GEORGIA INSTITUTE OF TECHNOLOGY

OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

☒ ORIGINAL ☐ REVISION NO. ______

Project No. G-35-630

GTRI/~~GIT~~ DATE 10 / 06 / 83

Project Director: Dr. Douglas Davis

School/~~Lab~~ Geophysical Sciences

Sponsor: Coordinating Research Council, Inc.

Type Agreement: Contract No. CAPA-19-80 (3-83)

Award Period: From 6/28/83 To ~~9/28/84~~ ~~12-28-85~~ ~~12-8-86~~ 9-28-87 (Performance) 9/28/84 (Reports)

Sponsor Amount:

	This Change	Total to Date
Estimated:	$	$
Funded:	$ 165,079	$ 165,079

Cost Sharing Amount: $ ______ Cost Sharing No: ______

Title: "Atmospheric Nitrogen Oxides: Their Detection and Chemistry"

ADMINISTRATIVE DATA

OCA Contact Frank Huff X4820

1) Sponsor Technical Contact:

2) Sponsor Admin/Contractual Matters:

Alan E. Zengel
Secretary and General Manager
Coordinating Research Council, Inc.
219 Perimeter Center Parkway
Atlanta, GA 30346
396-3400

Defense Priority Rating: ______

Military Security Classification: ______

(or) Company/Industrial Proprietary: ______

RESTRICTIONS

See Attached -- Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with sponsor; disposition of any equipment acquired shall be subject of separate negotiation upon completion of contract. See Article III.

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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 2/1/88

Project No. G-35-630 School/~~Lab~~ Geo. Sci.

Includes Subproject No.(s) E-16-699/Bailey/AE & A-3743/Sinclair/ EML

Project Director(s) D. Davis GTRC/~~GIT~~

Sponsor Coordinating Research Council, Inc.

Title Atmospheric Nitrogen Oxides--Their Detection and Chemistry

Effective Completion Date: 7/28/87 (Performance) 7/28/87 (Reports)

Grant/Contract Closeout Actions Remaining:

- ☒ None
- ☐ Final Invoice or Copy of Last Invoice Serving as Final
- ☐ Release and Assignment
- ☐ Final Report of Inventions and/or Subcontract: Patent and Subcontract Questionnaire sent to Project Director ☐
- ☐ Govt. Property Inventory & Related Certificate
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G-35-630

CRC PROGRESS REPORT

June 1 → July 7, 1984

Prepared by:
D. D. Davis
M. O. Rodgers
J. D. Bradshaw

Georgia Institute of Technology
School of Geophysical Sciences
Atlanta, Georgia, 30332.

JUNE 1 TO JULY 7, 1984 PROGRESS REPORT

In our recently submitted CRC "continuation" proposal, we outlined several tasks that were to be initiated in the June-July time frame. This progress report is being written with the intention of bringing the CRC Committee up to date on our activities during this time period.

As noted in our proposal, a major focus of our activity during June and July was to be on field sampling at Stone Mountain. In this regard, we are very pleased with the progress to date although we must add that the Stone Mountain field station is still in a state of transition. Our only major disappointment has been the absence of thunderstorm activity in Georgia during June. In the month of June only one major storm was encountered, that being on June 29. Early July has been more active, but the storms have generally been very localized. One of the most significant events was the passage of a cold front through the Stone Mountain area on Saturday, July 7, 1984. Further comments on these major meteorological events will be presented later in the discussion.

Concerning our laser development activities, significant progress has been made on both the NO_2 and NO_3 detection fronts. Short term, we have altered the NO TP-LIF system such that it can be operated either as an NO sensor or as a detector for NO_2 and NO_3 although in the case of NO_3 the system must still be considered to be in a preliminary form. To detect NO_2 or NO_3 the approach taken still involves the photofragmentation LIF scheme. Unlike the original scheme, however, the current approach uses three photons rather than two. This system has now been successfully used for the last 2 1/2 weeks to measure NO_2. Although this modified approach does not have the sensitivity (e.g. 350 ppt NO_2) of the originally proposed dual excimer PF-LIF system (2 to 4 pptv); nevertheless, it has been shown to be more than adequate for Stone Mountain observations, i.e. no NO_2 levels have yet been encountered which have been outside the detection range of this system. A very important advantage of the ongoing NO_2 system (above and beyond its selectivity) involves the fact that the hardware configuration can be switched from NO to NO_2 in ~ 1.5 minutes. The NO sensitivity in this modified scheme is in the 20 to 30 ppt range for a 5 minute integration period. This can be compared to a dedicated TP-LIF sampling scenario for NO where the detection limit of the current Stone Mt. system is in the 4 to 5 pptv range for a 5 minute integration period. We see this new laser configuration, therefore, as a very workable system for sampling at Stone Mountain.

As noted above, our NO_3 results at this point are preliminary and calibration procedures must be established before absolute concentration levels can be quoted. NO_3 has only been observed very late at night (actually in the early morning hours) and on both occasions when measurements were made very abrupt decreases in the signal level were seen at or near sunrise. The switching time from an NO/NO_2 configuration to an NO_3 sampling mode is ~ 10 minutes. Thus, we now believe that with modest refinement and calibration of the NO_3 sensor, the first modelling of the nighttime NO, NO_2, NO_3, O_3 system should become possible. On or near July 12 we will also be adding HNO_3 measurements (for a one week period) to the above list. In the latter case, it will be interesting to see if there are any correlations between NO_3 levels, dew point, and gas phase HNO_3. These initial measurements of HNO_3 will be carried out by Dr. Barry Huebert using his high vol filter matte collection technique.

In spite of the above progress on NO_3 we believe it advisable to continue our dedicated program for developing two photon PF-LIF NO_3 and HNO_2 sensors. Both "detection limit" and "time resolution" arguments suggest the desirability of perfecting these sensors. It now appears that the first test of both the NO_3 and HNO_2 two-photon PF-LIF sensors will be possible by the first week in August.

Our measurement program at Stone Mountain was activated ~ mid-June with NO and O_3 measurements being recorded together with the meteorological parameters, dew point, wind speed, and direction. Since then, we have added condensation nuclei and NO_2 measurements routinely, and NO_3 measurements on a spot-time basis at night. In addition, we have now set up procedures for collecting rain samples when such events occur. Thus far, only three events have occurred. During two of these samples were collected and shipped to Dr. Mohnen's lab for analysis. Additional instruments to be added during the next month include UV and visible flux meters, a cloud water collector, continuous pH readings on rain and cloud samples, a CO monitor, and a central microcomputer for continuous recording and analysis of the above data. The latter interface is, in itself, a significant task, but we are optimistic that it can be achieved by late summer or very early fall.

Since mid-June we've been able to obtain enough data to establish the general diurnal trends in NO, NO_2, and O_3 for summer time conditions at Stone Mountain. Meteorologically, this reflects the strong influence of the Bermuda high pressure cell off the East Coast of the U.S.A. Notable among the trends in NO is the observation of rising levels of NO in the early morning hours, reflecting both the photolysis of NO_2 and rush hour traffic into Atlanta. The NO typically peaks out at 1 to 3 ppbv around 8:45 a.m. and then steadily falls as the day progresses. By 12:00 noon, plateau levels ranging from 100 to 600 pptv are reached and this is maintained throughout the day until near sunset. After sunset, NO levels typically drop to the 5 to 40 pptv level with very early morning values (2:00 a.m. to 5:30 a.m.) running 4 to 15 pptv. Our observations of O_3 show that this species does not disappear during the night, levels typically range from 30 to 60 ppbv. The highest mid-day O_3 levels have been around 100 ppbv. NO_2 levels peak in the early morning hours (5 to 8 ppbv) and, like NO, then steadily fall off as mid-day (12:00 noon) approaches, reaching levels of 1 to 4 ppbv. The NO_2 level is observed to slowly decrease throughout the night.

One of the major surprises in our observations thus far has been the systematically low levels of NO observed throughout the day. We also note that the resulting very low levels of NO at night together with moderate levels of O_3 and NO_2, lead one to expect that conditions should be very favorable for the generation of reasonably high levels of NO_3. The preliminary measurements recorded of NO_3 would seem to be in accord with this, but as stated several times earlier, a careful calibration of this system must be carried out before a definitive statement can be made.

Concerning measurements during major meteorological events, there have been three that are worthy of some discussion: June 29, July 3, and July 7. Both the June 29 and July 7 events were triggered by cold fronts moving across the state of Georgia from the Northwest. Both fronts moved through the Stone Mountain area during mid-morning hours, i.e. 8:30 to 10:00 a.m. On June 29, ~ .25 inches of rain fell on Stone Mountain, and for brief periods of the storm, clouds at the height of the sampling station were encountered. Throughout the storm, lightning was quite prevalent. For ~ 85% of the time during which the front was positioned near Stone Mountain, the only NO_X species monitored was NO. These observations showed rather low levels of NO (i.e. in the 300 to 700 pptv range), however, significant fluctuations in O_3 were observed (e.g. 30 to 60 ppbv). Near the end of the storm, the laser configuration was switched into the NO_2 PF-LIF mode. By contrast, the first measurement of NO_2 was ~ 23 ppbv, a level which over the next 10 minutes steadily decreased to a rather stable 6 to 8 ppbv. The roll-off in the level of NO_2 was observed to be closely correlated with a major decrease in rain activity and the overall intensity of the storm.

The frontal system on July 7, was somewhat different from that on June 29, in that although very heavy rain and lightning activity had been reported as the front passed through Tennessee and northern Alabama, only moderate rain and low levels of lightning were observed as it passed through the Stone Mountain area. Nevertheless, very low levels of O_3 were observed, with one sampling period showing 0 to 3 ppbv. During the latter period, a dense cloud enveloped the sampling station and

NO levels as high as 6 ppbv were observed (this represents the highest level of NO seen over a three week sampling period). Using our modified laser configuration, NO and NO_2 were sequentially measured throughout the July 7 storm. While in the NO_2 sampling mode, we found that the levels present were sufficiently high as to partially saturate our photon counting electronics. Taking the counter reading without correction gives a lower limit estimate on the NO_2 concentration level of 105 ppbv. Folding in what is referred to as a pile-up correction for the pulse counting electronics gives an estimated value for the NO_2 level of 150 to 200 ppbv*. Since the latter meteorological event occurred on Saturday morning, the possibility that the NO_2 level had a local anthropogenic source appears to be quite small. Concurrent CO measurements during future events should conclusively prove this point. At this time, it appears quite probable that the source of the NO_x was lightning in origin; however, long range transport cannot at this time be totally ruled out. In this context, we would stress that during non-event sampling days (i.e. clear sky) the highest levels of NO_2 observed have been ~ 15 ppbv and this occurred only once.

July 3 proved to be another interesting event in that this storm is what may be called a highly localized thunder shower due to local late afternoon convective activity. This storm was sufficiently small that clear sky could be seen on both sides of the main cloud as it approached Stone Mountain. The cloud base, unlike the frontal systems, was estimated to be at least 1000' overhead the field station. During this event, ~ .20 inches of rain again fell, however, measurements of NO and NO_2 showed no increase beyond a factor of two of those observed before the storm hit.

Based on the above observations as related to electrified clouds, we now feel we have gained some very important quality to semi-quantitative data showing the potential significance of the lightning source. This experience has shown that

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* We have now implemented a change in the detection electronics so that at high NO_2 or NO levels we can collect the signal simultaneously on an analogue device, eliminating the need to correct our photon counting data for pile-up problems.

NO_2, in general, is a better species to monitor than NO but obviously both are important. The dynamics of the cloud formation are also seen to be quite important as related to how efficiently air parcels exposed to lightning are transported to the altitude at which sampling is occuring. (Obviously, this is a major advantage that airborne sampling has over fixed site sampling.) Finally, as noted earlier, CO measurements now appear to be of considerable importance as a means of convincingly demonstrating that the source of NO_x during lightning episodes is indeed derived from lightning rather than long range transport of anthropogenic pollution.

In general, future research activities for our program will continue to be focused in four areas:

(a) clear air NO_x/NO_y chemistry;

(b) in-cloud NO_x/NO_y chemistry;

(c) NO_x sources with the major emphasis being on electrified clouds;

and (d) the further development of NO_3 and HNO_2 PF-LIF sensors.

As noted earlier in the text, we believe we are now closing in on the NO, NO_2, NO_3, O_3 nighttime chemical system. Modelling of this system could provide important answers to questions related to the nighttime cycling of NO_x/NO_y species. We have also indicated the high likelihood of looking at NO_3, HNO_3, dew point correlations. If reproducible/meaningful correlations are found, this system should provide some challenging modelling opportunities as related to NO_x sinks. Our lightning studies will continue with our full attention being focused on these major meteoroligical events whenever they occur. We believe, however, that any modelling activities are still considerably downstream due to the need for a substantial data base. We must note also that the latter effort is being somewhat slowed down due to the fact that the lightning monitoring network in Georgia is still not tied into the central SUNY monitoring system. As stated in our renewal proposal, all equipment is now installed in Georgia, but problems persist with the AT&T telephone hook-up. We have just recently been told it will be two to three more months before this is achieved.

We close this brief updating report with the statement that although a great many scientific questions raised in our proposal on NO_x/NO_y chemistry remain unanswered at this time, we believe we are now obtaining some very important characterization data which will help to better define the experimental framework for our studies downstream. Quite noteworthy, we believe, is the fact that the instrumentation development, the aircraft sampling, and the Stone Mountain field sampling programs have all established very significant momentum by the end of the first contract year.

(b)"A Multi-Photon Laser-Induced Fluorescence Technique for Rapid Measurements of NO, NO_2, and NO_3".

Acknowledgment for Support: CRC.

(c)"Direct In-Cloud Measurements of NO and NO_2 in Southeastern U.S.A. under Conditions Involving Lightning".

Acknowledgment for Partial Support: CRC and NSF.

Concerning the first paper, one might argue that this work is outside the scope of our CRC proposal. We believe, however, that two aspects of this work are quite relevant to our CRC effort. The first of these involves the further documenting of the soundness of the TP-LIF NO sensor as an instrument capable of making reliable NO measurements under nearly all types of meteorological conditions. The second point involves the importance of better defining the NO_x reference frame in which measurements in rural Southeastern U.S.A. can be compared. The Southeastern U.S.A., like most of the U.S.A., presents a complex picture of NO_x sources and sinks. By removing the anthropogenic and the natural terrestial biogenic sources of NO (as is the case when sampling over the open Pacific Ocean) we have been able to make one of the first assessments of the magnitude of NO_x sources at remote tropospheric sites. Thus, it represents base line data to compare with.

Concerning papers (b) and (c), it should be apparent from the enclosed progress report that both are quite relevant to the proposed CRC program. Note that in the case of paper (c), we will be reporting on the average levels and fluctuations in NO and/or NO_2 during several electrical storms. At this time our data base is still too small to consider any major modelling effort. The acknowledgment of NSF support is included because the data base we will be drawing from will go back to our early observtions of NO during one major electrical storm in October 1982. At that time NSF was the principal supporter of our TP-LIF NO sensor.

Question (3) When do you expect your year-end report to be submitted?

Reply: Initially, we thought this could be achieved by early August. With the substantial amount of data now collected at Stone Mountain, we should like to delay submitting our report until mid or late August.

Question (4) It was pointed out in the proposal that additional flight time may be obtained during the year from other sources. Where are the resources for this additional flight time to come from?

Reply: Either Georgia Tech or NASA will likely contribute another 10 to 12 hours of flight time.

Question (5) What is the extent to which negotiations have taken place between Ga. Tech and York University (Harold Schiff) about utilization of the Ga. Tech aircraft?

Reply: Dr. Schiff was invited down to Georgia Tech during the winter of 1984. At that time he was shown both the Stone Mountain field station and the Georgia Tech Convair 240. My impressions from that meeting were that there appeared to be more interest in the use of our aircraft than the Stone Mountain station. This seems to reflect the ease with which the diode laser could be moved into the aircraft vs. the Stone Mountain sampling tower. The total cost for the interface and shaking out of Schiff's instrument has recently been re-evaluated by my staff to be $21,600. This includes $9,600 for 6 test flight hours, $3,000 for shop and ground interface charges, $2,000 for my staff's designing and stress analysis of interface fixtures, and $7,000 in overhead charges. We believe that Dr. Schiff's participation in some of the proposed airborne sampling operations could add significantly to the scientific depth of the program and would thus highly encourage it.

MEMORANDUM

TO: Tim Belian

FROM: D. D. Davis D.D. Davis

February 11, 1985

SUBJECT: Quarterly Report on Project # CAPA-22/23-83 for the time period September - December, 1984.

During the fall 1984 quarter there were five areas of activity:

(1) Laboratory studies of the PF-LIF NO_3 Detection System.

(2) Laboratory studies of the PF-LIF HNO_2 Detection System.

(3) Nighttime Field Measurements of NO at Stone Mountain.

(4) Completion of the SUNY Albany lightning detection network.

and (5) Research Manuscript writing.

Each of these areas of activity is discussed to varying degrees in the text provided below.

(1) Laboratory Studies of the PF-LIF NO_3 Detection System.

As noted in our original proposal to CRC, the crucial element in the successful development of a photofragmentation LIF NO_3 sensor is the photoproduction of vibrationally excited NO, e.g.

$$NO_3 + h\nu \rightarrow NO\ v'' = 2 \text{ or } 3 + O_2$$

According to early work by Magnotta and Johnston (1980), the NO_3 species fragments into NO and O_2 in a spectral region centered about 589 nm. Extensive tests completed at Georgia Tech during the fall now indicate that this earlier work by Magnotta and Johnston is incorrect.

Scans of a photolysis laser covering 532 nm up to ~ 630 nm have shown that although NO formation in the $v''= 2$ level occurs, this NO is generated entirely by a two photon absorption process involving NO_2. (NO_2 is typically present as an impurity in any sample of NO_3.) The two photon process involving the NO_2 molecule was demonstrated by our varying the laser energy and observing a square power dependence in the LIF NO signal level. This experiment was performed both with gas samples involving NO_3 with impurity NO_2 as well as with pure NO_2 samples. The square power dependence was observed in both cases.

Upon close inspection of Johnston's earlier work one discovers that the sum of the primary quantum yields (i.e. $NO_3 + h\nu \rightarrow NO + O_2$, Φ_1; and $NO_3 + h\nu \rightarrow NO_2 + O$, Φ_2) for NO_3 dissociation in the visible region actually exceed unity. Some investigators have speculated that the reason for this apparent anomaly is that the cross section for NO_3 is in error. We now believe that two-photon absorption by small amounts of NO_2 were responsible for the reported production of NO in Johnston's experiments and therefore resulted in evaluated primary quantum yields which exceeded unity. This conclusion is quite consistent with our results since Johnston's experiments also employed a high enery pulsed laser as a photolysis source.

Given the above fundamental finding on NO_3, it is now apparent that the proposed PF-LIF technique cannot be successfully applied to the detection of the NO_3 molecule. In our judgment, however, the chemistry of nighttime NO_3 has grown to such importance during the last 3 years to our understanding of the NO_x/NO_y chemical system that we believe alternate ways of measuring this species must be considered. We currently think that the preferred approach will be some form of long-path absorption. This method has been successfully employed by the Germans, by Jim Pitt's University of California group, and by John Noxon at NOAA. The major disadvantage of each of the latter efforts has been in the use of very large distances (5-17 km) to achieve the necessary absorbance by NO_3. Thus, we are now examining the use of a multi-pass laser based system which could be limited geometrically to the top of Stone Mountain. The physical dimensions between mirrors would be $\sim$ .1 km. With 10 round trip passes, this would result in a total absorption path of 2 km. With improved detection optics and processing electronics, our current calculations suggest that 3 to 5 pptv of

NO_3 could be detected. The need for NO_3 measurements over a limited physical path length will become more apparent in our subsequent discussions of nighttime NO measurements. Suffice it to say, at the moment we are carrying out further feasibility calculations on detecting NO_3 via the modified differential absorption method. The final decision to proceed on this track will be determined by the outcome of these calculations, the cost for setting up this system, and further input from CRC.

(2) Laboratory Studies of a PF-LIF HNO_2 Detection System.

Initial results from our studies of HNO_2 have been more encouraging than those on NO_3. Using a laser photolysis wavelength of 355 nm, we have established that a measurable yield of NO in the $v''= 2$ level can be produced. Unfortunately, we have also found that NO_2 produces small quantities of NO in the $v''= 2$ level at 355 nm. The ratio of $\frac{HNO_2(v''=2)}{NO_2(v''=2)}$ at 355 nm has been measured at ~ 20:1. By moving the photolysis wavelength to 353 (the XeF excimer laser line), however, this ratio could be increased to 40:1, due to the higher absorption cross for HNO_2. However, considering the fact that the available data on HNO_2 and NO_2 levels would suggest that HNO_2 is 40 to 200 times lower in concentration than NO_2, this would limit the detection of HNO_2 to 50 to 100 pptv.

At the present time, two alternatives to the above scenario are being examined: (a) moving the photolysis wavelength to the 368 nm band of HNO_2; and (2) use of the second photofragment from HNO_2 (i.e. OH) as a means of detecting nitrous acid,

$$HNO_2 + h\nu \rightarrow NO + OH$$

The disadvantage of the first approach is that there are no strong laser lines in this spectral region; thus, the overall sensitivity of this system for detecting HNO_2 could still remain low even if a more favorable $\frac{HNO_2(v''= 2)}{NO_2(v''= 2)}$

ratio were to be realized. For this reason, we believe that the second approach, involving the detection of the OH photofragment, is more likely to result in a highly sensitivie HNO_2 sensor. The effort required to explore the second option is very modest since a complete LIF OH detection system already exists in our laboratory. Current calculations suggest that a PF-LIF HNO_2 sensor, using OH detection, should have an HNO_2 detection capability of $\sim$ 10 pptv with 10 minute time resolution.

(3) Nighttime NO Field Measurements

Based on nighttime NO measurements by our group at Wallops Island, VA. in July 1983, and at Stone Mountain during June, July and August of 1984, a major scientific question has developed as related to nighttime N_xO_y chemistry. Current theory indicates that if local NO sources are absent, the level of NO at night should be negligible (e.g. < 1 pptv). The basis for the above argument is quite simply that at night the normal NO_x sequence of reactions,

(a) $NO + O_3 \rightarrow NO_2 + O_2 \qquad \tau = 30$ to 100 sec.

(b) $NO_2 + h\nu \rightarrow NO + O$

(c) $O + O_2 \xrightarrow{M} O_3$

is short-circuited at step (b) due to the absence of UV radiation. Under these conditions, all NO should be systematically titrated via rx. with O_3 to NO_2. Thus, so long as there is an excess of natural O_3 over NO, the levels of NO should remain very low.

At Wallops Island, VA., our group, as well as other investigators using modified chemiluminescence detectors, observed nighttime NO levels ranging from 9 to 15 pptv. At Stone Mountain during the summer of 1984, our group measured nighttime levels typically in the 20 to 50 pptv range.

Given these nighttime NO data, one may question whether these measurements are all in error or, alternatively, non-representative due to there being local

NO sources near the measurement site. It was with this background that our group initiated an extensive effort to determine the credibility of the previous nighttime NO measurements. This most recent NO measurement effort took place during October and November of 1984 and encompassed ~ 18 nights of measurements with each night involving ~ 6 hours of data on the average. A typical sampling night covered the time period 00:00 hours to 05:30 hours. During the fall NO sampling period, a total of seven different variations in operating conditions were carried out. These results are summarized below:

Type of Test	Observed Deviation
- Seven fold increase in sampling flow rate	≦ ± 25%
- Two fold decrease in sampling flow rate	≦ ± 30%
- Laser energy decrease of 2 to 4 fold	≦ ± 25%
- Roof top inlet vs. immediate side window inlet	≦ ± 20%
- All stainless steel vs. stainless steel/teflon sampling line	≦ ± 30%
- All teflon vs. teflon/stainless steel sampling line	≦ ± 20%
- Heated vs. unheated teflon sampling line	≦ ± 30%

As noted by the test results, no significant deviation in system performance was observed throughout these experiments. However, one test result not included in the above summary involved a nighttime run under heavy cloud conditions. In this case, a factor of two lower value of NO was observed in the nighttime level of NO using an all teflon sampling line versus that of a teflon line containing three stainless steel swageloks.* Nevertheless, on a second night involving heavy clouds (~ 1 week later), no difference was found in these two different

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* We now believe that the observed > in NO seen in the presence of stainless steel was most likely due to the surface decomposition of HNO_2. This hypothesis will be tested as soon as we have an on-line HNO_2 detector.

sampling lines. Based on these results we have taken the conservative approach and have now configured all sampling lines such that only teflon and quartz are used.

Based on the above results, we have concluded that the NO levels measured at Stone Mountain at night during the time period of October to November 1984 are free from major chemical interferences and/or local contamination effects.

The average level of NO observed over this time period was ~ 28 pptv, with low values of 12 pptv and high values of ~ 71 pptv. The average level of O_3 for the 18 nights of sampling was ~ 20 ppbv, with a low of 12 and a high of 46 ppbv. Also quite important to the nighttime NO observations are meteorological data showing that in virtually all cases during the times that sampling occurred on top of Stone Mountain, the site was above the nocturnal boundary layer.

The significance of these non-zero values of nighttime NO relate to the general question of nighttime N_xO_y chemistry; and, in particular, to the chemistry of NO_3. Recent field and laboratory kinetic studies, for example, have suggested that the key reactions involving NO_3 include:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \overset{M}{\leftrightarrow} N_2O_5$$

$$NO_3 + H_2O \xrightarrow{\text{hetero}} \text{Products}$$

$$NO_3 + \text{hydrocarbons} \rightarrow HNO_3 + \text{R radicals}$$

However, at a few parts per trillion of NO, the reaction

$$NO + NO_3 \rightarrow 2NO_2$$

completely controls the levels of NO_3. At this time, there appear to be two possible explanations for these high levels of nightime NO:

(a) Yet unidentified problems in the experimental measurements;

or (b) Yet unknown nighttime chemical rxs. which return some fraction of NOy or NO_2 species to the NO form, e.g.

$NO_2 + X \rightarrow NO + XO$

New nighttime experiments on the ground and in some cases the air, are now being planned for late winter, spring, and the summer of 1985, in an effort to further understand these nighttime NO results.

(4) SUNY Albany Lightning Detection Network.

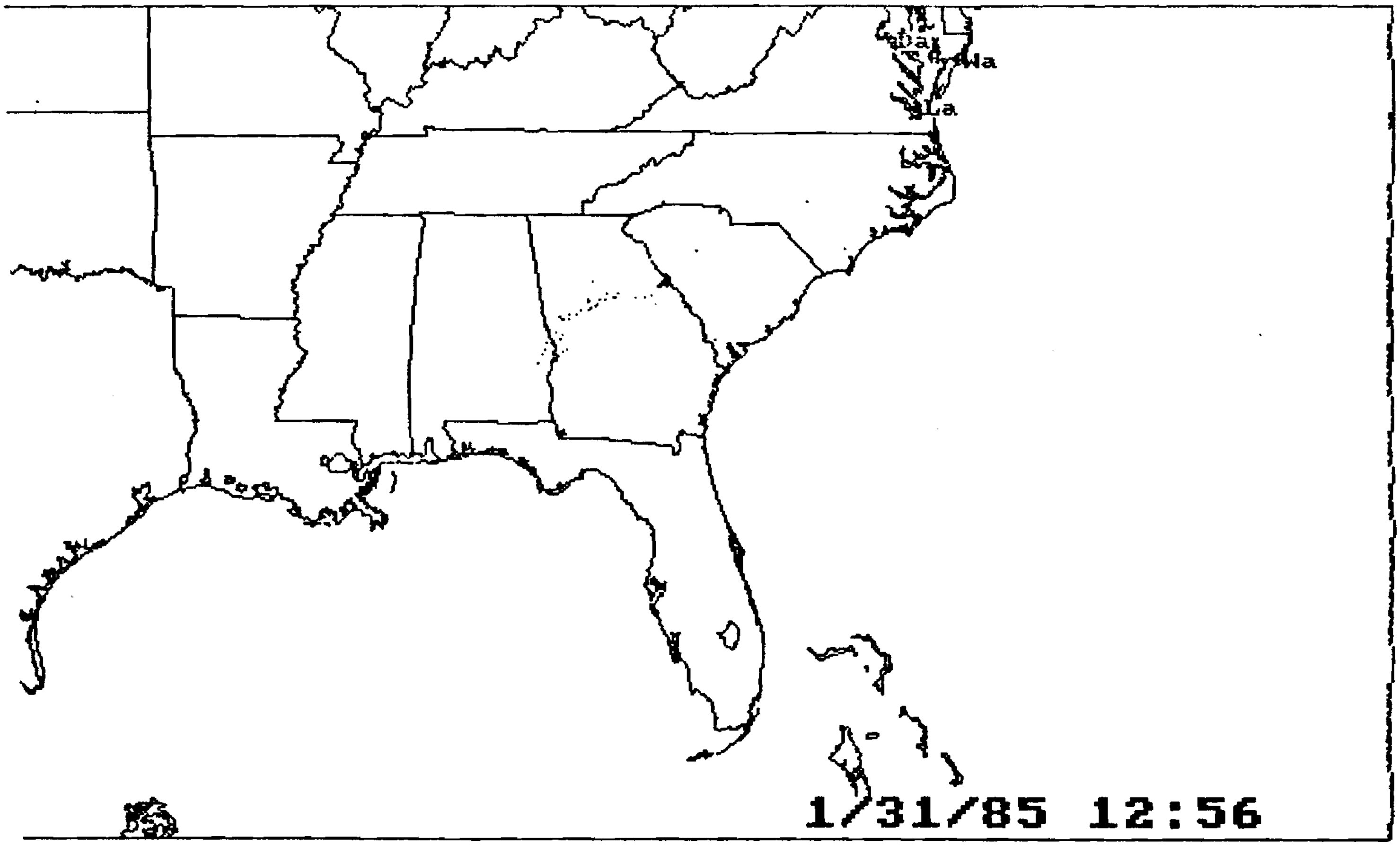
During the September - December 1984 time period, the final telephone hookups for the South Carolina and Georgia monitoring stations were completed. An example of a lightning strike profile for the Georgia area on January 31, 1985 is attached. All lightning strikes in the southeast will now be permanently recorded at the central receiving station in Albany and can be made available to Georgia Tech on request.

(5) Manuscript Writing.

Two manuscripts related to our CRC activities have been pursued during the fall 1984 quarter. The first of these is entitled "A Two Photon/Laser-Induced Fluorescence Field Instrument for Ground-Based and Airborne Measurements of Atmospheric NO" and is enclosed for your inspection. This NO instrument development activity, will be submitted to JGR.

The second paper is entitled "Nighttime NO: Its Impact on the Levels of NO_2, NO_3, and N_2O_5". Some of the results in this paper were presented at the December 1984 AGU meeting in San Francisco. At this time, the latter paper is in the third draft stage of completion and is expected to be completed within ~ two weeks time. A copy of this paper will be forwarded to CRC at that time.

UNY-Albany Lightning Detection Network



Ron Hendersen
78) 457-4812

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MEMORANDUM

TO: Tim Belian, Coordinating Research Council
FROM: D. D. Davis, Georgia Tech
SUBJECT: Winter Quarter (1985) Progress Report.

During the first quarter (January, February, March) of 1985 we had hoped to carry out at least four weeks of measurements during the peak winter months of January and February. Unfortunately, the water lines supplying the top of Stone Mountain were frozen and ruptured early in January, which prevented the operation of our water-cooled Nd:YAG laser during the nearly one month water outage. As a result of this outage, we redirected our attention toward several other areas. Some of these activities continued even after the water lines were repaired since considerable momentum had been established. The major areas of activity have been:

(1) A Beckman IR Dual-Isotope/Gas-Filter CO Monitor was placed in service and calibrated. This system has undergone field tests for nearly 1 1/2 months and now is providing continuous real time CO data at the field station. The system has, in fact, demonstrated sufficient stability to be allowed to operate unattended throughout the night.

(2) A major shortcoming of the Stone Mountain facility (lack of continuous automated data collection) has been eliminated. As of late March, all instruments which operate either in a continuous or semi-continuous mode have been interfaced with a data logging computer. Currently, variables which can be continuously recorded and stored include: Wind Speed, Wind Direction, Temperature, Dew Point, Barometric Pressure, UV Flux, Visible Flux, Carbon Monoxide, Ozone, NO, and NO_2. Still requiring manual

operations are the high-vol HNO_3 filter sampling system, the condensation nuclei counter, and the cloud and rain water sampling systems.

In addition to the automatic recording and storage system now in operation, real time displays of up to three variables are available on a graphics display terminal. This is soon to be supplemented by an HP graphics plotter.

(3) The previously described NO/NO_2 LIF sensor which had a 5 minute cycling time, alternating between NO and NO_2, has undergone a major instrument improvement program during the winter quarter. Modifications have been made to allow NO measurements on every laser shot and NO_2 on every other laser shot. Thus, the time separation between NO and NO_2 measurements is at worst 0.1 sec. In addition, other modifications to the fluorescence chamber (i.e. the number of PMTs), the collection optics, and improved synchronization between the NO_2 photolysis and the NO detecting laser pulses, have significantly improved the sensitivity of the NO_2 system along with more modest improvements for NO. In the case of NO_2, our previous sensitivity was 700 to 1000 pptv for an ~ 5 min integration period. With the use of a KrF excimer as the photolysis source (soon to be tested), the sensitivity of the NO_2 PF/TP-LIF system should be in the 2 to 4 pptv range for a 5 minute integration. The NO sensor, as a result of our now being able to generate 1.08μ radiation via Raman shifting of 574 nm dye radiation is now very close to the sensitivity of our earlier airborne system, i.e. 1 to 2 pptv per 5 min.

Quite significant in the above developments is the fact that the major improvements in sensitivity for both the NO and NO_2 means that <u>one common set of laser hardware</u> can now be flown aboard the Ga. Tech aircraft which will permit simultaneous measurements of NO and NO_2. Originally it was believed that two completely independent laser systems would be required. Thus, considerable aircraft space will be made available for other potentially important measurement systems, e.g. OH sensor, real time HNO_3 or real time HNO_2.

Currently the group is actively preparing for a major spring airborne sampling operation as well as carrying out limited field measurements at Stone Mountain. The summer should see another major Stone Mountain sampling operation.

Also currently being developed and prepared for testing is an HNO_2 sensor. This system will involve PF-LIF detection of the OH photofragment rather than the NO fragment as originally proposed. This system should be available for field tests in late June or early July 1985.

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404/894-3893

MEMORANDUM

Project G35-630

TO: Mr. Tim Belian, Coordinating Research Council
FROM: D. D. Davis, Geophysical Sciences, Georgia Inst. of Technology
DATE: February 21, 1986
SUBJECT: Georgia Tech Fall Quarter Report to CRC

During the Fall Quarter (Sept., Oct., Nov.), three areas of activity were pursued: (1) Laboratory tests to establish the feasibility of developing a PF-LIF HNO_2 sensor based on the detection of the OH photofragment; (2) Stone Mountain tests to establish instrument boundary conditions for the detection of NO_3; and (3) further nighttime measurements of NO at the Stone Mountain field sampling station.

Concerning area (1), all laboratory feasibility studies were completed during the Fall. The goal of this activity was demonstrating that the UV photofragmentation LIF technique could be used to detect HNO_2 via the approach:

$$HNO_2 + h\nu_1 \xrightarrow{\lambda \simeq 355nm} OH\ (v''=0) + NO$$

$$OH(X,v''=0) + h\nu_2 \xrightarrow{\lambda \simeq 282nm} OH(A,\ v'=1)$$

$$OH(A,v'=1,0) \rightarrow OH(X,v''=1,0) + h\nu_3(\lambda = 309nm)$$

The laboratory tests indicated that the OH radical from HNO_2 could be detected according to the above scheme without interference from O_3, H_2O_2, HNO_3, etc., due to the photolysis beam at 355 nm. As expected, however, care must be exercised at the OH probe wavelength of 282 nm, where $O(^1D)$ produced from the photolysis of O_3 can generate measurable levels of OH via the reaction:

$$O(^1D) + H_2O \rightarrow 2OH.$$

Although measurable levels can under certain conditions be produced, this interference is easily quantified in this system by comparing the OH signal with and without the photolysis beam (e.g. $\lambda = 353$ nm). With the latter problem now under control, we are moving the PF-LIF HNO_2 system into an extensive calibration phase. Thus, some time during the Winter quarter we should see the completion of the first generation PF-LIF HNO_2 in downtown Atlanta. This will be achieved by using an air sampling line which has been routed through the wall of the lab so as to sample air outside our building on the Georgia Tech campus. Upon completion of several data runs on the Tech campus, the PF-LIF HNO_2 system will be repackaged and moved to Stone Mountain. Measurements at the latter location will therefore take place throughout much of the Spring.

The NO_3 tests atop Stone Mountain were designed to determine the type of light source to be used in the long-path differential absorption technique and to establish the minimum possible absorption that could be detected under actual atmospheric conditions. To achieve the latter, we successfully negotiated with the PAR company to provide us on short term loan an optical multichannel analyzer (OMA), a diode detection array, and an appropriate monochromator. Concerning the light source to be used with this equipment, although we had earlier thought that a broad band dye laser would be the preferred choice, a closer examination of this option indicated that we would not be able to operate the dye laser system with a sufficient bandwidth to enable a reliable subtraction of the background absorption from the total absorption in the spectral region where NO_3 absorbs (e.g. $\lambda = 623 \rightarrow 662$). Thus, in the final analysis we chose a light source recommended by the German Group at KFA, namely, an Iodine high intensity CW light source. After approximately one month's worth of tests, using this advanced electronic system, we have been able to demonstrate that the OMA and diode array detector system, under controlled conditions, is capable of measuring differential absorption levels in the 8×10^{-6} to 2×10^{-5} range. Upon using a reflecting mirror in an actual atmospheric situation on top of the mountain, the minimum differential absorption was closer to 10^{-4}, a value typically reported by the Germans (Perner, Platt, Enhalt et al.) The difference between these two estimates (one order of magnitude) can be viewed as the influence of the real atmosphere on such measurements, but we are currently optimistic that we will be able to approach very closely the OMA diode array detection limit with further modifications to the initially tested monitoring system. For example, with rapid switching of the PAR system (i.e. every 200 ms), one should be able to significantly reduce the effects of lamp instabilities, detector instabilities, and other general electronic noise sources. However, even at 10^{-4} as a minimal differential absorption, over a .5 km path length, the above system will be able to detect 10 pptv of NO_3. Thus, we are more optimistic at this time that a successful N_xO_y experiment can be performed at Stone Mountain. Based on the above tests all equipment has been ordered for the NO_3 detection system. Delivery is expected during January and February 1986, at which time activity will start in setting up the final system at Stone Mountain.

Concerning further efforts to understand nighttime levels of NO, we were surprised during the Fall of 1985, to discover the presences of a gas furnace in one of the buildings on top of the mountain. Earlier, we had been told by the Park Service that all heating on top of the mountain was electric. It turns out all but one building is electric, but the one heated by gas is quite sizable. Efforts were initiated, therefore, to carry out nighttime NO measurements before the furnace was activated (mid-to-late Oct.) and to compare these results with those after the furnace was turned on for Winter heating. These tests clearly showed that the pre-turn on period typically had substantially lower levels of NO, by factors of 2 to 3 on the average. Recall in our original data set, we had observed a major difference in the level of nighttime NO in the Fall of 1984 vs the Spring of 1985. We now know that the 1985 Fall data was significantly influenced by the operation of the gas furnace. The current 1986 Fall data (before the furnace was activated) are in good agreement with the Spring 1985 data which gave average nighttime levels of NO of 8 to 12 pptv.

The gas furnace is normally activated over the months of late Oct., Nov., Dec., Jan., Feb. and early March. Thus, the furnace presented a major threat to our nighttime N_xO_y chemistry study, particularly that involving NO_3 since high levels of NO would rapidly destroy any NO_3. For this reason the project director, D. Davis, had several meetings with the Park Service, in which the case was made that only in the event of freezing weather is there any need for heat in the building that the furnace is coupled to. To make a very long story short, we convinced the Park management that they could save money on their heating fuel bill and at the same time we could continue an aggressive research program on nighttime N_xO_y chemistry if a timer switch was installed on the furnace which allowed it to normally operate only during the day. Thus, the furnace now cuts off ~ $^1/_2$ hour before sunset and turns on ~ 1 hour after sunrise, leaving the night hours atop Stone Mountain free of any NO source and thereby permitting us to pursue nighttime N_xO_y chemistry during virtually the entire calendar year. There is an outside air sensor, however, that is wired into this new system such that once 31°F is reached, a relay in the system overrides the timer switch at night, thus keeping water pips from freezing. This typically happens only ~ 2 weeks out of the year. When the latter does happen, a red light immediately flashes in our lab and outside experiments can be terminated.

The authors note that further measurements of NO during December and January have shown this new furnace control system to work very effectively and nighttime NO levels in the early Winter have not been found to be appreciably different than those observed in the Spring and early Fall of 1985.

G-35-6

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MEMORANDUM

TO: Tim Belian, Coordinating Research Council
FROM: D. D. Davis, Project Director

Project Title:
Atmospheric Nitrogen Oxides:
Their Detection and Chemistry

DATE: April 22, 1986
SUBJECT: Winter 1985 - 1986 Quarterly Report

During the 1985 - 1986 Winter Quarter two areas of activity were under active investigation: (1) development of the long path differential absorption (LPDA) NO_3 detection system on top of Stone Mountain; and (2) development and testing of the UV photofragmentation/laser-induced flourescence HNO_2 sensor. Concerning the first area of investigation, all equipment needed to complete the NO_3 system was received during the Winter Quarter and active tests were initiated to establish that each major component met the specifications for performance given to the manufacturer. New equipment now on hand includes: an EG&G optical multichannel analyzer equipped with a diode array detection systlem, a 1/3 meter monochromator, a 10" telescope, and an HP microcomputer system with appropriate software to make it compatible with the EG&G OMA. All components have now been certified as meeting the requirements of the LPDA NO_3 system. Work is now going forward on establishing the mounting of the main reflector on the Stone Mountain cable car tower. Thus, we expect the first complete test of the NO_3 system by middle to late Spring of 1986.

On the HNO_2 front, we have now successfully developed a UV photofragmentation/laser-induced flourescence sensor for HNO_2 based on the detection of the photofragment OH, i.e.

$$HNO_2 + h\nu_1 \xrightarrow{\lambda_1=355nm} OH + NO$$

$$OH + h\nu_2 \xrightarrow{\lambda_2=282nm} OH^*$$

$$OH^* \longrightarrow OH + h\nu_3 \ (\lambda=310nm)$$

Currently, both the 355nm, and 282nm wavelengths are being generated by a single YAG laser. The 355nm beam is the third harmonic wavelength of the YAG laser and is therefore fixed frequency. However, new experiments using a frequency-shifting crystal assembly will soon allow the photolysis wavelength to be shifted to 368.5nm, which corresponds to yet another strong absorption band of HNO_2.

The 282nm radiation in this system is generated by the 532nm (Nd:YAG 2nd harmonic) pumping of a dye laser which delivers a tunable output at 564nm. The latter wavelength is frequency doubled to give the final tunable OH excitation wavelength centered at 282nm ($Q_1$1 transition).

At the present time, this system is being used on the Georgia Tech Campus to look at nighttime levels of HNO_2 in the near downtown Atlanta area. Currently, ~15 nights of data have been collected involving 2 or more hours of monitoring. Of this total, there are <u>two</u> cases where complete diurnal profiles have been recorded and approximately 5 others where pre-sunset to 12:00 a.m. runs were made. Maximum values of HNO_2 have been in the 5 to 6 ppbv range with more common values being 1 - 2 ppbv. The HNO_2 detection limit of the presently configured system is in the range of 50 to 100 pptv; however, this system is yet to be fully optimized. With the addition of a second laser as the photolysis source (e.g. an XeF eximer) plus modest changes in the collection optics, the PF/LIF should be able to achieve a 10 to 20 pptv detection limit. Supporting measurements being made in conjunction with the more recent HNO_2 observations include HNO_3(g), NO^-, SO_4^-, O_3, Dew Point, T, NO_x, NO_2, NO, SO_2, as well as UV and visible solar flux. Movement of the HNO_2 sensor to Stone Mountain is expected in late Spring or early Summer, depending on when the NO_3 detection system is complete.

G-35-620

Summer 1986 Quarterly Report

To:

Coordinating Research Council

From:

Dr. D. D. Davis

School of Geophysical Sciences

Georgia Institute of Technology

Atlanta, GA 30332

During the summer quarter 1986 (June-August), three areas of activity were pursued: (1) final engineering modifications to the development of an LIF instrument that can make simultaneous measurements of NO/NO_2; (2) extensive measurements of $NO/NO_2/O_3$/UV flux and ancillary measurements to test the fast photochemical theory as related to nitrogen oxide species; and (3) analysis of HONO data collected during the winter and fall quarters 1986.

Concerning the first area of activity, the photofragmentation/two-photon laser-induced fluorescence system was upgraded in its performance specs to yield a far more sensitive instrument for the simultaneous collection of NO and NO_2 data. Previously, this system utilized a single YAG laser and one tunable dye laser to achieve the necessary wavelengths at 226 nm, 1.08 μ, and 355 nm, the latter wavelength being used to photofragment NO_2 to yield detectable NO. This single YAG/PDL system, however, had an ~ 70 pptv detection limit for NO_2 and ~ 5 to 10 pptv detection limit for NO. In our final design, we added a rebuilt Spectra Physics EXC-I excimer laser (now capable of 200 Hz operation) as a means of photofragmenting NO_2 at an output wavelength of 353 nm. This system was tested extensively this summer by comparing it against two different types of chemiluminescence NO_2 detectors as well as an NO_2 measuring diode laser system. Although it is still somewhat early to draw any final conclusions, it appears that the PF/TP-LIF sensor will emerge from this intercomparison as one of the preferred NO_2 instruments. The system, which has now been tested both on the ground and on an airborne platform, showed a detection limit of 2 to 3 pptv for NO and 10 to 12 pptv for NO_2, a major improvement over the original design.

In conjunction with the development of a highly sensitive instrument for the simultaneous detection of NO and NO_2, we also successfully completed the first extensive set of measurements in which NO, NO_2, O_3, UV flux, plus other chemical and physical parameters, were measured simultaneously. This data base was collected over a wide range of environmental conditions which included very clean air measured over the Eastern Pacific Ocean to varying degrees of polluted air measured over California and the Southwestern region of the U.S.A., i.e. Arizona and Nevada. Thus, we have a data set that encompasses one of the most extensive ranges of NO and NO_2 concentrations ever collected for purposes of testing photochemical theory. Equally important, we believe that one can have a high degree of confidence in both the NO and NO_2 measurements. The analysis of this data base will begin fall quarter 1986.

Concerning the final area of activity, HONO data analysis, this work has just gotten underway and will become part of Mike Rodgers' Ph.D thesis. Through the late winter and early spring months of 1986, average nighttime levels near downtown Atlanta were in the 2 ppbv range with peak levels on one or two nights reaching 9 ppbv. Based on the limited modelling exercises completed to date, there is strong evidence indicating that on average, the OH produced from the early to mid morning photolysis of HONO significantly exceeds that from the primary source $\left(\begin{array}{l} O_3 + h\nu \dashrightarrow O'D \\ \qquad\qquad\quad -H_2O\rightarrow 2OH \end{array}\right)$. At this time, therefore, one could tentatively conclude that HONO photolysis is the major driving force for smog production at the beginning of each day in a city such as Atlanta.

Fall 1986 Quarterly Report

To:

Coordinating Research Council

From:

Dr. D.D. Davis

School of Geophysical Sciences

Georgia Institute of Technology

Atlanta, GA 30332

During the fall quarter of 1986 (September - November) activity on this project was continued in three areas: (1) completion of airborne data collection operations using the 2nd generation NO/NO_2 detection system; (2) initiation of data reduction activities on the airborne NO/NO_2 data to test the experimental observations against photochemical theory; (3) completion of the first phase of our data analysis and modelling activities on the HONO data base recently collected with our newly developed PF-LIF HNO_2 sensor.

The first area of activity was completed early in the fall quarter. The simultaneously collected NO/NO_2 measurements were carried out in conjunction with a NASA airborne NO_2 instrument intercomparison program. (The Georgia Tech instrument in this intercomparison was the two/photon/photofragmentation laser-induced fluorescence (TP/PF-LIF) sensor.) This airborne field-sampling operation provided the opportunity to simultaneously measure NO and NO_2 concentrations over a wide variety of chemical environments including both clean and anthropogenically impacted air masses. The flights involved both maritime and continental regions. During the program the TP/PF-LIF instrument generally performed well, although early in the program the instrument's performance was compromised by problems arising from the use of a newly developed airborne excimer laser. The latter problem was largely corrected by in-the-field modifications to the design of the system. These changes allowed subsequent flights to proceed without incident.

The analysis of these NO/NO_2 measurements, the second area of activity in our program, was initiated early in the fall quarter. This analysis has been aimed at testing the credibility of photochemical theory in explaining the observed ratios of NO_2 to NO. As mentioned previously, these data were collected over a wide range of environmental conditions, including measurements in clean air over the Eastern Pacific Ocean as well as anthropogenically impacted continental air masses over California, Nevada, Utah and Colorado. In addition, data were taken on a transect of the United States during a flight between California and Virginia. These data thus represents one of the most extensive airborne data bases ever collected for purposes of testing photochemical theory. We anticipate that a detailed analysis of this new data base will be completed by mid-1987.

The final area of activity, analysis of the HONO measurement data, was largely completed by the end of the fall quarter. This analysis was compiled as a Ph.D. thesis and is included as an appendix to this report. In addition, two scientific papers covering these data are in various stages of preparation and are expected to be submitted to major scientific journals during January of 1987. This analysis has shown that for the nighttime HONO levels observed in Atlanta during the late winter and early spring of 1986 (normally in the range of 1 - 8 ppbv with with typical peak nighttime levels reaching approximately 2 ppbv, it is highly likely that the OH produced from early to mid-morning photolysis of HONO greatly exceeds that due to photolysis of ozone. HONO photolysis is therefore probably the major initiator of photochemical smog formation in a city such as Atlanta.

