instrument operational problems resulted in few overlapping data periods. Some techniques were more operational than others, but only a few "potentially" valid measurements of OH with signal-to-noise ratio >1 were made during the workshop. While it was not possible to define the levels of ambient OH experienced at Wallops, meteorological conditions and supporting data measurements were similar to those discussed in preworkshop site selection Science Team meetings and thus would suggest that OH values within the range of detection of one or more of the techniques did occur during the formal OH test periods. The overall conclusion for OH from the Wallops activities is that it is not possible to assess the capability of any of the three techniques for measuring global tropospheric levels of OH, and that the state of readiness of the techniques for supporting a GTE scientific global air monitoring mission must be questioned.

CO Techniques

Eight formal (16 hours of concentrated data) CO intercomparison tests were conducted at Wallops covering a range of meteorological conditions and air quality scenarios. Four techniques participated: one laser absorption and three grab-sample approaches. Each technique sampled the same air mass from a common manifold. Intercomparison test conditions included ambient, spiked-ambient, and spiked-nitrogen test scenarios. Supporting data were available for all the tests to assist the investigators in interpreting instrument performance. Ambient CO mixing ratios during the formal tests ranged from about 150 to 300 ppbv. GTE delta mixing ratios during the spiked tests ranged from 20 to 400 ppbv. The accuracy and precision of the GTE deltas were approximately 10 and 3 percent, respectively. Data analyses focused on overlapping data periods among the instruments, and data periods of large ambient CO variations were excluded from the analyses.

The exchange-of-standard portion of the workshop showed that statistically at a 2σ (standard deviation) confidence level no biases existed among the techniques or between any one technique and the gas standards. A figure of merit of 6 percent was calculated from the standards test and used as an estimate of the level of agreement among the techniques under laboratory conditions. This figure of merit provided a reference point for interpreting the results of the formal intercomparison tests. Based on the eight tests, the overall level of agreement among the techniques was generally 12 to 18 percent. The 12-percent level was noted under conditions of the spiked-nitrogen tests in which any effects of ambient variability have been eliminated and represents the level of agreement that might be obtained in the field if the temporal resolution (sampling times) of the four techniques are identical. More realistically, since three of the techniques were finite sampling techniques and normalizing temporal resolution was difficult, the 18-percent level of agreement is probably more applicable to a field mission. Any major biases among the techniques were of the proportional type similar to those that might occur as the result of calibration differences or inlet line losses. Observed proportional biases were statistically significant at a 95-percent confidence level as determined by linear regression analyses with the GTE deltas as a common reference. Small offset biases of a few ppbv may be present among the techniques but were considered insignificant compared with ambient CO mixing ratios. However, noted along with the 12- to 18-percent level of agreement, was an unexplained daily or test-to-test variation in agreement among the techniques. For one test this agreement approached 38 percent.

NO Techniques

Three NO techniques participated in the intercomparisons: one LIF and two chemiluminescent approaches. Eight formal intercomparison tests were conducted and involved over 22 hours of concentrated data gathering. As a result of a damaged laser, the LIF technique was operational for only the last four tests. Each technique sampled a common air mass from a common manifold. Test conditions included ambient and spiked-ambient test runs in which ambient mixing ratios ranged from 5 to 100 pptv and GTE deltas, from 10 to 200 pptv. Test accuracies, supporting data, and analyses were similar to those of the CO tests. The exchange-of-standards portion of the workshop showed no statistically significant biases among the techniques or between any one technique and the gas standards. A 6-percent figure of merit was calculated from the standard results and was an estimate of the level of agreement among the techniques under laboratory conditions. Based on the intercomparison results, an overall level of agreement among the techniques of about 20 percent was noted as determined by linear regression analyses with the GTE delta mixing ratios as a common reference. Proportional biases among the techniques were noted and were statistically significant at a 95-percent level. Offset biases were small (≈6 pptv). The data suggest that the LIF (GA TECH) technique was consistently low as compared with the chemiluminescent techniques (WALLOPS or NOAA/NCAR) when measuring GTE delta mixing ratios, and NOAA/NCAR was generally high compared with WALLOPS. The level of agreement among the techniques is within the stated accuracy and precision of the NO techniques (as stated to GTE by the investigators); namely, a 20- to 30-percent absolute accuracy for each technique, precisions of 6 to 8 pptv at 20 to 30 pptv, and artifact signals at the 5- to 6-pptv level.

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TABLE 1.- WORKSHOP PARTICIPANTS

Principal investigator	Affiliation	Measurement	Technique
[*]Malcolm J. Campbell	Washington State University, Pullman, Washington	OH	Radiochemical tracer [WASH]
[*]Douglas D. Davis	Georgia Institute of Technology, Atlanta, Georgia	OH	Single photon, laser-induced fluorescent [GA TECH]
[*]Charles C. Wang	Ford Motor Company, Dearborn, Michigan	OH	Laser-induced fluorescent [FORD]
[*]Douglas D. Davis	Georgia Institute of Technology, Atlanta, Georgia	NO	Two-photon, laser-induced fluorescent [GA TECH]
[*]Mack McFarland,[†] Mary Anne Carroll, and Brian A. Ridley	NOAA/NCAR, Boulder, Colorado	NO	Chemiluminescent [NOAA/NCAR]
[*]Arnold L. Torres	NASA Wallops Flight Facility, Wallops Island, Virginia	NO	Chemiluminescent [WALLOPS]
[*]Glen W. Sachse	NASA Langley Research Center, Hampton, Virginia	CO	Laser differential absorption [LANGLEY]
Estelle P. Condon	NASA Ames Research Center, Moffett Field, California	CO, CH_4	Grab samples—chromatograph [AMES 1 & 2]
Reinhold A. Rasmussen	Oregon Graduate Center, Beaverton, Oregon	CO, NMHC	Cryogenic grab samples—chromatograph [OGC]
Gerald L. Gregory	NASA Langley Research Center, Hampton, Virginia	O_3	Chemiluminescent and UV absorption
Sherwin M. Beck	NASA Langley Research Center, Hampton, Virginia	H_2O	Frost-point hygrometers
James E. Mentall	NASA Goddard Space Flight Center, Greenbelt, Maryland	UV flux	Grating spectrometer
Gerald L. Gregory	NASA Langley Research Center, Hampton, Virginia	Aerosol size	Forward scattering spectrometer
William H. Zoller	University of Maryland, College Park, Maryland	Aerosol composition	Filter samples
Wesley R. Cofer III	NASA Langley Research Center, Hampton, Virginia	CH_4 & NMHC	On-line gas chromatograph
David S. McDougal	NASA Langley Research Center, Hampton, Virginia	Meteorological parameters	

[*] Critical measurements PI.

[†] McFarland is currently employed by E. I. du Pont de Nemours & Co., Wilmington, Delaware.

TABLE 2.- WORKSHOP STANDARDS

Carbon monoxide:	
GTE primary	9.67 ± 0.09 ppmv CO in N_2
GTE Ames blind	1.10 ± 0.01 ppmv CO in N_2
GTE Langley blind	9.67 ± 0.09 ppmv CO in N_2
GTE Oregon Graduate Center blind	1.10 ± 0.01 ppmv CO in N_2
MAPS primary	1.28 ± 0.03 ppmv CO in air
MAPS 285	285 ppbv CO in air
Nitric oxide:	
GTE primary	9.49 ± 0.16 ppmv NO in N_2
GTE Georgia Tech blind	4.71 ± 0.09 ppmv NO in N_2
GTE NOAA/NCAR blind	4.68 ± 0.09 ppmv NO in N_2
GTE Wallops blind	4.71 ± 0.09 ppmv NO in N_2

Dilution system supply gases:

Standard	Supplier specification	Postworkshop NBS analysis
NO	9.068 ppmv NO 9.216 ppmv NO_x <1 ppmv NO_2 Balance nitrogen NBS traceable	9.14 ± 0.16 ppmv NO
CO	102.6 ppmv CO Balance nitrogen NBS traceable	102.9 ± 1 ppmv CO
Ultra-zero N_2	99.999% nitrogen <0.05 ppmv CO	

TABLE 3.- SUPPORTING MEASUREMENTS

Measurement/technique	Sampling location (a)	Capabilities
O_3/chemiluminescent and UV absorption	Free air Station 8.5 Station 36	Range: 2 ppbv to 1 ppmv Accuracy: 5 percent Precision: 2 percent
Temperature/resistance probe	Free air Station 8.5 Station 36	Range: ±50°C Accuracy: ±0.1°C
Dew point/frost point	Free air Station 8.5 Station 36	Range: -40°C to 60°C Accuracy: 0.4°C Response: 1°C/min
Wind speed and direction/ 3-cup anemometer and vane	Free air	Range: 2 to 200 mph Accuracy: Speed, 1 percent Direction, 3°
CO/grab-sample—GC analysis	Free air Station 30 Station 36	Range: >10 ppbv Accuracy: 10 percent
Trace gases/grab-sample—GC analysis	Free air Station 36	Depends on species
CH_4 & NMHC/on-line GC	Station 36	Range: >30 ppbv Accuracy: 2 percent
UV flux/grating spectrometer	Free air	Range: 270 to 350 nm Resolution: 2 nm
Aerosols, number density, and size distribution/ forward scattering spectrometer probe	Free air	Size range: 0.5 to 45 m Accuracy: 3 percent of count Response: 90 sec count period
Aerosols chemical composition/filter sample	Free air	Depends on species

[a] Free air - sample taken in ambient air, no sampling manifold; station x - sample taken from 75-mm ID main manifold and x meters from the inlet.

TABLE 4.- SUMMARY OF MANIFOLD LOSS TESTS

(a) Carbon monoxide

Calculated[a] manifold mixing ratio, ppmv	Ratio of average measured manifold carbon monoxide mixing ratio to calculated manifold carbon monoxide mixing ratio at station -				
	1	2	3	4	5
104.8	0.889	0.889	0.889	0.891	0.890
104.1	0.888	0.886	0.889	0.884	0.888
49.1	0.907	0.910	0.907	0.907	0.906
17.6	0.848	0.848	0.847	0.848	0.846
3.2	0.854	0.858	0.861	0.852	0.865

(b) Nitric oxide

Calculated[a] manifold mixing ratio, ppbv	Ratio of average measured manifold nitrogen oxide mixing ratio to calculated manifold nitric oxide mixing ratio at station -				
	1	2	3	4	5
377	1.044	1.042	1.042	1.035	1.038
383	1.114	1.114	1.117	1.118	1.116
96.3	0.954	0.960	0.947	0.964	0.964
49.1	0.936	0.919	0.941	0.954	0.936
9	0.945	0.998	1.020	0.892	0.988

[a] Based on test plan provided to the contractor: absolute accuracy of mixing ratios are ±10 percent; precision of measurements between stations ±2 percent.

TABLE 5.- TYPICAL RESULTS FROM TRACE GAS ANALYSES AT VARIOUS SAMPLING LOCATIONS

[Data of July 8, 1983]

Location	Time of sample (EDT), hr	Mixing ratios for -							
		CH_4, ppmv	CO, ppbv	CO_2, ppmv	N_2O, ppbv	F-12, pptv	F-11, pptv	CH_3CCl_3, pptv	CCl_4, pptv
75-mm ID main sampling manifold, ≈36 m from inlet	1148 to 1154	1727	236	342	336	452	242	293	156
75-mm ID individual PI (short) sampling cane, 5 m from inlet	1201 to 1206	1721	203	341	337	450	240	288	158
Tower, ambient air, ≈3 m above surface	1300 to 1306	1717	225	340	338	438	236	266	154

TABLE 6.- INTERCOMPARISON TEST SUMMARY

(a) Carbon monoxide

Date	Local EDT, hr	Type	Nominal ambient CO mixing ratio, ppbv	Range of spiked additions, ppbv
July 8	1000 to 1200	Ambient, spiked[a]	230 to 180	140 to 40
July 11	1000 to 1200	Nitrogen, spiked[a,b]		70 to 20
July 11	1400 to 1500	Ambient[a]	200 to 150	
July 12	2000 to 2310	Ambient, spiked[a]	240 to 160	90 to 20
July 14	0900 to 1000	Ambient[a]	300 to 180	
July 14	1300 to 1535	Nitrogen, spiked[b]		70 to 20
July 18	1530 to 1930	Nitrogen, spiked[b]		380 to 20
July 27	1700 to 2015	Ambient[c]	320 to 260	520 to 20

[a] Ames 1 data contaminated.
[b] OGC unreliable for CO in nitrogen.
[c] Ames 1 and 2 data unreliable.

TABLE 6.- Continued

(b) Nitric oxide

Date	Local EDT, hr	Type	Nominal ambient CO mixing ratio, pptv	Range of spiked additions, pptv
July 26	2100 to 2300	Ambient[d]	15 to 10	
July 27	1900 to 2000	Ambient[d]	10 to 120	
July 27	2230 to 0050	Ambient, spiked[d]	15 to 10	150 to 40
July 28	1200 to 1605	Ambient, spiked[e]	100 to 70	210 to 30
July 28	2000 to 0005	Ambient, spiked	15 to 5	42 to 10
July 29	1200 to 1400	Ambient	60 to 20	
July 29	1400 to 1730	Ambient, spiked	60 to 30	130 to 40
July 29	2030 to 0010	Ambient, spiked	15 to 10	120 to 20

[d] GA TECH NO system not operational.

[e] GA TECH NO operational for last step change, but test step invalid because of ambient variation.

TABLE 6.- Concluded

(c) Hydroxyl radical

Date	Local EDT, hr	Range of nominal ambient conditions at -			
		T, °C	DP, °C	O_3, ppbv	Particle count, number/cm^3
July 15	1000 to 1300[f,g,h] 1400 to 1645	34 to 31	21 to 15	104 to 52	2.6 to 1.2
July 16	1200 to 1530[f,g,h]	36 to 34	23 to 21	97 to 75	35 to 12
July 20	1100 to 1600[f,h]	34 to 28	27 to 22	76 to 48	85 to 36
July 21	1400 to 1530[g,h]	34 to 33	23 to 22	75 to 64	14 to 8
July 21	1530 to 2115[g,h]	33 to 27	26 to 23	93 to 61	51 to 15
July 22	1100 to 1700	30 to 26	13 to 10	65 to 33	1.3 to 0.7
July 22	1700 to 1935	28 to 26	15 to 13	71 to 62	1.6 to 0.7

[f] WASH system not on site.
[g] FORD system operational but SNR < 1.
[h] GA TECH OH system not operational.

TABLE 7.- VARIABILITY OF GTE DELTA MIXING RATIOS FOR SPIKED TESTS

(a) Carbon monoxide

Test date	Test	Mixing ratio,[a] ppbv		
		Av	Max	Min
July 8	C-3	41.6	42.2	40.8
		94.8	96.0	93.8
		140.6	141.6	139.7
July 11	X-3	17.8	18.7	17.6
		44.8	45.6	43.8
		69.6	70.1	68.9
July 12	C-4	23.0	23.4	22.7
		46.5	47.2	45.8
		92.9	94.4	91.9
		46.9	47.7	45.8
		23.2	24.3	22.9
July 14	X-3	11.1	17.3	16.7
		47.7	47.9	47.3
		69.7	69.9	69.1
July 18	X-3	17.0	18.2	16.6
		126.1	127.0	123.3
		268.2	170.0	263.0
		378.6	381.2	365.7
July 27	C-4	164.3	165.2	164.2
		23.2	24.2	22.3
		71.1	72.9	70.2
		516.0		
		116.4	116.9	115.5
		69.7	71.1	69.2

[a] Listed in sequence; i.e., 1st delta, 2d delta, etc.

TABLE 7.- Concluded

(b) Nitric oxide

Test date	Test	Mixing ratio,[a] pptv		
		Av	Max	Min
July 27	N-4	42.6 145.6	42.8 147.2	42.4 145.6
July 28	N-3	34.9 211.0 84.8	35.2 211.6 85.0	34.5 209.9 84.5
July 28	N-4	11.1 39.8 11.3	11.4 40.0 11.4	11.0 39.6 11.2
July 29	N-3	132.2 42.7 83.7	135.5 43.3 84.4	130.6 41.9 83.4
July 29	N-4	21.1 116.1 41.6	21.2 116.8 41.9	21.0 115.4 41.4

[a] Listed in sequence; i.e., 1st delta, 2d delta, etc.

TABLE 8.- SYNOPTIC WEATHER OVERVIEW FOR WALLOPS, JULY 5-29, 1983

Date	Location of high or cold-front passage	Type of continental high	Synoptic winds	General description	Max T, °C	Daily DP, °C	Relative humidity, percent
July 5	Cold-front passage	Polar	SW-W	Warm/humid	28	23	66
6	Michigan	Polar	N	Cool/humid	26	21	65
7	Ohio	Polar	N	Cool/dry	24	18	39
8	West Virginia	Polar	NE-E	Cool/dry	25	16	47
9	Tennessee Valley	Polar	W-NW	Warm/dry	29	18	45
10	Cold-front passage	Polar	N	Cool/dry	24	13	41
11	Pennsylvania	Tropical	NW	Warm/dry	28	14	34
12	Virginia	Tropical	NW-W	Hot/dry	31	19	44
13	Off southeast coast	Tropical	SW	Hot/humid	33	22	46
14	Applachian states	Polar	N	Warm/dry	29	14	31
15	Tennessee valley	Tropical	W	Hot/dry	33	19	37
16	Tennessee valley	Tropical	NW	Hot/dry	35	21	37
17	Tennessee valley	Tropical	NW	Hot/moderate	34	22	43
18	Tennessee valley	Tropical	NW	Hot/moderate	33	21	43
19	Mississippi	Tropical	SW-NE	Hot/humid	29	26	78
20	Texas	Tropical	W-NW	Hot/humid	32	23	55
21	Mississippi valley	Tropical	NW	Hot/moderate	32	22	48
22	Cold-front passage	Polar	NW	Cool/dry	28	11	41
23	Pennsylvania	Polar	NW	Cool/moderate	27	17	46
24	Cold-front passage	Tropical	NW	Hot/humid	31	21	46
25	Minnesota	Polar	NE	Cool/humid	26	19	64
26	Lake Superior	Polar	NE	Cool/moderate	27	18	48
27	Pennsylvania	Polar	Variable	Warm/humid	29	20	49
28	Off Virginia coast	Polar	SW	Warm/humid	28	21	58
29	Off Virginia coast	Polar	SW	Warm/humid	29	21	58

TABLE 9.- SUMMARY OF SUPPORTING MEASUREMENT RESULTS

[NA indicates data not available or not required by test]

Date	Test	Temperature, °C		Dew point, °C		Wind speed, m/s		Wind direction, deg		Ozone, ppbv		Aerosols, number/cm^3						CH$_4$, ppm		NO, pptv (a)		CO, ppbv (b)	
		Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Av	1σ	Max	Min	% in 0.5-1 μm	% in 1-1.5 μm	Max	Min	Max	Min	Max	Min
July 8	C-3	27.7	24.9	15.6	11.8	2.0	0.2	179	15	76	39	1.4	0.4	2.02	0.89	60	10	1.72	1.69	NA	NA	(c)	(c)
11	[d]X-3																						
11	C-1	29.9	27.0	18.0	13.7	2.2	0.2	300	117	58	54	1.1	0.2	1.60	0.79	60	15	NA	NA	NA	NA	(c)	(c)
12	C-4	24.3	23.4	22.8	22.1	2.8	1.0	236	210	57	48	25	4.8	36.4	17.8	85	7	1.74	1.72	NA	NA	(c)	(c)
14	C-1	29.3	27.3	18.1	15.2	2.4	0.8	68	21	40	35	1.3	0.4	1.87	0.85	72	9	1.84	1.76	NA	NA	(c)	(c)
14	[d]X-3																						
15	OH-1	34.4	31.2	20.5	15.1	3.6	0.4	321	246	104	52	1.7	0.4	2.61	1.15	66	8	1.74	1.69	286	98	292	192
16	OH-2	35.9	34.2	23.3	20.8	4.4	1.6	330	287	97	75	21	6.0	34.6	12.0	97	2	1.81	1.78	204	136	385	325
18	[d]X-3																						
20	OH-3	33.9	27.8	26.7	22.1	3.8	0.4	360	190	76	48	[c]50	[c]20	[e]85.1	[e]36.2	90	8	1.75	1.72	577	140	328	215
21	OH-4	34.0	33.0	23.2	22.3	2.6	1.2	305	240	75	64	10	1.8	13.8	7.8	80	7	1.72	1.70	306	145	230	189
21	OH-5	33.4	27.0	25.6	23.2	3.0	0.8	280	192	93	61	33	10	[f]50.8	[f]15.4	88	7	1.72	1.70	136	28	289	194
22	OH-6	30.1	26.4	13.3	10.3	4.4	0.8	360	286	65	33	0.69	0.17	1.27	0.47	65	8	1.76	1.69	310	168	220	135
22	OH-7	28.2	26.4	15.2	12.8	4.2	1.2	332	298	71	62	1.04	0.30	1.62	0.73	75	7	1.75	1.72	175	90	236	206
26	N-2	23.7	23.0	19.5	18.8	2.0	1.0	209	189	79	75	7.00	0.81	9.11	5.67	88	7	1.80	1.76	(c)	(c)	NA	
27	C-4	28.0	24.9	22.3	21.2	3.3	1.7	210	179	82	71	5.61	0.38	6.19	4.92	85	7	1.76	1.72	NA	NA	(c)	(c)
27	N-2	29.5	25.0	22.0	21.4	2.8	1.8	205	190	74	72	5.95	0.24	6.19	5.55	85	7	1.76	1.72	(c)	(c)	NA	NA
27	N-4	24.6	24.1	21.8	20.7	3.6	2.0	209	192	68	62	0.63	NA	5.34	3.39	75	11	NA	NA	(c)	(c)	NA	NA
28	N-3	28.7	27.2	21.7	19.0	4.6	2.2	202	182	58	44	2.70	0.34	3.16	1.88	76	10	NA	NA	(c)	(c)	NA	NA
28	N-4	24.3	23.4	21.2	19.9	2.7	1.4	203	187	50	39	3.80	0.46	4.93	3.18	78	9	NA	NA	(c)	(c)	NA	NA
29	N-1	28.8	26.5	21.9	20.3	3.3	1.9	208	177	47	44	2.92	0.11	3.13	2.71	76	10	1.78	1.74	(c)	(c)	NA	NA
29	N-3	28.8	27.1	21.4	19.3	3.7	1.9	201	173	47	41	2.43	0.24	2.90	2.02	75	10	1.78	1.73	(c)	(c)	NA	NA
29	N-4	24.7	24.1	22.2	20.8	3.9	2.5	201	180	34	29	3.32	0.82	4.68	2.61	50	22	1.76	1.71	(c)	(c)	NA	NA

[a] WALLOPS and NOAA/NCAR.

[b] LANGLEY CO technique.

[c] Not supporting measurement; critical measurement for test being conducted.

[d] Data do not apply as tests were in dry nitrogen.

[e] For time period 1215 to 1600: considerable variation $\bar{X}$ = 50 particles/cm^3, 1σ = 20; for time period 1100 to 1215 particle count is much lower: max, 25 particles/cm^3, min, 7 particles/cm^3.

[f] Gradually increase with time: Average = 33 part/cm^3; 1σ = 10.

TABLE 10.- RESULTS OF STANDARD EXCHANGE

(a) Carbon monoxide

Designation	NBS value[a,b], ppmv	Measured mixing ratio, ppmv,[b] for -		
		AMES 1 and 2	LANGLEY	OGC
GTE primary	9.67 ± 0.09	9.52 ± 0.2	9.74 ± 0.18	9.62 ± 0.005 9.72 + 0.005
GTE Ames blind[c,d]	1.10 ± 0.01	1.13 ± 0.03	1.15	
GTE Langley blind[d]	9.67 ± 0.09		9.69 ± 0.23	
GTE OGC blind[c,d]	1.10 ± 0.01			1.19 ± 0.002 1.20 ± 0.002
MAPS primary	1.28 ± 0.03		1.31	1.21
MAPS 285[e]	285 ppbv		292 ppbv	269 ppbv 274 ppbv

(b) Nitric oxide

Designation	NBS value[a,b], ppmv	Measured mixing ratio, ppmv,[b] for -		
		GA TECH	NOAA/NCAR	WALLOPS
GTE primary[d]	9.49 ± 0.16	9.4 ± 0.5	9.65 ± 0.68	9.44
GTE Ga Tech blind[d]	4.71 ± 0.09	4.4 ± 0.2		
GTE NOAA/NCAR blind[d]	4.68 ± 0.09		4.81	
GTE Wallops blind[d]	4.71 ± 0.09			4.71

[a] Mixing ratio traceable to NBS standard reference material.
[b] Mixing ratio in ppmv unless noted otherwise.
[c] Same standard used for Ames and OGC.
[e] Mixed in air.
[d] Mixed in N_2.

TABLE 11.- OH INTERCOMPARISON RESULTS (10^7 OH/cm^3)

Date	Local EDT, hr	WASH (a)	FORD	GA TECH
July 21	1932	2.1	(b)	(c)
	2051	1.02		
July 22	1003 to 1204		(b)	
	1123	1.21		
	1229 to 1332		(b)	
	1308	.63		
	1347	.47		
	1354 to 1454		2.8 ± 1.8	
	1409	.72		
	1410 to 1505			1.35 ± 0.29
	1515 to 1617		(b)	
	1510 to 1610			1.21 ± 0.17
	1521	1.86		
	1750 to 1920		(b)	
	1810	4.21		
	1830 to 2019			<0.33
	1835	.95		
	1907	1.25		

[a] All results should be considered as upper limits due to impurities (e.g., labelled light hydrocarbons) which are not totally rejected by the carbon dioxide purification system.

[b] SNR < 1.

[c] GA TECH not operational.

TABLE 12.- DIFFERENCE BETWEEN INVESTIGATOR MEASUREMENT AND GAS STANDARD

(a) Carbon monoxide

Gas standard	Difference between standard and -		
	AMES 1 and 2, percent	LANGLEY, percent	OGC, percent
GTE primary	-1.6	0.7	-0.5 0.5
GTE Ames blind	2.6	4.5	7.9 9.1
GTE Langley blind		0.2	
MAPS primary	[a]0	2.3	-5.5
MAPS 285	[a]0	2.5	-5.6 -3.9
Average[b]	0.5 ± 3.0 (2)	2.0 ± 1.7 (5)	0.3 ± 6.1 (7)

(b) Nitric oxide

Gas standard	Difference between standard and -		
	GA TECH, percent	NOAA/NCAR, percent	WALLOPS, percent
GTE primary	-1.0	1.7	-0.5
GTE Ga Tech blind	-6.6		
GTE NOAA/NCAR blind		2.8	
GTE Wallops blind			0.0
Average[b]	-3.8 ± 4.0 (2)	2.3 ± 0.8 (2)	-0.3 ± 0.4 (2)

[a] By definition, Ames-supplied standard is the Ames measured mixing ratio.

[b] Number in parentheses is the number of data points used for each calculation.

TABLE 13.- CO INTERCOMPARISON RESULTS FOR PHASE 1

[Method 1, average percentage error, data category 3]

Parameter	AMES 1	AMES 2	LANGLEY	OGC
N	0	19	19	19
D, percent		-8.7	+5.1	+3.6
σ_D, percent		4.9	4.4	7.6
95-percent CI		-11.1 to +6.3	3 to +7.2	-0.1 to +7.2

TABLE 14.- CO INTERCOMPARISON RESULTS FOR PHASE 2

[Method 3 linear regression, data category 3]

Parameter	LANGLEY vs AMES 2	LANGLEY vs OGC	AMES 2 vs OGC
Intercept A, ppbv ..	-40.5	+16.0	+44.6
σ_A, ppbv	8.0	13.3	15.4
Slope B	1.06	0.89	0.90
σ_B	0.03	0.05	0.08
r	0.9909	0.9559	0.9445
N	19	30	19

TABLE 15.- CO INTERCOMPARISON RESULTS FOR PHASE 3 AND DATA CATEGORY 2

[Method 2, linear regression]

(a) Linear regression results

Parameter	LANGLEY	AMES 2	OGC
Intercept A, ppbv	-0.44	-5.38	+3.11
σ_A, ppbv	1.86	4.62	3.27
Slope B	1.02	1.19	1.01
σ_B	0.02	0.08	0.04
r	0.9959	0.9836	0.9856
N	20	10	19

(b) 95-percent confidence level criterion test for intercepts

Technique	95-percent CI on intercepts, ppbv	95-percent CI includes 0	Statistically significant
LANGLEY	-1.3 to +0.43	Yes	No
AMES 2	-8.7 to -2.1	No	Yes
OGC	+1.5 to +4.7	No	Yes

(c) 95-percent confidence level criterion test for slopes

Technique	95-percent CI on slopes	95-percent CI includes 1	Statistically significant
LANGLEY	1.01 to 1.03	No	Yes
AMES 2	1.13 to 1.25	No	Yes
OGC	0.99 to 1.03	Yes	No

TABLE 16.- CO INTERCOMPARISON RESULTS FOR PHASE 3 AND DATA CATEGORY 4

[Method 2, linear regression]

(a) Linear regression results

Parameter	LANGLEY	AMES 1	AMES 2
Intercept A, ppbv	-0.87	+5.43	+2.48
σ_A, ppbv	0.35	3.57	1.92
Slope B	0.91	0.79	0.81
σ_B	<0.01	0.02	0.01
r	0.9999	0.9964	0.9989
N	10	7	8

(b) 95-percent confidence level criterion test for intercepts

Technique	95-percent CI on intercepts, ppbv	95-percent CI includes 0	Statistically significant
LANGLEY	-1.2 to -0.60	No	Yes
AMES 1	+2.1 to +8.7	No	Yes
AMES 2	+0.9 to +4.1	No	Yes

(c) 95-percent confidence level criterion test for slopes

Technique	95-percent CI on slopes	95-percent CI includes 1	Statistically significant
LANGLEY	0.90 to 0.92	No	Yes
AMES 1	0.77 to 0.81	No	Yes
AMES 2	0.80 to 0.82	No	Yes

TABLE 17.- CO INTERCOMPARISON RESULTS

[Method 2, average percentage error]

(a) Data category 2

Parameter	AMES 1	AMES 2	LANGLEY	OGC
N	0	10	22	21
D, percent		+4.0	+3.1	+8.4
σ_D, percent		30.3	12.3	17.0

(b) Data category 4

Parameter	AMES 1	AMES 2	LANGLEY	OGC
N	7	8	10	0
D, percent	-0.43	+3.6	-7.2	
σ_D, percent	26.6	24.0	2.5	

TABLE 18.- COMPARISON OF TEST-BY-TEST DIFFERENCES FOR CO TECHNIQUES FOR AMBIENT AND SPIKED AMBIENT

Test date	OGC vs LANGLEY		AMES 2 vs LANGLEY		AMES 2 vs OGC	
	<DIFF>		<DIFF>		<DIFF>	
	ppbv	Percent	ppbv	Percent	ppbv	Percent
7-08-83	2.9 ± 8.9	0.5 ± 3.2	-14.0 ± 6.5	-5.7 ± 1.8	-20.8 ± 12.8	-7.6 ± 5.2
7-11-83	36.6 ± 1.2	17.6 ± 1.1	-28.9 ± 3.3	-20.5 ± 3.3	-56.5 ± 14.9	-38.2 ± 13.2
7-12-83	-12.8 ± 6.0	-7.2 ± 4.2	-32.2 ± 6.3	-20.0 ± 5.9	-17.0 ± 5.1	-10.0 ± 3.3
7-14-83	-22.0 ± 2.1	-10.5 ± 2.9	-33.9 ± 2.1	-12.5 ± 1.8	-12.5 ± 1.8	-6.4 ± 1.8
7-27-83	-23.3 ± 6.7	-8.7 ± 3.8				

TABLE 19.- NO INTERCOMPARISON RESULTS FOR PHASE 1

[Method 1, average percentage error, data category 3]

Parameter	WALLOPS	NOAA/NCAR	GA TECH
N	21	21	21
D, percent	6.9	3.6	-9.6
σ_D, percent	8.3	12.9	9.8
95-percent CI	3.1 to 10.7	-2.3 to 9.5	-5.1 to 14.1

TABLE 20.- NO INTERCOMPARISON RESULTS FOR PHASE 2

[Method 3, linear regression]

(a) Data category 1 (ambient, unspiked)

Parameter	GA TECH vs WALLOPS	GA TECH vs NOAA/NCAR	WALLOPS vs NOAA/NCAR
Intercept A, pptv ...	2.22	-1.89	-6.00
σ_A, pptv	4.44	3.69	4.11
Slope B	1.07	1.18	1.23
σ_B	0.26	0.20	0.23
r	0.9359	0.9480	0.9934
N	10	30	10

(b) Data category 2 (ambient, spiked)

Parameter	GA TECH vs WALLOPS	GA TECH vs NOAA/NCAR	WALLOPS vs NOAA/NCAR
Intercept A, pptv ...	0.51	-5.24	-5.94
σ_A, pptv	2.34	2.48	2.73
Slope B	1.15	1.33	1.16
σ_B	0.05	0.05	0.04
r	0.9919	0.9923	0.9995
N	9	9	9

TABLE 21.- NO INTERCOMPARISON RESULTS FOR PHASE 3 FROM LINEAR REGRESSION ANALYSIS

[Method 2, data category 3]

(a) Linear regression results

Parameter	WALLOPS	NOAA/NCAR	GA TECH
Intercept A, ppbv ..	0.34	0.09	3.34
σ_A, ppbv	1.84	1.59	2.62
Slope B	0.90	1.04	0.84
σ_B	0.03	0.02	0.04
r	0.9989	0.9976	0.9888
N	21	21	16

(b) 95-percent confidence level criterion test for intercepts

Technique	95-percent CI on intercepts, pptv	95-percent CI includes 0	Statistically significant
WALLOPS	-0.5 to +1.2	Yes	No
NOAA/NCAR	-0.6 to +0.8	Yes	No
GA TECH	+1.9 to +4.7	No	Yes

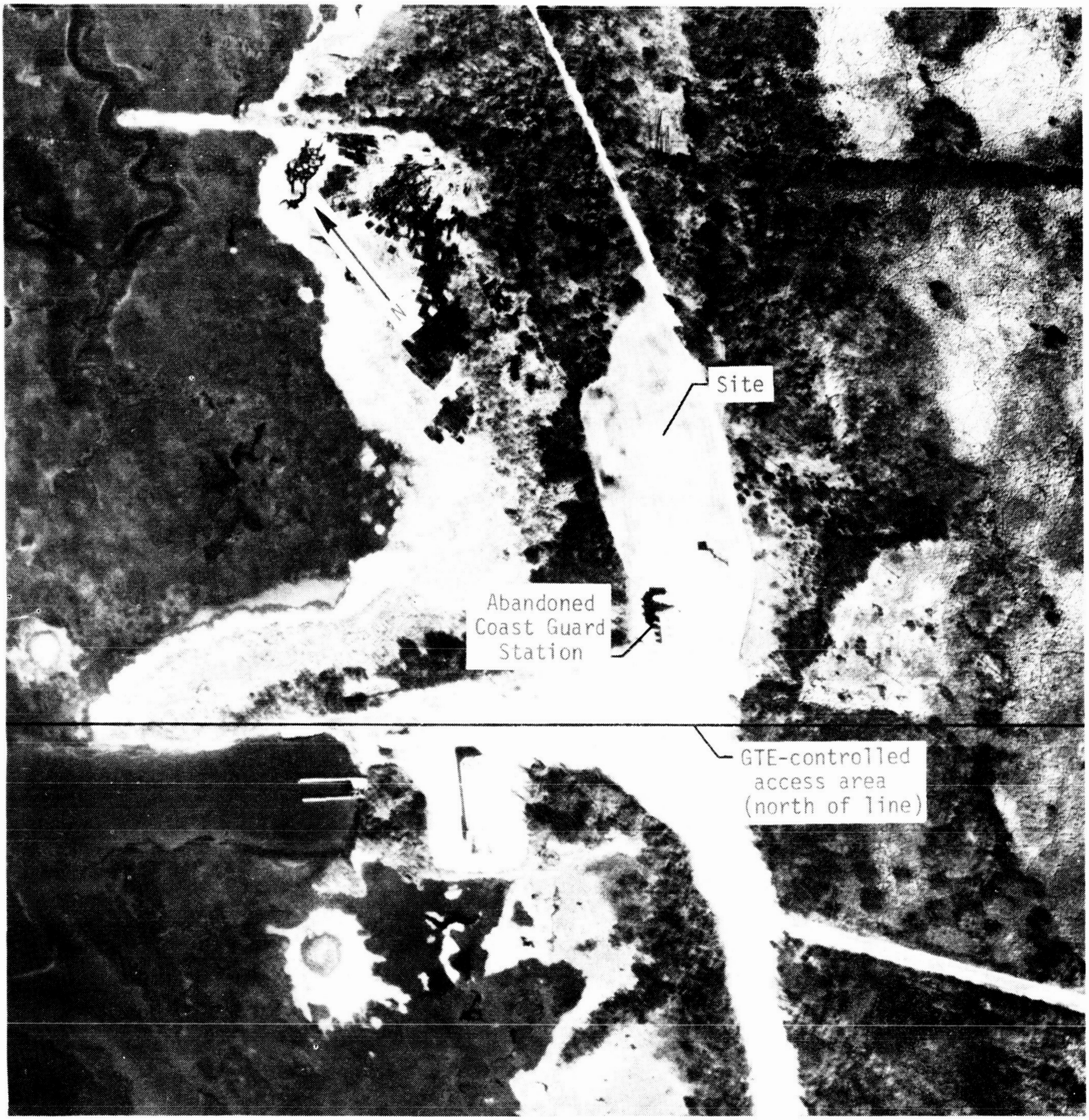
(c) 95-percent confidence level criterion test for slopes

Technique	95-percent CI on slopes	95-percent CI includes 1	Statistically significant
WALLOPS	0.89 to 0.91	No	Yes
NOAA/NCAR	1.03 to 1.05	No	Yes
GA TECH	0.80 to 0.86	No	Yes

TABLE 22.- NO INTERCOMPARISON RESULTS FOR PHASE 3 FROM AVERAGE PERCENTAGE ERROR ANALYSIS

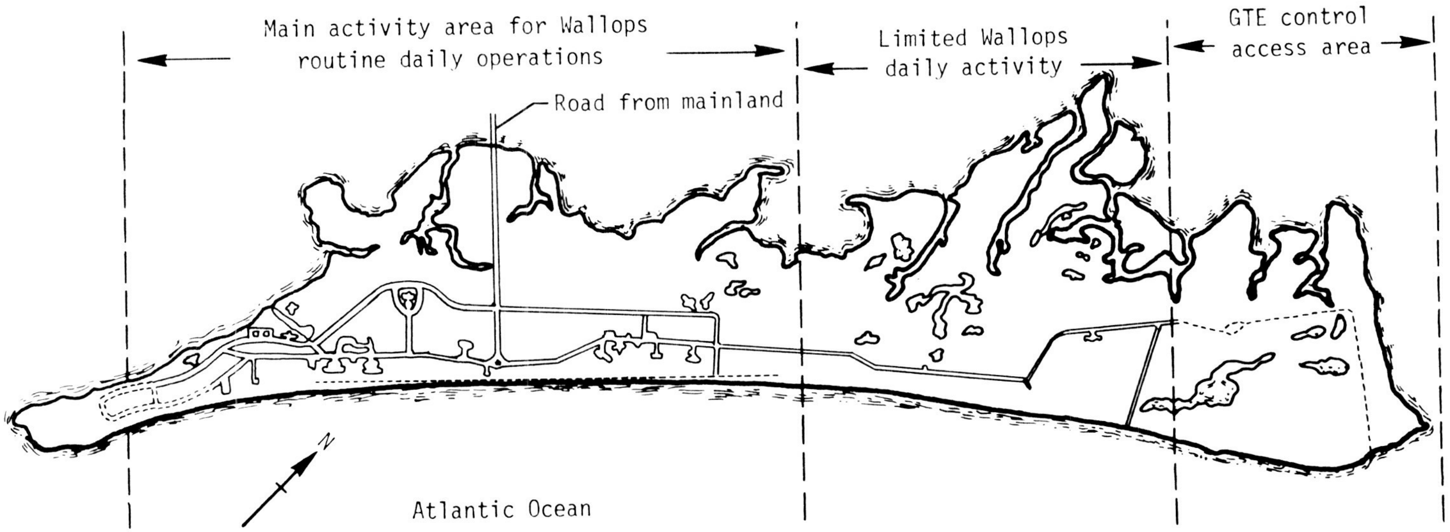
[Method 2, data category 3]

Parameter	WALLOPS	NOAA/NCAR	GA TECH
N	26	26	17
D, percent	-10.6	-0.7	-23.9
σ_D, percent	9.8	14.2	14.4

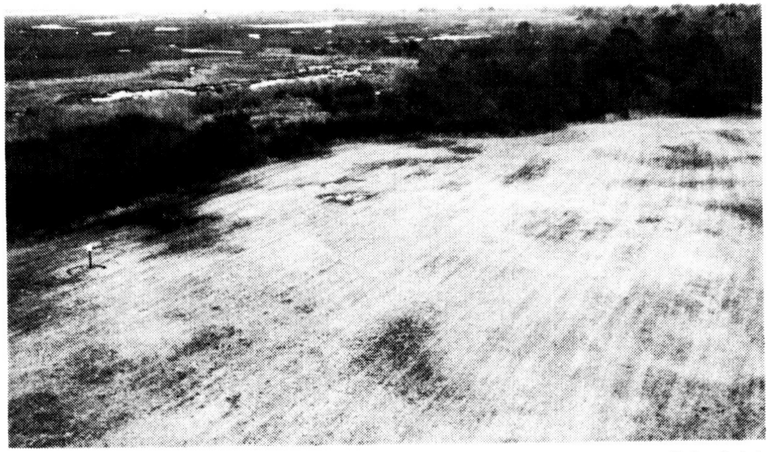


(a) Aerial view prior to construction.

Figure 1.- Test site for workshop.

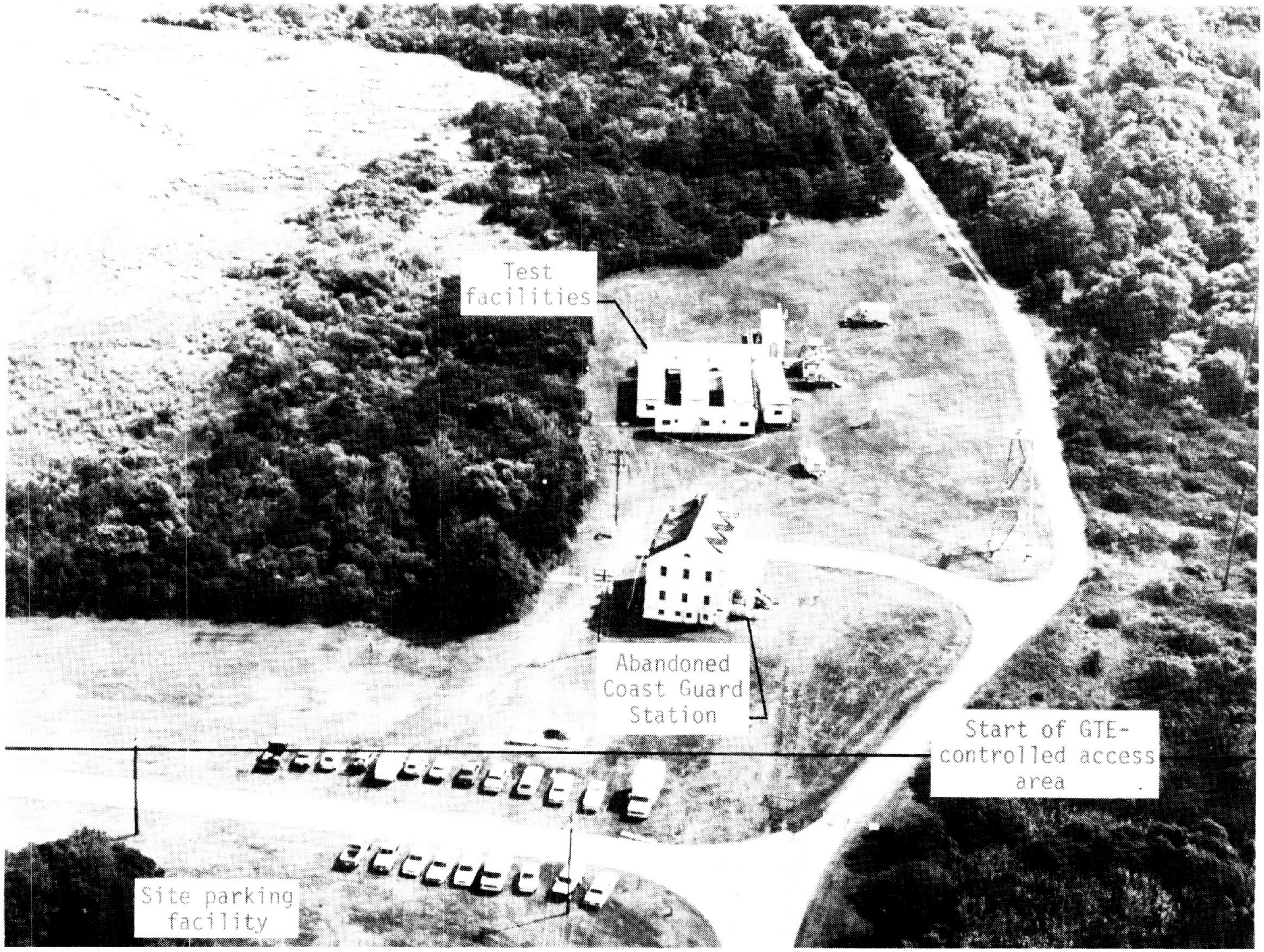


(b) Map of Wallops Island.


L-86-344

(c) Close-up of site prior to construction (looking north).

Figure 1.- Continued.