FINAL YEAR END REPORT

for

CONTRACT PERIOD JULY 1, 1983 THROUGH AUGUST 1984

Prepared for:

COORDINATING RESEARCH COUNCIL
219 Perimeter Center Parkway NE
Atlanta, GA. 30346.

Prepared by:

DOUGLAS DAVIS, PROJECT DIRECTOR
School of Geophysical Sciences
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Atlanta, GA. 30332.

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PROJECT SUMMARY

The primary objectives of the Georgia Tech CRC program are: (1) the development of new instrumental capability for measuring key atmospheric nitrogen species; and (2) the improvement of our understanding of the cycling of atmospheric nitrogen. During the first year considerable progress has been made on both program goals. Several of the more important of these achievements have been summarized below.

Sensor Development

Two of the pivotal species in the atmospheric cycling of nitrogen are NO and NO_2. At the start of the CRC program a ground-based field-operational two photon/laser-induced fluorescence (TP-LIF) NO sensor and a laboratory prototype photofragmentation laser-induced fluorescence (PF-LIF) NO_2 sensor were on hand at Georgia Tech. During the first year of our program the ground-based field-operational TP-LIF NO sensor underwent major design changes which resulted in two major technological advances in this instrument: (1) the sensitivity was improved by a factor of five (permitting pptv levels of NO to be sample with two to three minute time resolution), and (2) the ground-based NO system was made aircraft compatible. The latter development was deemed essential both for the purpose of investigating the N_xO_y chemistry of clouds and for studying the nighttime $NO/NO_2/NO_3$ chemical system.

Concerning instrumental developments on the detection of NO_2, a modified PF-LIF sensor was put in place at Stone Mountain in late June of 1984. Although this first generation system had a sensitivity of $\sim$ .5 ppbv, it was found to be quite adequate for measurements at Stone Mountain based on the levels typically observed there. A still more sensitive PF-LIF NO_2 sensor to be used in making airborne NO_2 measurements is now in the design stage and should be ready for our first airborne NO/NO_2 measurements in the spring of 1985. The latter system will have an improved detection limit for NO_2 of a few pptv with 2 to 3 minute time resolution. One of the unique advances in the development of the Stone

Mountain NO_2 sensor, which also will be incorporated into the airborne instrument, is that the same basic laser hardware used in the detection of NO is also employed in the NO_2 system. The only significant difference between the two systems is that the TP-LIF NO sensor uses two laser photons; whereas, the NO_2 sensor requires three, the third photon being used for the photolysis of NO_2. Thus, we have achieved the consolidation of NO and NO_2 measuring sensors into one package.

Development on the NO_3 and HONO detection systems is now in the final set up stage; thus we anticipate having detailed results available on both of these systems at the time of our fall quarterly report.

Field Measurements

Field measurements during the July 1983 to August 1984 time frame have involved both airborne platforms, with sampling occurring over remote Pacific Ocean regions, and ground-based sampling at the Georgia Tech Stone Mountain field station.

Airborne Measurements - the results from our airborne measurements (for which NASA provided the aircraft platform at no charge to CRC) were significant in two respects: (1) they enabled us to critically examine the field-operational characteristics of the TP-LIF NO system under a wide range of atmospheric conditions; and (2) they provided a unique opportunity to look at natural tropospheric sources of NO in the absence of anthropogenic influences.

Concerning the first area of investigation, the results from the airborne flights exceeded even Ga. Tech's expectations. The airborne system was demonstrated to be an all-weather, all-environmental instrument. Rain, clouds, ice, and dust/aerosol conditions had little influence on the signal limited characteristics of the TP-LIF NO sensor. In addition, comparisons with the much older technology of chemiluminescence NO detection, showed agreement to be within the ± 20% range even at levels of 5 to 10 pptv. There is, in fact, no comparable agreement reported in the literature between two totally different analytical techniques in the measurement of any trace atmospheric chemical species at these concentration levels.

The NO field observations recorded during the NASA airborne sampling flights revealed three decisive pieces of information on natural NO tropospheric NO sources: (1) extremely low levels of NO were observed in the Pacific marine boundary layer (e.g. 4 pptv on the average) suggesting that remote marine waters are at best a very weak natural source of NO. (2) Upon entering air masses which were characteristic of descending air from the upper free troposphere or lower stratosphere, major increases in NO as well as in O_3 were observed. The latter observations suggest that, as proposed by other investigators, the transport of NO_x rich air from the stratosphere must be considered a potential significant source of NO_x in remote regions of the global troposphere. And (3), the observation that upon penetrating electrified clouds very large increases in the average levels of NO were recorded. This third observation points to what we now believe is the other large natural source of NO_x in remote regions of the troposphere, namely, lightning.

Stone Mountain Measurements - The summer measurements program at Stone Mountain covered the time period of June 12 to August 1, 1984. During this time period, NO, NO_2, O_3, as well as meteorological data were routinely measured with more limited observations being recorded of gas phase HNO_3 and aqueous phase NO_3^{-1}, SO_4^{-2}, Na^+, Ca^{+2}, Cl^{-1}, NH_4^+, and K^+. The above time period was unique in that the month of June 1984 represented one of the driest summer months in Georgia's weather history; whereas July was one of the wettest. Our preliminary observations during this time period are summarized below. These observations relate to both NO_x sources as well as the cyclic chemistry of N_xO_y species during daylight and nighttime conditions.

(1) Most of the thunderstorm activity during July was related to the passage of major frontal systems through Gerogia. NO_x observations during several of these thunderstorms showed no systematic trends. On some

occasions, highly elevated levels of both NO and NO_2 were coincident with a given thunderstorm. At other times, major increases were seen only in the level of NO_2 and for still other storms no significant increase in either NO or NO_2 was observed.

On several occasions major spikes in NO and NO_2 also were seen immediately before a storm hit and for several hours afterwards. It now appears that the above observations are consistent with a cloud dynamic/-lightning model involving cloud to cloud lightning occurring between ~6 and 13 km and with downdraft air in the cumulonimbus rainshaft entering the cloud from the sides over an altitude range of 2 to 6 km. Thus, the effective transport of high altitude lightning generated NO_x to the low altitudes where sampling is occuring could be a rather sporadic event.

(2) The observed trend in the summer 1984 data set which shows much higher levels of NO during the month of July relative to June, strongly suggests that these elevated levels of NO_x were the result of the numerous frontal systems that moved through the state of Georgia during the July time period. Possible explanations for this behavior include:

(i) long range transport of NO_x pollutants by these frontal systems;

(ii) production of high levels of NO_x species due to extensive thunderstorm activity;

or (iii) major changes in the flux of NO_x species from natural biological sources due to changes in soil moisture levels.

Of the possibilities, (i) and (ii) appear to be by far the more likely. This tentative conclusion is based on the fact that a biological source is unlikely to produce the sharp spikes in NO and NO_2 observed so frequently during the 6/29 - 8/01 time period.

(3) The observed NO/NO_2 ratios at Stone Mountain during the summer of 1984 suggest that RO_2 and HO_2 reactions are important in promoting the oxidation of NO to NO_2 during daylight hours.

(4) The levels of NO observed at Stone Mountain at night suggest that nighttime levels of NO_3 may frequently be controlled by the $NO + NO_3$ reaction rather than by hydrocarbon or atmospheric moisture levels. The source of this nighttime NO is at this time unknown but may involve nighttime NO_x reactions. A more extensive examination of these nighttime levels of NO is being planned for the fall of 1984.

I. INSTRUMENT DEVELOPMENT

A. Airborne Two Photon/Laser-Induced Fluorescence NO System

1. Introduction

The following text addresses in detail the new airborne two photon/laser-induced fluorescence (TP-LIF) NO system. Although not explicitly outlined in our original proposal to CRC as a development task, this system is a critical part of our proposed airborne measurements of NO_x species in cloud environments. As such, the successful development of this instrument represents a significant milestone in our CRC program. This effort was made possible as a result of major funding from NASA and the use of very modest funds from CRC. An important fringe benefit resulting from this joint effort has been the official blind intercomparison of the TP-LIF NO system with other state-of-the-art NO sensors. The results from this intercomparison demonstrated that the TP-LIF NO sensor is a highly credible instrument, its standards of performance being those that future instruments will be evaluated against.

Some of the outstanding features of the TP-LIF system which showed up during the intercomparison period include: (1) the insensitivity to altitude changes (i.e. calibration number was constant); (2) the lack of a noise background (i.e. on the average 1 signal count per 100,000 laser shots, this being PMT dark count); (3) the absence of any interference signal; (4) the insensitivity to clouds, rain, and aircraft turbulence; and (5) the ability to achieve a detection limit which scales linearly with integration time. Based on the above profile, we might view the TP-LIF NO sensor as an all-weather all-chemical environment NO measuring system. Even so, improvements of 100 to 200 are possible if the system were to be moved into an eddy-correlation flux measuring sensor.

2. General Description of Hardware and Technique

The TP-LIF NO sensor is based on the principle that a molecule which has more than one bonding excited state can be pumped into the upper state with the resulting fluorescence being blue shifted relative to any of the pumping wavelengths (see Fig. 1). Once this blue shifted fluorescence is generated, one can successfully discriminate against all other noise sources using long wavelength blocking filters in conjunction with solar blind photomultiplier tubes. Obviously, the trick to achieving the above pumping scheme, with high efficiency, is in the use of very high photon fluxes which are at the same time delivered in the few nanosecond time regime. The latter characteristic permits the ultimate selectivity in the detection of a diatomic or simple polyatomic species by taking advantage of the high resolution spectroscopic features of these molecules.

In the case of NO, the two level pumping scheme involves the first excited state ($A^2\Sigma$) and the $D^2\Sigma$ upper state (see Fig. 1). The first level is reached using a wavelength of 226 nm; whereas, the second can be excited with infrared wavelengths ranging from ∿ 1.06 to 1.15μ.

In the ground based system used at our Stone Mountain field sampling station we opted to keep the system simple by using the left over 1.06μ radiation from the Nd:Yag laser as the second pump wavelength. The 226 nm radiation, on the other hand, was generated by pumping a dye laser with the second harmonic from a Nd:Yag laser with the resulting 574 nm tunable radiation then being frequency doubled. This doubled output was frequency mixed with the unused 1.06μ fundamental from the Yag laser to produce the desired wavelength at 226 nm.

The airborne system (see Figs. 2 and 3) used in the Ames/Hawaii NASA flights, in addition to being reduced to a 3'x 8' optical table rather than the more typical 4' x 12' surface area, differed from the Stone Mountain system in that the IR wavelength used to reach the $D^2\Sigma$ Level of NO was generated by a second Yag/dye laser system.

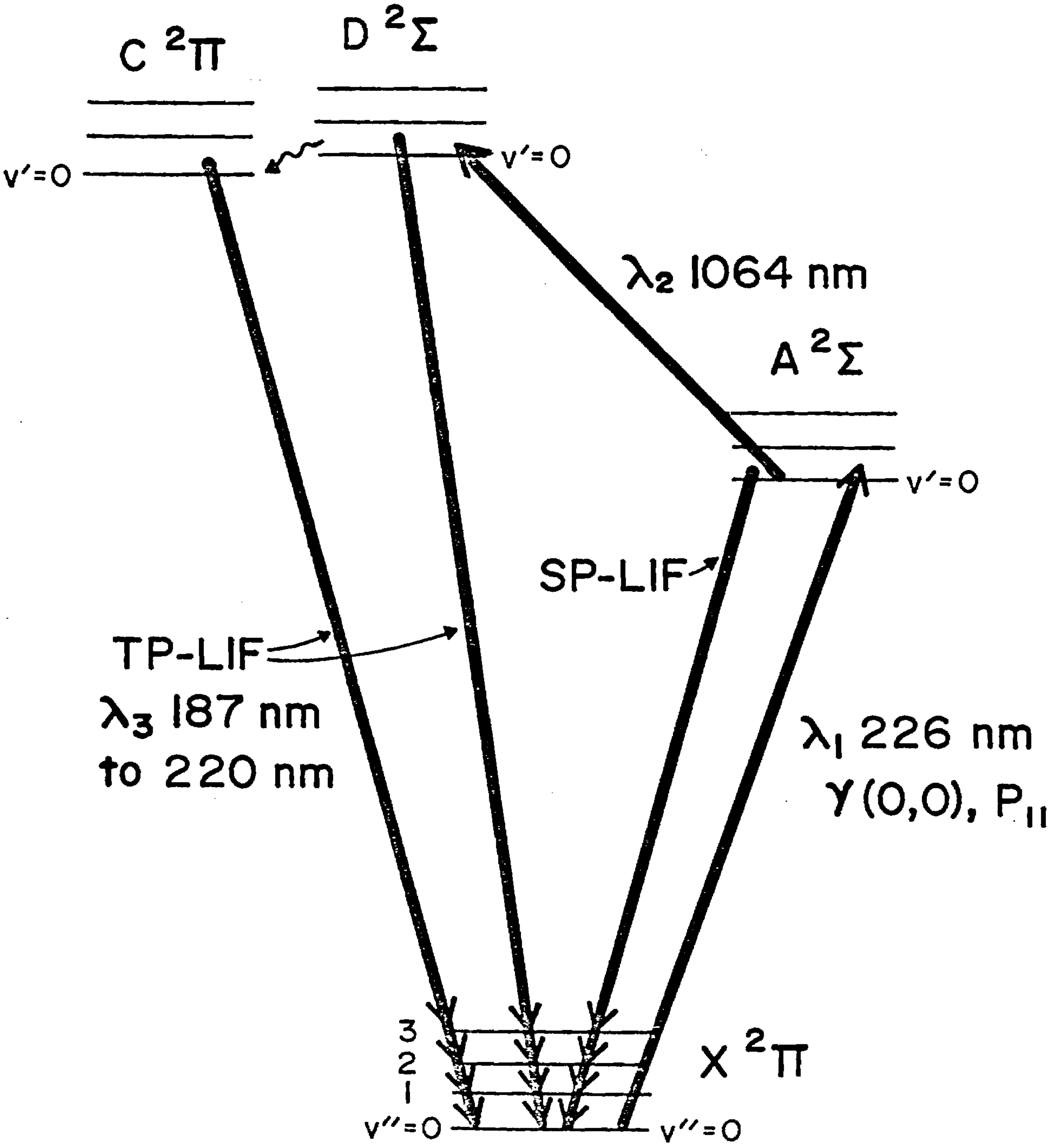

Fig. 1. Energy Diagram for the Sequential Two Photon/Laser-Induced Fluorescence Detection of NO. Note, Fluorescence at 187 to 220 nm is blue-shifted relative to the pumping wavelengths at 226 and 1064nm.

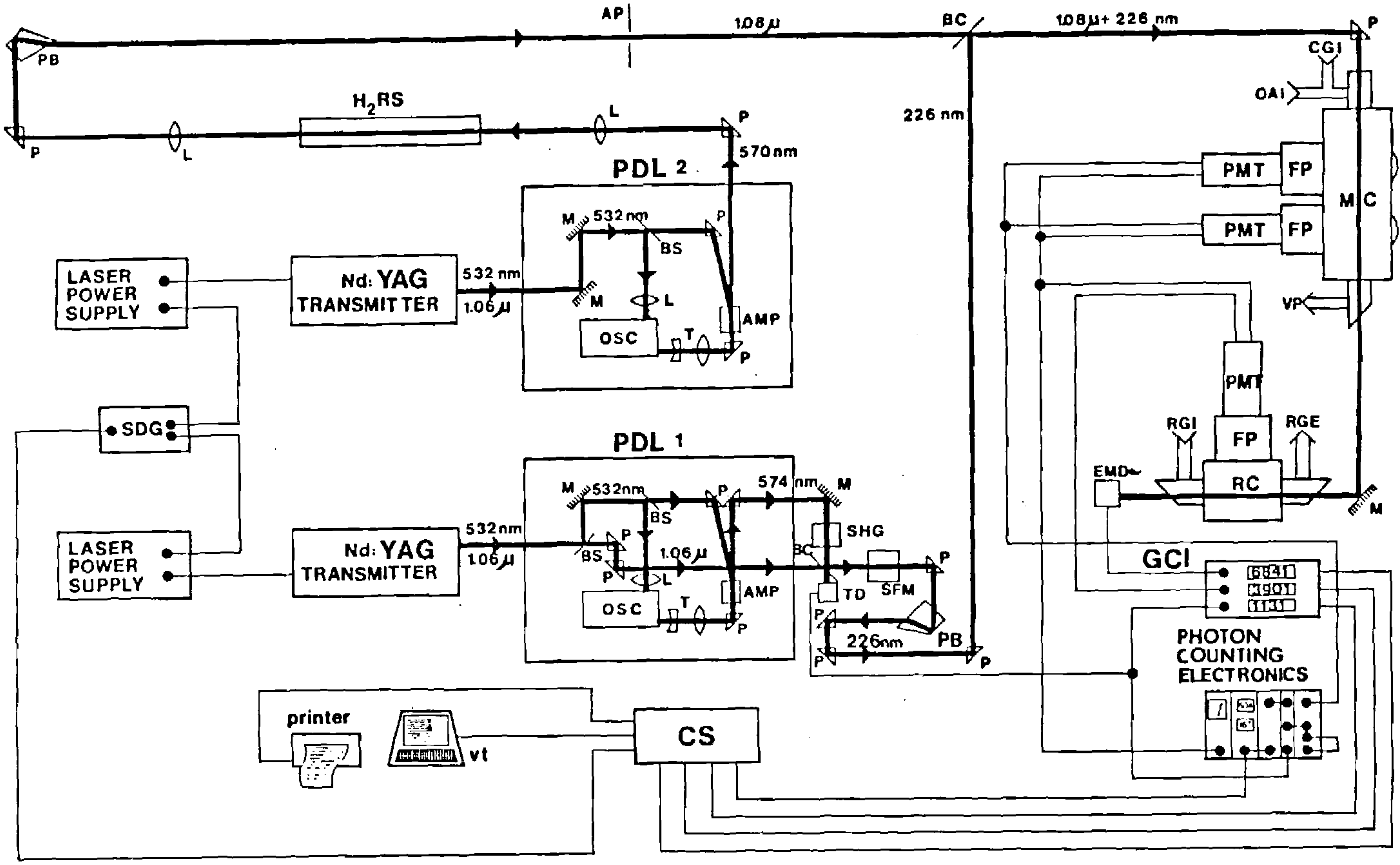

Figure 2: TP - LIF NO measurement instrumentation: (AMP) dye laser amplifier; (AP) aperture; (AT) laser beam attenuator, (BC) beam combining mirror; (BS) beam splitter mirror; (CS) computer system; (CGI) calibration gas inlet; (EMD) energy monitor diode; (FP) collection - optics/ Filter - pack; (GCI) gated charge - integrator; (GLP) Glan laser-polarizer; (H_2RS) Hydrogen Faman-Shifter; (HVP) High voltage power supply; (L) focusing lens; (LP) printer; (M) dichroic mirror; (MC) main sampling chamber; (OAI) outside air inlet; (P) turning prism; (PB) Pellin-Broca dispersing prism; (PC) Pockel cell; (PMT) photomultiplier tube; (PDL) pulsed dye laser; (RC) reference cell; (SDG) synchronization and delay generator; (SHG) second harmonic generation crystal; (RGE) reference gas exhaust; (RGI) reference gas inlet; (T) beam-expansion telescope; (TD) trigger diode; (VP) vacuum pump; (VT) video terminal.

(Reproduced from J. Geophys. Res. 1985)

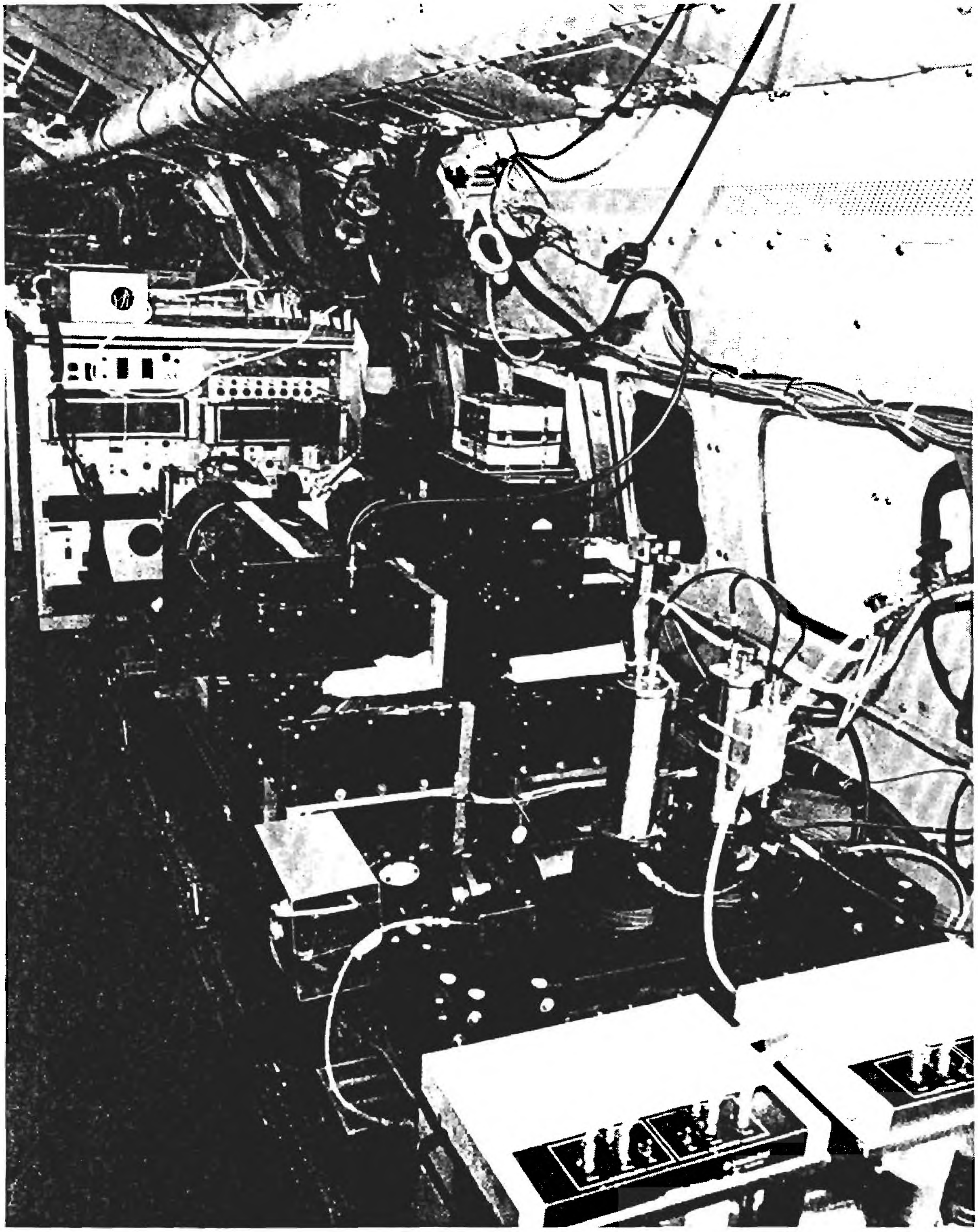

FIG. 3 TP-LIF NO Instrument Aboard Convair 990 Aircraft

Thus, the airborne system had double selectivity. The IR wavelength in the airborne system was generated by again pumping a dye laser with the second harmonic of a Yag laser (532 nm), and then taking the output at 580 nm and injecting it into a H_2 Raman shifter. From the spectrally separated output, the second Stokes line at ~ 1.1μ was then combined with the 226 nm beam and injected sequentially into the ambient air fluorescence chamber and then into the NO reference chamber. The latter element served to define any changes in the sensitivity of the TP-LIF sensor that resulted from changes in the IR or UV energy, changes in the time separation* between the IR and UV beams, or changes in the overlap of the two beams. Thus, all drifts in the system were continuously monitored using the reference cell signal and all ambient signal levels could be converted into absolute concentration levels using an appropriately adjusted calibration number. On the average, the overall drift in the reference cell signal was no more than ± 15%. Only when major laser problems developed was it seen to be greater than the above cited value and even then tests have shown that the reference cell signal could still be used to properly adjust the calibration number.

The advantages of the Ames/Hawaii airborne system over the ground-based system are threefold: (1) As stated above, since both the infrared and UV beams are tunable, the airborne system has double selectivity. (2) The tunable infrared laser system allows one to maximize the efficiency for pumping NO from the $A^2\Sigma$ into the $D^2\Sigma$ state. In fact, the sensitivity of this system was a factor of four higher than for the Wallops Island configuration. And (3), the very large absorption cross section available in the 1.08 to 1.10μ region permitted saturation conditions to be reached for the A → D transition. Under these conditions, the signal level for a given amount of NO is found to be nearly independent of changes in the IR laser energy for energy

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* Typically, the time separation between the UV and IR beams was held at 2 ns with a drift of ± 2 ns. This 2 ns was measured from the center of each temporal laser profile, both of which were ~ 11 ns full width half max.

changes of a factor of two to three.

Quite obviously, the major disadvantage of the airborne TP-LIF system is that twice the amount of laser hardware is required for the experiment and this additional hardware must be maintained. The more complex TP-LIF system was chosen for the airborne intercomparison due to its higher sensitivity, thus reflecting our anticipation of very low levels of NO in the marine boundary layer. As seen from our summary of airborne NO data, the latter hypothesis was correct.

In concluding our comments on hardware differences between the original ground-based system and the airborne sensor, we should point out that the one other area where alterations were made was in the dynamic dilution system used to perform absolute calibrations of the TP-LIF sensor. The system used at Wallops Island was what one might call a "bread-board" system. In this case, the individual mass flow meters were connected with long lengths of teflon tubing. In the airborne experiments, the dynamic dilution system was condensed into a 5" x 17" x 12" module. This resulted in a reduction in connecting tubing from 25' to 3'. A final change involved the substitution of one of the flow meters for one which had a flow range more appropriately suited to sampling conditions on the aircraft.

3. Evaluation of Background Noise Sources

Due to the combination of a long wavelength blocking filter (e.g. 5 OD units at 226 nm) and a fast roll-off solar blind PMT, the TP-LIF scheme permited discrimination against all Rayleigh- and Stokes-shifted Raman noise sources as well as spectrally white fluorescence noise from aerosols, chamber walls and other trace gases. In addition, this filter/PMT combination gave effective blocking of the first and second anti-Stokes Raman scatter lines from both N_2 and O_2. This leaves only very weak multiphoton absorption processes by unidentified trace gases as a possible source of laser generated noise. Thus far, we have never observed any backgrounds (above the time gated dark count of the PMT's) for the 1.1μ laser system during numerous hours of testing at our Stone Mountain field sampling station or during ground based tests at Ames/Hawaii.

As a further check, during the first few flights in the Ames/Hawaii operation, we operated our system in a 10/5 Hz mode where the signal and background due to the 226 nm laser beam were recorded on alternating shots (the 5 Hz repetition rate laser being the 1.1μ wavelength). In these tests covering over 4 1/2 hours of total integration time, the recorded background counts = 0*.

In other tests we have consistently found that upon tuning the UV wavelength off the P branch NO band head, we obtain the same background levels as those observed when the 226 nm beam was positioned on an NO absorption band. Only in the latter test was the IR beam blocked.

The time gated PMT dark count gives a lower limit noise of $\leq$ 1 ct/2 hr. with the laser operated at a rep rate of 10 pps. This lower background noise limit was realized in the relatively clean air over the Pacific during the Fall Ames/Hawaii NO intercomparison. Thus, throughout the Fall intercomparison mission the TP-LIF system was an NO signal limited technique _not_ a background limited technique.

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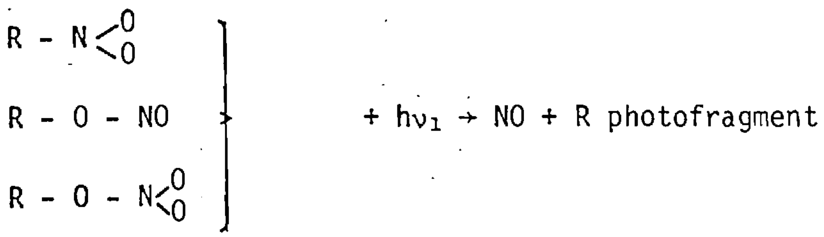
*During flight 6, we note that there was a brief period where a low background count rate was observed, but this was determined to be due to the 226 nm beam clipping a collimating ring. This problem was resolved and never surfaced for the remainder of the flights.

4. Evaluation of Potential Chemical Interferences

Several chemical interference tests were carried out on this system. For each chemical system examined, the basic process tested involved four steps, e.g.

(1)



$$\left.\begin{array}{l} \mathrm{R - N}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}} \\ \mathrm{R - O - NO} \\ \mathrm{R - O - N}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}} \end{array}\right\} + h\nu_1 \rightarrow \mathrm{NO} + \mathrm{R}\ \text{photofragment}$$

(2) $\mathrm{NO} + h\nu_1 \rightarrow \mathrm{NO}\ A^2\Sigma$

(3) $\mathrm{NO}\ A^2\Sigma + h\nu_2 \rightarrow \mathrm{NO}\ D^2\Sigma$

(4) $\mathrm{NO}\ D^2\Sigma \rightarrow \mathrm{NO}X^2\Pi + h\nu_3$

From this, it can be seen that the interference signal depends on the square power of the UV laser energy and on the first power of the IR. The results reported here relate to the following laser parameters: UV beam diameter of 5 mm, UV energy 0.90 mJ. In each case the ratio given represents the concentration of interfering species required, relative to that of NO, to give the same signal as that from NO itself. Thus, in the first example, involving HNO_3, the interference measurement indicates that over 2800 times more HNO_3 is needed to produce an equivalent signal to that from one part natural NO. Concentration levels for other compounds are given below:

$HNO_3 > 2800/1$

$CH_3NO_2 > 17{,}000/1$

$C_2H_5NO_2 > 17{,}000/1$

$CH_3ONO = 360/1$

$CH_3ONO_2 > 28{,}000/1$

$NO_2 \geqslant 4000/1$

$SO_2 > 17{,}000/1$

Based on these results, together with a consideration of the abundance of each of the above species in the clean troposphere, we have concluded that none of these molecules should have presented an interference problem to the TP-LIF NO system during the Ames/Hawaii mission. The highest interference species, methyl nitrite (CH_3ONO), might initially be viewed with some alarm but in assessing this species concentration level in the atmosphere the following points must be considered: (1) there is no efficient mechanism for forming this species under atmospheric conditions, and (2) the strong absorption by this species in the near UV relegates it to the category of a short-lived species. Both of these factors suggest that the levels of methyl nitrite in the atmosphere should be no greater than a few pptv. Our 1-D chemical model at Georgia Tech tends to corroborate this point of view.

Two additional molecules of possible concern for which tests have not as yet been carried out are peroxyacetyl nitrate (PAN) and nitrous acid (HONO). The relative magnitude of these potential interfering species can be estimated based on the efficiency of photolysis, E_p, and the quantum efficiency for NO production in the k level being excited, Φ_p, where:

$$E_p = 1 - \exp - \frac{\sigma_{\lambda_1} P_{\lambda_1}}{a_{\lambda_1}}$$

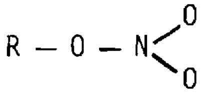
(Here $p\lambda_1$ is the number of photons per laser shot at λ_1, $\sigma\lambda_1$ is the absorption cross section at λ_1 and $a\lambda_1$ is the laser beam diameter for wavelength λ_1.)

and the interference ratio is given by:

$$\frac{D_{\lambda_3}(NO)}{D_{\lambda_3}(RNO_x)} = \frac{1}{E_p \Phi}$$

In the case of nitrous acid $E_p = 6 \times 10^{-3}$ and Φ_p is estimated to have a value ≤ 0.1, based on our results on methyl nitrite. The latter species, we believe, should define a reasonable template molecule for modelling the simple photodissociative behavior of RONO species such as nitrous acid. We would therefore estimate an interference ratio value for nitrous acid $\geqslant$ 1600/1, i.e. there would have to be 1600 times more HONO to give same signal as 1 part NO. Given a photostationary concentration of $\leqslant$ 10 pptv (the highest levels predicted by our 1-D chemical model for clean tropospheric conditions), we see that HONO should not have presented interference problems to the TP-LIF NO system.

In the case of PAN, the value of E_p is calculated to be 3×10^{-3}. To estimate the quantum efficiency for production of NO in pumpable quantum states we have used methyl nitrate as our template molecule. Its structure is of the type:



Thus, based on our methyl nitrate results, we have back calculated a Φ_p value of $\leq$ .02. This gives a final interference ratio for PAN of$\geq$ 16,000/1.Since the results of Singh and Hanst (1981)* suggest an upper concentration level of 200 pptv for PAN in the clean troposphere, it is again apparent that PAN should not result in a measurable interference in the TP-LIF detection of NO under normal tropospheric conditions.

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*Singh, H. and P.L. Hanst, Geophys. Res. Letters, 8, p. 941, 1981

5. Reference Cell Considerations

The TP-LIF signal strength is proportional to the product of the spatially and temporally overlapped energy densities. However, the non-linearity of P_{λ_2} for the tunable 1.1μ system precludes any use of a referencing system that uses the simple product of the P_{λ_1} and P_{λ_2} monitored energies. Thus, a reference cell which is to accurately monitor changes in overall system performance must meet the following criteria:

(1) correct for any drift in either λ_1 or λ_2 laser wavelengths;

(2) give an accurate correction for variations in P_{λ_1} and P_{λ_2} when P_{λ_2} is non linear;

(3) have nearly identicial characteristics as the ambient chamber, both in regard to the temporal and spatial overlap of the λ_1 and λ_2 laser pulses

(4) have long term stability in both its physical and chemical characteristics

and (5) have a precision which is $\leq \pm 2\%$

Our first attempt at developing such a reference cell involved air mixtures spiked with NO. This system failed criterion (4) due to a build-up of O_3 from the 226 nm photolysis of O_2. This problem is avoided at gas flow rates of > 2 standard liters per minute, however, the costly consumption of large gas quantities coupled with the ability of this flow to act as a non-trivial local pollution source necessitated another choice of gas mixtures.

The electronic quenching rate, $Q = k_q[M]$ for the A state in 1 atm. of dry air is $Q_A = 7.5 \times 10^8$ s^{-1} and for the D state $Q_D = 3.0 \times 10^9$ s^{-1}. A mixture of ~ 11% CO_2 in N_2 gives $Q_A = 1.0 \times 10^9$ s^{-1} and $Q_D = 2.5 \times 10^9$ s^{-1}. This buffer gas mixture exhibited loss of NO at flow rates less than ~ 200 cc/min. A mixture of He + 11% CO_2 was found to give the best chemical stability yielding values of $Q_A = 1.0 \times 10^9$ s^{-1} and $Q_D = 1.7 \times 10^9$ s^{-1}. Thus, primary standard quality mixtures of 10 ppmv NO in He + 11% CO_2 were commercially obtained and used throughout all field experiments as a reference cell gas mixture.

Using the above gas mixture and an optical/PMT assembly nearly identical to that used on the main sample chamber, resulted in a signal level of ~ 200 photon/pulse for the tunable 1.1μ TP-LIF system. The photon statistics S/N ratio was therefore > 100 (for a 1 min. integration).

As noted earlier, the tunable 1.1μ system also has the additional complexity of temporal synchronization between the two driver lasers. In the airborne system the two ILS Nd:YAG lasers were typically operated with a 2 ns delay, with the UV laser leading. Short term jitter was less than ± 2 ns and long term stability was typically ≤ 4 ns/hour. The error in the reference cell correction resulting from poor temporal overlap between lasers was found to be only 20% for a factor of 5 decrease in the observed signal at 1 atm. pressure. These overlap conditions were generated by our purposely moving the lasers out of synchronization by ± 8 ns. These extreme timing conditions were not found to occur during any flight operation, nevertheless, systematic checks of the timing between lasers were made approximately once every hour.

In conclusion, the reference system described above met all the criteria necessary in order to accurately correct for changes in laser system performance. In addition, the pressure in the reference cell was maintained at the same pressure as that outside the aircraft, thereby giving accurate corrections when changing pressure altitude.

6. Analysis of Precision and Absolute Accuracy for the TP-LIF NO System

(a) Precision of Measurement

In the TP-LIF system, the determination of the absolute concentration of ambient NO depends on basically two factors: (1) the measurement of a signal strength (photons/unit time) and (2) an accurate calibration factor (photons/unit time/molecule/cm^3). The precision in our determination of [NO] is simply the precision in our measurement of signal strength. For our system, which is NO signal limited, the standard deviation, σ, of the photon population (described by a Poisson distribution) can be taken as $\sigma = \sqrt{N}$ where N is the number of photons counted for a given integration time. Within the linear regime of photon counting the fractional precision of this measurement is simply $\sqrt{N}/N$.

(b) Accuracy of Measurement

The absolute accuracy of our TP-LIF measurement is solely dependent on the accuracy of our calibration factor. The accuracy of the TP-LIF calibration factor depends on the accuracy of the following variables: (i) the reference cell correction factor; (ii) the flow system dilution factor; (iii) the value for concentration in the standard gas mixture; and (iv) the integrity of [NO] in the sample chamber compared to that in the ambient air; RC, DF, $[NO]_{std}$, $[NO]_{sample}$, respectively. Each of these variables can be treated as independent quantities.

(i) Error in the Reference Cell Correction:

The fractional precision of our reference cell measurement is typically ± 0.3%. The ability of this reference measurement to accurately correct for changes in the system has been observed to be less than 20% for factors of 5 change in detection sensitivity. This represents a very worst case situation where as noted earlier we purposely varied the UV and IR laser synchronization by ± 8 ns. On the average the system performance over a data run varied by only ± 15%, not a factor of five. Thus, using the 15% variability value, we estimate a very conservative upper limit fractional error for the reference cell correction to be ± 4.5%.

(ii) Dilution Factor Error:

The dilution factor, DF, is derived from the product of two sets of flow meter ratios. But, since these flow meters were all cross calibrated against a common reference system, any systematic errors in calibration should all be in one direction (i.e. either + or -). The systematic errors in the dilution factor, therefore, should be very near zero. However, each of these cross comparisons had a random error of ± 2% due to our precision in cross calibrating these devices. We have assigned a combined uncertainty in the value for the dilution factor of ± 4%.

(iii) Error in the NO Standard Gas Mixture Value:

As previously mentioned, our primary standard NO mixture has been compared to a NASA provided NBS traceable standard whose value is known to be ± 2%. The uncertainty in our cross calibration of these primary standard values to our working standard is ± 5%, and is purely due to photon statistics of our measurement combined with our flow meter uncertainties, both of which are random in nature.

(iv) Error in the [NO] Sampled Due to Sample Integrity:

This error term takes into account all systematic loss process of NO in our flow system prior to sampling (e.g. reaction with O_3, wall loss, etc.) as well as all artificially produced levels of NO (e.g. laser photolytic chemical interference, leaks of cabin air, etc.). To a large extent the systematic errors due to any loss mechanisms will be corrected for via our use of the standard addition calibration technique. Errors due to NO production sources have also been discussed as being negligible. We therefore estimate a conservative upper limit for these effects of ± 2%.

(v) Overall Accuracy of Calibration Factor:

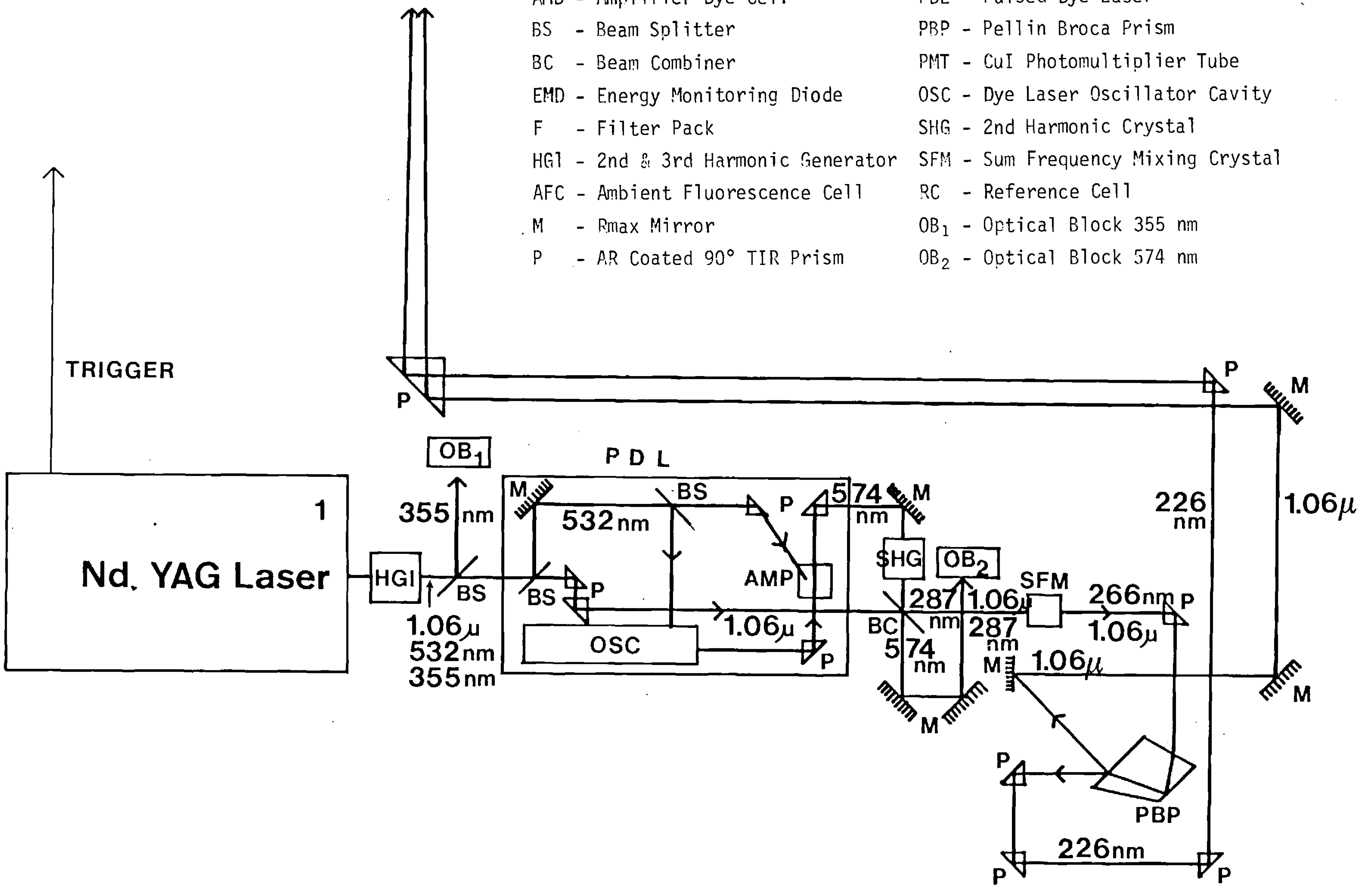
Taking these four variables (RC, DF, $[NO]_{std}$, and $[NO]_{sample}$) as independent quantities, we estimate via propagation error analysis, the overall accuracy of our TP-LIF system to be ± 8%. However, since the in-flight standard-addition calibrations also have an additional uncertainty of ± 3 to 5% due to photon statistics, the final accuracy for a given calibration is evaluated at ± 9.5%. This represents the 68% confidence limit, and we believe more realistically the 90% confidence limit should be given as the final accuracy figure. Thus, the 90% value is ± 16%.

B. Ground Based Photofragmetation/Two-Photon/Laser-Induced Fluorescence Detection of NO_2 and NO_3

(1) In our original proposal, it was indicated that both NO_2 and NO_3 would be sampled using the photofragmentation LIF technique. This goal is still being actively pursued and will result in extremely sensitive sensors for both species (e.g. in the few pptv level). The one disadvantage that the latter approach has, however, is that one cannot quickly switch from the NO_2 to the NO_3 mode of operating. Switching times have been estimated to be 1/2 to 1 hour. Of equal importance is the fact that to measure NO and NO_2, two separate instruments will be required, i.e. TP-LIF for NO and photofragmentation/laser-induced fluorescence (PF-LIF) for NO_2. The latter situation is demanding in terms of available equipment and is also more demanding in terms of operator personnel

To overcome this problem, we have initiated an instrument modification effort which has resulted in a compromise between sensitivity and instrument switching time. This new system which has been labelled photofragmentation/two-photon/LIF has been designed around the original ground-based TP-LIF NO sensor. Recall, that the latter system makes use of a tunable 226 nm beam in conjunction with a fixed wavelength 1.06μ beam (the fundamental wavelength of a Nd;YAG laser). In the modified sensor, one may switch from NO to NO_2 in approximately 2 minutes, with the return to the NO mode being about the same time.