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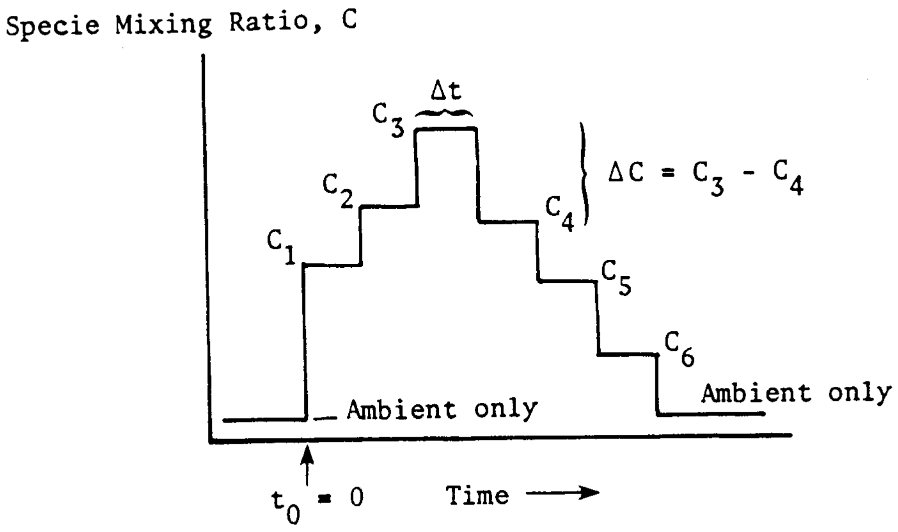
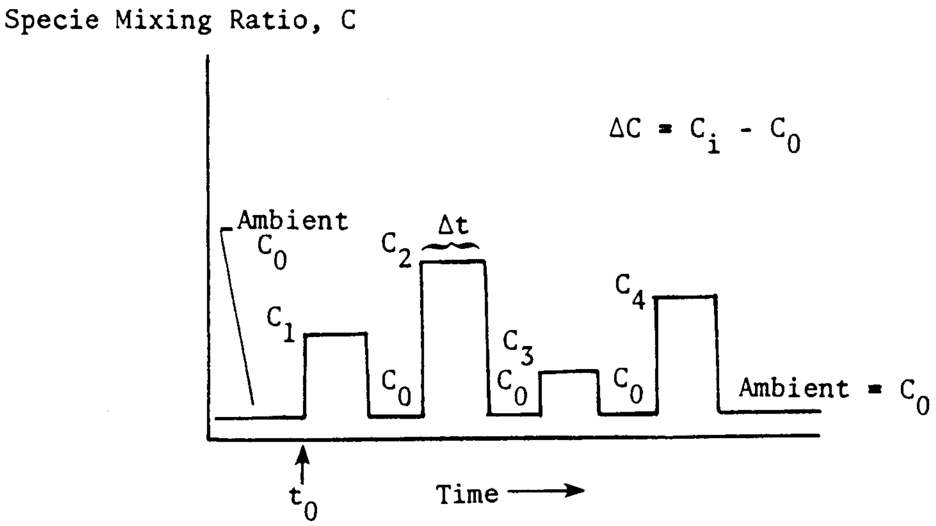
(d) Completed site (looking northeast).

Figure 1.- Concluded.

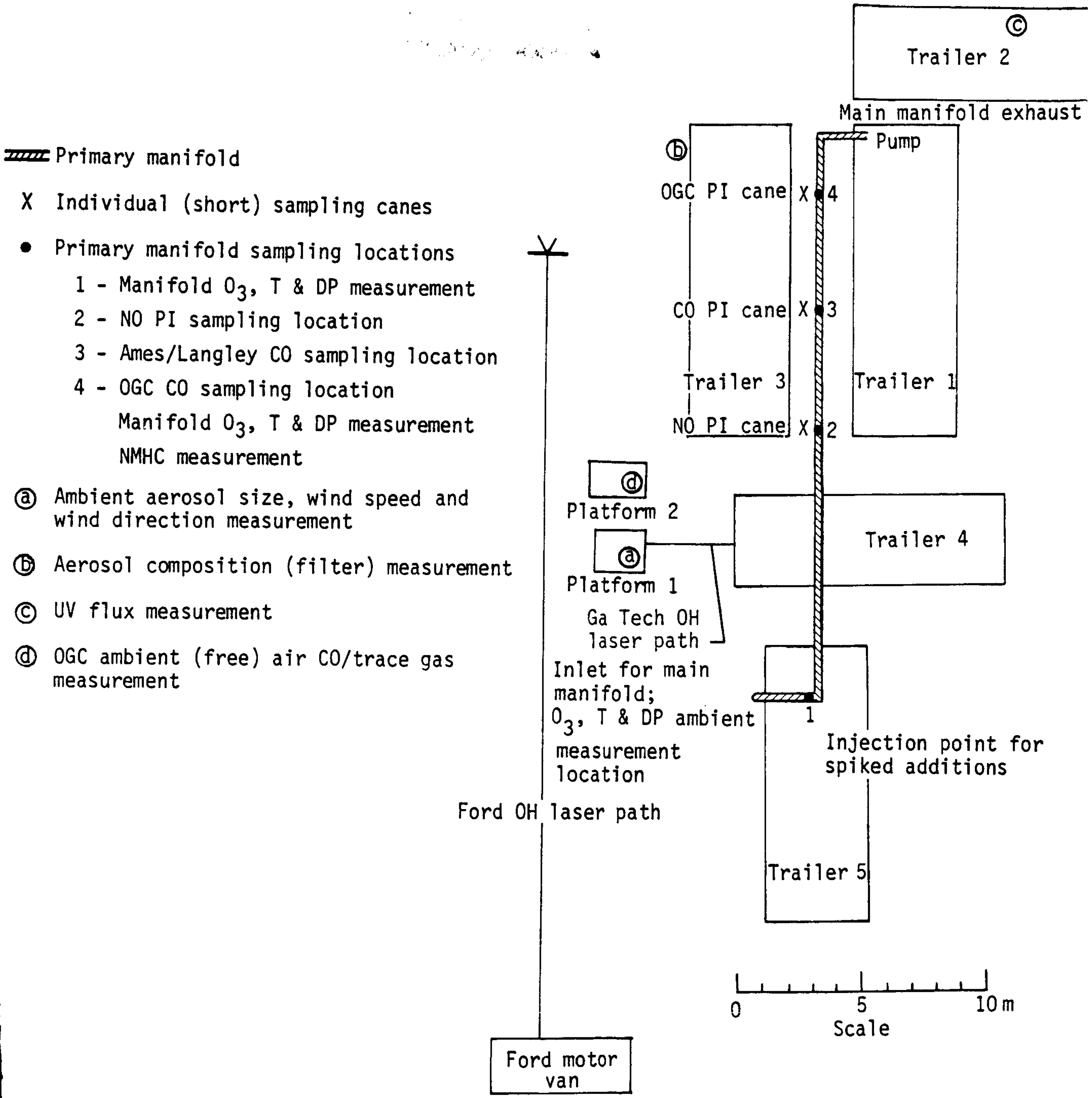


(a) Sequential additions.



(b) Alternating additions.

Figure 2.- Typical spiked-ambient intercomparison tests.



(a) Site layout (scale approximate).

Figure 3.- Wallops intercomparison site.

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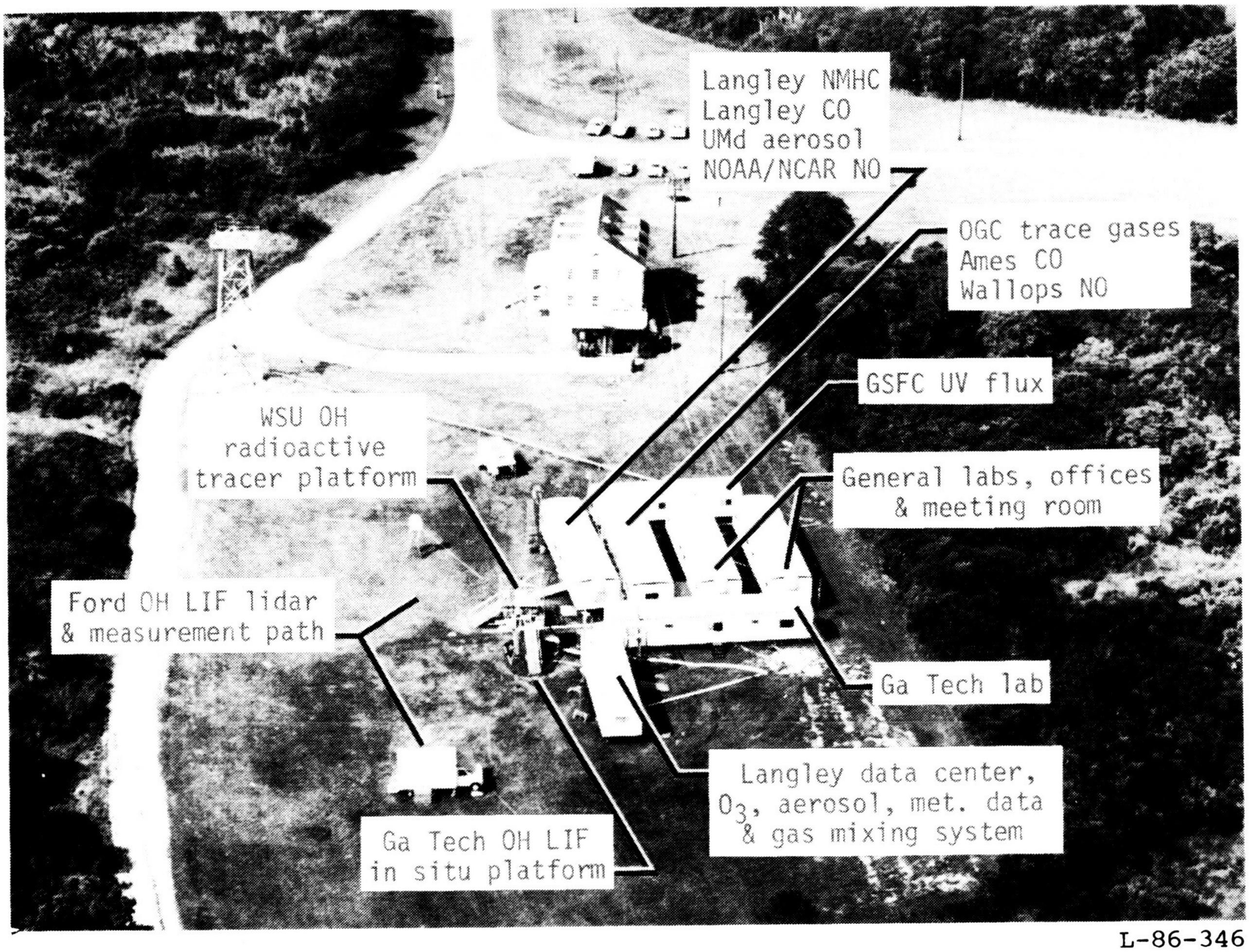

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(b) Photograph of site (looking south).

Figure 3.- Concluded.

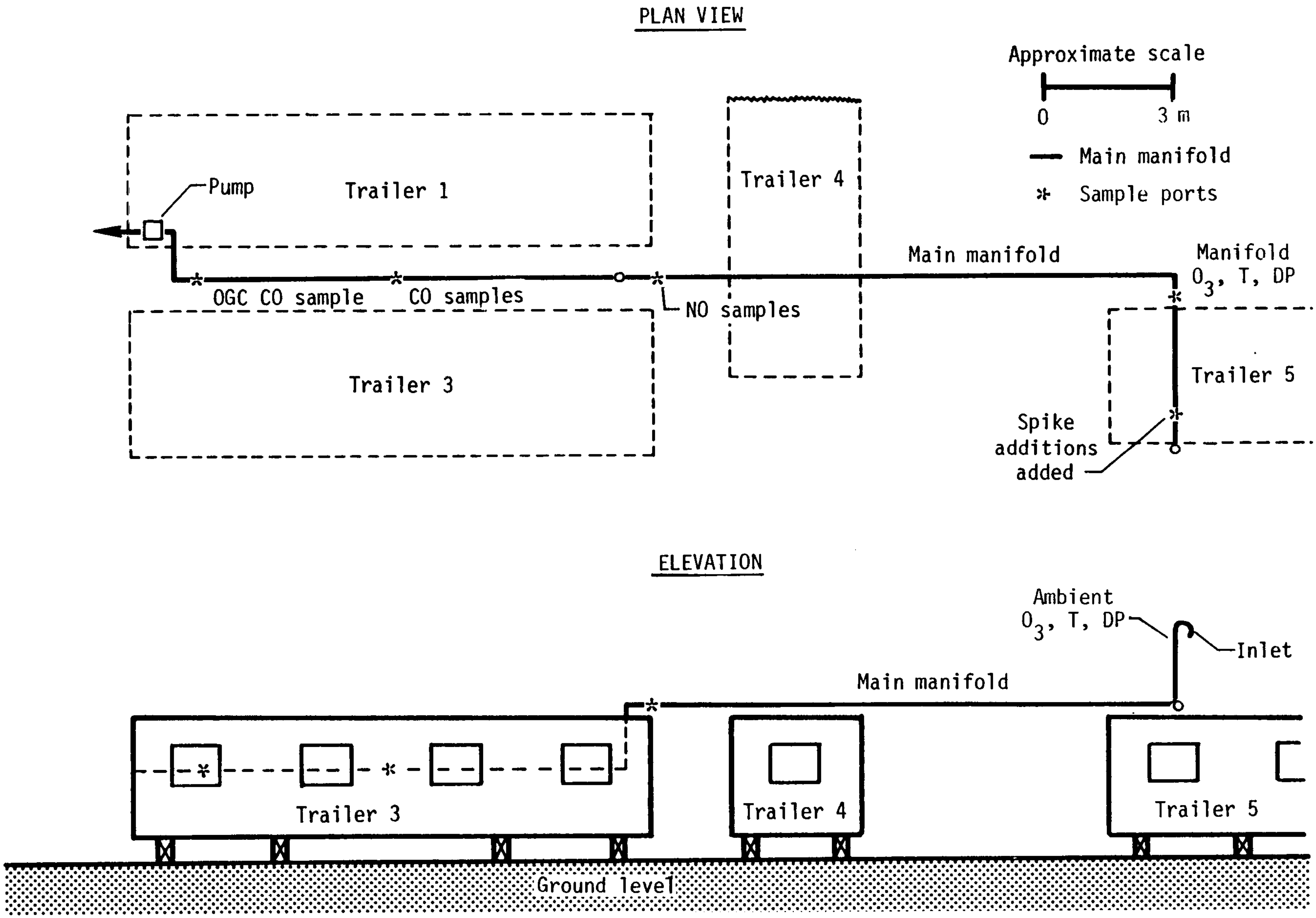
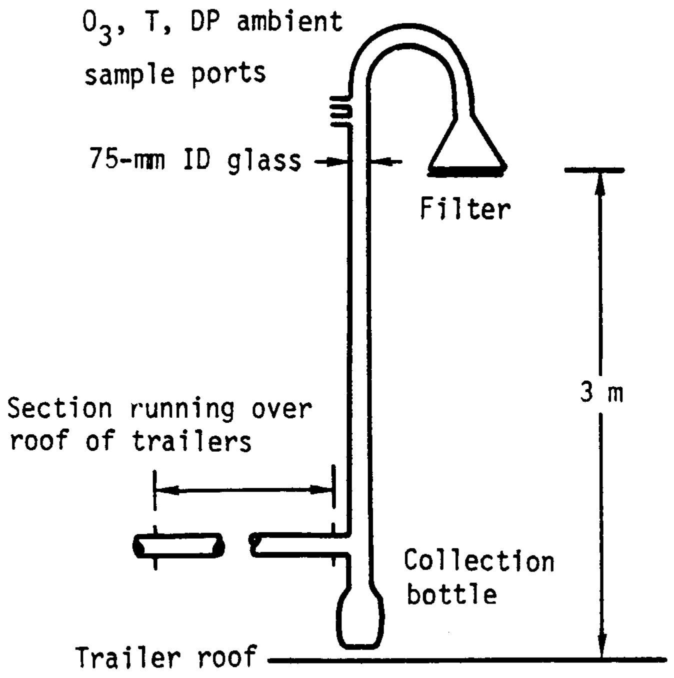
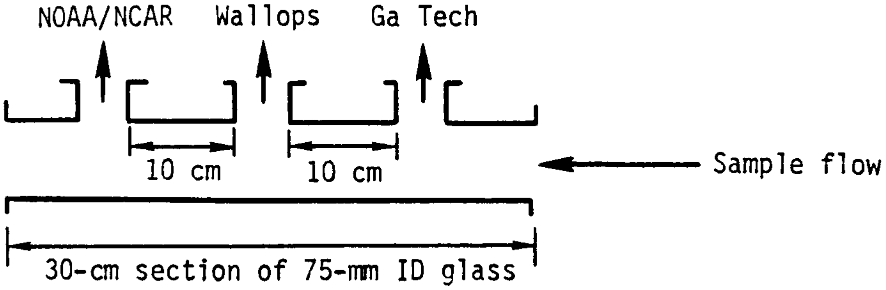


Figure 4.- Plan view and elevation sketch of main manifold.



(a) Inlet (primary manifold).



(b) Nitric oxide PI sample ports (typical).

Figure 5.- Sample inlets and ports (primary manifold).

Parameters for NO change of 10 pptv

Parameter	Flow, cm^3/min	NO mixing ratio
NO supply (Q_1)	60	9.07 ppmv
Zero gas (Q_A)	0	0
Exit 1st stage (X_1)		9.07 ppmv
Test mix (Q_2)	60	9.07 ppmv
Ultra-zero gas (Q_8)	9000	0
Exit 2d stage (X_2)		60 ppbv
Test mix (Q_3)	400	60 ppbv
Manifold air (Q_M)	2.3×10^6	(*)
Manifold change (X_M)		10.6 pptv

*Assumed zero for step-change calculation.

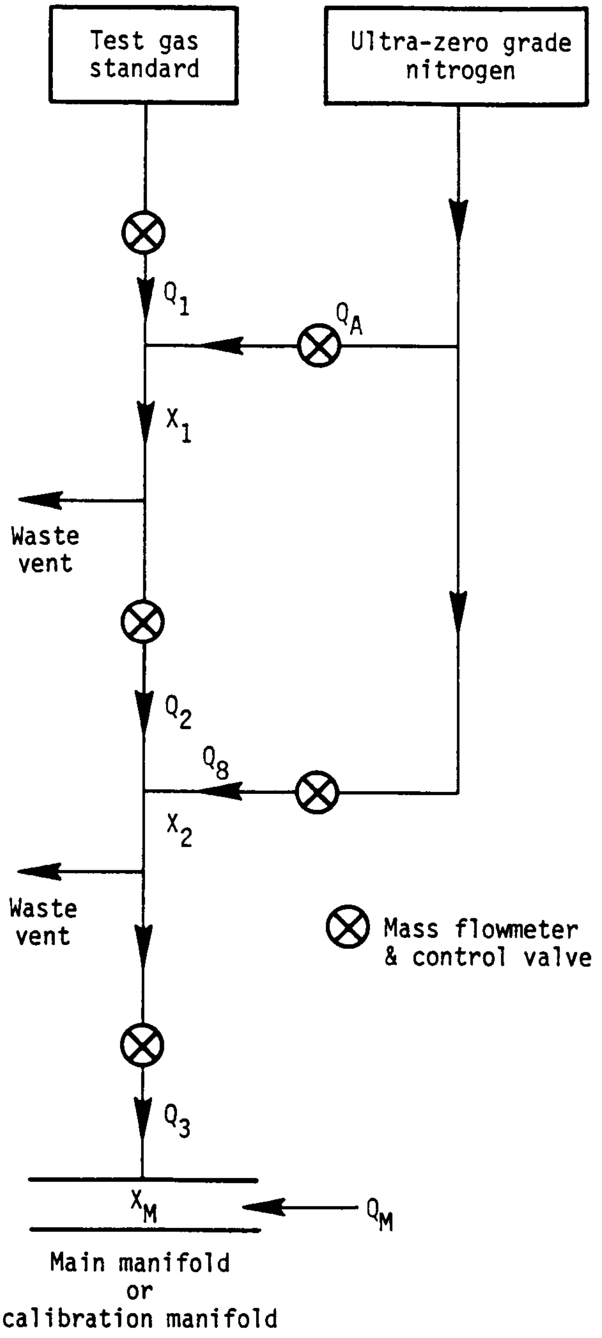


Figure 6.- Schematic of gas dilution system.

Mon. June 13
*DACOM/CO on-site

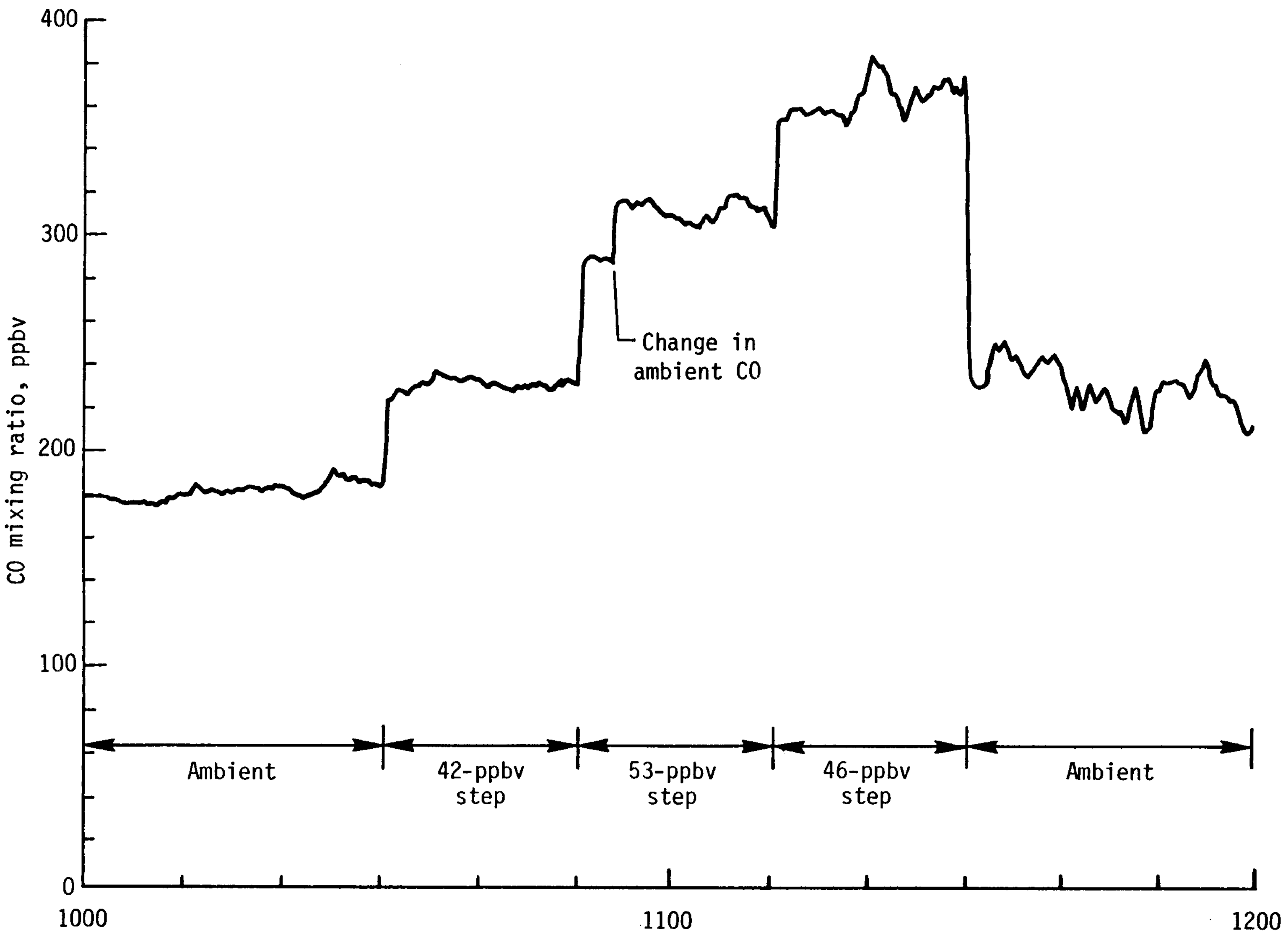
Mon. June 27
*Ford/OH on-site

Tue. June 28
*Site complete as per doc.

Fri. July 1
*Ga Tech OH/NO on-site

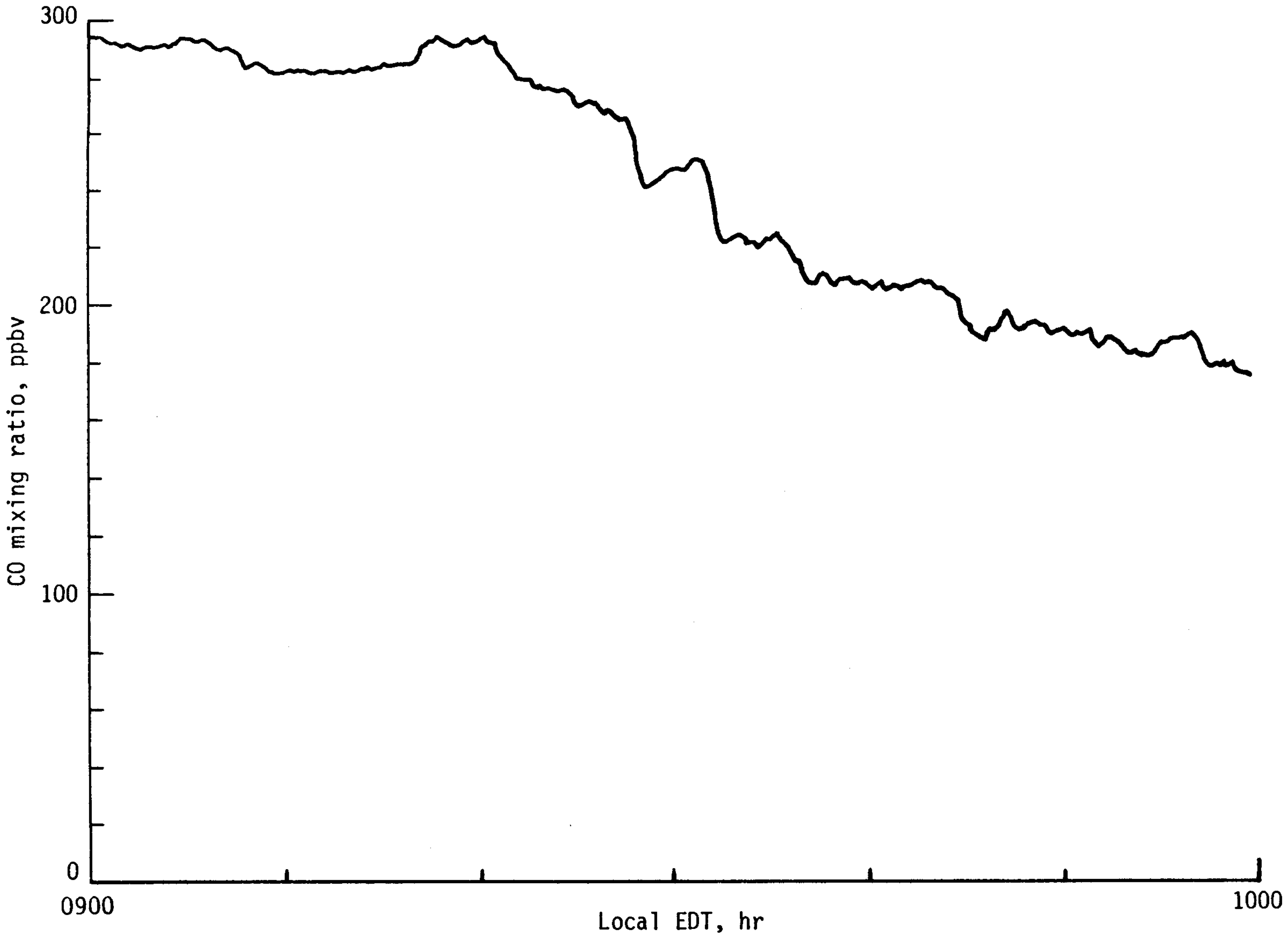
SATURDAY	SUNDAY	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
July 2 --- No scheduled activities ---	**July 3**	**July 4**	**July 5** *Langley NMHC on-site	**July 6** *Ames CO on-site *CO procedures checkout with DACOM	**July 7** *OGC CO & trace gases on-site *GSFC UV flux on-site	**July 8** *CO/C-3 test *Wallops NO on-site *UMd aerosol on-site
July 9 --- No scheduled activities ---	**July 10**	**July 11** *CO/X-3 test *CO/C-1 test *NOAA/NCAR on-site	**July 12** *CO/C-4 test *Request for 24-hr met. & O_3 data	**July 13** *NO test procedure checked out with NOAA/NCAR & Wallops inst.	**July 14** *CO/C-1 test *CO/X-3 test	**July 15** *OH-1 (1000-1300) & (1400-1645)
July 16 *OH-2 (1200-1530)	**July 17** *No scheduled test	**July 18** *OH-3 cancelled (Ga Tech laser contamination) *OH support data for Ford (1200-1400) *CO/X-3 test	**July 19** *Ga Tech laser contamination *OH support data for Ford (1200-1500) *Rain @ 1500	**July 20** *OH-3 (1100-1600)	**July 21** *WSU on-site (0800) *OH-4 (1400-1730) *OH-5 (1730-2115)	**July 22** *OH-6 (1100-1700) *OH-7 (1700-1935) *Completion of OH test
July 23 *No scheduled test	**July 24** *Ga Tech lost laser	**July 25** *Ga Tech lost laser	**July 26** *NO/N-2 test chem only *Ga Tech replacement laser in transit	**July 27** *NO/N-2 test chem only (1900-2000) *NO/N-4 test chem only (2230-0050) *Ga Tech replacement laser on-site *CO/C-4 test	**July 28** *NO/N-3 (1200-1605) *LIF on line @ 1500 *NO/N-4 test (2000-0005)	**July 29** *NO/N-4 (1200-1400) *NO/N-3 (1400-1730) *NO/N-4 (2030-0010) *GTE/IIW complete

Figure 7.- Calendar of events.



(a) Spiked-ambient test run.

Figure 8.- CO ambient variability maximum levels observed. Data source: LANGLEY.



(b) Ambient-only test run.

Figure 8.- Concluded.

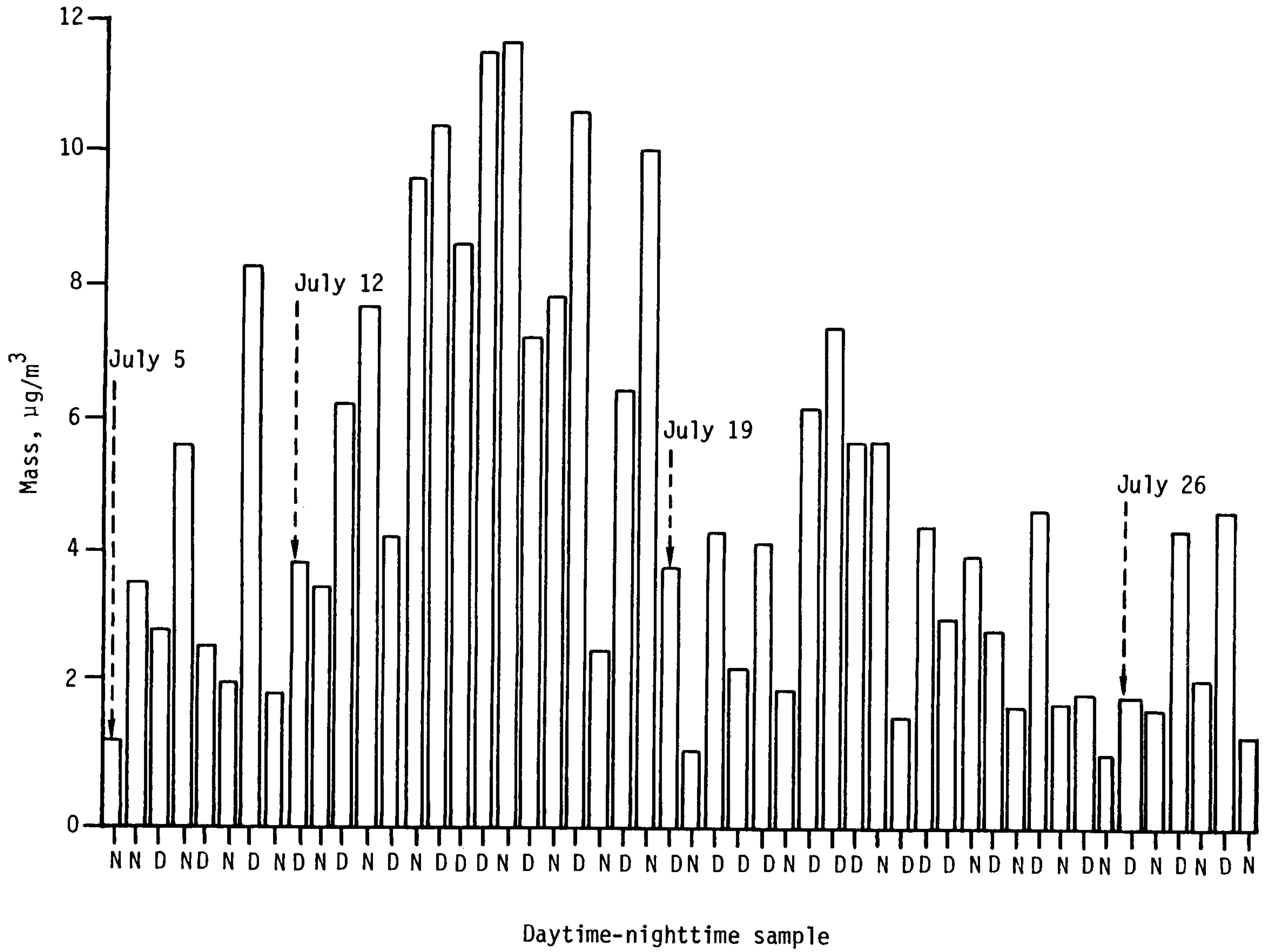


Figure 9.- Particulate loading of crustal dust (≈12-hr sample).

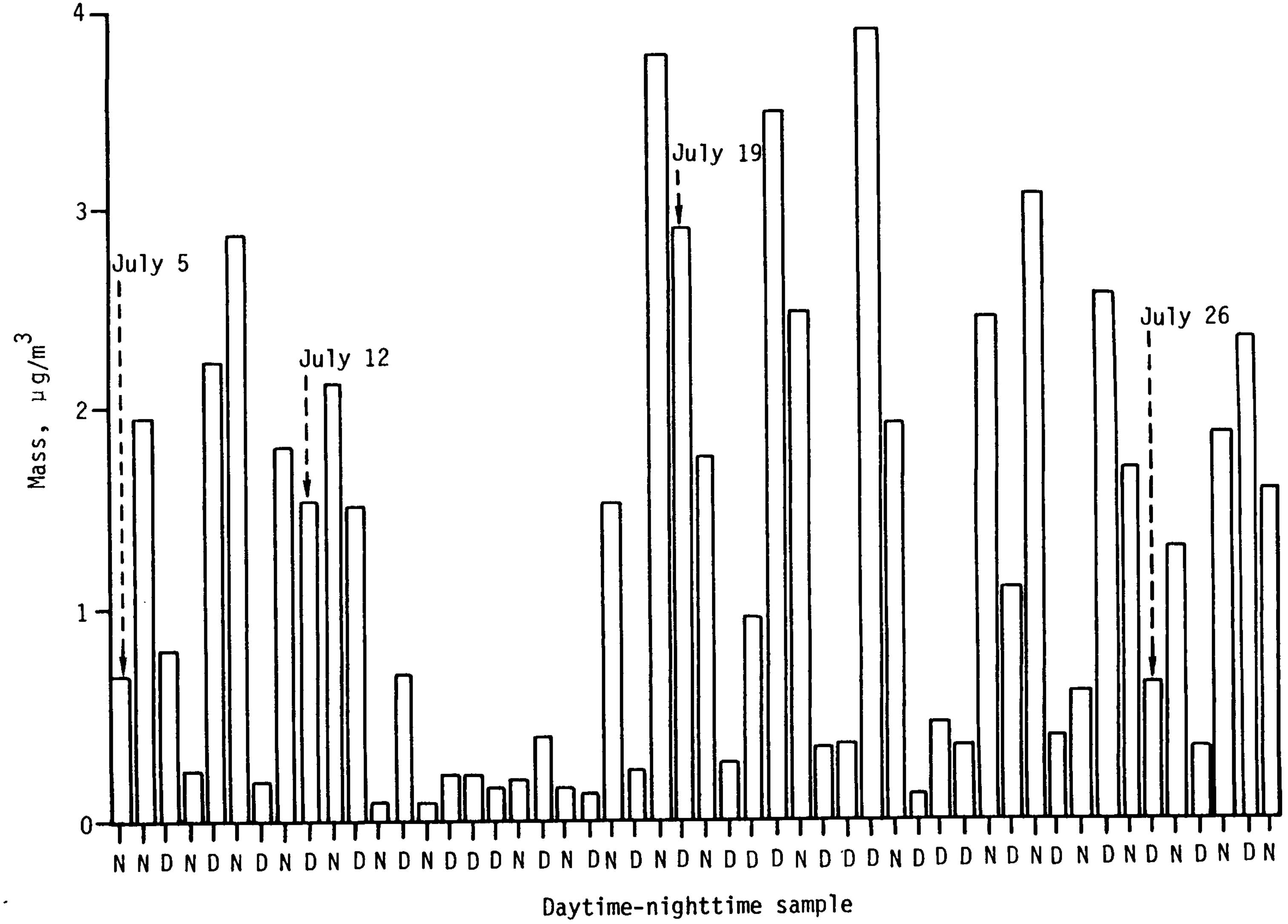


Figure 10.- Particulate loading of sea salt (≈12-hr sample).

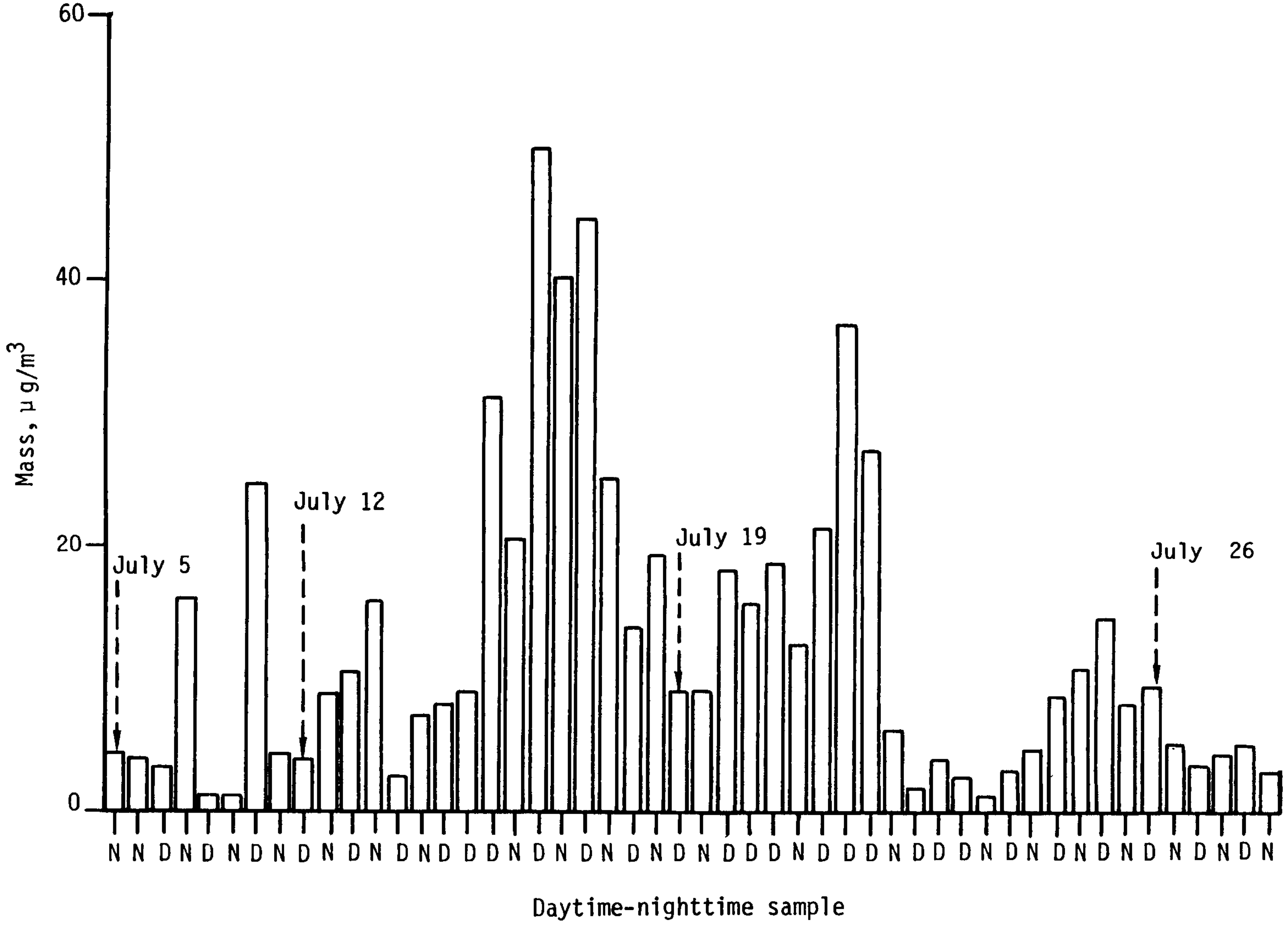


Figure 11.- Particulate loading of sulfate (≈12-hr sample).