The basic optical layouts for the three different modes of operation (NO, NO_2 and NO_3) are shown in Figures 4, 5, and 6. In the NO mode, the fundamental YAG wavelength (1.06μ) is first frequency doubled and tripled in element HG-1. The third harmonic wavelength at 355 nm is split off on mirror BC but is blocked with element OB_1. The first and second harmonics pass through BC and enter the dye laser housing where the 1.06 nm beam is routed through the dye laser in a non-interactive mode. The second harmonic (532 nm) is used to drive the active medium in the dye laser resulting in tunable 574 nm radiation. The latter tunable



AMD	Amplifier Dye Cell
BS	Beam Splitter
BC	Beam Combiner
EMD	Energy Monitoring Diode
F	Filter Pack
HG1	2nd & 3rd Harmonic Generator
AFC	Ambient Fluorescence Cell
M	Rmax Mirror
P	AR Coated 90° TIR Prism
PDL	Pulsed Dye Laser
PBP	Pellin Broca Prism
PMT	CuI Photomultiplier Tube
OSC	Dye Laser Oscillator Cavity
SHG	2nd Harmonic Crystal
SFM	Sum Frequency Mixing Crystal
RC	Reference Cell
OB_1	Optical Block 355 nm
OB_2	Optical Block 574 nm

FIG. 4, TP/LIF NO SYSTEM

AFC - Ambient Fluorescence Chamber
EMD - Energy Monitoring Diode
F - Filter Pack
PMT - CuI Photomultiplier Tube
RC - Reference Cell

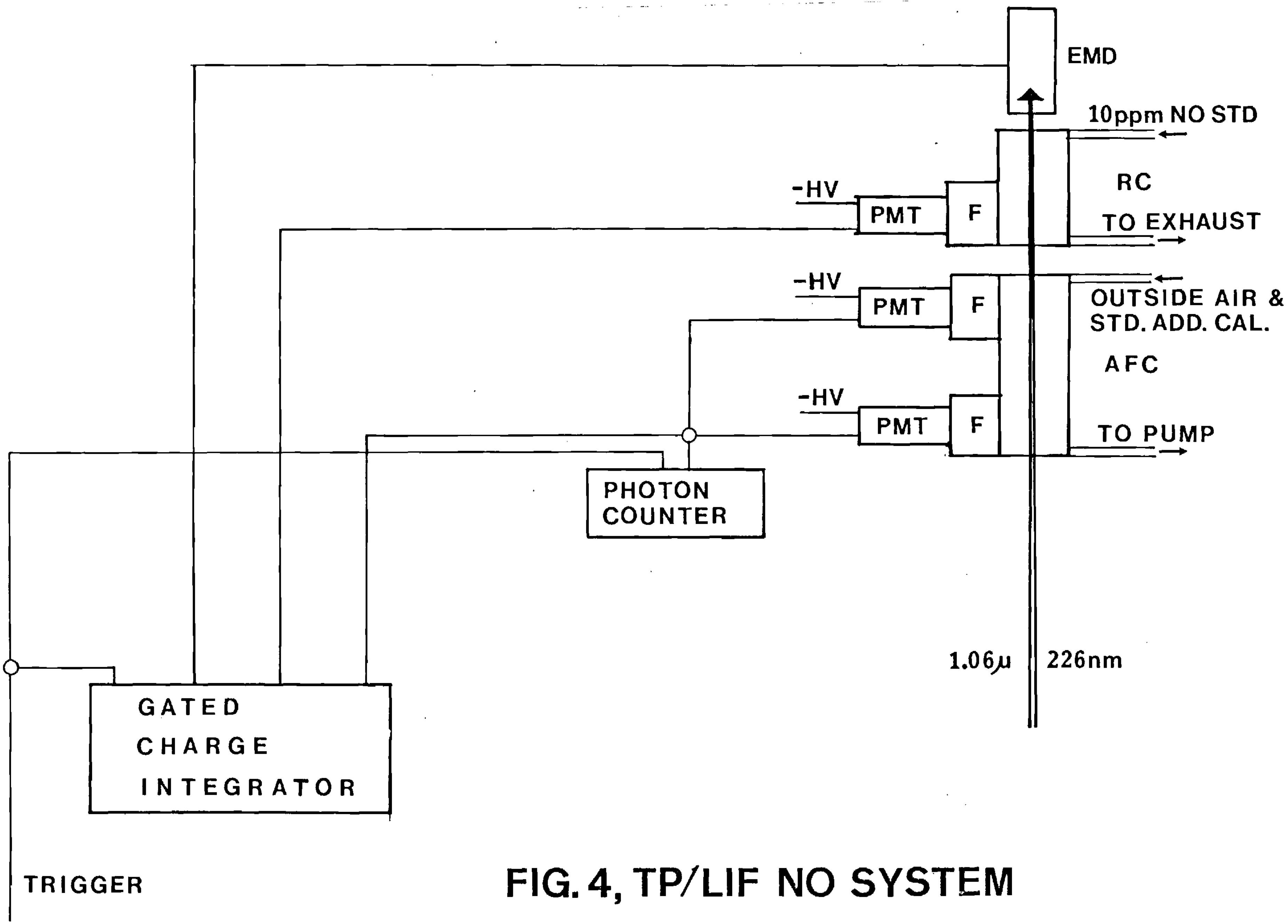
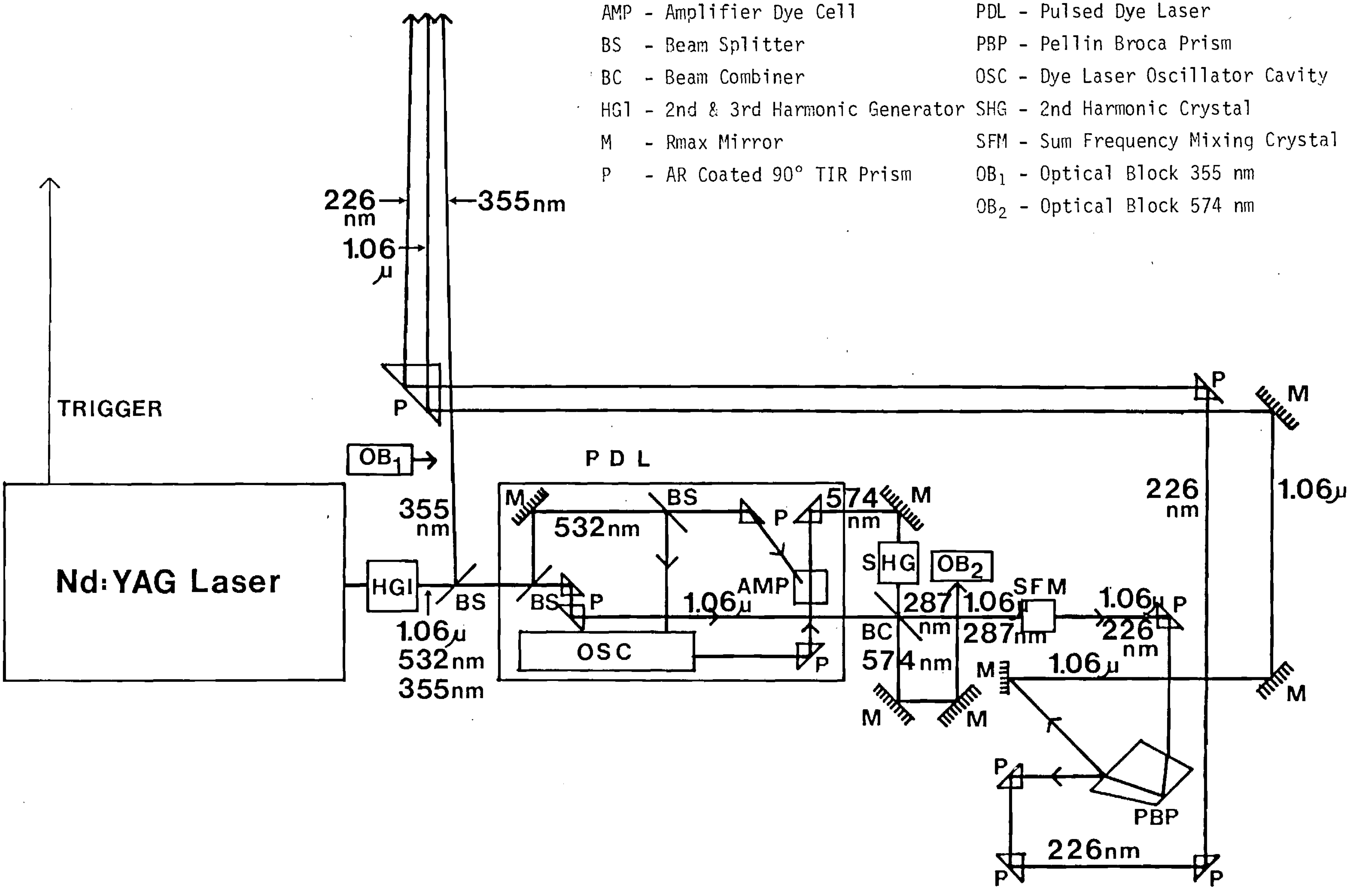


FIG. 4, TP/LIF NO SYSTEM



AMP	-	Amplifier Dye Cell
BS	-	Beam Splitter
BC	-	Beam Combiner
HG1	-	2nd & 3rd Harmonic Generator
M	-	Rmax Mirror
P	-	AR Coated 90° TIR Prism
PDL	-	Pulsed Dye Laser
PBP	-	Pellin Broca Prism
OSC	-	Dye Laser Oscillator Cavity
SHG	-	2nd Harmonic Crystal
SFM	-	Sum Frequency Mixing Crystal
OB_1	-	Optical Block 355 nm
OB_2	-	Optical Block 574 nm

FIG. 5, PF-TP/LIF NO_2 SYSTEM

AFC - Ambient Fluorescence Chamber

EMD - Energy Monitoring Diode

F - Filter Pack

PMT - CuI Photomultiplier Tube

RC - Reference Cell

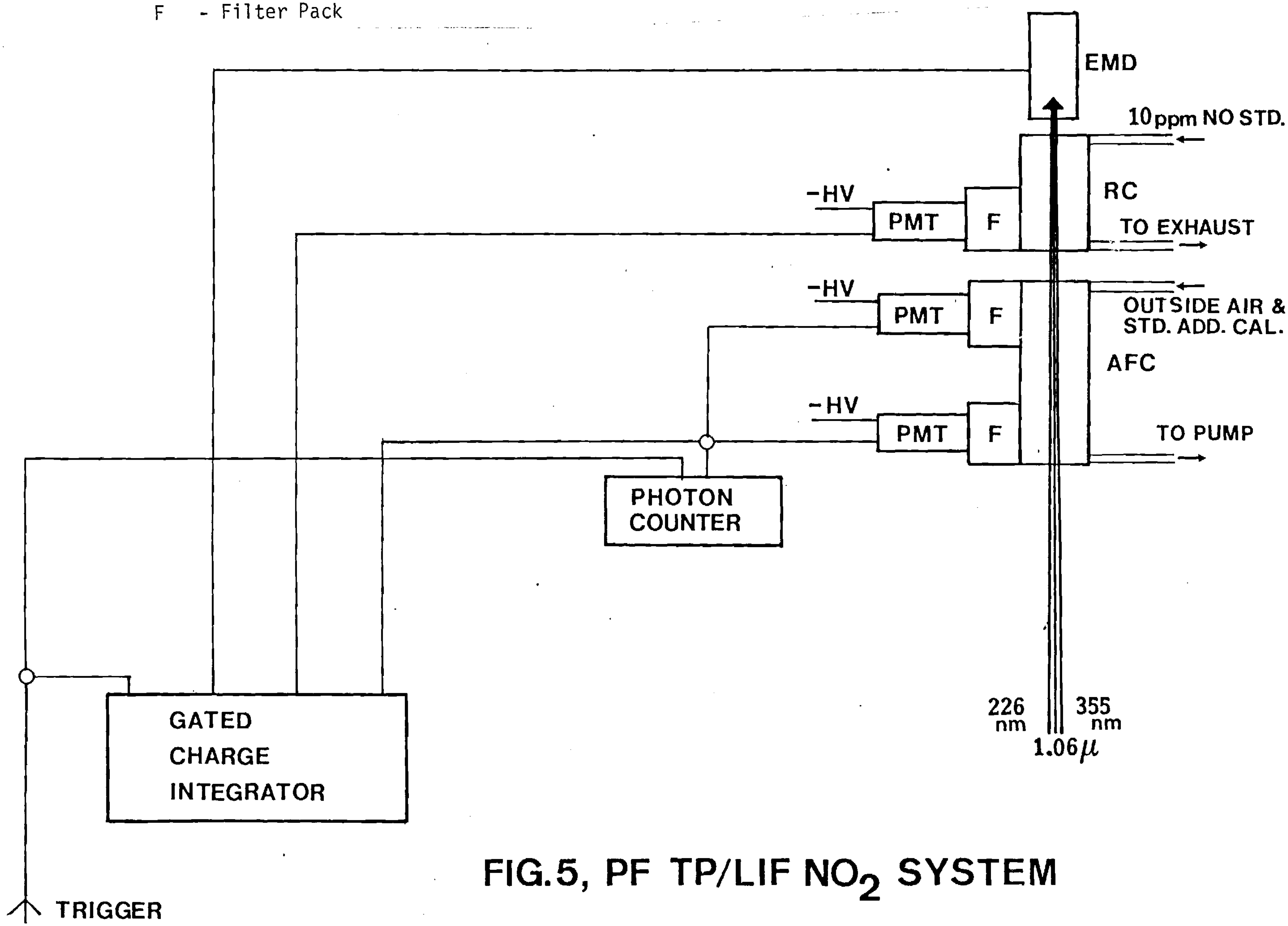
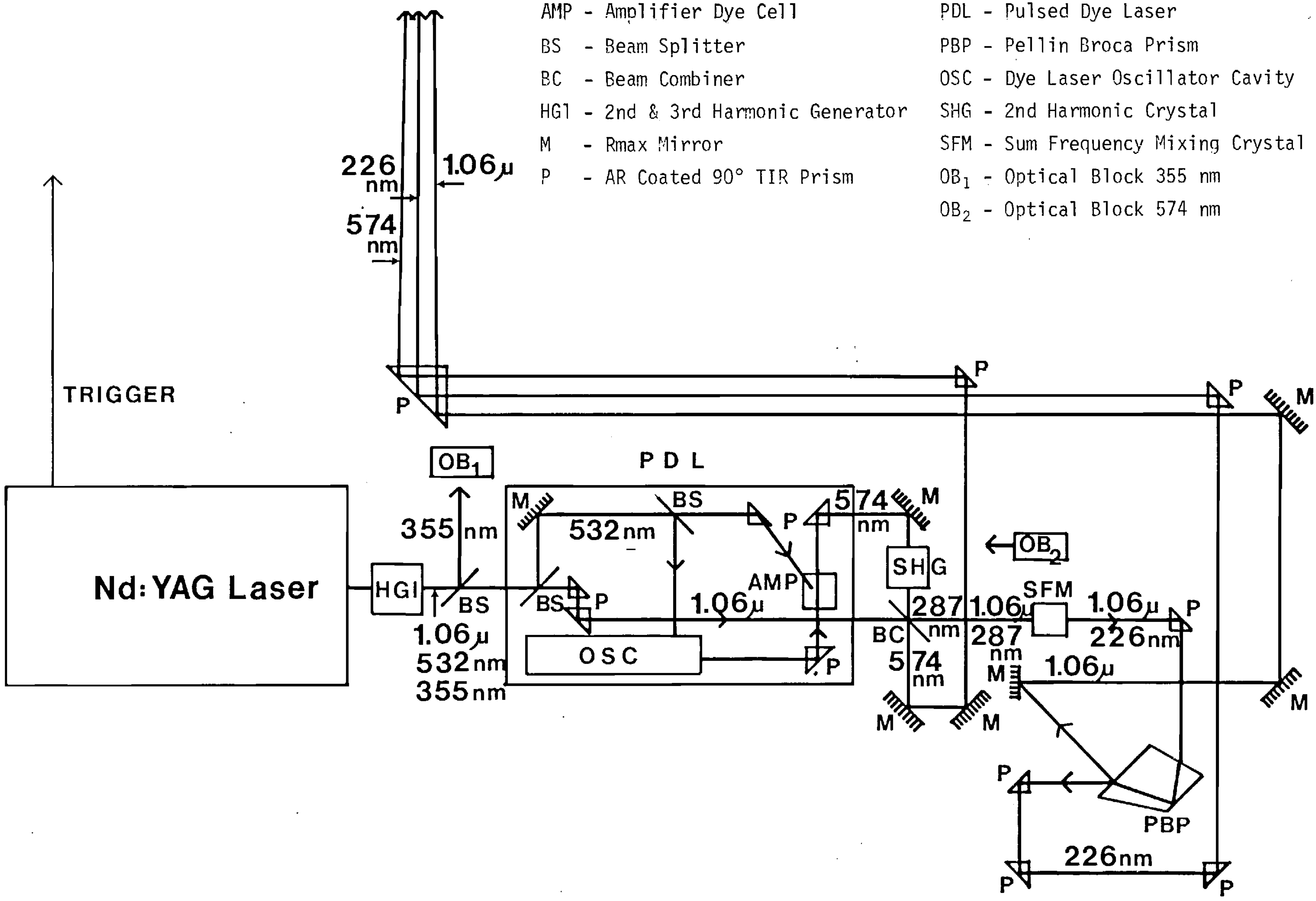


FIG.5, PF TP/LIF NO_2 SYSTEM



AMP	Amplifier Dye Cell	PDL	Pulsed Dye Laser
BS	Beam Splitter	PBP	Pellin Broca Prism
BC	Beam Combiner	OSC	Dye Laser Oscillator Cavity
HG1	2nd & 3rd Harmonic Generator	SHG	2nd Harmonic Crystal
M	Rmax Mirror	SFM	Sum Frequency Mixing Crystal
P	AR Coated 90° TIR Prism	OB_1	Optical Block 355 nm
		OB_2	Optical Block 574 nm

FIG. 6, PF-TP/LIF NO_3 SYSTEM

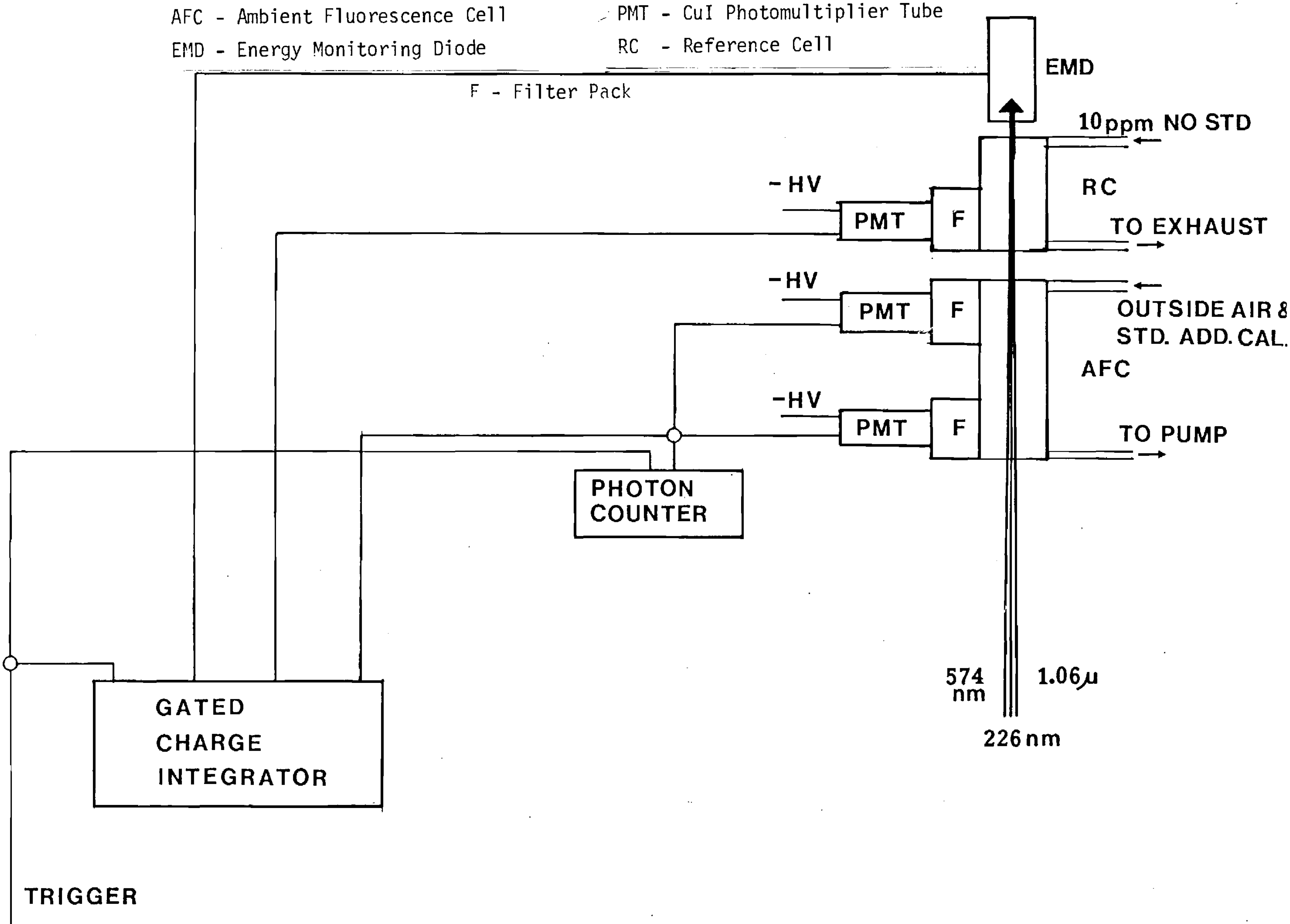


FIG. 6 PF/LIF NO_3 SYSTEM

wavelength is frequency doubled (element SHG) and the resulting 287 nm beam is then recombined on mirror BC. (∿ 20 mJ of 574 nm radiation passes through mirror BC and is then blocked in the NO running mode at OB_2.) The combined 287 nm and 1.06μ beams are injected into a sum frequency crystal (element SFC), producing tunable 226 nm radiation. Both the 226nm and 1.06μ beams are finally separated from other wavelengths using a Pellin Broca Prism and then recombined again in the ambient sampling chamber and reference chamber via prism optical sterring elements. Thus, in the NO configuration only 226 and 1.06μ beams enter the sampling chamber. The 226 nm beam pumps NO from the X to A state and the fixed frequency 1.06μ beam drives the NO from the A state into the upper lying D level. As discussed in Section IA, fluorescence in this system is sampled at ∿ 190 nm (i.e. blue shifted).

In the NO_2 mode of operation, the major change made to the system is that of unblocking the 355 nm beam (element OB_1). In this case, the third wavelength is overlapped with the 1.06μ and 226 nm beams. The 355 nm beam serves as the photofragmentation wavelength for NO_2 . Although the resulting NO is formed in the v" = 0 and 1 levels, only the v" = 0 state can be excited with the 226/1.06 wavelength combination. (Recall that in the normal PF-LIF sensor the photolysis wavelength is 308 nm and in this system only the v" = 3 NO states are sampled). In the PF/TP-LIF system, then, a signal is produced from natural ground state NO as well as from v" = 0 NO generated from the 355 nm photolysis of NO_2 . The signal corresponding to NO_2 is therefore the difference between the total signal (with 355 nm photolysis) versus that for natural NO where the 355 nm beam is blocked. Under typical operating conditions, the integration time required for NO is 5 min.; thus the average separation between NO and NO_2 measurements is a minimum of 5 minutes. However, because of the background scatter from the 355 nm beam an additional time of 2 1/2 minutes is frequently required for purposes of extracting a final NO_2 signal. Using the laser sequencing just described (e.g. 226nm, 1.06μ beams: 226nm, **1.06μ, 355nm beams,** and 355nm beam only), one problem can delevop with the measurement of NO and NO_2 is that of the NO level undergoing a major change during an NO_2 integration period. In fact, this occurred on a limited number of occasions (see e.g. July 7 NO_2 data). Under these conditions the NO_2 levels reported could have been too high by as much as 35%. To avoid this problem in the future, the blocking and unblocking of the 355 nm photolysis beam will be performed via a computer controlled solenoid beam chopper. In the latter configuration, the NO, NO + NO_2, and 355 scatter signals will be recorded sequentially for times of 30 seconds only. The computer can then be used to integrate as many of these 30 second intervals as required to get a meaningful S/N ratio. Obviously, still more sophisticated beam choppers could be used (e.g. one which would switch every other laser shot (100 ms)), if still higher time resolution for NO and NO_2 were deemed necessary.

To convert the NO TP-LIF sensor into the NO_3 mode, optical block OB_1 remains in place but OB_2 is removed. The latter move permits 574 nm radiation, which is transmitted by the beam combining mirror BC, to be combined via prism folders with the 226 nm and 1.06μ beams. The 574 nm beam serves the same purpose as the 355 beam for NO_2, that is, it photofragments NO_3 to form NO in the $v''= 0$ and higher states*. At 574 nm, however, NO_2 only fluoresces it cannot be photofragmented. There are, in fact, no other known atmospheric nitrogen oxide species that can be photofragmented at 574 nm other than NO_3. Thus, the signal derived from the 574, 226, 1.06μ wavelength combination defines the levels of ground state natural NO plus $v''= 0$ NO produced from NO_3. As in the case for NO_2, an indpendent measurement of NO therefore permits an evaluation of the NO_3 concentration provided the system has been properly calibrated for NO_3. The latter exercise is still to be completed. Even so, we can report that measurable levels (i.e. S/N > 2/1) of NO_3 have been observed at night on four separate occasions.

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* The statement that NO_3 photofragments to form NO in excited vibrational states is based on theoretical arguments. We are just now testing this system to establish the validity of these arguments.

The PF/TP-LIF detection limit for the gases NO, NO_2, and NO_3 is a function of both integration time and the 226 nm, 1.06μ, 355 nm and 574 nm energies. Under optimum operating conditions (laser operating at max. energy) the NO detection limit is ~ 10 pptv per 5 min. integration time. More typically, however, the laser energy employed was below the maximum level and the detection limit was in the 25 to 60 pptv range. At night when NO levels were quite low, we either increased the laser energy or, alternatively, increased the integration time so as to gain further sensitivity.

For NO_2, under optimum operating conditions, the detection limit is ~ 400 pptv per 5 min. Again, with more typical energies employed it was 600 to 800 pptv per 5 min. As with NO, the above detection limit could be systematically improved by increasing the integration time. We note that although further improvements can be made in the NO_2 system at this time based on the levels of NO_2 observed at Stone Mountain it does not appear to be a high priority. For example, it was very seldom that the NO_2 levels fell below the detection limit of the existing PF/TP-LIF sensor.

The NO_3 system, as discussed earlier, has not been fully calibrated as of now and thus no definitive statement can be made about its detection limit.

2. Potential Chemical Interferences

<u>NO</u>

A very large number of trace gas species have been experimentally tested for interference in the measurement of NO by the TP-LIF method. This group includes HNO_3, CH_3ONO, CH_3NO_2, CH_3ONO_2, $C_2H_5NO_2$, NO_2, and SO_2. For atmospheric conditions, the only species which was found to potentially produce a measurable interference was NO_2. (CH_3ONO also resulted in a measurable NO signal; however, its atmospheric concentration is estimated to be too low to be of any significance.) In the case of NO_2, the interference ratio was $\leq$ 1/1000, i.e. 1000 parts of NO_2 gives an equivalent signal to 1 part NO. At night, which would represent the worst situation, 10 ppbv of NO_2 would give an NO equivalent signal of $\leq$ 10 pptv. For most studies, therefore, this would represent an insignificant correction.

If very low levels of NO needed to be measured (free of interference corrections) the 1.10μ/226 nm TP/LIF airborne NO system could be employed. Because the 226 nm energy can be greatly reduced in this system, due to the much higher cross section at 1.10μ vs. 1.06μ, the interference signal resulting from the 226 nm photolysis of NO_2 is substantially reduced, the interference signal going approximately as the square power of the 226 nm energy. In this case, for an NO_2 level of 10 ppbv, the estimated interference signal would be equivalent to ~ 2 pptv of NO.

Two molecules for which interference tests have not been carried out are HNO_2 and PAN. The HNO_2 species is clearly a source of NO due to its known photofragmentation into OH and NO radicals. In this case, the interference can be evaluated by scaling the HNO_2 molecule to NO_2 in terms of cross-sections and concentration levels. In the evaluation here we have assumed that the quantum yield for the production of NO in a pumpable quantum state is the same for HNO_2 and NO_2. With this assumption, we find that the cross-section for HNO_2 is ~ 7 times greater than that for NO_2 at 226 nm. The concentration of HNO_2 relative to NO_2 is more difficult to evaluate since the only simultaneous measurements of HNO_2 and NO_2 are those reported by Platt and Perner (JGR, 1980) and Perner and Platt (GRL, 1979). The highest ratio reported by these authors (e.g. HNO_2/NO_2) was 1/40 with more typical values being 1/500. Taking the most favorable situation (i.e. one giving the highest interference), we would adopt the ratio of 1/40. Making the assumption of a similar quantum yield for pumpable NO together with the above cross-section and concentration considerations, we estimate that the interference from HNO_2 would be ~ 6 times lower than for NO_2. If this value is scaled to an NO_2 concentration level of 10 ppbv, the estimated maximum interference is ~ 2.5 pptv equivalent NO.

In the case of PAN, we have scaled the interference from the template molecule CH_3ONO_2 for which we have experimental results. Again, using similar arguments as used above for HNO_2, we have evaluated the interference ratio for PAN to be $\geqslant$ 4000/1. That is, one would need to have $\geqslant$ 4000 PAN molecules to give an equivalent signal to one molecule of natural NO. Thus, taking the PAN concentration to be $\sim$ equal to the NO_2 level, for NO_2 levels of 10 ppbv the PAN interference is calculated to be $\leq$ 2.5 pptv equivalent NO.

Based on the above results, we believe that interference problems in detecting NO in the presence of NO_2, HNO_2, PAN, etc., should be insignificant for nearly all studies being proposed to CRC. As noted earlier, however, if a situation does arise where a reduction in interference is required, the TP-LIF airborne NO system will be available for use.

NO_2

Although far less interference testing has been completed on the PF/TP-LIF NO_2 sensor, the situation here is more favorable in that at the photolysis wavelength, 355 nm,very few atmospheric nitrogen species absorb. The principal ones are HNO_2, NO_3, and N_2O_5. Both NO_3 and N_2O_5 have vanishingly small cross-sections at 355 nm, in comparison to NO_2 , and their atmospheric concentration levels are estimated to be nearly two orders of magnitude lower than that of NO_2. The combined effect of cross-section and concentration therefore reduces the interference from these two species to that of being negligibly small.

HNO_2, on the other hand, has an absorption cross-section at 355 nm which is only two times smaller than that for NO_2. However, using the results of Perner and Platt, where the reported upper limit $[HNO_2]/[NO_2]$ value is 1/40, one would estimate that the HNO_2 interference level in the NO_2 measurement is less than 1.3%. For example, for 10 ppbv of NO_2, the interference from HNO_2 would be .13 ppbv.

NO_3

As noted previously, we know of no atmospheric nitrogen oxide species which photofragments at 574 nm other than NO_3. At this time, therefore, we do not expect the interference question will be a serious problem in the detection of NO_3. However, one can perhaps make the argument that two photon processes may come into play at some level of detection and thus tests will be carried out to test this possibility using those atmospheric species present at high concentration levels, e.g. NO_2.

(Note added in proof - Since the writing of this initial report, we have determined that at 574 as well as at longer wavelengths NO_2 undergoes a two photon absorption process that generates NO in the $V'' = 2$ and $v'' = 3$ level. All existing evidence points toward NO_3 not photofragmenting to give NO and therefore the PF-LIF approach would now appear to be unuseable for the detection of the NO_3 molecule, see Fall 1984 Quarterly Report for details).

3. Calibration

NO

Calibration of the TP-LIF NO system involves the well established method of standard addition. In this method, a standard gas mixture consisting of 1 ppm of NO in N_2 is passed through a two stage dynamic dilution system resulting in NO levels in the tens of pptv range. The NO calibration gas is injected at the inlet of the ambient NO sampling line, thus ensuring that the calibration is carried out under atmospheric conditions of pressure, temperature, and chemical composition.

Approximately once a month the secondary NO standard is calibrated against an NBS certified primary standard (44 ppmv), thus all measurements are ultimately referenced to an NBS standard gas mixture.

NO_2

Calibration of the PF/TP-LIF NO_2 system is very similar to that for NO in that the standard addition technique is employed. In the case of NO_2, the secondary standard (~ 44 ppmv) is again a pre-made bottled gas mixture of NO_2 in N_2. Unlike the NO system, however, the primary standard consists of an NO_2 permeation tube operated at constant temperature.

NO_3

The calibration of the NO_3 sensor is a far more difficult task than that for NO_2 or NO. In the former case, it is not possible to buy a standard gas mixture with a certified level of NO_3 in it. NO_3 is a moderately reactive gas and must therefore be generated in-situ for calibration purposes. Our current approach to the NO_3 calibration problem involves the thermal decomposition of N_2O_5. This system is still in the developmental stage but we expect that alterations will be needed in this scheme as further testing is completed.

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*The N_2O_5 in this system is generated via the gas phase reaction of NO_2 with O_3 and the subsequent reaction of the product NO_3 species with additional NO_2. In our procedure the above gas mixture is distilled back and forth through three traps, one of which is held at 195K to collect the N_2O_5 product. Typically, six transfers through this system are needed to get relatively pure N_2O_5 .

C. Laboratory Photofragmentation/Laser-Induced Fluorescence (PF-LIF) NO_3 and HNO_2 Systems.

In the PF-LIF technique, two laser photons are employed to achieve fluorescence. Potentially, therefore, two-level spectral discrimination is possible in all applications of this methodology. The first photon is used to photofragment the "primary" species to be detected; the second photon is used to electronically excite one of the photofragments to a bonding excited state. A critical aspect of this method involves energizing the "primary" species to an extent that when photofragmentation occurs, one of the photofragments is born with excess vibrational energy (i.e. vibrationally hot). Under these conditions, the second laser photon can have a wavelength, λ_2, such that $\lambda_2 > \lambda_3$ where λ_3 is the fluorescence wavelength. This means that quite unlike conventional single-photon laser-induced fluorescence, the fluorescence from the PF-LIF system is blue shifted. If at the same time the photolysis wavelength, λ_1, can also be selected such that $\lambda_1 > \lambda_3$, near complete discrimination can be achieved against conventional background noise sources such as Rayleigh and Raman scatter and "white" fluorescence derived from the λ_2 laser. The latter type discrimination is achieved through the use of long wavelength solution blocking filters in conjunction with solar-blind photomultiplier tubes. Taking this approach, we have been able to routinely achieve 15 or more optical density units of discrimination between the sampled λ_3 fluorescence and background signals generated by the λ_1 and λ_2 lasers. Under the above conditions, remaining noise sources consist of PMT dark count anti-Stokes Raman scatter, and higher order multi-photon events involving other atmospheric trace gas species. Extensive laboratory tests involving artificial gas mixtures, air samples from the lab, and those pulled in from outside the building all indicate that these noise sources are extremely small (e.g. 1 noise photon in ~ 36,000 laser shots). We have thus demonstrated for at least the NO_2 molecule, the PF-LIF technique is signal limited under typical sampling conditions rather than the conventional from the other.

Thus far, only the PF-LIF NO_2 system has been extensively studied in the laboratory. Based on tests now complete and the scaling of these results to the energies and rep-rates available from our new excimers, we estimate the detection limit for NO_2 will be at or below the 1 pptv level. If the primary photochemical steps are demonstrated to be efficient, similar detection limits would be expected for the NO_3 and HNO_2 systems.

As noted in earlier progress reports, a key element in the successful application of the TP-LIF detection scheme to NO_3 and HNO_2 involves these species photofragmenting to form vibrationally hot NO. In regard to HNO_2, we have just recently been encouraged by the laboratory results by Zare et al. at Stanford. In the latter study HNO_2 was photofragmented at 248 and 353 nm and the nascent quantum state distribution of the OH fragment was examined. These results showed that the OH species was formed only in the v"=0 quantum state and was born rotationally hot. This strongly suggests that the NO species is probably generated vibrationally hot.

Studies are now under way in our laboratory to demonstrate that the latter hypothesis is, in fact, correct as related to the HNO_2 molecule. With our current hardware arrangement, we should also be able to quickly test the NO_3 species to determine if hot NO molecules are produced at 589 nm. These results are expected during the fall of 1984.

signal-to-noise limited.

PF-LIF sampling schemes for the molecules NO_3, and HNO_2 are summarized below:

$$HNO_2 + h\nu_1 \xrightarrow{\lambda_1 = 353nm} NO\ (v'' = 2 \text{ or } 3)^* + OH$$

$$NO(v''=3) + h\nu_2 \xrightarrow{\lambda_2 = 259nm} NO^{\ddagger}\ (v' = 0)$$

$$NO^{\ddagger}\ (v'=0) \longrightarrow NO\ (v''=0) + h\nu_3 \text{ where } \lambda_3 = 226 \text{ nm}$$

$$NO_3 + h\nu_1 \xrightarrow{\lambda_1 = 589nm} NO\ (v''=2 \text{ or } 3)^* + O_2$$

$$NO\ (v''=3) + h\nu_2 \xrightarrow{\lambda_2 = 259nm} NO^{\ddagger}\ (v'=0)$$

$$NO^{\ddagger}\ (v' = 0) \longrightarrow NO\ (v''=0) + h\nu_3 \text{ where } \lambda_3 = 226 \text{ nm}$$

From the above schemes, it can be seen that only the λ_1 photolysis wavelength is uniquely different for each system. The λ_2 electronic pumping wavelength as well as the detected fluorescence wavelength, λ_3, can be made the same and thereby greatly simplify the laser hardware and the detection optics and PMT requirements of these two systems. The authors note that the PF-LIF NO_2 system also uses the same NO pumping wavelength (i.e. 259 nm) and thus employs the same detection optics.

Concerning interference in the above detection schemes, for the NO_3 molecule where photofragmentation occurs at 589 nm it is not energetically possible** to form NO(v"=3) from HNO_2 or NO_2. At 353 nm, on the other hand, it is not energetically possible to form NO(v"=3) from NO_2. And, since at 353 nm the HNO_2 cross section is over two orders of magnitude greater than that for NO_3,the primary quantum yield for NO production from NO_3 represents a negligible interference. From the above discussion we can conclude that the proposed schemes for detecting NO_3 and HNO_2 are uniquely tailored to the detection of each species without interference

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*Note, that other v" NO levels are formed at this wavelength; we have only shown those that are most suitable for PF-LIF detection.

**This statement is based on single photon absorption processes only. As noted earlier in the text, we will be examining the possibility that two photon absorption processes could be a potential problem.

II. FIELD MEASUREMENTS

A. Airborne NO Observations

As noted in our second year renewal proposal and follow-up year-end progress report, the airborne measurements of NO using our newly designed TP-LIF NO sensor, have provided us with an extremely useful NO data base. One of the primary objectives of our CRC program has been that of obtaining a better understanding of natural NO sources. In the latter regard, the Fall 1983 field sampling operation involving airborne measurements over the eastern and central Pacific, have given us an initial picture of the relative magnitude of several natural NO sources, in the absence of anthropogenic influences. We note again that this information was acquired at no direct expense to CRC insofar as all flight hours on the Convair 990 were covered by NASA. An overview of some of the more significant results is provided in the following text. Further details on these measurements will be given in subsequent CRC reports.

1. Average and Maximum/Minimum NO levels as a Function of Altitude, Geographical Location and Time-of-Day.

(a) Pacific Ocean (Northern Hemisphere 15 to 38°N)

(i) Day Time (typically 10:00 to 15:00 hrs.)

20,000'

Flight #7 (48 min.)

Ave. [NO]: 22 pptv
Max. [NO]: 30 pptv
Min. [NO]: 5 pptv

Flight #11 (7 min.)

Ave. [NO]: 5 pptv
Max. [NO]: 9 pptv
Min. [NO]: 4 pptv

Weighted Ave. 20 pptv

∿ 30,000'

Flight #8 (210 min.)

Ave. [NO]: 16 pptv
Max. [NO]: 75 pptv
Min. [NO]: 4 pptv

Flight # 9 (14 min.)

Ave. [NO]: 45 pptv
Max. [NO]: 58 pptv
Min. [NO]: 39 pptv

Flight #11 (110 min.)

Ave. [NO]: 70 pptv

Max. [NO]: 891 pptv

Min. [NO]: 4 pptv

Flight #11 minus electrified cloud data:

Ave. [NO]: 23 pptv

Max. [NO]: 85 pptv

Min. [NO]: 4 pptv

Flight #13 (116 min.)

Ave. [NO]: 35 pptv

Max. [NO]: 69 pptv

Min. [NO]: 11 pptv

All Data Weighted Ave. 35 pptv

[Non-Cloud Weighted Ave. 24 pptv]

1000 to 6000'

Flight # 7 (18 min.)

Ave. [NO]: 4.5 pptv

Flight #9 (8 min.)

Ave. [NO]: 3.2 pptv

(10 min.)

Ave. [NO]: 1.7 pptv

Flight #11 (14 min.)

Ave. [NO]: 5.5 pptv

Weighted Ave. 4.0 pptv

(ii) Nighttime

∿ 20,000'

Flight #5 (60 min.)

Ave. [NO]: 1.6 pptv

Flight #13 (7 min.)

Ave. [NO]: 1.2 pptv

Weighted Ave. = 1.5 pptv

∿ 32,000'

Flight #13 (11 min.)

Ave. [NO]: .8 pptv

Weighted Ave. = .8 pptv

1,000'

Flight # 5 (50 min.)

Ave. [NO]: 2.8 pptv

Weighted Ave. = 2.8 pptv

(b) Continental (Central California)

(i) Daytime (10:00 to 14:00 hrs.)

20,000' (25 min.)

Ave. [NO]: 7.5 pptv

Max. [NO]: 12 pptv

Min. [NO]: 9.3 pptv

Weighted Ave. 7.5 pptv

8,500' (28 min)

Ave. [NO]: 6.5 pptv

Max. [NO]: 11 pptv

Min. [NO]: 5.2 pptv

Weighted Ave. 6.5 pptv

4,100' (28 min.)

Ave. [NO]: 22 pptv

Max. [NO]: 101 pptv

Min. [NO]: 9.3 pptv

Weighted Ave. 22 pptv

2. Overview of Results

There are three areas of the airborne NO measurements that lend themselves to further discussion: (a) natural sources of NO over the remote Pacific; (b) average levles and variability in NO; and (c) photochemical production of O_3 over the remote Pacific.

(a) From the average NO levles given in section II A-1, a reasonably clear picture emerges concerning natural NO sources over the remote eastern and central Pacific Ocean in the northern hemisphere. This picture might be somewhat altered by seasonal trends but we believe that the semi-quantitative picture presented here will in subsequent studies be found to be basically sound.

The three most decisive pieces of NO data related to natural sources are: (1) extremely low levels of NO in the marine boundary layer (e.g. 4.0 pptv as an average); (2) observed maxima in the NO mixing ration when encountering descending air masses; and (3) observed major increases in the NO mixing ratio upon penetrating electrified clouds.

The first observation strongly suggests that the ocean surface is not itself a significant source of NO or NO_2. This is not surprising when one examines the region of the Pacific over which sampling flights were conducted. This region may be defined as being encompassed by the northern-hemispheric Pacific gyre. This region is known for its lack of upwelling water and thus nutrient levels are very low. Consequently, primary productivity is very low in these waters. Low primary productivity may be directly equated to a weak biological source strength for all reduced gas species, NO included.

The observed maximum in the NO mixing ratio at high altitudes is consistent with much other data collected over the Pacific (see, for example, Project GAMETAG) which indicates that over the eastern and central Pacific a large scale meteorological trend involving subsidence is fairly common. In these regions, air is transported down from the upper free-troposphere which in many cases has mixed with the lower stratosphere. Since the lower stratosphere is rich in both O_3 and NO_x/NO_y species, one expects to see positive correlations between O_3 and NO and negative correlations between these two variable and H_2O levels. Both correlations have, in fact, been observed. One would conclude, therefore, that the mixing of air parcels between the stratosphere and troposphere probably define one of the significant sources of NO for remote regions of the Pacific Ocean.

In still other Flights (e.g. Flight #11), we see evidence supporting our contention that another significant source of NO in remote Pacific areas is that defined by lightning. In the case of flight #11, the penetration of the anvils of two independent cumulonimbus clouds resulted in very abrupt increases in the mixing ratio of NO. In both cases, the increase in NO was positively correlated with H_2O and there was no correlation with O_3.

Nevertheless, based on the limited data available, it is still quite difficult to quantify the relative magnitudes of the descending air versus electrified cloud NO sources. Our current belief, however, is that lightning (electrified clouds) is probably the more important source but this is likely to be highly dependent on latitude. Presently we are working on modelling the NO data collected during the penetration of the electrified clouds.

In concluding this overview on NO natural sources, we note that both stratospheric intrusion and lightning are far more prevalent over continental areas than over oceans. This is particularly true at mid-latitudes and sub-tropical latitudes. Thus, a major question that may be raised is what is the influence of natural NO sources over continental areas such as the USA? Certainly, in the case of lightning, current models have sufficiently large uncertainties in them as to not exclude this source as being significant in rural areas.

(b) Average Levels and Variability in NO

As presented in section IIA-1, there are clearly major differences in the average levels of NO in the marine boundary layer vs. that at high altitude. Taking 20,000' as our free-tropospheric altitude, the comparison with the boundary layer is 4 pptv vs. 20 pptv, respectively. At 30,000', the comparison is 4 pptv vs. 24 pptv (excluding the electrified cloud data) or 4 pptv vs. 35 pptv if one includes the block of data taken in the electrified cumulonimbus clouds. If electrified clouds release NO to the atmosphere more efficiently near the cloud top, then it may be that over the long term one would expect to find higher levels of NO at 30,000' than 20,000'. Higher levels of NO at higher altitudes is consistent with the idea that descending air masses from the upper troposphere/lower stratosphere are also a significant tropospheric NO source.

The observation of an increasing NO mixing ratio with altitude is contrary to earlier theoretical predictions on the tropospheric distribution of NO. It is however, in agreement with a limited number of balloon borne NO observations. In the latter case, though, the measurements have all been over continental areas and have involved sampling only in the middle and upper free-troposphere.

The current airborne measurements over the remote Pacific suggest that surface sources are very weak or non-existent and that the photochemical conversion of NO_x to HNO_3 or heterogeneous conversions of NO_x to HNO_3, followed by washout/-rainout, result in persistently low levels of NO in the remote Pacific marine-boundary layer. The much higher levels of NO observed in the middle and upper free troposphere are consistent with a picture involving both lightning and stratospheric injection as significant sources of NO over remote regions of the Pacific and of less efficient removal processes for nitrogen oxide species at these high altitudes.

The variability in NO levels in the troposphere, is clearly seen to be as much as a factor of 500 over short sampling distances. The latter gradient is reflected in the levels observed in the tropical-marine boundary layer versus that observed in or near electrified clouds. Thus, considering the fact that the marine surface is a very weak (and perhaps non-existent) source, and that lightning and stratospheric intrusions represent highly localized strong sources of NO, one might conclude that the daytime variability of NO in a given region probably exceeds a factor of 500 on many occasions.

As a final comment on average NO levels and its variability, the data collected over central California seems noteworthy. From the data summary given earlier, it can be seen that at 20,000' and 8,500' the average levels of NO do not deviate significantly, e.g. ∿ 7 pptv. Although from such a small data set one cannot draw any final conclusions, it is interesting that in spite of there being major surface sources of NO in the area, the efficiency with which this NO reached higher altitudes was quite low.

(c) Photochemical O_3 Production over the Remote Pacific

The photochemical generation of O_3 is dependent on the following key reactions:

(i) $HO_2 + NO \rightarrow NO_2 + OH$

(ii) $RO_2 + NO \rightarrow NO_2 + RO$

(iii) $NO_2 + h\nu \rightarrow NO + O$

(iv) $O + O_2 \overset{M}{\rightarrow} O_3$

That is, only when NO_2 is generated via rxs. (i) and (ii) can there be a net production of O_3. Whether or not the rates of rxs. (i) and (ii) are sufficiently fast to yield significant NO_2 (and hence O_3) depends on the rates of competing reactions. The competing rxs. are of the type:

(v) $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

(vi) $RO_2 + RO_2 \rightarrow$ products

(vii) $RO_2 + HO_2 \rightarrow RO_2H + O_2$

Thus, for low levels of NO, rxs. (i) and (ii) are typically not competitive with (v), (vi) and (vii), and very little photochemically generated O_3 occurs. We note also that for very low levels of hydrocarbons, the levels of RO_2 species are very low and therefore even if the dominant reaction is (ii) vs. (vi) or (vii), the total rate of production of NO_2 is likely to be small from mechanism (i) → (iv).

At this time, we have not yet been provided with all supporting data from the NASA Fall flights and therefore detailed modelling studies have not been possible. However, based on previous marine atmospheric modelling efforts by our group, several general comments seem to be appropriate.

(1) The systematically low levels of NO found in the pacific marine boundary layer suggest that it is highly unlikely that significant photochemical generation of O_3 occurs. The low levels of ambient O_3 observed are quite consistent with this conclusion.

(2) On the average, the higher levels of NO observed in the free-troposphere are probably still too low to cause the major photochemical production of O_3. Nevertheless, this photochemical source in many cases could become comparable to the photochemical destruction of O_3.

(3) The most likely scenario leading to the net photochemical production of O_3 over the Pacific may involve localized hot spot production. Thus, in regions where excessive levels of NO may be present, e.g. due to lightning or stratospheric intrusions, the short term photochemical production of O_3 could be quite significant.

B. Stone Mountain Field Measurements

1. Atmospheric Parameters Measured Over the Time Period 6/12 → 8/01 (1984)

Shown in Table I is a summary of the variables measured at our Stone Mountain field station* over the time period 6/12/84 to 8/01/84. Note that the symbols used to indicate the number of hours a specific variable was measured do not typically reflect continuous monitoring. Due to most instruments at the field station not being interfaced with our microcomputer at that time, most measurements were recorded by hand in a data log book. This somewhat tedious task resulted in a moderate amount of dead time in the recording of some variables. This was particularly true of the reported "condensation nuclei" measurements and to a somewhat lesser degree the wind direction, wind speed, dew point, and temperature.

Concerning measurements of NO and NO_2, there were periods of time when the PF/TP-LIF system was undergoing calibration and/or was down because of laser problems. Thus, some interruptions in these measurements also will be seen.

Recognizing the limitations of this mode of operating, a major effort is under way to interface our Stone Mountain instrument array with a data logging computer system. The latter system will be designed to have a data link with one of several computers on the Tech campus for purposes of further analysis and final storage.

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* The Georgia Tech Atmospheric Field-Sampling Station at Stone Mountain is located ~18 miles ENE of the city of Atlanta, near the town of Stone Mountain. The station itself is located in an abandoned forestry observation tower on top of Stone Mountain and is 870 feet above the surrounding terrain. The lab area is 20' x 20' in size.

TABLE I. SUMMARY OF VARIABLES MEASURED AT STONE MOUNTAIN OVER THE TIME PERIOD OF 7/12 TO 8/01 (1984)

	JUNE																			JULY															
	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
O_3	* *	* *	O	O	+	—	O	+	*	*	*	O	+	+	*	* *	* *	O	*	O	—	O	—	O	O	*	—	—	—	—	—	* *	* *	—	* *
WS	* *	* *	—	—	+	—	O	+	*	+	*	O	+	+	*	* *	* *	O	*	O	—	O	—	O	O	*	—	—	—	—	—	* *	* *	—	* *
WD	* *	* *	—	O	+	—	O	+	*	+	*	O	+	+	*	* *	* *	O	*	O	—	O	—	O	O	*	—	—	—	—	—	* *	* *	—	* *
RH	* *	* *	—	O	—	—	O	+	*	+	*	O	+	+	*	* *	* *	O	*	O	—	O	—	O	O	*	—	—	—	—	—	* *	* *	—	* *
T	* *	* *	—	O	—	—	O	+	*	+	*	O	+	+	*	* *	* *	O	*	O	—	O	—	O	O	*	—	—	—	—	—	* *	* *	—	* *
NO	* *	* *	—	O	+	—	O	+	*	+	*	O	+	+	*	* *	* *	O	*	O	—	O	—	O	—	*	—	—	—	—	—	* *	* *	—	* *
NO_2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	+	* *	* *	O	*	O	—	O	—	—	O	*	—	—	—	—	—	* *	* *	O	* *
uV	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	*	*	O	* *
HNO_3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	O	* *	* *	—	* *
Rain	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	R S T	R S T	—	—	—	—	—	R S T	—	—	R S T
CN	* *	* *	—	—	—	—	—	—	*	+	*	O	+	+	*	* *	* *	—	—	—	—	—	—	O	O	*	—	—	—	—	—	* *	—	—	* *

	JULY															AUGUST
	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	1
O_3	* *	+	—	O	—	—	—	—	—	—	O	—	—	O	O	O
WS	* *	+	—	O	—	—	—	—	—	O	O	—	—	O	O	O
WD	* *	+	—	O	—	—	—	—	—	—	O	—	—	O	O	O
RH	* *	+	—	O	—	—	—	—	—	—	O	—	—	O	O	O
T	* *	+	—	O	—	—	—	—	—	—	O	—	—	O	O	O
NO	* *	+	—	—	—	—	—	—	—	—	O	—	—	O	O	O
NO_2	* *	+	—	—	—	—	—	—	—	—	O	—	—	O		O
uV	* *	+	—	O	—	—	—	—	—	—	O	—	—	O	O	O
HNO_3	* *	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Rain	—	R S T	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CN	* *	—	—	O	—	—	—	—	—	—	O	—	—	O	O	O

KEY ≥ 20hrs = *
* ≥10hrs = * <10hrs = + <5hrs = O — = no measurement R S T = Rain Sample Taken

2. High Resolution Diurnal Plots for Selected Days

Figures A - H, show representative Stone Mountain field data recorded on 8 different sampling days, some of which were $\sim$ 24 hours in duration.* Figure A, for example, shows a 26 hr sampling period in which only one significant interruption occurred in the data taking, e.g. 21:00 to 00:00 hrs. The NO data plotted in Figure A are typical of those collected throughout the dry period in June (6/12-6/28). Of particular interest here is the early morning peaking in the level of NO (1.6 ppbv) and the low levels of NO that are then observed during the remainder of the afternoon, in this case averaging $\sim$ 180 pptv. O_3 levels are moderate ($\sim$65 ppbv) and are seen to increase slightly during the day and then to decrease during night hours.