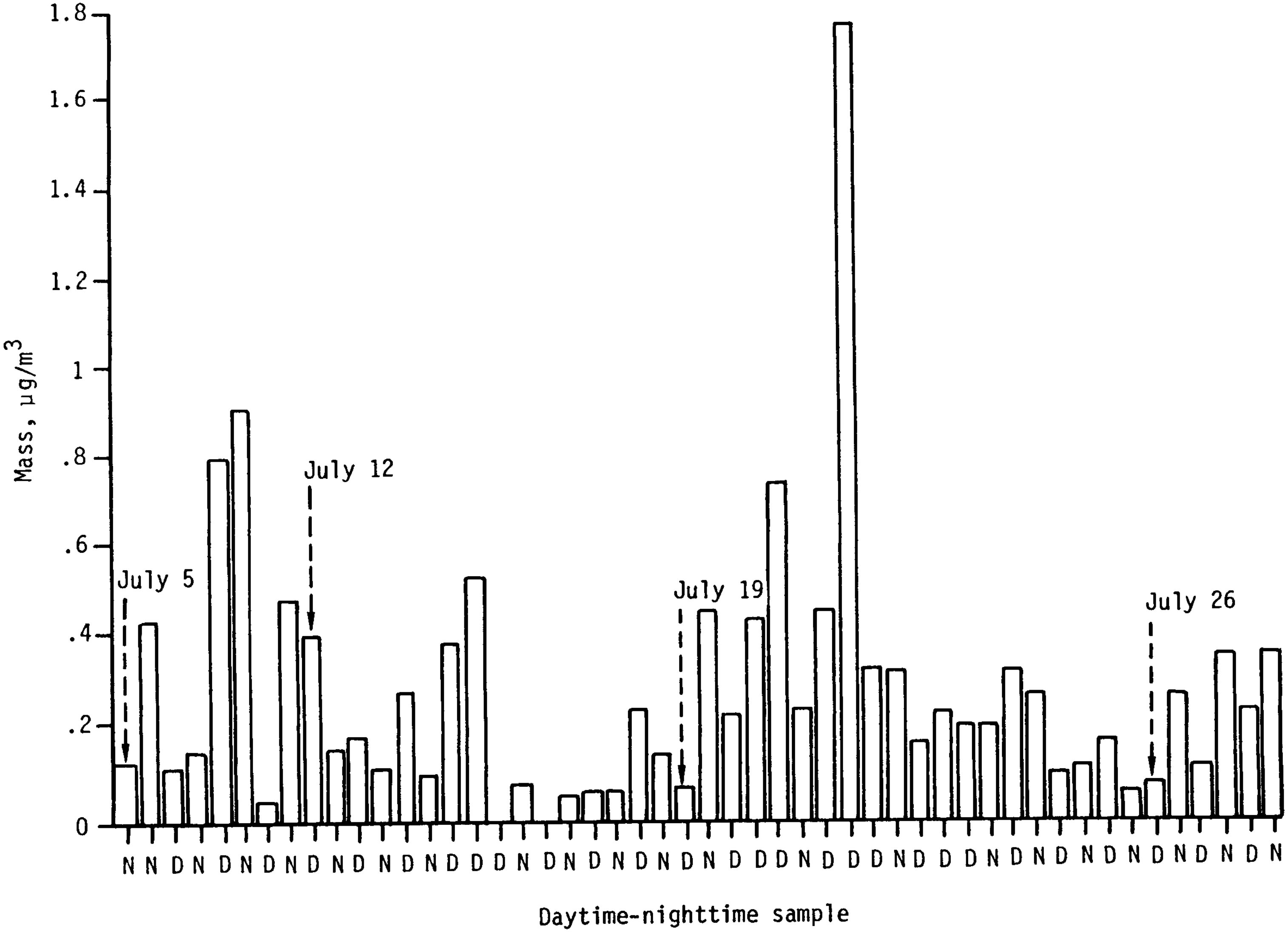
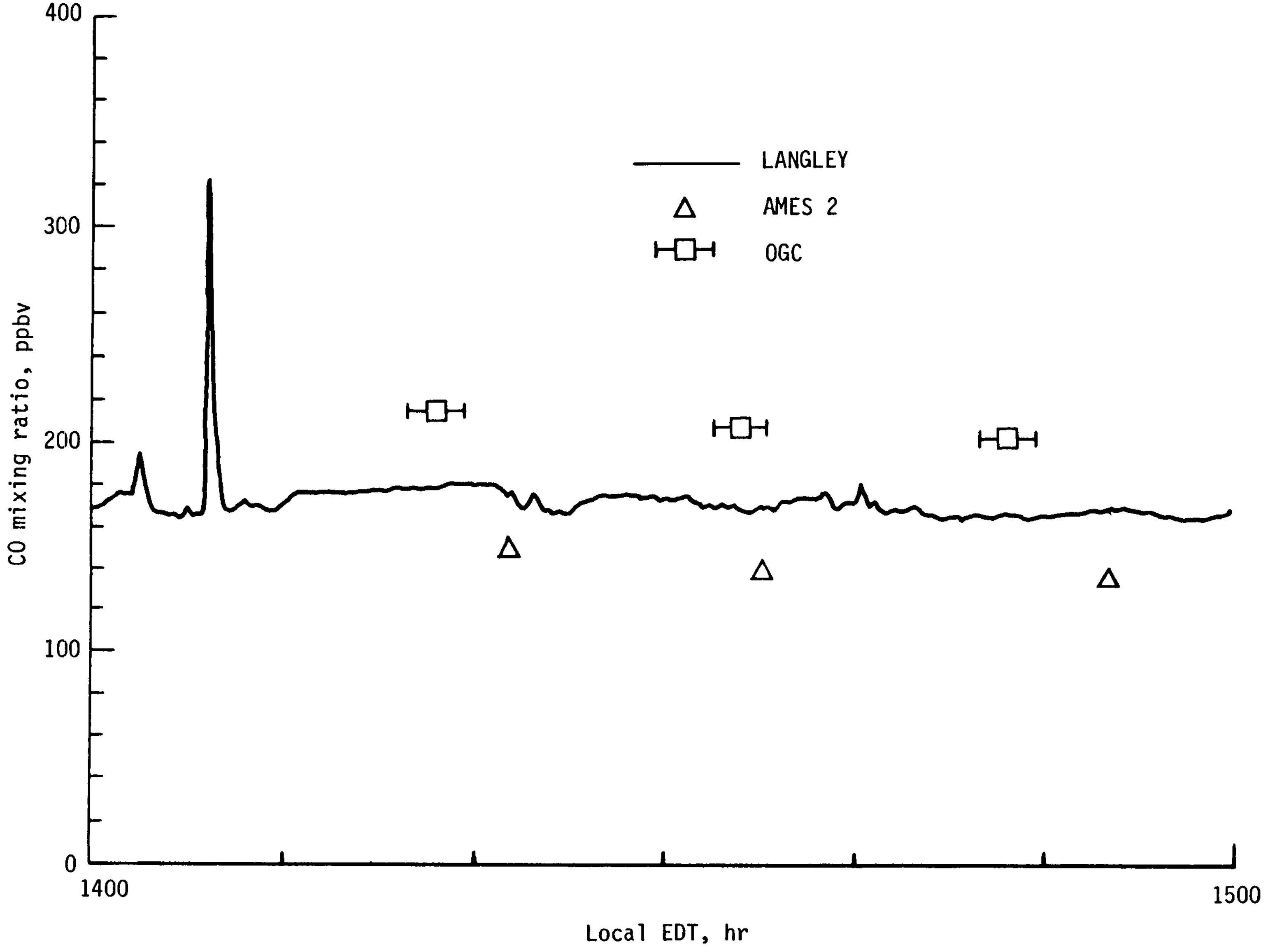
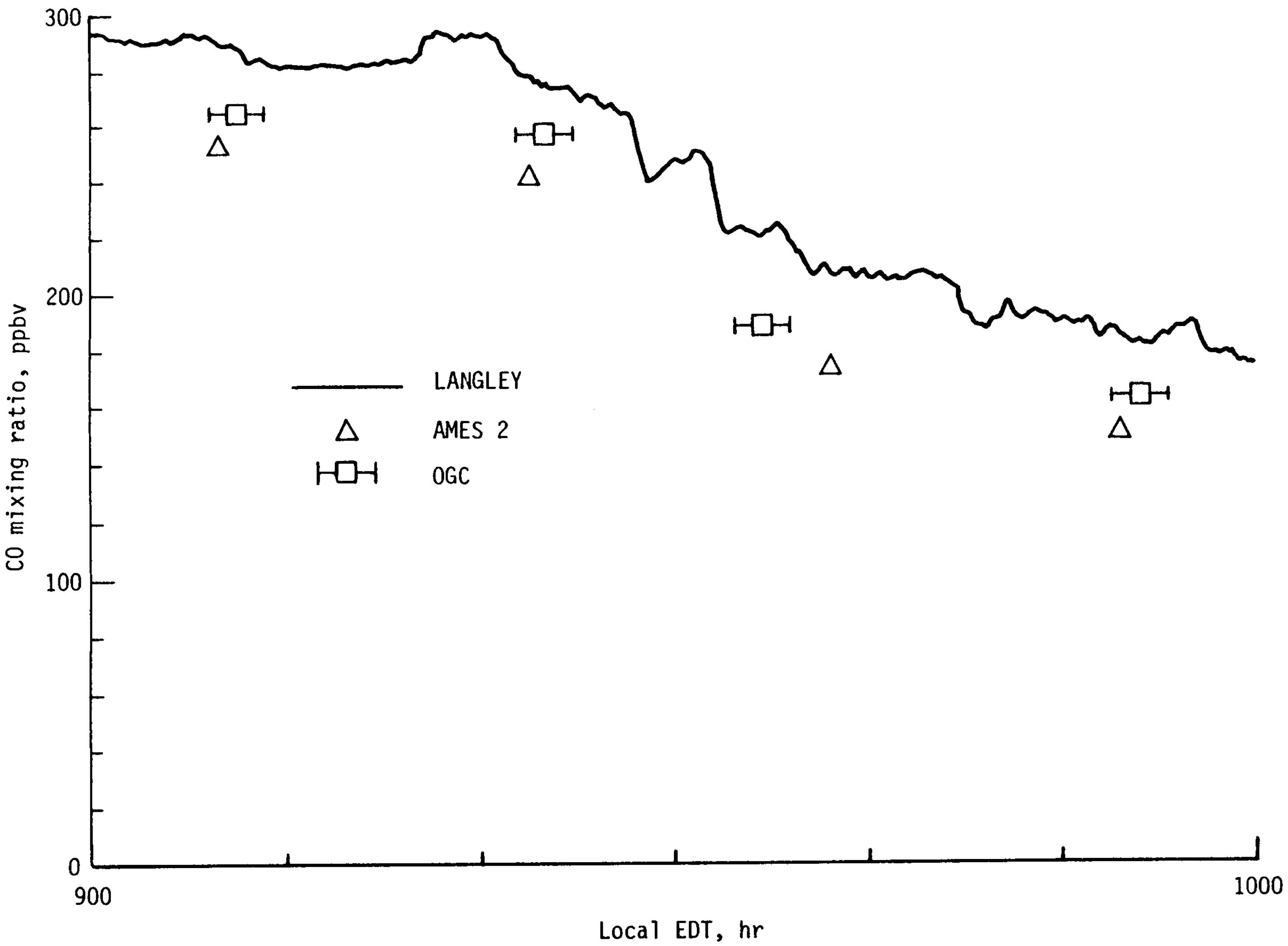


Figure 12.- Particulate loading of nitrate (≈12-hr sample).



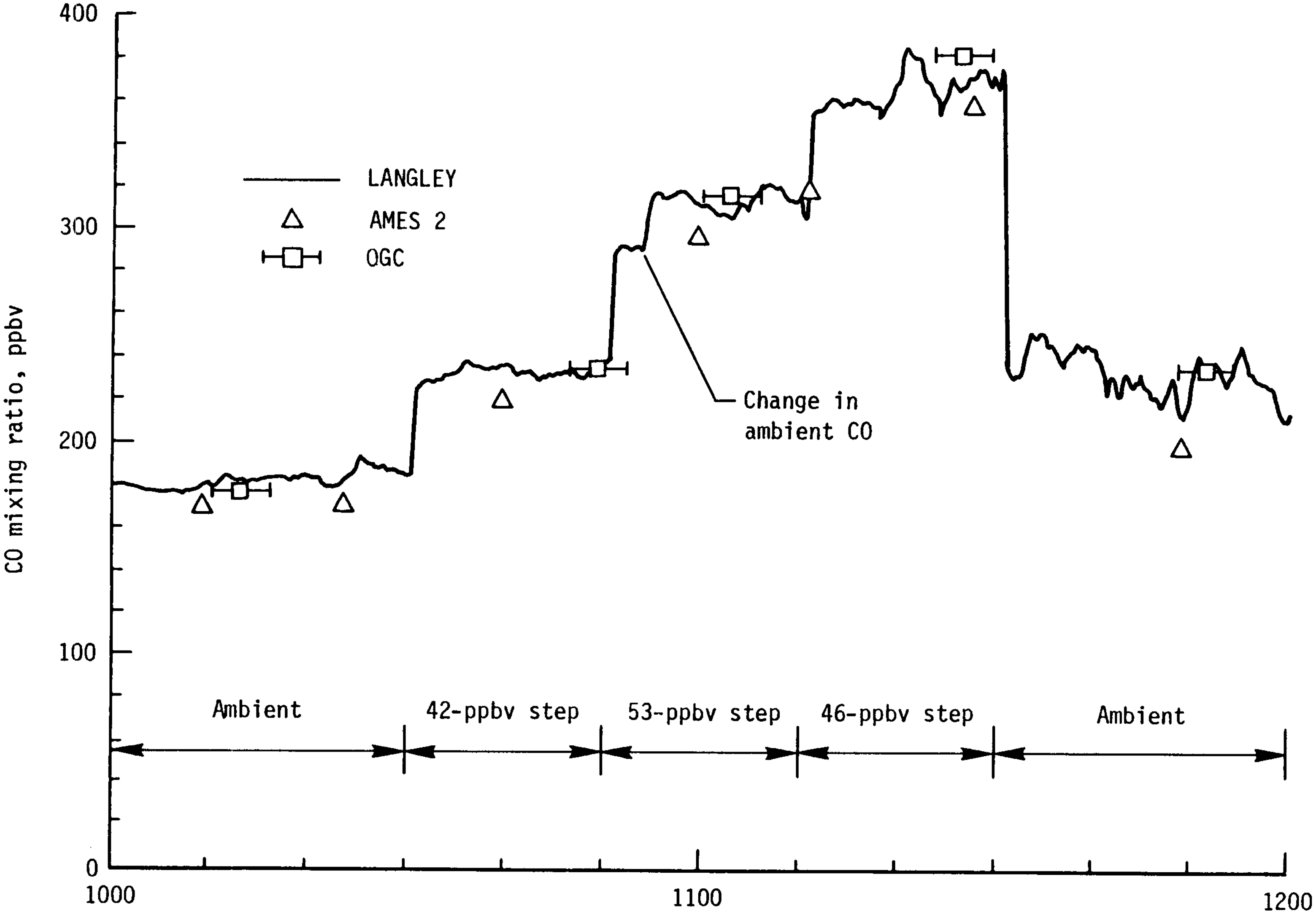
(a) Test C-1, July 11, 1983.

Figure 13.- Carbon monoxide results for ambient test.



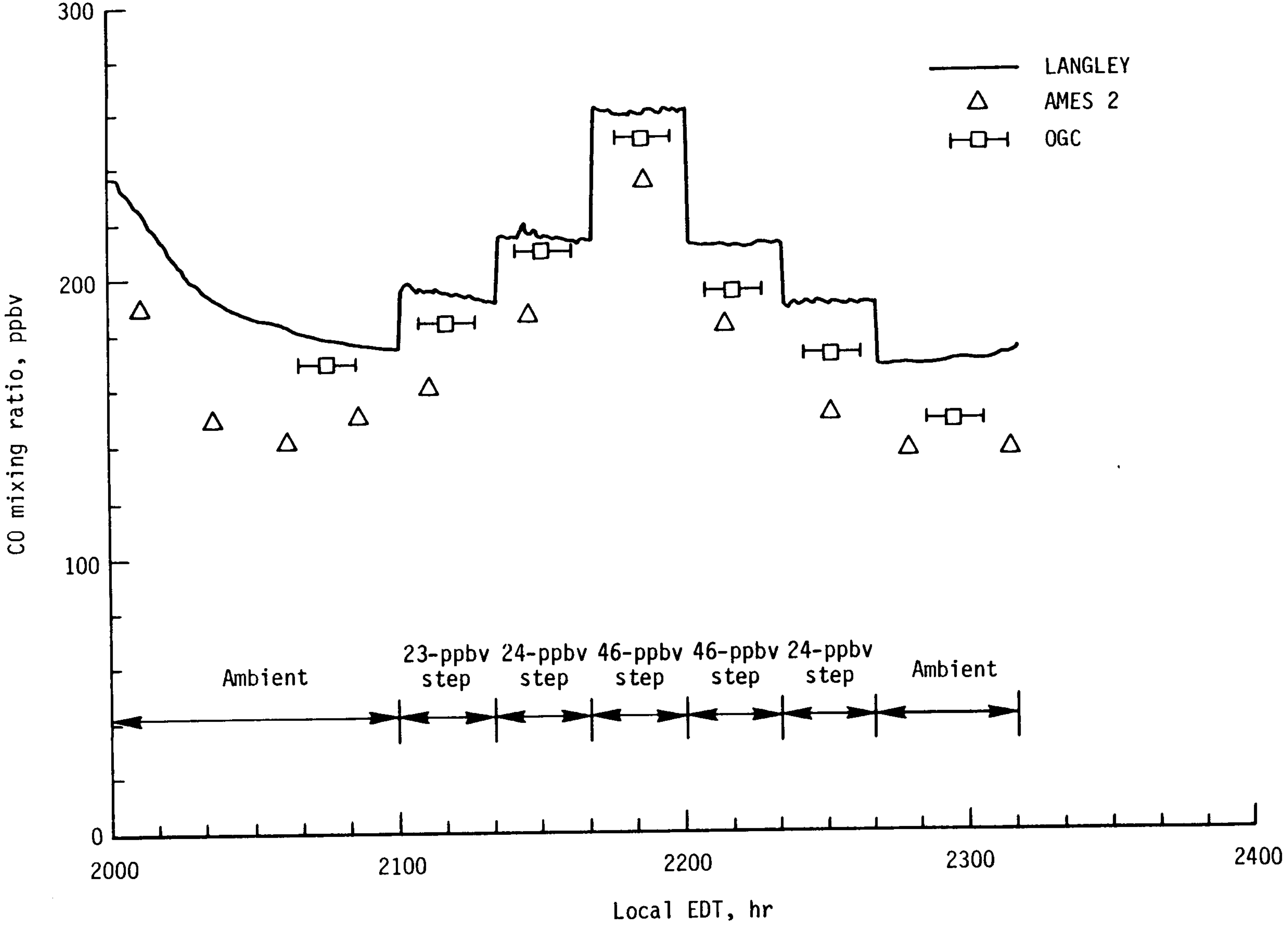
(b) Test C-1, July 14, 1983.

Figure 13.- Concluded.



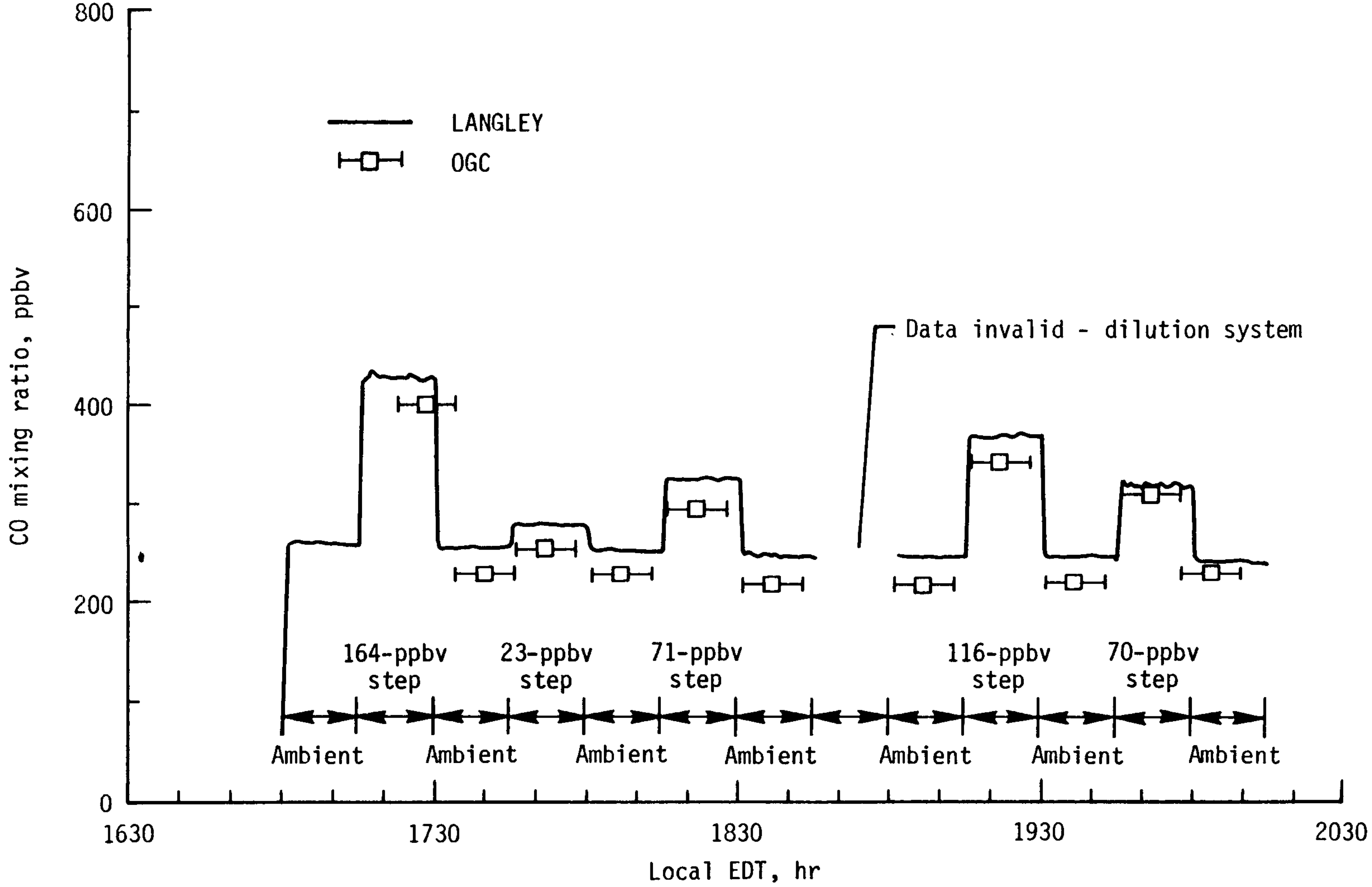
(a) Test C-3, July 8, 1983.

Figure 14.- Carbon monoxide results for spiked-ambient test.



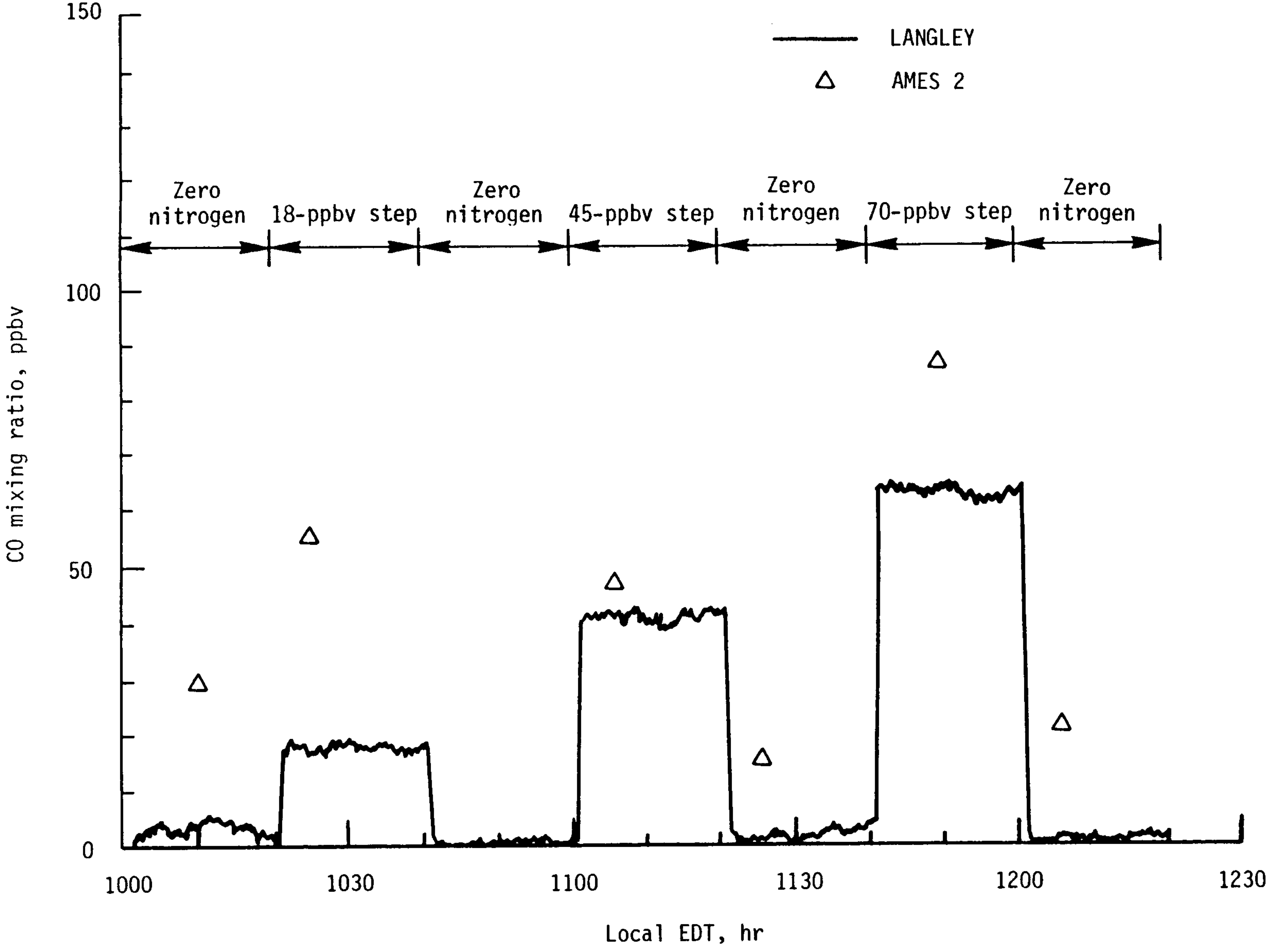
(b) Test C-4, July 12, 1983.

Figure 14.- Continued.



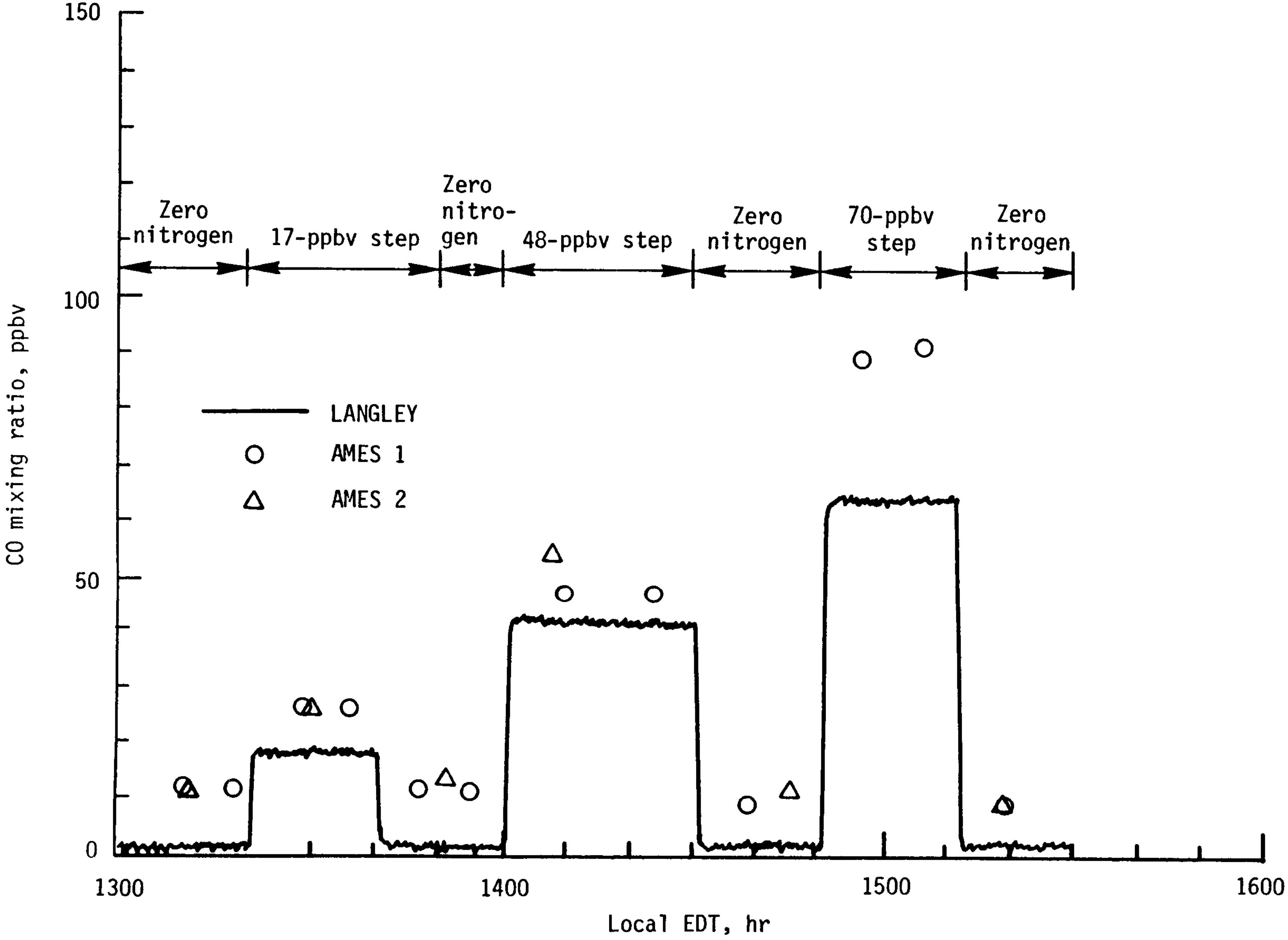
(c) Test C-4, July 27, 1983.

Figure 14.- Concluded.



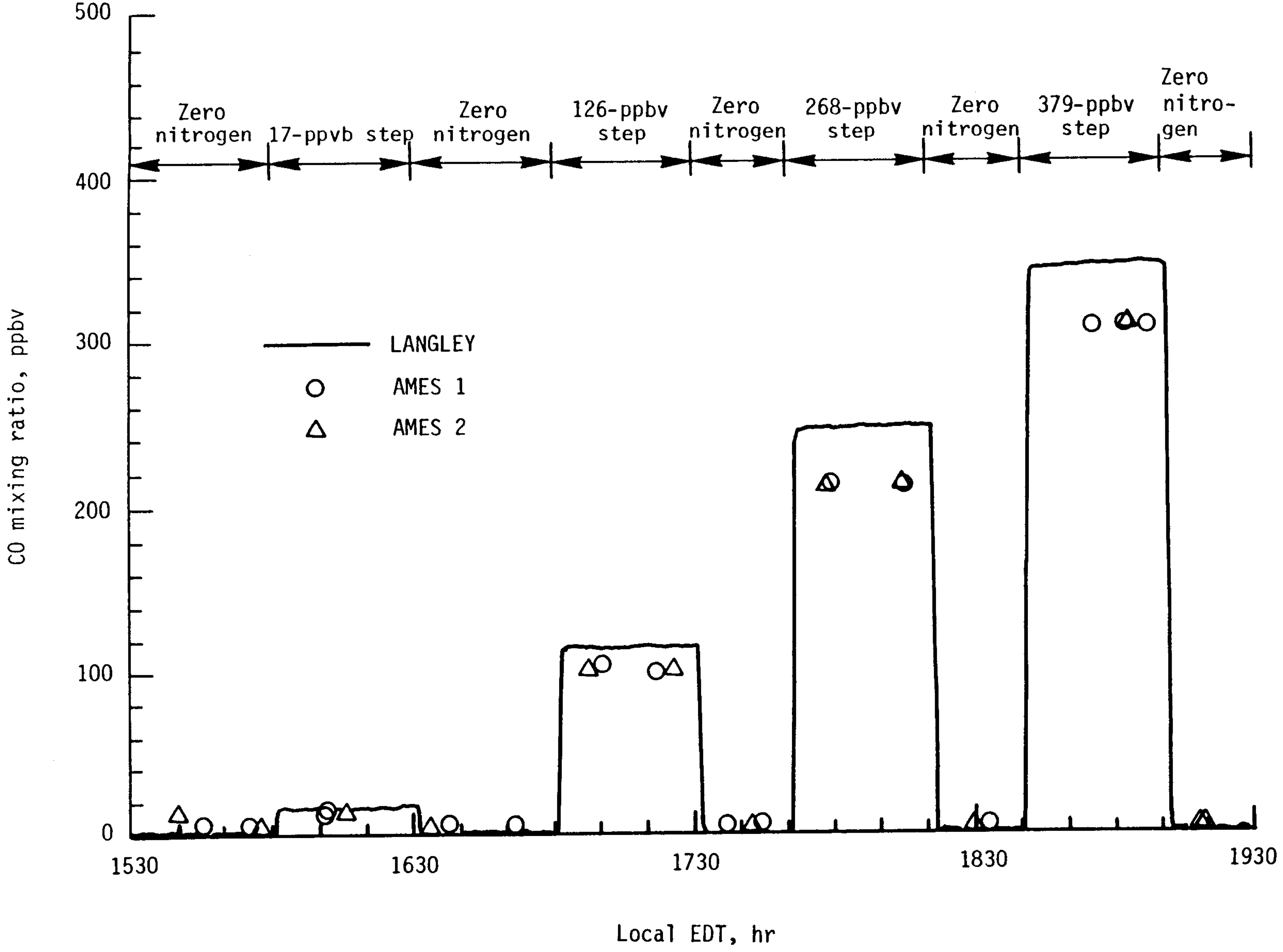
(a) Test X-3, July 11, 1983.

Figure 15.- Carbon monoxide results for spiked-nitrogen test.



(b) Test X-3, July 14, 1983.

Figure 15.- Continued.



(c) Test X-3, July 18, 1983.

Figure 15.- Concluded.

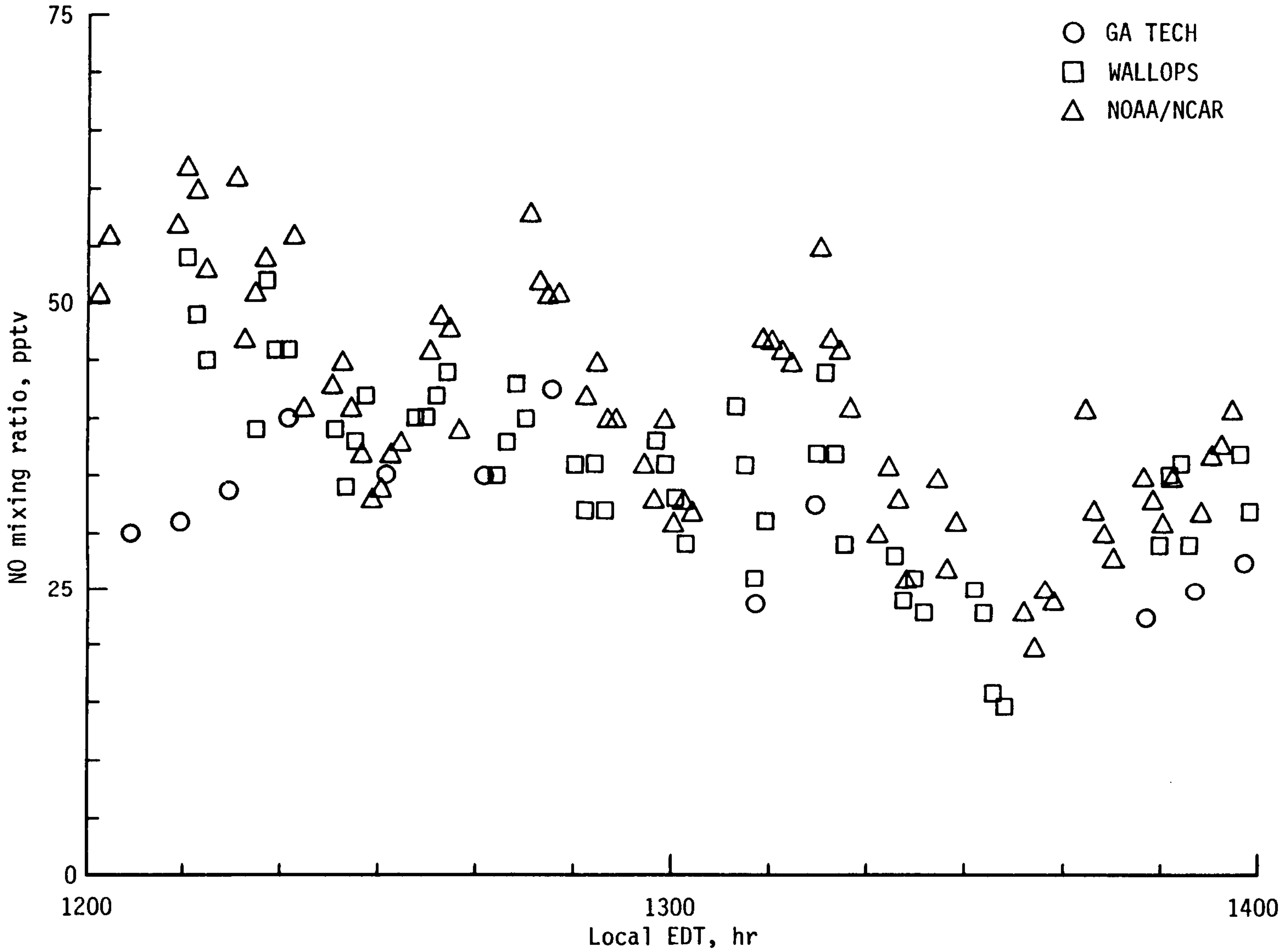
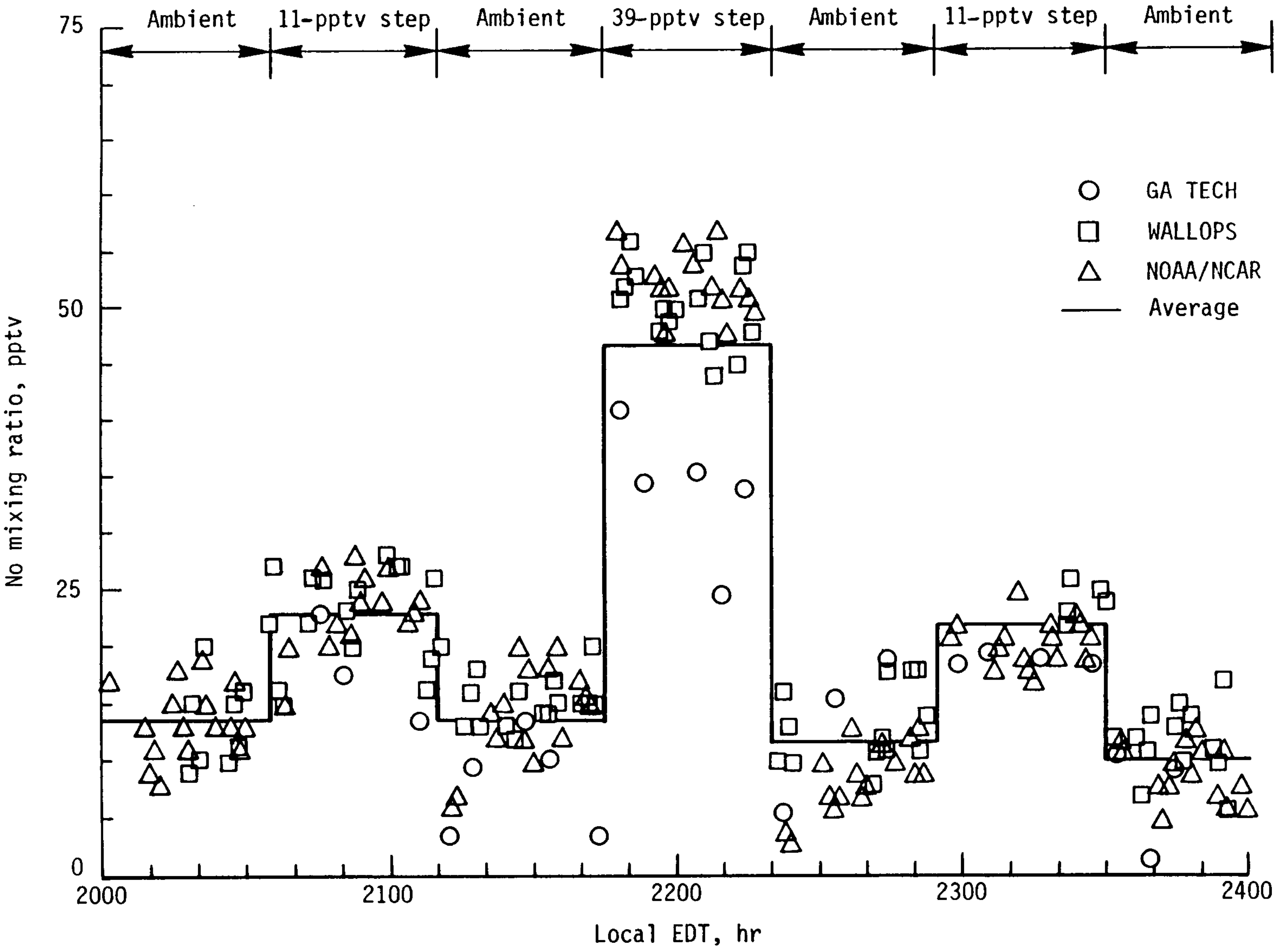
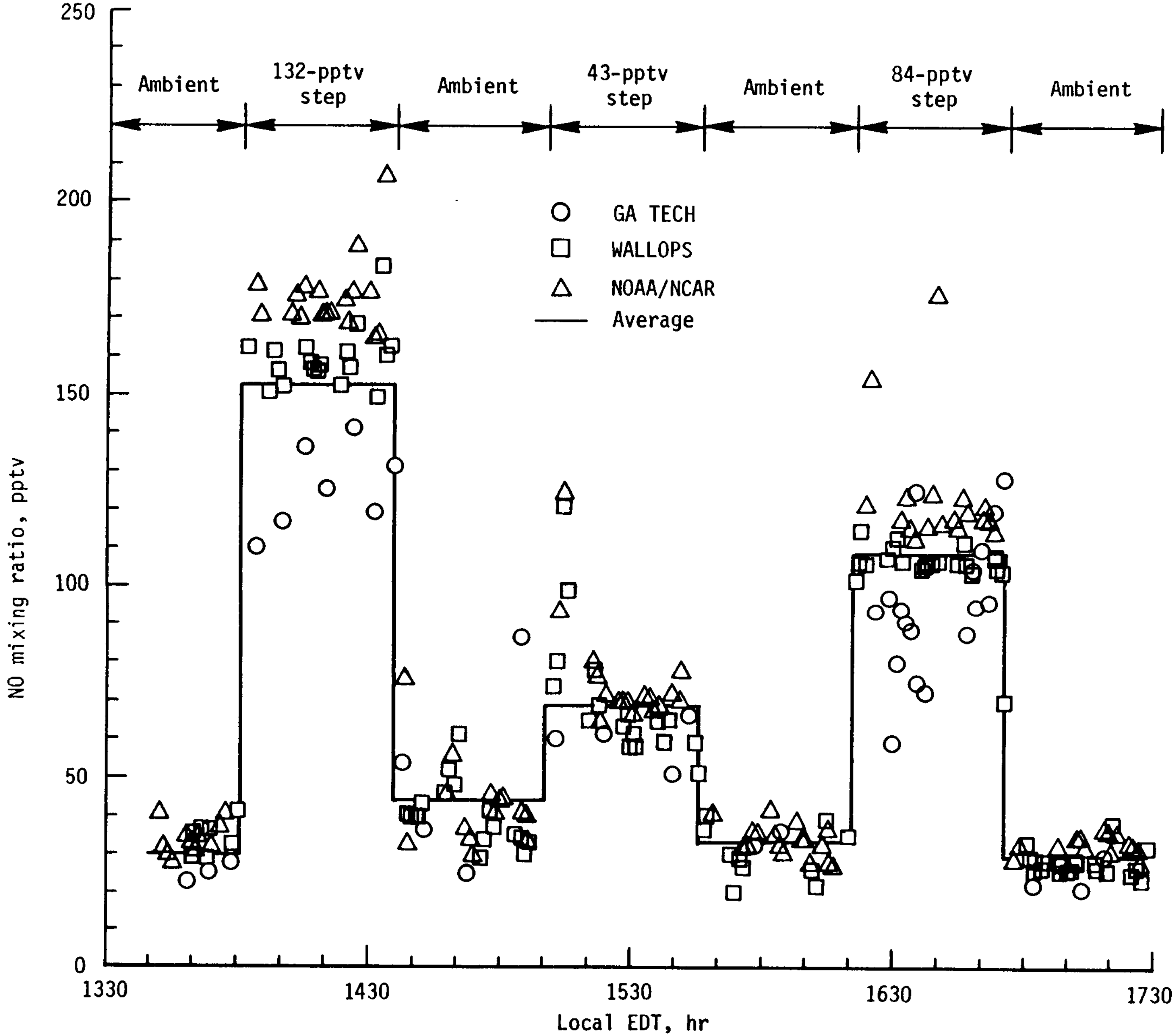


Figure 16.- Nitric oxide results for ambient test N-1, July 29, 1983.



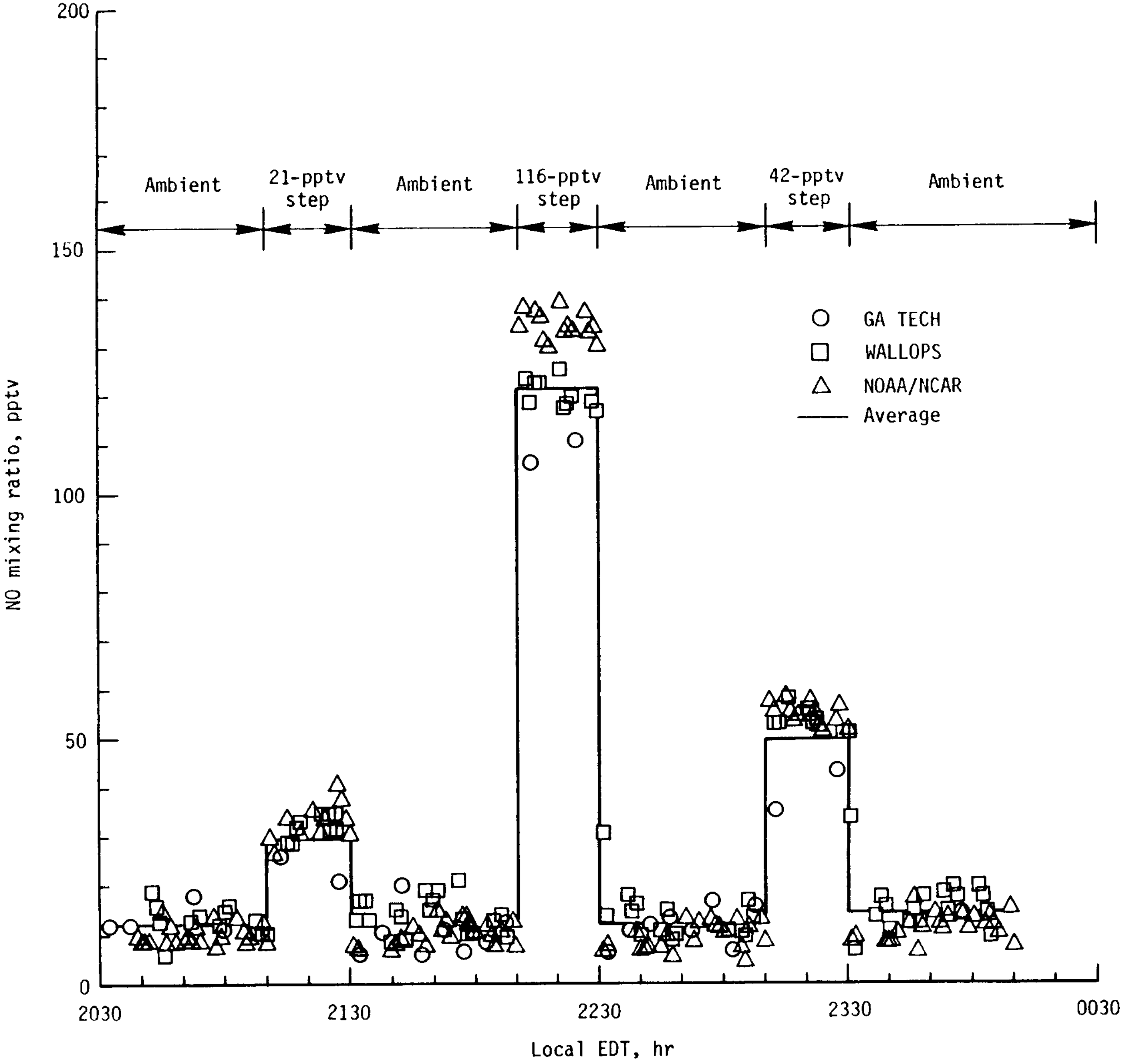
(a) Test N-4, July 28, 1983.

Figure 17.- Nitric oxide results for spiked-ambient test.



(b) Test N-3, July 29, 1983.

Figure 17.- Continued.



(c) Test N-4, July 29, 1983.

Figure 17.- Concluded.