Figure B presents data from June 29 which represents the beginning of the summer wet period. Between the hours of 10:00 and 10:45, a thunderstorm occurred in the Stone Mountain area which produced a very modest increase in the NO level and a rather substantial increase in NO_2. In this case, NO_2 levels of 25 ppbv were reached. During this same time period we see that the O_3 level fluctuated between 60 and 30 ppbv. A final interesting feature in the June 29 data is the major peak in NO occurring at $\sim$ 11:45. (NO_2 data were not being recorded at that time.) Levels of NO, in this instance, reached $\sim$ 4 ppbv. These levels were observed while sampling in low lying status clouds, formed from the local heavy precipitation.

July 3rd, shown in Fig. C, represents another data run in which a thunderstorm occurred in the Stone Mountain area. In this case there was no

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* (The entire data base for the time period 6/12 → 8/01 is available to the interested reader as a separate supplement to this report from the main office of CRC.)

FIG. A: JUNE 12,1984

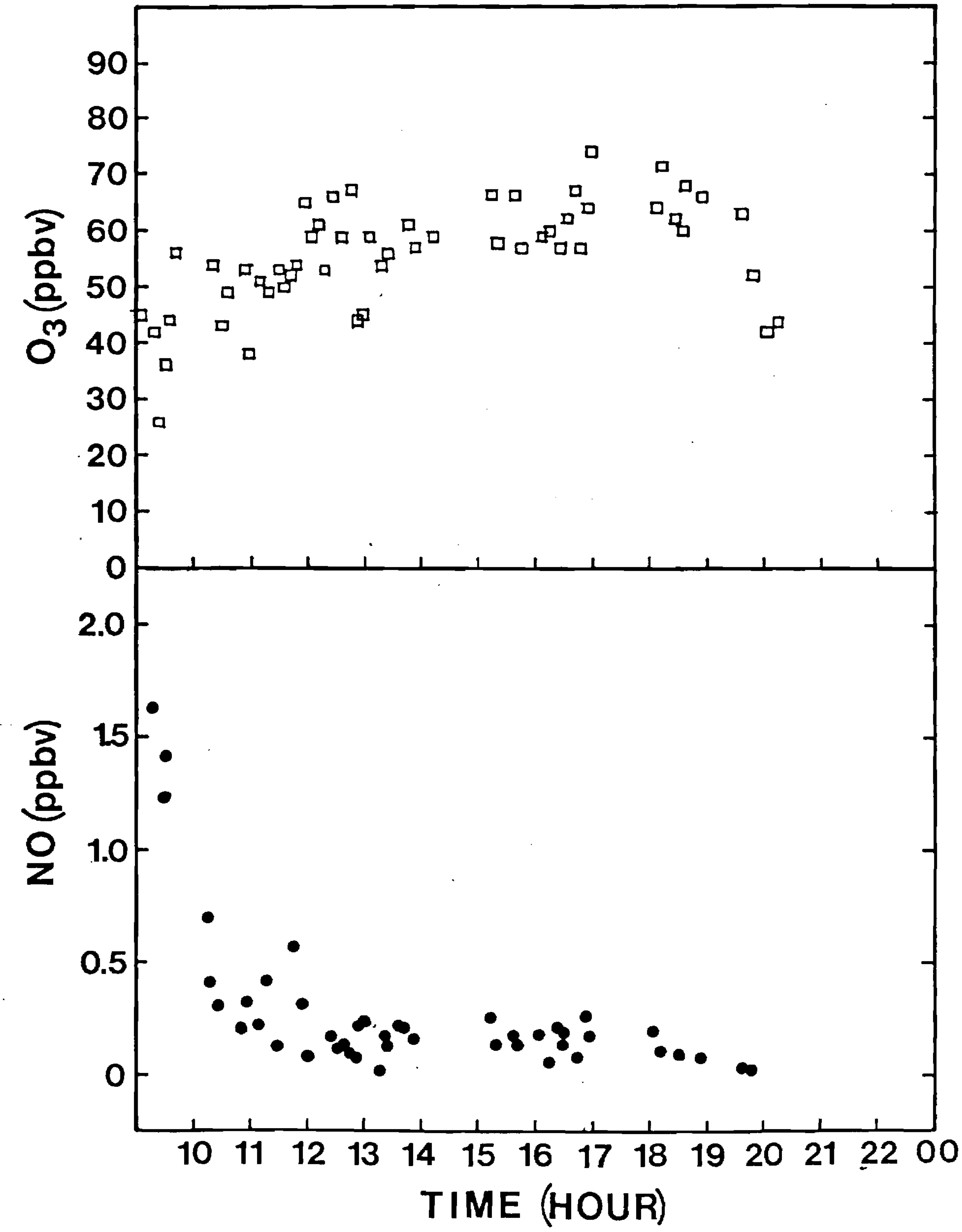
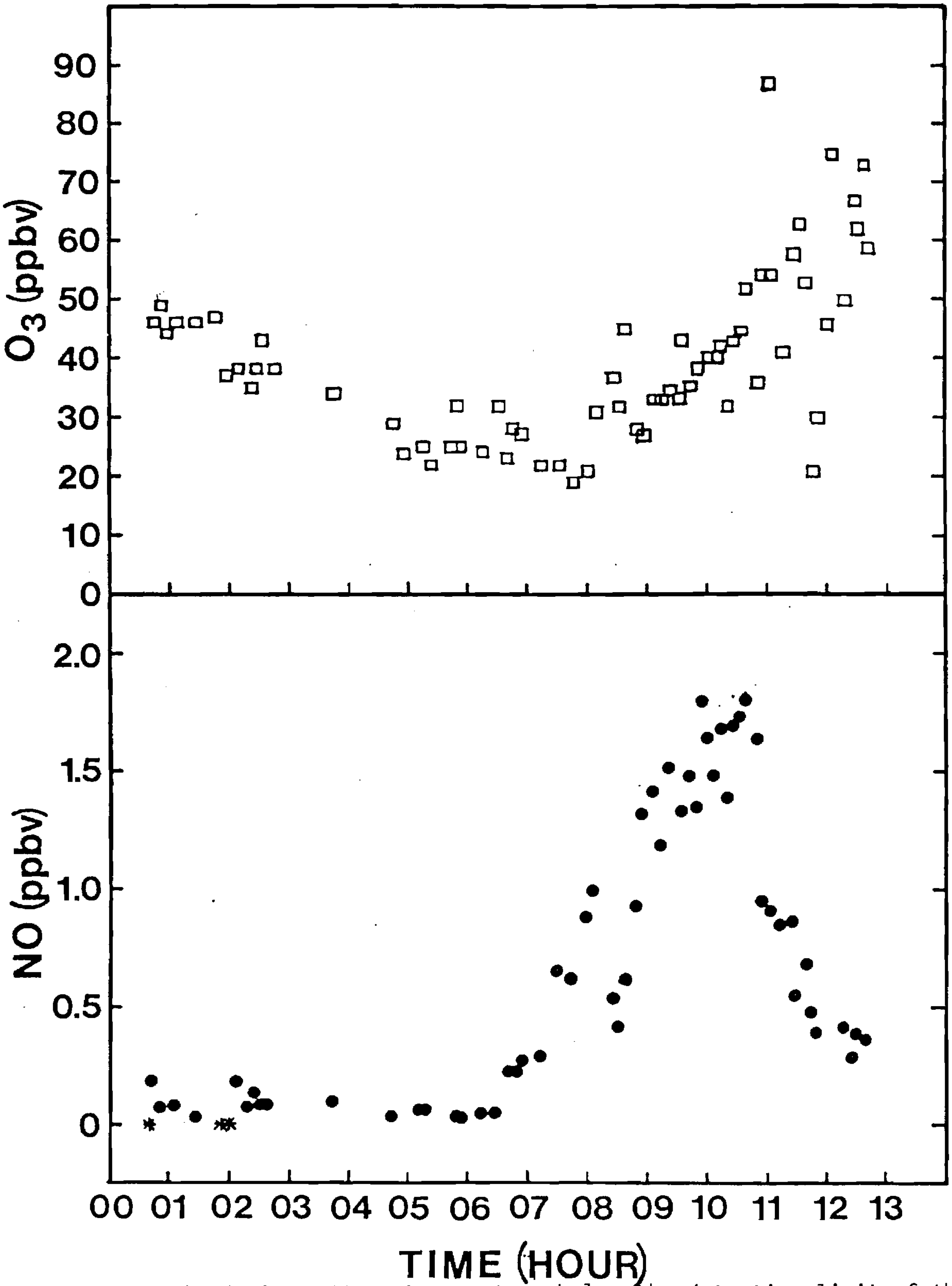


FIG. A: JUNE 13, 1984



* Level of NO_2 and/or NO was at or below the detection limit of the instrument during this run.