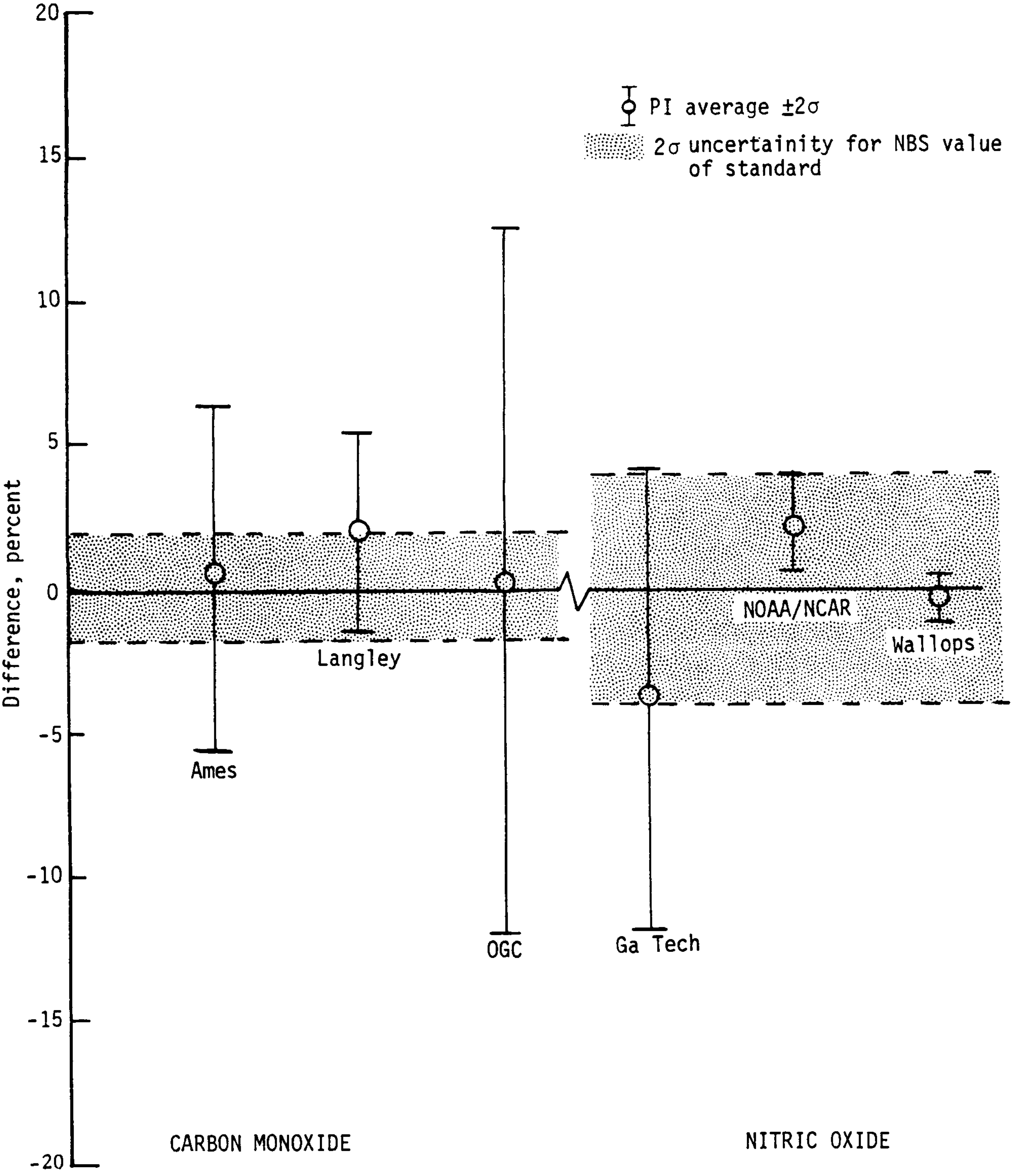


Figure 18.- Comparison of average difference between PI's measurements and between PI's measurement and gas standard (2σ level).

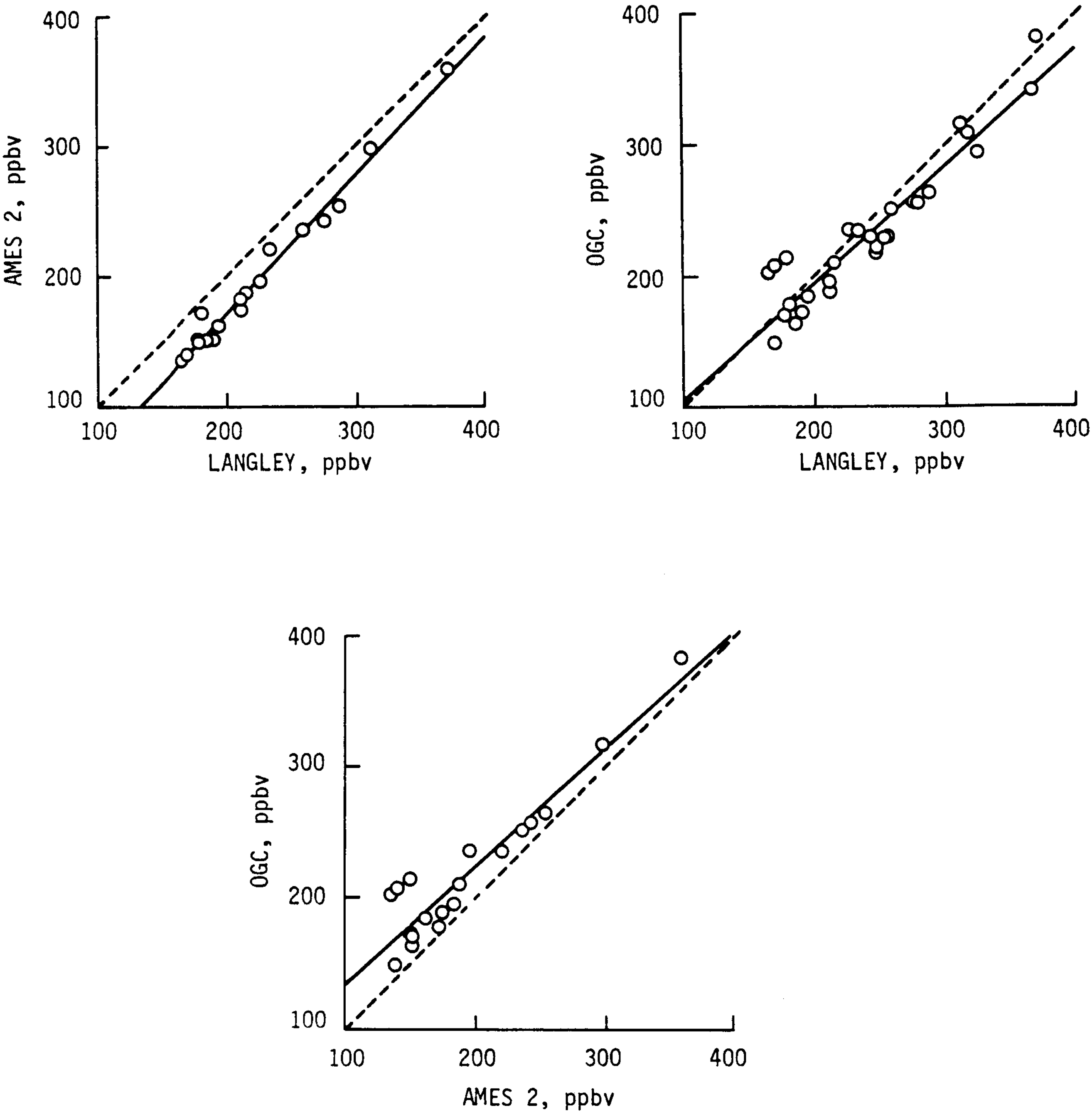


Figure 19.- Linear regression analysis of CO with data from ambient and spiked-ambient tests.

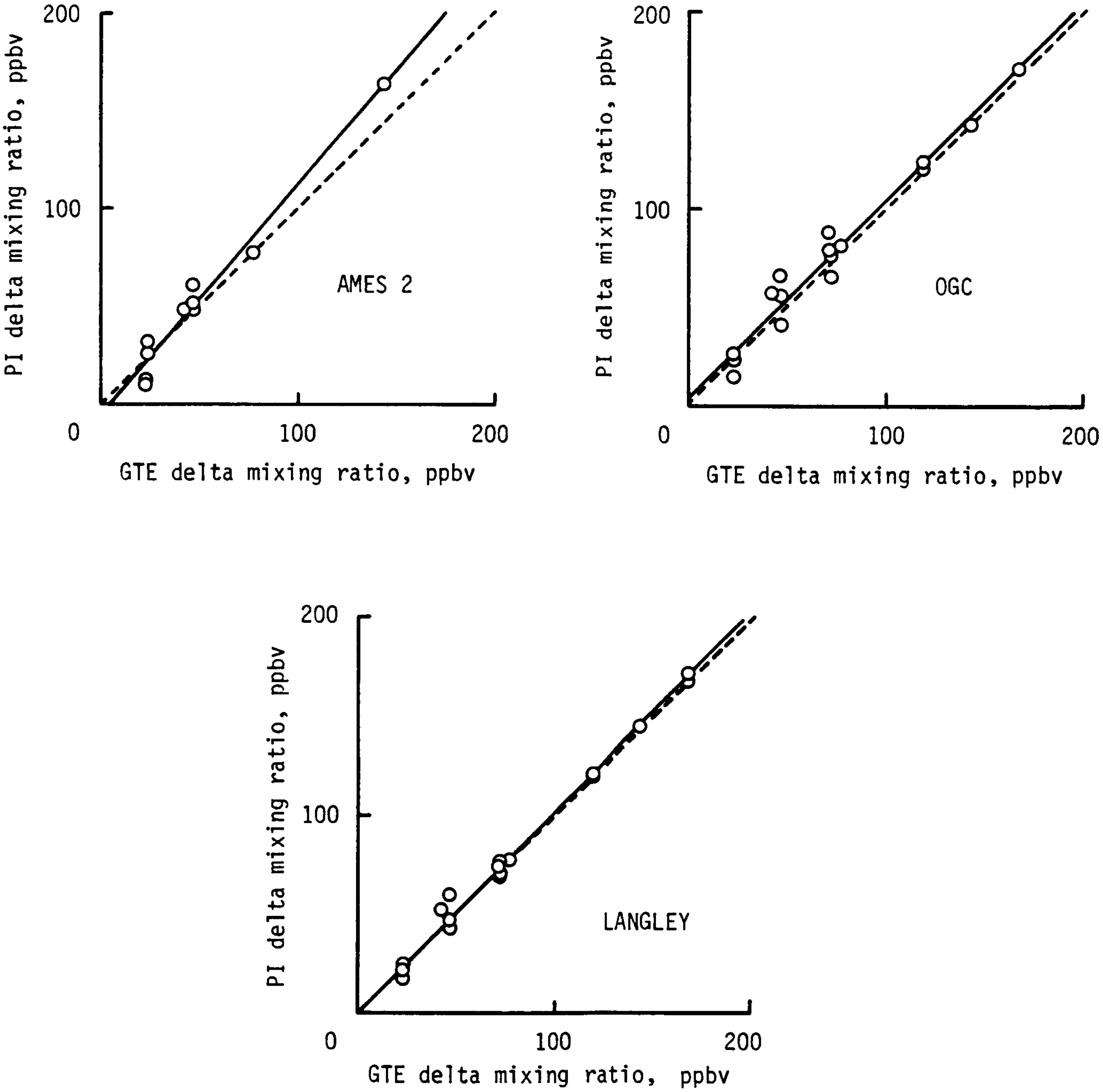


Figure 20.- Linear regression analysis of CO with data from spiked-ambient tests.

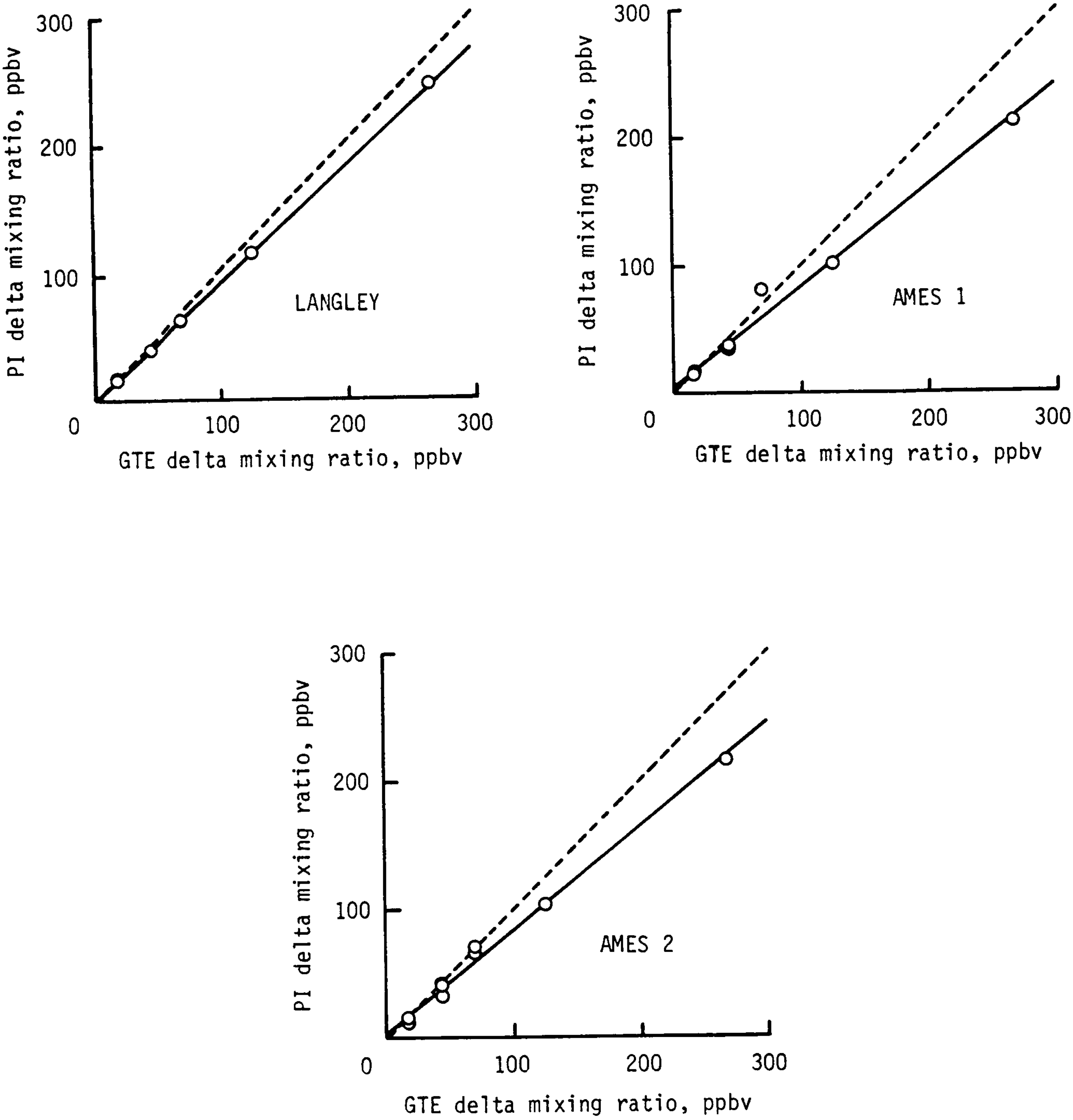


Figure 21.- Linear regression analysis of CO with data from spiked-nitrogen tests.

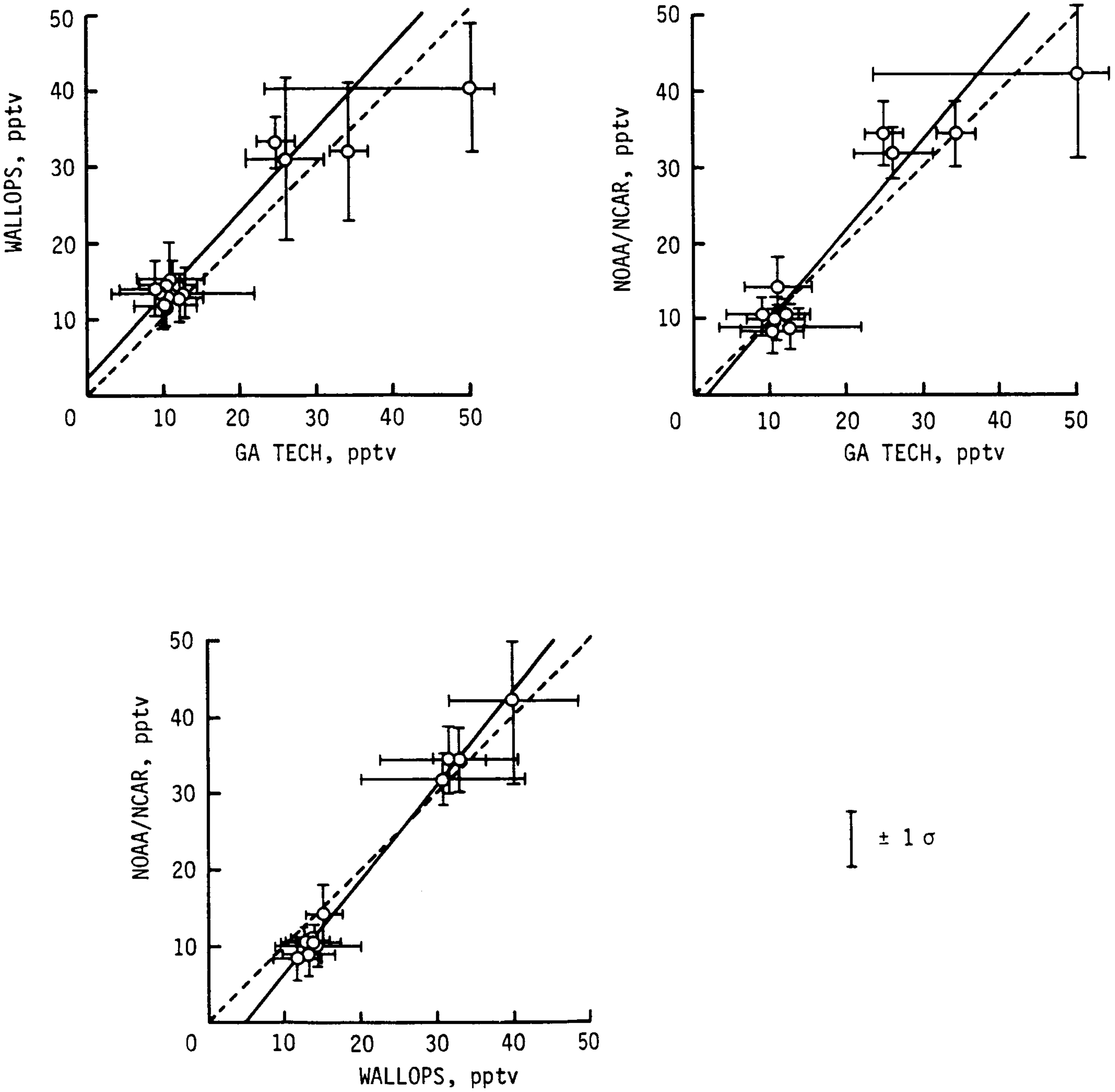


Figure 22.- Linear regression analyses of NO with data from ambient tests. NO < 50 pptv.

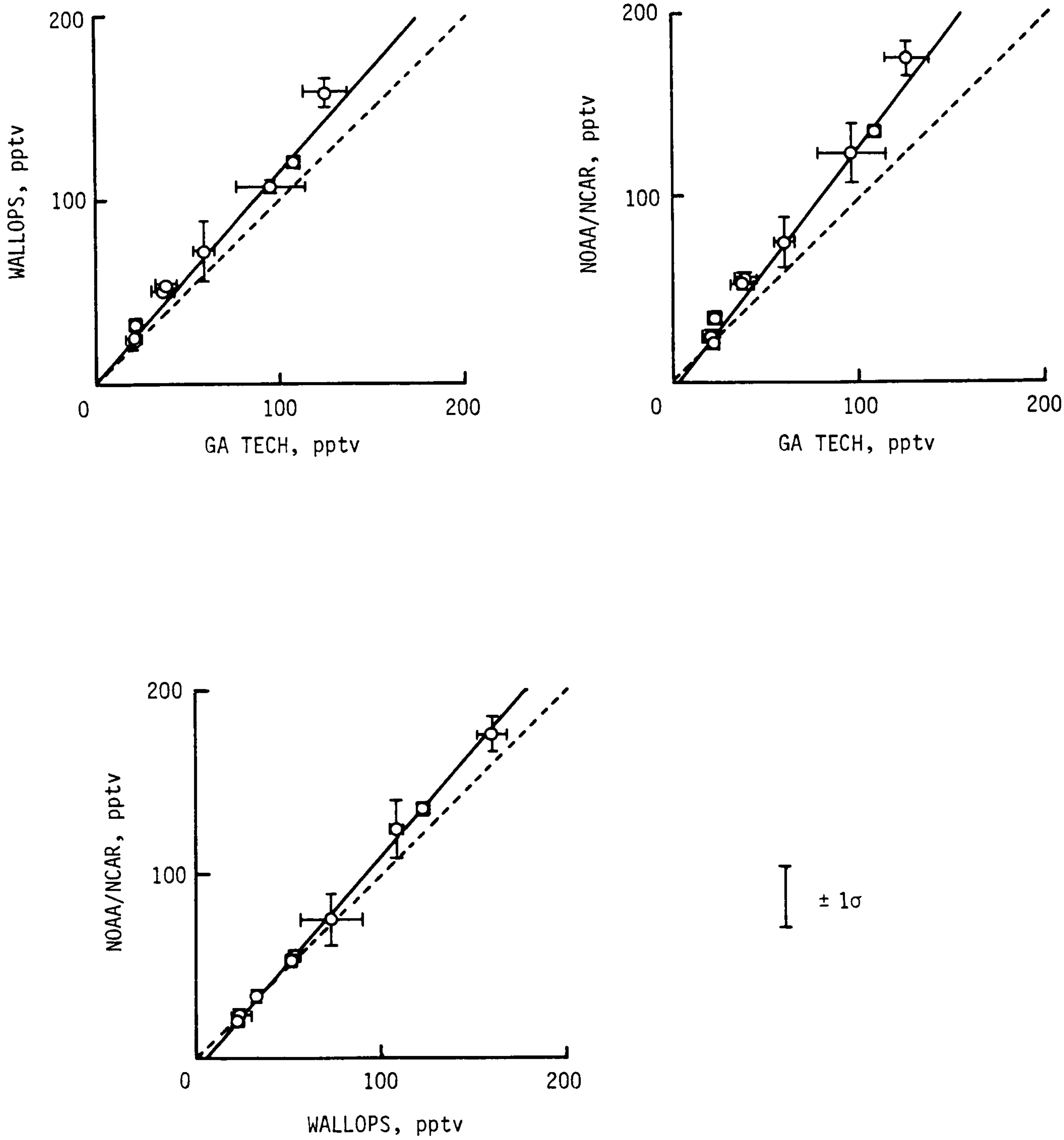


Figure 23.- Linear regression analyses of NO with data from spiked-ambient tests.

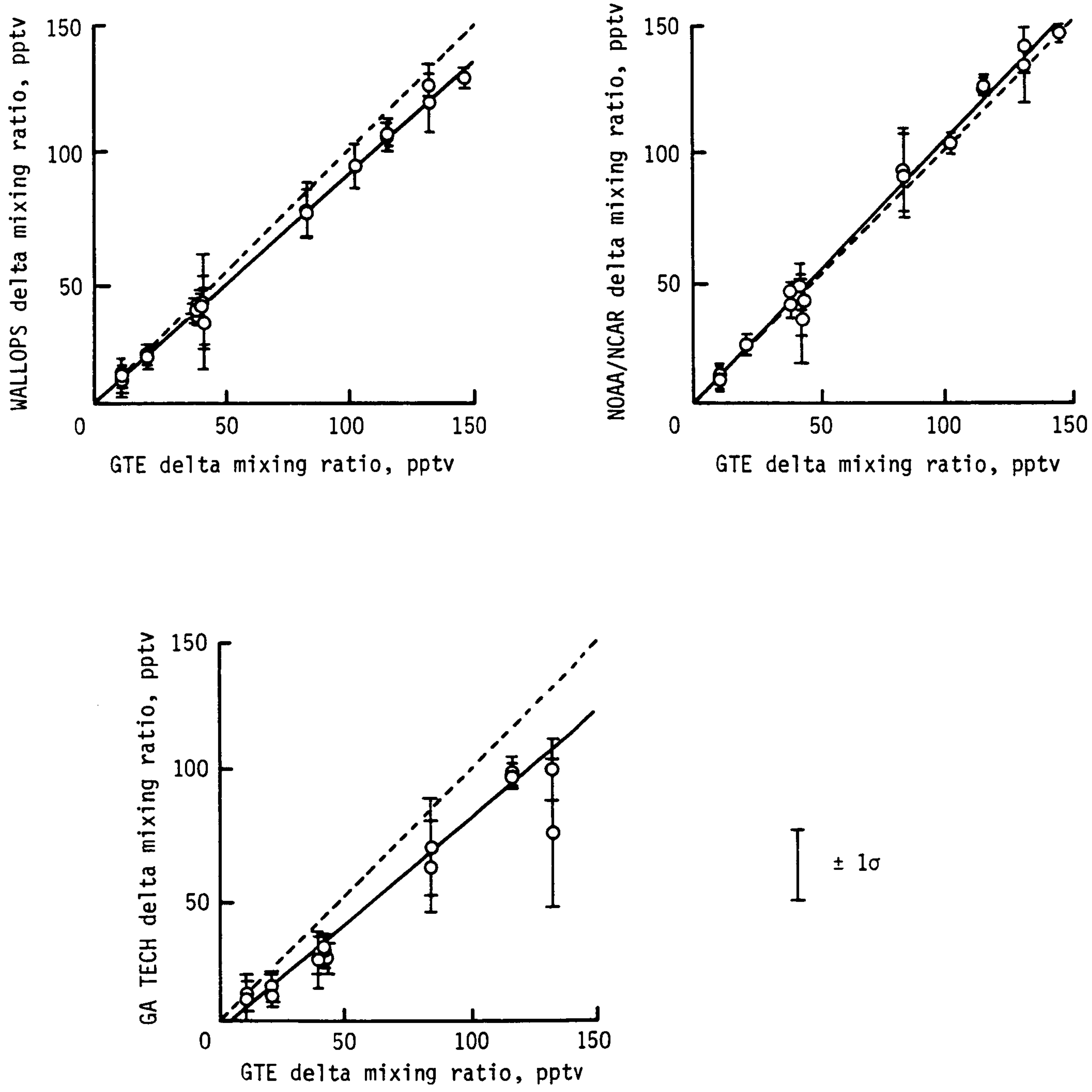


Figure 24.- Linear regression analyses of NO with data from spiked-ambient tests.

APPENDIX A

CO AND NO FORMAL TEST SEQUENCES

The test sequence for each of the eight formal CO and NO intercomparison tests are given in tables A1 and A2. The test designation code is as follows:

N-series tests are intercomparison tests for NO using the 75-mm ID primary manifold

C-series tests are intercomparison tests for CO using the 75-mm ID primary manifold

X-3-series tests are intercomparison tests for NO in nitrogen using the 25-mm ID calibration manifold

A 1 or 2 used in conjunction with the N- or C-series tests indicate ambient intercomparisons in which no spiked mixing ratios were added to the manifold; the 1 indicates daytime tests; 2, nighttime tests

A 3 or 4 used with N- or C-series test indicates spiked addition tests; the 3 is for daytime tests; 4, nighttime tests

Identified in the tables are those tests or test sequences which were excluded from the intercomparison analyses presented in the text. Data which were not available as the result of instrument problems are also noted in the last column. The nature of these problems is discussed in appendix B.

Figures A1 through A4 are plots of the NO data sets not used in the intercomparison analyses presented in the main text. As discussed in the text, these four NO tests did not include GA TECH (i.e., LIF technique) data. These data can be used to provide additional intercomparison between the two chemiluminescent techniques. All the valid CO data reported to the project for the formal CO intercomparison test periods are given in tables A3 through A10. Listed sample times are the midpoint times of the AMES 1 and OGC sample times (1 and 6 min, respectively) and the sample injection time for AMES 2. The LANGLEY data have been averaged over the appropriate sample times of the other techniques, for nitrogen (X-series) tests, they have been averaged over the entire step. All the valid NO data reported to the project for the formal NO intercomparison test periods are given in tables A11 through A13. The WALLOPS, NOAA/NCAR, and GA TECH results are given in the respective tables.

TABLE A1.- CO TEST SEQUENCE

Date	Test code	Step duration, min	Test value[a] of CO mixing ratio, ppbv, for -													Local EDT, hr	No data
			Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 10	Step 11	Step 12	Step 13		
July 8	C-3	[b]20	Ambient	41.6	94.8	140.6	Ambient									1000 to 1200	AMES 1
July 11	X-3	20	Nitrogen	17.8	Nitrogen	44.8	Nitrogen	69.6	Nitrogen							1000 to 1220	AMES 1 OGC
July 11	C-1	60	Ambient													1400 to 1500	AMES 1
July 12	C-4	[c]20	Ambient	23	46.5	92.9	46.9	23.2	Ambient							2000 to 2310	AMES 1
July 14	C-1	60	Ambient													0900 to 1000	AMES 1
July 14	X-3	[d]20	Nitrogen	17.1	Nitrogen	47.7	Nitrogen	69.7	Nitrogen							1300 to 1535	OGC
July 18	x-3	[e]30	Nitrogen	17.0	Nitrogen	126.1	Nitrogen	268.2	Nitrogen	378.6	Nitrogen					1530 to 1930	OGC
July 27	C-4	15	Ambient	164.3	Ambient	23.2	Ambient	71.1	Ambient	[f]516.0	Ambient	116.4	Ambient	69.7	Ambient	1700 to 2015	AMES 1 AMES 2

[a] Ambient, ambient air only; numeral entry, delta added to ambient or nitrogen; nitrogen, nitrogen only.
[b] Sampling period for steps 1 and 5 is 30 min.
[c] Sampling period for step 1 is 60 min; for step 7, 30 min.
[d] Sampling period for step 4 is 30 min; for step 6, 21 min; for step 7, 24 min.
[e] Sampling period for steps 5, 7, and 9 is 20 min.
[f] Test sequence invalid because of GTE flowmeter.

TABLE A2.- NO TEST SEQUENCE

Date	Test code	Step duration, min	Test value[a] of NO mixing ratio, pptv, for -							Local EDT, hr	No data
			Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7		
July 26[b]	N-2	120	Ambient							2100 to 2300	GA TECH
July 27[b]	N-2	60	Ambient							1900 to 2000	GA TECH
July 27[b]	N-4		Ambient	42.6	145.6	Ambient				2230 to 0050	GA TECH
July 28[b]	N-3	35	Ambient	34.9	Ambient	211	Ambient	[b]84.8	Ambient	1200 to 1605	GA TECH steps 1 to 5
July 28	N-4	35	Ambient	11.1	Ambient	39.3	Ambient	11.3	Ambient	2000 to 0005	
July 29	N-1	120	Ambient							1200 to 1400	
July 29	N-3	35	132.2	Ambient	42.7	Ambient	83.7	Ambient		1400 to 1730	
July 29	N-4	35	Ambient	21.1	Ambient	116.1	Ambient	41.6	Ambient	2000 to 0005	

[a] Ambient, ambient air only; numeral, delta added to ambient.

[b] Data not used for intercomparison analyses.

C-2

TABLE A3.- CO DATA[1] FOR TEST C-3, JULY 8, 1983

Condition	Local EDT, hr min sec	CO mixing ratio, ppbv, for -		
		LANGLEY	AMES 2	OGC
Step 1	100900	180.0	172.0	
(ambient)	101300	183.0		177.8
	102323	182.7	173.0	
Step 2	103922	235.6	221.0	
(delta)	104900	242.0		235.0
Step 3	105905	311.3	298.0	
(delta)	110230	310.0		316.6
	111023	347.8	320.0	
Step 4	112600	368.0		382.4
(delta)	112706	370.7	359.0	
Step 5	114844	212.7	200.0	
(ambient)	115100	230.0		235.5
	120413		192.0	

[1] AMES 1 data invalid.

TABLE A4.- CO DATA[a] FOR TEST X-3, JULY 11, 1983

Condition	Local EDT, hr min sec	CO mixing ratio, ppbv, for -	
		LANGLEY	AMES 2
Step 1 (nitrogen)	(b) 101002	3.0	(c)
Step 2 (delta)	(b) 102506	17.0	56.0
Step 3 (nitrogen)	(b) 104545	0.5	(c)
Step 4 (delta)	(b) 110548	40.7	47.5
Step 5 (nitrogen)	(b) 112537	1.0	16.0
Step 6 (delta)	(b) 114923	63	87.0
Step 7 (nitrogen)	(b) 120554	1.0	22.0

[a] AMES 1 and OGC data invalid.

[b] LANGLEY data averaged over entire step, excluding the first and last 30-sec transit periods.

[c] AMES 2 sample invalid.

TABLE A5.- CO DATA[a] FOR TEST C-1, JULY 11, 1983

Condition	Local EDT, hr min sec	CO mixing ratio, ppbv		
		LANGLEY	AMES 2	OGC
Ambient	141800	179.0		214.1
	142146	175.9	150.0	
	143400	170.0		207.8
	143509	168.5	140.0	
	144800	165.0		202.6
	145324	168.4	136.0	

[a] AMES 1 data invalid.

TABLE A6.- CO DATA[a] FOR TEST C-4, JULY 12, 1983

Condition	Local EDT, hr min sec	CO mixing ratio, ppbv, for -		
		LANGLEY	AMES 2	OGC
Step 1 (ambient)	191500			195.8
	200600	224.5	191.0	
	202115	193.0	151.0	
	203637	182.7	143.0	
	204500	179.0		169.7
	205125	176.6	152.0	
Step 2 (delta)	210621	195.9	162.0	
	211000	195.0		184.4
Step 3 (delta)	212711	216.3	188.0	
	213000	215.0		210.2
Step 4 (delta)	215100	260.0		251.2
	215117	258.9	236.0	
Step 5 (delta)	220820	211.6	184.0	
	221000	212.0		195.5
Step 6 (delta)	223050	190.8	152.0	
	223100	191.0		172.6
Step 7 (ambient)	224709	168.2	139.0	
	225700	170.0		148.8
	220850	172.4	139.0	

[a] AMES 1 data invalid.

TABLE A7.- CO DATA[a] FOR TEST C-1, JULY 14, 1983

Condition	Local EDT, hr min sec	CO mixing ratio, ppbv, for -		
		LANGLEY	AMES 2	OGC
Ambient	090632	289.3	254.0	
	090730	288.0		264.4
	092223	279.0	243.0	
	092315	276.0		257.1
	093430	212.0		188.9
	093758	206.7	175.0	
	095253	184.4	152.0	
	095400	186.0		163.7

[a] AMES 1 data invalid.

TABLE A8.- CO DATA[a] FOR TEST X-3, JULY 14, 1983

Condition	Local EDT, hr min sec	CO mixing ratio, ppbv, for -		
		LANGLEY	AMES 1	AMES 2
Step 1 (nitrogen)	(b)	1.0		
	131020		11.7	
	131128			11.8
	111815		11.7	
Step 2 (delta)	(b)	18.0		
	132847		26.0	
	133025			26.0
	133610		26.0	
Step 3 (nitrogen)	(b)	1.0		
	134700		11.7	
	135133			14.0
	135455		11.0	
Step 4 (delta)	(b)	41.0		
	140756			54.6
	140955		47.0	
	142402		47.0	
Step 5 (nitrogen)	(b)	2.0		
	143850		9.0	
	144530			11.8
Step 6 (delta)	(b)	64.0		
	145630		89.0	
	150615		91.0	
	(c)			(c)
Step 7 (nitrogen)	(b)	2.0		
	151830			9.5
	151910		9.0	

[a] OGC data invalid.

[b] LANGLEY data averaged over entire step, excluding the first and last 30-sec transit periods.

[c] AMES 2 sample not taken.

TABLE A9.- CO DATA[a] FOR TEST X-3, JULY 18, 1983

Condition	Local EDT, hr min sec	CO mixing ratio, ppbv, for -		
		LANGLEY	AMES 1	AMES 2
Step 1 (nitrogen)	(b)	1.0		
	154530		0	
	155520		0	
	155750			0
Step 2 (delta)	(b)	16.0		
	161130		12.0	
	161210		15.0	
	161544			
Step 3 (nitrogen)	(b)	1.0		
	163350		0	0
	163745		0	
	165150			
Step 4 (delta)	(b)	115.0		
	170716			103.0
	171020		104.0	
	172147		99.0	
	172530			103.0
Step 5 (nitrogen)	(b)	0		
	173710		0	
	174222			0
	174420		0	
Step 6 (delta)	(b)	247.0		
	175806			213.0
	175920		213.0	
	181424			217.0
	181515		212.0	
Step 7 (nitrogen)	(b)	1.0		
	183003			0
	183300		0	
Step 8 (delta)	(b)	345.0		
	185520		307.0	
	190222		309.0	
	190225			312.0
	190700		308.0	
Step 9 (nitrogen)	(b)	1.0		
	191740		(c)	0
	191920			0

[a] OGC data invalid.

[b] LANGLEY data averaged over entire step, excluding the first and last 30-sec transit periods.

[c] AMES 1 sample not taken.

TABLE A10.- CO DATA[a] FOR TEST C-4, JULY 27, 1983

Condition	Local EDT, hr min sec	CO mixing ratio, ppbv, for -	
		LANGLEY	OGC
Step 1 (ambient)	171000	260.5	
Step 2 (delta)	172830	429.0	400.9
Step 3 (ambient)	174000	257.0	230.2
Step 4 (delta)	175200	279.5	255.8
Step 5 (ambient)	180700	254.0	229.6
Step 6 (delta)	182200	325.0	294.8
Step 7 (ambient)	183700	248.5	218.8
Step 8[b] (delta)	185200	810.0	788.0
Step 9 (ambient)	190700	247.0	218.8
Step 10 (delta)	192200	368.0	342.6
Step 11 (ambient)	193700	248.0	222.0
Step 12 (delta)	195200	317.5	310.1
Step 13 (ambient)	200700	243.0	230.7

[a] AMES 1 and 2 data invalid.

[b] Not included in analyses because of GTE flowmeter operational problem.

TABLE A11.- WALLOPS NO DATA FOR INTERCOMPARISON TESTS

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
Test N-2, July 26, ambient		
204237	204337	25.0
204308	204408	18.0
204339	204439	18.0
204411	204511	14.0
204442	204542	8.0
204513	204613	21.0
204547	204647	12.0
204618	204718	10.0
205058	205158	14.0
205129	205229	13.0
205201	205301	11.0
205232	205332	24.0
205303	205403	22.0
205334	205434	23.0
205405	205505	13.0
205436	205536	13.0
205917	210017	22.0
205948	210048	19.0
210022	210122	28.0
210053	210153	23.0
210124	210224	34.0
210155	210255	22.0
210226	210326	17.0
210258	210358	20.0
210738	210838	22.0
210809	210909	21.0
210840	210940	15.0
210911	211011	7.0
210945	211045	16.0
211016	211116	15.0
211047	211147	11.0
211119	211219	9.0
211559	211659	20.0
211630	211730	14.0
211701	211801	18.0
211733	211833	16.0
211804	211904	27.0
211835	211935	40.0
211909	212009	24.0
211940	212040	13.0
212420	212520	26.0
212451	212551	16.0
212522	212622	16.0
212554	212654	17.0
212625	212725	20.0
212656	212756	17.0
212727	212827	19.0
212758	212858	13.0
213239	213339	26.0
213310	213410	11.0
213344	213444	10.0
213415	213515	22.0
213446	213546	19.0
213517	213617	10.0
213548	213648	14.0
213620	213720	13.0
214100	214200	23.0
214131	214231	13.0
214202	214302	12.0
214233	214333	16.0
214307	214407	10.0
214338	214438	10.0
214409	214509	9.0
214441	214541	14.0
214921	215021	17.0
214952	215052	19.0
215023	215123	17.0
215055	215155	18.0
215126	215226	17.0
215157	215257	18.0
215231	215331	23.0
215302	215402	18.0
215742	215842	26.0
215813	215913	15.0
215844	215944	22.0
215916	220016	26.0
215947	220047	24.0
220018	220118	18.0
220049	220149	15.0
220120	220220	20.0
220601	220701	20.0
220632	220732	14.0
220706	220806	19.0
220737	220837	14.0
220808	220908	19.0
220839	220939	19.0
220910	221010	20.0
220942	221042	20.0
221422	221522	18.0
221453	221553	27.0
221524	221624	20.0
221555	221655	22.0

TABLE A11.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
221629	221729	24.0
221700	221800	17.0
221732	221832	15.0
221803	221903	26.0
222243	222343	20.0
222314	222414	15.0
222345	222445	21.0
222417	222517	16.0
222448	222548	19.0
222519	222619	19.0
222553	222653	13.0
222624	222724	21.0
223104	223204	20.0
223135	223235	19.0
223207	223307	14.0
223238	223338	18.0
223309	223409	27.0
223340	223440	20.0
223411	223511	18.0
223443	223543	14.0
223923	224023	21.0
223954	224054	20.0
224028	224128	19.0
224059	224159	25.0
224130	224230	15.0
224201	224301	16.0
224233	224333	26.0
224304	224404	15.0
224744	224844	16.0
224815	224915	15.0
224846	224946	16.0
224918	225018	13.0
224951	225051	15.0
225023	225123	14.0
225054	225154	21.0
225125	225225	15.0
225605	225705	19.0
225708	225808	11.0
225739	225839	17.0
225810	225910	16.0
225841	225941	27.0
Test N-2, July 27, ambient		
185442	185542	78.0
185543	185643	74.0
185644	185744	75.0
185746	185846	77.0
190152	190252	70.0
190254	190354	69.0
190355	190455	64.0
190457	190557	71.0
190901	191001	68.0
191002	191102	74.0
191106	191206	78.0
191207	191307	69.0
191612	191712	76.0
191713	191813	79.0
191814	191914	80.0
191916	192016	79.0
192322	192422	75.0
192424	192524	68.0
192525	192625	73.0
192626	192726	73.0
193033	193133	64.0
193134	193234	63.0
193236	193336	70.0
193337	193437	65.0
193741	193841	64.0
193842	193942	66.0
193946	194046	63.0
194048	194148	66.0
194452	194552	64.0
194553	194653	62.0
194655	194755	57.0
194756	194856	58.0
195203	195303	50.0
195304	195404	53.0
195405	195505	51.0
195507	195607	49.0
195913	200013	46.0
Test N-4, July 27, step 1 (ambient)		
223842	223942	19.0
223943	224043	19.0
224044	224144	12.0
224146	224246	22.0
224653	224753	12.0
224755	224855	16.0
224856	224956	15.0
224958	225058	19.0
225505	225605	16.0
225607	225707	19.0

TABLE A11.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
225708	225808	15.0
225809	225909	11.0
230317	230417	21.0
230419	230519	[a]33.0
Test N-4, July 27, step 2 (delta)		
230520	230620	51.0
230621	230721	51.0
231129	231229	55.0
231231	231331	54.0
231332	231432	53.0
231433	231533	48.0
231939	232039	53.0
232043	232143	53.0
232144	232244	51.0
232245	232345	51.0
232751	232851	56.0
232852	232952	52.0
232956	233056	47.0
233057	233157	50.0
233603	233703	45.0
233704	233804	51.0
233909	234009	[a]49.0
Test N-4, July 27, step 3 (delta)		
234415	234515	140.0
234516	234616	142.0
234618	234718	144.0
234719	234819	146.0
235227	235327	143.0
235328	235428	142.0
235430	235530	146.0
235531	235631	148.0
0039	0139	145.0
0140	0240	141.0
0242	0342	141.0
0343	0443	141.0
0851	0951	142.0
0952	1052	140.0
1054	1154	143.0
1155	1255	140.0

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
Test N-4, July 27, step 4 (ambient)		
1703	1803	13.0
1804	1904	8.0
1906	2006	9.0
2007	2107	18.0
2512	2612	14.0
2616	2716	11.0
2717	2817	11.0
2819	2919	15.0
3324	3424	19.0
3426	3526	18.0
3529	3629	19.0
3631	3731	11.0
4136	4236	15.0
4238	4338	14.0
4339	4439	11.0
4948	5048	11.0
5050	5150	10.0
5151	5251	11.0
5253	5353	17.0
Test N-3, July 28, step 1 (ambient)		
114945	115045	98.0
115046	115146	87.0
115147	115247	95.0
115552	115652	218.0
115655	115755	106.0
115757	115857	95.0
120206	120306	83.0
120307	120407	84.0
120408	120508	78.0
120815	120915	111.0
120916	121016	95.0
121018	121118	80.0
121422	121522	71.0
121523	121623	73.0
121627	121727	67.0
122031	122131	59.0
122133	122233	62.0
122234	122334	66.0

[a] GTE delta changed during sampling period.

TABLE A11.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
122641	122741	70.0
122742	122842	74.0
122844	122944	73.0
123248	123348	71.0
123349	123449	62.0
123451	123551	[a]87.0
Test N-3, July 28, step 2 (delta)		
123857	123957	103.0
123959	124059	97.0
124100	124200	101.0
124504	124604	105.0
124608	124708	824.0
124710	124810	1428.0
125114	125214	92.0
125215	125315	89.0
125317	125417	89.0
125723	125823	90.0
125825	125925	95.0
125926	130026	95.0
130330	130430	87.0
130432	130532	97.0
130535	130635	94.0
130941	131041	[a]77.0
Test N-3, July 28, step 3 (ambient)		
131042	131142	70.0
131144	131244	71.0
131550	131650	82.0
131652	131752	76.0
131753	131853	79.0
133136	133236	106.0
133237	133337	118.0
133339	133439	126.0
133743	133843	103.0
133847	133947	112.0
133948	134048	109.0
134352	134452	104.0
134454	134554	[a]258.0
Test N-3, July 28, step 4 (delta)		
134555	134655	289.0
135002	135102	283.0
135103	135203	288.0
135205	135305	288.0
135609	135709	272.0
135710	135810	271.0
135814	135914	271.0
140218	140318	265.0
140320	140420	264.0
140421	140521	267.0
140828	140928	251.0
140929	141029	258.0
141030	141130	242.0
141435	141535	247.0
141536	141636	257.0
141637	141737	246.0
Test N-3, July 28, step 5 (ambient)		
142044	142144	67.0
142145	142245	65.0
142247	142347	71.0
142651	142751	65.0
142755	142855	70.0
142856	142956	64.0
143301	143401	57.0
143402	143502	65.0
143503	143603	56.0
144847	144947	57.0
144948	145048	64.0
145052	145152	73.0
145456	145556	[a]125.0
Test N-3, July 28, step 6 (delta)		
145557	145657	138.0
145659	145759	131.0
150105	150205	121.0
150207	150307	126.0
150308	150408	124.0
150712	150812	120.0
150814	150914	119.0
150915	151015	121.0

[a] GTE delta changed during sampling period.

TABLE A11.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
151322	151422	116.0
151423	151523	127.0
151524	151624	121.0
151929	152029	121.0
152033	152133	481.0
152134	152234	727.0
152640	152740	130.0
152741	152841	128.0
Test N-3, July 28, step 7 (ambient)		
153148	153248	79.0
153249	153349	86.0
153350	153450	90.0
153755	153855	99.0
153856	153956	95.0
154000	154100	86.0
154404	154504	65.0
154506	154606	69.0
154607	154707	62.0
155016	155116	69.0
155118	155218	70.0
155219	155319	65.0
155623	155723	61.0
155725	155825	66.0
155826	155926	58.0
160233	160333	54.0
160334	160434	56.0
160435	160535	50.0
Test N-4, July 28, step 1 (ambient)		
201732	201832	9.0
201834	201934	15.0
201935	202035	10.0
202036	202136	20.0
202544	202644	10.0
202645	202745	15.0
202747	202847	11.0
202848	202948	16.0
203356	203456	22.0
203457	203557	[a]27.0

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
Test N-4, July 28, step 2 (delta)		
203559	203659	16.0
203700	203800	15.0
204208	204308	22.0
204309	204409	26.0
204411	204511	26.0
204512	204612	26.0
205020	205120	23.0
205151	205221	20.0
205223	205323	25.0
205324	205424	35.0
205830	205930	28.0
205933	210033	33.0
210035	210135	27.0
210136	210236	27.0
210642	210742	16.0
210743	210843	19.0
210847	210947	26.0
210948	211048	[a]20.0
Test N-4, July 28, step 3 (ambient)		
211454	211554	13.0
211555	211655	16.0
211656	211756	18.0
211800	211900	13.0
212306	212406	13.0
212407	212507	13.0
212508	212608	12.0
212610	212710	16.0
213118	213218	14.0
213219	213319	14.0
213320	213420	17.0
213422	213522	15.0
213930	214030	15.0
214031	214131	15.0
214132	214232	20.0
214234	214334	15.0
Test N-4, July 28, step 4 (delta)		
214742	214842	51.0
214843	214943	52.0
214945	215045	56.0

[a] GTE delta changed during sampling period.

TABLE A11.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
215046	215146	53.0
215557	215657	48.0
215659	215759	50.0
215800	215900	49.0
215901	220001	50.0
220407	220507	51.0
220511	220611	55.0
220612	220712	47.0
220713	220813	44.0
221219	221319	45.0
221320	221420	54.0
221424	221524	55.0
221525	221625	48.0
Test N-4, July 28, step 5 (ambient)		
222031	222131	10.0
222133	222233	16.0
222234	222334	13.0
222338	222438	10.0
224023	224123	8.0
224125	224225	11.0
224226	224326	12.0
224327	224427	18.0
224835	224935	18.0
224936	225036	18.0
225038	225138	11.0
225139	225239	14.0
Test N-4, July 28, step 6 (delta)		
231901	232001	22.0
232002	232102	22.0
232103	232203	23.0
232205	232305	26.0
232712	232812	21.0
232814	232914	25.0
232915	233015	[a]24.0
Test N-4, July 28, step 7 (ambient)		
233016	233116	12.0
233524	233624	12.0
233626	233726	7.0
233727	233827	11.0
233828	233928	14.0
234336	234436	13.0
234438	234538	15.0
234539	234639	10.0
234640	234740	14.0
235148	235248	11.0
235250	235350	10.0
235351	235451	17.0
235452	235552	6.0
Test N-1, July 29, ambient		
120901	121001	54.0
121002	121102	49.0
121104	121204	45.0
121612	121712	39.0
121713	121813	52.0
121814	121914	46.0
121916	122016	46.0
122424	122524	39.0
122525	122625	34.0
122626	122726	38.0
122728	122828	42.0
123236	123336	40.0
123337	123437	40.0
123438	123538	42.0
123540	123640	44.0
124048	124148	35.0
124149	124249	38.0
124250	124350	43.0
124352	124452	40.0
124857	124957	36.0
125001	125101	32.0
125102	125202	36.0
125204	125304	32.0
125709	125809	38.0
125811	125911	36.0
125914	130014	33.0
130016	130116	29.0
130521	130621	41.0
130724	130824	26.0
130828	130928	31.0
131333	131433	37.0
131435	131535	44.0
131536	131636	37.0

[a]GTE delta changed during sampling period.

TABLE A11.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
131637	131737	29.0
132145	132245	28.0
132247	132347	24.0
132348	132448	26.0
132449	132549	23.0
132957	133057	25.0
133059	133159	23.0
133200	133300	16.0
133301	133401	15.0
134847	134947	29.0
134950	135050	35.0
135052	135152	36.0
135153	135253	29.0
135659	135759	37.0
135800	135900	32.0
Test N-3, July 29, step 1 (delta)		
135904	140004	[a]41.0
140005	140105	162.0
140511	140611	150.0
140612	140712	161.0
140713	140813	156.0
140817	140917	152.0
141323	141423	162.0
141424	141524	158.0
141525	141625	156.0
141627	141727	157.0
142135	142235	152.0
142236	142336	161.0
142337	142437	157.0
142439	142539	168.0
142947	143047	149.0
143048	143148	183.0
143149	143249	160.0
143251	143351	162.0
Test N-3, July 29, step 2 (ambient)		
143759	143859	40.0
143900	144000	39.0
144001	144101	40.0
144103	144203	43.0
144611	144711	46.0
144712	144812	52.0
144813	144913	48.0
144915	145015	61.0
145420	145520	29.0
145524	145624	34.0
145625	145725	41.0
145727	145827	37.0
150232	150332	35.0
150334	150434	34.0
150437	150537	30.0
150539	150639	33.0
Test N-3, July 29, step 3 (delta)		
151044	151144	74.0
151146	151246	80.0
151247	151347	121.0
151351	151451	99.0
151856	151956	65.0
151958	152058	78.0
152059	152159	69.0
152200	152300	62.0
152708	152808	63.0
152810	152910	67.0
152911	153011	61.0
153520	153620	65.0
153622	153722	59.0
153723	153823	65.0
153824	153924	70.0
154332	154432	59.0
154434	154534	[a]51.0
Test N-3, July 29, step 4 (ambient)		
154535	154635	37.0
154636	154736	40.0
155144	155244	30.0
155246	155346	20.0
155347	155447	29.0
155448	155548	27.0
161034	161134	26.0
161135	161235	22.0

[a] GTE delta changed during sampling period.

TABLE A11.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
161237	161337	28.0
161340	161440	39.0
161846	161946	35.0
161947	162047	[a]102.0
Test N-3, July 29, step 5 (delta)		
162048	162148	115.0
162150	162250	106.0
162658	162758	108.0
162759	162859	110.0
162900	163000	112.0
163002	163102	107.0
163510	163610	105.0
163611	163711	106.0
163712	163812	106.0
163814	163914	107.0
164322	164422	106.0
164423	164523	112.0
164524	164624	106.0
164626	164726	104.0
165235	165335	105.0
165336	165436	104.0
165438	165538	[a]70.0
Test N-3, July 29, step 6 (ambient)		
165943	170043	33.0
170047	170147	29.0
170148	170248	27.0
170250	170350	28.0
170755	170855	28.0
170857	170957	26.0
171000	171100	26.0
171102	171202	29.0
171607	171707	27.0
171709	171809	29.0
171810	171910	26.0
171914	172014	38.0
172419	172519	25.0
172521	172621	26.0
172622	172722	24.0
172723	172823	32.0

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
Test N-4, July 29, step 1 (ambient)		
204115	204215	19.0
204217	204317	16.0
204318	204418	13.0
204419	204519	6.0
204927	205027	9.0
205029	205129	13.0
205130	205230	9.0
205231	205331	14.0
205739	205839	12.0
205841	205941	15.0
205942	210042	16.0
210043	210143	13.0
210551	210651	13.0
210653	210753	11.0
210754	210854	11.0
210855	210955	10.0
Test N-4, July 29, step 2 (delta)		
211403	211503	29.0
211505	211605	29.0
211606	211706	32.0
211707	211807	33.0
212213	212313	31.0
212317	212417	35.0
212418	212518	32.0
212519	212619	35.0
Test N-4, July 29, step 3 (ambient)		
213025	213125	13.0
231126	213226	17.0
213230	213330	17.0
213331	213431	13.0
213837	213937	9.0
213938	214038	15.0
214039	214139	14.0
214143	214243	9.0
214649	214749	19.0
214750	214850	15.0
214851	214951	17.0
214953	215053	19.0

[a] GTE delta changed during sampling period.

TABLE A11.- Concluded

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
215501	215601	21.0
215602	215702	13.0
215703	215803	10.0
215805	215905	10.0
220313	220413	13.0
220414	220514	10.0
220515	220615	14.0
220617	220717	10.0
Test N-4, July 29, step 4 (delta)		
221125	221225	124.0
221226	221326	119.0
221327	221427	123.0
221429	221529	123.0
221937	222037	126.0
222038	222138	118.0
222139	222239	119.0
222241	222341	120.0
222746	222846	119.0
222850	222950	117.0
Test N-4, July 29, step 5 (ambient)		
222951	223051	[a]31.0
223053	223153	14.0
223558	223658	18.0
223700	223800	15.0
223803	223903	16.0
223905	224005	10.0
224410	224510	11.0
224512	224612	15.0
224613	224713	9.0
224717	224817	10.0
230302	230402	11.0
230404	230504	10.0
230505	230605	17.0
230606	230706	14.0
Test N-4, July 29, step 6 (delta)		
231114	231214	53.0
231216	231316	53.0
231317	231417	56.0
231418	231518	58.0
231926	232026	56.0
232028	232128	53.0
232129	232229	54.0
232230	232330	52.0
232736	232826	51.0
232840	232940	51.0
232941	233041	[a]34.0
Test N-4, July 29, step 7 (ambient)		
233042	233142	7.0
233548	233648	14.0
233649	233749	18.0
233753	233853	16.0
233854	233954	11.0
234400	234500	13.0
234501	234601	15.0
234602	234702	13.0
234706	234806	18.0
235212	235312	19.0
235313	235413	15.0
235414	235514	20.0
235516	235616	18.0
10024	0124	20.0
10124	0225	18.0
0226	0326	15.0
0328	0428	10.0

[a] GTE delta changed during sampling period.

TABLE A12.- NOAA/NCAR NO DATA FOR INTERCOMPARISON TESTS

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
Test N-2, July 26, ambient		
205800	205900	16.0
205900	210000	10.0
210600	210700	15.0
210700	210800	10.0
210800	210900	12.0
210900	211000	13.0
211200	211300	15.0
211300	211400	7.0
211400	211500	11.0
211500	211600	10.0
211800	211900	16.0
211900	212000	12.0
212000	212100	11.0
212100	212200	9.0
212900	213000	7.0
213000	213100	10.0
213700	213800	12.0
213800	213900	7.0
213900	214000	15.0
214000	214100	10.0
214300	214400	17.0
214400	214500	14.0
214500	214600	9.0
214600	214700	15.0
214900	215000	14.0
215000	215100	19.0
215100	215200	13.0
215200	215300	12.0
220000	220100	7.0
220100	220200	7.0
220800	220900	9.0
220900	221000	11.0
221000	221100	8.0
221100	221200	14.0
221400	221500	15.0
221500	221600	22.0
221600	221700	13.0
221700	221800	9.0
222000	222100	11.0
222100	222200	11.0
222200	222300	14.0
222300	222400	9.0
223100	223200	11.0
223200	223300	9.0
223900	224000	12.0
224000	224100	10.0
224100	224200	10.0
224200	224300	11.0
224500	224600	12.0
224600	224700	10.0
224700	224800	9.0
224800	224900	11.0
225100	225200	8.0
225200	225300	11.0
225300	225400	12.0
225400	225500	9.0
Test N-2, July 27, ambient		
190000	190100	149.0
190100	190200	148.0
190800	190900	155.0
190900	191000	154.0
191000	191100	161.0
191100	191200	160.0
191400	191500	174.0
191500	191600	175.0
191600	191700	176.0
191700	191800	187.0
192000	192100	181.0
192100	192200	184.0
192200	192300	185.0
192300	192400	180.0
193100	193200	155.0
193200	193300	155.0
193900	194000	151.0
194000	194100	145.0
194100	194200	150.0
194200	194300	141.0
194600	194700	135.0
194700	194800	137.0
194800	194900	124.0
194900	195000	133.0
195200	195300	127.0
195300	195400	119.0
195400	195500	116.0
195500	195600	116.0
Test N-4, July 27, step 1 (ambient)		
223000	223100	12.0
223100	223200	14.0

TABLE A12.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
223800	223900	13.0
223900	224000	11.0
224000	224100	14.0
224100	224200	13.0
224400	224500	13.0
224500	224600	14.0
224600	224700	13.0
224700	224800	14.0
225000	225100	16.0
225100	225200	22.0
225200	225300	14.0
225300	225400	14.0
Test N-4, July 27, step 2 (delta)		
230700	230800	55.0
230800	230900	59.0
231500	231600	56.0
231600	231700	51.0
231700	231800	49.0
231800	231900	54.0
232100	232200	51.0
232200	232300	56.0
232300	232400	58.0
232400	232500	52.0
232700	232800	58.0
232800	232900	58.0
232900	233000	53.0
233000	233100	53.0
Test N-4, July 27, step 3 (delta)		
234200	234300	162.0
234300	234400	160.0
235000	235100	161.0
235100	235200	158.0
235200	235300	154.0
235300	235400	159.0
235600	235700	156.0
235700	235800	156.0
235800	235900	155.0
235900	0000	158.0
0200	0300	154.0
0300	0400	155.0
0400	0500	154.0
0500	0600	156.0

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
Test N-4, July 27, step 4 (ambient)		
1700	1800	11.0
1800	1900	12.0
2500	2600	12.0
2600	2700	14.0
2700	2800	9.0
2800	2900	7.0
3100	3200	15.0
3200	3300	10.0
3300	3400	7.0
3400	3500	10.0
3700	3800	13.0
3800	3900	10.0
3900	4000	13.0
4000	4100	9.0
Test N-3, July 28, step 1 (ambient)		
120000	120100	98.0
120100	120200	100.0
120800	120900	132.0
120900	121000	120.0
121000	121100	88.0
121100	121200	85.0
121400	121500	93.0
121500	121600	91.0
121600	121700	85.0
121700	121800	88.0
122000	122100	83.0
122100	122200	78.0
122200	122300	82.0
122300	122400	79.0
Test N-3, July 28, step 2 (delta)		
123700	123800	108.0
123800	123900	99.0
124500	124600	102.0
124600	124700	692.0
124700	124800	1732.0
124800	124900	809.0
125100	125200	109.0
125200	125300	102.0
125300	125400	100.0
125400	125500	109.0
125700	125800	97.0

TABLE A12.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
125800	125900	102.0
125900	130000	100.0
130000	130100	105.0
Test N-3, July 28, step 3 (ambient)		
131200	131300	73.0
131300	131400	77.0
132000	132100	98.0
132100	132200	95.0
132200	132300	99.0
132300	132400	93.0
132600	132700	102.0
132700	132800	100.0
132800	132900	102.0
132900	133000	103.0
133200	133300	107.0
133300	133400	149.0
133400	133500	123.0
133500	133600	117.0
Test N-3, July 28, step 4 (delta)		
134700	134800	328.0
134800	134900	323.0
135500	135600	312.0
135600	135700	310.0
135700	135800	310.0
135800	135900	308.0
140100	140200	296.0
140200	140300	309.0
140300	140400	297.0
140400	140500	302.0
140700	140800	293.0
140800	140900	283.0
140900	141000	291.0
141000	141100	279.0
Test N-3, July 28, step 5 (ambient)		
142200	142300	70.0
142300	142400	72.0
143000	143100	75.0
143100	143200	73.0
143200	143300	66.0
143300	143400	59.0
143600	143700	73.0
143700	143800	71.0
143800	143900	71.0
143900	144000	70.0
144200	144300	75.0
144300	144400	75.0
144400	144500	71.0
144500	144600	65.0
Test N-3, July 28, step 6 (delta)		
145900	150000	119.0
150000	150100	122.0
150700	150800	146.0
150800	150900	144.0
150900	151000	162.0
151000	151100	157.0
151300	151400	170.0
151400	151500	174.0
151500	151600	183.0
151600	151700	185.0
151900	152000	210.0
152000	152100	412.0
152100	152200	1191.0
152200	152300	1412.0
Test N-3, July 28, step 7 (ambient)		
153200	153300	84.0
153300	153400	89.0
154000	154100	85.0
154100	154200	85.0
154200	154300	80.0
154300	154400	77.0
154600	154700	69.0
154700	154800	64.0
154800	154900	67.0
154900	155000	69.0
155200	155300	72.0
155300	155400	68.0
155400	155500	65.0
155500	155600	62.0
Test N-4, July 28, step 1 (ambient)		
200000	200100	17.0
200100	200200	17.0
200800	200900	13.0

TABLE A12.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
200900	201000	9.0
201000	201100	11.0
201100	201200	8.0
201400	201500	15.0
201500	201600	18.0
201600	201700	13.0
201700	201800	11.0
202000	202100	19.0
202100	202200	15.0
202200	202300	13.0
202300	202400	13.0
202600	202700	13.0
202700	202800	17.0
202800	202900	11.0
202900	203000	13.0
Test N-4, July 28, step 2 (delta)		
203700	203800	15.0
203800	203900	20.0
204500	204600	27.0
204600	204700	20.0
204700	204800	20.0
204800	204900	22.0
205100	205200	21.0
205200	205300	28.0
205300	205400	24.0
205400	205500	26.0
205700	205800	24.0
205800	205900	24.0
205900	210000	27.0
210000	210100	27.0
210300	210400	22.0
210400	210500	23.0
210500	210600	24.0
210600	210700	24.0
Test N-4, July 28, step 3 (ambient)		
211200	211300	6.0
211300	211400	7.0
212000	212100	14.0
212100	212200	12.0
212200	212300	12.0
212300	212400	15.0
212600	212700	20.0
212700	212800	12.0

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
212800	212900	18.0
212900	213000	10.0
213200	213300	18.0
213300	213400	15.0
213400	213500	20.0
213500	213600	12.0
213800	213900	17.0
213900	214000	17.0
214000	214100	16.0
214100	214200	15.0
Test N-4, July 28, step 4 (delta)		
214700	214800	57.0
214800	214900	54.0
215500	215600	53.0
215600	215700	52.0
215700	215800	48.0
215800	215900	52.0
220100	220200	56.0
220200	220300	54.0
220300	220400	54.0
220400	220500	54.0
220700	220800	52.0
220800	220900	57.0
220900	221000	51.0
221000	221100	48.0
221300	221400	52.0
221400	221500	51.0
221500	221600	51.0
221600	221700	50.0
Test N-4, July 28, step 5 (ambient)		
222200	222300	4.0
222300	222400	3.0
223000	223100	10.0
223100	223200	7.0
223200	223300	6.0
223300	223400	7.0
223600	223700	13.0
223700	223800	9.0
223800	223900	7.0
223900	224000	8.0
224200	224300	12.0
224300	224400	11.0
224400	224500	11.0

TABLE A12.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
224500	224600	10.0
224800	224900	12.0
224900	225000	9.0
225000	225100	13.0
225100	225200	9.0
Test N-4, July 28, step 6 (delta)		
225700	225800	21.0
225800	225900	22.0
230600	230700	18.0
230700	230800	20.0
230800	230900	21.0
231100	231200	25.0
231200	231300	19.0
231300	231400	18.0
231400	231500	17.0
231700	231800	22.0
231800	231900	21.0
231900	232000	19.0
232000	232100	22.0
232300	232400	23.0
232400	232500	22.0
232500	232600	19.0
232600	232700	21.0
Test N-4, July 28, step 7 (ambient)		
233200	233300	12.0
233300	233400	11.0
234000	234100	8.0
234100	234200	5.0
234200	234300	8.0
234300	234400	10.0
234600	234700	12.0
234700	234800	9.0
234800	234900	13.0
234900	235000	11.0
235200	235300	7.0
235300	235400	7.0
235400	235500	11.0
235500	235600	6.0
235800	235900	8.0
235900	0000	6.0
0000	0100	3.0
0100	0200	4.0

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
Test N-1, July 29, ambient		
120000	120100	51.0
120100	120200	56.0
120800	120900	57.0
120900	121000	62.0
121000	121100	60.0
121100	121200	53.0
121400	121500	61.0
121500	121600	47.0
121600	121700	51.0
121700	121800	54.0
122000	122100	56.0
122100	122200	41.0
122400	122500	43.0
122500	122600	45.0
122600	122700	41.0
122700	122800	37.0
122800	122900	33.0
122900	123000	34.0
123000	123100	37.0
123100	123200	38.0
123400	123500	46.0
123500	123600	49.0
123600	123700	48.0
123700	123800	39.0
124400	124500	58.0
124500	124600	52.0
124600	124700	51.0
124700	124800	51.0
125000	125100	42.0
125100	125200	45.0
125200	125300	40.0
125300	125400	40.0
125600	125700	36.0
125700	125800	33.0
125800	125900	40.0
125900	130000	31.0
130000	130100	33.0
130100	130200	32.0
130800	130900	47.0
130900	131000	47.0
131000	131100	46.0
131100	131200	45.0
131400	131500	55.0
131500	131600	47.0
131600	131700	46.0

TABLE A12.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
131700	131800	41.0
132000	132100	30.0
132100	132200	36.0
132200	132300	33.0
132300	132400	26.0
132600	132700	35.0
132700	132800	27.0
132800	132900	31.0
133500	133600	23.0
133600	133700	20.0
133700	133800	25.0
133800	133900	24.0
134100	134200	41.0
134200	134300	32.0
134300	134400	30.0
134400	134500	28.0
134700	134800	35.0
134800	134900	33.0
134900	135000	31.0
135000	135100	35.0
135300	135400	32.0
135400	135500	37.0
135500	135600	38.0
135600	135700	41.0
Test N-3, July 29, step 1 (delta)		
140200	140300	179.0
140300	140400	171.0
141000	141100	171.0
141100	141200	176.0
141200	141300	170.0
141300	141400	178.0
141600	141700	177.0
141700	141800	171.0
141800	141900	171.0
141900	142000	171.0
142200	142300	175.0
142300	142400	169.0
142400	142500	177.0
142500	142600	189.0
142800	142900	177.0
142900	143000	165.0
143000	143100	166.0
143100	143200	207.0

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
Test N-3, July 29, step 2 (ambient)		
143700	143800	76.0
143800	143900	33.0
144600	144700	46.0
144700	144800	46.0
144800	144900	56.0
145100	145200	37.0
145200	145300	34.0
145300	145400	30.0
145400	145500	33.0
145700	145800	46.0
145800	145900	41.0
145900	150000	44.0
150000	150100	45.0
150300	150400	37.0
150400	150500	41.0
150500	150600	40.0
150600	150700	33.0
Test N-3, July 29, step 3 (delta)		
151200	151300	94.0
151300	151400	125.0
152000	152100	80.0
152100	152200	77.0
152200	152300	65.0
152300	152400	72.0
152600	152700	70.0
152700	152800	70.0
152800	152900	70.0
152900	153000	67.0
153200	153300	72.0
153300	153400	71.0
153400	153500	68.0
153500	153600	69.0
153800	153900	72.0
153900	154000	69.0
154000	154100	78.0
154100	154200	69.0
Test N-3, July 29, step 4 (ambient)		
154700	154800	40.0
154800	154900	41.0
155500	155600	32.0
155600	155700	33.0

TABLE A12.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
155700	155800	36.0
155800	155900	36.0
160100	160200	42.0
160200	160300	36.0
160300	160400	33.0
160400	160500	31.0
160700	160800	39.0
160800	160900	34.0
160900	161000	34.0
161000	161100	28.0
161300	161400	33.0
161400	161500	37.0
161500	161600	28.0
161600	161700	27.0
Test N-3, July 29, step 5 (delta)		
162200	162300	122.0
162300	162400	155.0
163000	163100	118.0
163100	163200	124.0
163200	163300	115.0
163300	163400	113.0
163600	163700	116.0
163700	163800	125.0
163800	163900	177.0
163900	164000	117.0
164200	164300	118.0
164300	164400	116.0
164400	164500	124.0
164500	164600	120.0
164800	164900	118.0
164900	165000	122.0
165000	165100	118.0
165100	165200	115.0
Test N-3, July 29, step 6 (ambient)		
165700	165800	29.0
165800	165900	33.0
170500	170600	26.0
170600	170700	31.0
170700	170800	33.0
170800	170900	27.0
171100	171200	35.0
171200	171300	35.0
171300	171400	33.0
171400	171500	29.0
171700	171800	37.0
171800	171900	36.0
171900	172000	31.0
172000	172100	36.0
172300	172400	33.0
172400	172500	32.0
172500	172600	27.0
172600	172700	29.0
Test N-4, July 29, step 1 (ambient)		
203800	203900	10.0
203900	204000	9.0
204000	204100	9.0
204100	204200	9.0
204400	204500	15.0
204500	204600	9.0
204600	204700	12.0
204700	204800	9.0
205000	205100	10.0
205100	205200	9.0
205200	205300	12.0
205300	205400	9.0
205600	205700	14.0
205700	205800	8.0
205800	205900	10.0
205900	210000	12.0
210200	210300	14.0
210300	210400	11.0
210400	210500	9.0
210500	210600	10.0
210800	210900	13.0
210900	211000	9.0
Test N-4, July 29, step 2 (delta)		
211000	211100	30.0
211100	211200	27.0
211400	211500	34.0
211500	211600	31.0
211600	211700	33.0
211700	211800	31.0
212000	212100	36.0
212100	212200	35.0
212200	212300	31.0
212300	212400	34.0

TABLE A12.- Continued

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
212600	212700	41.0
212700	212800	38.0
212800	212900	34.0
212900	213000	31.0
Test N-4, July 29, step 3 (ambient)		
213000	213100	8.0
213100	213200	7.0
213800	213900	10.0
213900	214000	7.0
214000	214100	8.0
214100	214200	9.0
214400	214500	12.0
214500	214600	11.0
214600	214700	10.0
214700	214800	8.0
215000	215100	15.0
215100	215200	11.0
215200	215300	13.0
215300	215400	10.0
215600	215700	14.0
215700	215800	14.0
215800	215900	12.0
215900	220000	11.0
220200	220300	12.0
220300	220400	10.0
220400	220500	8.0
220500	220600	11.0
220800	220900	13.0
220900	221000	8.0
Test N-4, July 29, step 4 (delta)		
221000	221100	135.0
221100	221200	139.0
221400	221500	138.0
221500	221600	137.0
221600	221700	132.0
221700	221800	131.0
222000	222100	140.0
222100	222200	134.0
222200	222300	135.0
222300	222400	134.0
222600	222700	138.0
222700	222800	134.0
222800	222900	135.0
222900	223000	131.0
Test N-4, July 29, step 5 (ambient)		
223000	223100	7.0
223100	223200	8.0
223800	223900	11.0
223900	224000	7.0
224000	224100	8.0
224100	224200	8.0
224400	224500	8.0
224500	224600	10.0
224600	224700	8.0
224700	224800	6.0
225000	225100	14.0
225100	225200	11.0
225200	225300	9.0
225300	225400	13.0
225600	225700	14.0
225700	225800	12.0
225800	225900	12.0
225900	230000	11.0
230200	230300	14.0
230300	230400	8.0
230400	230500	5.0
230500	230600	12.0
230800	230900	14.0
230900	231000	9.0
Test N-4, July 29, step 6 (delta)		
231000	231100	58.0
231100	231200	56.0
231400	231500	59.0
231500	231600	56.0
231600	231700	54.0
231700	231800	55.0
232000	232100	58.0
232100	232200	56.0
232200	232300	53.0
232300	232400	52.0
232600	232700	54.0
232700	232800	57.0
232800	232900	51.0
232900	233000	52.0

TABLE A12.- Concluded

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
Test N-4, July 29, step 7 (ambient)		
233000	233100	9.0
233100	233200	10.0
233800	233900	9.0
233900	234000	9.0
234000	234100	9.0
234100	234200	11.0
234400	234500	13.0
234500	234600	18.0
234600	234700	7.0
234700	234800	12.0
235000	235100	15.0
235100	235200	13.0
235200	235300	12.0
235300	235400	14.0
235600	235700	15.0
235700	235800	15.0
235800	235900	12.0
235900	0000	14.0
0200	0300	13.0
0300	0400	14.0
0400	0500	12.0
0500	0600	11.0
0800	0900	16.0
0900	1000	8.0

TABLE A13.- GA TECH NO DATA FOR INTERCOMPARISON TESTS

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
Test N-3, July 28, step 6 (delta)		
145500	150000	97.0
150000	150500	121.0
151100	151600	85.0
151700	152200	198.0
152800	153000	145.0
Test N-3, July 28, step 7 (ambient)		
153000	153500	50.0
154000	154500	71.0
155600	160100	49.0
160100	160600	62.0
Test N-4, July 28, step 2 (delta)		
204300	204800	25.8
204800	205300	20.5
210400	210900	16.5
Test N-4, July 28, step 3 (ambient)		
211000	211500	6.5
211500	212000	12.5
212600	213100	16.5
213100	213600	13.3
214300	214500	6.5
Test N-4, July 28, step 4 (delta)		
214600	215100	44.0
215100	215600	37.5
220200	220700	38.5
220700	221200	27.5
221200	221700	37.0
Test N-4, July 28, step 5 (ambient)		
222000	222500	8.5
222500	223000	1.8
223100	223600	18.5
224200	224700	22.0

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
Test N-4, July 28, step 6 (delta)		
225700	230200	21.5
230300	230800	22.5
231400	231900	22.0
232500	233000	21.5
Test N-4, July 28, step 7 (ambient)		
233000	233500	13.8
233700	234200	4.5
234200	234700	12.5
235900	240400	11.0
Test N-1, July 29, ambient		
120200	120700	29.0
120700	121200	30.0
121200	121700	32.7
121800	122300	39.0
122800	123300	34.0
123800	124300	34.0
124500	125000	41.5
130600	131100	22.7
131200	131700	31.5
134600	135100	21.5
135100	135600	24.0
135700	140000	26.5
Test N-3, July 29, step 1 (delta)		
140100	140600	109.0
140700	141200	115.5
141200	141700	135.0
141700	142200	124.0
142300	142800	140.0
142800	143300	118.0
143300	143500	130.0
Test N-3, July 29, step 2 (ambient)		
143500	144000	52.7
144000	144500	35.3
144500	150000	24.0
150200	150700	85.3

TABLE A13.- Concluded

Sample EDT, hr min sec		NO mixing ratio, pptv
Start	Stop	
Test N-3, July 29, step 3 (delta)		
151000	151500	59.0
152100	152600	60.2
152700	153200	56.5
153700	154200	50.0
154200	154400	65.3
Test N-3, July 29, step 4 (ambient)		
155600	156100	31.5
160200	160700	35.2
Test N-3, July 29, step 5 (delta)		
162300	162800	92.7
162800	162900	96.4
162900	163000	58.4
163000	163100	79.0
163100	163200	93.3
163200	163300	89.7
163300	163400	88.0
163400	163500	124.0
163500	163600	74.0
163600	163800	71.5
164600	164700	86.5
164700	164800	103.7
164800	164900	94.0
164900	165000	109.0
165100	165200	95.3
165200	165300	119.0
165400	165500	127.7
Test N-3, July 29, step 6 (ambient)		
170000	170500	21.5
170500	171000	30.2
171100	171600	20.2
171600	172100	29.0
Test N-4, July 29, step 1 (ambient)		
203000	203500	11.0
203500	204000	11.0
205000	205500	17.0
205700	210200	10.0
Test N-4, July 29, step 2 (delta)		
211100	211600	25.0
212500	213000	20.0
Test N-4, July 29, step 3 (ambient)		
213000	213500	5.0
213500	214000	9.5
214000	214500	19.0
214485	214985	5.0
215000	215500	10.0
215500	216000	5.5
220000	220500	7.5
220500	221000	11.5
Test N-4, July 29, step 4 (delta)		
221100	221600	105.5
222200	222700	110.0
Test N-4, July 29, step 5 (ambient)		
223000	223500	5.5
223500	224000	10.0
224000	224500	11.0
224485	224985	12.5
225000	225500	10.0
225500	226000	16.0
230000	230500	6.0
230500	231000	15.0
Test N-4, July 29, step 6 (delta)		
231000	231500	34.5
232500	233000	42.5

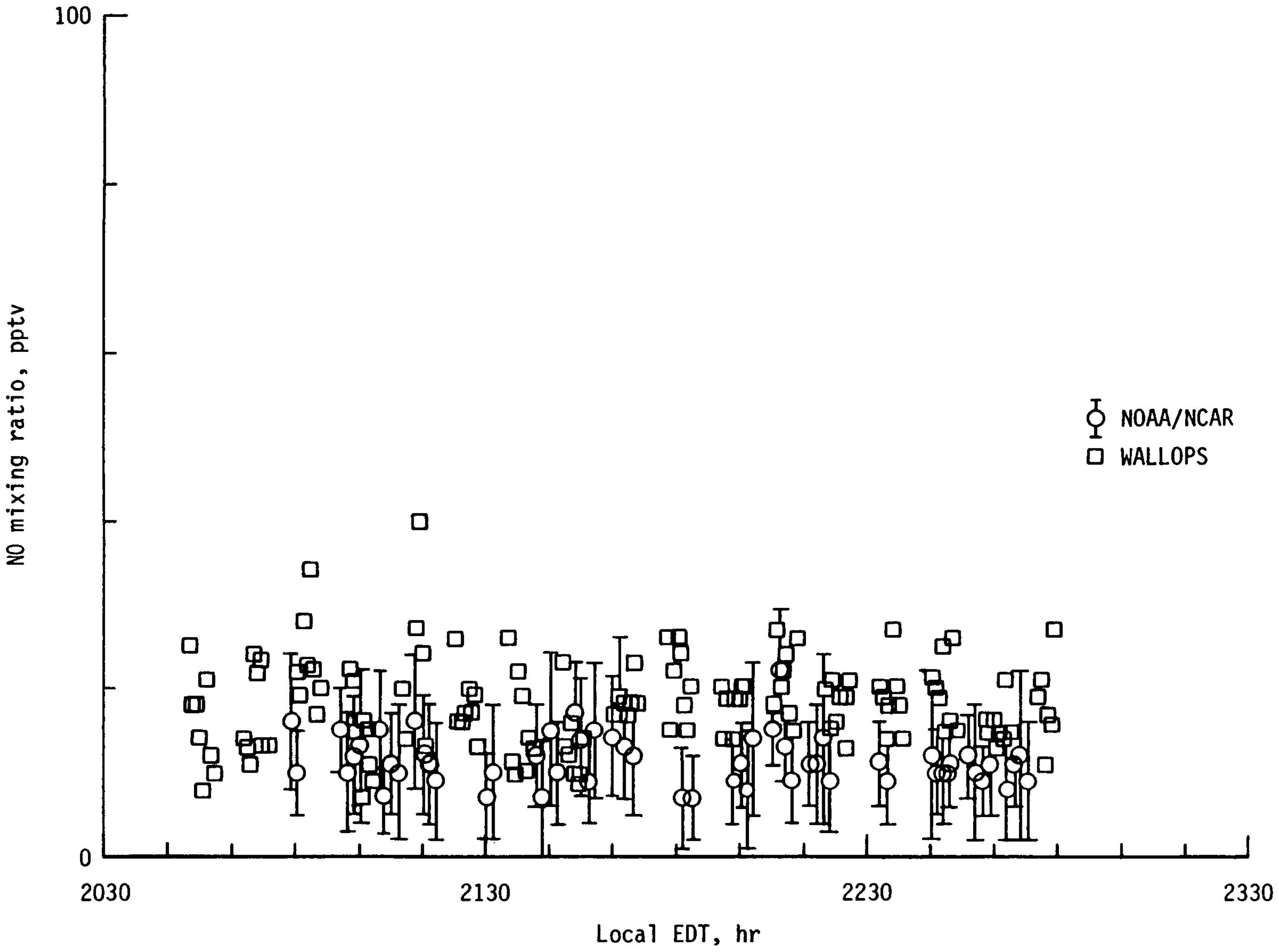


Figure A1.- Nitric oxide results from ambient test N-2 of July 26, 1983.

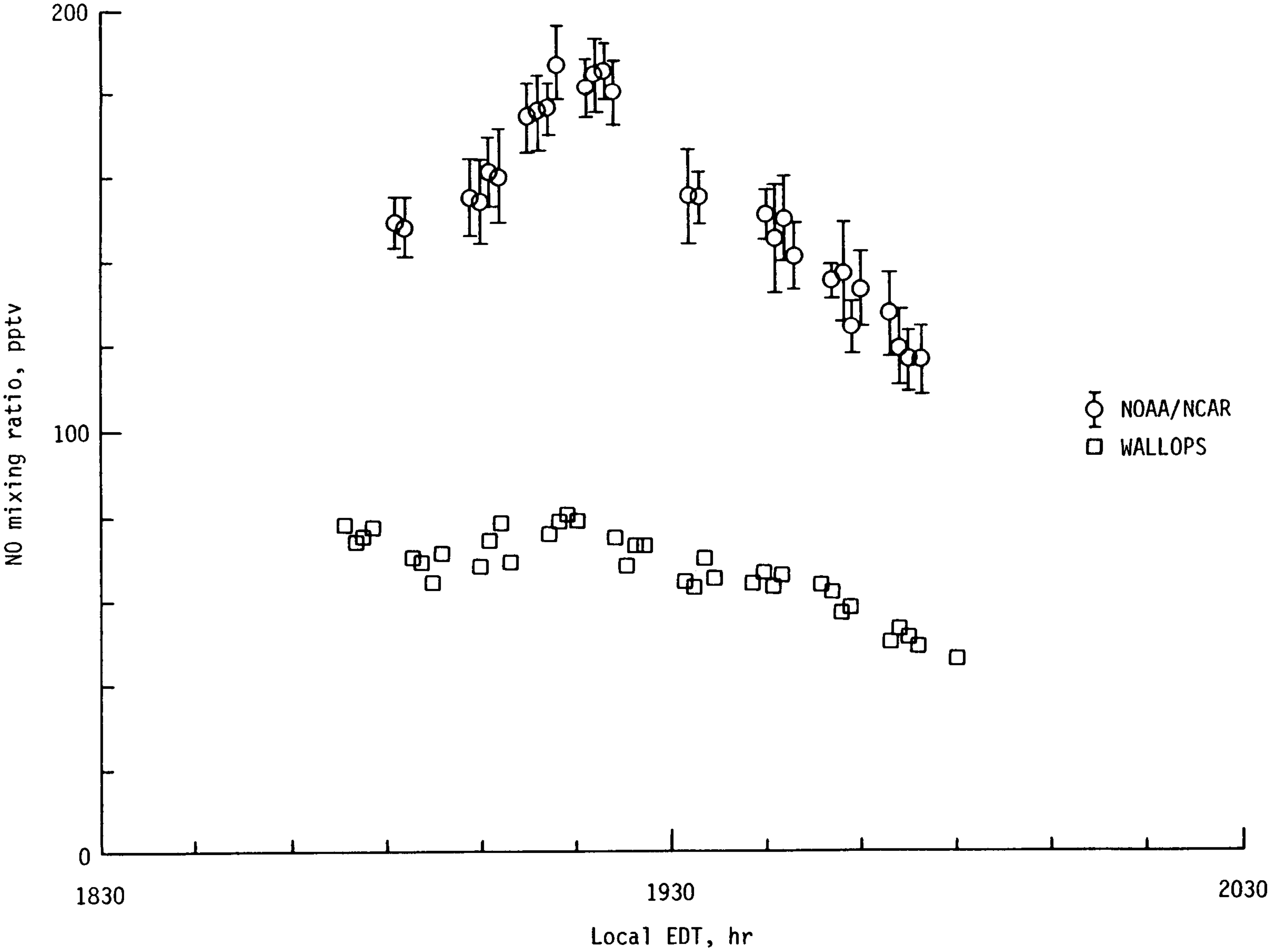


Figure A2.- Nitric oxide results from ambient test N-2 of July 27, 1983.

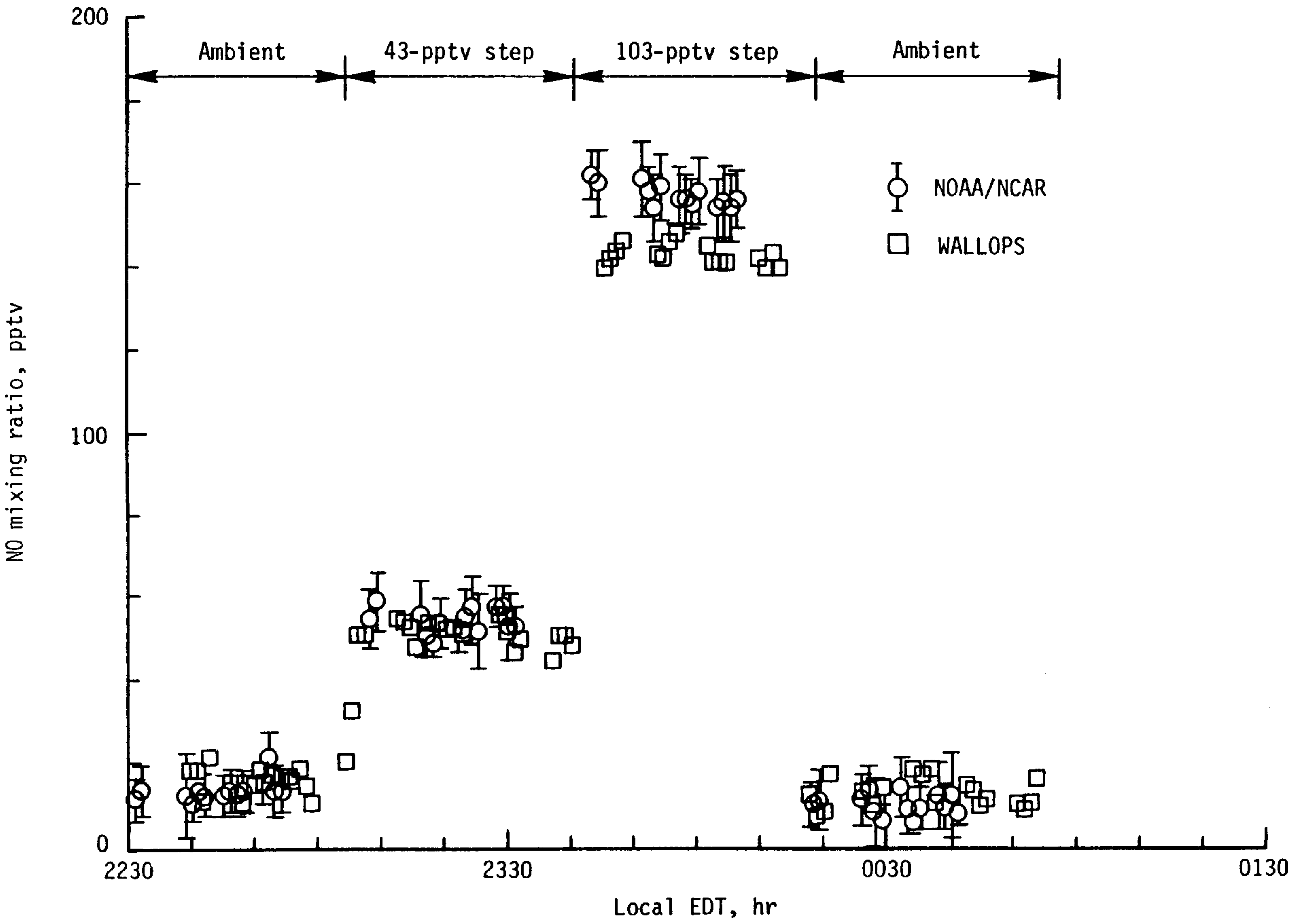


Figure A3.- Nitric oxide results from spiked-ambient test N-4 of July 27, 1983.

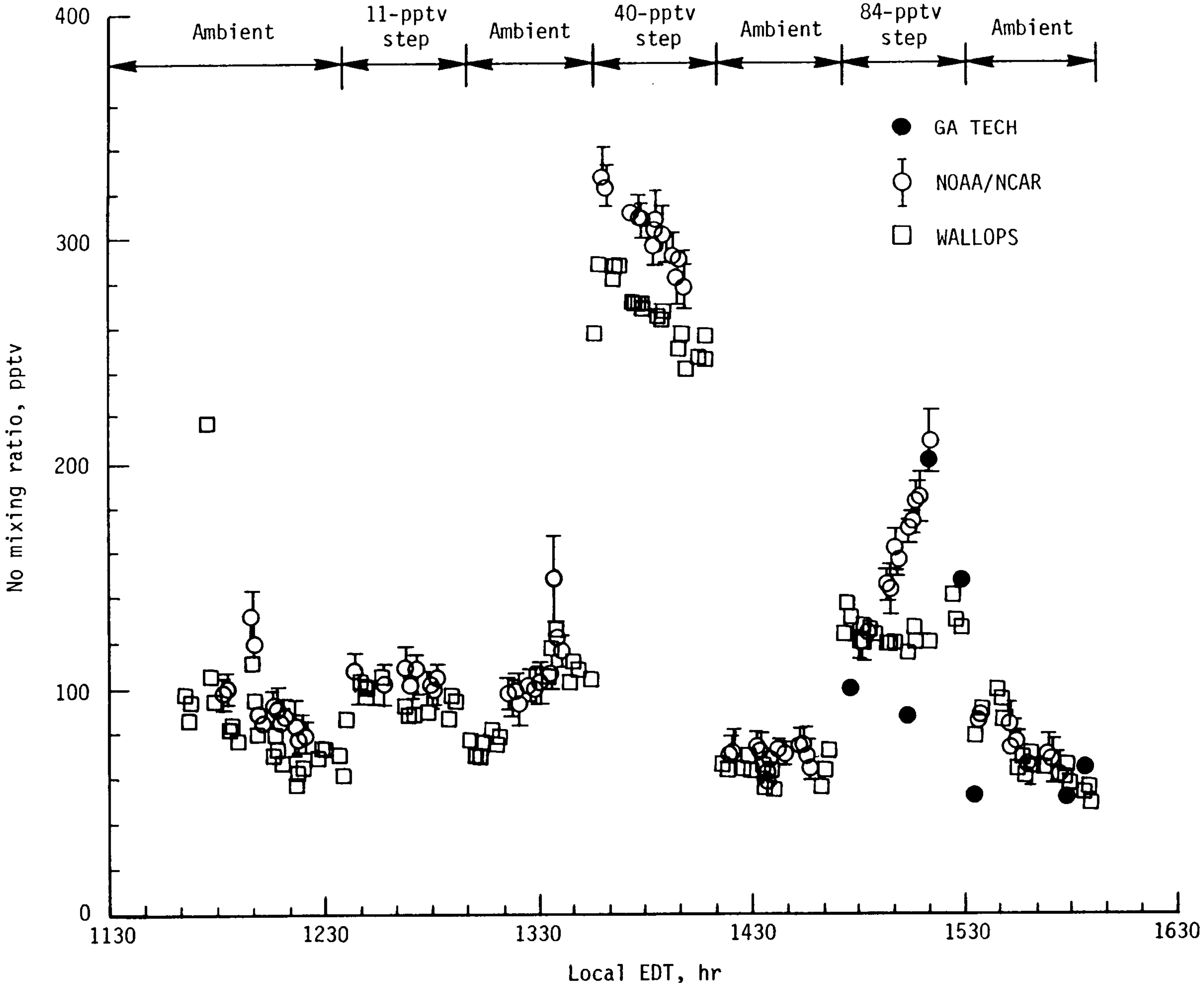


Figure A4.- Nitric oxide results from spiked-ambient test N-3 of July 28, 1983.