FIG. B: JUNE 29,1984

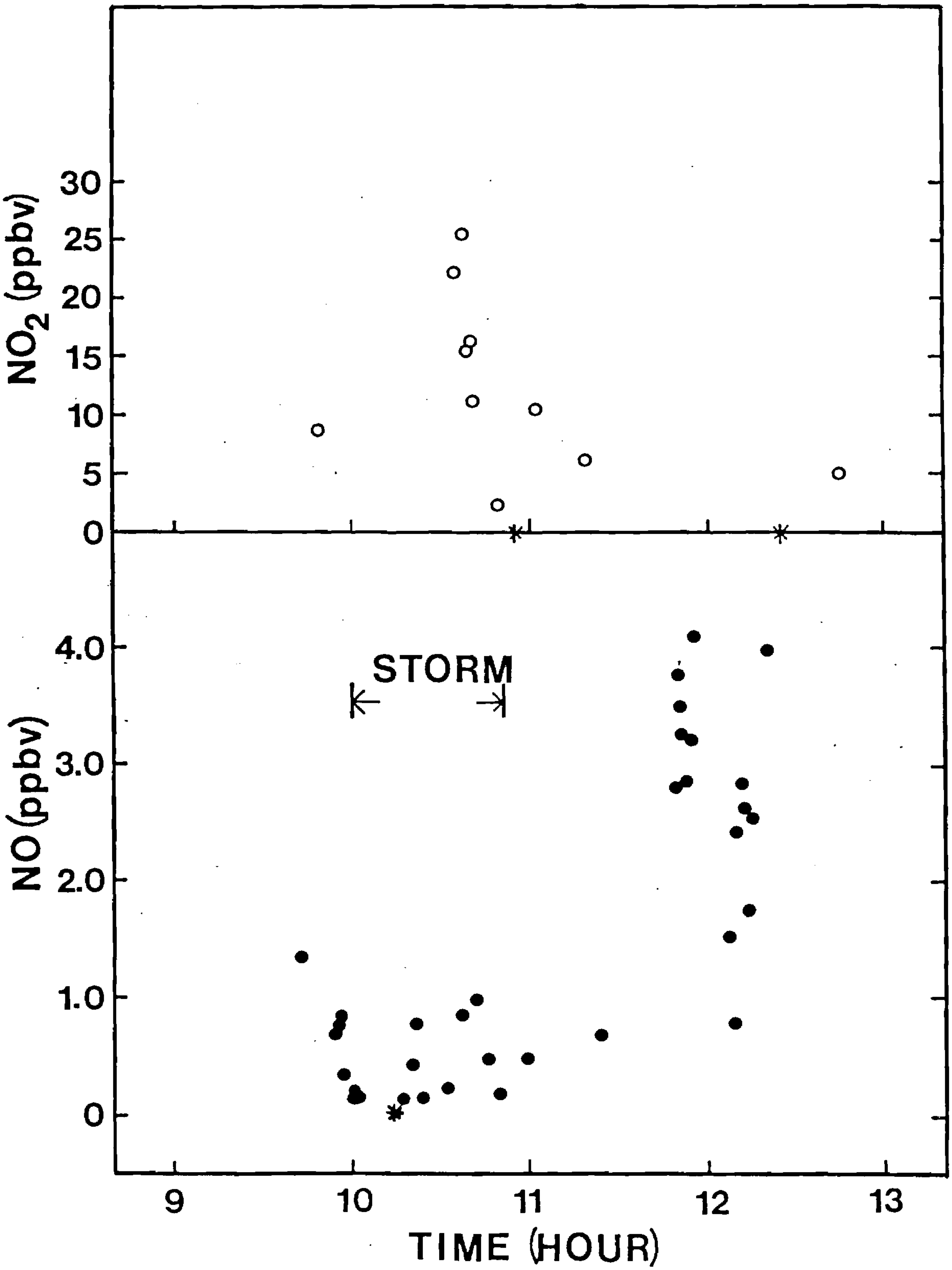


FIG. B: JUNE 29,1984

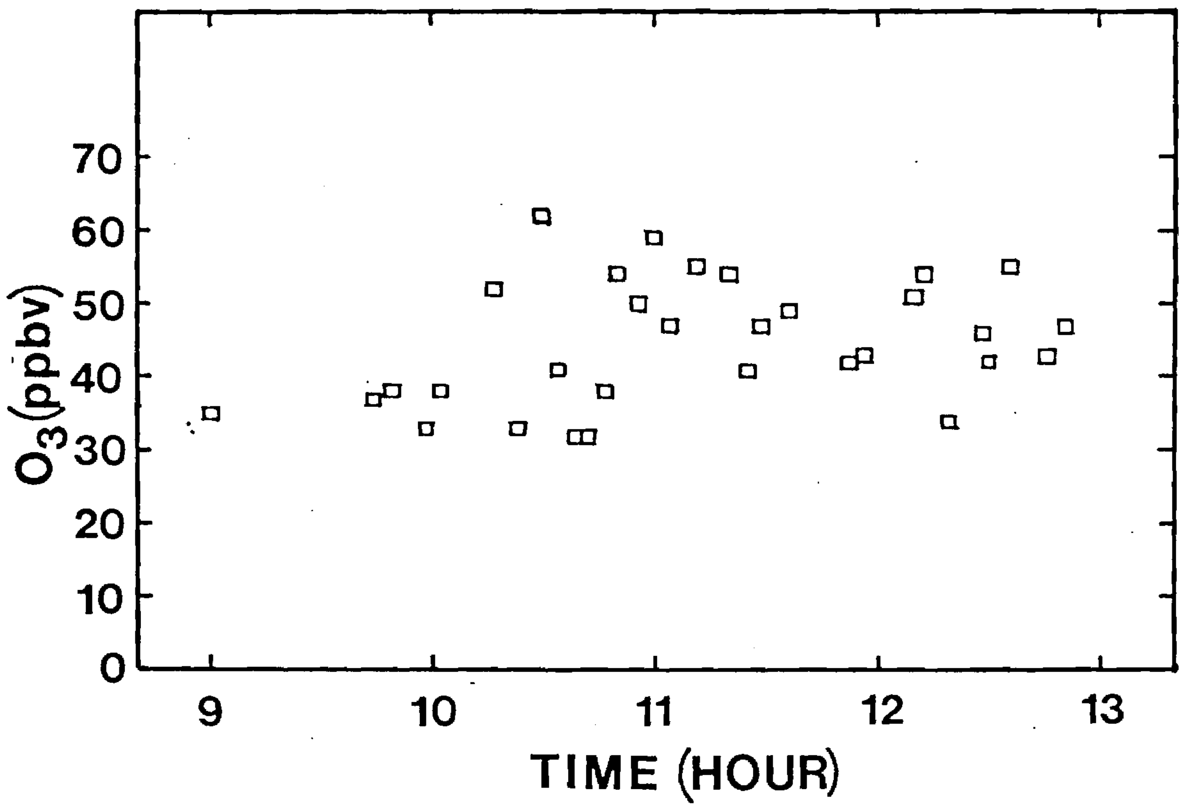


FIG. C: JULY 3, 1984

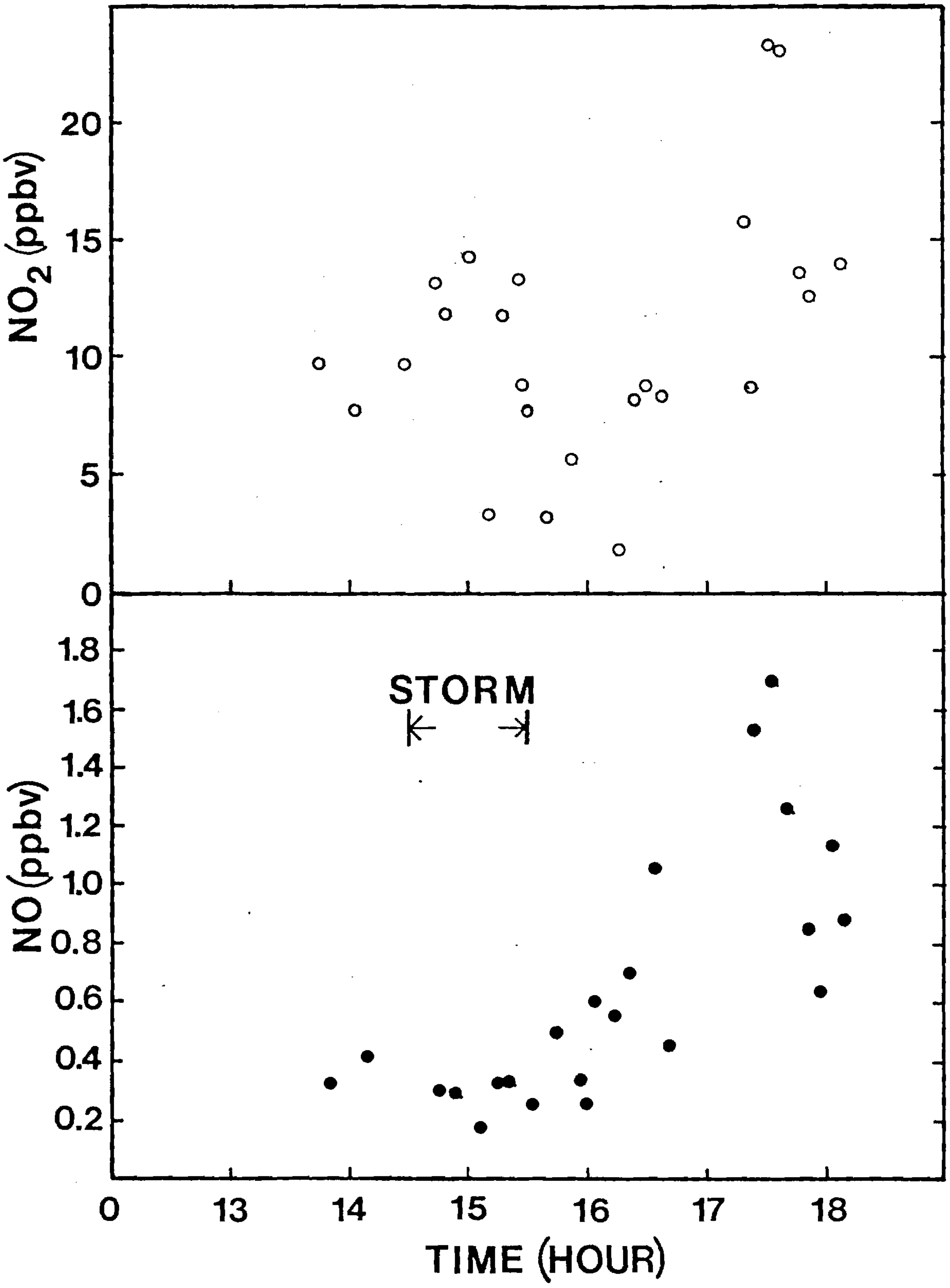


FIG. C: JULY 3, 1984

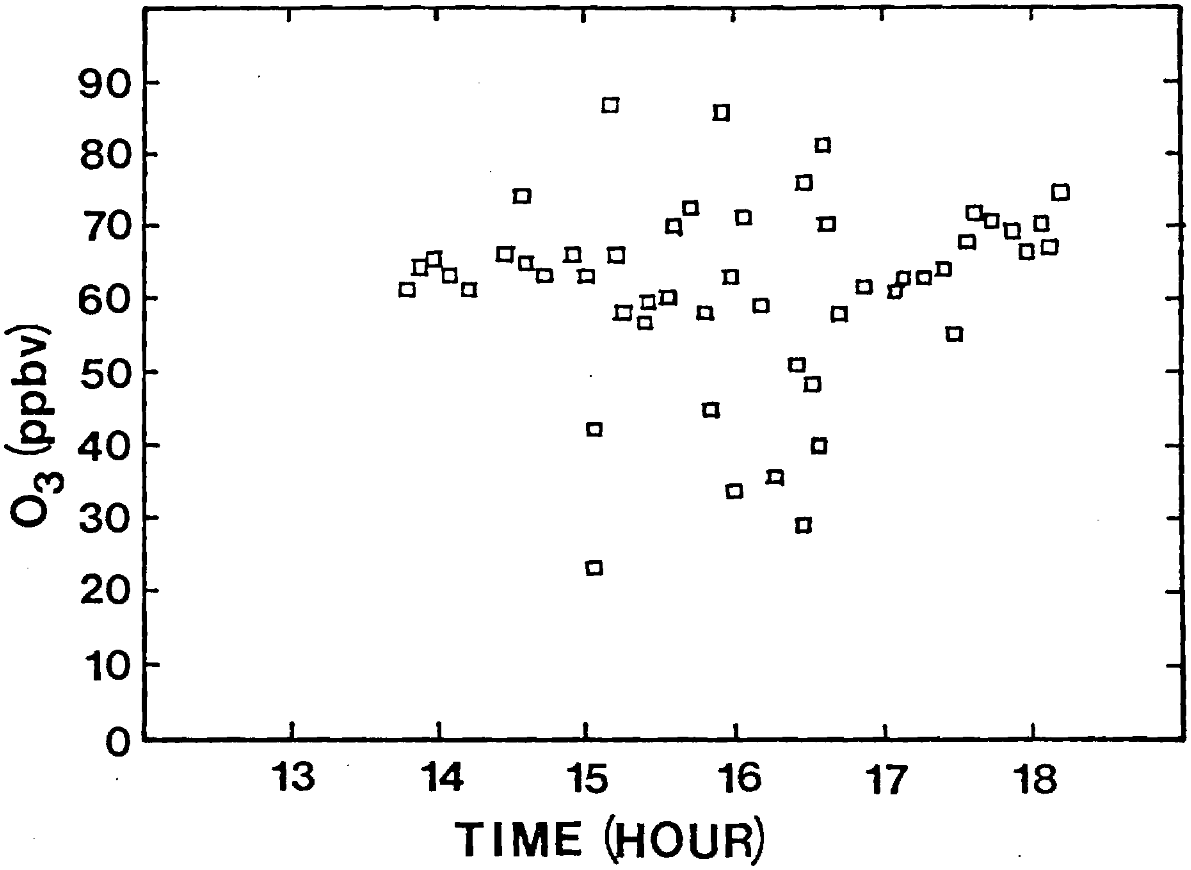


FIG. D: JULY 7, 1984

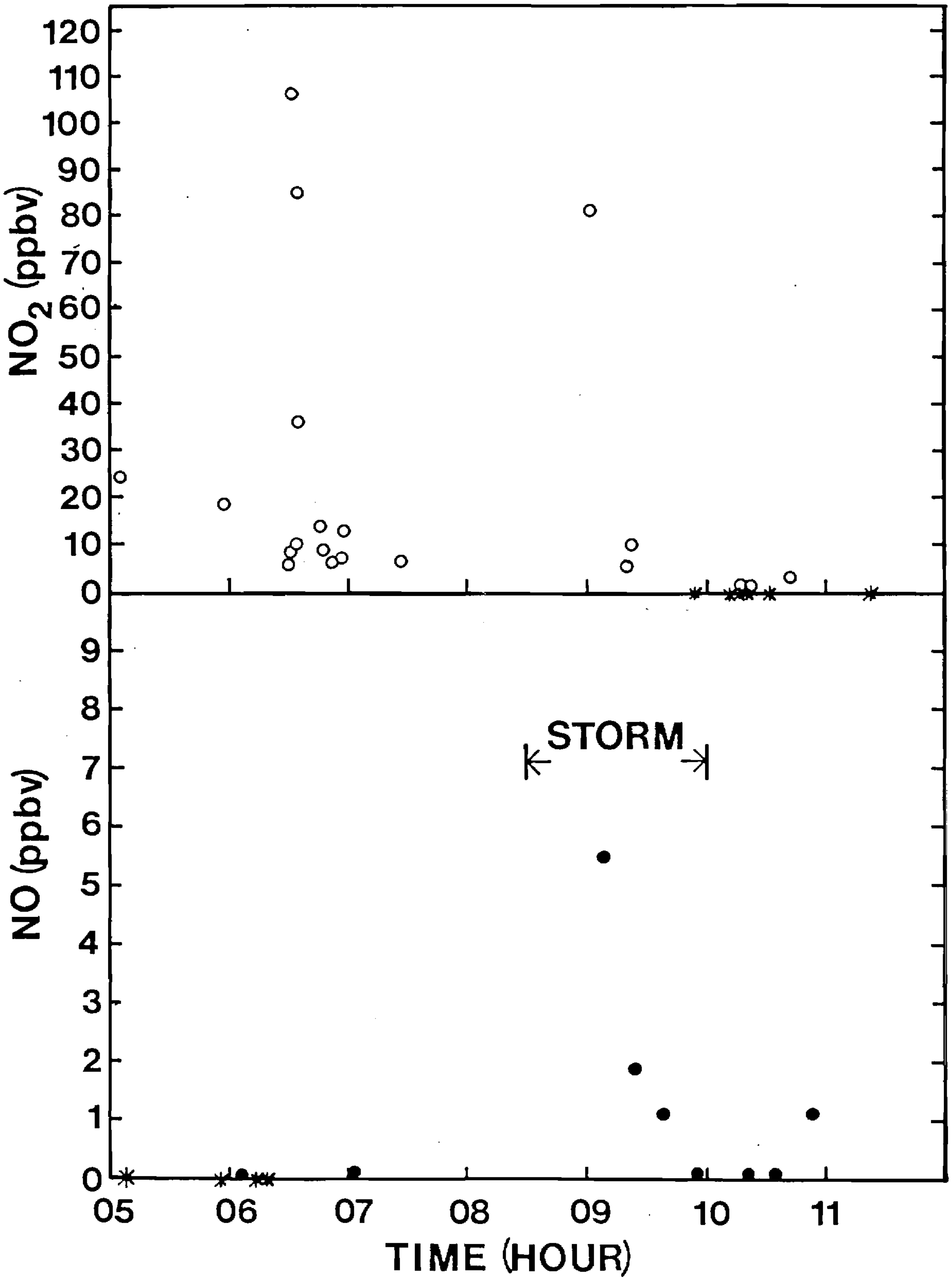


FIG. D: JULY 7, 1984

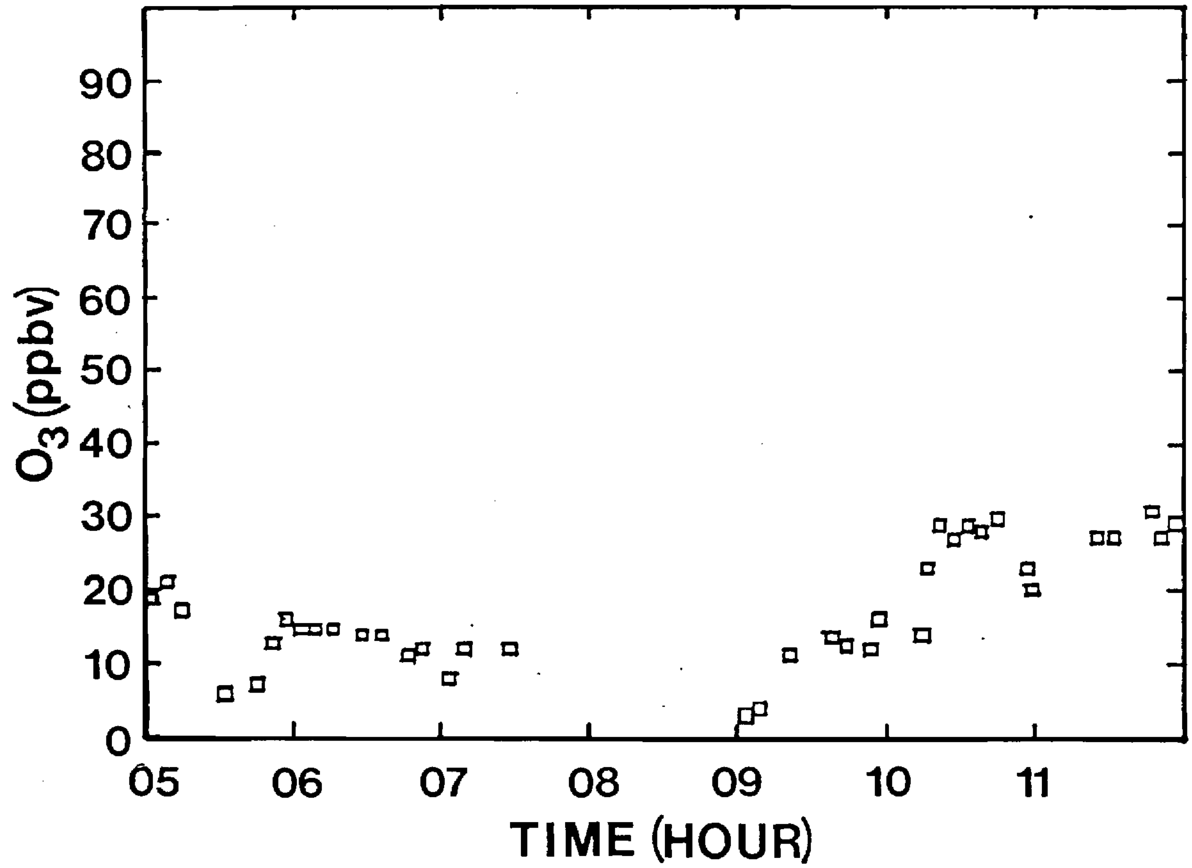


FIG. D: JULY 7, 1984

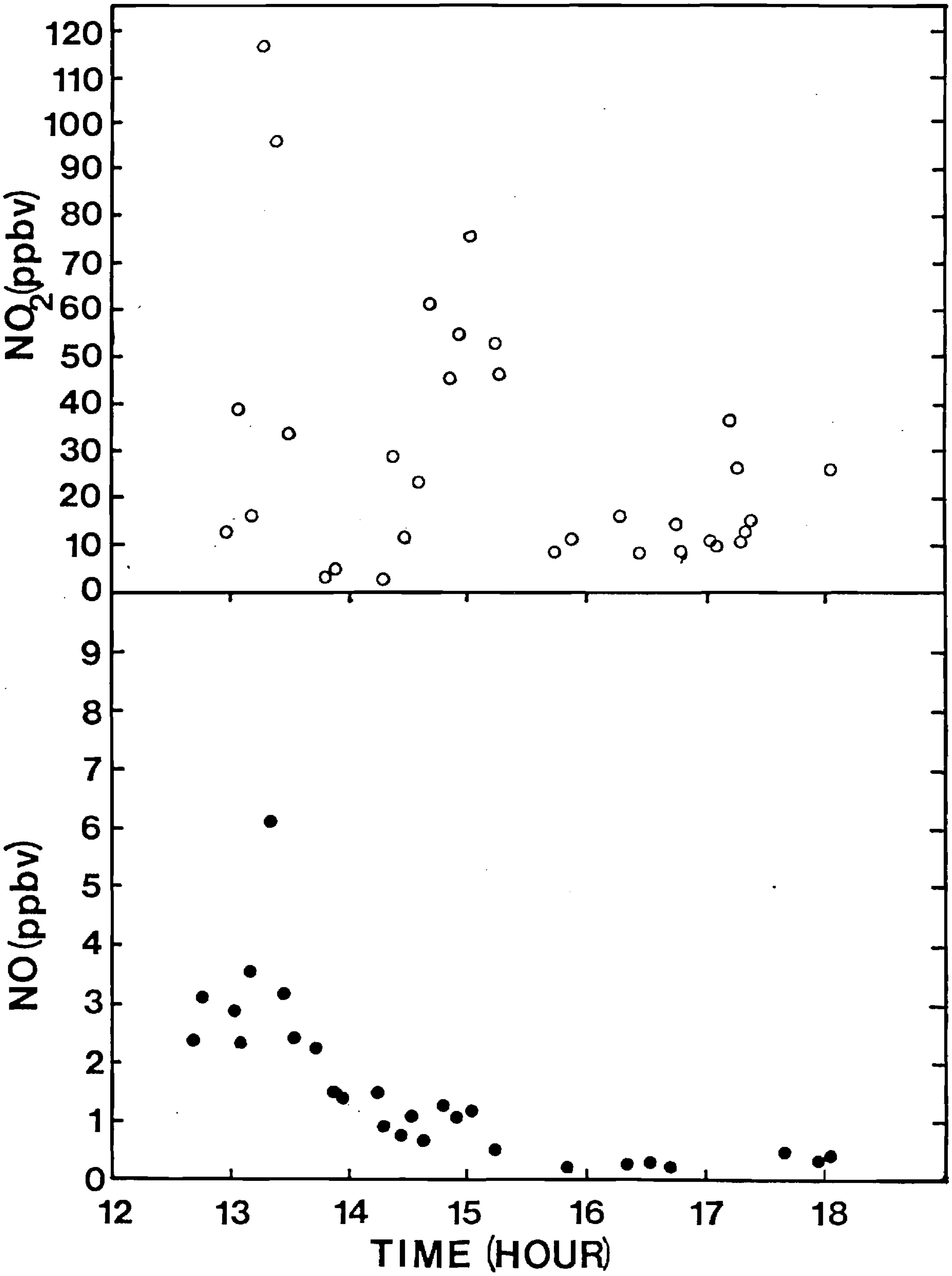


FIG D: JULY 7, 1984

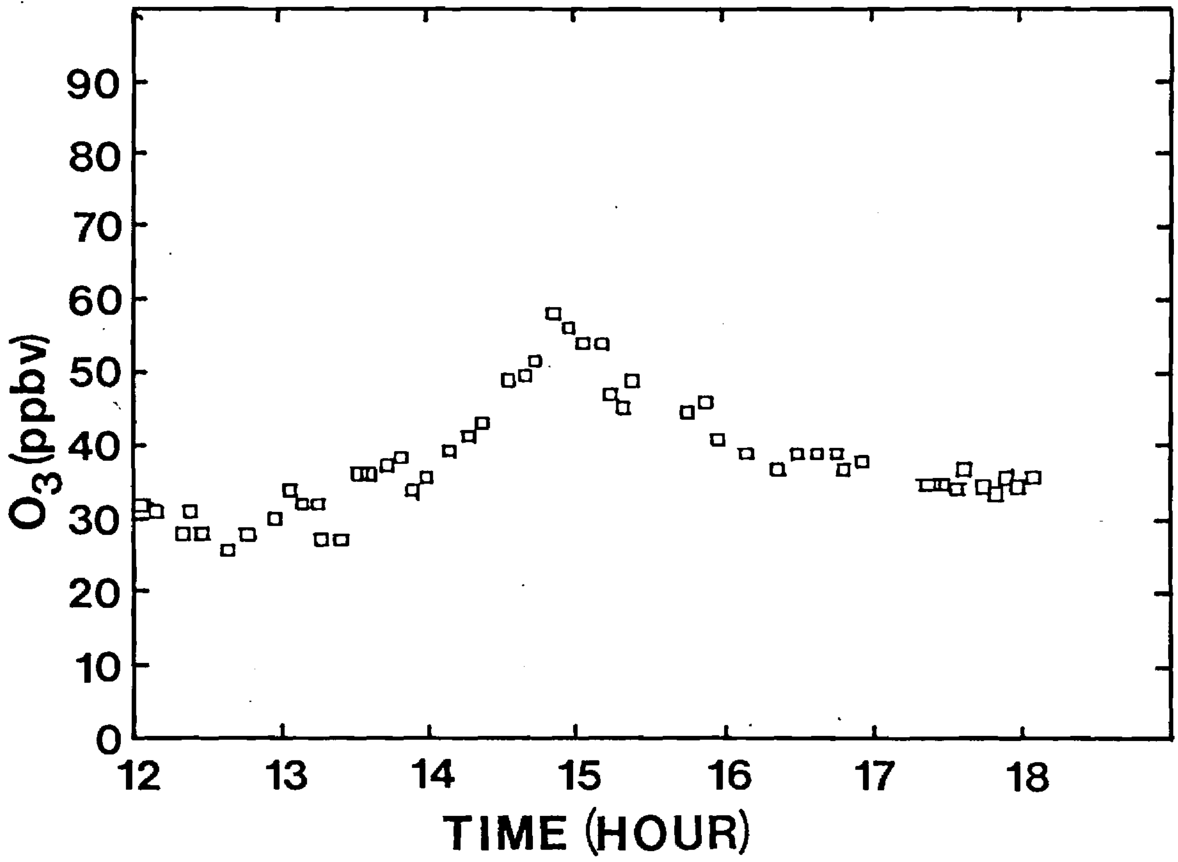


FIG. E: JULY 13, 1984

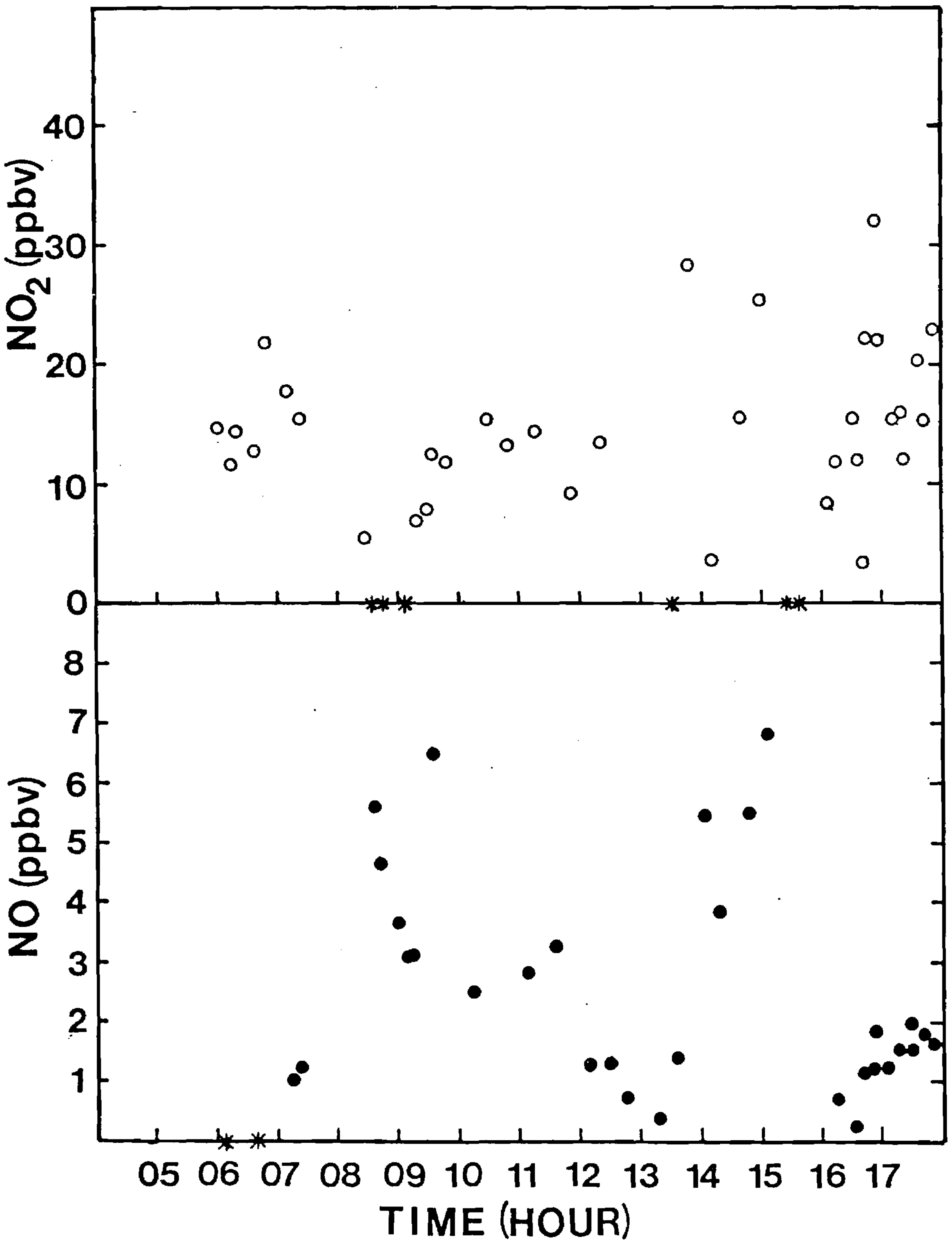


FIG. E: JULY 13, 1984

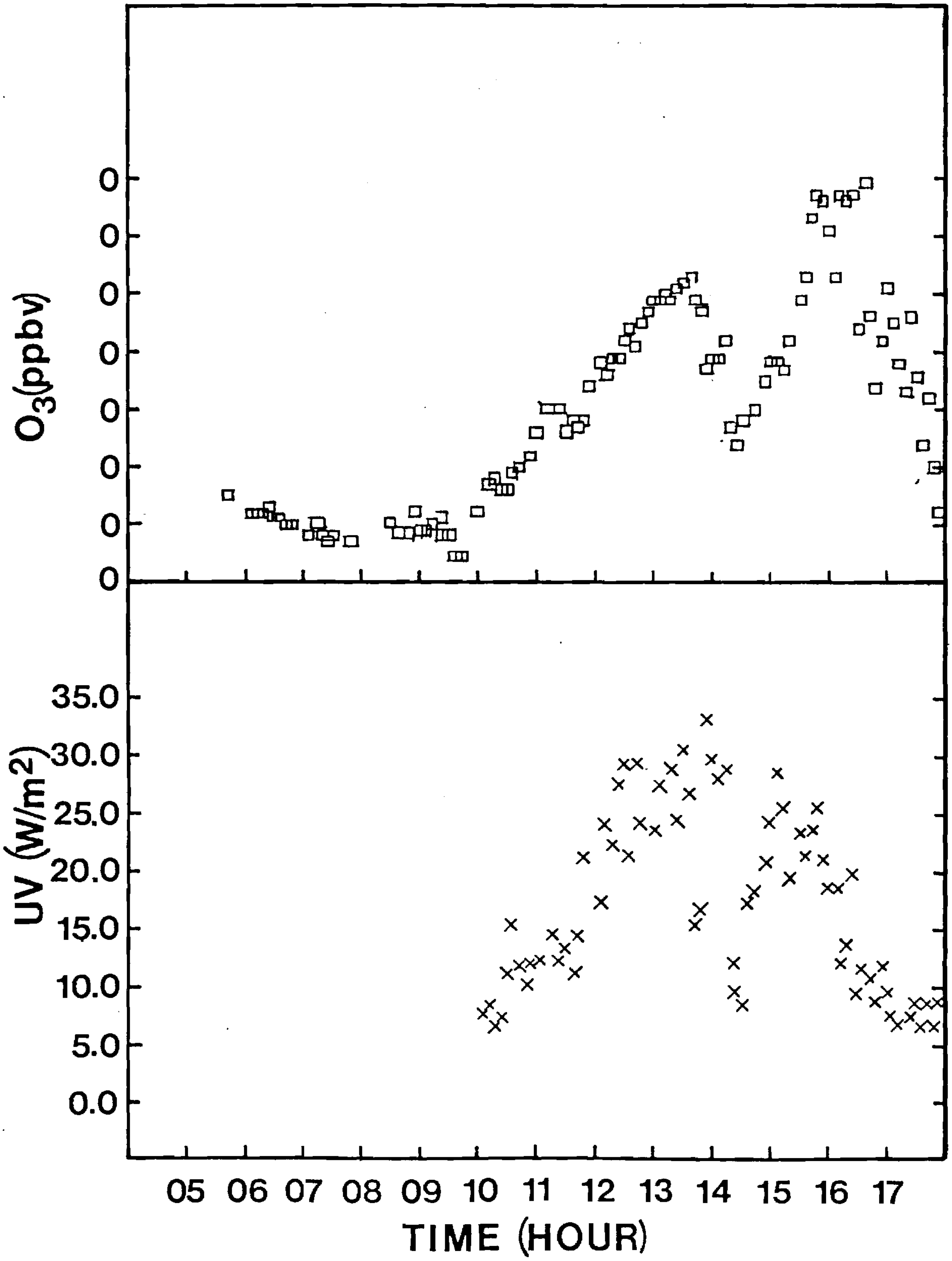


FIG. E: JULY 13, 1984

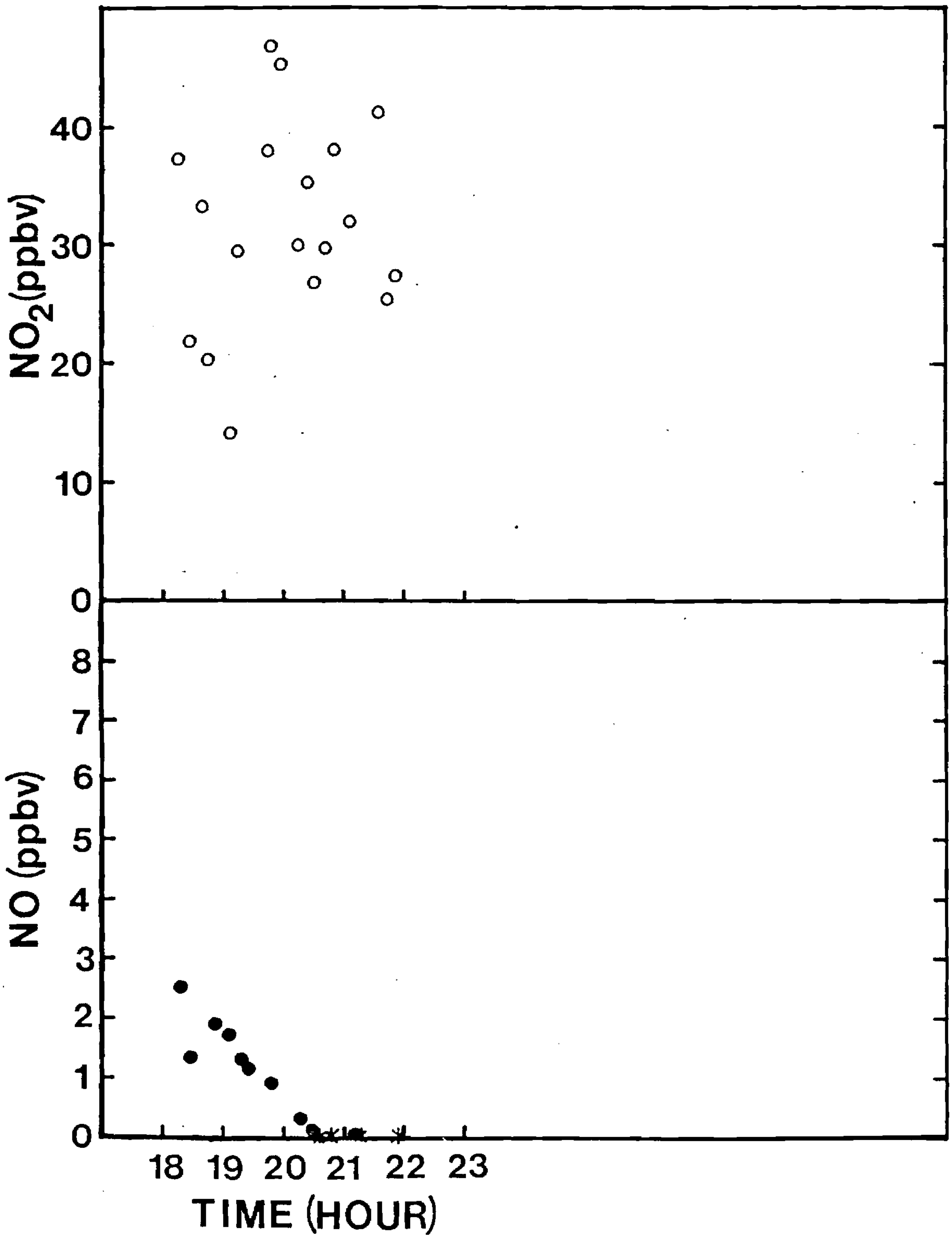


FIG. E: JULY 13, 1984

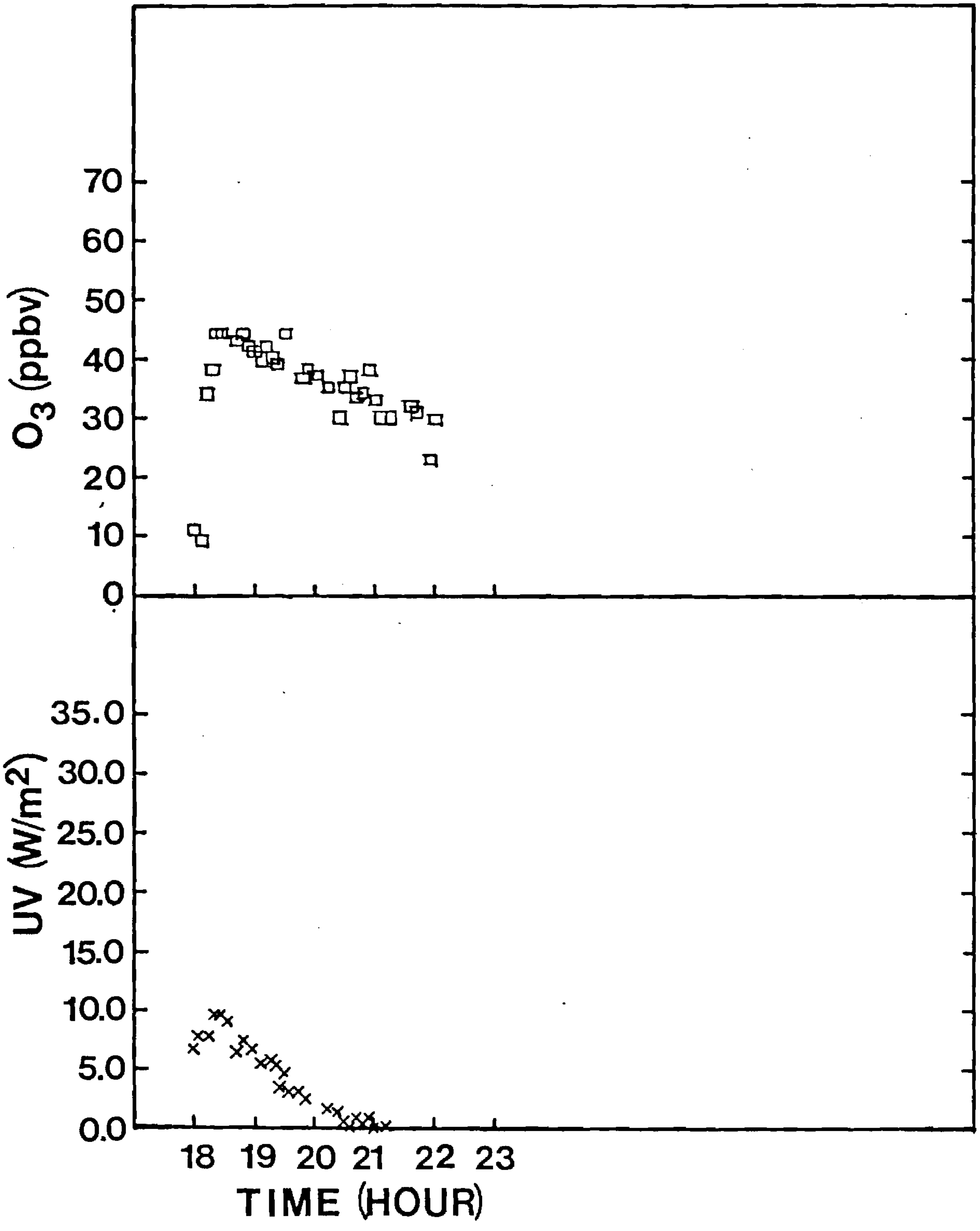


FIG. F: JULY 14, 1984

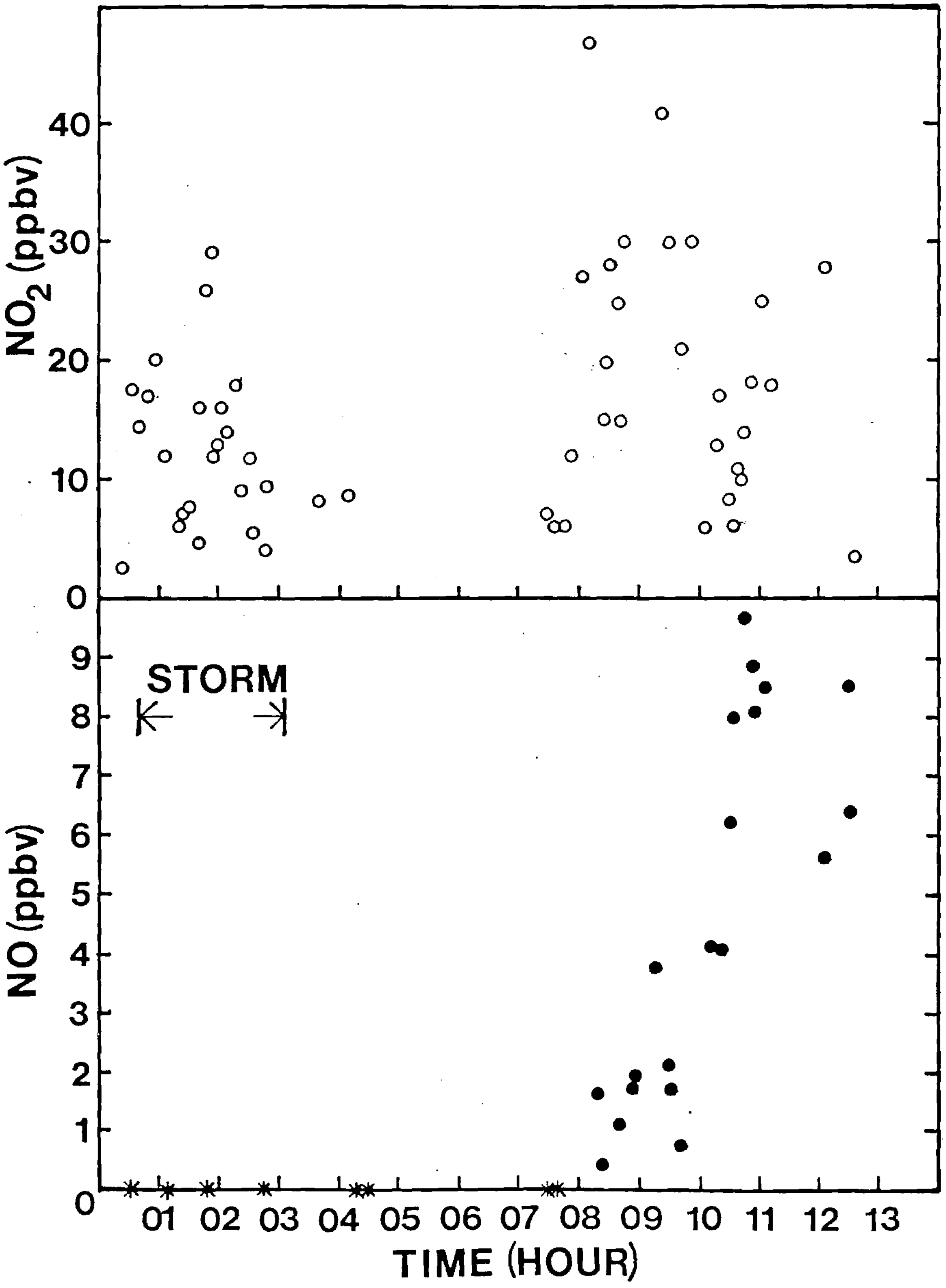


FIG. F: JULY 14, 1984

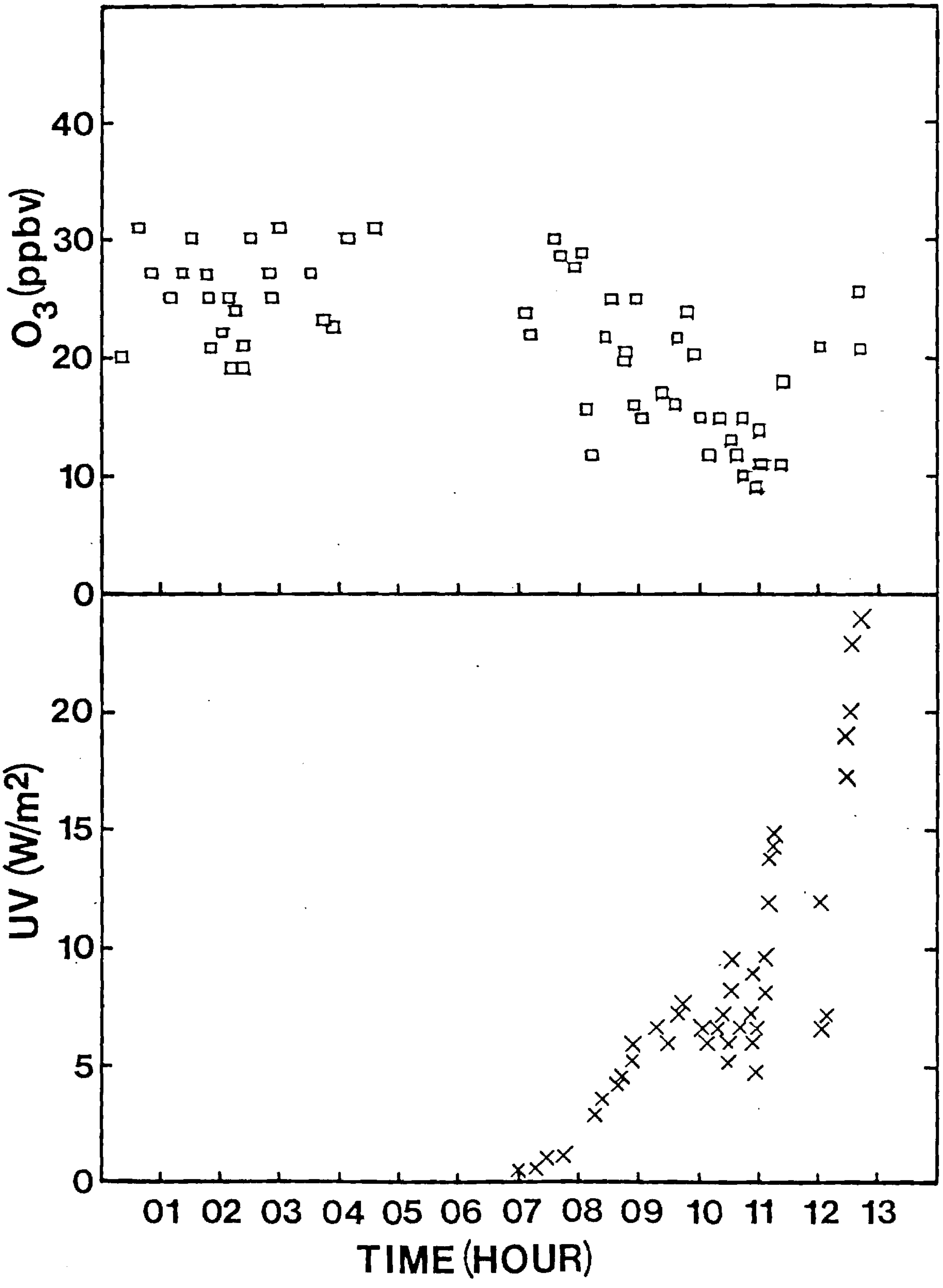


FIG. G: JULY 17, 1984

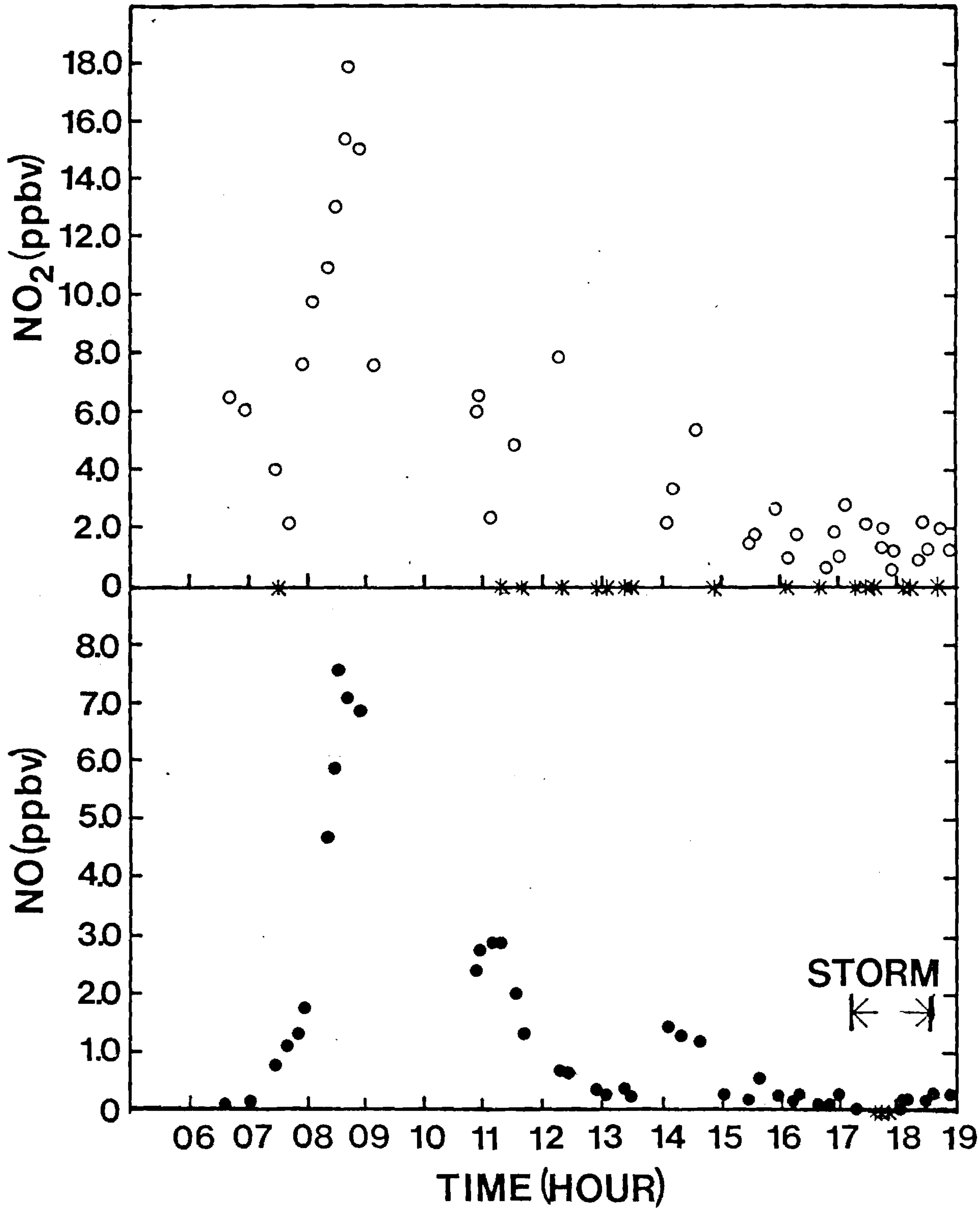


FIG. G: JULY 17, 1984

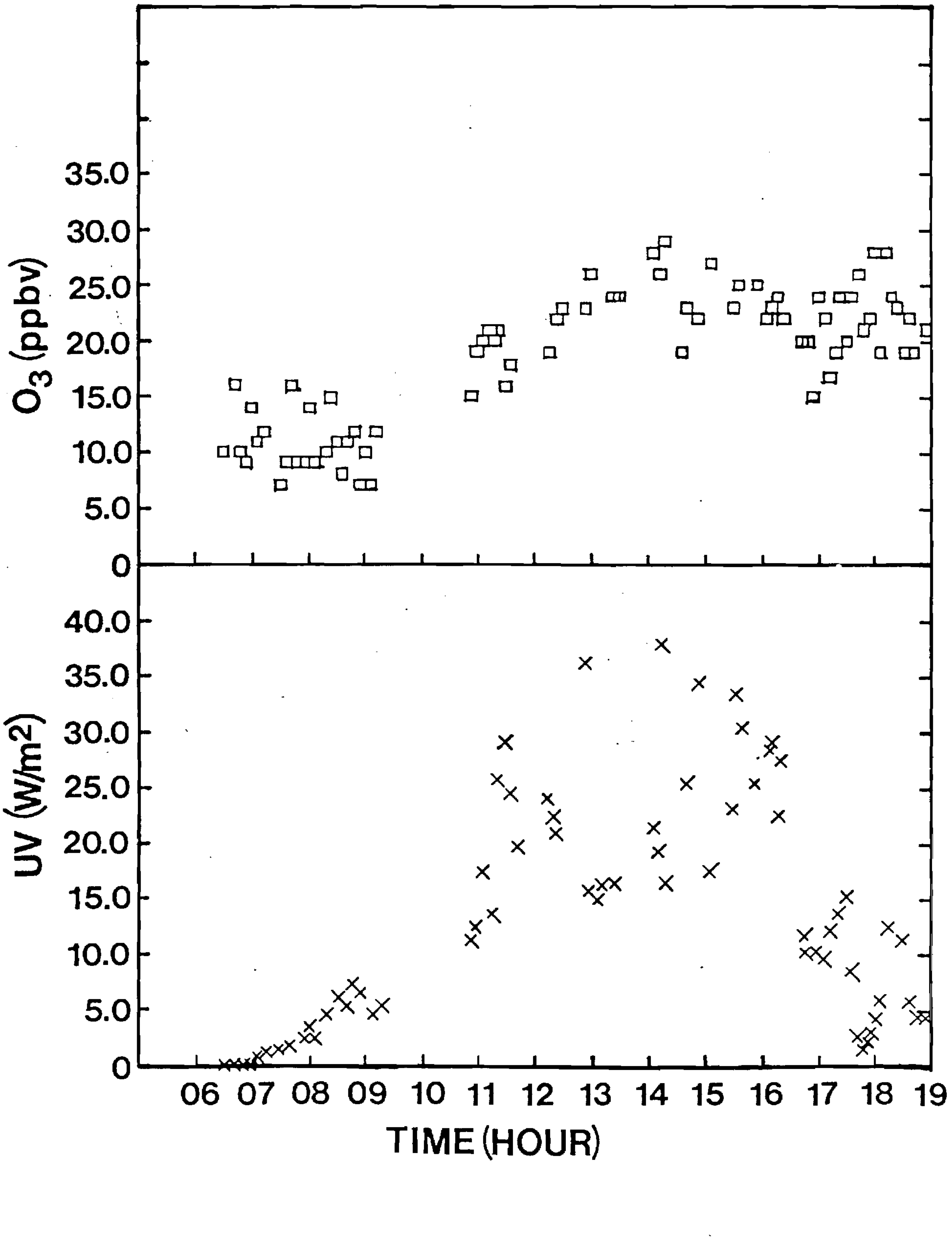


FIG. H: JULY 27, 1984

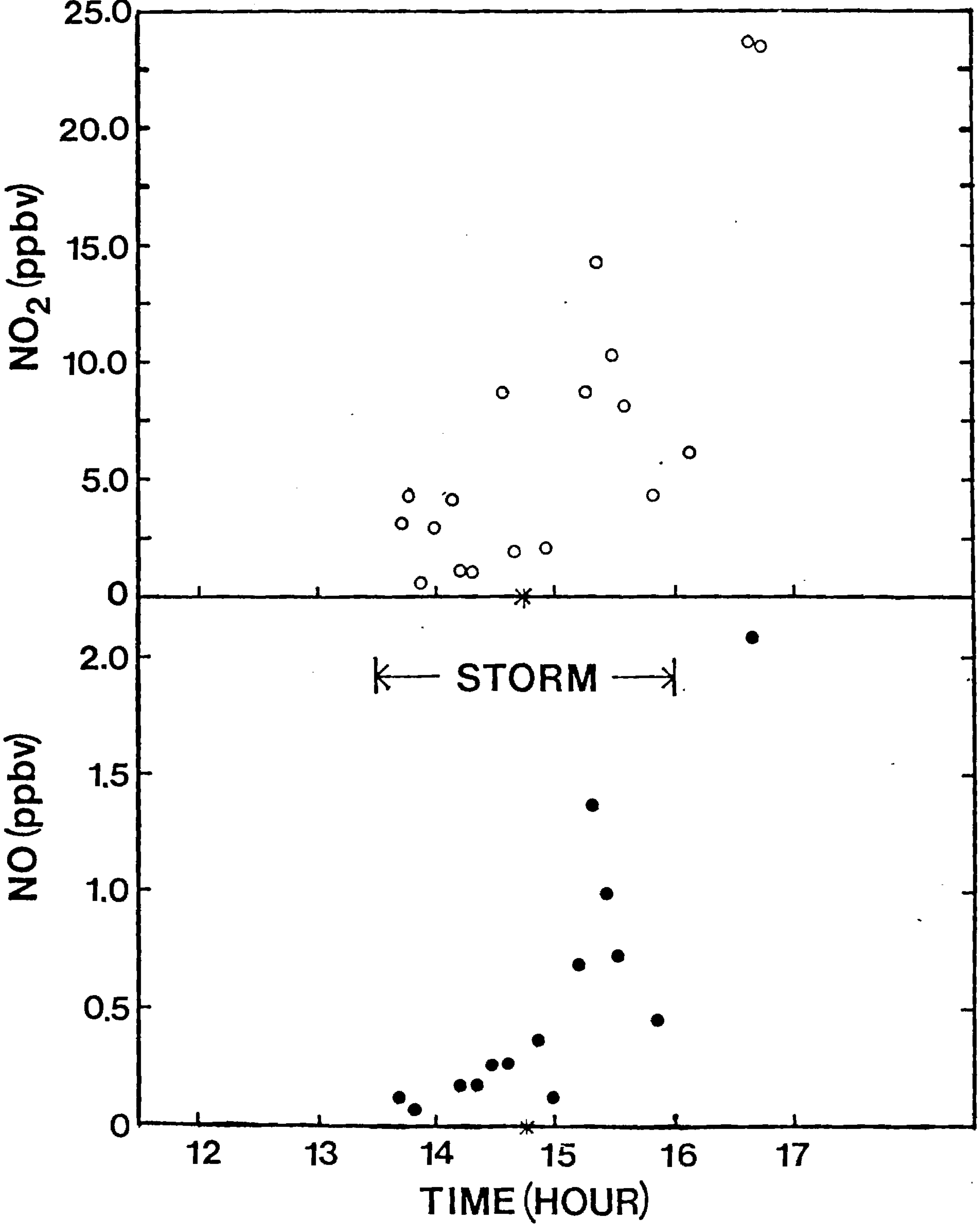
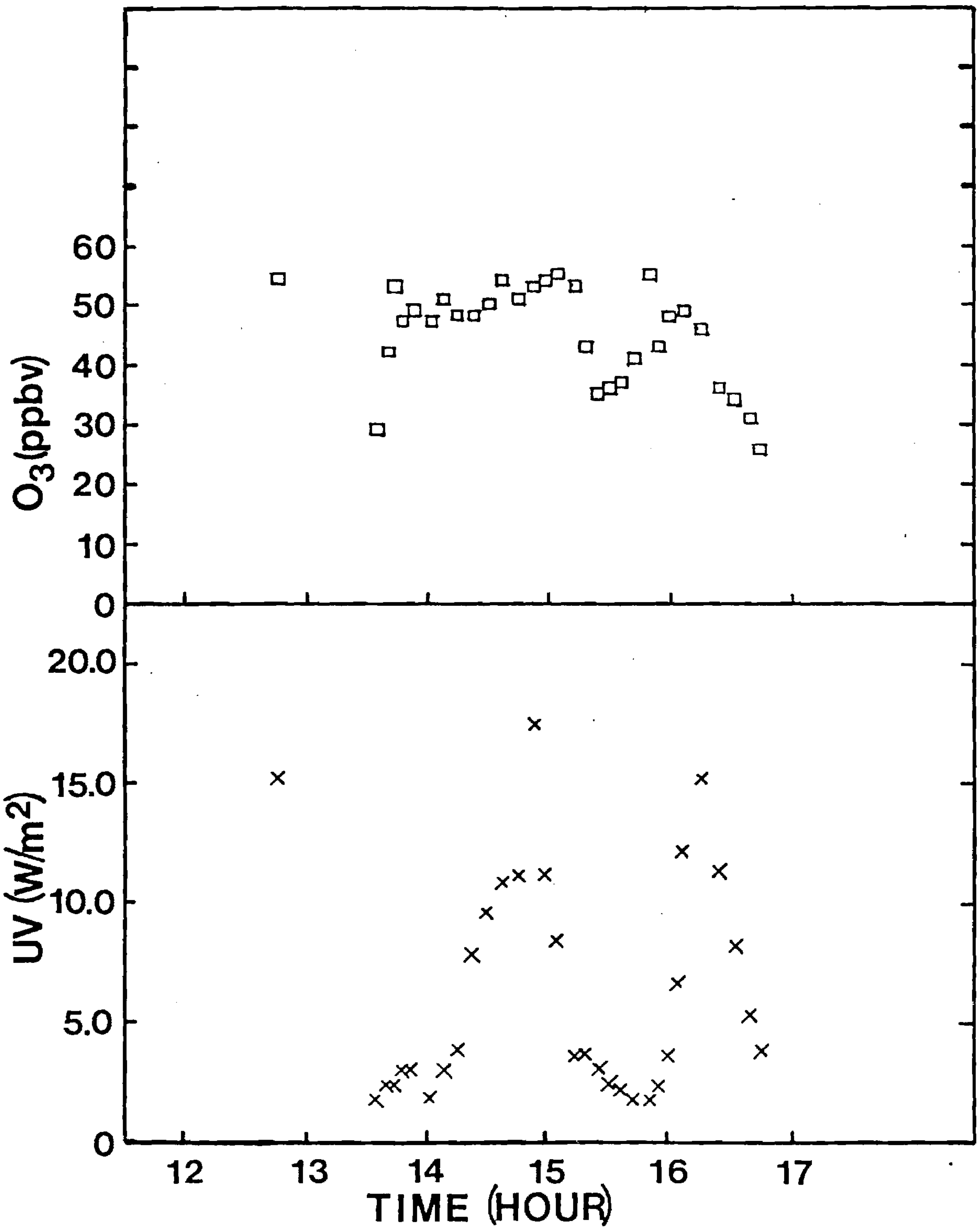


FIG. H: JULY 27, 1984



change in the NO levels and only a small increase in the NO_2 (e.g. ~ 8 ppbv → 13 ppbv). The storm occurred between 14:30 and 15:30 hours; however, the highest levels in NO and NO_2 occurred at ~ 17:30. The latter increase occurred under clear air conditions. By contrast, we note that the largest fluctuations in O_3 occurred during or right after the storm. At the time of the clear air NO/NO_2 peaks, the O_3 levels were reasonably constant at 70 ppbv.

Figure D shows data from July 7. Once again a thunderstorm occurred in the Stone Mountain area but in this case it was accompanied by considerable thunderstorm activity throughout most parts of central and northern Georgia. Here we see a very large clear air NO_2 spike preceding the storm at ~6:30 with yet another increase in both NO and NO_2 being observed during the storm itself (8:30 → 10:00). It is interesting to note that at one point during the storm the level of O_3 was in the 2 - 4 ppbv range. Later in the day, again under clear air conditions, we see two very large spikes in NO_2 (115 ppbv in one case and 75 ppbv in the other). The NO_2 spikes are positively correlated with much smaller but yet significant peaks in NO of 6 ppbv and 1.2 ppbv. A very significant positive correlation is also observed between O_3 and the second NO_x peak at ~15:00 hrs.

July 13th, shown in Figure E, was a non-storm day but it was sandwiched in time between two storms. Here we see spikes in NO (up to 6 to 7 ppbv) and highly fluctuating levels of NO_2. The second major spike in NO is negatively correlated with O_3 (see e.g. 14:30 hrs.). It is also negatively correlated with the UV flux. Moderate to high levels of NO_2 (40 ppbv) are observed to persist into the early evening hours.

Figure F represents a continuation of the data collection effort initiated on July 13. On the 14th a major storm occurred in the very early morning hours (00:45 → 03:00). NO levels in this case are seen to be very low (below our detection limit at that time); whereas, some peaking in NO_2 is observed during the storm with a maximum value of 30 ppbv being reached at 02:00 hrs. Moderate to high levels of NO_2 persisted throughout the morning hours (8:00 to 11:30) although a significant decrease is seen at $\sim$ 10:30. This decrease in NO_2 is seen to be negatively correlated with a sharp rise in NO (up to 10 ppbv). Likewise, O_3 levels were also negatively correlated with the sharp rise in NO.

On July 17, Figure G, a storm occurred between 17:15 and 18:30 hours. On this occasion there was no increase seen in the levels of either NO or NO_2. The morning peak in NO and NO_2 is similar to that observed on other data collection mornings.

The final plot shown on July 27, shows storm activity occurring from 13:30 through 16:00 hours. Peaks in both NO and NO_2 are observed during the storm as well as after the storm at $\sim$ 16:30. These peaks are seen to be negatively correlated with O_3 and UV flux.

3. Diurnal Trends

(1a) Weekdays (non-frontal conditions)

The diurnal trend in NO may be characterized as consisting of an early morning bulge (6:30 - 11:00 hrs) followed by much lower but fairly constant levels throughout mid-day with an occasional late afternoon peaking. After sunset, the NO level typically dropped abruptly and then was observed to fluctuate throughout the night at very low levels. The levels observed during the early morning bulge ranged from 1 to 5 ppbv but more commonly were 1 to 2 ppbv. Mid-day values ranged from .125 to .500 ppbv but again were more commonly observed to be in the .125 to .300 ppbv range. Nighttime levels were typically less than 50 pptv with occasional values reaching the 10 pptv level.

The data on NO_2 for non-frontal conditions is quite limited and therefore any comments on its diurnal trends must be considered very preliminary in nature. Based on this limited data, it appears that an early morning bulge in NO_2 is observed (6:30 - 11:00 hrs) with somewhat lower but highly fluctuating values being seen throughout the remainder of the day.

(2a) Saturday/Sunday (non-frontal conditions)

There are too few NO and NO_2 data on weekends to assess any diurnal trends.

(1b) Weekdays (frontal conditions)

In contrast to the above observations, during the time period when several frontal systems passed through Georgia in rapid succession, no simple diurnal trend was observed in NO. Nighttime levels were again very low in comparison to daytime levels and the early morning bulge in NO was also observed. The morning peak in NO, however, was much larger than noted earlier, reaching 20 ppbv in one case. Perhaps still more significant were the much higher average levels of NO seen in the time period of 11:00 → 19:00 hrs. The average NO value was typically in the 1 ppbv range with 1/2 hour spikes occurring during mid-day which reached 7 ppbv.

Concerning NO_2 trends, like NO there typically was an early morning bulge, however, some of the largest peaks in NO_2 were observed during the very early morning hours, mid-day and at night. Values of 40 to 105 ppbv were measured on several occasions.

(2b) Saturday/Sunday (frontal conditions)

No systematic maximum was observed in the level of NO during the early morning hours of 6:30 - 11:00 hrs. It must be noted, though, that for those mornings that data were collected it was quite cloudy. Thus, the average levels observed during the morning were not much different than those in the afternoon. As observed on weekdays, short lived spikes (5 to 40 minutes in duration) were observed throughout the day. Several of these spikes reached levels of 6 to 8 ppbv during mid-day hours.

As in the case of NO, no systematic early morning peaking was seen in the levels of NO_2. Also like NO, several mid-day and, in some cases, early morning spikes were observed. Some of these spikes reached levels of 100+ ppbv.

4. Major Meteorological Events (Frontal System Passage)

Summarized in Table II is a simple correlation chart which shows the changes in NO and NO_2 levels observed during the passage of each storm through the Atlanta area during the time period of 6/29 to 8/01. Also inducated on the chart are any significant changes in the levels of NO and NO_2 occurring before or after each storm. As dicussed later in the text, during the time period 6/29 → 8/01 no less than seven frontal systems moved through the Atlanta area bringing, in most cases, considerable rain and lightning to the area. Typically, however, each of these frontal systems produced more severe weather in areas to the northwest and west of Atlanta. Thus, in the Atlanta area itself, we were frequently exposed to the major after-effects of these frontal systems. For this reason, we have opted to examine our NO_x data both in terms of the levels present before and after each local (Stone MOuntain) storm event.

From the results summarized in Table II, it is apparent that no systematic trend emerges in the NO/NO_2 levels as observed during storm events. In some cases increases in both NO and NO_2 were seen. In other cases, only NO_2 increases were observed. There were still other events where no significant increase in either NO or NO_2 levels was seen. And, on numerous occasions significant changes in the levels of NO and NO_2 were observed either before or after a local storm event.

Summary:

Although we are still in need of a far more extensive data base, at this time we believe that our NO and NO_2 observations during the passage of electrified frontal systems are not inconsistent with the hypothesis that electrified clouds can be a significant source of atmospheric NO_x. The somewhat random occurrence of NO_x increases during thunderstorms may be explicable in terms of the dynamic and electrical characteristics of summer thunderstorms. For example, based on detailed lightning studies by other investigators, it now appears that most cloud-to-cloud lightning strokes occur between the altitudes of 6 and 13 Km. Thus, the transport of this upper level NO_x source to the altitude at which sampling is occurring (.6 Km, top of Stone Mountain) is critically dependent on the detailed dynamics of a given thunderstorm. Information now provided to us by cloud dynamists at the National Center for Atmospheric Research suggests that most of the downward air flow which accompanies the rain shaft of a cumulonimbus enters the cloud from the sides between the altitudes of 2 to 6 Km. This suggests that in many cases the downdraft air column may never ever pass through those regions of the cloud where cloud-to-cloud lightning strikes have occurred.

We offer the above comments not as proof that we now understand the lightning NO_x source; rather we put them forward as a working hypothesis which will require much more data to validate.

TABLE II CORRELATIONS BETWEEN ELECTRICAL/RAIN STORMS AND LEVELS OF NO/NO_2

Date	Approx. Time	Stone Mtn. Rain	Stone Mtn. Lightning	Significant Changes in [NO] During Activity		Significant Changes in [NO] Before or After Activity	
				NO	NO_2	NO	NO_2
6/29	Morning	✓	✓	+	+	+	NR
7/01	Afternoon	✓	✓	-	-	+	NR
7/03	Afternoon	✓	✓	-	+(S)	+	+
7/05	Late Afternoon	(Occurred Immed. before Data Collection)	✓	NR	NR	-	NR
7/06	Afternoon	✓	✓	NR	-	NR	+
7/07	Morning	✓	(low level)	+	+	+	+
7/14	V.Early Morning	✓(Heavy)	✓(Heavy)	-	+(S)	+	+
7/16	Afternoon	✓	✓	+	+	-	+
7/17	Early Evening	✓	X	-	-	-	-
7/18	Early Morning	✓	✓	-	+(S)	-	+
7/27	Afternoon	✓	✓	+	+		
7/30	Afternoon	✓	X	+	NR		
7/31	Afternoon	✓	X	-	-		
8/01	Afternoon	✓	X	+	+		

\+ indicates significant change in concentention level observed, i.e. $>$ factor of two

\- indicates no change in level observed.

NR indicates no data recorded.

5. "Long Term" Trends

In an effort to determine what influence wind direction, time of week (i.e. weekday vs. weekend), and changes in meteorological conditions had on the observed NO and NO_2 levels, we have analyzed the existing data set in terms of two temporal sampling periods covering each day measurements were recorded. These sampling windows were selected on the basis of: (1) that the number of days NO and/or NO_2 measurements were recorded during the time period was moderately large; and (2) that the levels of NO or NO_2 were markedly different for each sampling window. Based on these two criteria, temporal sampling windows of 8:00 to 11:00 and 12:00 to 18:00 hrs were chosen. The morning sampling period may be characterized as one having high NO and NO_2 levels; whereas, the mid-day period typically showed low levels of NO and moderate levels of NO_2.

In addition to the just-mentioned breakdown into two diurnal time periods, we have also sub-divided the entire data set into two calendar periods: 6/12 to 6/28 and 6/29 to 8/01. The latter breakdown reflects a major change in meteorological conditions in Georgia during the 50 day sampling period. The JUne time period was representative of an extremely dry summer month. The July time period, on the other hand, was one of the wettest summer months ever recorded in Georgia. These results have been presented in Tables IIIa and IIIb.

The phrase "long term" has been employed in this discussion in the very limited context of addressing the question of whether systematic changes occurred in the average levels of NO over the sampling period of 50 days. As noted earlier, we believe this question has considerable significance since the 50 day period spans two of the most unique months in Georgia's weather. One might say, in fact, we were very lucky to have chosen these months for our initial sampling effort.

As noted earlier, our local meteorological data indicates that over the sampling period of June 12 through June 28 no rainfall was measured at Stone

Table IIIa, Trends in NO, NO_2, and O_3 Over the Time Period 6/12 to 8/01

Time Period 12:00 to 18:00 hrs.	NO(ppbv)	NO_2 (ppbv)	O_3 (ppbv)
All Wind Directions/All Days 6/12 to 6/28	.34	2.8 (1)	67
W to NW (4) " " " (All Days)	.38	—	74
S to SW (6) " " " (All Days)	.21	2.8(1)	68
N,NE,E,SE(4) " " " (All Days)	.47		60
All Wind Directions/All Days 6/29 to 8/01	1.5	9.1	43
W to NW (6) " " " (All Days)	1.1	11	52
S to SW (5) " " " (All Days)	1.9	11	39
N,NE,E,SE (3) " " "	1.4	4.3	32
Time Period 8:00 - 11:00 hrs.			
All Wind Directions/All Days 6/12 - 6/28	1.2	7.0(2)	45
W to NW (1) " " " (All Days)	2.9		65
S to SW (4) " " " (All Days)	1.0	7.0(2)	40
N,NE,E,SE (4) " " " (All Days)	1.0		47
All Wind Directions/All Days 6/29 - 8/01	4.6	15	23
W to NW (2) " " " (All Days)	2.5	22	13
S to SW (6) " " " (All Days)	5.2	12	25
N,NE,,E,SE (1)" " " (All Days)	.38	15	34

Table IIIb, Trends in NO, NO_2, and O_3 Over the Time Period 6/12 to 8/01

Time Period: 12:00 to 18:00 hrs.

		NO(ppbv)	NO_2 (ppbv)	O_3 (ppbv)
All Wind Directions (All Days but Sat. & Sun.)	6/12 to 6/28	.29	2.8(1)	70
All Wind Directions (Sat. & Sundays only)	" " "	.41	——	58
All Wind Directions (All Days but Sat. & Sun.)	6/29 to 8/01	.84	7.5	38
All Wind Directions (Sat. & Sundays only)	" " "	2.9	13	52

Time Period: 8:00 to 11:00 hrs.

		NO(ppbv)	NO_2 (ppbv)	O_3 (ppbv)
All Wind Directions (All Days but Sat. & Sun.)	6/12 to 6/28	1.2	7.0(2)	46
All Wind Directions (Sat. & Sundays only)	" " "	——	——	——
All Wind Directions (All Days but Sat. & Sun.)	6/29 to 8/01	6.2	15	24
All Wind Directions (Sat. & Sundays only)	" " "	2.0	14	22

Mountain; whereas, from June 29 through August 1, fourteen rain events were recorded with several others being missed because personnel were not on hand at the station at the time the rain event occurred. The rain activity during the June 29 → August 1 time period was somewhat complex in that it typically did not originate from a localized summer-convective thunderstorm but rather was initiated by a succession of weak cold frontal systems that moved throught he state of Georgia during this time period. Although detailed meteorological records are still being assembled, it appears that 6 to 7 such systems swept through the state during July and early August of 1984. Thus, because of the temporal closeness of these frontal systems, we have opted to look at this wet period as one block of data and the dry period as a second block.

From Table III, it can be seen that for the sampling window 12:00 → 18:00 hrs, data was recorded on 14 days during the calendar periods of June 12 → June 28 and also June 29 → August 1. For the window 8:00 → 11:00 hours, the statistics are somewhat worse with only 9 days of sampling occuring. For both diurnal sampling windows, however, a similar trend is seen in the relative NOlevels, e.g.$\sim$ 3.8 times higher NO being observed for the period 6/29 → 8/01. The authors note that the higher NO_x levels seen during the 8:00 → 11:00 vs. 12:00 → 18:00 sampling windows reflect either the effects of morning rush hour traffic into Atlanta or some other natural phenomenon related to sunrise, such as the breakup of the nocturnal boundary layer. (Both of these possibilities are being investigated.)

By taking the average wind vector over each sampling period, we have attempted to determine if there were any systematic trends in the levels of NO as a function of wind direction. As seen from Table IIIa, no significant trend appears to be present. However, considering the small number of days for each wind direction, we do not believe that one can draw any final conclusions from this data set.

As suggested earlier, of several possible environmental influences on the Stone Mountain NO_x data base, we see Atlanta's rush hour traffic as potentially one of the major sources. To further assess the impact of this source, we examined the Stone Mountain data base in terms of weekdays versus weekends. This analysis is presented in Table IIIb. For the sampling period 12:00 to 18:00 hours, the average weekday NO level is seen to increase a factor of 2.9, favoring 6/29, → 8/01. By contrast, the Saturday/Sunday sampling scenario shows the NO level increasing by a factor of 7.1, again favoring the 6/29 → 8/01 period.

For the sampling window (8:00 - 11:00), inadequate Saturday/Sunday data exist for the 6/12 → 6/28 time period to carry out a comparison. However, for weekdays the trend is similar to that cited earlier. For example, the increase in NO is seen to be a factor of 5.2, the 6/29 - 8/01 period again being higher.

The trend in NO_2 is also seen to be one involving increasing levels during the wet period, 6/29 → 8/01. But, as discussed previously, the limited data available for NO_2 in the 6/12 → 6/28 time period hardly justify any conclusions regarding this species.

A final analysis shown in Tables IIIa and IIIb involves the trend in O_3 during the wet and dry months. We see, for example, that for all sampling scenarios considered there is a systematic decrease in O_3 ranging from 35 to 50% for the period 6/12 - 6/28 relative to 6/29 - 8/01. This trend would appear to be chemically consistent with the systematic increases observed in NO for the same calendar time.

6. HNO_3 Measurements

Nitric acid measurements were carried out on July 12, 13, 14, 16, and 17. The method employed for these measurements involved high-volume (high-vol) sampling with chemically treated filter-mattes. The system used in this study was designed by Dr. Barry Huebert and all analyses were carried out in his laboratory at Colorado College.

The high-vol technique uses two removable filters which are placed in a sampling manifold attached to a high-vol pump. The quantity of air pulled through the filters is determined with a mass flow controller, which is positioned between the manifold and pump. The first filter in the manifold is constructed from teflon and is designed to collect aerosol species having diameters $\geqq .01\mu$. The second, and in some cases third, filter in the sampling train is made from a nylon type material and is designed to chemically trap all gas phase species that are strongly acidic.

The high-vol system used by Huebert is one of the most extensively tested in the country and has undergone extensive calibrations using HNO_3 permeation tubes.

As shown in Table IV, the HNO_3 levels measured during the time period of 7/12 to 7/17 show considerable variability, ranging from a high of 9.14 ppbv to a low of .23 ppbv. These results most likely reflect the high solubility of HNO_3 in liquid aerosols and the efficient scavenging of HNO_3 by washout and rainout processes. The low HNO_3 values for sample 20 (July 13), samples 27, 28 and 29 (July 16), and samples 30, 31, 33, 35 and 37 on July 17 would appear to be strong evidence supporting the importance of these removal processes.

Upon eliminating those samples where washout/rainout processes were prominent, one finds that the levels of HNO_3 observed at Stone Mountain were exceptionally high in comparison to measurements made by Huebert in locations such as Oak Ridge, Tennessee; Champaign, Illinois; Pawnee Grasslands (Fort

Collins, Colorado); Niwot Ridge, Colorado; and the Boulder Atmospheric Observation Tower, Boulder, Colorado.

As discussed in Section IIB(9), we cannot at this time determine whether these high levels of HNO_3 were due to NO_x generated from lightning or due to the long range transport of NO_x/HNO_3 species from regions to the North and West of the State of Georgia. By adding SO_2, CO, and N_2O to our existing array of measurements, however, we hope to resolve this question during the coming year.*

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* CO serves as a good indicator of auto pollution; whereas SO_2 is a good indicator of power plant plumes. N_2O, on the other hand, is like NO in that it is produced very efficiently from lightning.

TABLE IV, HNO_3 MEASUREMENTS

Date	Sample #	Time	$[HNO_3]$(ppbv)	Meterological Information
7/12 (84)	1	14:35 → 15:08	3:81 ± .01	Haze
"	3	15:22 → 15:52	3.71	Haze
"	4	17:43 → 18:22	1.81	Lightning(distant)
7/13	5	03:56 → 04:26	.50	Clear
"	8	09:13 → 09:42	2.19	Haze
"	12	11:28 → 12:01	3.42	Low clouds
"	13	13:05 → 13:35	4.42	Broken clouds
"	14	15:35 → 16:05	9.14	Windy, broken clouds
"	15	17:13 → 17:43	2.04	Haze,T.Storms, Atl.
"	16	19:01 → 19:31	5.33	Cloudy, Haze
"	17	21:33 → 22:03	3.78	Clear, Big T.Storm,S.
"	18	23:15 → 23:43	5.63	T.Storm to SW
7/14	19	01:19 → 01:49	1.18	Storm Approaching
"	20	02:07 → 02:37	.84	Rain, Lightning
"	21	06:05 → 06:40	2.25	Drizzle
"	22	07:23 → 07:53	1.90	Fog below,haze above
"	24	10:38 → 11:08	3.09	Haze
7/16	25	11:50 → 12:20	4.96	Haze
"	26	12:21 → 12:51	3.06	Haze
"	27	20:06 → 20:38	.57	Rain at 15:20→16:20
"	28	20:47 → 21:19	.48	85% Rel. H.
"	29	21:27 → 23:33	.35	85% Rel. H.
7/16 (17)	30	23:46 → 01:23	.35	80% Rel. H.
7/17	31	01:28 → 02:02	.37	High winds,95% Rel.H.
"	33	04:00 → 04:30	.53	High winds,95% Rel.H.
"	35	04:38 → 05:08	.37	Heavy Haze
"	37	08:25 → 08:55	.23	Low lying stratus

7. Rain Samples

Rain samples were collected on each of the following days: 7/6, 7/7, 7/13, 7/14, 7/16, 7/18, 7/30, 7/31, 8/01. Each sample was analyzed within one week of its collection time and during the interim was stored in a refrigerator at 277K. All rain samples were analyzed in Dr. Mohnen's laboratory at SUNY, Albany. Variables measured included: pH, Cl^-, NO_3^-, SO_4^{-2}, NO^+, NH_4^+, and K^+. The method of analysis for all cations and anions was that of ion-chromatography. Dr. Mohnen's group is one of several laboratories in the U.S.A. that has been actively involved in establishing reliable analytical procedures for rain water analysis and is thus one of the better established laboratories for performing this type of analysis.

A summary of the rain sample analyses from Stone Mountain is given in Table V. Although at this time there has been no extensive examination of these data, two points are perhaps worth mentioning: (1) the ratio of NO_3^- to SO_4^{-2} observed in our rain samples does not suggest that the air masses being sampled were in recent contact with plumes from large coal-fired power plants. The argument here is that due to the much higher ratio of SO_2/NO_x in power plant plumes, precipitation in air which has been influenced by these plumes typically yields SO_4^{-2}/NO_3^- ratios of 3/1 to 4/1. The reader will note that in some cases the Stone Mountain data actually shows SO_4^{-2}/NO_3^- ratios of less than unity, see, for example, 7/14, 7/30, and 8/01 data.

A second point to be made about the rain data is that, as expected, we see a strong positive correlation between the absolute levels of $NO_3^- + SO_4^{-2}$ and the acidity of the rain. The lowest pH level observed of 3.69 was found in a sample collected on 7/16. This same sample had one of the highest levels of $NO_3^- + SO_4^{-2}$. It is also interesting to note that immediately before the rain storm on 7/16, gas phase HNO_3 levels were running 3 to 5 ppbv. Immediately after the rain they were .5 ppbv or lower.

TABLE V RAIN SAMPLE ANALYSIS

				Concentration μM/ℓ					
Date	Time	Sample #	pH	Cl^-	NO_3^-	SO_4^{-2}	Na^+	NH_4^+	K^+
7/6(84)	14:30	1	4.00	*	36.5	48.1	*	8.07	*
7/7	9:50	1	4.54	*	7.93	14.0	*	1.01	*
7/14	01:30	1	3.98	4.45	42.9	37.0	1.37	2.86	<1.0
		2	4.02	5.40	49.5	41.1	2.1	2.1	1.0
7/16	15:10	1	3.75	8.69	59.7	83.0	4.02	19.4	<1.0
		2	3.69	13.3	61.0	88.0	6.51	8.20	<1.0
7/18	4:30	3	4.58	4.48	12.3	22.8	10.5	1.32	2.68
		4	4.48	3.49	14.4	29.0	7.66	7.27	2.44
7/30	14:12	A_1	5.50	8.7	11.1	5.7	8.0	3.6	<1.0
		B_1	5.26	8.5	10.5	5.2	8.0	3.4	<1.0
7/31	16:35	A	4.08	9.70	39.0	57.0	11.7	18.8	<1
		B	4.02	12.4	43.9	66.1	13.3	22.6	<1
8/01	14:03	1	5.10	3.0	5.6	8.5	6.9	3.9	<1
"	15:24	2	5.01	2.4	7.8	2.0	1.7	< 1	<1
		3	5.01	2.2	8.3	2.6	1.6	< 1	<1

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* Samples contaminated by finger print therefore cl^-, Na^+, and K^+ unreliable.

8. N_xO_y Photochemistry

There are two facets of the N_xO_y chemical cycle that may be examined in the context of the 6/12 - 8/01 Stone Mountain data base.

(1) Does the simple photstationary state relationship

$$\frac{NO}{NO_2} = \frac{J}{k[O_3]} \qquad \text{I}$$

give an accurate representation of daytime NO_x chemistry?

And (2) Do we now understand the key elements of nighttime N_xO_y chemistry, e.g.

(a) $NO + O_3 \rightarrow NO_2 + O_2$

(b) $NO_2 + O_3 \rightarrow NO_3 + O_2$

(c) $NO_3 + NO_2 \overset{M}{\rightarrow} N_2O_5$

(d) $N_2O_5 \rightarrow NO_2 + NO_3$

(e) $NO_3 + RH \rightarrow HNO_3 + R\cdot$

(f) $NO_3 + H_2O \xrightarrow{\text{heterog.}} \text{Products}$

(g) $N_2O_5 + H_2O \xrightarrow{\text{heterog.}} 2HNO_3$

Concerning the first question, as of this writing the summer 1984 Stone Mountain data base has not been analyzed in the detail required to evaluate equation I. This exercise will be carried out for all days where NO, NO_2, O_3, and UV solar flux data are available, e.g. the time period July 13 → Aug. 1. Nevertheless, it is of perhaps qualitative interest that in quickly surveying the Stone Mountain data there are 15 cases where mid-day levels of NO and NO_2 were sufficiently constant with time that ratios for NO/NO_2 could be reliably evaluated. Of these, four showed values of $\geqq 1/20$, five others gave ratios $\geqq 1/10$, three gave a ratio of $\geqq 1/5$, and two gave ratio values of $\sim 1/3$. This preliminary analysis suggests that in most cases the experimentally measured ratios for NO/NO_2 will not be in good agreement with those predicted by equation I. Thus, this qualitative assessment suggests that the oxidation of NO to NO_2 via reaction with RO_2 and HO_2 radicals will likely prove to be an important factor in controlling the atmospheric ratio of NO/NO_2 for the summertime Stone Mountain data set.

The second question raised, related to nighttime N_xO_y chemistry, is also a very important one in that during the last 3 to 4 years both field and laboratory studies of the NO_3 species indicate that earlier hypotheses on the controlling factors for this species are probably in error. The early thinking on this chemistry encompassed the idea that there should be a rapid conversion of NO to NO_2 at night via rx. (a), followed by a slow decay of this NO_2 throughout the night due to its conversion to NO_3 via rx. (b) and also due to its reaction with NO_3 itself, thus forming N_2O_5. N_2O_5 was believed to slowly disappear via heterogeneous reactions with H_2O to form HNO_3. Thus, the early chemical models on this chemistry predicted appreciable levels of NO_3 and N_2O_5 being built up during the night.

During the last 3 to 4 years, field measurements of NO_3 have shown that the levels of this species are one or more orders of magnitude lower in concentration than predicted from the early models. In addition, it has been found that NO_3 very quickly achieves a stationary state concentration level early in the evening.

More recently, the above behavior has been explained in terms of the interaction of NO_3 with H_2O (e.g. heterogeneously) and, perhaps more importantly, as a result of the NO_3 species reacting with a wide assortment of hydrocarbons, e.g. rx. (e). Laboratory kinetic data, in fact, strongly support the latter argument and suggest that the NO_3/hydrocarbon reaction could be one of the major sources of HNO_3 in the troposphere, comparable to, if not larger than, that resulting from the daytime $OH + NO_2 \rightarrow HNO_3$ rx.

The significance of the Stone Mountain data, as related to the question of NO_3, lies in the observed nighttime levels of NO. These ranged from 10 to 70 pptv with an average value of 35 pptv. However, given the very fast reaction

$$NO + NO_3 \rightarrow 2NO_2$$

only a few pptv of NO can act to totally control the level of NO_3 in the nighttime atmosphere. If true, the hydrocarbon/NO_3 production of HNO_3 could again become a minor channel for HNO_3 formation.

We are left, then, with the following questions: (1) are the measurements of nighttime NO at Stone Mountain reliable? and (2) if the NO measurements are correct, where is this NO coming from? New field experiments are now being planned for the fall of 1985 in an effort to answer these questions.

9. Preliminary Conclusions

This first 50 day "exploratory" field-sampling period encompassed major changes in both sampling hardware and sampling strategy. And, in spite of the evolutionary nature of this effort, the authors believe that some highly significant scientific data were generated. These data have already caused us to make major adjustments in our future sampling strategy.

As of this writing, the authors would not want to underscore any final conclusions that might be drawn from this first data set, but several preliminary conclusions can be put forward.

(a) In the absence of major thunderstorm (frontal) activity, the daytime trends in NO at Stone Mountain appear to be reasonably well understood in terms of local sources and chemical sinks/transformations.

(b) It now appears that it may not be possible to cleanly define the impact of electrified clouds on local levels of NO_x based only on ground level observations made during thunderstorm events.

(c) The observed trend in the summer 1984 data set showing much higher levels of NO during the month of July relative to June, strongly suggests that these elevated levels of NO_x were the result of the numerous frontal systems that moved through the state of Georgia during the July time period. Possible explanations for this behavior include:

(i) long range transport of NO_x pollutants by these frontal systems;

(ii) production of high levels of NO_x species due to extensive thunderstorm activity;

or (iii) major changes in the flux of NO_x species from natural biological sources due to changes in soil moisture levels.*

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* Of the possibilities listed, (i) and (ii) appear to be by far the more likely. This tentative conclusion is based on the fact that a biological source is unlikely to produce the sharp spikes in NO and NO_2 observed so frequently during the 6/29 - 8/01 time period.

(d) The observed NO/NO_2 ratios at Stone Mountain during the summer of 1984 suggest that RO_2 and HO_2 reactions are important in promoting the oxidation of NO to NO_2.

and (e) The levels of NO observed at Stone Mountain at night suggest that nighttime levels of NO_3 may very frequently be controlled by the NO + NO_3 reaction rather than by hydrocarbon or atmospheric moisture levels.

APPENDIX A

STONE MOUNTAIN FIELD DATA

Time Period 6/12 - 8/01

2-
[illegible]

Prepared for:

COORDINATING RESEARCH COUNCIL
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Prepared by:

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```
THIS DATA WAS RECORDED ON 06/12_13/84


                                REL.                UV.
   TIME          WIND   TEMP    HUM.   C.C.N.    FLUX     [O3]     [NO]      +/-     [NO2]      +/-

     (DEGREES)(MPH)(K)      (%)    (#/CM2)(W/M2)  (PPB)    (PPB)    (PPB)    (PPB)    (PPB)


   10:00        NR   NR     NR      NR     NR      NA      45        NA       NA       NA        NA
   10:15        NR   NR     NR      NR     NR      NA      42     1.619     .115       NA        NA
   10:21        NR    0     NR      NR     NR      NA      26        NR       NR       NA        NA
   10:30        NR    0    301      35     NR      NA      35     1.220     .099       NA        NA
   10:31         "    "      "       "      "       "      24         "        "        "         "
   10:32         "    "      "       "      "       "      55         "        "        "         "
   10:33         "    "      "       "      "       "      30         "        "        "         "
   10:35        NR    0     NR      NR     NR      NA      41     1.407     .107       NA        NA
   10:36         "    "      "       "      "       "       "         "        "        "         "
   10:37         "    "      "       "      "       "      55         "        "        "         "
   10:38         "    "      "       "      "       "      40         "        "        "         "
   10:40        NR   NR     NR      NR     NR      NA      56        NR       NR       NA        NA
   11:16        60   NR     NR      NR     NR      NA      NR      .703     .074       NA        NA
   11:21        NR   NR     NR      NR     NR      NA      54      .415     .055       NA        NA
   11:27        80   NR    308      42     NR      NA      43      .322     .048       NA        NA
   11:32        NR   NR     NR      NR     NR      NA      49        NR       NR       NA        NA
   11:53        NR   NR     NR      NR     NR      NA      53      .212     .037       NA        NA
   11:58        NR   NR     NR      NR     NR      NA      38      .331     .049       NA        NA
   12:11        NR   NR     NR      NR     NR      NA      51      .237     .040       NA        NA
   12:17        NR   NR     NR      NR     NR      NA      49      .424     .056       NA        NA
   12:31        NR   NR     NR      NR     NR      NA      53      .144     .029       NA        NA
   12:34        NR   NR    309      33     NR      NA      50        NR       NR       NA        NA
   12:42        NR   NR     NR      NR     NR      NA      52        NR       NR       NA        NA
   12:48        NR   NR     NR      NR     NR      NA      54      .568     .066       NA        NA
   12:57        NR   NR     NR      NR     NR      NA      65      .314     .047       NA        NA
   13:03        NR   NR    306      30     NR      NA      59      .093     .022       NA        NA
   13:10        NR   NR    305      40     NR      NA      57        NR       NR       NA        NA
   13:11         "    "      "       "      "       "      64         "        "        "         "
   13:16        NR   NR     NR      NR     NR      NA      62        NR       NR       NA        NA
   13:17         "    "      "       "      "       "      47         "        "        "         "
   13:18         "    "      "       "      "       "      50         "        "        "         "
   13:27        NR   NR     NR      NR     NR      NA      70      .169     .032       NA        NA
   13:28         "    "      "       "      "       "      62         "        "        "         "
   13:32        NR   NR    305      38     NR      NA      59      .110     .024       NA        NA
   13:37        NR   NR     NR      NR     NR      NA      59      .128     .034       NA        NA
   13:44        NR   NR     NR      NR     NR      NA      67      .102     .023       NA        NA
   13:51        NR    4     NR      NR     NR      NA      44      .093     .022       NA        NA
   13:56        NR   NR     NR      NR     NR      NA      32      .212     .037       NA        NA
   13:57         "    "      "       "      "       "      57         "        "        "         "
    4:03        NR   NR     NR      NR     NR      NA      56      .246     .041       NA        NA
    4:04         "    "      "       "      "       "      61         "        "        "         "
    4:17        NR   NR     NR      NR     NR      NA      54      .008     .003       NA        NA
    4:24        NR   NR     NR      NR     NR      NA      56      .169     .032       NA        NA
    4:27        NR   NR     NR      NR     NR      NA      54      .127     .027       NA        NA
    4:37       170    4    304      43     NR      NA      NR      .220     .038       NA        NA
    4:44       200    4    303      38     NR      NA      61      .212     .037       NA        NA
    4:53       178    4     NR      NR     NR      NA      57      .161     .032       NA        NA
    5:00        NR   NR     NR      NR     NR      NA      NR        NR       NR       NA        NA
```

15:13	NR	NR	NR	NR	NR	NA	59	NR	NR	NA	NA
15:14	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
16:14	176	9	304	38	NR	NA	66	.264	.038	NA	NA
16:20	160	6	NR	NR	NR	NA	58	.141	.026	NA	NA
16:37	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
16:40	173	10	NR	NR	NR	NA	66	.166	.029	NA	NA
16:47	179	8	NR	NR	NR	NA	57	.141	.026	NA	NA
17:00	NR	NR	NR	40	NR	NA	NR	NR	NR	NA	NA
17:07	160	6	NR	NR	NR	NA	59	.178	.030	NA	NA
17:08	"	"	"	"	"	"	59	NR	NR	"	"
17:09	"	"	"	"	"	"	57	"	"	"	"
17:10	"	"	"	"	"	"	60	"	"	"	"
17:13	166	8	NR	NR	NR	NA	57	.061	.015	NA	NA
17:14	"	"	"	"	"	"	62	"	"	"	"
17:15	160	6	"	"	"	"	61	"	"	"	"
17:16	170	7	"	"	"	"	"	"	"	"	"
17:19	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
17:25	184	8	NR	NR	NR	NA	56	.221	.034	NA	NA
17:26	200	7	"	"	"	"	"	"	"	"	"
17:27	"	9	"	"	"	"	55	"	"	"	"
17:28	"	10	"	"	"	"	60	"	"	"	"
17:30	189	8	NR	NR	NR	NA	54	.135	.026	NA	NA
17:31	184	12	"	"	"	"	64	"	"	"	"
17:32	185	10	"	"	"	"	"	"	"	"	"
17:33	197	12	"	"	"	"	61	"	"	"	"
17:34	198	11	NR	NR	NR	NA	67	.178	.030	NA	NA
17:35	197	9	"	"	"	"	64	"	"	"	"
17:40	NR	NR	NR	NR	NR	NA	67	NR	NR	NA	NA
17:47	192	8	NR	NR	NR	NA	57	.086	.019	NA	NA
17:53	180	13	NR	NR	NR	NA	64	.258	.037	NA	NA
17:58	180	7	NR	NR	NR	NA	74	.166	.029	NA	NA
19:06	190	9	NR	NR	NR	NA	64	.201	.030	NA	NA
19:12	NR	NR	299	46	NR	NA	71	.109	.021	NA	NA
19:25	NR	NR	NR	NR	NR	NA	62	NR	NR	NA	NA
19:32	NR	NR	NR	NR	NR	NA	60	.098	.019	NA	NA
19:36	NR	NR	299	50	NR	NA	68	NR	NR	NA	NA
19:41	NR	NR	NR	NR	NR	NA	NR	NR	NA	NA	NA
19:55	NR	NR	NR	NR	NR	NA	66	.071	.028	NA	NA
20:37	194	12	NR	NR	NR	NA	63	.038	.027	NA	NA
20:48	192	14	296	50	450	NA	52	.027	.018	NA	NA
20:54	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
21:03	NR	NR	NR	NR	NR	NA	42	NR	NR	NA	NA
21:15	NR	NR	NR	NR	NR	NA	44	NR	NR	NA	NA
21:23	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
0:40	NR	NR	NR	NR	NR	NA	NR	BDL	BDL	NA	NA
0:45	NR	NR	NR	NR	NR	NA	46	.180	.043	NA	NA
0:50	140	8	NR	NR	NR	NA	44	.062	.029	NA	NA
0:51	"	"	"	"	"	"	53	"	"	"	"
0:57	NR	NR	NR	NR	NR	NA	44	NR	NR	NA	NA
1:06	161	10	297	62	NR	NA	46	.068	.030	NA	NA
1:07	"	"	"	"	"	"	45	"	"	"	"
1:11	NR	NR	NR	NR	NR	NA	46	NR	NR	NA	NA
1:25	NR	NR	NR	NR	NR	NA	46	.025	.025	NA	NA
1:35	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
1:45	NR	NR	NR	NR	NR	NA	46	NR	NR	NA	NA
1:46	"	"	"	"	"	"	48	"	"	"	"
:50	NR	NR	NR	NR	NR	NA	NR	BDL	BDL	NA	NA
:58	NR	NR	NR	NR	NR	NA	37	BDL	BDL	NA	NA
2:08	NR	NR	NR	NR	NR	NA	38	.173	.057	NA	NA
2:20	NR	NR	NR	NR	NR	NA	35	.069	.046	NA	NA

02:25	NR	NR	NR	NR	NR	NA	38	.138	.056	NA	NA
02:34	184	15	612	66	NR	NA	43	.069	.039	NA	NA
02:40	NR	NR	NR	NR	NR	NA	38	.069	.046	NA	NA
03:45	NR	NR	NR	NR	NR	NA	34	.099	.046	NA	NA
04:45	200	16	NR	NR	NR	NA	29	.037	.024	NA	NA
04:50	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
04:55	NR	NR	NR	NR	NR	NA	24	NR	NR	NA	NA
05:15	NR	NR	NR	NR	NR	NA	25	.059	.025	NA	NA
05:22	210	16	295	60	NR	NA	23	.059	.030	NA	NA
05:24	"	"	"	"	"	"	21	NR	NR	"	"
05:40	NR	NR	NR	NR	NR	NA	25	NR	NR	NA	NA
05:50	210	16	NR	NR	NR	NA	32	.043	.020	NA	NA
05:55	NR	NR	NR	NR	NR	NA	25	.043	.024	NA	NA
06:00	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
06:15	NR	NR	NR	NR	NR	NA	25	.053	.025	NA	NA
06:16	"	"	"	"	"	"	22	"	"	"	"
06:30	NR	NR	NR	NR	NR	NA	32	.048	.025	NA	NA
06:40	210	14	NR	NR	NR	NA	23	.223	.041	NA	NA
06:46	NR	NR	NR	NR	NR	NA	26	.234	.041	NA	NA
06:47	"	"	"	"	"	"	29	"	"	"	"
06:51	NR	NR	NR	NR	NR	NA	30	.234	.041	NA	NA
06:57	NR	NR	NR	NR	NR	NA	23	.266	.040	NA	NA
07:15	NR	NR	NR	NR	NR	NA	22	.287	.044	NA	NA
07:35	NR	NR	NR	NR	NR	NA	22	.654	.075	NA	NA
07:47	NR	NR	NR	NR	NR	NA	19	.622	.071	NA	NA
08:00	210	11	NR	NR	NR	NA	20	.883	.084	NA	NA
08:01	"	"	"	"	"	"	22	"	"	"	"
08:10	NR	NR	NR	NR	NR	NA	31	1.000	.090	NA	NA
08:27	210	8	NR	NR	NR	NA	37	.543	.070	NA	NA
08:32	NR	NR	NR	NR	NR	NA	32	.410	.062	NA	NA
08:37	NR	NR	NR	NR	NR	NA	45	.612	.069	NA	NA
08:50	220	7	301	30	NR	NA	28	.941	.110	NA	NA
08:56	NR	NR	NR	NR	NR	NA	27	1.319	.120	NA	NA
09:11	210	3	NR	NR	NR	NA	33	1.417	.110	NA	NA
09:16	230	5	NR	NR	NR	NA	33	1.189	.110	NA	NA
09:24	228	2	NR	NR	NR	NA	35	1.508	.120	NA	NA
09:30	266	1	NR	NR	NR	NA	33	NR	NR	NA	NA
09:36	250	0	NR	NR	NR	NA	43	1.326	.110	NA	NA
09:41	230	1	NR	NR	NR	NA	38	NR	NR	NA	NA
09:44	277	2	306	33	NR	NA	34	1.470	.120	NA	NA
09:49	190	2	NR	NR	NR	NA	38	1.348	.120	NA	NA
09:57	207	3	305	25	NR	NA	NR	1.803	.120	NA	NA
0:02	202	3	NR	NR	NR	NA	40	1.652	.120	NA	NA
0:10	230	3	NR	NR	NR	NA	40	1.485	.110	NA	NA
0:15	196	4	306	25	NR	NA	42	1.682	.120	NA	NA
0:22	93	1	NR	NR	NR	NA	32	1.394	.120	NA	NA
0:27	190	3	306	28	NR	NA	43	1.697	.120	NA	NA
0:34	215	2	NR	NR	NR	NA	44	1.735	.120	NA	NA
0:39	203	3	NR	NR	NR	NA	52	1.811	.120	NA	NA
0:44	155	3	NR	NR	NR	NA	47	1.818	.120	NA	NA
0:52	164	2	NR	NR	NR	NA	36	1.652	.120	NA	NA
0:58	125	5	NR	NR	NR	NA	54	.947	.095	NA	NA
1:04	119	4	NR	NR	NR	NA	87	.917	.095	NA	NA
:09	124	3	305	25	NR	NA	54	.917	.095	NA	NA
:16	120	2	NR	NR	NR	NA	41	.848	.091	NA	NA
:26	126	4	NR	NR	NR	NA	57	.864	.091	NA	NA
:27	"	"	"	"	"	"	60	"	"	"	"
:33	148	5	305	34	NR	NA	63	.545	.072	NA	NA
:39	140	5	NR	NR	NR	NA	53	.682	.081	NA	NA
:45	114	4	NR	NR	NR	NA	21	.492	.073	NA	NA

11:52	123	6	306	32	NR	NA	30	.386	.064	NA	NA
12:00	127	9	NR	NR	NR	NA	46	NR	NR	NA	NA
12:06	140	NR	NR	NR	NR	NA	75	NR	NR	NA	NA
12:20	112	3	NR	NR	NR	NA	50	.424	.065	NA	NA
12:26	128	4	NR	NR	NR	NA	67	.288	.055	NA	NA
12:30	328	1	NR	NR	NR	NA	62	.386	.063	NA	NA
12:37	334	4	NR	NR	NR	NA	73	NR	NR	NA	NA
12:42	338	2	NR	NR	NR	NA	59	.364	.062	NA	NA

* * *

NR = NOT RECORDED

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BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

HIS DATA WAS RECORDED ON 06/15/84

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	$[O_3]$	[NO]	+/-	$[NO_2]$	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM^2)	(W/M^2)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
14:50	180	4	306	40	NR	NA	49	.176	.022	NA	NA
15:00	NR	6	NR	NR	NR	NA	48	.127	.019	NA	NA
15:12	202	8	306	42	NR	NA	49	.165	.021	NA	NA
15:19	211	8	306	35	NR	NA	46	.165	.021	NA	NA
15:30	184	9	305	40	NR	NA	47	STD	STD	-	-
15:38	190	6	305	NR	NR	NA	44	.334	.029	NA	NA
15:47	192	7	305	45	NR	NA	42	.248	.025	NA	NA
16:07	179	8	306	40	NR	NA	47	.424	.032	NA	NA
16:14	204	10	306	44	NR	NA	45	.227	.024	NA	NA
16:22	207	7	305	40	NR	NA	47	.178	.022	NA	NA
16:26	204	6	305	38	NR	NA	47	.158	.021	NA	NA
16:32	195	6	305	38	NR	NA	49	.123	.019	NA	NA
16:54	208	5	307	36	NR	NA	41	.134	.020	NA	NA
17:00	NR	NR	NR	NR	NR	NA	51	NR	NR	NA	NA
17:07	173	7	307	42	NR	NA	47	.246	.025	NA	NA
17:17	200	7	306	38	NR	NA	48	.313	.028	NA	NA
17:23	196	6	305	41	NR	NA	47	.336	.029	NA	NA
7:33	180	6	305	40	NR	NA	47	STD	STD	-	-
7:42	204	6	305	40	NR	NA	47	.176	.022	NA	NA
7:45	208	3	305	45	NR	NA	48	.190	.023	NA	NA
7:51	192	5	305	42	NR	NA	46	NR	NR	NA	NA

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" = THE SAME AS THE PRECEDING VALUE

BDL = BELOW THE DETECTION LIMIT

HIS DATA WAS RECORDED ON 06/16/84

TIME	WIND (DEGREES)	(MPH)	TEMP (K)	REL. HUM. (%)	C.C.N. (#/CM^2)	UV. FLUX (W/M^2)	[O_3] (PPB)	[NO] (PPB)	+/- (PPB)	[NO_2] (PPB)	+/- (PPB)
14:03	190	7	306	35	NR	NA	68	.262	.030	NA	NA
14:09	188	4	306	33	NR	NA	62	.195	.027	NA	NA
14:20	203	2	306	26	NR	NA	63	.185	.026	NA	NA
14:30	137	1	306	38	NR	NA	62	STD	STD	–	–
14:40	201	7	306	38	NR	NA	61	.185	.026	NA	NA
14:47	204	3	306	38	NR	NA	65	.917	.055	NA	NA
14:53	215	8	306	40	NR	NA	48	.192	.027	NA	NA
14:59	NR	NR	NR	61	NR	NA	NR	NR	NR	NA	NA
15:09	NR	NR	NR	53	NR	NA	NR	NR	NR	NA	NA
15:14	208	8	304	42	NR	NA	44	.099	.020	NA	NA
15:20	200	9	304	40	NR	NA	42	.147	.024	NA	NA
15:26	214	10	305	36	NR	NA	49	.153	.024	NA	NA
15:32	215	14	305	42	NR	NA	46	.157	.024	NA	NA
15:43	213	9	304	35	NR	NA	48	STD	STD	–	–
15:52	222	10	305	40	NR	NA	48	.201	.027	NA	NA
16:00	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
16:22	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
.6:35	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
.6:47	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
7:00	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
7:31	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
7:43	207	15	304	45	NR	NA	63	NR	NR	NA	NA
0:02	205	15	303	41	NR	NA	67	NR	NR	NA	NA
0:10	207	15	303	45	NR	NA	68	NR	NR	NA	NA
0:16	207	15	302	42	NR	NA	67	NR	NR	NA	NA
0:22	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA

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" = THE SAME AS THE PRECEDING VALUE

BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

IS DATA WAS RECORDED ON 06/18/84

TIME		WIND	TEMP	REL. HUM.	C.C.N.	UV. FLUX	[O$_3$]	[NO]	+/-	[NO$_2$]	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM^2)	(W/M^2)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
15:00	290	7	305	46	NR	NA	83	.312	.045	NA	NA
15:06	270	5	305	46	NR	NA	77	.312	.045	NA	NA
15:17	276	2	305	42	NR	NA	87	STD	STD	-	-
15:25	324	7	304	50	NR	NA	87	.369	.048	NA	NA
15:31	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
15:42	320	6	305	40	NR	NA	89	.375	.049	NA	NA
15:47	NR	6	305	42	NR	NA	92	.431	.052	NA	NA
15:55	268	5	306	41	NR	NA	88	.358	.048	NA	NA
6:25	301	6	305	42	NR	NA	87	NR	NR	NA	NA
6:44	304	5	305	42	NR	NA	93	.403	.050	NA	NA
6:54	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
7:00	285	13	304	45	NR	NA	86	NR	NR	NA	NA
7:16	293	16	303	NR	NR	NA	89	NR	NR	NA	NA

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STD = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE

BDL = BELOW THE DETECTION LIMIT

IS DATA WAS RECORDED ON 06/19/84

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	$[O_3]$	[NO]	+/-	$[NO_2]$	+/-
	(DEGREES)	(MPH)	(K)	(%)	$(\#/CM^2)$	(W/M^2)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
12:18	332	6	305	33	NR	NA	60	.309	.036	NA	NA
12:58	329	9	303	38	NR	NA	55	.168	.028	NA	NA
13:02	NR	NR	NR	NR	NR	NA	NR	NR	NA	NA	NA
13:06	290	8	304	37	NR	NA	64	STD	STD	–	–
13:17	325	9	303	33	NR	NA	62	.321	.037	NA	NA
13:39	332	5	304	34	NR	NA	65	.321	.037	NA	NA
13:35	281	4	305	40	NR	NA	68	.336	.037	NA	NA
13:42	287	10	305	41	NR	NA	62	.298	.035	NA	NA
13:47	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
13:54	17	9	305	36	NR	NA	68	.302	.036	NA	NA
14:00	47	6	304	45	NR	NA	69	.485	.044	NA	NA
14:05	69	9	305	40	NR	NA	68	.363	.039	NA	NA
16:33	275	15	306	38	NR	NA	73	.256	.033	NA	NA
16:38	264	15	307	37	NR	NA	69	.279	.034	NA	NA
.6:45	268	10	307	NR	NR	NA	73	STD	STD	–	–
7:00	NR	NR	NR	NR	NR	NA	NR	STD	STD	–	–
7:09	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
7:15	280	9	310	38	NR	NA	81	.303	.039	NA	NA
7:20	275	8	309	38	NR	NA	81	.263	.033	NA	NA
7:25	303	9	307	35	NR	NA	88	.248	.033	NA	NA
7:30	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
7:41	292	8	308	40	NR	NA	94	STD	STD	–	–
7:15	278	10	306	38	NR	NA	96	.347	.038	NA	NA
7:21	NR	NR	NR	NR	NR	NA	97	.355	.038	NA	NA
7:26	273	10	NR	NR	NR	NA	95	.382	.040	NA	NA
7:41	281	9	NR	NR	NR	NA	99	NR	NR	NA	NA
7:48	NR	NR	NR	NR	NR	NA	96	.359	.039	NA	NA
:49	"	"	"	"	"	"	89	.408	.041	"	"
:54	NR	NR	NR	NR	NR	NA	91	.332	.037	NA	NA
:59	NR	NR	NR	NR	NR	NA	97	.244	.032	NA	NA
:00	"	"	"	"	"	"	96	NR	NR	"	"
:04	275	9	NR	NR	NR	NA	93	.347	.038	NA	NA
:05	"	"	"	"	"	"	89	STD	STD	–	–
:07	NR	NR	304	42	NR	NA	89	NR	NR	NA	NA
:20	281	10	304	40	NR	NA	77	.225	.029	NA	NA
:21	"	"	"	"	"	"	80	NR	NR	"	"
:22	"	"	"	"	"	"	77	"	"	"	"

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[illegible]

TIME	WIND (DEGREES)	(MPH)	TEMP (K)	REL. HUM. (%)	C.C.N. (#/CM²)	UV. FLUX (W/M²)	[O$_3$] (PPB)	[NO] (PPB)	+/- (PPB)	[NO$_2$] (PPB)	+/- (PPB)
09:10	310	12	300	45	NR	NA	58	NR	NR	NA	NA
09:11	"	"	"	"	"	"	48	"	"	"	"
09:20	307	10	NR	NR	NR	NA	57	NR	NR	NA	NA
09:21	"	"	"	"	"	"	52	"	"	"	"
09:22	"	"	"	"	"	"	57	"	"	"	"
09:29	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
09:33	NR	NR	NR	NR	NR	NA	57	NR	NR	NA	NA
09:34	"	"	"	"	"	"	62	"	"	"	"
09:53	NR	NR	NR	NR	NR	NA	67	NR	NR	NA	NA
09:55	322	11	NR	NR	NR	NA	57	4.662	.194	NA	NA
09:56	"	"	"	"	"	"	71	"	"	"	"
09:57	"	"	"	"	"	"	67	"	"	"	"
09:58	"	"	"	"	"	"	63	3.892	.178	"	"
10:14	318	9	NR	NR	NR	NA	65	2.625	.149	NA	NA
10:15	"	"	"	"	"	"	70	"	"	"	"
0:23	327	9	305	32	NR	NA	68	1.931	.130	NA	NA
0:24	"	"	"	"	"	"	70	NR	NR	"	"
0:25	"	"	"	"	"	"	57	"	"	"	"
0:26	"	"	"	"	"	"	70	"	"	"	"
0:27	"	"	"	"	"	"	68	"	"	"	"
0:28	"	"	"	"	"	"	69	"	"	"	"
0:29	"	"	"	"	"	"	89	"	"	"	"
0:30	311	9	NR	NR	5400	NA	68	2.045	.133	NA	NA
0:31	"	"	"	"	"	"	74	NR	NR	"	"
0:32	"	"	"	"	"	"	73	"	"	"	"
0:33	"	"	"	"	"	"	62	"	"	"	"
0:40	305	9	NR	NR	NR	NA	73	1.778	.126	NA	NA
:41	"	"	"	"	"	"	"	NR	NR	"	"
:42	"	"	"	"	"	"	72	"	"	"	"
:43	"	"	"	"	"	"	69	"	"	"	"
:48	325	8	303	38	NR	NA	71	1.564	.119	NA	NA
:55	319	7	302	38	NR	NA	66	1.557	.119	NA	NA
:00	328	8	303	33	NR	NA	76	1.778	.126	NA	NA
:06	NR	NR	NR	NR	2400	NA	75	1.648	.122	NA	NA
:07	"	"	"	"	"	"	83	NR	NR	"	"
:08	"	"	"	"	"	"	73	"	"	"	"
:16	327	13	NR	NR	NR	NA	64	1.091	.103	NA	NA
:17	"	"	"	"	"	"	80	NR	NR	"	"
:18	"	"	"	"	"	"	69	"	"	"	"
:23	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
:26	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
29	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
32	334	6	303	35	NR	NA	71	1.012	.062	NA	NA
33	"	"	"	"	"	"	76	NR	NR	"	"
34	"	"	"	"	"	"	84	"	"	"	"
35	"	"	"	"	"	"	81	"	"	"	"
36	"	"	"	"	"	"	71	"	"	"	"
37	"	"	"	"	"	"	76	.897	.059	"	"
38	"	"	"	"	"	"	74	NR	NR	"	"

11:37		"	"	"	"	"	72	"	"	"	"
11:40	313	12	NR	NR	NR	NA	74	NR	NR	NA	NA
11:41	"	"	"	"	"	"	72	"	"	"	"
11:42	"	"	"	"	"	"	75	"	"	"	"
11:43	"	"	"	"	"	"	66	"	"	"	"
11:50	313	9	NR	NR	NR	NA	70	.705	.053	NA	NA
11:51	"	"	"	"	"	"	75	NR	NR	"	"
11:52	"	"	"	"	"	"	77	"	"	"	"
11:53	"	"	"	"	"	"	74	"	"	"	"
11:54	"	"	"	"	"	"	76	"	"	"	"
11:55	"	"	"	"	"	"	87	.365	.048	"	"
12:00	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
12:02	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
12:05	323	12	304	32	NR	NA	78	NR	NR	NA	NA
12:14	316	10	303	32	NR	NA	81	.509	.046	NA	NA
12:15	"	"	"	"	"	"	77	NR	NR	"	"
12:16	"	"	"	"	"	"	61	"	"	"	"
12:17	"	"	"	"	"	"	59	"	"	"	"
12:18	"	"	"	"	"	"	71	"	"	"	"
12:19	"	"	"	"	"	"	76	"	"	"	"
12:20	"	"	"	"	"	"	75	"	"	"	"
12:21	"	"	"	"	"	"	37	"	"	"	"
2:22	"	"	"	"	"	"	72	"	"	"	"
2:23	"	"	"	"	"	"	76	"	"	"	"
2:24	"	"	"	"	"	"	"	"	"	"	"
2:25	"	"	"	"	"	"	41	"	"	"	"
2:26	"	"	"	"	"	"	81	"	"	"	"
2:30	NR	NR	NR	NR	NR	NA	77	.436	.043	NA	NA
2:31	"	"	"	"	"	"	87	NR	NR	"	"
2:32	"	"	"	"	"	"	67	"	"	"	"
2:33	"	"	"	"	"	"	77	"	"	"	"
2:34	"	"	"	"	"	"	83	.405	.042	"	"
2:40	NR	NR	NR	NR	NR	NA	72	.297	.037	NA	NA
2:45	NR	NR	NR	NR	NR	NA	83	NR	NR	NA	NA
:53	NR	NR	NR	NR	NR	NA	78	NR	NR	NA	NA
:30	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
:36	315	6	NR	NR	NR	NA	63	NR	NR	NA	NA
:40	309	8	305	41	NR	NA	84	NR	NR	NA	NA
:41	"	"	"	"	"	"	59	NR	NR	NA	NA
:44	NR	NR	NR	NR	NR	NA	67	NR	NR	NA	NA
:47	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
:49	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
:56	336	3	306	34	NR	NA	74	NR	NR	NA	NA
:03	294	5	305	38	NR	NA	73	.363	.040	NA	NA
:08	317	10	305	42	NR	NA	65	.272	.036	NA	NA
17	301	9	305	35	NR	NA	67	NR	NR	NA	NA
25	281	8	305	35	NR	NA	67	.236	.036	NA	NA
30	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
40	310	5	307	34	NR	NA	59	.345	.039	NA	NA
45	322	7	306	32	NR	NA	27	.230	.034	NA	NA
55	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
06	309	12	306	35	NR	NA	71	.300	.032	NA	NA
16	316	6	306	34	NR	NA	71	NR	NR	NA	NA
29	303	12	306	NR	NR	NA	[illegible]	NR	NR	NA	NA
35	299	3	306	34	NR	NA	77	.359	.050	NA	NA
32	351	4	307	30	NR	NA	52	.271	.047	NA	NA
[illegible]	313	11	307	35	NR	NA	75	.337	.043	NA	NA
[illegible]	[illegible]	4	306	37	NR	NA	76	.338	.044	NA	NA
5	312	8	306	40	NR	NA	71	NR	NR	NA	NA
1	320	11	306	33	NR	NA	31	NR	NR	NA	NA

16:13	[illegible]	7	306	34	NR	NA	77	.350	.050	NA	NA
16:37	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
16:40	273	12	305	29	NR	NA	82	.301	.047	NA	NA
16:47	306	11	307	34	NR	NA	73	.277	.046	NA	NA
16:53	311	11	307	36	NR	NA	80	.296	.047	NA	NA
17:00	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
17:05	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
17:10	267	10	309	35	NR	NA	79	.189	.041	NA	NA
17:16	271	11	309	35	NR	NA	66	.175	.040	NA	NA
17:23	NR	8	307	38	NR	NA	74	.199	.041	NA	NA
17:27	300	8	306	32	NR	NA	69	.291	.047	NA	NA
18:05	310	7	NR	NR	NR	NA	NR	.300	.036	NA	NA
18:35	310	7	306	36	NR	NA	78	.323	.038	NA	NA
18:43	NR	NR	NR	NR	NR	NA	78	.400	.041	NA	NA
18:44	"	"	"	"	"	"	83	NR	NR	"	"
18:45	"	"	"	"	"	"	85	"	"	"	"
18:48	NR	NR	NR	NR	NR	NA	86	.273	.035	NA	NA
18:49	"	"	"	"	"	"	94	NR	NR	"	"
18:57	NR	NR	NR	NR	NR	NA	86	.169	.029	NA	NA
19:03	NR	NR	NR	NR	NR	NA	83	.177	.029	NA	NA
19:04	"	"	"	"	"	"	79	NR	NR	"	"
19:05	"	"	"	"	"	"	66	"	"	"	"
19:08	285	11	306	36	NR	NA	76	.219	.032	NA	NA
19:09	"	"	"	"	"	"	87	"	"	"	"
9:13	NR	NR	NR	NR	NR	NA	83	.188	.030	NA	NA
9:14	"	"	"	"	"	"	75	NR	NR	"	"
9:15	"	"	"	"	"	"	89	"	"	"	"
9:19	NR	NR	NR	NR	NR	NA	75	.192	.030	NA	NA
9:27	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
0:14	328	10	303	45	NR	NA	67	.092	.023	NA	NA
0:19	NR	NR	NR	NR	NR	NA	75	.058	.020	NA	NA
0:20	"	"	"	"	"	"	73	NR	NR	"	"
0:25	NR	NR	NR	NR	NR	NA	70	.054	.022	NA	NA
0:30	NR	NR	NR	NR	NR	NA	NR	.085	.022	NA	NA
0:35	NR	NR	301	57	NR	NA	48	NR	NR	NA	NA
:45	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
:52	NR	NR	NR	NR	NR	NA	49	NR	NR	NA	NA
:07	145	11	299	60	NR	NA	53	BDL	BDL	NA	NA
:08	"	"	"	"	"	"	49	NR	NR	"	"
:20	155	9	NR	NR	NR	NA	46	.219	.032	NA	NA
:21	149	9	"	"	"	"	52	NR	NR	NA	NA
:22	"	"	"	"	"	"	59	NR	NR	NA	NA
:25	NR	NR	NR	NR	NR	NA	57	.119	.025	NA	NA
:30	150	13	NR	NR	NR	NA	56	.188	.030	NA	NA
:40	144	11	298	64	NR	NA	44	BDL	BDL	NA	NA
:50	137	12	NR	NR	NR	NA	NR	NR	NR	NA	NA
02	146	14	NR	NR	NR	NA	64	NR	NR	NA	NA
12	NR	NR	NR	NR	NR	NA	55	.031	.017	NA	NA
17	NR	NR	298	62	NR	NA	59	.031	.017	NA	NA
23	NR	NR	NR	NR	NR	NA	57	.019	.016	NA	NA
28	NR	NR	NR	NR	NR	NA	55	BDL	BDL	NA	NA
34	136	12	NR	NR	NR	NA	49	.027	.017	NA	NA
40	NR	NR	NR	NR	NR	NA	56	NR	NR	NA	NA
55	148	14	NR	NR	NR	NA	53	BDL	BDL	NA	NA

NR = NOT RECORDED

NA = NOT AVAILABLE

STD = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE

BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

THE DATA WAS RECORDED ON 06/21/84

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	[O_3]	[NO]	+/-	[NO_2]	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM²)	(N/M²)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
08:25	150	11	297	100	NR	NA	33	NR	NR	NA	NA
08:30	"	"	"	"	"	"	40	"	"	"	"
08:37	NR	NR	NR	NR	NR	NA	41	NR	NR	NA	NA
09:14	NR	NR	NR	NR	NR	NA	44	NR	NR	NA	NA
09:25	182	3	303	42	NR	NA	49	NR	NR	NA	NA
09:30	186	0	303	50	NR	NA	50	NR	NR	NA	NA
09:38	142	0	303	48	NR	NA	49	NR	NR	NA	NA
09:46	155	3	303	48	NR	NA	53	.674	.055	NA	NA
09:47	"	"	"	"	"	"	54	NR	NR	"	"
09:48	"	"	"	"	"	"	37	"	"	"	"
09:49	"	"	"	"	"	"	42	"	"	"	"
09:50	"	"	"	"	"	"	52	"	"	"	"
09:51	"	"	"	"	"	"	40	"	"	"	"
9:52	"	"	"	"	"	"	44	.601	.052	"	"
9:53	"	"	"	"	"	"	45	NR	NR	"	"
9:54	"	"	"	"	"	"	46	"	"	"	"
9:55	"	"	"	"	"	"	48	"	"	"	"
9:56	"	"	"	"	"	"	50	"	"	"	"
9:57	"	"	"	"	"	"	43	"	"	"	"
9:58	"	"	"	"	"	"	51	.506	.048	"	"
9:59	"	"	"	"	"	"	"	NR	NR	"	"
0:07	170	2	303	43	NR	NA	43	NR	NR	NA	NA
0:08	"	"	"	"	"	"	59	"	"	"	"
0:09	"	"	"	"	"	"	50	"	"	"	"
0:10	"	"	"	"	"	"	"	"	"	"	"
0:11	"	"	"	"	"	"	43	"	"	"	"
0:12	"	"	"	"	"	"	51	"	"	"	"
:13	"	"	"	"	"	"	48	"	"	"	"
:20	211	3	303	42	NR	NA	46	.387	.042	NA	NA
:21	"	"	"	"	"	"	49	NR	NR	"	"
:22	"	"	"	"	"	"	54	"	"	"	"
:23	"	"	"	"	"	"	55	"	"	"	"
:24	"	"	"	"	"	"	52	"	"	"	"
:25	"	"	"	"	"	"	46	.369	.041	"	"
:26	"	"	"	"	"	"	63	NR	NR	"	"
:30	NR	NR	NR	NR	NR	NA	45	NR	NR	NA	NA
:31	"	"	"	"	"	"	48	"	"	"	"
:32	"	"	"	"	"	"	56	"	"	"	"
:33	"	"	"	"	"	"	51	"	"	"	"
34	"	"	"	"	"	"	"	"	"	"	"
31	110	3	303	45	NR	NA	74	.359	.040	NA	NA
36	67	3	303	40	NR	NA	67	.323	.038	NA	NA
41	109	2	303	42	NR	NA	57	NR	NR	NA	NA
51	97	3	303	40	NR	NA	70	.346	.039	NA	NA
03	159	7	304	49	NR	NA	67	.323	.038	NA	NA
11	106	2	304	41	NR	NA	68	.270	.034	NA	NA
16	226	6	305	42	NR	NA	64	.247	.033	NA	NA
24	90	2	305	39	NR	NA	69	.279	.035	NA	NA

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	NA	NA
12:48	131	3	305	42	NR	NA	77	.270	.035	NA	NA
13:55	119	1	305	38	NR	NA	91	.208	.033	NA	NA
14:01	105	1	305	40	NR	NA	99	.271	.038	NA	NA
14:07	128	4	305	50	NR	NA	96	NR	NR	NA	NA
14:19	154	6	305	40	NR	NA	94	.417	.046	NA	NA
14:45	209	2	306	40	NR	NA	101	.271	.038	NA	NA
14:51	223	5	307	45	NR	NA	109	.083	.021	NA	NA
14:58	273	3	307	41	NR	NA	109	.219	.034	NA	NA
15:05	217	2	306	45	NR	NA	115	NR	NR	NA	NA
5:12	261	5	306	45	NR	NA	110	.109	.024	NA	NA
5:19	356	4	305	50	NR	NA	105	.094	.022	NA	NA
5:50	258	6	308	48	NR	NA	117	.308	.040	NA	NA
5:55	247	4	307	40	NR	NA	124	.172	.030	NA	NA
6:00	261	3	307	34	NR	NA	120	.177	.030	NA	NA
6:06	315	3	306	NR	NR	NA	127	.167	.029	NA	NA
6:25	343	25	298	60	NR	NA	94	.141	.027	NA	NA
6:30	353	24	298	60	NR	NA	58	.188	.031	NA	NA
6:38	108	24	297	78	NR	NA	39	.156	.029	NA	NA
6:44	110	28	297	80	NR	NA	66	.125	.025	NA	NA
6:49	115	15	297	81	NR	NA	66	.198	.032	NA	NA
6:55	116	16	297	79	450	NA	76	.162	.029	NA	NA
7:00	123	14	297	80	NR	NA	66	.255	.036	NA	NA
7:17	103	16	298	75	NR	NA	81	.104	.023	NA	NA
7:32	111	11	298	63	NR	NA	78	.302	.040	NA	NA
7:35	162	19	298	85	NR	NA	71	.026	.012	NA	NA
:38	130	16	300	86	NR	NA	62	.266	.037	NA	NA
:45	115	14	297	85	NR	NA	63	.375	.044	NA	NA
:58	NR	NR	NR	NR	450	NA	NR	NR	NR	NA	NA
:04	130	11	297	95	NR	NA	54	.605	.056	NA	NA
:09	127	14	298	95	NR	NA	61	.813	.065	NA	NA
:16	119	13	298	90	NR	NA	57	.751	.063	NA	NA
:17	"	"	"	"	"	"	44	NR	NR	"	"
:18	"	"	"	"	"	"	55	"	"	"	"
:19	"	"	"	"	"	"	62	"	"	"	"
:20	"	"	"	"	"	"	65	"	"	"	"
:21	"	"	"	"	"	"	73	.839	.066	"	"
:22	"	"	"	"	"	"	41	NR	NR	"	"
:23	"	"	"	"	"	"	75	"	"	"	"
:24	"	"	"	"	"	"	52	"	"	"	"
25	"	"	"	"	"	"	60	"	"	"	"
26	"	"	"	"	"	"	62	"	"	"	"
27	"	"	"	"	"	"	44	"	"	"	"
28	"	"	"	"	"	"	76	.712	.069	"	"
29	"	"	"	"	"	"	5	NR	NR	"	"
30	"	"	"	"	"	"	55	"	"	"	"
31	"	"	"	"	"	"	59	"	"	"	"
32	"	"	"	"	"	"	67	"	"	"	"
33	"	"	"	"	"	"	39	"	"	"	"
34	"	"	"	"	"	"	67	.829	.066	"	"
35	"	"	"	"	"	"	51	NR	NR	"	"
59	107	11	297	90	NR	NA	44	NR	NR	NA	NA
00	"	"	"	"	"	"	48	"	"	"	"
01	"	"	"	"	"	"	53	"	"	"	"
02	"	"	"	"	"	"	43	"	"	"	"
05	118	9	297	90	NR	NA	40	.271	.044	NA	NA
15	130	12	296	100	NR	NA	47	.010	.007	NA	NA
50	NR	NR	NR	NR	NA	NA	43	BDL	BDL	NA	NA
51	"	"	"	"	"	"	55	NR	NR	"	"

NR = NOT RECORDED

NA = NOT AVAILABLE

STD = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE

BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

```
IS DATA WAS RECORDED ON 06/22/84

                                      REL.               UV.
TIME          WIND   TEMP   HUM.    C.C.N.    FLUX    [O3]      [NO]      +/-      [NO2]     +/-

  (DEGREES)(MPH)(K)      (%)     (#/CM3)(W/M2)  (PPB)     (PPB)     (PPB)     (PPB)   (PPB)


09:20       115    6    295     100     NR      NA      30          NR        NR        NA        NA
10:04       123    7    296      90     NR      NA      45       2.646      .116        NA        NA
10:05        "     "     "        "      "       "      42          NR        NR         "         "
10:06        "     "     "        "      "       "      39           "         "         "         "
10:07        "     "     "        "      "       "      38           "         "         "         "
10:08        "     "     "        "      "       "      42           "         "         "         "
10:09        "     "     "        "      "       "      39           "         "         "         "
 0:10        "     "     "        "      "       "      45       2.005      .101         "         "
 0:11        "     "     "        "      "       "      47           "         "         "         "
 0:12        "     "     "        "      "       "      40           "         "         "         "
 0:13        "     "     "        "      "       "      48           "         "         "         "
 0:14        "     "     "        "      "       "      49           "         "         "         "
 0:15        "     "     "        "      "       "       "       1.338      .083         "         "
 0:16        "     "     "        "      "       "      46           "         "         "         "
 0:17        "     "     "        "      "       "      44           "         "         "         "
 0:18        "     "     "        "      "       "      48           "         "         "         "
 0:19        "     "     "        "      "       "      27           "         "         "         "
 0:20        "     "     "        "      "       "      46           "         "         "         "
 0:21        "     "     "        "      "       "      48       1.297      .092         "         "
  :29       120    6    298      79     NR      NA      48          NR        NR        NA        NA
  :30        "     "     "        "      "       "      53           "         "         "         "
  :31        "     "     "        "      "       "      49           "         "         "         "
  :35       113    9    297      58     NR      NA      53        .805      .064        NA        NA
  :36        "     "     "        "      "       "      49          NR        NR         "         "
  :37        "     "     "        "      "       "      52           "         "         "         "
  :38        "     "     "        "      "       "      49           "         "         "         "
  :39        "     "     "        "      "       "      55           "         "         "         "
  :40        "     "     "        "      "       "      46           "         "         "         "
  :50       110    6     NR      NR     NR      NA      49        .559      .054        NA        NA
  :55        NR   NR     NR      NR     NR      NA      50        .579      .055        NA        NA
  :17       128   12    297      83     NR      NA      52        .697      .060        NA        NA
  :18        "     "     "        "      "       "      54        .492      .051         "         "
  .19        "     "     "        "      "       "      53           "         "         "         "
   20        "     "     "        "      "       "      58           "         "         "         "
   21        "     "     "        "      "       "      51           "         "         "         "
   22        "     "     "        "      "       "      60           "         "         "         "
   23        "     "     "        "      "       "      52           "         "         "         "
   24        "     "     "        "      "       "      54        .534      .053         "         "
   25        "     "     "        "      "       "      51           "         "         "         "
   26        "     "     "        "      "       "      53           "         "         "         "
   27        "     "     "        "      "       "       "           "         "         "         "
   28        "     "     "        "      "       "      56           "         "         "         "
   29        "     "     "        "      "       "      55           "         "         "         "
   30        "     "     "        "      "       "      47        .662      .058         "         "
   31        "     "     "        "      "       "      56           "         "         "         "
   [illegible] "  "     "        "      "       "      [illegible]  "         "         "         "
   33       112   12    297      NR     NR      NA      52        .851      .066        NA        NA
   [illegible] "        "        "      "       "      75          NR        NR         "         "
```

11:42	"	"	"	"	"	"	57	"	"	"	"
11:43	"	"	"	"	"	"	"	"	"	"	"
11:44	"	"	"	"	"	"	48	"	"	"	"
11:45	"	"	"	"	"	"	56	"	"	"	"
11:46	"	"	"	"	"	"	52	"	"	"	"
11:47	"	"	"	"	"	"	44	"	"	"	"
11:48	"	"	"	"	"	"	53	"	"	"	"
11:49	"	"	"	"	"	"	48	"	"	"	"
11:50	"	"	"	"	"	"	51	"	"	"	"
11:51	"	"	"	"	"	"	50	"	"	"	"
11:52	"	"	"	"	"	"	33	"	"	"	"
11:53	"	"	"	"	"	"	52	"	"	"	"
11:54	"	"	"	"	"	"	47	"	"	"	"
11:55	"	"	"	"	"	"	55	"	"	"	"
11:56	"	"	"	"	"	"	48	"	"	"	"
11:57	"	"	"	"	"	"	54	"	"	"	"
12:15	129	10	297	88	NR	NA	57	.477	.049	NA	NA
.2:16	"	"	"	"	"	"	54	NR	NR	"	"
.2:17	"	"	"	"	"	"	57	"	"	"	"
2:18	"	"	"	"	"	"	55	"	"	"	"
2:19	"	"	"	"	"	"	50	"	"	"	"
2:20	"	"	"	"	"	"	47	.569	.054	"	"
2:21	"	"	"	"	"	"	56	"	"	"	"
2:29	94	6	298	80	NR	NA	52	NR	NR	NA	NA
2:30	"	"	"	"	"	"	59	"	"	"	"
2:31	"	"	"	"	"	"	56	"	"	"	"
2:32	"	"	"	"	"	"	57	"	"	"	"
2:43	137	9	298	90	NR	NA	51	2.708	.118	NA	NA
2:44	"	"	"	"	"	"	59	NR	NR	"	"
2:45	"	"	"	"	"	"	56	"	"	"	"
2:46	"	"	"	"	"	"	57	"	"	"	"
:47	"	"	"	"	"	"	54	"	"	"	"
:57	128	13	298	90	NR	NA	49	.287	.038	NA	NA
:58	"	"	"	"	"	"	54	NR	NR	"	"
:59	"	"	"	"	"	"	47	"	"	"	"
:00	"	"	"	"	"	"	64	"	"	"	"
:04	127	7	298	80	NR	NA	60	.385	.044	NA	NA
:10	133	7	298	85	2400	NA	63	.334	.043	NA	NA
:41	117	15	299	80	NR	NA	55	.251	.036	NA	NA
:52	123	15	299	80	NR	NA	49	.338	.042	NA	NA
:04	121	13	298	80	NR	NA	51	.297	.039	NA	NA
:19	125	13	299	78	NR	NA	55	.405	.046	NA	NA
:23	109	13	299	78	NR	NA	49	.462	.047	NA	NA
:29	113	13	299	80	NR	NA	46	.241	.035	NA	NA
:34	115	16	298	88	NR	NA	50	.313	.040	NA	NA
47	125	18	298	97	NR	NA	48	NR	NR	NA	NA
06	112	20	298	95	NR	NA	53	.369	.044	NA	NA
12	109	17	297	100	NR	NA	51	.297	.039	NA	NA
20	123	23	296	100	NR	NA	49	.462	.047	NA	NA
25	115	17	297	100	NR	NA	47	.497	.051	NA	NA
30	121	22	296	100	NR	NA	49	.338	.041	NA	NA
00	113	19	296	100	NR	NA	44	NR	NR	NA	NA
05	114	13	296	120	NR	NA	43	.510	.056	NA	NA
11	120	15	295	100	NR	NA	47	.488	.055	NA	NA
16	125	13	295	100	NR	NA	46	.364	.043	NA	NA
[illegible]	120	14	294	100	NR	NA	72	.382	.047	NA	NA
[illegible]	NR	NR	NR	NR	NR	NA	NR	.354	.070	NA	NA
[illegible]	NR	NR	NR	NR	NR	NA	49	.549	.074	NA	NA
[illegible]	"	"	"	"	"	"	50	NR	NR	"	"
[illegible]	134	15	290	100	NR	NA	47	.579	.053	NA	NA