APPENDIX B

INSTRUMENT AND PROCEDURAL PROBLEMS RESULTING IN UNREPORTED OR INVALID DATA

As noted in the text and in appendix A, instrument and/or procedural problems did occur at Wallops and resulted in data not being reported or in data being marked invalid for intercomparison purposes. This appendix discusses the nature of these problems.

CO Techniques

During the first five CO tests (see table A1), preliminary data from AMES 1 were submitted with the caveat that there was evidence (i.e., high methane levels) of contamination of the grab samples by room air. Since AMES 2 was operational, the GTE workshop staff continued formal CO intercomparison tests, and required the Ames investigator to participate in these tests while at the same time diagnose the AMES 1 sample problem. Changes implemented in the procedures used to obtain an AMES 1 sample from the GTE manifolds as well as changes to the inlet lines from the GTE manifolds eliminated the source of contamination, during the last three tests. As a result of the contamination, AMES 1 data for these five tests were not included in the CO data set. Data from AMES 1 and 2 for the last test were invalid because of problems that arose with the GC system used to analyze samples obtained by both methods. The Ames investigator noted prior to the last test that the GC needed major maintenance (2 days). The GTE workshop staff met with the CO investigators to discuss the pros and cons of conducting this test in view of the anticipated GC problem. It was agreed that the last test would be conducted with the caveat that the Ames data could be withdrawn if the investigator felt the GC was providing unreliable data. In the formal submission of data (30 days after the workshop), the AMES 1 and 2 data were noted as invalid. The GTE workshop staff concurred and results were not included in the intercomparison data set.

From the formal submission of data, the CO mixing ratios reported by OGC during each of the spiked-nitrogen tests were noted to be significantly higher than those predicted from the GTE dilution system, and intercomparison results in nitrogen versus air (as compared with the other techniques) were substantially different. As a result, laboratory studies were conducted by the OGC investigator to evaluate the performance of liquid nitrogen cryogenic trapping (part of OGC sampling procedures) in a CO/N_2 versus CO/air medium. The accuracy of the cryogenic approach requires 100 percent collection efficiency of the sample constituents in order to maintain their relative concentrations after collection. The tests indicated that the difference between solidification temperature of N_2 and air resulted in overestimating the mixing ratio of CO in the original source. This finding was consistent with the OGC results obtained at Wallops during the nitrogen tests. Accordingly, all OGC data reported for the nitrogen tests were declared invalid and were omitted from the CO data set.

In terms of test procedures, only one test sequence has been declared invalid and that is step 8 (516 ppbv GTE delta) of the July 27 test C-4 (see table A1). Intercomparison results for this step were inconsistent compared with those for the other CO tests. The source of the problem was traced to an unreliable flowmeter which was used only for this one delta step. This flowmeter was not included in the NBS test of the GTE dilution system but was part of the GTE spare equipment, which was implemented into the workshop procedures to obtain a relatively high CO mixing ratio of 516 ppbv. Postworkshop calibrations showed the flowmeter to be nonrepeatable to the extent that it was immediately scrapped. As such, the GTE workshop staff considers the 516 ppbv delta to be questionable and has declared the data for this step invalid.

NO Techniques

As noted in table A2, the GA TECH technique was not operational for the first four NO tests. In switching the LIF laser from an OH to an NO sampling configuration, laser damage was noted. The investigator immediately notified the GTE staff that the LIF NO technique would be down for several days while a replacement laser could be removed from a lab system at Georgia Tech in Atlanta, transported to Wallops, and integrated into the system. On July 26, the GTE workshop staff started the formal NO tests even though the LIF technique would not be operational for the first few tests. The GA TECH LIF technique became operational for the last step of test N-3 of July 28. However, intercomparison data for this step were not included in the CO data set as they were marked invalid because of ambient variations.

OH Techniques

Numerous instrument problems occurred during the OH tests. These problems were frequent and varied in nature, to the extent that a discussion of them is somewhat lengthy. As a result the authors have elected to summarize the OH test activities by reproducing the Official OH Test Log. The following paragraphs are a summary of the events recorded in this log. All times are local eastern daylight in hours.

Test OH-1: July 15, 1983

```
1000 * Start of test
     * Ga Tech correcting minor problems observed last night -
       expects to be on line at 1200
1020 * Ford doing N2 Raman runs, should shortly be on-line for OH
1035 * Ford on-line measuring OH
1105 * Ford will be off-line for 10 min to change a filter
1108 * Ford on-line measuring OH
1140 * Ford will be off-line for 10 min
1150 * Ford on-line measuring OH; maximizing parameters (reason
       for sequence of off/on events)
1250 * Ford asked permission to go off-line to cool laser and make
       adjustments
     * Ford asked that we check Ga Tech status before allowing Ford
       to go off-line.
     * Ga Tech said earliest possible time was 1430
1300 * Project stopped test OH-1 with plans to resume at 1400
     * Ford given permission to go off-line
1400 * Test OH-1 resumed - test extended to 1600 hr
1425 * Ford on-line making OH measurements
1515 * Project checked with Ga Tech, almost but not operational yet
1552 * Ga Tech will be on-line in 5 min
1602 * Ga Tech on-line making OH measurements
1610 * Project confirmed both Ford and Ga Tech on-line
1615 * Ford having electrical pick-up problems but still on-line
```

1628 * Project requested of OH PI's an estimate of how much longer to run OH-1
* PI's suggested 15 min longer
1645 * Test completed

Test OH-2: July 16, 1983

1200 * Start of test
1246 * Ga Tech expects to be on-line in 20 min
1309 * Ga Tech on-line measuring OH
1331 * Ga Tech off-line; requests test be extended to 1500
1336 * Project checked with Ford; would like an extension also
* Test extended to 1500
1351 * Ga Tech on-line measuring OH
1410 * Ford on-line measuring OH
1441 * Ford requested a 30-min extension of test
* Ga Tech agreed; was also about to request an extension
1442 * Test extended to 1530
1530 * Test completed

Test OH-3: July 20, 1983

1100 * Start of test
1101 * Ford on-line measuring OH since 1058
1145 * Ford doing N_2 Raman runs for next 20 min
1211 * Ford on-line measuring OH since 1208
1308 * Ford doing N_2 Raman runs for next 20 min
1325 * Ford on-line measuring OH
1337 * Ga Tech will be on-line in 30 min; if so will request test be extended to 1600
1412 * Ga Tech expects to be on-line in 15 min
1425 * Ford doing N_2 Raman runs for next 20 min
1438 * Ga Tech will be on-line at 1440
1440 * Ford on-line measuring OH
1444 * Ga Tech on-line measuring OH
1445 * Test extended to 1530
1450 * Ga Tech off-line; will be back on-line in 10 min
1515 * Test extended to 1600
1600 * Test completed

Test OH-4: July 21, 1983

1400 * Start of test
1409 * Ford on-line measuring OH
1500 * Due to laser alignment problems, Ga Tech will not participate in OH-4 and will use time to prepare for OH-5
1506 * Ford off-line for calibration data for 20 min
1528 * Ford will continue calibration data since no other OH instruments are on-line
1546 * Ford on-line making OH measurements
1553 * Washington State ready to make OH measurements
1620 * Washington State sample GT-1
1630 * Project asked Ford to stay on-line until 1700 so that Washington State could get another sample
* Test OH-5 scheduled to start at 1730

1645 * Ga Tech on-line measuring OH
* Project extended test OH-4 to 1730
1649 * Washington State sample GT-2
1651 * Washington State off-line until 1730 to take a break
1714 * Ga Tech off-line at 1650; only made 1 run
1730 * Test completed

Test OH-5: July 21, 1983

1730 * Start of test
1732 * Ford will start N_2 Raman runs at 1745
1810 * Washington State on the platform working since 1730
1821 * Ford on-line measuring OH
1822 * Washington State sample GT-3; will take another sample in 30 min
1907 * Ford will stay on-line measuring OH until 2000 and then run N_2 Raman
1917 * Ga Tech on-line measuring OH; request 1-hr test extension
1932 * Washington State sample GT-4
2005 * Project extended test to 2115
2019 * Ford starting N_2 Raman runs
2032 * Ga Tech starting line assignments; will be back measuring OH in 15 min
2036 * Ford on-line measuring OH
2051 * Washington State sample GT-7
2115 * Test complete

Test OH-6: July 22, 1983

1100 * Start of test
1103 * Ford on-line measuring OH
1123 * Washington State sample GT-8; next sample in 20 min
1151 * Washington State sample GT-9; next sample in 35 min
1210 * Ford expects to start N_2 Raman runs
1230 * Ford on-line measuring OH
1308 * Washington State sample GT-10
1330 * Ford off-line for calibration run
1347 * Washington State sample GT-11
1354 * Ford on-line measuring OH
1408 * Ga Tech on-line measuring OH; request a 1-hr test extension
1409 * Washington State sample GT-12
1455 * Ford off-line for calibration runs
1458 * Expect next Washington State sample in 20 min
1513 * Project extended test to 1700
1515 * Ford on-line measuring OH
1521 * Washington State sample GT-13
1617 * Ga Tech injecting propylene for next 1 hr
* Project extended test to 1700
* Test OH-7 will start at 1700 and end at 2000
1620 * Ford and Washington State will be off-line while Ga Tech injecting propylene; Ford, calibrating; Washington State, minor repairs
1700 * Test completed

Test OH-7: July 22, 1983

1700 * Start of test
     * Ga Tech on-line measuring OH while injecting propylene; on-line since 1408
     * Ford will continue N_2 Raman runs until Ga Tech stops injecting propylene
1750 * Ga Tech on-line measuring OH (no propylene injection); will run 1 hr, then do O_3 interference tests; OK with Ga Tech to stop test OH-7 after ambient OH runs
     * Ford on-line measuring OH; OK with Ford to stop test early
1810 * Washington State sample GT-15
1835 * Washington State sample GT-16
1908 * Washington State sample GT-17
1925 * Ford will do N_2 Raman run and then shut down for the night
1935 * Test completed
     * Ga Tech still on-line measuring OH

APPENDIX C

PRINCIPAL INVESTIGATORS' DESCRIPTION OF ANALYSIS PROCEDURES FOR PREWORKSHOP EXCHANGE OF STANDARDS

As requested by the GTE workshop staff, each CO and NO investigator provided along with the preworkshop analysis of the gas standards a discussion of the procedures used for the analyses. This appendix presents a summary of these discussions. Values for the various standards as reported by the investigators are given in table 2 and will be referred to as necessary for these discussions. OGC was not requested to participate in the preworkshop exchange of standards.

AMES 1 and 2

The preworkshop analyses of the GTE primary and GTE Ames blind standards were performed with the same technique as used with AMES 1. The indicated uncertainties in the reported values (table 2) were based on four analytical runs (one sample) for each GTE standard and 7 runs of the PI's internal standard. The precision for the four runs was typically 0.49 percent. The mixing ratio of the internal standard was 5.76 ppmv and the typical precision for 7 runs was 0.50 percent.

LANGLEY

Calibration.- LANGLEY was calibrated by flowing precision mixtures of a CO standard (PI's internal standard) and zero air through the optical white cell which was maintained at an internal pressure of 50 torr. The PI's standard and zero air were procured from a commercial vendor with certified analyses traceable to NBS. The analyses indicated a CO mixing ratio of 1.382 ppmv for the CO standard and a CO mixing ratio below 0.050 ppmv for the zero air. After repeated measurements of the zero air, the CO mixing ratio was determined to be 0.006 ppmv.

The dilution was accomplished by monitoring the flow rate from the CO standard and zero air with mass flowmeters. The flowmeters had full-scale ranges of 500 cm^3/min for the CO standard and 2000 cm^3/min for the zero air. These flowmeters had a manufacturer-specified accuracy of 1 percent of full scale. The accuracy had been improved beyond 1 percent by using a multipoint calibration of the flowmeters.

The LANGLEY instrument was "zeroed" by trapping 500 torr of the zero air in the white cell. The transfer function of the instrument was such that its response was inversely proportional to pressure. Thus the zero air had an instrument response equivalent to 0.006 ppmv at the normal white cell operating pressure of 50 torr but gave an instrument response equivalent to 0.0006 ppmv at 500 torr. During the flowing dilution runs, the total flow rate (CO standard plus zero air) was held constant at a nominal value of 1375 cm^3/min by a flow controller while the flow from the CO standard was manually set by adjusting a metering value.

The CO mixing ratio X in ppmv of the diluted gas was calculated by using the following expression:

$$X = F(1.382) + (1 - F)(0.006) \tag{C1}$$

where F is the dilution factor A/B (A is the flow rate of the CO standard and B is the total flow rate) and 1.382 and 0.006 are the mixing ratios of the gas standard and zero air, respectively. The dilution factors and CO mixing ratios and the instrument output Y generated during a calibration are given in table C1. A linear regression of these data results in the following equation:

$$Y = 0.16 + 10.001X \tag{C2}$$

where Y is measured in millivolts and X in ppmv.

Measurement of GTE primary CO standard.- The current configuration of the LANGLEY instrument had been selected for optimum response for CO mixing ratios in the range of 0 to 2 ppmv. Accordingly a direct measurement of the GTE primary standard forced the response into a slightly nonlinear region. To circumvent this problem, we diluted the primary standard in a manner similar to that described earlier. The five lowest dilution factors used in the calibration discussed earlier were repeated as closely as possible with our manual flow control. All dilutions were kept under 1.5 ppmv so as to remain in the linear response region of the instrument. Rather than repeating the same dilution five times, five different dilutions were produced. If this were not done, the constant flow-rate-reading error at a specific dilution would result in a systematic measurement error. The five dilution factors and the respective instrument responses are listed in table C2. For these data,

$$X = FX_p + (1 - F)0.006 \tag{C3}$$

where X_p is the mixing ratio of the GTE primary standard. Substituting X from equation (C2) for X in equation (C3) and combining terms gives

$$Y = 0.22 + 10.001(X_p - 0.006)F \tag{C4}$$

A linear relationship exists between F and Y, and by solving for the optimum slope B ($B = 10.001(X_p - 0.006)$) with the method of least squares, the best estimate of X_p may be inferred. The results are $B = 96.67$ with $\sigma_B = 0.807$ (where σ_B is the estimate of the standard deviation of B). The 90-percent confidence limit on B is 96.67 ± 1.72. Evaluating the expression for B gives the 90-percent confidence limits on X_p as 9.67 ± 0.17 ppmv.

Measurement of GTE Langley blind CO standard.- The GTE Langley blind CO standard was measured in the same way as the primary standard. Four dilution factors were used. The dilution factors and instrument responses are given in table C2. Analysis of the data gives the following results:

(1) $B = 96.902$, $\sigma_B = 0.970$

(2) 90-percent confidence limits on $B = 96.90 \pm 2.28$

(3) 90-percent confidence limits on $X_p = 9.69 \pm 0.23$ ppmv

WALLOPS

Measurement of GTE primary NO standard.- The GTE primary NO standard was analyzed by the chemiluminescent technique with an EPA protocol NO standard (traceable to NBS) of 9.746 ppmv certified to a 1-percent accuracy. The analysis used a switching arrangement to alternately direct gas from the two cylinders (GTE primary and EPA protocol) through a single dilution stage to the detector inlet, switching at 10-min intervals. Two or three 1-min signal integrations were recorded after flushing inlet line and sample chamber 7 to 8 min. The ratio of the cylinder mixing ratios was obtained from the ratio of the signals. The EPA standard was measured before and after measurement of the GTE standard and these readings averaged to account for slow instrument drifts. Although the two cylinders were close enough in mixing ratio that instrument nonlinearities were not a factor, a check of linearity was made for completeness. The GTE primary standard was found to be 9.44 ± 0.01 ppmv where the uncertainty level was a 90-percent confidence interval for a six-sample set.

Measurement of GTE Wallops blind NO standard.- The analysis of the GTE Wallops blind NO standard was also referenced to the 9.746-ppmv EPA protocol standard. These analyses were performed while on-site at Wallops on July 7 and 24. The NO intercomparisons started on July 26. Instrument response was measured for the GTE and EPA standards over a dilution range of three orders of magnitude by using a two-stage mass-flow dilution system. The diluent gas was zero air. A valve arrangement allowed flow to the dilution system to be directed from either the GTE or EPA gas cylinder. The instrument background (in the absence of NO) was periodically determined and subtracted from the total signal. The results are given in tables C3 and C4 and figures C1 and C2. Determination of the GTE mixing ratio was based on the slopes of the curves and was 4.66 ppmv (July 7, fig. C1) and 4.71 ppmv (July 24, fig. C2).

NOAA/NCAR

Measurement of GTE primary NO standard.- The fittings on the GTE-supplied regulator were cleaned with ethanol and a cotton swab. The regulator was mounted on the GTE standard gas cylinder and evacuated to pressures less than 50 millitorr for 3 days by using a liquid nitrogen-trapped vacuum pump. The regulator was purged occasionally during this time. The regulator and NO cylinder were connected to the NOAA/NCAR chemiluminescent detector, in parallel with a laboratory's own calibration standard. (See fig. C3.) The gas flow in each line was regulated by a separate mass-flow controller. A relative calibration of these controllers had been made for this intercomparison. The flows were kept constant and, by using three-way valves as shown, each NO mixture could either be sent to the detector or dumped to an exhaust line. Initially both NO flows were sent to the exhaust and the background count (zero air only) rate was measured. Then, one at a time in alternating order, the NO flows were diverted to the detector and the instrument response measured. Three to five repetitive cycle measurements were made. The variation among replicate measurements was less than 0.5 percent. This test sequence was repeated for five separate in-house NOAA/NCAR standards. Test results are summarized in table C5. The specifications of five in-house standards are listed in the table. The older standards, 1 and 2, had also been frequently compared with those of calibrated NO_2 permeation tubes via gas-phase titration, and standard 1 had been previously intercompared with other institution's standard (agreed to within 5 percent). The gas supplier of all five standards state a 4-percent accuracy for the mixing ratio.

The precision of the multiple ratios measured for each NOAA standard was sufficiently small that it could be neglected as a source of uncertainty in the GTE-NOAA/NCAR intercomparison. All the uncertainty arose from the fact that the results obtained by using each of the five standards differed. To obtain a best single NOAA/NCAR value for the mixing ratio of the GTE primary NO standard, the following procedure was used.

The mixing ratios listed on the right-hand side of table C5 have been averaged, with double weight placed on the results from standards 1 and 2, with which we have had the most experience and ancillary intercomparisons. The resulting weighted mean is 9.29 ppmv. A 10-percent uncertainty, 0.93 ppmv, encompasses essentially all the separate determinations in table C5; hence, this uncertainty corresponds to a high confidence level, such as 90 or 95 percent.

Measurement of GTE NOAA/NCAR blind NO standard.- The NO mixing ratio of the GTE NOAA/NCAR blind standard was measured by repeatedly comparing the instrument responses with those for the diluted samples of the blind and two NO calibration standards that had been previously compared with the GTE primary NO standard. The experimental setup and procedures were similar to those used for the GTE primary analysis. The blind and two in-house standards were diluted by a factor of about 3000 with a single stage of dilution. The blind was compared with the first standard three times resulting in a determined mixing ratio for the blind of 4.83 ± 0.03 ppmv. Six comparisons with the other standard yielded a mixing ratio for the blind of 4.79 ± 0.04 ppmv. With the two in-house standards as transfer standards from the GTE NO primary standard, the NOAA/NCAR blind NO standard is 4.81 ± 0.24 ppmv.

In association with the analysis of the blind standard, a linearity check of the NOAA/NCAR instrument was performed. Tests required two stages of dynamic dilution in order to obtain mixing ratios in the range of 60 to 6 ppbv. The resulting response curve for the instrument was

$$\text{Signal (counts)} = 6417 \text{ (NO mixing ratio in ppmv)} \pm 17.81 \text{ CPS} \qquad \text{(C5)}$$

with a correlation coefficient of 0.9999. The instrument was found linear in the test range and within the uncertainties associated with the dilution technique.

GA TECH

The results of the GA TECH LIF measurements of the primary and blind standards are given in table 2. The standards were diluted to 1 to 5 ppbv by using a two-stage dynamic dilution system and zero air prior to analysis. Quoted uncertainties are 1σ values associated with six separate determinations, each determination based on a 10-min integrated sampling period.

TABLE C1.- LANGLEY CALIBRATION DATA FOR GTE STANDARDS ANALYSIS

CO mixing ratio, X, ppmv	Dilution factor, F	Instrument output, Y, mV
Zero air[a] 500 torr[b]	NA[c]	0.009
Zero air[a] 500 torr[b]	NA[c]	.009
0.0317	0.0187	.336
.0575	.0374	.606
.0831	.0600	.855
.10086	.00746	1.11
.2100	.1482	2.12
.3097	.2207	3.09
.4082	.2923	4.05
.5084	.3652	5.07
1.3820	1.0000	13.85

[a] Equivalent CO mixing ratio = 0.0006 ppmv.
[b] Equivalent CO mixing ratio = 0.0060 ppmv.
[c] Not applicable.

TABLE C2.- LANGLEY RESULTS FROM ANALYSIS OF GTE STANDARDS

(a) GTE primary CO standard

Dilution factor, F	Instrument response, Y, mV
0.0191	1.785
.0382	3.675
.0572	5.595
.0762	7.545
.1515	14.715

(b) GTE Langley blind CO standard

Dilution factor, F	Instrument response, Y, mV
0.0191	1.92
.0382	3.84
.0762	7.58
.1504	14.58

TABLE C3.- WALLOPS RESULTS FROM ANALYSIS OF GTE WALLOPS BLIND NO STANDARD ON JULY 7, 1983

Dilution factor, F	Instrument count rate, CPS, for -		NO mixing ratio,[a] pptv
	GTE blind	EPA protocol	
3.35×10^{-3}	29 300	60 910	32 600
1.67×10^{-3}	14 560	30 090	16 280
9.96×10^{-4}	8 680	17 780	9 710
1.65×10^{-4}	1 260	2 704	1 610
1.32×10^{-4}	1 164	2 401	1 290
1.06×10^{-4}	939	1 915	1 030
6.64×10^{-5}	594	1 247	647
3.35×10^{-5}	295	624	328
1.36×10^{-5}	130	250	133
8.34×10^{-6}	65	145	81
6.94×10^{-6}	61	121	68
6.94×10^{-6}	53	116	68

[a] Based on EPA protocol cylinder, NO (pptv) = $(9.746 \times 10^{6})F$.

TABLE C4.- WALLOPS RESULTS FROM ANALYSIS OF GTE WALLOPS BLIND NO STANDARD ON JULY 24, 1983

Dilution factor, F	Instrument count rate, CPS, for -		NO mixing ratio,[a] pptv
	GTE blind	EPA protocol	
5.39×10^{-3}	38 950	80 570	52 500
4.04×10^{-3}	29 170	60 520	39 400
2.69×10^{-3}	19 580	40 550	26 200
1.34×10^{-3}	9 610	19 960	13 100
1.06×10^{-4}	(b)	1 530	1 030
5.34×10^{-5}	(b)	816	520
3.23×10^{-5}	(b)	492	315
1.62×10^{-5}	(b)	262	158
5.58×10^{-6}	(b)	96	54
2.79×10^{-6}	(b)	44	27

[a] Based on EPA protocol cylinder, NO (pptv) = $(9.746 \times 10^{6})F$.
[b] GTE standard not tested.

TABLE C5.- NOAA/NCAR RESULTS FROM ANALYSIS OF GTE PRIMARY NO STANDARD

NOAA/NCAR standard			GTE NO primary[a] standard	
Standard	Date	Mixing ratio, ppmv	Mixing ratio, ppmv	Difference, $\frac{\text{Measured} - 9.49}{9.49}$, percent
1	March 20, 1978	1.92	10.2	7.5
2	August 4, 1980	2.01	9.05	-4.6
3	August 9, 1982	2.60	8.32	-12.3
4	August 9, 1982	2.61	8.40	-11.5
5	March 21, 1983	2.15	9.80	3.3

[a] GTE primary mixing ratio given as 9.49 ± 0.16 ppmv.

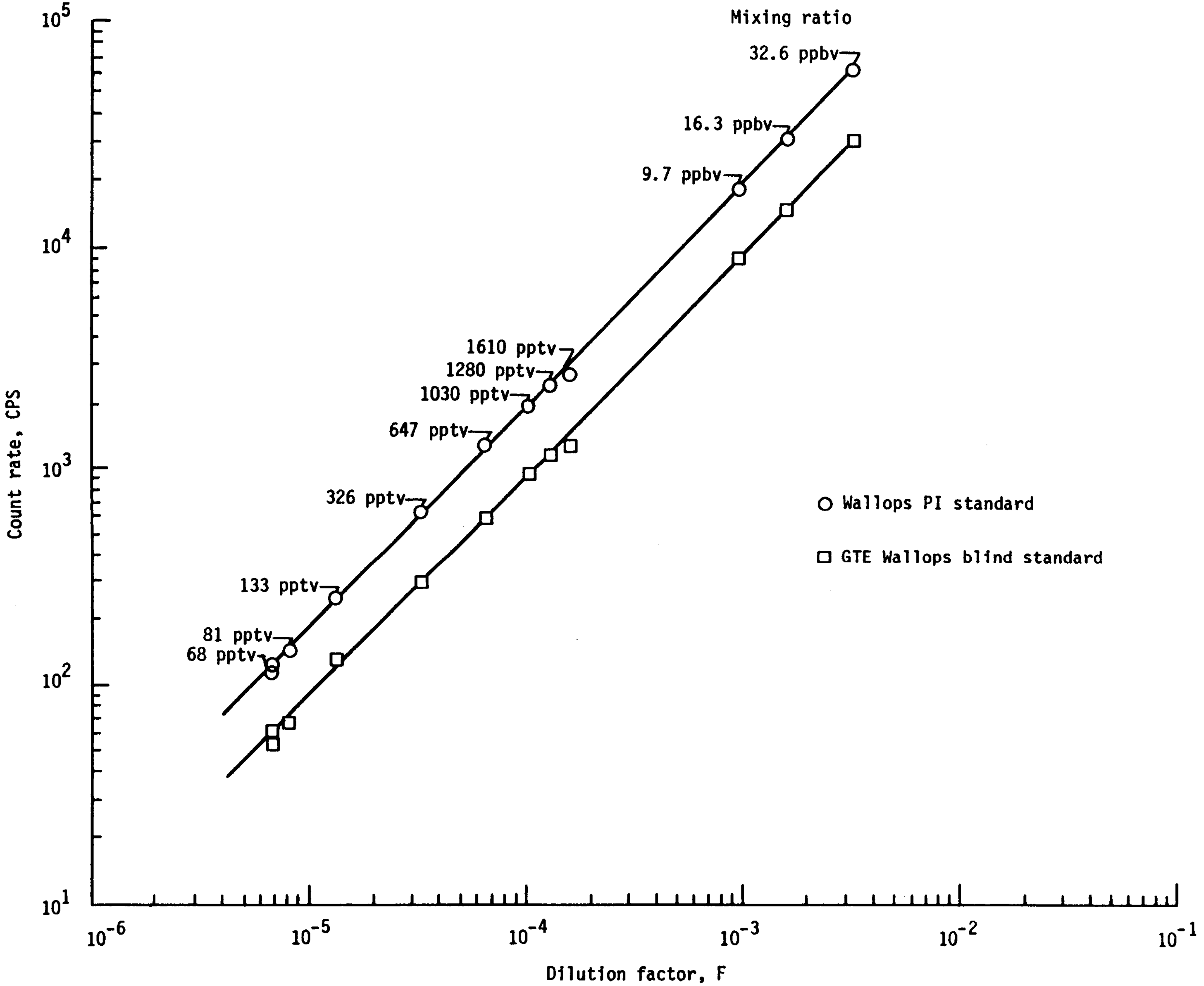


Figure C1.- Measurement results of Wallops GTE blind standard tests, July 7, 1983.

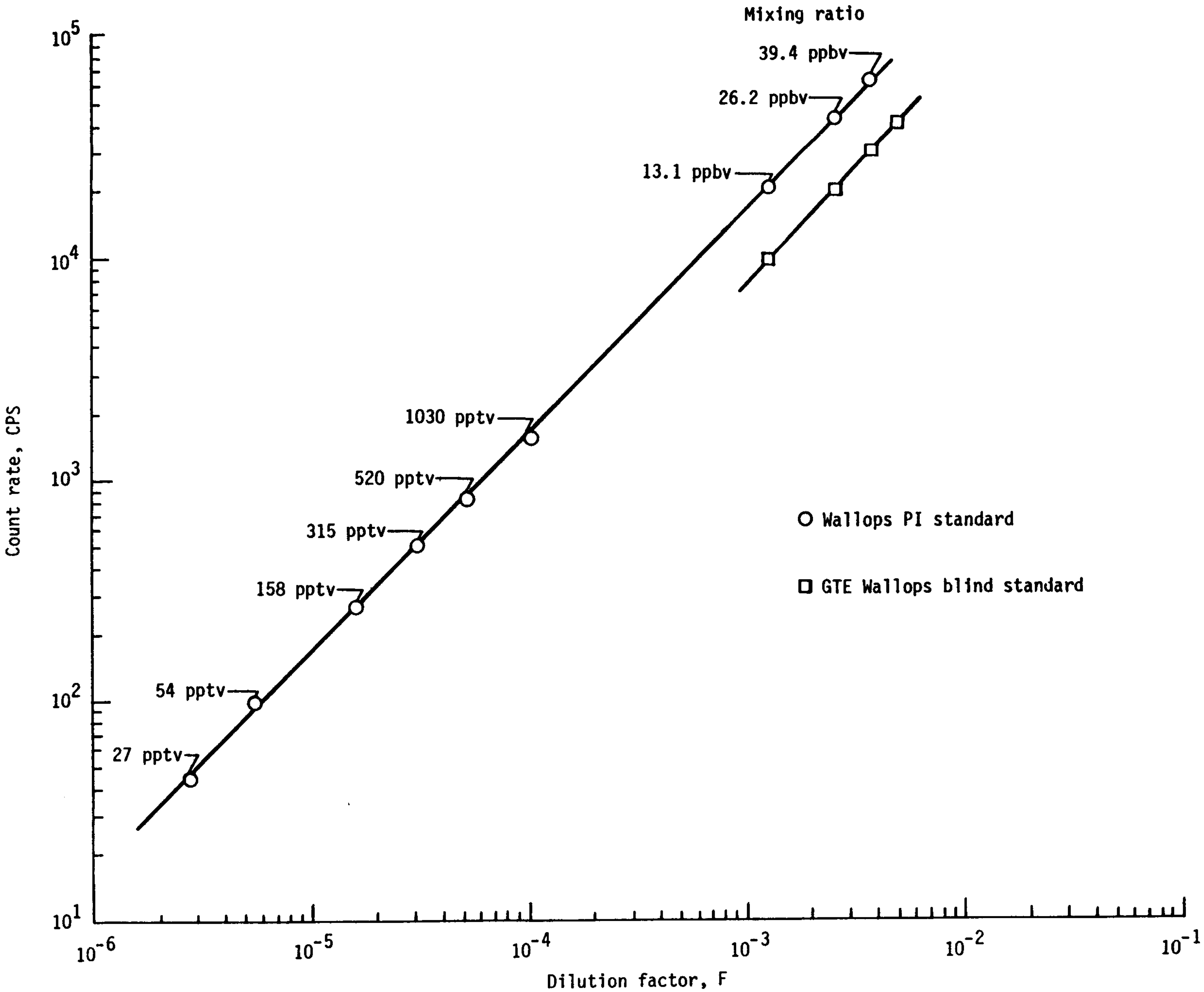


Figure C2.- Measurement results of GTE blind standard tests, July 24, 1983.

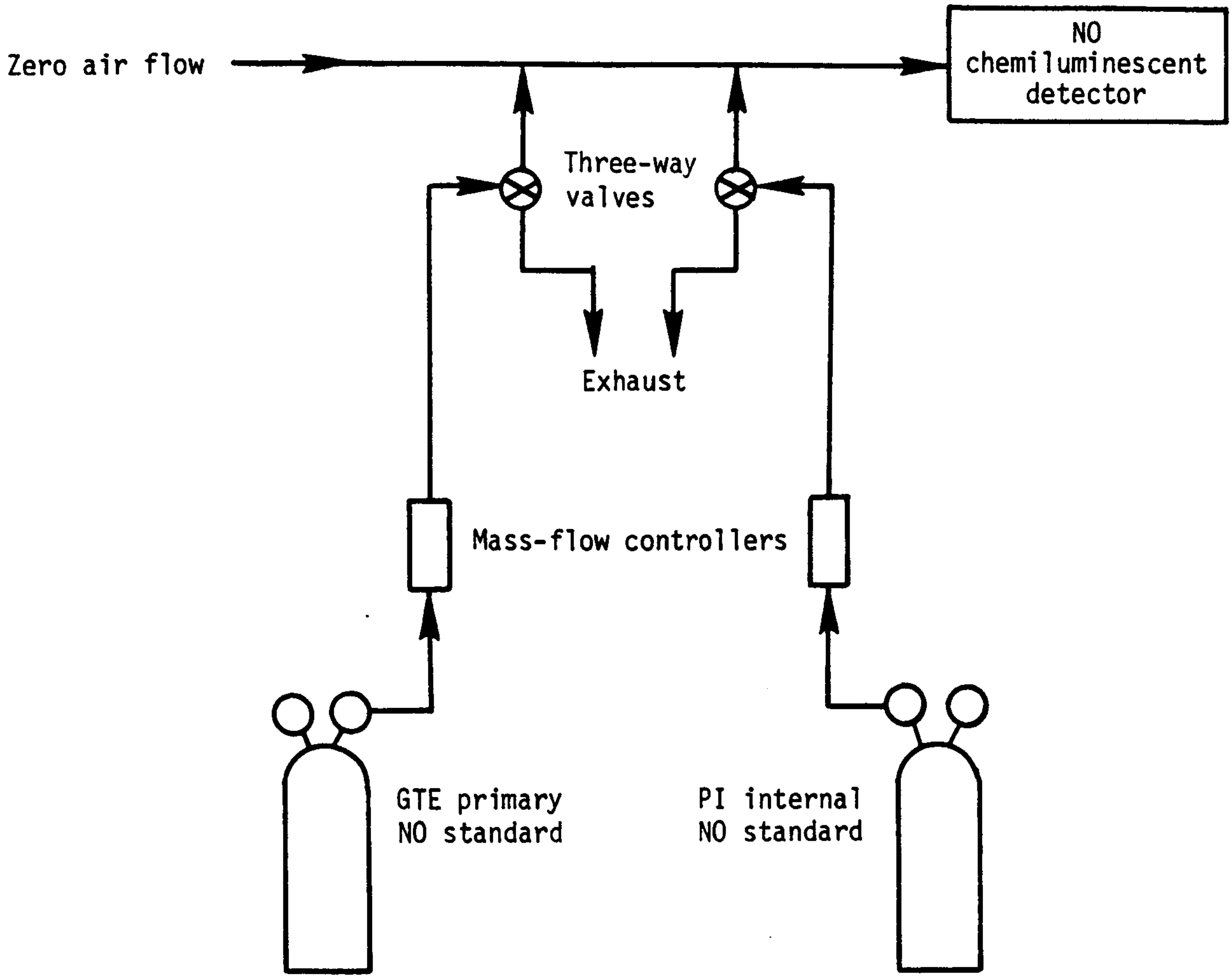


Figure C3.- Experimental setup for NOAA/NCAR tests of GTE-supplied standards.

APPENDIX D

DAILY METEOROLOGICAL CHARTS

Figures D1 through D26 are copies of the daily weather charts which were obtained from NOAA and represent the synoptic conditions from July 4 through July 29, 1983. Each figure includes the following charts for the indicated date:

1. The 0700 EST surface chart

2. The 0700 500-millibar chart

3. The daily temperature extreme chart

4. A precipitation chart

Table D1 is a reproduction of a NOAA write-up which is furnished with the charts.

TABLE D1.- REPRODUCTION OF NOAA SUPPLIED WRITE-UP FOR METEOROLOGICAL CHARTS

The charts in this publication are the principal charts of the former Weather Bureau publication, "Daily Weather Map." They are the Surface Weather Map, the 500-Millibar Height Contours chart, the Highest and Lowest Temperatures chart, and the Precipitation Areas and Amounts chart. All charts for each day are arranged on a single page. They are copied from operational weather maps prepared by the National Meteorological Center, National Weather Service. The symbols on the Surface Weather Map and the 500-Millibar Height Contours chart are standard international symbols. Official copies of an explanatory sheet are available from National Oceanic and Atmospheric Administration, Central Logistics Supply Center, 619 Hardesty Street, Kansas City, MO 64124. Sales copies may be ordered from Public Documents Department, U.S. Government Printing Office, Washington, D.C. 20402, single copy 40 cents. Orders of 100 copies or more mailed to one address are discounted at 25 percent. Make checks payable to "Superintendent of Documents."

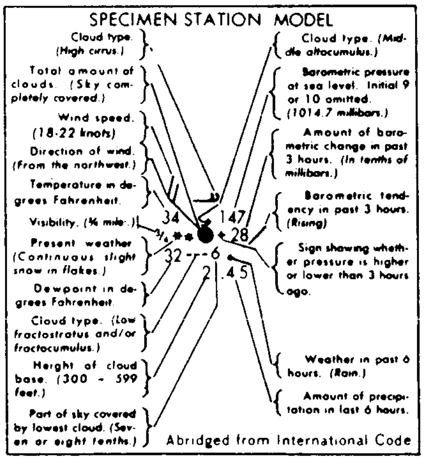
The Surface Weather Map shows station data and the analysis for 7:00 a.m., EST. Tracks of well-defined low pressure areas are indicated by chain of arrows; locations of these centers at 6, 12, and 18 hours preceding map time are indicated by small white crosses in black squares. Areas of precipitation are indicated by shading. The weather reports printed here are only a fraction of those on which the analyses are based. Occasional apparent discrepancies between the printed station data and the analyses result from absence of station reports not included here because of lack of space.

The 500-Millibar Height Contours chart shows height contours and isotherms of the 500-millibar surface at 7:00 a.m., EST. Height contours are shown as continuous lines labeled in feet above sea level. Isotherms are shown as dashed lines labeled in degrees Celsius. Arrows show the wind direction and speed at the 500-millibar level.

The Highest and Lowest Temperatures chart shows the maximum temperature for the 12-hour period ending at 7:00 p.m. EST of the previous day and the minimum temperature for the 12-hour period ending 7:00 a.m. EST. The names of the reporting points are shown on the Surface Weather Map. The maximum temperature is plotted above the station location, and the minimum temperature is plotted below.

The Precipitation Areas and Amounts chart shows areas (shaded) that had precipitation during the 24 hours ending at 7:00 a.m., EST, with amounts to the nearest hundredth of an inch. Incomplete totals are underlined. "T" indicates a trace of precipitation. Dashed lines, in season, show the depth of snow on the ground in inches at 7:00 a.m., EST.

SPECIMEN STATION MODEL



Abridged from International Code

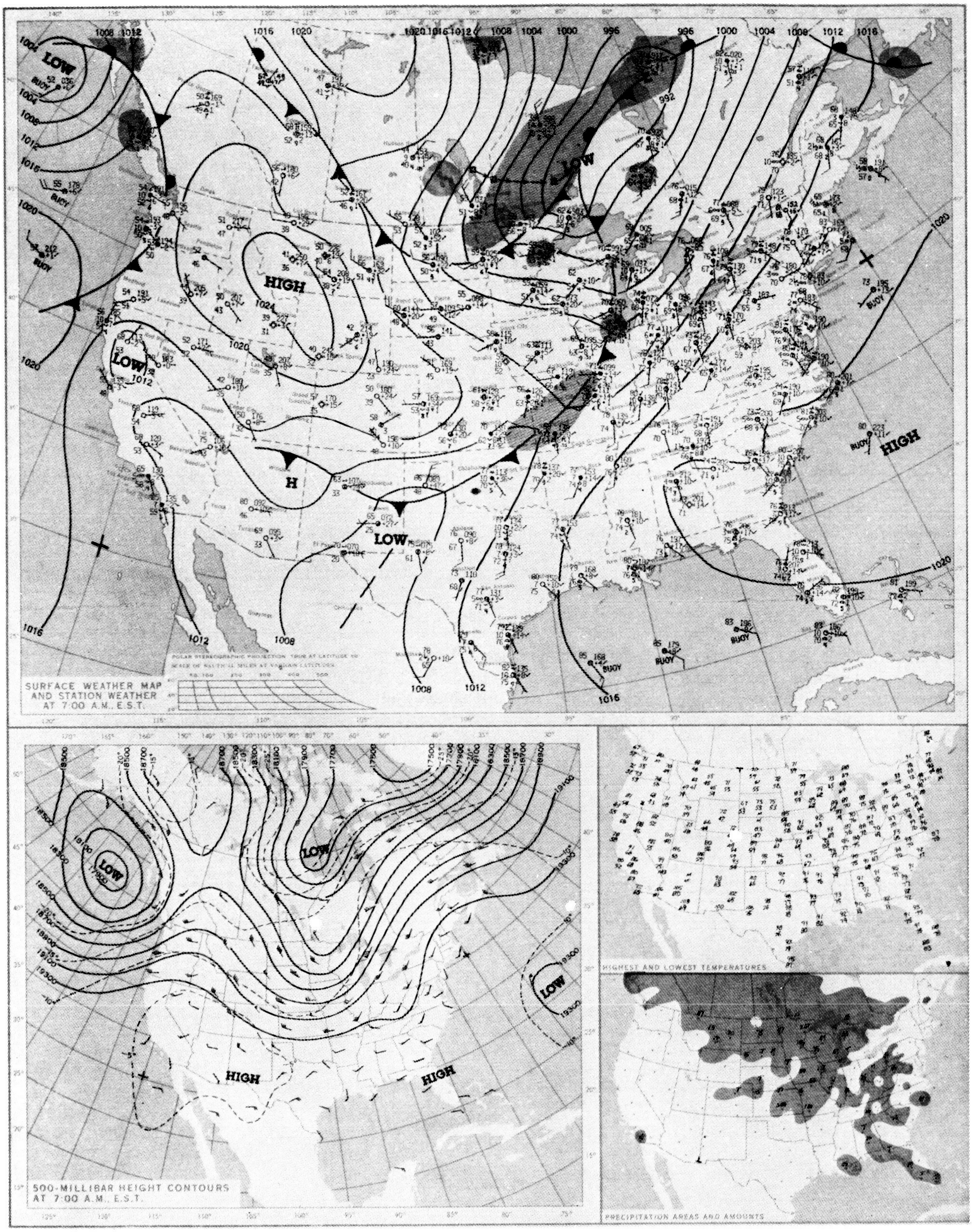


Figure D1.- Weather chart for July 4, 1983.

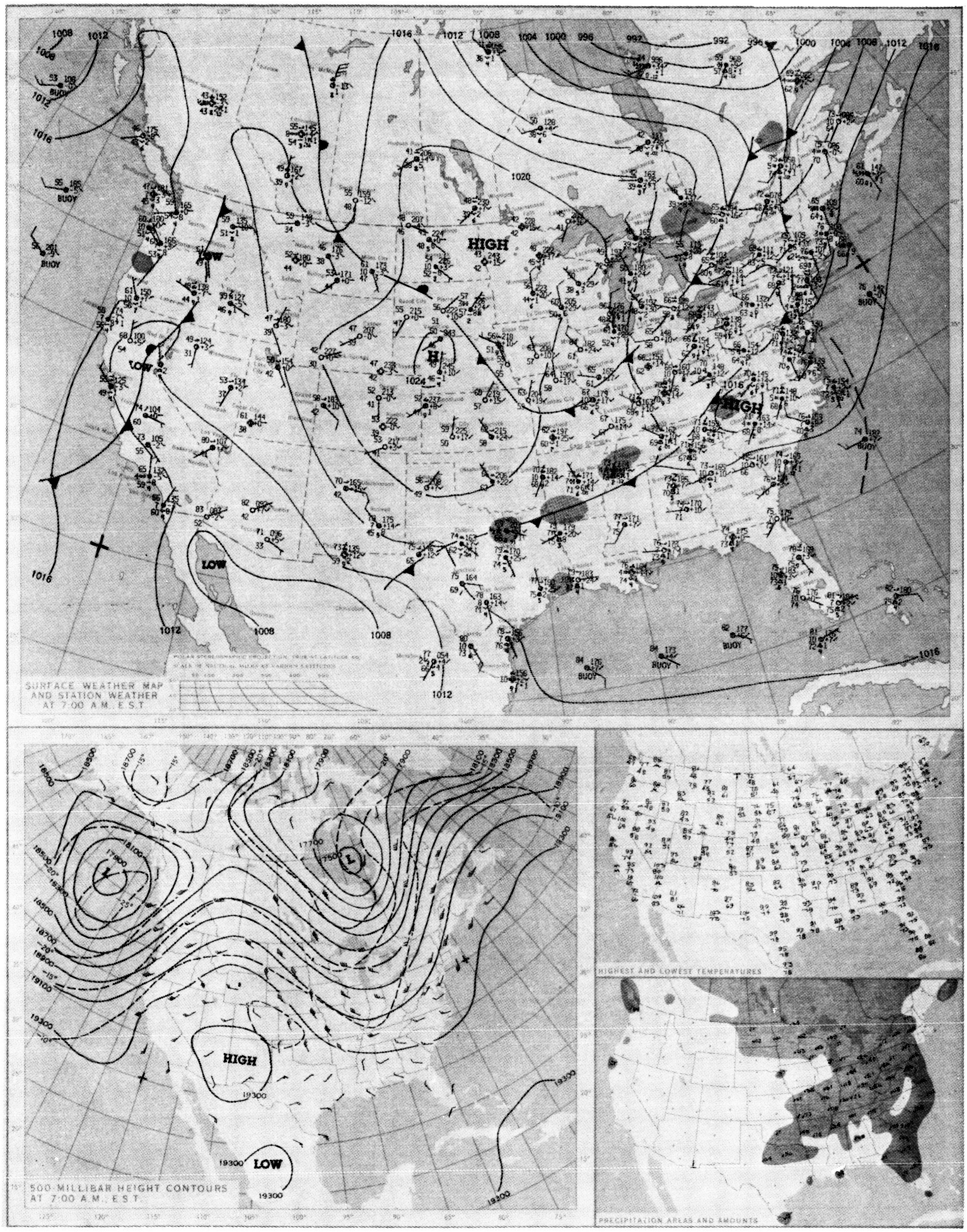


Figure D2.- Weather chart for July 5, 1983.