```
18:47                                                   46        .897  .056
19:30    140   14    295    100    NR     NA      51        .564  .054       NA        NA
19:33     NR   NR     NR     NR    NR     NA      54        .528  .052       NA        NA
```

```
NR = NOT RECORDED

NA = NOT AVAILABLE

STD  = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE

BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT
```

IS DATA WAS RECORDED ON 06/23/84

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	[O_3]	[NO]	+/-	[NO_2]	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM²)	(W/M²)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
15:00	175	6	301	53	NR	NA	62	1.009	.053	NA	NA
15:07	NR	NR	NR	NR	NR	NA	54	NR	NR	NA	NA
15:12	NR	NR	NR	NR	NR	NA	54	NR	NR	NA	NA
15:20	NR	NR	NR	NR	NR	NA	53	NR	NR	NA	NA
15:30	130	8	NR	NR	NR	NA	55	NR	NR	NA	NA
15:42	NR	NR	NR	NR	NR	NA	56	NR	NR	NA	NA
15:56	NR	NR	301	65	NR	NA	54	.240	.026	NA	NA
5:57	"	"	"	"	"	"	55	NR	NR	"	"
5:58	"	"	"	"	"	"	"	"	"	"	"
5:59	"	"	"	"	"	"	53	"	"	"	"
6:00	"	"	"	"	"	"	54	"	"	"	"
6:01	"	"	"	"	"	"	55	"	"	"	"
6:02	"	"	"	"	"	"	58	.109	.017	"	"
6:03	"	"	"	"	"	"	56	NR	NR	"	"
6:04	"	"	"	"	"	"	54	"	"	"	"
6:05	"	"	"	"	"	"	58	"	"	"	"
6:06	"	"	"	"	"	"	57	"	"	"	"
:07	"	"	"	"	"	"	59	"	"	"	"
:08	"	"	"	"	"	"	56	.176	.022	"	"
:09	"	"	"	"	"	"	57	NR	NR	"	"
:17	133	7	300	70	NR	NA	57	.243	.026	NA	NA
:18	"	"	"	"	"	"	62	NR	NR	"	"
:19	"	"	"	"	"	"	59	"	"	"	"
:30	NR	NR	NR	NR	NR	NA	68	NR	NR	NA	NA
:31	"	"	"	"	"	"	58	"	"	"	"
:32	"	"	"	"	"	"	59	"	"	"	"
:33	"	"	"	"	"	"	58	"	"	"	"
:52	NR	NR	301	70	NR	NA	59	.229	.025	NA	NA
:53	"	"	"	"	"	"	58	NR	NR	"	"
54	"	"	"	"	"	"	63	"	"	"	"
55	"	"	"	"	"	"	59	"	"	"	"
56	"	"	"	"	"	"	63	"	"	"	"
07	NR	NR	NR	NR	NR	NA	60	.178	.022	NA	NA
08	"	"	"	"	"	"	62	STD	STD	—	—
09	"	"	"	"	"	"	54	"	"	NA	NA
26	NR	NR	NR	NR	NR	NA	NR	.151	.020	NA	NA
30	170	11	298	73	NR	NA	53	NR	NR	NA	NA
35	NR	NR	NR	NR	NR	NA	53	NR	NR	NA	NA
41	165	12	NR	NR	NR	NA	52	NR	NR	NA	NA
46	NR	NR	NR	NR	NR	NA	48	NR	NR	NA	NA
30	NR	NR	NR	NR	NR	NA	44	NR	NR	NA	NA

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" = THE SAME AS THE PRECEDING VALUE

BDL = BELOW THE DETECTION LIMIT

IS DATA WAS RECORDED ON 06/24/84

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	$[O_3]$	[NO]	+/-	$[NO_2]$	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM²)	(W/M²)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
12:45	302	8	300	58	NR	NA	64	1.729	.082	NA	NA
12:46	"	"	"	"	"	"	62	NR	NR	"	"
12:47	"	"	"	"	"	"	74	"	"	"	"
12:48	"	"	"	"	"	"	80	"	"	"	"
12:49	"	"	"	"	"	"	75	"	"	"	"
12:50	"	"	"	"	"	"	73	"	"	"	"
12:51	"	"	"	"	"	"	54	1.545	.078	"	"
2:52	"	"	"	"	"	"	66	NR	NR	"	"
2:53	"	"	"	"	"	"	58	"	"	"	"
2:54	"	"	"	"	"	"	68	"	"	"	"
2:55	"	"	"	"	"	"	73	"	"	"	"
2:56	"	"	"	"	"	"	72	"	"	"	"
2:57	"	"	"	"	"	"	69	1.090	.065	"	"
2:58	"	"	"	"	"	"	68	NR	NR	"	"
2:59	"	"	"	"	"	"	79	"	"	"	"
3:00	"	"	"	"	"	"	51	.914	.060	"	"
3:06	290	9	301	58	NR	NA	72	NR	NR	NA	NA
3:07	"	"	"	"	"	"	"	"	"	"	"
3:08	"	"	"	"	"	"	75	"	"	"	"
3:09	"	"	"	"	"	"	71	1.027	.064	"	"
3:10	"	"	"	"	"	"	70	NR	NR	"	"
:13	NR	NR	NR	NR	1600	NA	NR	NR	NR	NA	NA
:22	325	6	300	60	NR	NA	86	.800	.056	NA	NA
:23	"	"	"	"	"	"	68	NR	NR	"	"
:24	"	"	"	"	"	"	77	"	"	"	"
:25	"	"	"	"	"	"	78	"	"	"	"
:26	"	"	"	"	"	"	81	"	"	"	"
:30	NR	NR	NR	NR	NR	NA	62	.690	.052	NA	NA
:31	"	"	"	"	"	"	74	NR	NR	"	"
:32	"	"	"	"	"	"	71	"	"	"	"
:33	"	"	"	"	"	"	64	"	"	"	"
:34	"	"	"	"	"	"	74	"	"	"	"
:35	"	"	"	"	"	"	66	.510	.045	"	"
:36	"	"	"	"	"	"	69	NR	NR	"	"
:43	311	6	301	53	NR	NA	71	NR	NR	NA	NA
44	"	"	"	"	"	"	69	"	"	"	"
45	"	"	"	"	"	"	71	"	"	"	"
46	"	"	"	"	"	"	67	"	"	"	"
47	"	"	"	"	"	"	77	"	"	"	"
48	"	"	"	"	"	"	74	"	"	"	"
49	"	"	"	"	"	"	71	"	"	"	"
52	309	7	300	62	NR	NA	75	.690	.052	NA	NA
53	"	"	"	"	"	"	70	NR	NR	"	"
54	"	"	"	"	"	"	67	"	"	"	"
55	"	"	"	"	"	"	57	"	"	"	"
1[illegible]	311	12	300	10	NR	NA	60	NR	NR	NA	NA
17	NR	NR	NR	NR	NR	NA	73	NR	NR	NA	NA
20	NR	NR	NR	NR	NR	NA	65	NR	NR	NA	NA

14:30	312	9	301	58	NR	NA	57	.934	.062	NA	NA
14:40	320	10	301	60	NR	NA	54	.369	.033	NA	NA
14:53	67	7	301	60	NR	NA	64	NR	NR	NA	NA
15:04	86	9	300	68	NR	NA	28	NR	NR	NA	NA
15:15	87	5	302	62	NR	NA	60	NR	NR	NA	NA
15:35	73	10	302	54	NR	NA	54	NR	NR	NA	NA
15:45	79	6	301	55	NR	NA	47	NR	NR	NA	NA
15:58	93	7	301	58	NR	NA	57	NR	NR	NA	NA
17:14	46	7	303	58	NR	NA	54	NR	NR	NA	NA
17:26	63	6	304	60	NR	NA	58	NR	NR	NA	NA
17:35	88	7	304	51	NR	NA	64	NR	NR	NA	NA
17:55	77	5	305	52	NR	NA	59	NR	NR	NA	NA
18:13	81	10	305	51	NR	NA	60	NR	NR	NA	NA
18:20	86	8	305	50	NR	NA	72	NR	NR	NA	NA
18:35	75	8	301	55	NR	NA	57	NR	NR	NA	NA
19:00	NR	NR	NR	NR	1000	NA	NR	NR	NR	NA	NA

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STD = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE

BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

HIS DATA WAS RECORDED ON 06/25/84

TIME	WIND (DEGREES)	(MPH)	TEMP (K)	REL. HUM. (%)	C.C.N. (#/CM^2)	UV. FLUX (W/M^2)	[O$_3$] (PPB)	[NO] (PPB)	+/- (PPB)	[NO$_2$] (PPB)	+/- (PPB)
10:20	85	10	302	45	NR	NA	48	2.364	.084	NA	NA
10:21	"	"	"	"	"	"	51	NR	NR	"	"
10:22	"	"	"	"	"	"	35	"	"	"	"
10:23	"	"	"	"	"	"	40	"	"	"	"
10:24	"	"	"	"	"	"	46	"	"	"	"
10:25	"	"	"	"	"	"	50	1.954	.076	"	"
10:36	85	9	300	42	8000	NA	53	NR	NR	NA	NA
0:37	"	"	"	"	"	"	52	1.277	.062	"	"
0:38	"	"	"	"	"	"	56	NR	NR	"	"
0:39	"	"	"	"	"	"	70	"	"	"	"
0:40	"	"	"	"	"	"	75	"	"	"	"
0:41	"	"	"	"	"	"	47	"	"	"	"
0:42	"	"	"	"	"	"	71	1.239	.061	"	"
0:43	"	"	"	"	"	"	41	NR	NR	"	"
0:44	"	"	"	"	"	"	60	"	"	"	"
0:45	"	"	"	"	"	"	59	"	"	"	"
0:46	"	"	"	"	"	"	58	"	"	"	"
0:47	"	"	"	"	"	"	53	"	"	"	"
0:48	"	"	"	"	"	"	51	.902	.052	"	"
:49	"	"	"	"	"	"	57	NR	NR	"	"
:50	"	"	"	"	"	"	80	"	"	"	"
:51	"	"	"	"	"	"	64	"	"	"	"
:52	"	"	"	"	"	"	50	"	"	"	"
:00	NR	NR	NR	NR	450	NA	54	.765	.048	NA	NA
:01	"	"	"	"	"	"	41	NR	NR	"	"
:02	"	"	"	"	"	"	73	"	"	"	"
:03	"	"	"	"	"	"	51	"	"	"	"
:04	"	"	"	"	"	"	56	"	"	"	"
:18	NR	NR	NR	NR	450	NA	NR	NR	NA	"	"
:23	86	9	300	39	NR	NA	53	.627	.044	NA	NA
24	"	"	"	"	"	"	54	NR	NR	"	"
25	"	"	"	"	"	"	62	"	"	"	"
26	"	"	"	"	"	"	48	"	"	"	"
27	"	"	"	"	"	"	58	"	"	"	"
28	"	"	"	"	"	"	57	"	"	"	"
29	"	"	"	"	"	"	60	.527	.041	"	"
30	"	"	"	"	"	"	61	NR	NR	"	"
31	"	"	"	"	"	"	61	"	"	"	"
06	90	6	301	44	NR	NA	63	.662	.045	NA	NA
07	"	"	"	"	"	"	64	NR	NR	"	"
08	"	"	"	"	"	"	60	"	"	"	"
09	"	"	"	"	"	"	53	"	"	"	"
10	"	"	"	"	"	"	68	"	"	"	"
1	"	"	"	"	"	"	62	"	"	"	"
2	"	"	"	"	"	"	66	.645	.045	"	"
11	92	8	300	41	NR	NA	70	.648	.045	NA	NA
12	"	"	"	"	"	"	64	NR	NR	"	"
3	"	"	"	"	"	"	62	"	"	"	"
4	"	"	"	"	"	"	62	"	"	"	"

12:26	"	"	"	"	"	"	66	"	"	"	"
12:27	"	"	"	"	"	"	65	.747	.048	"	"
12:28	"	"	"	"	"	"	60	NR	NR	"	"
12:29	"	"	"	"	"	"	68	"	"	"	"
12:30	"	"	"	"	"	"	69	"	"	"	"
12:31	"	"	"	"	"	"	69	.665	.045	"	"
12:37	62	14	300	40	NR	NA	71	NR	NR	NA	NA
12:38	"	"	"	"	"	"	69	"	"	"	"
12:39	"	"	"	"	"	"	74	"	"	"	"
12:48	297	16	300	36	NR	NA	63	.513	.040	NA	NA
12:49	"	"	"	"	"	"	60	NR	NR	"	"
12:50	"	"	"	"	"	"	"	"	"	"	"
12:51	"	"	"	"	"	"	"	"	"	"	"
12:52	"	"	"	"	"	"	62	.674	.046	"	"
3:06	281	8	301	28	1000	NA	62	.372	.035	NA	NA
3:07	"	"	"	"	"	"	61	NR	NR	"	"
3:08	"	"	"	"	"	"	69	"	"	"	"
3:09	"	"	"	"	"	"	66	"	"	"	"
3:10	"	"	"	"	"	"	74	"	"	"	"
3:11	"	"	"	"	"	"	68	"	"	"	"
3:12	"	"	"	"	"	"	71	.483	.039	"	"
3:31	270	15	304	42	NR	NA	64	NR	NR	NA	NA
3:37	286	12	301	38	NR	NA	64	NR	NR	NA	NA
3:50	290	10	302	40	NR	NA	66	NR	NR	NA	NA
3:58	288	10	301	NR	NR	NA	73	NR	NR	NA	NA
4:13	70	5	301	41	NR	NA	65	.574	.042	NA	NA
4:14	"	"	"	"	"	"	76	NR	NR	"	"
:15	"	"	"	"	"	"	69	"	"	"	"
:27	292	16	301	35	NR	NA	71	.648	.045	NA	NA
:28	"	"	"	"	"	"	73	NR	NR	"	"
:29	"	"	"	"	"	"	"	"	"	"	"
:30	"	"	"	"	"	"	68	"	"	"	"
:31	"	"	"	"	"	"	74	"	"	"	"
:32	"	"	"	"	"	"	69	.697	.046	"	"
:35	NR	NR	NR	NR	1400	NA	NR	NR	NR	NA	NA
:41	310	11	301	35	NR	NA	69	.665	.045	NA	NA
:42	"	"	"	"	"	"	66	NR	NR	"	"
:43	"	"	"	"	"	"	69	"	"	"	"
:44	"	"	"	"	"	"	71	"	"	"	"
:45	"	"	"	"	"	"	81	"	"	"	"
:46	"	"	"	"	"	"	79	"	"	"	"
47	"	"	"	"	"	"	64	.551	.041	"	"
48	"	"	"	"	"	"	80	NR	NR	"	"
49	"	"	"	"	"	"	56	"	"	"	"
44	310	10	302	38	NR	NA	74	.650	.045	NA	NA
45	"	"	"	"	"	"	73	NR	NR	"	"
46	"	"	"	"	"	"	70	"	"	"	"
47	"	"	"	"	"	"	66	"	"	"	"
48	"	"	"	"	"	"	68	"	"	"	"
49	"	"	"	"	"	"	78	"	"	"	"
50	"	"	"	"	"	"	"	.404	.036	"	"
35	299	5	302	43	NR	NA	76	.398	.036	NA	NA
59	300	10	302	40	NR	NA	80	.527	.040	NA	NA
05	277	11	302	37	NR	NA	77	.457	.038	NA	NA
16	259	11	304	42	NR	NA	72	.416	.036	NA	NA
30	235	14	305	40	NR	NA	73	.557	.042	NA	NA
10	308	12	304	40	NR	NA	75	.545	.039	NA	NA
1	326	10	303	38	NR	NA	71	NR	NR	NA	NA
4	316	10	304	41	NR	NA	73	NR	NR	NA	NA

17:45	313	13	304	42	NR	NA	66	NR	NR	NA	NA
18:01	318	16	302	42	1000	NA	60	NR	NR	NA	NA

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BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

IS DATA WAS RECORDED ON 06/26/84

TIME	WIND (DEGREES)	(MPH)	TEMP (K)	REL. HUM. (%)	C.C.N. (#/CM²)	UV. FLUX (W/M²)	$[O_3]$ (PPB)	[NO] (PPB)	+/- (PPB)	$[NO_2]$ (PPB)	+/- (PPB)
00:05	344	19	300	42	NR	NA	62	NR	NR	NR	NR
00:37	353	18	NR	NR	NR	NA	55	NR	NR	NR	NR
00:57	352	17	NR	NR	NR	NA	63	NR	NR	NR	NR
00:58	"	"	"	"	"	"	58	"	"	"	"
01:15	NR	NR	NR	NR	NR	NA	57	NR	NR	NR	NR
01:40	106	16	NR	NR	NR	NA	51	NR	NR	NR	NR
02:05	NR	NR	NR	NR	NR	NA	49	NR	NR	NR	NR
02:13	NR	NR	NR	NR	NR	NA	52	NR	NR	NR	NR
02:21	NR	NR	NR	NR	NR	NA	50	NR	NR	NR	NR
2:29	NR	NR	NR	NR	NR	NA	47	NR	NR	NR	NR
2:45	NR	NR	NR	NR	NR	NA	45	NR	NR	NR	NR
3:44	120	22	NR	NR	NR	NA	50	NR	NR	NR	NR
4:10	NR	NR	NR	NR	NR	NA	48	NR	NR	NR	NR
4:15	NR	NR	NR	NR	NR	NA	50	NR	NR	NR	NR
4:20	NR	NR	NR	NR	NR	NA	45	NR	NR	NR	NR
4:30	119	24	297	53	NR	NA	NR	NR	NR	NR	NR
5:00	NR	NR	NR	NR	NR	NA	56	NR	NR	NR	NR
5:28	125	23	NR	NR	NR	NA	45	NR	NR	NR	NR
5:37	120	22	NR	NR	NR	NA	49	NR	NR	NR	NR
6:05	123	24	NR	NR	NR	NA	47	NR	NR	NR	NR
6:12	NR	NR	NR	NR	NR	NA	50	NR	NR	.92	.25
6:37	NR	NR	NR	NR	NR	NA	46	NR	NR	1.76	.31
6:45	123	23	NR	NR	NR	NA	48	NR	NR	1.32	.28
7:03	NR	NR	NR	NR	NR	NA	NR	NR	NR	2.12	.34
7:17	122	25	297	50	NR	NA	48	NR	NR	2.68	.37
:25	127	26	NR	NR	NR	NA	47	NR	NR	NR	NR
:30	NR	NR	NR	NR	NR	NA	44	NR	NR	1.48	.36
:36	NR	NR	NR	NR	NR	NA	46	.124	.032	NR	NR
:43	128	25	NR	NR	NR	NA	NR	NR	NR	NR	NR
:46	NR	NR	NR	NR	NR	NA	44	NR	NR	NR	NR
:51	NR	NR	NR	NR	NR	NA	45	NR	NR	NR	NR
:55	131	26	NR	NR	NR	NA	44	.324	.067	NR	NR
:00	NR	NR	NR	NR	NR	NA	44	.325	.046	NR	NR
:05	130	26	NR	NR	NR	NA	47	NR	NR	NR	NR
:25	136	24	300	55	NR	NA	44	NR	NR	5.04	.60
:30	NR	NR	NR	NR	NR	NA	42	.449	.053	NR	NR
:40	135	21	NR	NR	NR	NA	39	NR	NR	NR	NR
:52	NR	NR	NR	NR	NR	NA	45	.671	.063	NR	NR
.03	138	16	297	58	NR	NA	45	NR	NR	6.32	1.02
06	NR	NR	NR	NR	NR	NA	NR	.861	.071	NR	NR
15	130	17	296	52	NR	NA	29	NR	NR	4.56	.70
21	133	13	296	52	NR	NA	49	.926	.073	NR	NR
26	128	18	296	NR	NR	NA	52	.747	.067	NR	NR
36	137	15	296	51	NR	NA	50	.351	.046	NR	NR
44	131	11	296	55	1400	NA	53	.314	.046	NR	NR
49	115	11	296	51	NR	NA	45	NR	NR	6.48	.62
51	136	18	296	51	NR	NA	45	.754	.042	NR	NR
00	133	15	296	45	NR	NA	53	NR	NR	3.36	.50
06	132	13	296	50	NR	NA	48	.292	.044	NR	NR