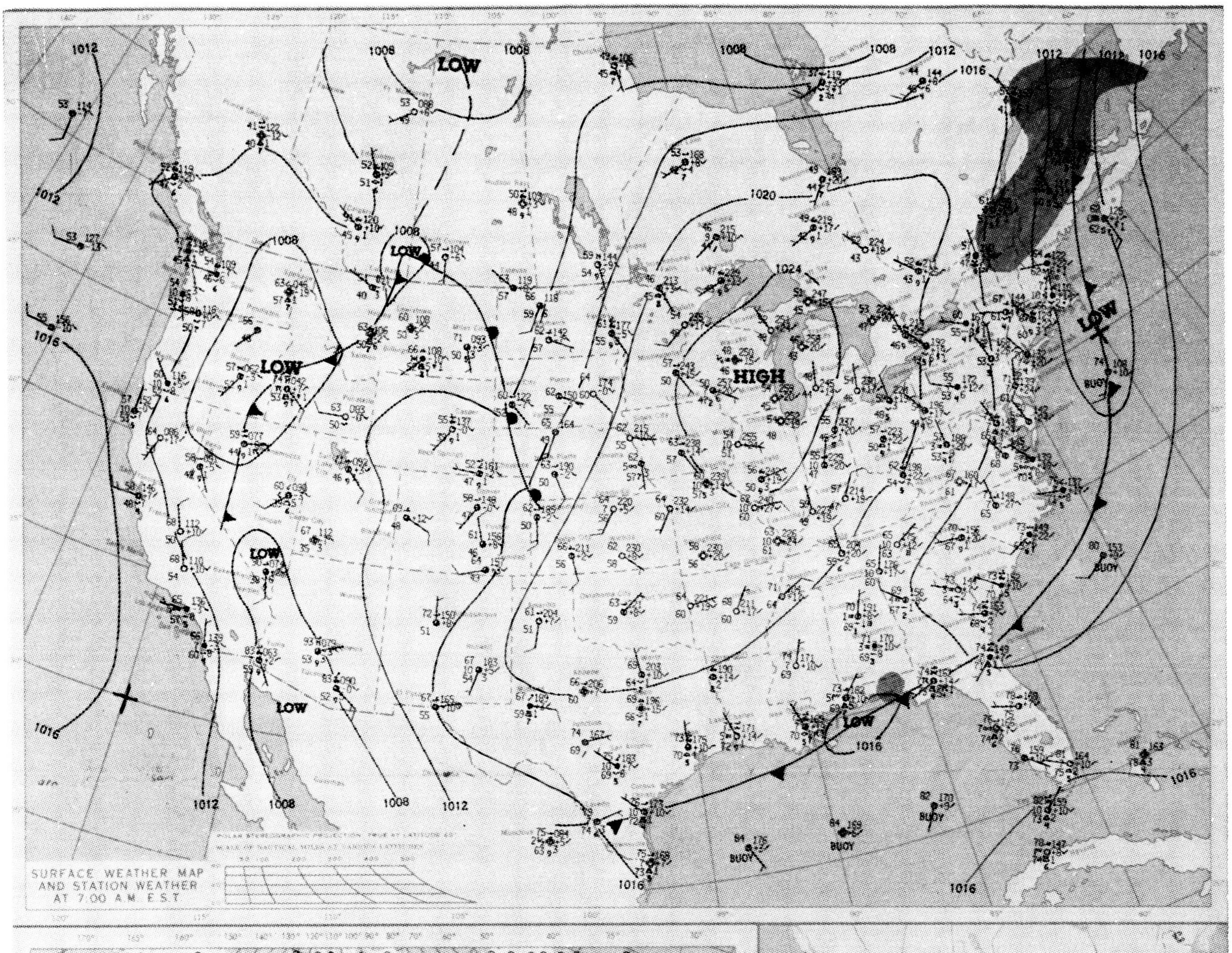


Figure D3.- Weather chart for July 6, 1983.

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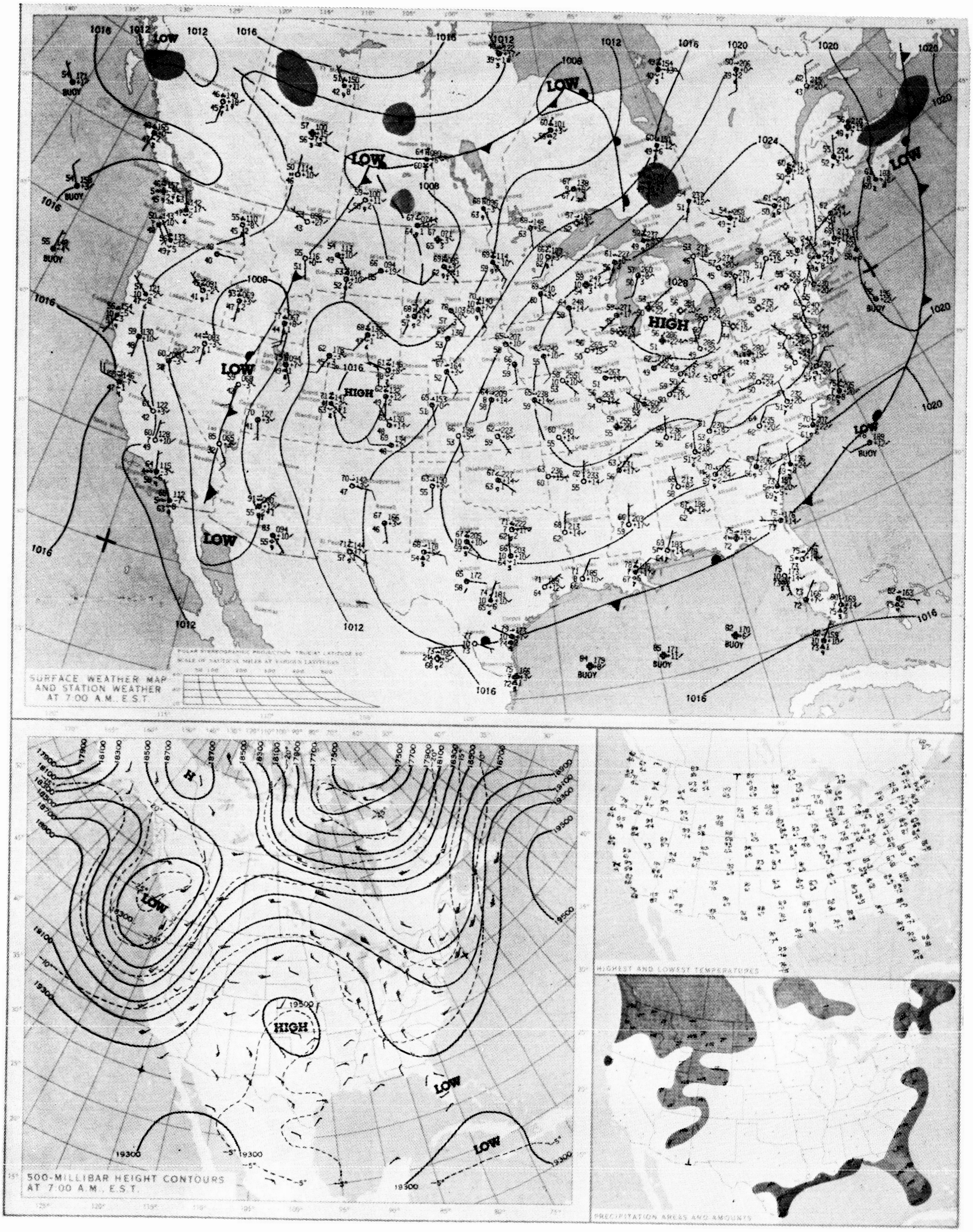


Figure D4.- Weather chart for July 7, 1983.

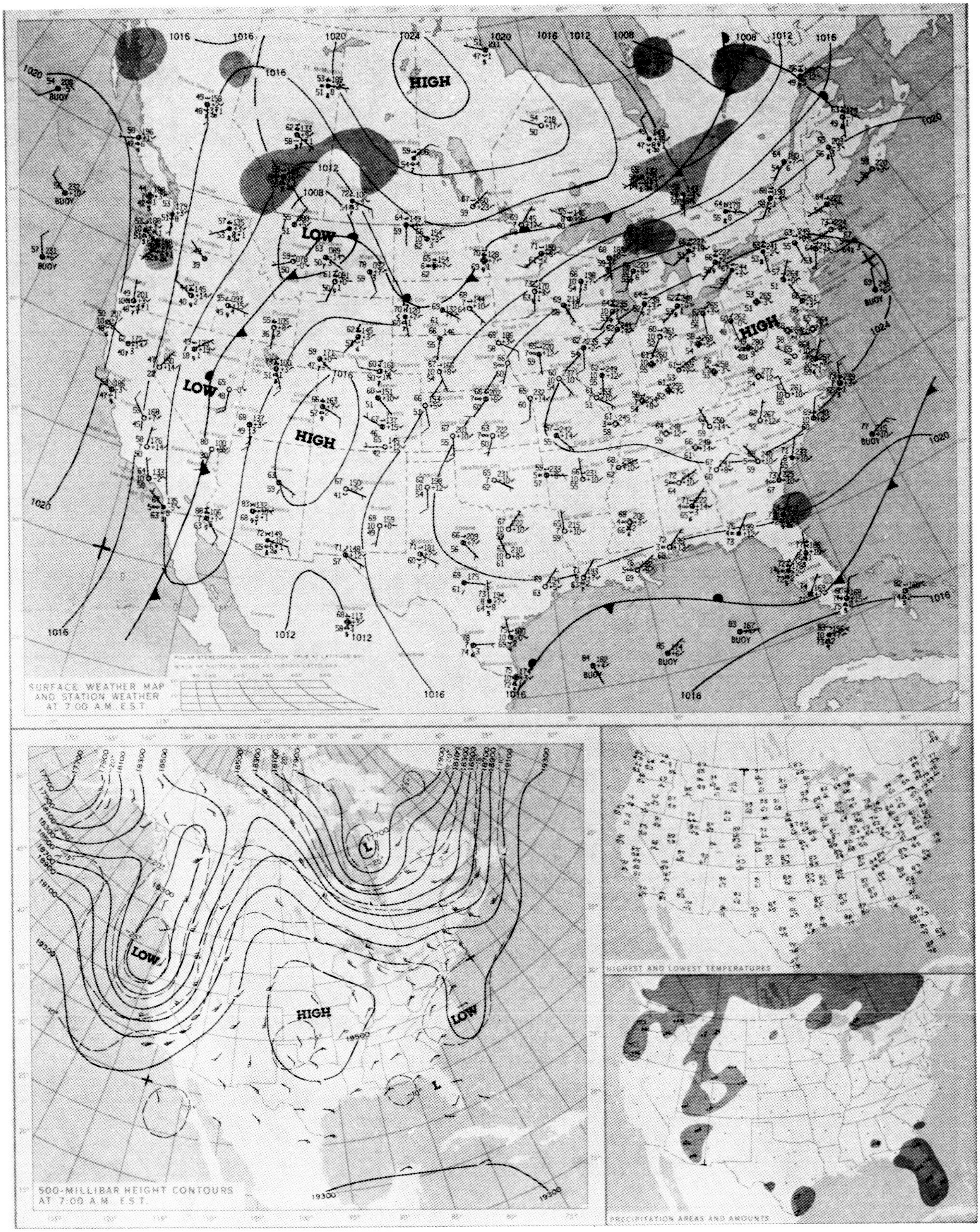


Figure D5.- Weather chart for July 8, 1983.

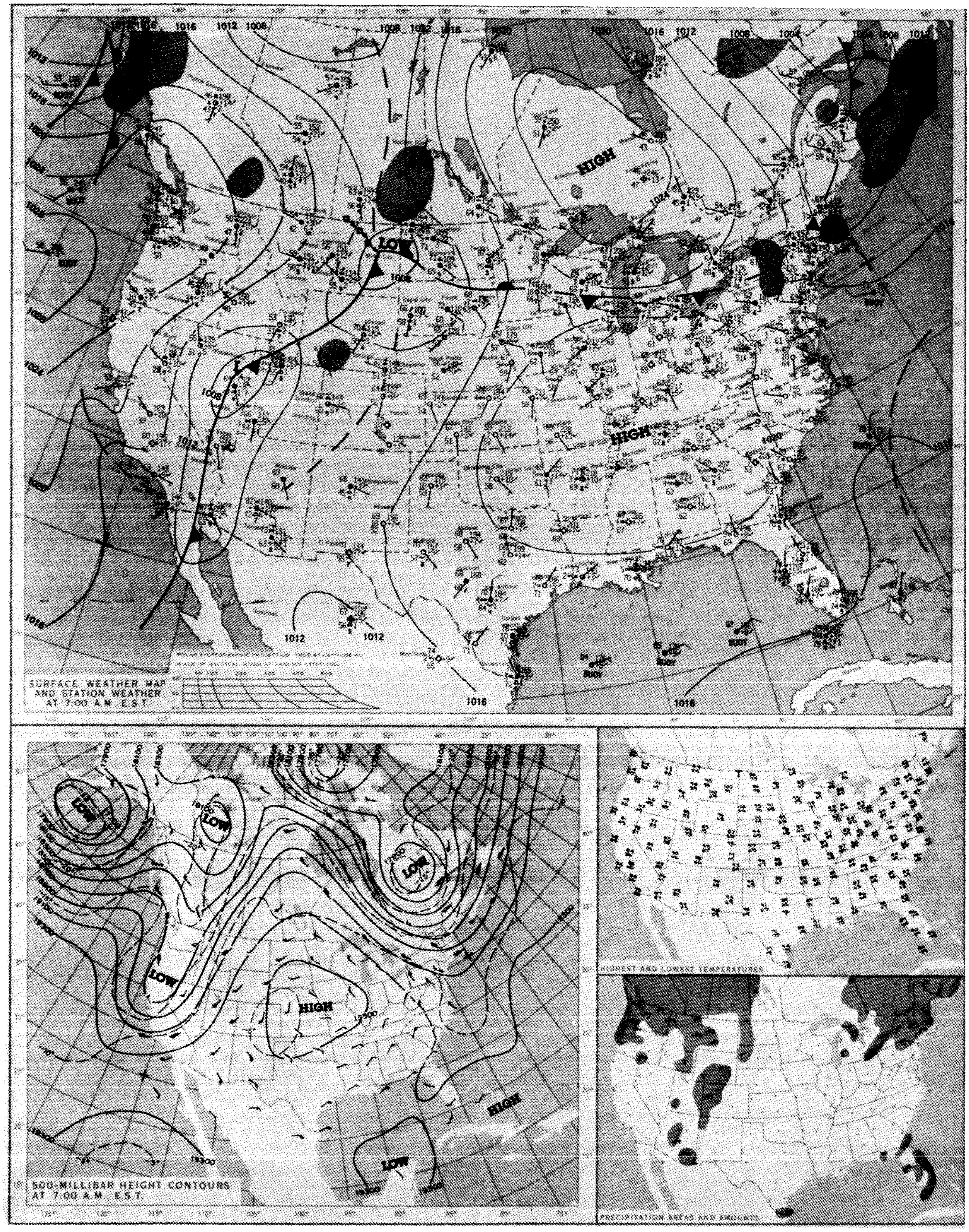


Figure D6.- Weather chart for July 9, 1983.

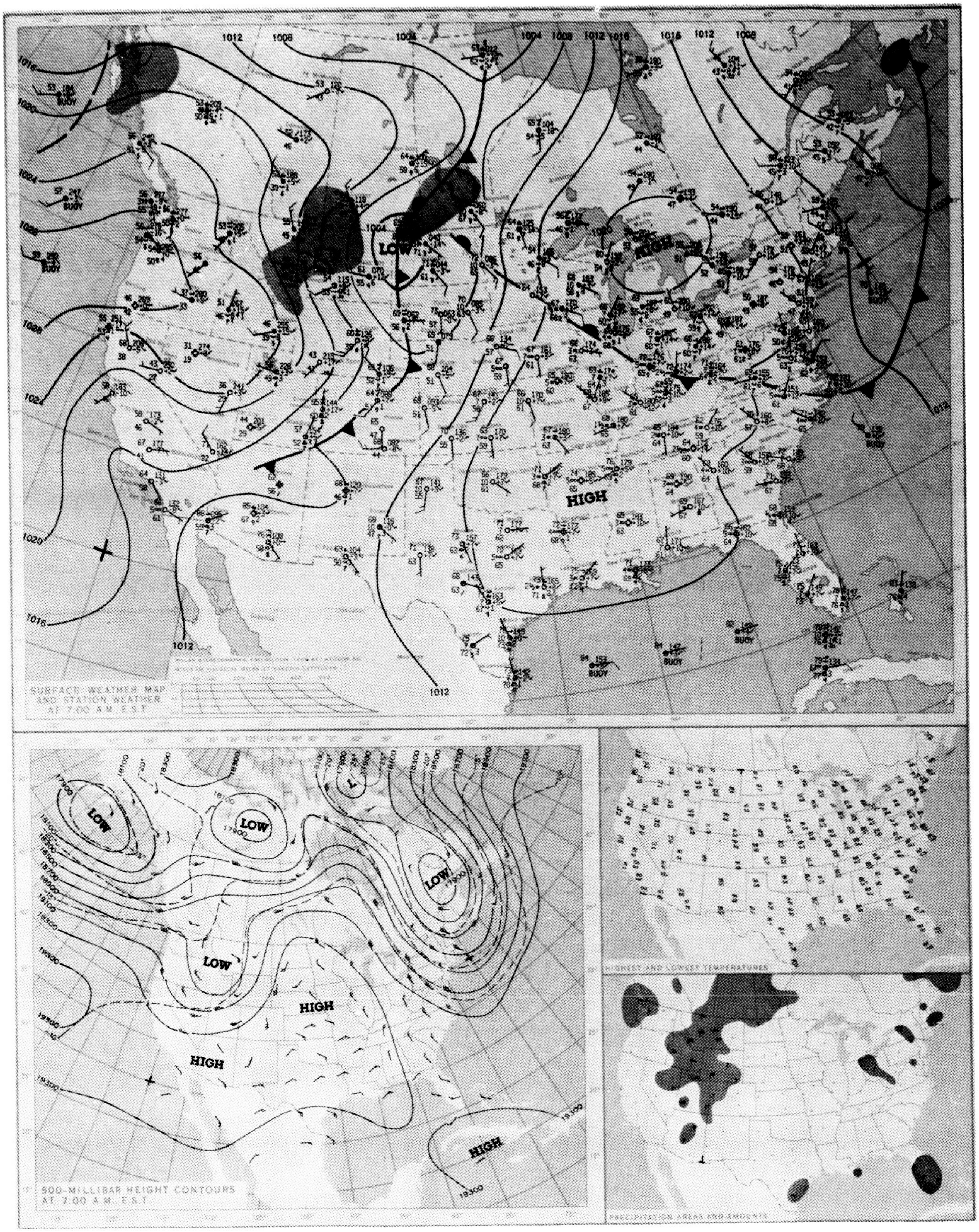


Figure D7.- Weather chart for July 10, 1983.

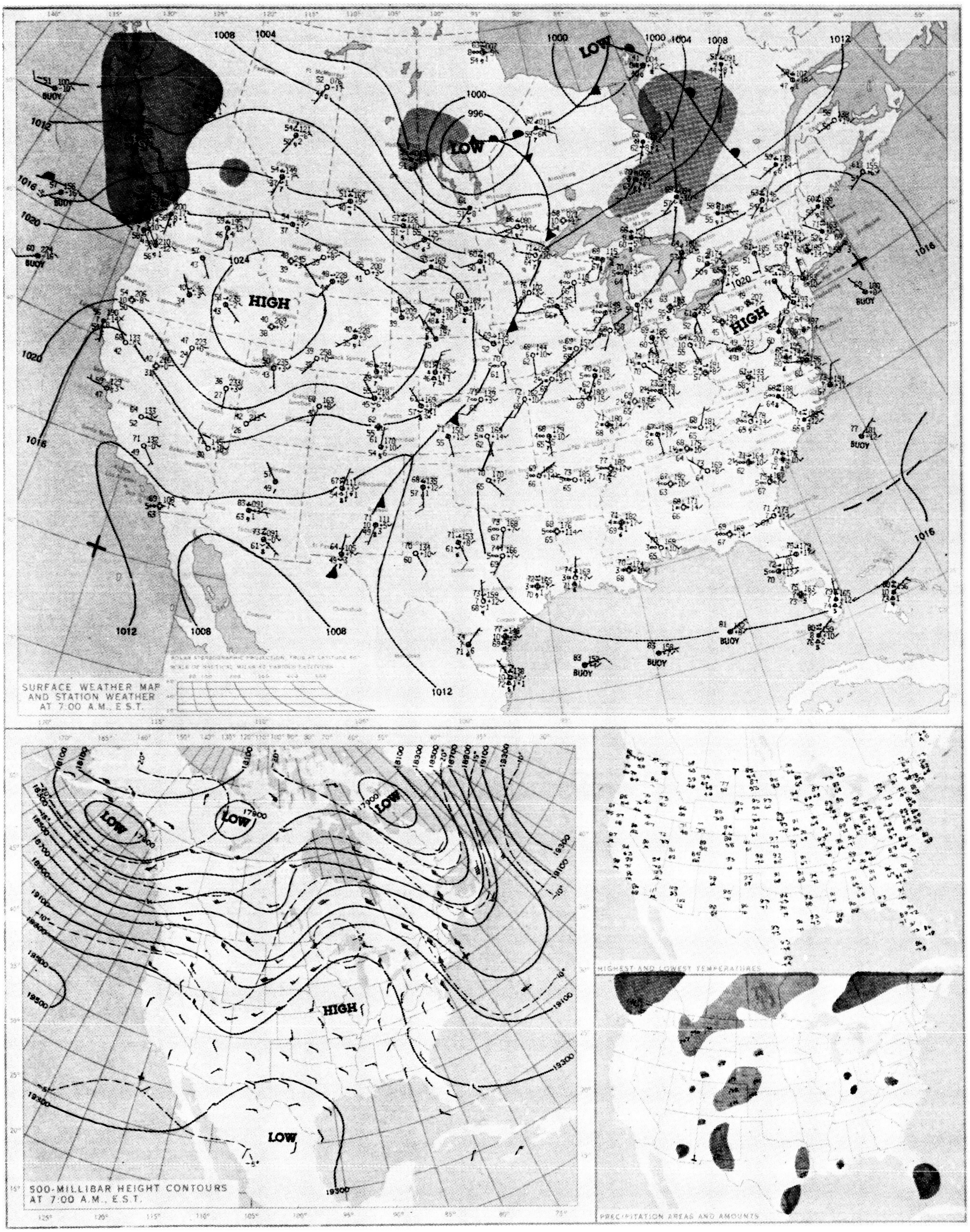
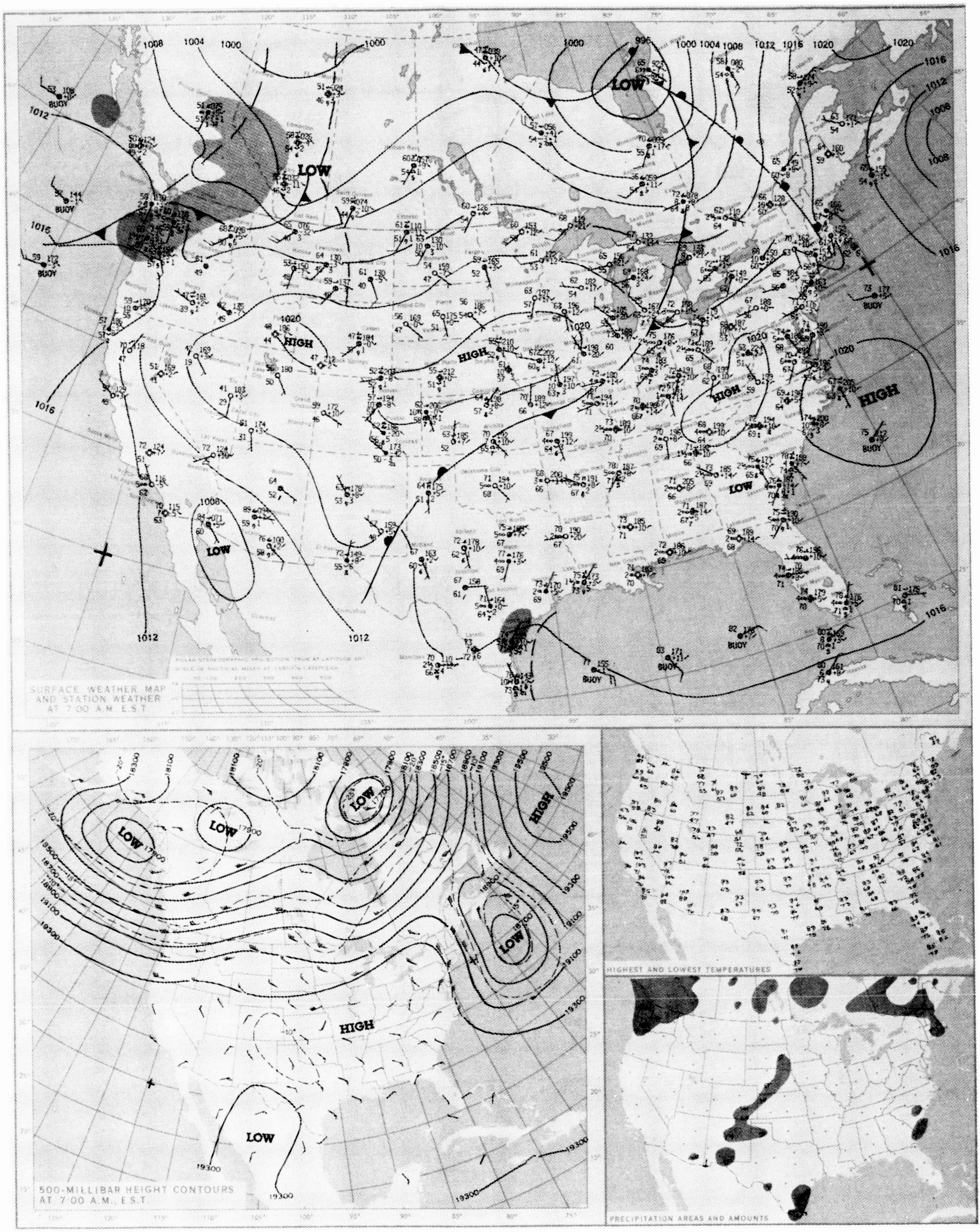


Figure D8.- Weather chart for July 11, 1983.



SURFACE WEATHER MAP AND STATION WEATHER AT 7:00 A.M. E.S.T.

500-MILLIBAR HEIGHT CONTOURS AT 7:00 A.M., E.S.T.

HIGHEST AND LOWEST TEMPERATURES

PRECIPITATION AREAS AND AMOUNTS

Figure D9.- Weather chart for July 12, 1983.

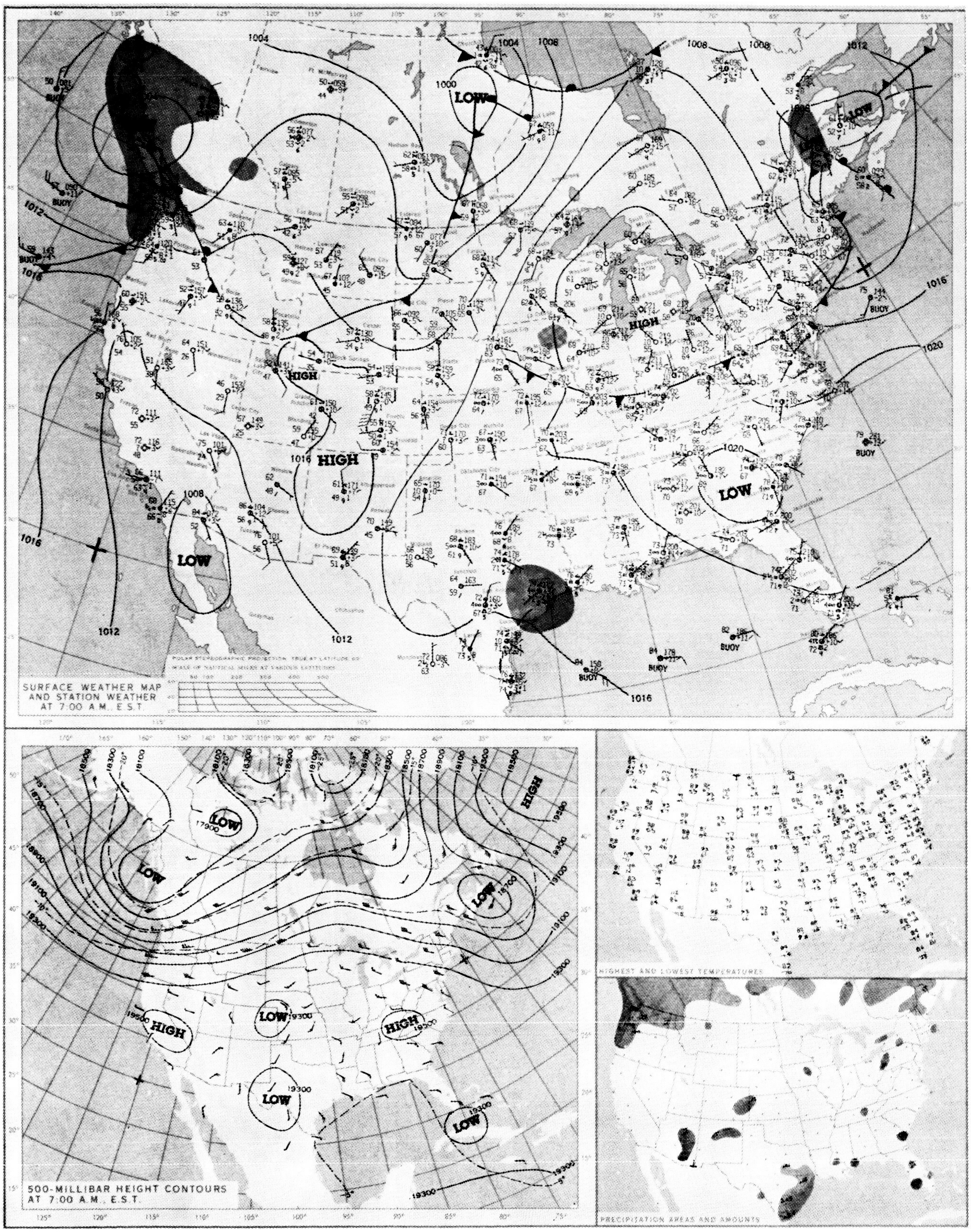


Figure D10.- Weather chart for July 13, 1983.

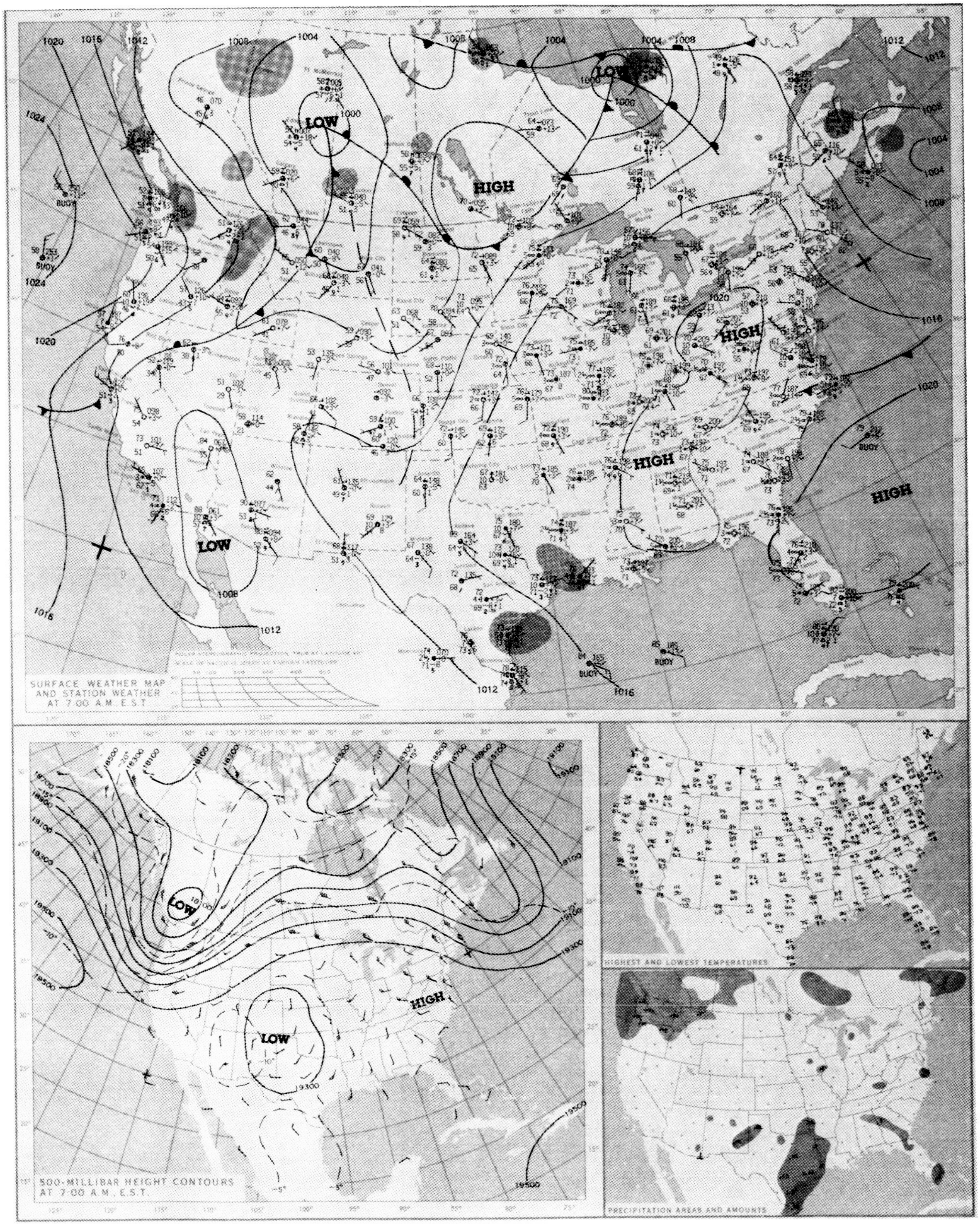
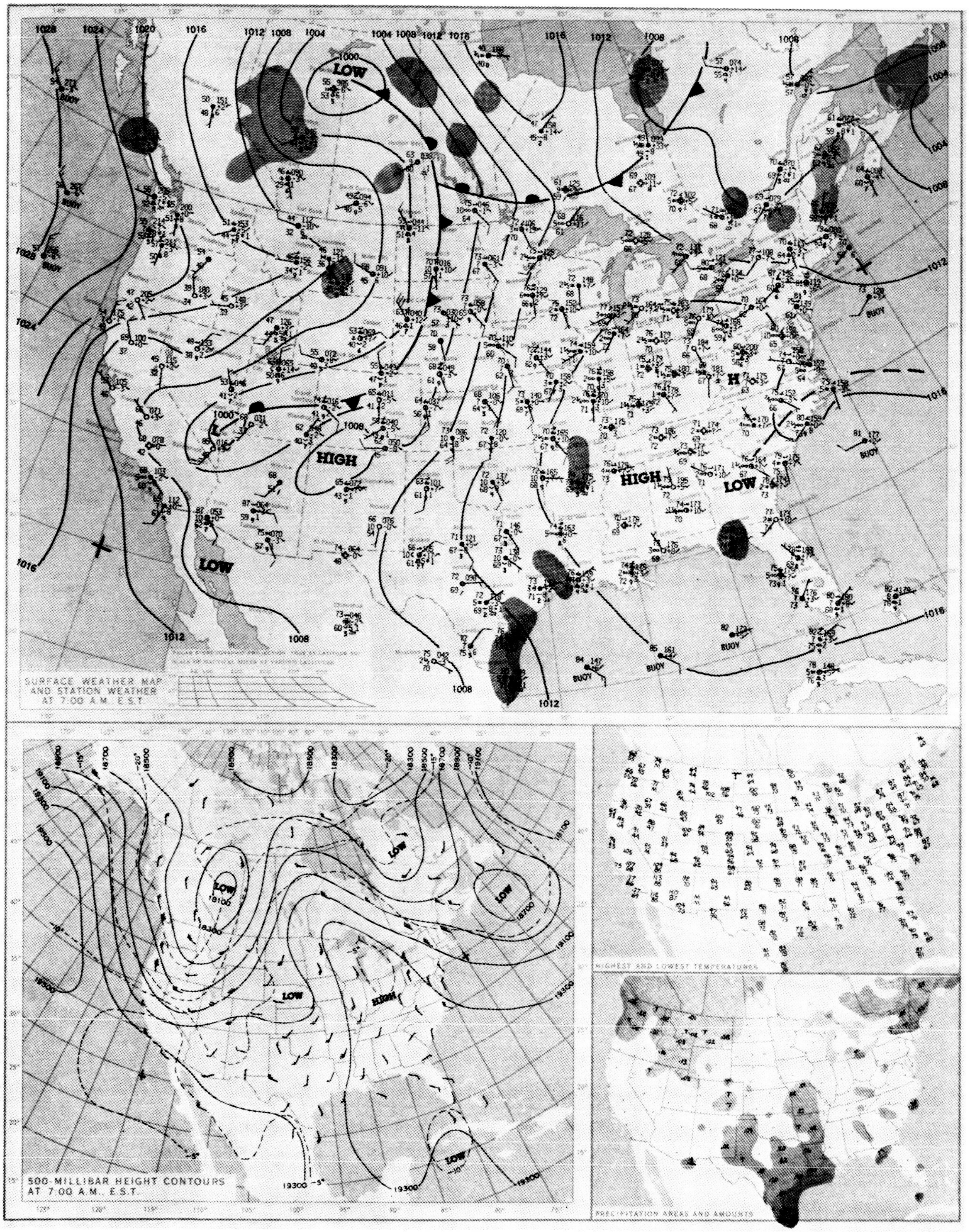


Figure D11.- Weather chart for July 14, 1983.



SURFACE WEATHER MAP AND STATION WEATHER AT 7:00 A.M. E.S.T.

500-MILLIBAR HEIGHT CONTOURS AT 7:00 A.M., E.S.T.

HIGHEST AND LOWEST TEMPERATURES

PRECIPITATION AREAS AND AMOUNTS

Figure D12.- Weather chart for July 15, 1983.

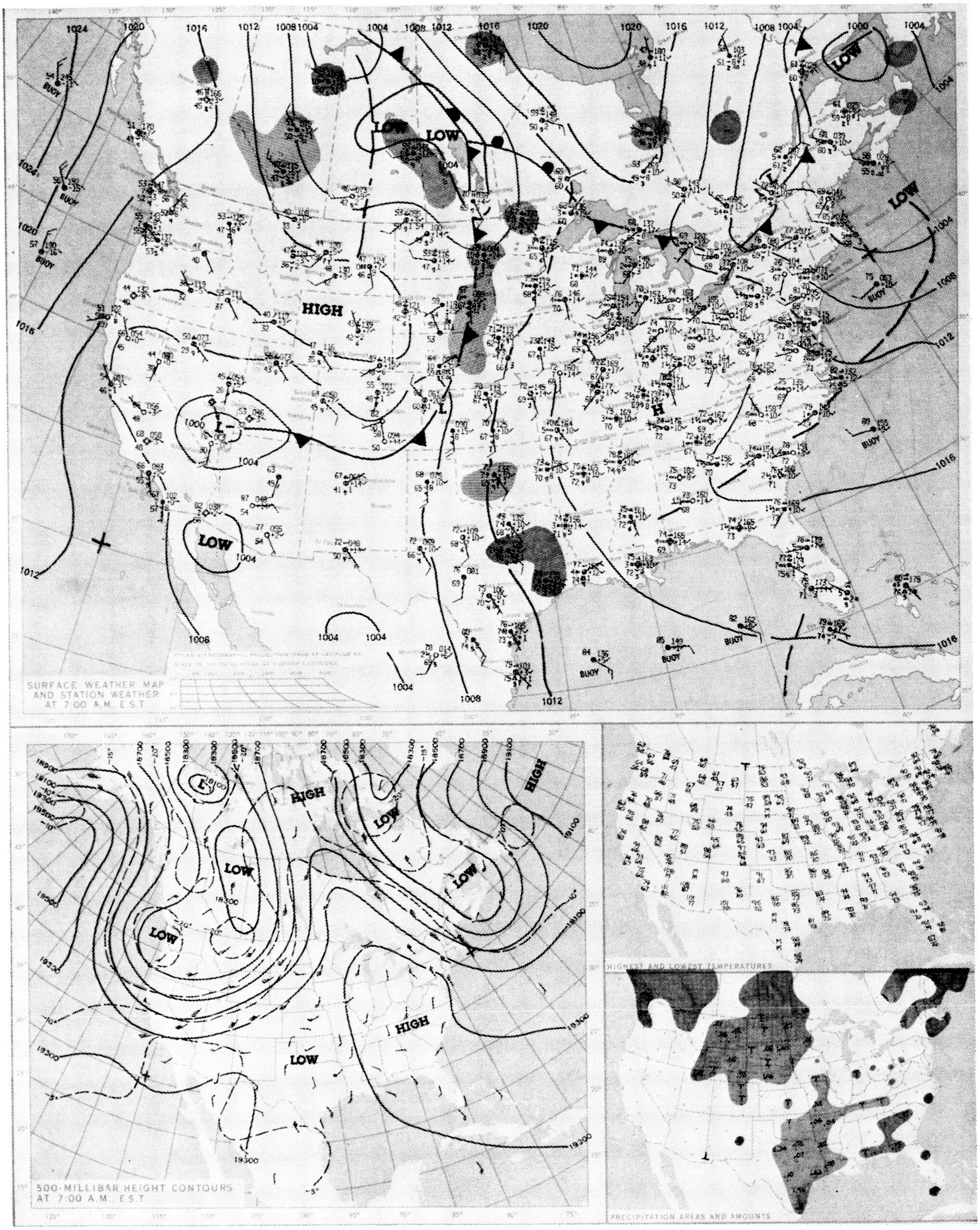


Figure D13.- Weather chart for July 16, 1983.

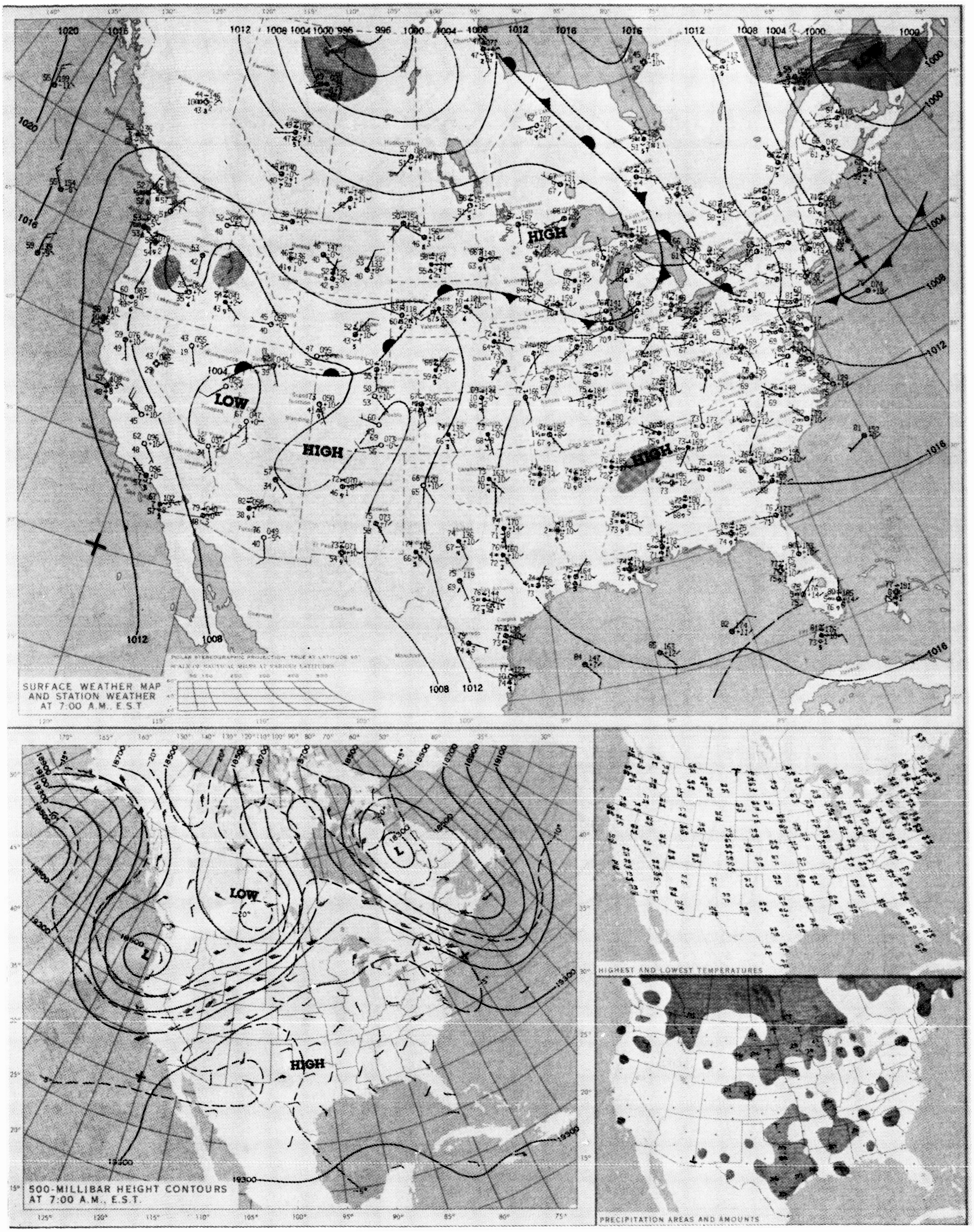


Figure D14.- Weather chart for July 17, 1983.

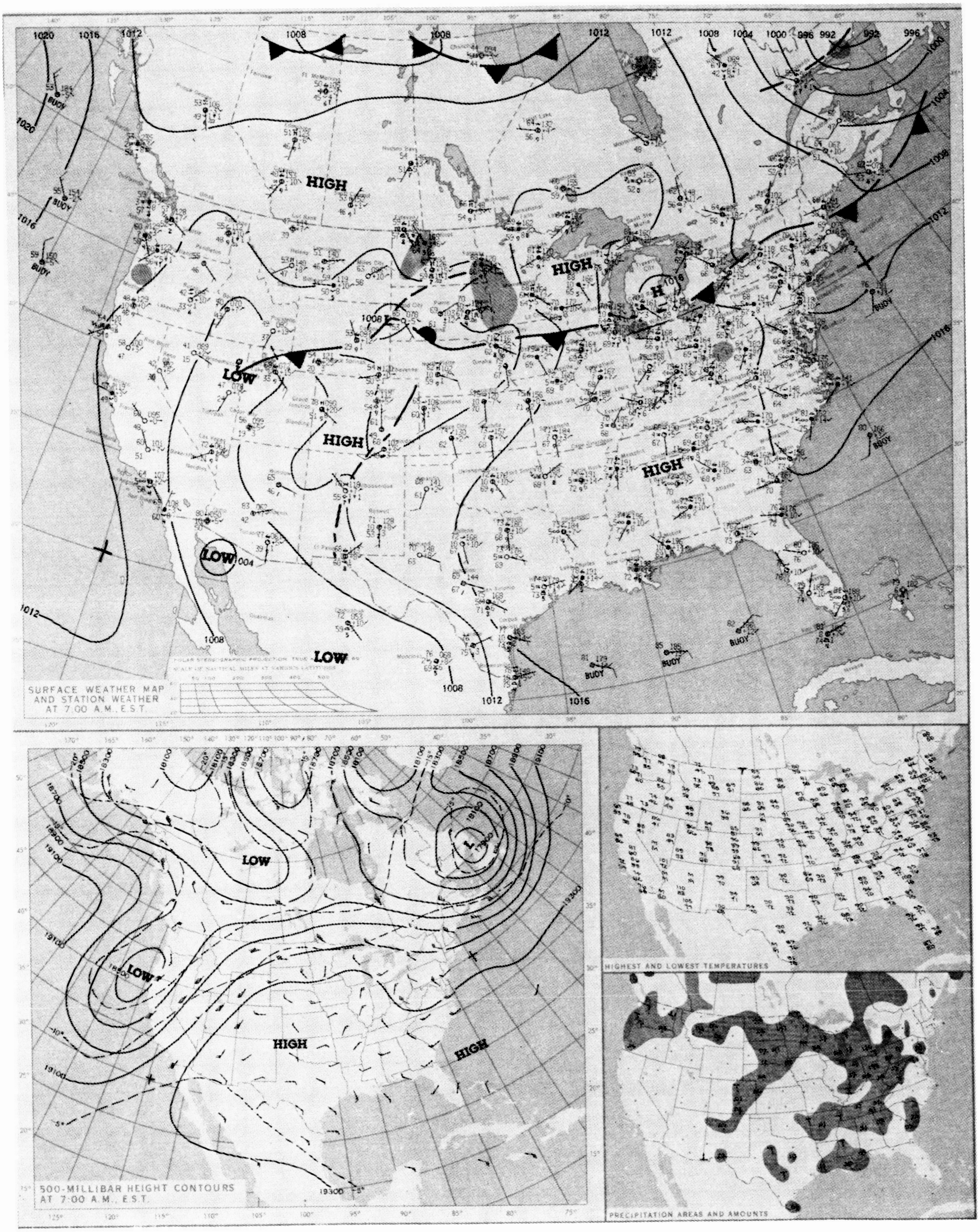


Figure D15.- Weather chart for July 18, 1983.

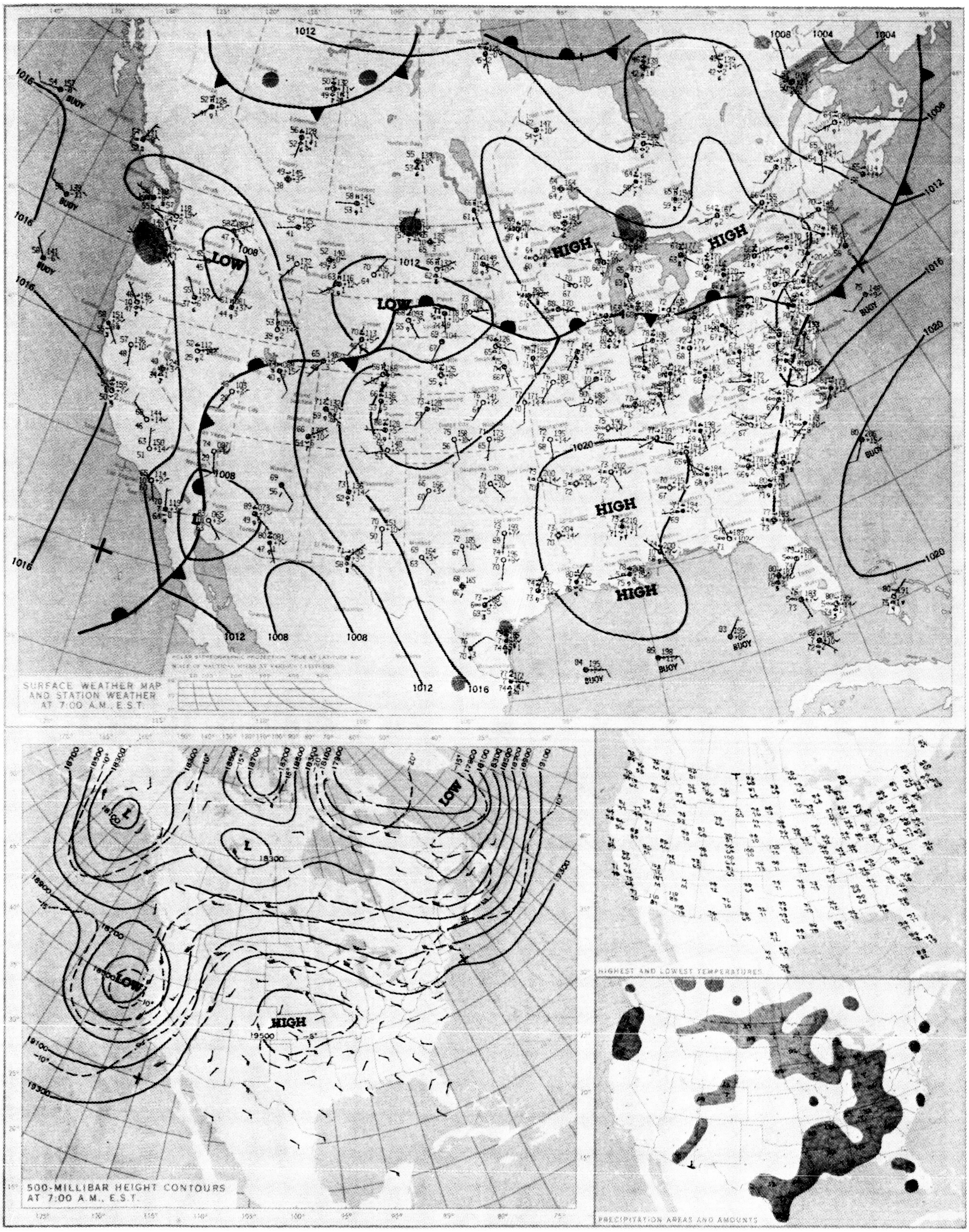


Figure D16.- Weather chart for July 19, 1983.

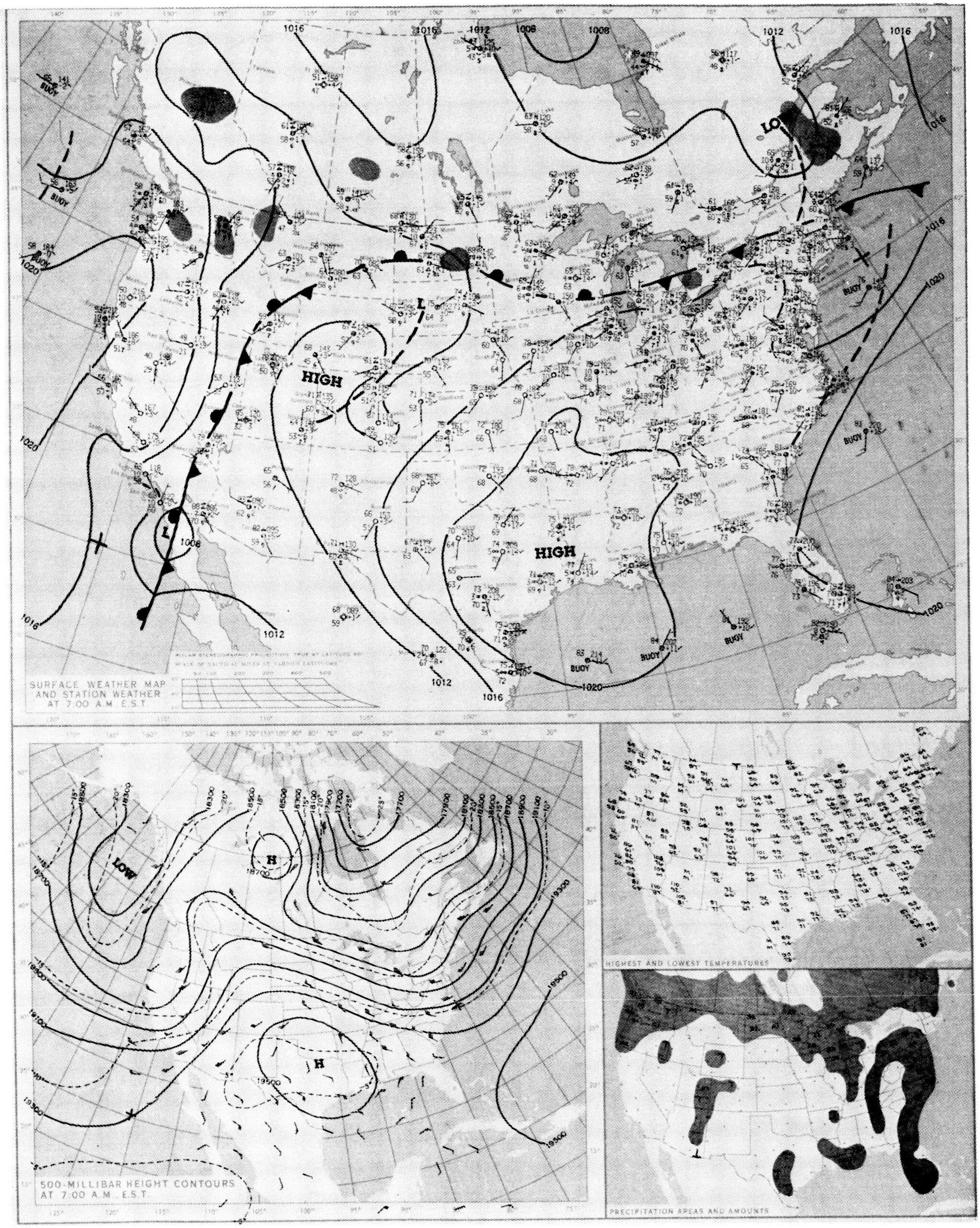


Figure D17.- Weather chart for July 20, 1983.

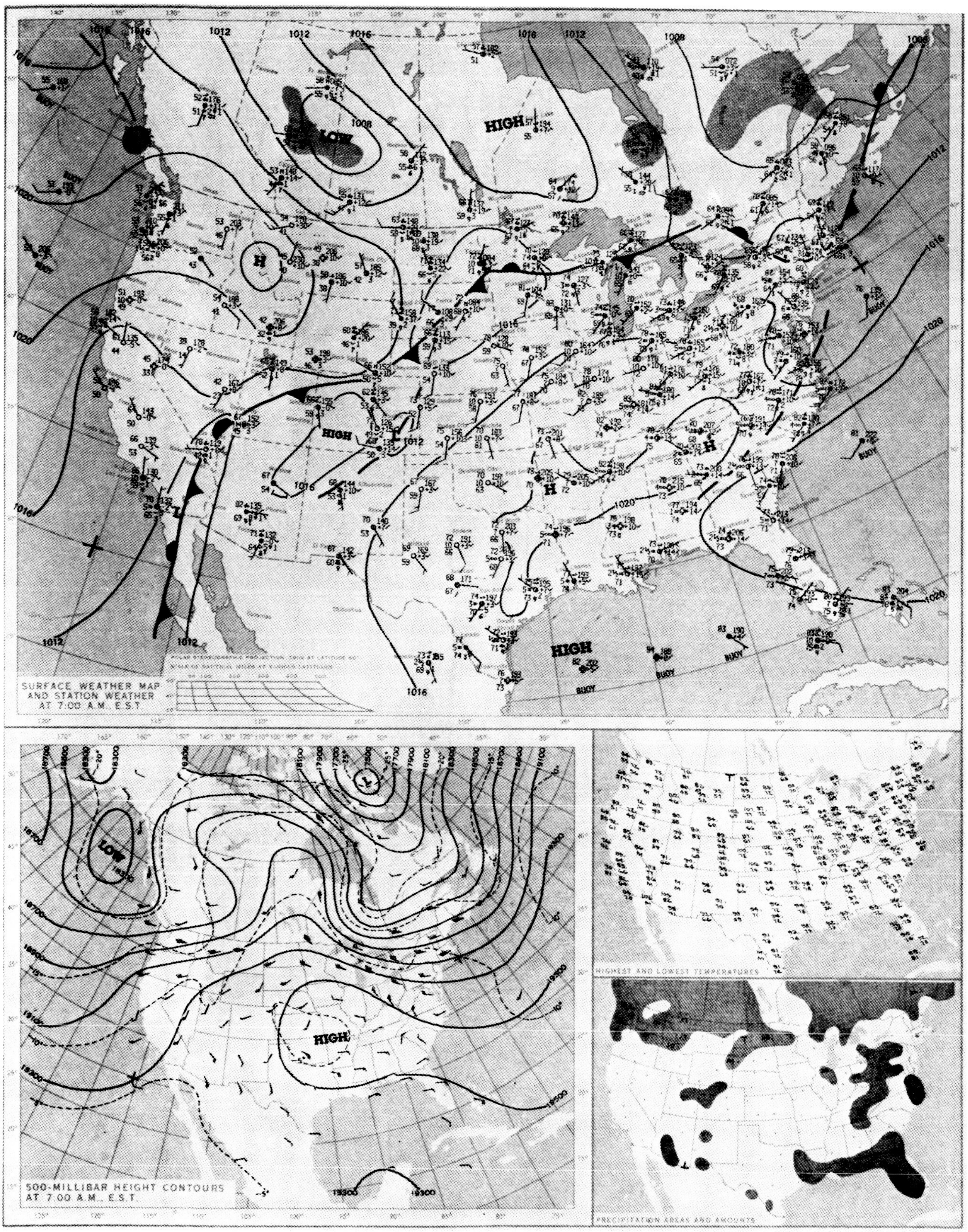


Figure D18.- Weather chart for July 21, 1983.

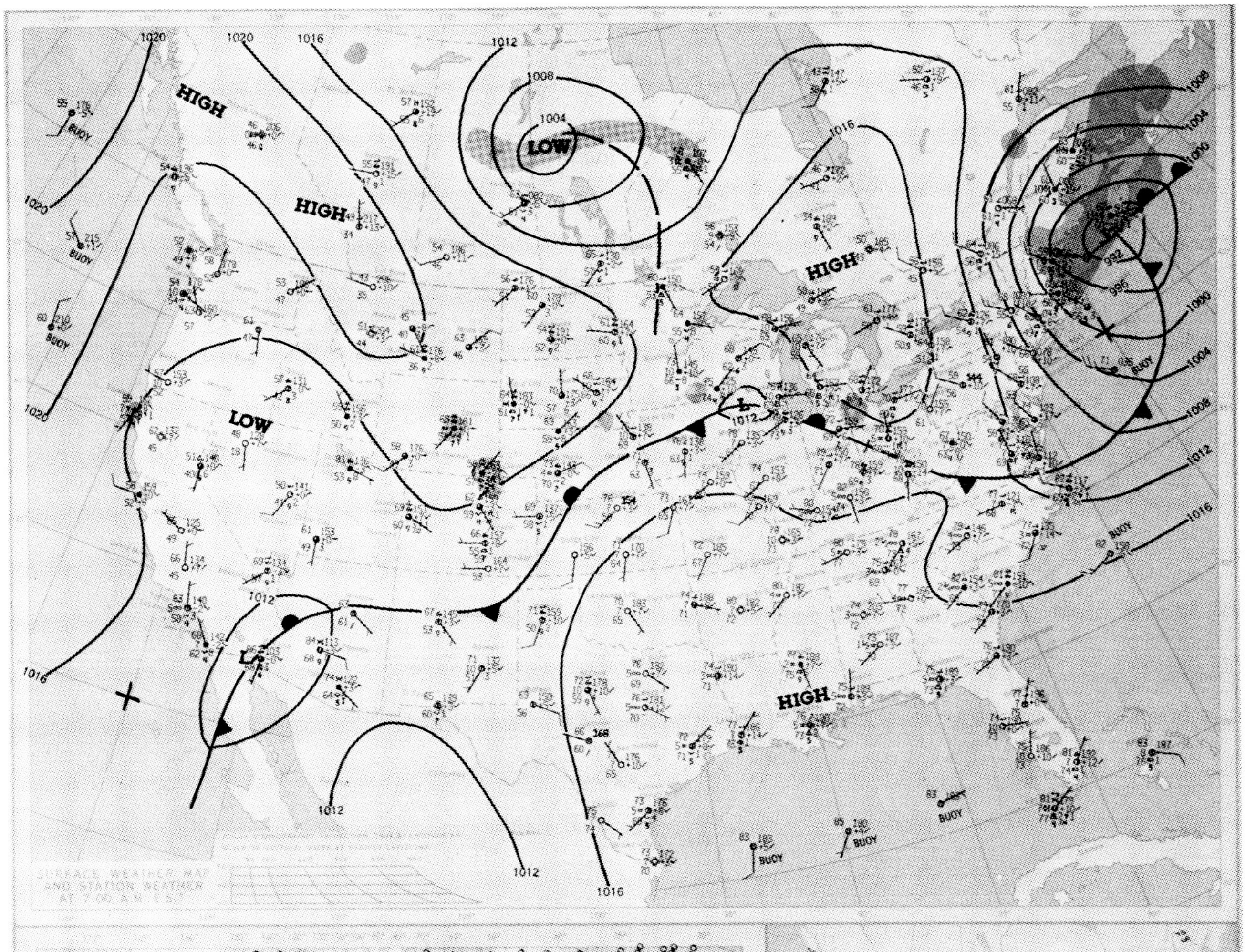


Figure D19.- Weather chart for July 22, 1983.

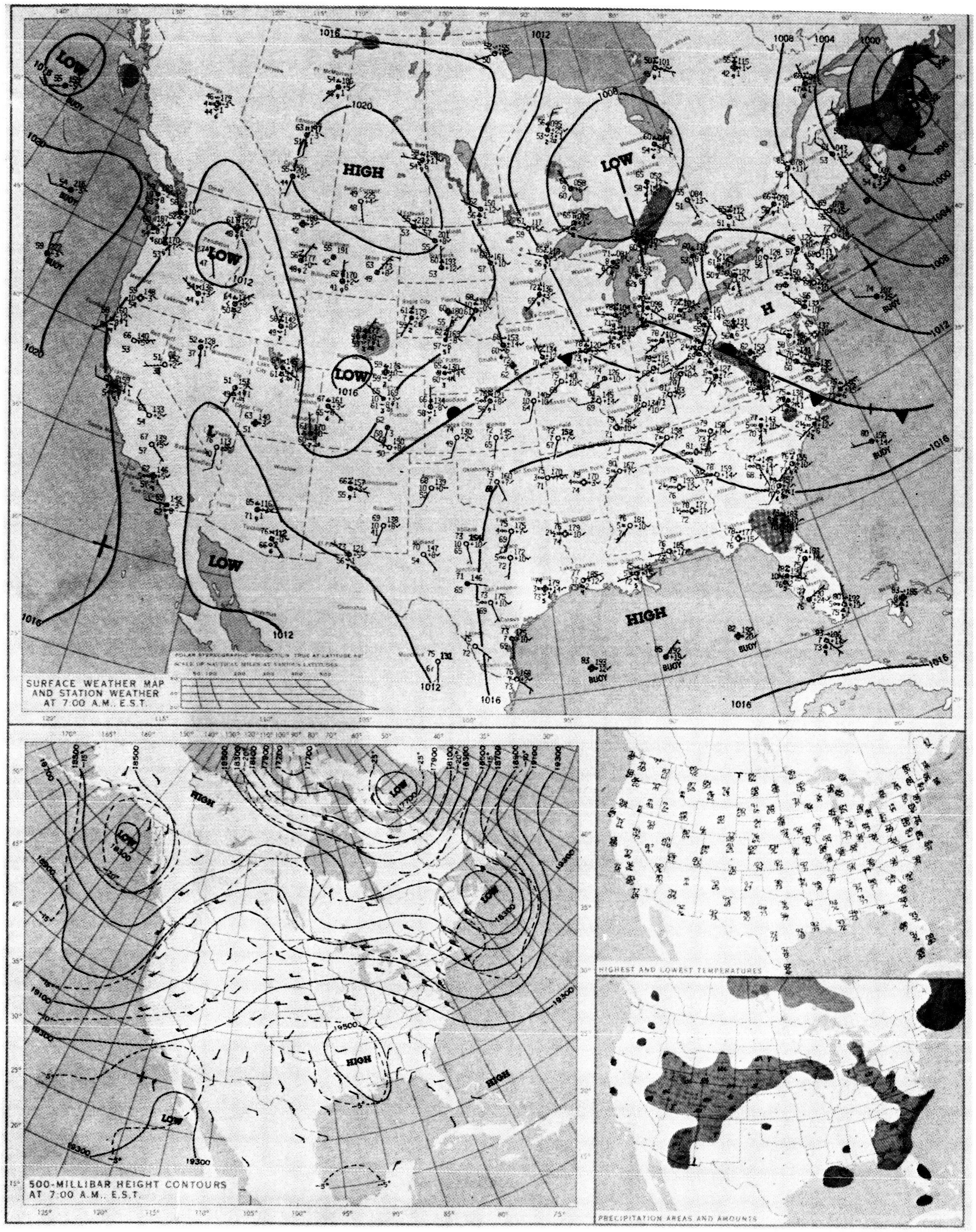
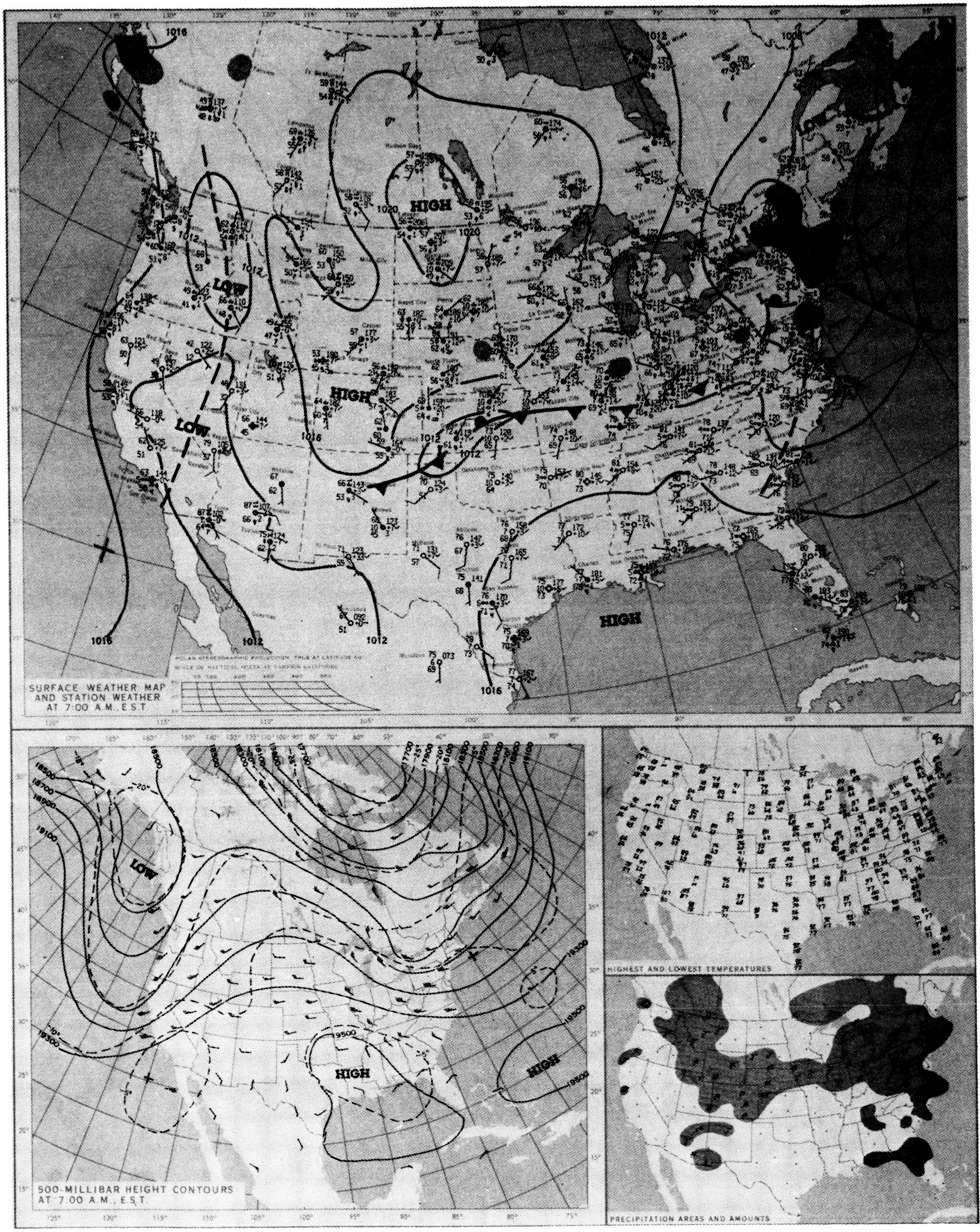


Figure D20.- Weather chart for July 23, 1983.



SURFACE WEATHER MAP AND STATION WEATHER AT 7:00 A.M., E.S.T.

500-MILLIBAR HEIGHT CONTOURS AT 7:00 A.M. E.S.T.

HIGHEST AND LOWEST TEMPERATURES

PRECIPITATION AREAS AND AMOUNTS

Figure D21.- Weather chart for July 24, 1983.

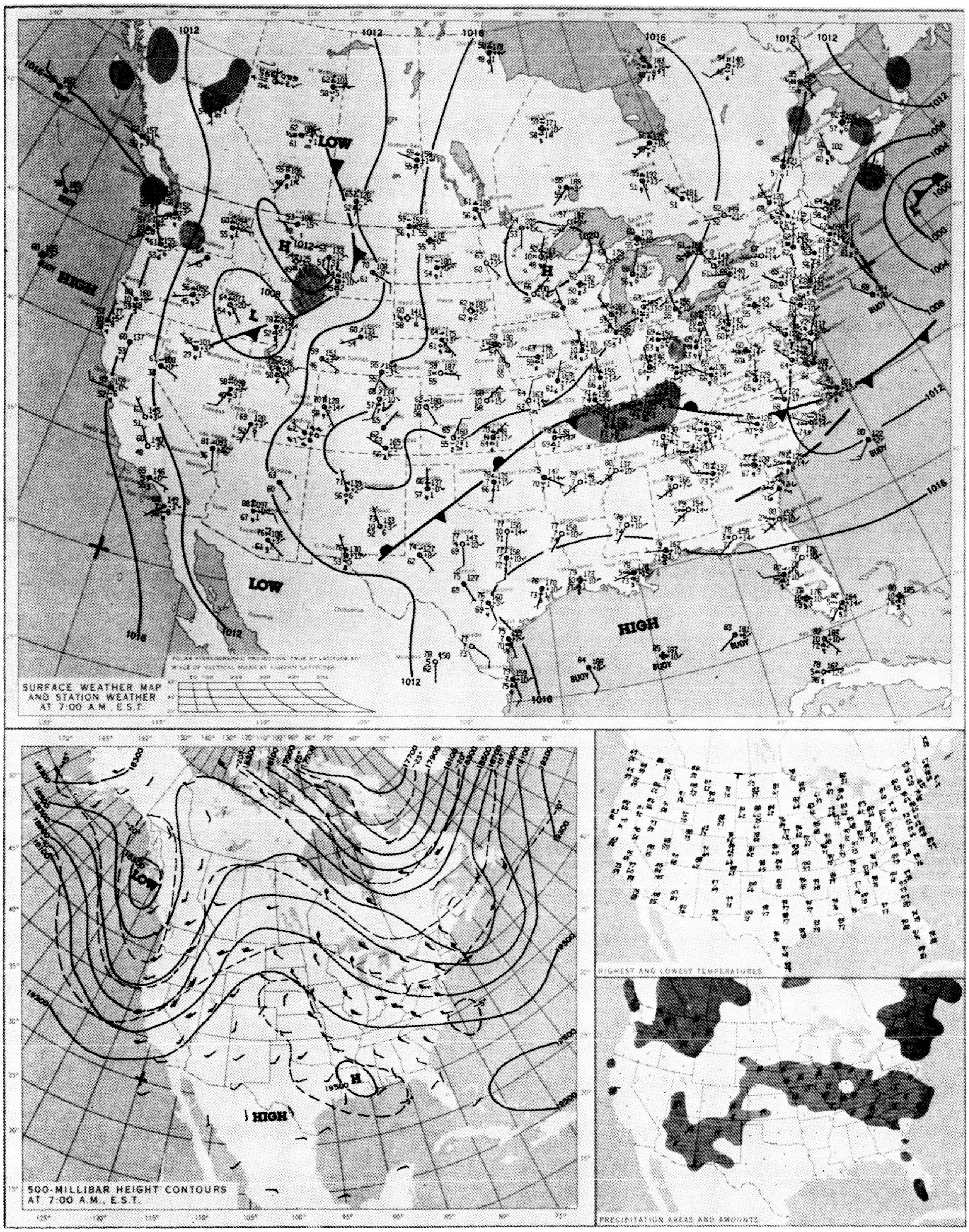


Figure D22.- Weather chart for July 25, 1983.

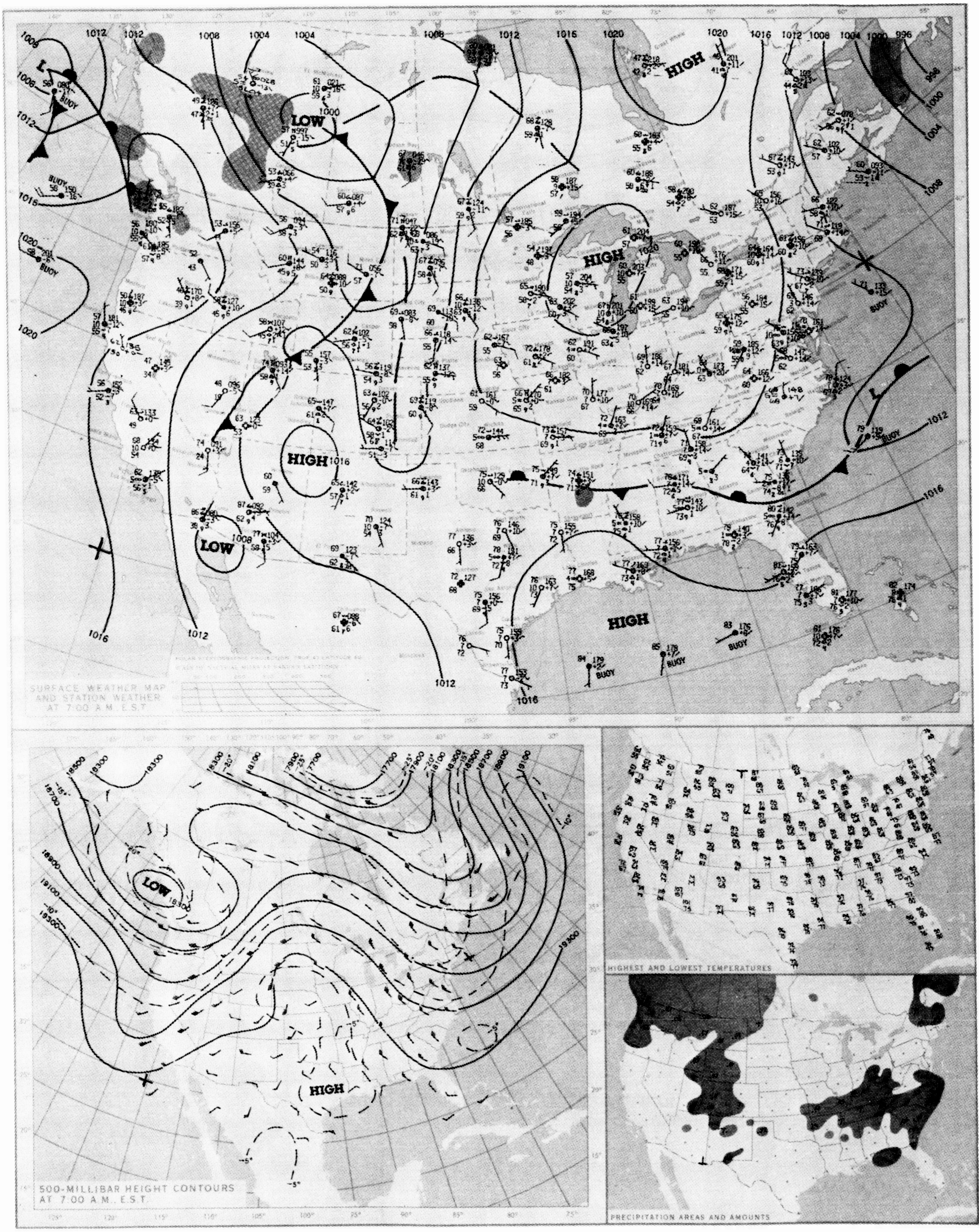


Figure D23.- Weather chart for July 26, 1983.

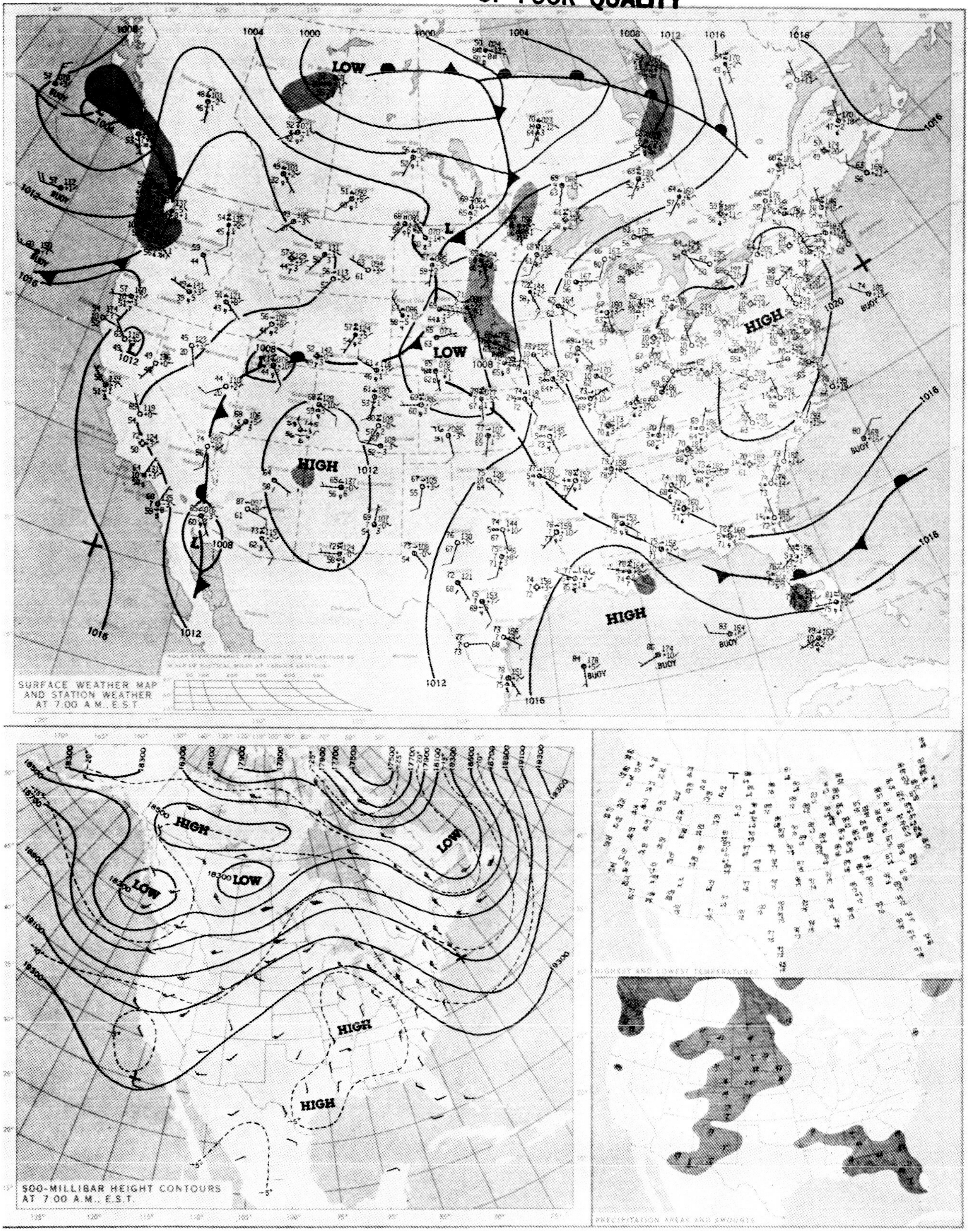


Figure D24.- Weather chart for July 27, 1983.

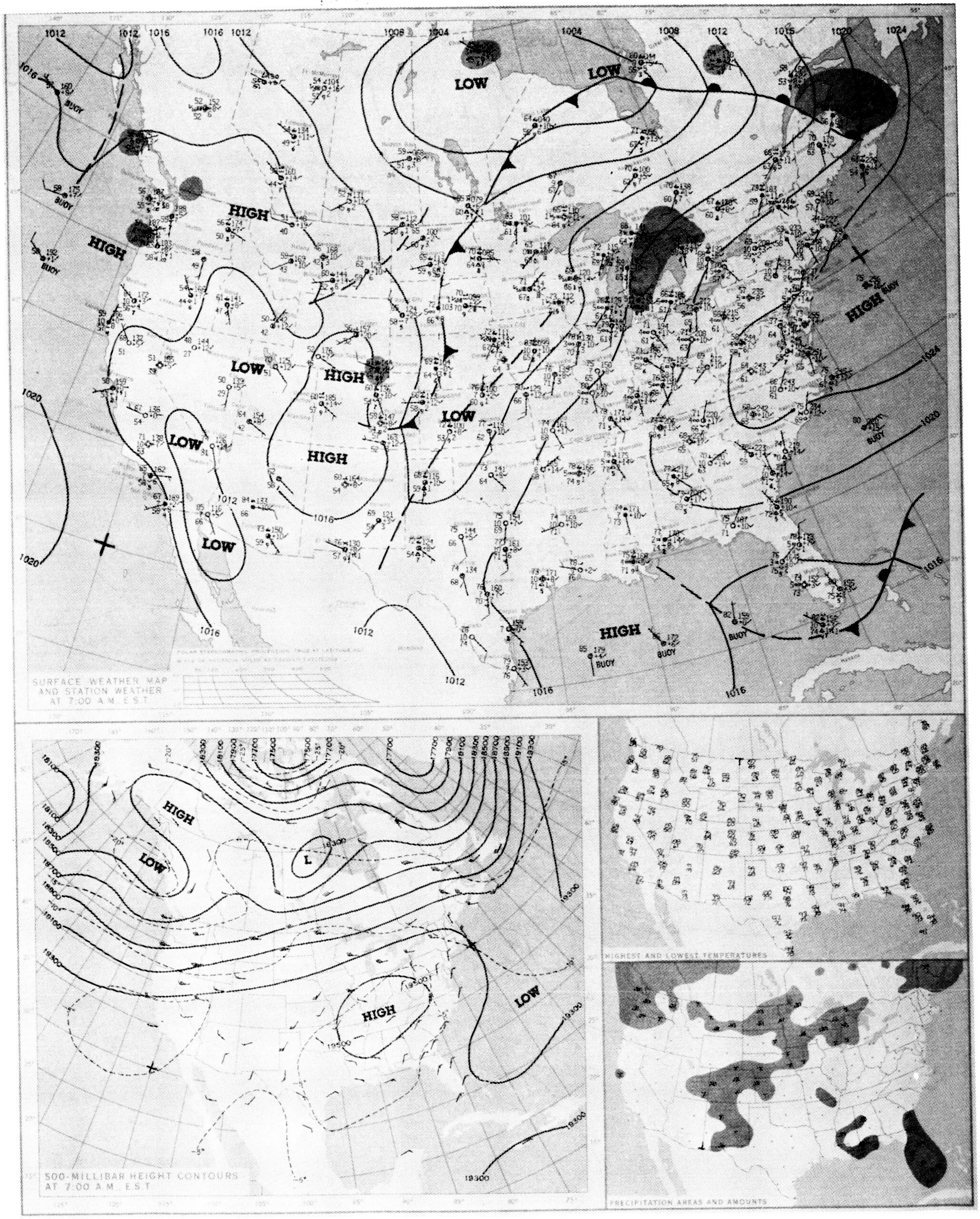


Figure D25.- Weather chart for July 28, 1983.

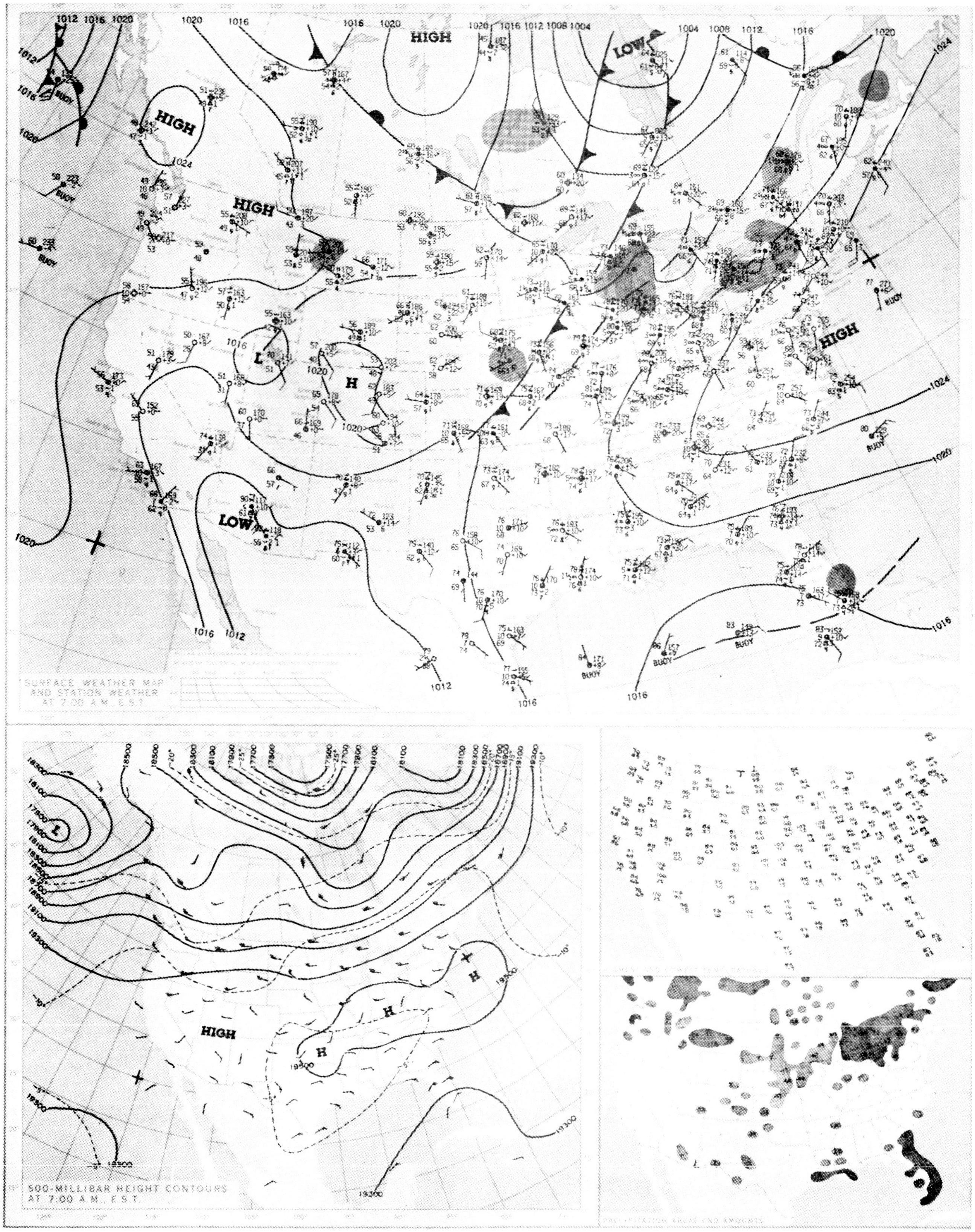


Figure D26.- Weather chart for July 29, 1983.

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16. Abstract

The report provides documentation of the first of three instrument intercomparisons conducted as part of NASA Global Tropospheric Experiment/Chemical Instrumentation Test and Evaluation (GTE/CITE-1). This ground-based intercomparison was conducted during July 1983 at NASA Wallops Flight Facility. Instruments intercompared included one laser system and three grab-sample approaches for CO; two chemiluminescent systems and one laser-induced fluorescent (LIF) technique for NO; and two different LIF systems and a radiochemical tracer technique for OH. The major objectives of this intercomparison was to intercompare ambient measurements of CO, NO, and OH at a common site by using techniques of fundamentally different detection principles and to identify any major biases among the techniques prior to intercomparison on an aircraft platform. Included in the report are comprehensive discussions of workshop requirements, philosophies, and operations as well as intercomparison analyses and results. In addition, the large body of nonintercomparison data incorporated into the workshop measurements is summarized. The report is an important source document for those interested in conducting similar large and complex intercomparison tests as well as those interested in using the data base for purposes other than instrument intercomparison.

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