```
10:29   147  14   298   43  450   NA   52     NR    NR    .88   .33
10:33   155  15   297   45   NR   NA   56   .130  .033    NR    NR
10:53   147  22   296   42   NR   NA   55     NR    NR  1.60   .35
10:58   146  20   297   41   NR   NA   64   .032  .023    NA    NA
11:38    NR  NR    NR   NR  150   NA   NR     NR    NR    NA    NA
11:50   174  10   298   38   NR   NA   62     NR    NR    NA    NA
12:10   155  12   298   41   NR   NA   61     NR    NR    NA    NA
12:20   152  14   299   40   NR   NA   66     NR    NR    NA    NA
12:35   154  14   299   40   NR   NA   64     NR    NR    NA    NA
12:45    NR  NR    NR   NR  200   NA   NR     NR    NR    NA    NA
15:26   160   9   303   44   NR   NA   68     NR    NR    NA    NA
15:46   109   2   303   36   NR   NA   68   .146  .034    NA    NA
15:59   149   3   304   36   NR   NA   67   .114  .032    NA    NA
16:10   129   3   304   40   NR   NA   66   .173  .036    NA    NA
16:22   135   5   304   42   NR   NA   67   .157  .035    NA    NA
16:35   218   8   304   41   NR   NA   69     NR    NR    NA    NA
16:48   185   6   305   63   NR   NA   70   .194  .038    NA    NA
17:01    NR  NR    NR   NR  150   NA   NR     NR    NR    NA    NA
17:12   180   7   305   40   NR   NA   65   .287  .044    NA    NA
.7:25   212   5   304   38   NR   NA   67   .152  .035    NA    NA
.7:35   184   4   303   42   NR   NA   67   .200  .038    NA    NA
 7:41   170   5   304   42   NR   NA   67   .168  .036    NA    NA
 7:50   140   2   302   40   NR   NA   68   .114  .032    NA    NA
 7:55   159   5   304   39   NR   NA   70   .325  .046    NA    NA
 8:00   166   4   304   36   NR   NA   66   .119  .032    NA    NA
```

NR = NOT RECORDED

NA = NOT AVAILABLE

STD = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE

BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

S DATA WAS RECORDED ON 06/27_28/84

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	[O_3]	[NO]	+/-	[NO_2]	+/-
	(DEGREES)	(MPH)	(K)	(%)	$(\#/CM^2)$	(W/M^2)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
03:15	207	17	NR	NR	NR	NA	44	NR	NR	NR	NR
04:02	202	18	299	86	NR	NA	45	.056	.016	NR	NR
04:07	NR	NR	NR	NR	NR	NA	38	NR	NR	NR	NR
04:14	NR	NR	NR	NR	NR	NA	39	.042	.015	NR	NR
04:20	199	18	NR	NR	NR	NA	41	NR	NR	NR	NR
4:30	NR	NR	NR	NR	NR	NA	42	NR	NR	NR	NR
5:05	197	16	299	85	NR	NA	40	.070	.018	NR	NR
5:15	NR	NR	NR	NR	NR	NA	42	NR	NR	NR	NR
5:23	NR	NR	NR	NR	NR	NA	36	NR	NR	10.22	1.30
5:28	202	16	NR	NR	NR	NA	39	BDL	BDL	NR	NR
5:40	NR	NR	NR	NR	NR	NA	38	NR	NR	11.61	1.38
5:45	NR	NR	NR	NR	NR	NA	39	NR	NR	11.61	1.38
5:50	NR	NR	NR	NR	NR	NA	35	BDL	BDL	NR	NR
6:10	209	13	NR	NR	NR	NA	42	NR	NR	13.01	1.44
6:15	NR	NR	NR	NR	NR	NA	36	-	-	STD	STD
:30	NR	NR	NR	NR	NR	NA	NR	NR	NR	6.24	1.16
:35	NR	NR	NR	NR	NR	NA	39	NR	NR	9.36	1.30
:42	NR	NR	NR	NR	NR	NA	38	BDL	BDL	NR	NR
:44	NR	NR	NR	NR	NR	NA	50	NR	NR	NR	NR
:47	NR	NR	NR	NR	NR	NA	39	NR	NR	NR	NR
:00	210	17	299	85	NR	NA	32	NR	NR	9.46	1.33
:15	210	16	NR	NR	NR	NA	36	NR	NR	10.97	1.39
:27	NR	NR	NR	NR	NR	NA	38	BDL	BDL	NR	NR
:00	212	9	NR	NR	NR	NA	28	.585	.099	NR	NR
:05	NR	NR	NR	NR	NR	NA	33	NR	NR	12.90	1.61
:10	202	11	NR	NR	NR	NA	34	NR	NR	NR	NR
:17	NR	NR	NR	NR	NR	NA	34	1.055	.125	NR	NR
:25	202	11	NR	NR	NR	NA	31	NR	NR	17.31	1.85
:30	NR	NR	NR	NR	NR	NA	33	1.017	.123	NR	NR
35	NR	NR	NR	NR	NR	NA	34	NR	NR	NR	NR
40	NR	NR	NR	NR	NR	NA	36	NR	NR	18.71	1.88
47	NR	NR	NR	NR	NR	NA	33	.839	.114	NR	NR
54	210	10	NR	NR	NR	NA	36	NR	NR	NR	NR
00	NR	NR	NR	NR	NR	NA	34	NR	NR	6.13	1.44
05	205	10	NR	NR	NR	NA	35	.623	.101	NR	NR
10	NR	NR	NR	NR	NR	NA	38	NR	NR	9.14	1.69
12	"	"	"	"	"	"	41	"	"	NR	NR
18	206	8	300	70	NR	NA	47	.941	.119	NR	NR
20	"	"	"	"	"	"	39	NR	NR	"	"
23	NR	NR	NR	NR	NR	NA	39	NR	NR	NR	NR
28	NR	NR	NR	NR	NR	NA	38	NR	NR	NR	NR
33	215	8	NR	NR	NR	NA	38	.445	.089	NR	NR
40	205	9	300	59	NR	NA	39	NR	NR	8.60	1.44
48	203	9	300	68	NR	NA	38	NR	NR	6.88	.79
54	186	8	300	50	NR	NA	43	.648	.102	NR	NR
9	220	12	301	52	NR	NA	47	NR	NR	3.44	1.16
4	208	9	301	50	NR	NA	45	.419	.090	NR	NR
9	220	10	301	45	NR	NA	52	NR	NR	NR	NR

10:35	221	10	300	55	NR	NA	38	NR	NR	NR	NR
10:42	199	9	300	62	NR	NA	47	.369	.038	NR	NR
0:57	202	8	300	50	NR	NA	44	NR	NR	4.84	1.23
1:02	210	11	300	45	NR	NA	52	.292	.077	NR	NR
1:16	216	14	300	42	NR	NA	35	STD	STD	—	—
1:24	177	7	300	50	NR	NA	55	.280	.076	NR	NR
2:26	210	11	301	52	NR	NA	57	.216	.028	NA	NA
2:35	212	14	302	48	NR	NA	67	.176	.027	NA	NA
2:46	226	12	303	48	NR	NA	78	.110	.022	NA	NA
2:57	236	13	304	48	NR	NA	56	.157	.026	NA	NA
3:10	215	18	303	45	NR	NA	70	.132	.024	NA	NA
3:20	223	18	304	53	NR	NA	64	.113	.022	NA	NA
3:28	210	10	303	45	NR	NA	62	STD	STD	—	—
:35	234	8	303	52	NR	NA	69	.150	.025	NA	NA
:48	214	25	304	44	NR	NA	63	.252	.032	NA	NA
:00	243	12	305	53	NR	NA	55	.168	.027	NA	NA
:06	NR	NR	NR	NR	150	NA	NR	NR	NR	NA	NA
:28	254	13	305	48	NR	NA	66	.183	.028	NA	NA
:34	NR	NR	NR	NR	450	NA	NR	NR	NR	NA	NA
:41	235	14	305	46	NR	NA	58	.227	.030	NA	NA
:50	225	17	305	42	NR	NA	64	.117	.023	NA	NA
:07	240	17	305	42	NR	NA	65	.205	.029	NA	NA
:25	NR	NR	NR	NR	250	NA	NR	.205	.029	NA	NA
:35	227	15	305	52	NR	NA	63	NR	NR	NA	NA
:50	240	10	305	42	NR	NA	71	.121	.023	NA	NA
05	226	9	305	40	NR	NA	65	.281	.033	NA	NA
20	250	12	305	44	NR	NA	73	.241	.031	NA	NA
30	265	14	305	42	NR	NA	77	.223	.030	NA	NA
45	NR	NR	NR	NR	150	NA	NR	NR	NR	NA	NA
51	231	8	306	48	NR	NA	76	.307	.035	NA	NA
06	216	6	306	41	NR	NA	76	.296	.034	NA	NA
12	240	14	307	48	NR	NA	70	.234	.031	NA	NA
20	234	12	305	42	NR	NA	75	.201	.029	NA	NA
30	231	11	305	42	NR	NA	73	.179	.027	NA	NA
40	247	8	305	45	NR	NA	72	.216	.030	NA	NA
50	226	9	305	42	NR	NA	71	.227	.030	NA	NA
00	224	11	305	50	NR	NA	71	.252	.032	NA	NA
00	212	10	301	47	NR	NA	75	NR	NR	NA	NA
0	185	14	NR	NR	NR	NA	58	NR	NR	NA	NA
5	190	11	297	64	NR	NA	48	.069	.020	NA	NA
0	NR	NR	NR	NR	NR	NA	46	NR	NR	NA	NA
8	NR	NR	NR	NR	NR	NA	46	NR	NR	NA	NA
3	194	11	NR	NR	NR	NA	40	.062	.019	NA	NA
3	NR	NR	NR	NR	NR	NA	45	.044	.018	NA	NA
9	NR	NR	NR	NR	NR	NA	43	NR	NR	NA	NA
5	NR	NR	NR	NR	NR	NA	42	BDL	BDL	NA	NA
2	212	15	NR	NR	NR	NA	43	STD	STD	—	—
0	NR	NR	NR	NR	NR	NA	42	NR	NR	NA	NA
5	NR	NR	NR	NR	NR	NA	44	NR	NR	NA	NA
	NR	NR	NR	NR	NR	NA	39	NR	NR	5.65	1.49
	NR	NR	NR	NR	NR	NA	41	BDL	BDL	NA	NA
	215	13	NR	NR	NR	NA	42	NR	NR	3.19	1.37
	NR	NR	NR	NR	NR	NA	42	NR	NR	NA	NA
	NR	NR	NR	NR	NR	NA	45	NR	NR	BDL	BDL
	NR	NR	NR	NR	NR	NA	38	—	—	STD	STD
	"	"	"	"	"	"	45	"	"	"	"
	NR	NR	NR	NR	NR	NA	43	—	—	STD	STD
	NR	NR	NR	NR	NR	NA	42	—	—	STD	STD
	NR	NR	NR	NR	NR	NA	39	NR	NR	NR	NR
	212	11	NR	NR	NR	NA	41	NR	NR	4.64	1.44

01:25	NR	NR	NR	NR	NR	NA	46	BDL	BDL	NR	NR
01:30	226	16	NR	NR	NR	NA	48	NR	NR	3.33	1.38
01:33	"	"	"	"	"	"	52	"	"	NR	NR
01:35	NR	NR	NR	NR	NR	NA	55	NR	NR	NR	NR
01:52	224	16	296	52	NR	NA	50	NR	NR	BDL	BDL
02:00	NR	NR	NR	NR	NR	NA	60	NR	NR	NR	NR
02:05	NR	NR	NR	NR	NR	NA	64	NR	NR	1.59	1.28
02:10	NR	NR	NR	NR	NR	NA	59	NR	NR	NR	NR
02:15	NR	NR	NR	NR	NR	NA	58	NR	NR	4.35	1.43
02:20	NR	NR	NR	NR	NR	NA	58	NR	NR	NR	NR
02:32	NR	NR	NR	NR	NR	NA	56	NR	NR	BDL	BDL
04:30	NR	NR	NR	NR	NR	NA	42	NR	NR	NR	NR
04:35	NR	NR	NR	NR	NR	NA	39	BDL	BDL	NR	NR
05:00	NR	NR	NR	NR	NR	NA	37	NR	NR	NR	NR
05:05	NR	NR	NR	NR	NR	NA	38	.036	.015	NR	NR
5:10	212	3	295	79	NR	NA	35	NR	NR	NR	NR
5:13	"	"	"	"	"	"	34	"	"	"	"
5:15	NR	NR	NR	NR	NR	NA	33	.027	.015	NR	NR
5:25	NR	NR	NR	NR	NR	NA	34	NR	NR	NR	NR
5:30	NR	NR	NR	NR	NR	NA	33	NR	NR	NR	NR
5:33	"	"	"	"	"	"	30	"	"	"	"
5:50	NR	NR	NR	NR	NR	NA	38	NR	NR	NR	NR
5:52	"	"	"	"	"	"	11	"	"	"	"
5:54	"	"	"	"	"	"	38	"	"	"	"
5:55	NR	NR	NR	NR	NR	NA	33	NR	NR	NR	NR
:00	NR	NR	NR	NR	NR	NA	33	.020	.015	NR	NR
:10	246	4	295	70	NR	NA	41	NR	NR	7.99	1.22
:15	NR	NR	NR	NR	NR	NA	27	.110	.048	NR	NR
:18	"	"	"	"	"	"	31	NR	NR	"	"
:20	NR	NR	NR	NR	NR	NA	36	NR	NR	NR	NR
:30	NR	NR	NR	NR	NR	NA	46	NR	NR	NR	NR
:33	NR	NR	NR	NR	NR	NA	48	NR	NR	NR	NR
:40	NR	NR	NR	NR	NR	NA	37	NR	NR	NR	NR
:45	NR	NR	NR	NR	NR	NA	32	NR	NR	NR	NR
:00	212	4	NR	NR	NR	NA	26	NR	NR	1.33	1.04
03	"	"	"	"	"	"	34	"	"	NR	NR
05	NR	NR	295	75	NR	NA	31	.475	.080	NR	NR
15	NR	NR	NR	NR	1000	NA	28	NR	NR	NR	NR
20	"	"	"	"	"	"	30	"	"	"	"
27	220	3	NR	NR	NR	NA	49	NR	NR	5.14	1.17
30	"	"	"	"	"	"	34	"	"	NR	NR
32	NR	NR	NR	NR	NR	NA	42	.287	.065	NR	NR
35	NR	NR	NR	NR	NR	NA	35	NR	NR	NR	NR
40	NR	NR	NR	NR	NR	NA	40	NR	NR	NR	NR
55	220	2	NR	NR	NR	NA	40	.530	.083	NR	NR
58	"	"	"	"	"	"	41	NR	NR	"	"
00	NR	NR	NR	NR	NR	NA	34	NR	NR	5.90	1.35
05	NR	NR	NR	NR	NR	NA	33	.994	.110	NR	NR
2	NR	NR	NR	NR	NR	NA	46	NR	NR	3.62	1.26
5	"	"	"	"	"	"	45	"	"	NR	NR
8	230	1	NR	NR	NR	NA	47	.453	.078	NR	NR
7	237	2	301	50	NR	NA	57	.475	.080	NR	NR
8	217	3	303	51	NR	NA	39	NR	NR	4.00	1.23
0	221	1	302	49	NR	NA	52	.740	.096	NR	NR
0	198	1	301	50	NR	NA	46	NR	NR	5.14	1.32
2	216	1	301	45	NR	NA	58	NR	NR	NR	NR
0	234	3	302	42	NR	NA	54	NR	NR	2.47	1.13
5	212	1	302	47	NR	NA	58	.475	.080	NR	NR
5	262	3	304	40	NR	NA	63	NR	NR	1.52	.95
5	232	6	304	36	NR	NA	69	.144	.052	NR	NR

12:05	241	8	303	39	NR	NA	71	NR	NR	2.95	1.03
12:15	246	5	304	38	NR	NA	79	.155	.053	NR	NR
12:20	NR	NR	NR	NR	270	NA	NR	NR	NR	NR	NR
12:38	219	10	304	42	NR	NA	75	NR	NR	2.66	1.01
12:46	243	5	305	38	NR	NA	80	NR	NR	NA	NA
13:44	202	4	305	48	NR	NA	81	NR	NR	NA	NA
13:45	"	"	"	"	"	"	"	.208	.035	"	"
13:46	"	"	"	"	"	"	80	NR	NR	"	"
13:47	"	"	"	"	"	"	83	"	"	"	"
13:48	"	"	"	"	"	"	79	"	"	"	"
13:49	"	"	"	"	"	"	84	"	"	"	"
3:50	"	"	"	"	"	"	83	.219	.036	"	"
3:51	"	"	"	"	"	"	80	NR	NR	"	"
3:52	"	"	"	"	"	"	87	"	"	"	"
3:53	"	"	"	"	"	"	80	"	"	"	"
3:54	"	"	"	"	"	"	82	"	"	"	"
3:55	"	"	"	"	"	"	83	.190	.034	"	"
3:56	"	"	"	"	"	"	89	NR	NR	"	"
3:57	"	"	"	"	"	"	84	"	"	"	"
3:58	"	"	"	"	"	"	87	"	"	"	"
3:59	"	"	"	"	"	"	84	"	"	"	"
4:00	"	"	"	"	"	"	87	.259	.038	"	"
4:01	"	"	"	"	"	"	81	NR	NR	"	"
4:02	"	"	"	"	"	"	85	"	"	"	"
4:03	"	"	"	"	"	"	84	"	"	"	"
:04	"	"	"	"	"	"	90	"	"	"	"
:05	"	"	"	"	"	"	86	.282	.040	"	"
:06	"	"	"	"	"	"	87	NR	NR	"	"
:07	"	"	"	"	"	"	86	"	"	"	"
:08	"	"	"	"	"	"	87	"	"	"	"
:09	"	"	"	"	"	"	88	"	"	"	"
:10	"	"	"	"	"	"	87	.208	.035	"	"
:11	"	"	"	"	"	"	82	NR	NR	"	"
:12	"	"	"	"	"	"	90	"	"	"	"
:13	"	"	"	"	"	"	86	"	"	"	"
14	"	"	"	"	"	"	90	"	"	"	"
15	"	"	"	"	"	"	88	.230	.037	"	"
16	"	"	"	"	"	"	91	NR	NR	"	"
17	"	"	"	"	"	"	87	"	"	"	"
18	"	"	"	"	"	"	90	"	"	"	"
19	"	"	"	"	"	"	92	"	"	"	"
20	"	"	"	"	"	"	91	.208	.035	"	"
21	"	"	"	"	"	"	95	NR	NR	"	"
22	"	"	"	"	"	"	99	"	"	"	"
23	"	"	"	"	"	"	98	"	"	"	"
24	"	"	"	"	"	"	95	"	"	"	"
25	"	"	"	"	"	"	94	.196	.034	"	"
6	"	"	"	"	"	"	96	NR	NR	"	"
7	"	"	"	"	"	"	97	"	"	"	"
8	"	"	"	"	"	"	100	"	"	"	"
9	"	"	"	"	"	"	98	"	"	"	"
0	"	"	"	"	"	"	102	.264	.040	"	"
1	"	"	"	"	"	"	103	NR	NR	"	"
2	"	"	"	"	"	"	102	"	"	"	"
3	"	"	"	"	"	"	103	"	"	"	"
4	NR	NR	NR	NR	450	NA	NR	.310	.046	NA	NA
9	307	2	305	41	NR	NA	115	NR	NR	NA	NA
0	"	"	"	"	"	"	114	"	"	"	"
1	"	"	"	"	"	"	116	"	"	"	"
2	"	"	"	"	"	"	118	"	"	"	"

15:03	"	"	"	"	"	"	119	"	"	"	"
15:06	222	9	305	42	NR	NA	111	STD	STD	–	–
15:07	"	"	"	"	"	"	110	"	"	NA	NA
15:08	"	"	"	"	"	"	113	"	"	"	"
15:09	"	"	"	"	"	"	115	"	"	"	"
15:10	"	"	"	"	"	"	"	"	"	"	"
15:15	NR	NR	NR	NR	NR	NA	117	NR	NR	NA	NA
15:16	"	"	"	"	"	"	115	"	"	"	"
15:17	"	"	"	"	"	"	119	"	"	"	"
15:21	235	6	305	41	NR	NA	119	.202	.039	NA	NA
15:22	"	"	"	"	"	"	120	NR	NR	"	"
15:23	"	"	"	"	"	"	115	"	"	"	"
15:24	"	"	"	"	"	"	116	"	"	"	"
5:25	"	"	"	"	"	"	126	"	"	"	"
15:26	"	"	"	"	"	"	130	.230	.039	"	"
5:27	"	"	"	"	"	"	128	NR	NR	"	"
5:30	"	"	"	"	"	"	132	"	"	"	"
5:31	"	"	"	"	"	"	131	"	"	"	"
5:32	"	"	"	"	"	"	129	"	"	"	"
5:33	"	"	"	"	"	"	131	"	"	"	"
5:34	NR	NR	NR	NR	NR	NA	135	NR	NR	NA	NA
5:44	NR	NR	NR	NR	3700	NA	NR	NR	NR	NA	NA

* * *

NR = NOT RECORDED

NA = NOT AVAILABLE

STD = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE

BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

S DATA WAS RECORDED ON 06/29/84

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	[O$_3$]	[NO]	+/-	[NO$_2$]	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM^2)	(W/M^2)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
3:30	250	3	NR	NR	NR	NA	34	NR	NR	NR	NR
9:00	78	10	291	65	NR	NA	35	NR	NR	NR	NR
9:44	36	8	291	95	NR	NA	37	1.343	.069	NR	NR
9:49	30	8	291	84	NR	NA	38	NR	NR	8.63	.89
9:55	46	16	291	95	NR	NA	33	.687	.211	NR	NR
9:56	"	"	"	"	"	"	24	.755	.228	"	"
9:57	"	"	"	"	"	"	39	.824	.238	"	"
9:58	"	"	"	"	"	"	33	.343	.154	"	"
9:59	"	"	"	"	"	"	37	"	"	"	"
0:00	"	"	"	"	"	"	35	"	"	"	"
0:01	"	"	"	"	"	"	45	.137	.097	"	"
0:02	"	"	"	"	"	"	39	.206	.119	"	"
0:03	"	"	"	"	"	"	34	.137	.097	"	"
0:15	NR	NR	NR	NR	NR	NA	54	BDL	BDL	NR	NR
0:17	"	"	"	"	"	"	66	"	"	"	"
0:19	"	"	"	"	"	"	36	.137	.097	"	"
:21	"	"	"	"	"	"	29	.412	.168	"	"
:23	"	"	"	"	"	"	"	.755	.228	"	"
:25	"	"	"	"	"	"	42	.137	.097	"	"
:27	"	"	"	"	"	"	65	"	"	"	"
:29	"	"	"	"	"	"	75	"	"	"	"
:31	"	"	"	"	"	"	46	"	"	"	"
:33	"	"	"	"	"	"	50	.206	.119	"	"
:36	85	6	NR	NR	NR	NA	26	NR	NR	22.06	3.12
:37	"	"	"	"	"	"	29	"	"	NR	NR
:38	"	"	"	"	"	"	31	"	"	25.58	3.29
:39	"	"	"	"	"	"	37	.824	.238	NR	NR
:40	"	"	"	"	"	"	32	NR	NR	15.67	2.69
:41	"	"	"	"	"	"	27	"	"	16.30	2.68
:42	"	"	"	"	"	"	30	"	"	11.19	2.39
43	"	"	"	"	"	"	40	.962	.257	NR	NR
45	NR	NR	NR	NR	NR	NA	34	NR	NR	NR	NR
47	NR	NR	NR	NR	NR	NA	42	.481	.182	NR	NR
50	NR	NR	NR	NR	NR	NA	54	NR	NR	2.24	1.47
51	NR	NR	NR	NR	NR	NA	NR	.275	.137	NR	NR
53	NR	NR	NR	NR	NR	NA	58	NR	NR	NR	NR
55	NR	NR	NR	NR	NR	NA	59	NR	NR	NR	NR
56	NR	NR	NR	NR	NR	NA	48	NR	NR	BDL	BDL
57	NR	NR	NR	NR	NR	NA	44	NR	NR	NR	NR
00	130	1	291	90	NR	NA	59	.481	.088	NR	NR
03	"	"	"	"	"	"	53	NR	NR	10.49	.97
05	145	3	291	75	NR	NA	41	NR	NR	NR	NR
11	NR	NR	NR	NR	NR	NA	55	NR	NR	NR	NR
20	104	5	292	85	NR	NA	54	NR	NR	6.01	.85
25	113	11	292	76	NR	NA	41	.673	.096	NR	NR
29	NR	NR	NR	NR	NR	NA	47	NR	NR	NR	NR
36	152	5	293	100	NR	NA	49	STD	STD	—	—
1	NR	NR	NR	NR	NR	NA	NR	NR	NR	NR	NR

11:50	123	3	294	76	NR	NA	42	2.797	.434	NR	NR
11:51	"	"	"	"	"	"	32	3.777	.509	"	"
11:52	"	"	"	"	"	"	37	3.503	.490	"	"
11:53	"	"	"	"	"	"	49	2.747	.434	"	"
11:54	"	"	"	"	"	"	50	2.816	.440	"	"
11:55	"	"	"	"	"	"	21	3.228	.471	"	"
11:56	"	"	"	"	"	"	64	4.121	.532	"	"
12:08	NR	NR	NR	NR	NR	NA	19	1.511	.322	NR	NR
12:09	"	"	"	"	"	"	82	.755	.228	"	"
12:10	"	"	"	"	"	"	91	2.404	.406	"	"
12:11	"	"	"	"	"	"	47	"	"	"	"
12:12	"	"	"	"	"	"	25	2.816	.440	"	"
2:13	"	"	"	"	"	"	56	2.610	.423	"	"
2:14	"	"	"	"	"	"	52	1.717	.343	"	"
2:17	204	5	296	72	NR	NA	42	STD	STD	—	—
2:19	"	"	"	"	"	"	46	2.541	.418	NR	NR
2:21	"	"	"	"	"	"	15	3.984	.523	NR	NR
2:25	200	2	296	56	NR	NA	49	NR	NR	BDL	BDL
2:26	"	"	"	"	"	"	45	"	"	NR	NR
2:27	NR	NR	NR	NR	NR	NA	45	NR	NR	NR	NR
2:28	227	0	296	69	NR	NA	46	NR	NR	NR	NR
2:29	"	"	"	"	"	"	"	"	"	"	"
2:30	"	"	"	"	"	"	42	"	"	"	"
2:35	306	1	296	58	NR	NA	55	NR	NR	NR	NR
2:45	253	1	NR	NR	NR	NA	43	NR	NR	4.97	1.40
2:50	NR	NR	NR	NR	NR	NA	47	NR	NR	NR	NR
:54	116	2	298	60	NR	NA	47	NR	NR	NR	NR
:55	"	"	"	"	"	"	57	"	"	"	"
:56	"	"	"	"	"	"	39	"	"	"	"
:57	"	"	"	"	"	"	58	"	"	"	"
:58	"	"	"	"	"	"	54	"	"	"	"
:00	83	1	298	56	NR	NA	48	NR	NR	NR	NR
:01	"	"	"	"	"	"	56	"	"	"	"
:02	"	"	"	"	"	"	49	"	"	"	"
:03	"	"	"	"	"	"	56	"	"	"	"
:11	NR	NR	NR	NR	NR	NA	50	NR	NR	NR	NR
:16	228	1	298	58	NR	NA	49	NR	NR	NR	NR
:17	"	"	"	"	"	"	50	"	"	"	"
:18	"	"	"	"	"	"	54	"	"	"	"
:19	"	"	"	"	"	"	"	"	"	"	"
:20	"	"	"	"	"	"	"	"	"	"	"
22	175	3	299	69	NR	NA	55	NR	NR	NR	NR
23	"	"	"	"	"	"	53	"	"	"	"
24	"	"	"	"	"	"	61	"	"	"	"
25	"	"	"	"	"	"	50	"	"	"	"
26	"	"	"	"	"	"	48	"	"	"	"
40	213	4	299	62	NR	NA	62	NR	NR	NR	NR
41	"	"	"	"	"	"	57	"	"	"	"
42	"	"	"	"	"	"	49	"	"	"	"
43	"	"	"	"	"	"	66	"	"	"	"
44	"	"	"	"	"	"	52	"	"	"	"
46	188	7	299	72	NR	NA	54	NR	NR	NR	NR
47	"	"	"	"	"	"	"	"	"	"	"
48	"	"	"	"	"	"	58	"	"	"	"
49	"	"	"	"	"	"	53	"	"	"	"
50	"	"	"	"	"	"	57	"	"	"	"
5	204	5	299	NR	NR	NA	NR	NR	NR	NR	NR
2	192	8	298	70	NR	NA	58	STD	STD	—	—
3	"	"	"	"	"	"	59	"	"	NR	NR
4	"	"	"	"	"	"	61	"	"	"	"

17:35	"	"	"	"	"	"	"	"	"	"	"
17:36	"	"	"	"	"	"	55	"	"	"	"
17:47	197	7	298	72	NR	NA	58	NR	NR	NR	NR
17:48	"	"	"	"	"	"	60	"	"	"	"
17:49	"	"	"	"	"	"	"	"	"	"	"
17:50	"	"	"	"	"	"	53	"	"	"	"
17:51	"	"	"	"	"	"	59	"	"	"	"
17:55	202	8	298	NR	NR	NA	63	NR	NR	NR	NR
17:56	"	"	"	"	"	"	55	"	"	"	"
17:57	"	"	"	"	"	"	61	"	"	"	"
17:58	"	"	"	"	"	"	58	"	"	"	"
17:59	"	"	"	"	"	"	"	"	"	"	"
18:06	202	8	298	71	NR	NA	58	–	–	STD	STD
18:07	"	"	"	"	"	"	"	NR	NR	"	"
18:08	"	"	"	"	"	"	57	"	"	"	"
18:09	"	"	"	"	"	"	59	"	"	"	"
18:10	"	"	"	"	"	"	57	"	"	"	"
8:11	"	"	"	"	"	"	61	"	"	"	"
8:13	186	8	297	78	NR	NA	60	–	–	STD	STD
8:14	"	"	"	"	"	"	59	NR	NR	"	"
8:15	"	"	"	"	"	"	"	"	"	"	"
8:16	"	"	"	"	"	"	64	"	"	"	"
8:17	"	"	"	"	"	"	58	"	"	"	"
8:20	185	8	297	80	NR	NA	56	–	–	STD	STD
8:28	187	10	297	80	NR	NA	55	–	–	STD	STD
8:29	"	"	"	"	"	"	56	NR	NR	"	"
8:30	"	"	"	"	"	"	58	"	"	"	"
8:31	202	9	297	80	NR	NA	58	–	–	STD	STD
8:32	"	"	"	"	"	"	55	NR	NR	"	"
8:33	"	"	"	"	"	"	51	"	"	"	"
8:34	"	"	"	"	"	"	49	"	"	"	"
8:35	"	"	"	"	"	"	58	"	"	"	"
8:40	193	9	298	85	NR	NA	52	–	–	STD	STD
8:48	190	10	297	90	NR	NA	60	NR	NR	NR	NR
8:49	"	"	"	"	"	"	59	"	"	"	"
:50	"	"	"	"	"	"	57	"	"	"	"
:51	"	"	"	"	"	"	54	"	"	"	"
:52	"	"	"	"	"	"	51	"	"	"	"

NR = NOT RECORDED

NA = NOT AVAILABLE

STD = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE

BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

S DATA WAS RECORDED ON 06/30/84

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	[O_3]	[NO]	+/-	[NO_2]	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM^2)	(W/M^2)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
08:15	344	8	291	100	NR	NA	29	NR	NR	NR	NR
08:30	NR	NR	NR	NR	NR	NA	49	NR	NR	NR	NR
08:50	NR	NR	NR	NR	NR	NA	38	.061	.028	NR	NR
8:52	"	"	"	"	"	"	11	NR	NR	"	"
8:54	"	"	"	"	"	"	36	"	"	"	"
8:57	NR	NR	NR	NR	NR	NA	22	NR	NR	.83	.66
8:59	"	"	"	"	"	"	79	"	"	NR	NR
9:01	"	"	"	"	"	"	10	"	"	"	"
9:03	"	"	"	"	"	"	70	"	"	"	"
0:45	55	8	NR	NR	NR	NA	6	NR	NR	2.18	.69
:46	"	"	"	"	"	"	44	"	"	.90	.62
0:52	NR	NR	NR	NR	NR	NA	43	1.216	.189	NR	NR
0:54	NR	NR	NR	NR	NR	NA	37	1.133	.183	NR	NR
0:55	"	"	"	"	"	"	24	NR	NR	"	"
1:04	NR	NR	NR	NR	NR	NA	49	NR	NR	BDL	BDL
1:05	"	"	"	"	"	"	43	"	"	.90	.57
1:06	"	"	"	"	"	"	39	1.077	.179	NR	NR
1:07	NR	NR	NR	NR	NR	NA	44	.802	.156	NR	NR
2:25	305	10	297	40	NR	NA	49	.580	.135	NR	NR
2:26	"	"	"	"	"	"	35	.525	.130	"	"
2:27	"	"	"	"	"	"	62	.691	.146	"	"
2:28	"	"	"	"	"	"	61	.746	.151	"	"
:32	NR	NR	NR	NR	NR	NA	54	NR	NR	1.65	.58
:33	"	"	"	"	"	"	76	"	"	6.83	.85
:34	"	"	"	"	"	"	NR	"	"	1.05	.54
:40	347	6	NR	NR	NR	NA	59	NR	NR	BDL	BDL
:41	NR	NR	NR	NR	NR	NA	60	NR	NR	1.58	.58
:43	NR	NR	NR	NR	NR	NA	63	NR	NR	NR	NR
:44	"	"	"	"	"	"	56	"	"	"	"
:54	NR	NR	NR	NR	NR	NA	50	.663	.144	NR	NR
:55	"	"	"	"	"	"	62	"	"	"	"
:56	"	"	"	"	"	"	56	.802	.156	"	"
:57	"	"	"	"	"	"	57	.691	.146	"	"
58	NR	NR	NR	NR	NR	NA	73	NR	NR	NR	NR
59	"	"	"	"	"	"	57	.553	.133	"	"
00	"	"	"	"	"	"	55	.636	.141	"	"
02	NR	NR	NR	NR	NR	NA	56	NR	NR	NR	NR
30	328	5	NR	54	NR	NA	58	.193	.087	NR	NR
31	"	"	"	"	"	"	54	.138	.078	"	"
35	NR	NR	NR	NR	NR	NA	52	NR	NR	NR	NR
36	NR	NR	NR	NR	NR	NA	52	NR	NR	NR	NR
37	NR	NR	NR	NR	NR	NA	67	NR	NR	2.03	.56
00	NR	NR	NR	NR	NR	NA	64	NR	NR	NR	NR
20	380	7	NR	NR	NR	NA	65	NR	NR	NR	NR
25	NR	NR	300	62	NR	NA	69	NR	NR	4.81	.92
30	NR	NR	NR	NR	NR	NA	68	.310	.046	NR	NR
33	"	"	"	"	"	"	66	NR	NR	"	"
55	374	9	NR	NR	NR	NA	61	.359	.049	NR	NR

16:58	"	"	"	"	"	"	72	NR	NR	NR	NR
17:00	NR	NR	NR	NR	NR	NA	69	NR	NR	9.69	1.18
17:03	"	"	"	"	"	"	67	"	"	NR	NR
17:05	NR	NR	NR	NR	NR	NA	63	.674	.091	NR	NR
17:06	"	"	"	"	"	"	61	NR	NR	3.38	.87
17:07	NR	NR	NR	NR	NR	NA	64	.310	.071	NR	NR
17:25	370	3	NR	NR	NR	NA	66	NR	NR	1.58	.80
17:26	NR	NR	NR	NR	NR	NA	64	.730	.095	NR	NR
17:30	NR	NR	NR	NR	NR	NA	63	1.050	.122	NR	NR
17:31	NR	NR	NR	NR	NR	NA	62	2.399	.165	NR	NR
17:33	NR	NR	NR	NR	NR	NA	56	2.155	.262	NR	NR
17:34	"	"	"	"	"	"	55	2.260	.268	"	"
17:35	NR	NR	NR	NR	NR	NA	61	1.824	.244	NR	NR
17:37	NR	NR	NR	NR	NR	NA	63	NR	NR	3.23	.77
17:38	NR	NR	NR	NR	NR	NA	58	1.631	.234	NR	NR
17:39	NR	NR	NR	NR	NR	NA	NR	NR	NR	5.11	.84
17:45	NR	NR	NR	NR	NR	NA	62	1.382	.219	NR	NR
18:07	NR	NR	NR	NR	NR	NA	62	NR	NR	NR	NR
8:08	NR	NR	NR	NR	NR	NA	61	NR	NR	6.61	.99
8:09	NR	NR	NR	NR	NR	NA	55	2.239	.267	NR	NR
8:10	NR	NR	NR	NR	NR	NA	49	NR	NR	6.83	.99
8:24	NR	NR	NR	NR	NR	NA	NR	2.128	.261	NR	NR
8:29	NR	NR	NR	NR	NR	NA	47	6.081	.431	NR	NR
9:08	NR	NR	NR	NR	NR	NA	58	NR	NR	3.53	.66
9:09	NR	NR	NR	NR	NR	NA	62	.940	.168	NR	NR
9:11	NR	NR	NR	NR	NR	NA	53	NR	NR	NR	NR
9:12	NR	NR	NR	NR	NR	NA	48	NR	NR	3.60	.53
9:13	NR	NR	NR	NR	NR	NA	53	1.299	.195	NR	NR

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S DATA WAS RECORDED ON 07/01/84


                                 REL.               UV.
 TIME          WIND   TEMP   HUM.   C.C.N.  FLUX    [O3]     [NO]     +/-     [NO2]    +/-

     (DEGREES)(MPH)(K)      (%)   (#/CM2)(W/M2)  (PPB)    (PPB)    (PPB)    (PPB)   (PPB)


13:58       274    2    301      NR     NR      NA     73         NR      NR       NR      NR
14:00        NR   NR     NR      63     NR      NA     NR         NR      NR       NR      NR
14:03       360    1     NR      NR     NR      NA     67         NR      NR       NR      NR
.4:06       358    2    302      50     NR      NA     53         NR      NR       NR      NR
.4:11        NR   NR     NR      NR     NR      NA     70         NR      NR       NR      NR
 4:13       162    1    300      NR     NR      NA     93         NR      NR       NR      NR
 5:17       267    6    296      80     NR      NA     53         NR      NR     7.02    1.72
 5:20       287    7    295      NR     NR      NA     54       .122    .069       NR      NR
 5:23        NR   NR     NR      NR     NR      NA     49         NR      NR       NR      NR
 5:35        NR   NR     NR      NR     NR      NA     NR         NR      NR     9.27    1.91
 5:42        NR   NR     NR      NR     NR      NA     58       .294    .095       NR      NR
 5:45        NR   NR     NR      NR     NR      NA     60         NR      NR     4.01    1.52
 5:47       289    9     NR      NR     NR      NA     67        BDL     BDL       NR      NR
 5:53       282    8     NR      NR     NR      NA     60         NR      NR       NR      NR
 5:56        NR   NR    293      68     NR      NA     62         NR      NR     5.01    1.50
 5:58        NR    7     NR      NR     NR      NA     65       .074    .060       NR      NR
  :02       246    3    294      81     NR      NA     67         NR      NR     3.51    1.50
  :05        NR   NR     NR      NR     NR      NA     55         NR      NR     6.52    1.74
  :09        NR   NR    293     100     NR      NA     41       .319    .098       NR      NR
  :11        NR   NR     NR      NR     NR      NA     43         NR      NR     8.52    2.01
  :15       153    5     NR      NR     NR      NA     45       .466    .115       NR      NR
  :18        NR   NR     NR      NR     NR      NA     58         NR      NR       NR      NR
  :21        NR   NR    292     100     NR      NA     54         NR      NR       NR      NR
  :26       148    5    291      NR     NR      NA     50       .172    .078       NR      NR
  :29        NR   NR     NR      NR     NR      NA     71         NR      NR     4.76    1.62
  :31        NR   NR     NR      NR     NR      NA     65       .294    .095       NR      NR
  :33       149    4    293      NR     NR      NA     64         NR      NR     8.52    2.05
  :36       131    5    292     100     NR      NA     63       .637    .132       NR      NR
  :39        NR   NR     NR      NR     NR      NA     48       .441    .112       NR      NR
  :41        NR   NR     NR      NR     NR      NA     51       .270    .092       NR      NR
  :47       143    5     NR      NR     NR      NA     63         NR      NR       NR      NR
   49       146    3    292      75     NR      NA     52         NR      NR       NR      NR
   51        NR   NR     NR      NR     NR      NA     52         NR      NR       NR      NR
   54        NR   NR    292      80     NR      NA     56       .221    .085       NR      NR
   56        NR   NR     NR      NR     NR      NA     53         NR      NR       NR      NR
   58        NR   NR     NR      NR     NR      NA     87       .319    .098       NR      NR
   02        NR   NR     NR      NR     NR      NA     66         NR      NR       NR      NR
   04        NR   NR     NR      NR     NR      NA     69         NR      NR       NR      NR
   09       157    3    294      83     NR      NA     55         NR      NR      BDL     BDL
   10        NR   NR     NR      NR     NR      NA     66         NR      NR       NR      NR
   12        NR   NR     NR      NR     NR      NA     68         NR      NR      BDL     BDL
   15        NR   NR     NR      NR     NR      NA     65       .147    .074       NR      NR
   18        NR   NR     NR      NR     NR      NA     64         NR      NR      BDL     BDL
   24        NR   NR     NR      NR     NR      NA     70         NR      NR       NR      NR
   26        NR   NR     NR      NR     NR      NA     89         NR      NR       NR      NR
   29       260    1     NR      NR     NR      NA     14         NR      NR       NR      NR
   30         "    "      "       "      "       "     43          "       "        "       "
   33       278    1     NR      NR     NR      NA    119         NR      NR     9.02    2.14
   34         "    "      "       "      "       "     53          "       "       NR      NR
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17:36	NR	NR	NR	NR	NR	NA	114	NR	NR	5.01	1.89
17:38	NR	NR	NR	NR	NR	NA	41	.564	.126	NR	NR
17:42	NR	NR	299	70	NR	NA	73	NR	NR	NR	NR
17:45	296	2	300	60	NR	NA	101	.809	.147	NR	NR
17:47	NR	NR	NR	NR	NR	NA	57	NR	NR	NR	NR
17:48	"	"	"	"	"	"	17	"	"	"	"
17:50	NR	NR	299	50	NR	NA	74	NR	NR	NR	NR
17:51	"	"	"	"	"	"	26	"	"	"	"
17:52	NR	NR	NR	NR	NR	NA	68	NR	NR	NR	NR
17:53	"	"	"	"	"	"	62	"	"	"	"
17:55	272	2	NR	NR	NR	NA	80	.294	.095	NR	NR
17:56	"	"	"	"	"	"	56	NR	NR	"	"
17:57	NR	NR	NR	NR	NR	NA	63	NR	NR	NR	NR
17:58	"	"	"	"	"	"	65	"	"	"	"
17:59	NR	NR	NR	NR	NR	NA	56	NR	NR	NR	NR
18:00	"	"	"	"	"	"	53	"	"	"	"

* * *

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IS DATA WAS RECORDED ON 7/03/84

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	[O$_3$]	[NO]	+/-	[NO$_2$]	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM^2)	(W/M^2)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
01:20	NR	NR	NR	NR	NR	NA	35	.170	.032	NR	NR
01:33	NR	NR	NR	NR	NR	NA	37	.165	.032	NR	NR
02:30	NR	NR	NR	NR	NR	NA	31	NR	NR	NR	NR
02:33	NR	NR	293	85	NR	NA	32	NR	NR	NR	NR
02:35	NR	NR	NR	NR	NR	NA	29	NR	NR	NR	NR
02:37	NR	NR	NR	NR	NR	NA	33	.047	.015	NR	NR
03:01	NR	NR	NR	NR	NR	NA	37	.020	.007	NR	NR
03:06	NR	NR	NR	NR	NR	NA	32	.018	.007	NR	NR
03:11	NR	NR	NR	NR	NR	NA	34	NR	NR	NR	NR
03:42	318	11	NR	NR	NR	NA	32	.008	.006	NR	NR
4:15	NR	NR	NR	NR	NR	NA	32	.023	.008	NR	NR
4:20	NR	NR	NR	NR	NR	NA	28	NR	NR	NR	NR
4:26	NR	NR	NR	NR	NR	NA	28	.020	.007	NR	NR
4:30	NR	NR	NR	NR	NR	NA	35	NR	NR	NR	NR
4:35	NR	NR	NR	NR	NR	NA	28	.020	.007	NR	NR
4:40	NR	NR	NR	NR	NR	NA	29	NR	NR	NR	NR
4:45	NR	NR	NR	NR	NR	NA	27	NR	NR	NR	NR
4:55	NR	NR	NR	NR	NR	NA	25	NR	NR	NR	NR
5:10	322	12	292	90	NR	NA	27	.029	.008	NR	NR
5:15	NR	NR	NR	NR	NR	NA	28	NR	NR	NR	NR
5:20	NR	NR	NR	NR	NR	NA	25	.022	.007	NR	NR
5:25	NR	NR	NR	NR	NR	NA	33	NR	NR	NR	NR
6:15	323	10	NR	NR	NR	NA	28	NR	NR	NR	NR
6:30	NR	NR	NR	NR	NR	NA	29	.016	.007	NR	NR
7:00	NR	NR	292	100	NR	NA	25	NR	NR	NR	NR
7:16	323	8	NR	NR	NR	NA	22	NR	NR	NR	NR
:24	NR	NR	NR	NR	NR	NA	21	NR	NR	NR	NR
:30	NR	NR	NR	NR	NR	NA	18	NR	NR	NR	NR
:33	NR	NR	NR	NR	NR	NA	17	NR	NR	NR	NR
:45	243	7	303	50	NR	NA	64	NR	NR	9.81	1.20
:46	"	"	"	"	"	"	57	"	"	NR	NR
:47	"	"	"	"	"	"	64	"	"	"	"
:48	"	"	"	"	"	"	65	"	"	"	"
:51	263	8	302	51	NR	NA	59	.355	.047	NR	NR
:52	"	"	"	"	"	"	61	NR	NR	"	"
:53	"	"	"	"	"	"	66	"	"	"	"
:54	"	"	"	"	"	"	67	"	"	"	"
:57	243	8	303	42	NR	NA	65	NR	NR	NR	NR
:58	"		"	"	"	"	66	"	"	"	"
:59	"	"	"	"	"	"	65	"	"	"	"
:00	"	"	"	"	"	"	66	"	"	"	"
:03	246	8	302	58	NR	NA	60	NR	NR	7.70	1.30
:04	"	"	"	"	"	"	63	"	"	NR	NR
05	"	"	"	"	"	"	62	"	"	"	"
06	"	"	"	"	"	"	63	"	"	"	"
09	226	8	300	48	NR	NA	60	.433	.052	NR	NR
10	"	"	"	"	"	"	"	NR	NR	"	"
11	"	"	"	"	"	"	57	"	"	"	"

14:12	"	"	"	"	"	"	52	"	"	"	"
14:13	NR	NR	302	50	NR	NA	68	NR	NR	NR	NR
14:25	266	4	302	NR	NR	NA	68	NR	NR	NR	NR
14:29	279	8	301	48	NR	NA	64	NR	NR	9.56	1.20
14:30	"	"	"	"	"	"	45	"	"	NR	NR
14:31	"	"	"	"	"	"	79	"	"	"	"
14:32	"	"	"	"	"	"	65	"	"	"	"
14:34	285	5	300	45	NR	NA	77	NR	NR	NR	NR
14:35	"	"	"	"	"	"	65	"	"	"	"
14:36	"	"	"	"	"	"	60	"	"	"	"
14:37	"	"	"	"	"	"	"	"	"	"	"
14:41	280	6	300	51	NR	NA	65	NR	NR	NR	NR
14:42	"	"	"	"	"	"	61	"	"	"	"
14:44	293	5	300	50	NR	NA	61	NR	NR	13.13	1.80
14:45	"	"	"	"	"	"	65	"	"	NR	NR
14:46	279	4	301	50	NR	NA	62	.298	.060	NR	NR
14:47	"	"	"	"	"	"	62	NR	NR	"	"
14:49	274	4	302	50	NR	NA	65	NR	NR	11.99	1.80
14:50	"	"	"	"	"	"	68	"	"	NR	NR
14:53	307	5	301	NR	NR	NA	67	.298	.060	NR	NR
.4:54	"	"	"	"	"	"	59	NR	NR	"	"
4:55	281	7	300	45	NR	NA	62	NR	NR	13.45	1.90
4:56	"	"	"	"	"	"	65	"	"	NR	NR
5:01	280	22	297	65	NR	NA	23	NR	NR	14.26	1.90
5:02	"	"	"	"	"	"	44	"	"	NR	NR
5:05	276	26	293	90	NR	NA	40	.170	.043	NR	NR
5:06	"	"	"	"	"	"	89	NR	NR	"	"
5:08	317	18	NR	NR	NR	NA	73	NR	NR	NR	NR
5:09	"	"	"	"	"	"	98	"	"	"	"
5:11	340	12	291	70	NR	NA	55	NR	NR	3.40	1.30
5:12	"	"	"	"	"	"	74	"	"	NR	NR
5:15	278	2	292	50	NR	NA	37	.341	.064	NR	NR
5:16	"	"	"	"	"	"	51	NR	NR	"	"
5:17	280	2	293	50	NR	NA	62	NR	NR	11.83	1.80
5:18	"	"	"	"	"	"	59	"	"	NR	NR
:20	280	5	294	50	NR	NA	53	.355	.066	NR	NR
:21	"	"	"	"	"	"	61	NR	NR	"	"
:25	289	5	295	60	NR	NA	65	NR	NR	8.91	1.80
:26	"	"	"	"	"	"	54	"	"	NR	NR
:30	295	4	296	50	NR	NA	66	NR	NR	7.62	1.70
:31	"	"	"	"	"	"	57	"	"	NR	NR
:32	"	"	"	"	"	"	52	"	"	"	"
:33	314	5	297	47	NR	NA	58	.270	.056	NR	NR
:34	"	"	"	"	"	"	65	NR	NR	"	"
:36	290	5	297	55	NR	NA	69	NR	NR	NR	NR
:37	"	"	"	"	"	"	71	"	"	"	"
40	294	6	297	65	NR	NA	76	NR	NR	3.24	1.60
41	"	"	"	"	"	"	85	"	"	NR	NR
44	299	7	297	67	NR	NA	54	.497	.080	NR	NR
45	"	"	"	"	"	"	60	NR	NR	"	"
47	295	NR	297	55	NR	NA	65	NR	NR	NR	NR
48	"	"	"	"	"	"	48	"	"	"	"
50	294	NR	297	55	NR	NA	40	NR	NR	NR	NR
51	"	"	"	"	"	"	49	"	"	"	"
53	294	6	297	51	NR	NA	73	NR	NR	5.83	1.50
54	"	"	"	"	"	"	98	"	"	NR	NR
56	280	5	298	50	NR	NA	59	.341	.064	NR	NR
57	"	"	"	"	"	"	65	NR	NR	"	"
00	284	5	299	55	NR	NA	34	.255	.054	NR	NR
01	"	"	"	"	"	"	67	NR	NR	"	"

16:03	288	6	299	55	NR	NA	71	.610	.089	NR	NR
16:04	"	"	"	"	"	"	76	NR	NR	"	"
16:07	280	5	300	55	NR	NA	60	STD	STD	–	–
16:08	"	"	"	"	"	"	57	"	"	NR	NR
16:13	276	5	301	55	NR	NA	31	.568	.086	NR	NR
16:14	"	"	"	"	"	"	41	NR	NR	"	"
16:16	276	5	302	48	NR	NA	32	NR	NR	1.78	1.60
16:17	"	"	"	"	"	"	40	"	"	NR	NR
16:20	275	7	302	NR	NR	NA	58	.710	.097	NR	NR
16:21	"	"	"	"	"	"	53	NR	NR	"	"
16:24	264	7	302	NR	NR	NA	40	NR	NR	8.27	1.80
16:25	"	"	"	"	"	"	29	"	"	NR	NR
16:28	259	8	302	50	NR	NA	85	.639	.091	NR	NR
16:29	"	"	"	"	"	"	68	NR	NR	"	"
16:31	255	5	302	NR	NR	NA	49	NR	NR	8.75	2.10
16:32	"	"	"	"	"	"	73	"	"	NR	NR
16:34	239	5	302	55	NR	NA	88	1.064	.120	NR	NR
16:35	"	"	"	"	"	"	40	NR	NR	"	"
16:38	253	6	302	NR	NR	NA	60	NR	NR	8.43	1.70
6:39	"	"	"	"	"	"	79	"	"	NR	NR
6:41	245	6	302	NR	NR	NA	54	.468	.077	NR	NR
6:42	"	"	"	"	"	"	62	NR	NR	"	"
6:58	279	5	303	50	NR	NA	53	–	–	STD	STD
6:59	"	"	"	"	"	"	70	"	"	"	"
7:01	258	7	303	55	NR	NA	58	–	–	STD	STD
7:02	"	"	"	"	"	"	68	"	"	"	"
7:04	242	5	303	45	NR	NA	56	–	–	STD	STD
7:05	"	"	"	"	"	"	53	"	"	"	"
7:07	240	5	303	NR	NR	NA	74	–	–	STD	STD
7:08	"	"	"	"	"	"	72	"	"	"	"
7:10	260	7	303	NR	NR	NA	63	–	–	STD	STD
7:11	"	"	"	"	"	"	70	"	"	"	"
7:13	260	5	304	50	NR	NA	55	–	–	STD	STD
7:14	"	"	"	"	"	"	66	"	"	"	"
:19	242	5	304	50	NR	NA	74	NR	NR	15.72	2.50
:20	"	"	"	"	"	"	52	"	"	NR	NR
:22	230	3	304	50	NR	NA	64	NR	NR	8.75	2.30
:23	"	"	"	"	"	"	67	"	"	NR	NR
:28	250	5	303	NR	NR	NA	58	1.533	.145	NR	NR
:29	"	"	"	"	"	"	51	NR	NR	"	"
:31	235	5	303	NR	NR	NA	71	NR	NR	23.50	2.70
:32	"	"	"	"	"	"	64	"	"	NR	NR
:34	245	5	304	NR	NR	NA	71	1.760	.156	NR	NR
:35	"	"	"	"	"	"	69	NR	NR	"	"
:37	262	5	304	55	NR	NA	74	NR	NR	23.18	2.80
:38	"	"	"	"	"	"	70	"	"	NR	NR
.40	255	5	304	NR	NR	NA	64	1.277	.132	NR	NR
41	"	"	"	"	"	"	86	NR	NR	"	"
44	261	4	304	NR	NR	NA	62	NR	NR	NR	NR
45	"	"	"	"	"	"	69	"	"	"	"
47	220	4	303	NR	NR	NA	71	NR	NR	13.61	2.30
48	"	"	"	"	"	"	"	"	"	NR	NR
50	225	6	302	NR	NR	NA	64	.866	.107	NR	NR
51	"	"	"	"	"	"	75	NR	NR	"	"
53	227	6	303	NR	NR	NA	55	NR	NR	12.64	2.10
54	"	"	"	"	"	"	80	"	"	NR	NR
58	218	6	303	50	NR	NA	69	.624	.090	NR	NR
59	"	"	"	"	"	"	66	NR	NR	"	"
01	219	5	303	50	NR	NA	65	NR	NR	BDL	BDL
02	"	"	"	"	"	"	69	"	"	NR	NR

```
18:04    220    7    303    48    NR    NA    72    1.135   .124    NR      NR
18:05     "     "     "      "     "     "    64       NR     NR     "       "
18:07    232    6    303    NR    NR    NA    72       NR     NR   14.10   2.40
18:08     "     "     "      "     "     "    67        "      "    NR      NR
18:10    210    6    303    55    NR    NA    70     .880   .108    NR      NR
18:11     "     "     "      "     "     "    79       NR     NR     "       "
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" = THE SAME AS THE PRECEDING VALUE

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IS DATA WAS RECORDED ON 07/05/84

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	$[O_3]$	[NO]	+/-	$[NO_2]$	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM²)	(W/M²)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
17:44	317	13	298	70	NR	NA	28	.170	.032	NR	NR
17:45	"	"	"	"	"	"	30	NR	NR	"	"
17:46	"	"	"	"	"	"	33	"	"	"	"
17:48	320	10	298	65	1600	NA	43	NR	NR	NR	NR
17:49	"	"	"	"	"	"	44	"	"	"	"
17:50	"	"	"	"	"	"	30	"	"	"	"
17:51	"	"	"	"	"	"	51	"	"	"	"
17:52	"	"	"	"	"	"	45	"	"	"	"
7:54	312	15	297	60	450	NA	49	.350	.044	NR	NR
7:55	"	"	"	"	"	"	32	NR	NR	"	"
7:56	"	"	"	"	"	"	55	"	"	"	"
7:57	"	"	"	"	"	"	31	"	"	"	"
7:58	"	"	"	"	"	"	40	"	"	"	"
8:02	310	11	297	75	NR	NA	42	.309	.042	NR	NR
8:03	"	"	"	"	"	"	41	NR	NR	"	"
8:04	"	"	"	"	"	"	21	"	"	"	"
8:05	"	"	"	"	"	"	29	"	"	"	"
8:06	"	"	"	"	"	"	87	"	"	"	"
8:07	295	15	297	60	NR	NA	31	.139	.030	NR	NR
8:08	"	"	"	"	"	"	"	NR	NR	"	"
8:09	"	"	"	"	"	"	27	"	"	"	"
8:10	"	"	"	"	"	"	26	"	"	"	"
8:11	"	"	"	"	"	"	43	"	"	"	"
:12	290	17	297	65	NR	NA	49	.345	.044	NR	NR
:13	"	"	"	"	"	"	46	NR	NR	"	"
:14	"	"	"	"	"	"	31	"	"	"	"
:15	"	"	"	"	"	"	37	"	"	"	"
:17	260	14	297	65	NR	NA	51	.253	.038	NR	NR
:18	"	"	"	"	"	"	28	NR	NR	"	"
:19	"	"	"	"	"	"	37	"	"	"	"
:20	"	"	"	"	"	"	44	"	"	"	"
:21	"	"	"	"	"	"	39	"	"	"	"
:22	300	10	296	70	NR	NA	17	NR	NR	NR	NR
:23	"	"	"	"	"	"	29	"	"	"	"
:24	"	"	"	"	"	"	40	"	"	"	"
25	"	"	"	"	"	"	60	"	"	"	"
29	320	5	294	65	NR	NA	57	NR	NR	NR	NR
33	NR	3	294	NR	NR	NA	22	NR	NR	NR	NR
49	NR	9	NR	NR	NR	NA	21	NR	NR	NR	NR
51	"	"	"	"	"	"	47	"	"	"	"
53	250	7	302	60	NR	NA	50	.108	.027	NR	NR
54	"	"	"	"	"	"	28	NR	NR	"	"
55	"	"	"	"	"	"	34	"	"	"	"
56	"	"	"	"	"	"	56	"	"	"	"
57	"	"	"	"	"	"	50	"	"	"	"
59	255	5	305	50	NR	NA	28	.253	.038	NR	NR
00	"	"	"	"	"	"	44	NR	NR	"	"
01	"	"	"	"	"	"	47	"	"	"	"

19:02	"	"	"	"	"	"	60	"	"	"	"
19:03	"	"	"	"	"	"	5	"	"	"	"
19:05	265	9	305	55	NR	NA	39	NR	NR	NR	NR
19:06	"	"	"	"	"	"	37	"	"	"	"
19:07	"	"	"	"	"	"	51	"	"	"	"
19:08	"	"	"	"	"	"	36	"	"	"	"
19:11	266	NR	305	NR	NR	NA	54	NR	NR	NR	NR
19:13	266	9	305	60	350	NA	35	STD	STD	–	–
19:14	"	"	"	"	"	"	26	"	"	NR	NR
19:15	"	"	"	"	"	"	44	"	"	"	"
19:16	"	"	"	"	"	"	31	"	"	"	"
19:17	"	"	"	"	"	"	43	"	"	"	"
19:27	267	8	302	60	NR	NA	40	.155	.031	NR	NR
19:28	"	"	"	"	"	"	43	NR	NR	"	"
19:29	"	"	"	"	"	"	"	"	"	"	"
19:30	"	"	"	"	"	"	40	"	"	"	"
19:31	"	"	"	"	"	"	"	"	"	"	"
19:32	260	8	304	55	NR	NA	38	.247	.038	NR	NR
19:33	"	"	"	"	"	"	28	NR	NR	"	"
19:34	"	"	"	"	"	"	31	"	"	"	"
19:35	"	"	"	"	"	"	37	"	"	"	"
19:36	"	"	"	"	"	"	79	"	"	"	"

* * *

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IS DATA WAS RECORDED ON 07/06/84

TIME	WIND (DEGREES)	(MPH)	TEMP (K)	REL. HUM. (%)	C.C.N. (#/CM²)	UV. FLUX (W/M²)	[O$_3$] (PPB)	[NO] (PPB)	+/- (PPB)	[NO$_2$] (PPB)	+/- (PPB)
14:43	215	17	302	45	NR	NA	52	NR	NR	NR	NR
14:50	240	23	299	55	NR	NA	49	NR	NR	BDL	BDL
14:51	"	"	"	"	"	"	56	"	"	NR	NR
14:55	238	42	293	70	NR	NA	67	NR	NR	NR	NR
14:56	"	"	"	"	"	"	76	"	"	"	"
15:02	NR	17	293	NR	NR	NA	47	NR	NR	NR	NR
15:06	220	18	293	65	NR	NA	54	NR	NR	NR	NR
15:08	220	21	294	NR	NR	NA	57	NR	NR	NR	NR
15:37	215	15	298	60	NR	NA	65	NR	NR	BDL	BDL
5:38	"	"	"	"	"	"	29	"	"	NR	NR
5:40	215	14	298	55	1900	NA	43	NR	NR	NR	NR
5:41	"	"	"	"	"	"	52	"	"	"	"
5:44	230	12	298	55	NR	NA	40	NR	NR	BDL	BDL
5:45	"	"	"	"	"	"	48	"	"	NR	NR
5:48	205	11	298	58	NR	NA	51	NR	NR	NR	NR
5:49	"	"	"	"	"	"	31	"	"	"	"
5:51	220	19	299	58	NR	NA	122	NR	NR	3.20	1.90
5:52	"	"	"	"	"	"	12	"	"	NR	NR
5:54	235	13	300	59	NR	NA	22	NR	NR	NR	NR
5:55	"	"	"	"	"	"	79	"	"	"	"
5:57	235	12	301	55	NR	NA	59	NR	NR	NR	NR
5:58	"	"	"	"	"	"	40	"	"	"	"
:04	240	10	300	55	3000	NA	33	NR	NR	4.40	2.60
:05	"	"	"	"	"	"	52	"	"	NR	NR
:08	225	10	300	58	NR	NA	38	NR	NR	NR	NR
:09	"	"	"	"	"	"	40	"	"	"	"
:11	235	13	300	NR	NR	NA	22	NR	NR	NR	NR
:12	"	"	"	"	"	"	36	"	"	"	"
:14	230	12	300	60	NR	NA	36	NR	NR	NR	NR
:15	"	"	"	"	"	"	31	"	"	"	"
:20	265	6	300	NR	NR	NA	35	NR	NR	NR	NR
:11	280	8	298	NR	NR	NA	23	NR	NR	4.20	1.60
:12	"	"	"	"	"	"	43	"	"	NR	NR
14	280	9	297	58	NR	NA	63	NR	NR	NR	NR
15	"	"	"	"	"	"	39	"	"	"	"
17	275	8	297	55	NR	NA	46	NR	NR	10.50	2.10
18	"	"	"	"	"	"	49	"	"	NR	NR
20	280	8	296	NR	NR	NA	39	NR	NR	NR	NR
21	"	"	"	"	"	"	48	"	"	"	"
23	280	10	296	55	NR	NA	39	NR	NR	22.30	2.70
24	"	"	"	"	"	"	43	"	"	NR	NR
31	260	11	298	NR	NR	NA	49	–	–	STD	STD
32	"	"	"	"	"	"	46	NR	NR	"	"
33	"	"	"	"	"	"	35	"	"	"	"
34	255	16	298	NR	NR	NA	42	–	–	STD	STD
35	"	"	"	"	"	"	37	"	"	"	"
37	250	11	298	NR	NR	NA	43	–	–	STD	STD
38	"	"	"	"	"	"	39	"	"	"	"
40	230	10	298	NR	NR	NA	41	–	–	STD	STD

17:41	"	"	"	"	"	"	49	"	"	"	"
17:54	240	9	299	NR	NR	NA	46	NR	NR	17.90	2.50
17:55	"	"	"	"	"	"	38	"	"	NR	NR
17:57	240	9	299	57	100	NA	41	NR	NR	10.80	2.10
17:58	"	"	"	"	"	"	43	"	"	NR	NR
18:00	240	10	299	57	NR	NA	42	NR	NR	10.30	2.10
18:01	"	"	"	"	"	"	47	"	"	NR	NR

* * *

NR = NOT RECORDED

NA = NOT AVAILABLE

STD = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE

BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

IS DATA WAS RECORDED ON JULY SEVENTH, NINETEEN HUNDRED A

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	[O_3]	[NO]	+/-	[NO_2]	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM²)	(W/M²)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
05:00	223	19	294	88	NR	NA	19	NR	NR	NA	NA
05:05	NR	NR	NR	NR	NR	NA	23	NR	NR	24.87	2.88
05:06	"	"	"	"	"	"	21	"	"	"	"
05:07	"	"	"	"	"	"	20	"	"	"	"
05:08	"	"	"	"	"	"	17	"	"	"	"
05:11	NR	NR	NR	NR	NR	NA	16	NR	NR	NR	NR
05:12	"	"	"	"	"	"	19	"	"	"	"
05:13	"	"	"	"	"	"	"	"	"	"	"
05:14	"	"	"	"	"	"	17	"	"	"	"
05:33	NR	NR	NR	NR	NR	NA	6	NR	NR	NR	NR
5:45	237	18	NR	NR	NR	NA	6	NR	NR	NR	NR
5:46	"	"	"	"	"	"	5	"	"	"	"
5:49	NR	NR	NR	NR	NR	NA	8	NR	NR	NR	NR
5:50	"	"	"	"	"	"	13	"	"	"	"
5:55	NR	NR	NR	NR	NR	NA	14	NR	NR	NR	NR
5:56	"	"	"	"	"	"	16	"	"	"	"
5:58	NR	NR	NR	NR	NR	NA	19	NR	NR	17.65	2.39
6:03	NR	NR	NR	NR	NR	NA	16	NR	NR	NR	NR
6:06	242	14	NR	NR	NR	NA	14	NR	NR	NR	NR
6:07	"	"	"	"	"	"	15	"	"	"	"
6:16	NR	NR	NR	NR	NR	NA	17	STD	STD	-	-
6:17	"	"	"	"	"	"	14	"	"	"	"
6:18	"	"	"	"	"	"	16	"	"	"	"
:25	NR	NR	NR	NR	NR	NA	14	NR	NR	NR	NR
:26	"	"	"	"	"	"	"	"	"	"	"
:30	NR	NR	NR	NR	NR	NA	14	NR	NR	5.08	1.36
:31	"	"	"	"	"	"	"	"	"	8.29	1.65
:32	"	"	"	"	"	"	"	"	"	10.96	1.85
:33	"	"	"	"	"	"	"	"	"	106.4	5.58
:34	"	"	"	"	"	"	"	"	"	84.76	5.04
:35	"	"	"	"	"	"	"	"	"	36.37	3.53
:45	239	12	NR	NR	NR	NA	8	NR	NR	15.78	2.55
:46	"	"	"	"	"	"	10	"	"	13.10	2.41
:47	"	"	"	"	"	"	12	"	"	9.36	2.19
:48	"	"	"	"	"	"	13	"	"	16.31	2.58
:52	NR	NR	NR	NR	NR	NA	11	NR	NR	6.69	2.02
:53	"	"	"	"	"	"	12	"	"	8.82	2.16
:54	"	"	"	"	"	"	"	"	"	8.29	2.12
:55	"	"	"	"	"	"	11	"	"	14.17	2.47
:56	252	15	"	"	"	"	9	"	"	13.10	2.41
:57	"	"	"	"	"	"	10	"	"	12.03	2.35
:03	NR	NR	NR	NR	NR	NA	4	.318	.051	NR	NR
04	"	"	"	"	"	"	11	"	"	"	"
08	NR	NR	NR	NR	NR	NA	11	NR	NR	NR	NR
09	"	"	"	"	"	"	14	"	"	"	"
28	260	14	NR	NR	NR	NA	14	NR	NR	6.95	2.04
29	"	"	"	"	"	"	11	"	"	7.49	2.07
30	"	"	"	"	"	"	NR	"	"	6.69	2.02

08:00	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
09:04	347	13	296	100	NR	NA	3	NR	NR	82.63	7.23
09:06	"	"	"	"	"	"	4	"	"	"	"
09:07	NR	NR	NR	NR	NR	NA	NR	5.419	.375	NR	NR
09:22	NR	NR	NR	NR	NR	NA	11	1.914	.218	NR	NR
09:23	"	"	"	"	"	"	"	"	"	5.64	2.14
09:24	"	"	"	"	"	"	"	"	"	9.50	3.18
09:38	352	24	NR	NR	NR	NA	14	NR	NR	NR	NR
09:40	"	"	"	"	"	"	11	1.143	.169	NR	NR
09:42	"	"	"	"	"	"	13	NR	NR	"	"
09:43	NR	NR	NR	NR	NR	NA	14	NR	NR	NR	NR
09:54	"	"	"	"	"	"	12	"	" "	NR	NR
09:55	NR	NR	NR	NR	NR	NA	17	.584	.061	NR	NR
09:56	"	"	"	"	"	"	15	"	"	"	"
10:14	330	11	291	100	NR	NA	14	NR	NR	BDL	BDL
10:15	"	"	"	"	"	"	25	"	"	"	"
10:16	341	14	"	"	"	"	22	"	"	"	"
0:17	"	"	"	"	"	"	25	"	"	1.48	7.85
0:18	"	"	"	"	"	"	22	"	"	BDL	BDL
0:19	"	"	"	"	"	"	26	"	"	"	"
0:22	339	17	290	95	NR	NA	29	.186	.107	NR	NR
0:23	343	16	290	100	NR	NA	29	NR	NR	.89	.84
0:24	"	"	"	"	"	"	28	"	"	BDL	BDL
0:25	"	"	"	"	"	"	25	"	"	"	"
0:26	"	"	"	"	"	"	31	"	"	"	"
0:27	"	"	"	"	"	"	32	"	"	"	"
0:29	354	18	290	80	NR	NA	30	NR	NR	NR	NR
0:31	360	17	290	75	NR	NA	27	NR	NR	BDL	BDL
0:32	"	"	"	"	"	"	29	"	"	"	"
:33	"	"	"	"	"	"	31	"	"	"	"
:34	"	"	"	"	"	"	29	"	"	"	"
:36	111	16	290	72	NR	NA	28	.224	.054	NR	NR
:37	"	"	"	"	"	"	29	"	"	"	"
:38	"	"	"	"	"	"	28	"	"	"	"
:39	"	"	"	"	"	"	25	"	"	"	"
:45	124	14	291	66	NR	NA	29	NR	NR	4.45	1.97
:46	"	"	"	"	"	"	30	"	"	"	"
:47	"	"	"	"	"	"	"	"	"	"	"
:48	"	"	"	"	"	"	29	"	"	"	"
:54	113	9	292	88	NR	NA	25	1.156	.121	NR	NR
:55	"	"	"	"	"	"	22	"	"	"	"
:56	"	"	"	"	"	"	21	"	"	"	"
57	"	"	"	"	"	"	19	"	"	"	"
24	147	2.	297	59	NR	NA	27	NR	NR	BDL	BDL
25	"	"	"	"	"	"	26	"	"	"	"
26	"	"	"	"	"	"	"	"	"	"	"
27	"	"	"	"	"	"	29	"	"	"	"
29	121	2	278	61	NR	NA	28	—	—	STD	STD
30	"	"	"	"	"	"	27	"	"	"	"
31	"	"	"	"	"	"	"	"	"	"	"
32	"	"	"	"	"	"	"	"	"	"	"
48	83	2	300	55	NR	NA	30	—	—	STD	STD
49	"	"	"	"	"	"	32	"	"	"	"
50	"	"	"	"	"	"	28	"	"	"	"
51	"	"	"	"	"	"	29	"	"	"	"
54	49	3	300	58	NR	NA	25	—	—	STD	STD
55	"	"	"	"	"	"	28	"	"	"	"
6	"	"	"	"	"	"	"	"	"	"	"
7	"	"	"	"	"	"	30	"	"	"	"
9	72	3	300	60	NR	NA	28	—	—	STD	STD

12:00	"	"	"	"	"	"	"	"	"	"	
12:01	"	"	"	"	"	"	"	"	"	"	"
12:02	"	"	"	"	"	"	34	"	"	"	"
12:07	63	2	300	50	NR	NA	32	NR	NR	NR	NR
12:08	"	"	"	"	"	"	33	"	"	"	"
12:09	"	"	"	"	"	"	28	"	"	"	"
12:10	"	"	"	"	"	"	30	"	"	"	"
12:12	44	2	300	50	NR	NA	28	–	–	STD	STD
12:13	"	"	"	"	"	"	33	"	"	"	"
12:14	"	"	"	"	"	"	27	"	"	"	"
12:15	"	"	"	"	"	"	"	"	"	"	"
12:19	40	3	300	53	NR	NA	28	–	–	STD	STD
12:20	"	"	"	"	"	"	30	"	"	"	"
12:21	"	"	"	"	"	"	31	"	"	"	"
12:22	"	"	"	"	"	"	32	"	"	"	"
12:24	46	4	299	42	NR	NA	32	–	–	STD	STD
12:25	"	"	"	"	"	"	31	"	"	"	"
12:26	"	"	"	"	"	"	26	"	"	"	"
12:27	"	"	"	"	"	"	"	"	"	"	"
12:35	50	5	NR	NR	NR	NA	26	NR	NR	NR	NR
12:38	30	6	299	45	NR	NA	23	NR	NR	BDL	BDL
2:39	"	"	"	"	"	"	32	"	"	"	"
2:41	35	6	299	48	NR	NA	29	2.406	.157	NR	NR
2:42	"	"	"	"	"	"	30	"	"	"	"
2:44	290	8	298	48	NR	NA	28	NR	NR	BDL	BDL
2:45	"	"	"	"	"	"	34	"	"	"	"
2:47	280	6	298	NR	NR	NA	27	3.033	.176	NR	NR
2:48	"	"	"	"	"	"	29	"	"	"	"
2:58	270	9	300	52	NR	NA	30	NR	NR	12.00	6.87
2:59	"	"	"	"	"	"	"	"	"	"	"
3:01	275	9	300	50	6400	NA	37	2.883	.172	NR	NR
3:02	"	"	"	"	"	"	33	"	"	"	"
3:03	277	6	300	48	NR	NA	32	NR	NR	41.20	7.19
3:04	"	"	"	"	"	"	"	"	"	"	"
3:06	262	8	300	42	3800	NA	34	2.337	.155	NR	NR
3:07	"	"	"	"	"	"	31	"	"	"	"
3:09	240	10	300	NR	NR	NA	31	NR	NR	16.00	7.59
:11	260	11	300	50	NR	NA	37	3.639	.192	NR	NR
:12	"	"	"	"	"	"	31	"	"	"	"
:14	270	7	300	NR	NR	NA	26	NR	NR	NR	NR
:15	"	"	"	"	"	"	28	"	"	"	"
:17	265	10	300	NR	NR	NA	26	NR	NR	115.6	11.3
:20	260	10	300	52	NR	NA	28	6.125	.248	NR	NR
:21	"	"	"	"	"	"	25	"	"	"	"
:24	250	8	300	50	NR	NA	33	NR	NR	96.00	9.19
:25	"	"	"	"	"	"	31	"	"	"	"
:27	253	12	300	50	NR	NA	32	3.221	.181	NR	NR
:28	"	"	"	"	"	"	33	"	"	"	"
:29	260	10	300	NR	NR	NA	34	NR	NR	34.40	7.05
:30	"	"	"	"	"	"	37	"	"	"	"
:32	250	8	300	53	NR	NA	36	2.396	.157	NR	NR
:33	"	"	"	"	"	"	35	"	"	"	"
:35	265	11	300	52	NR	NA	36	NR	NR	NR	NR
36	"	"	"	"	"	"	"	"	"	"	"
40	270	8	300	55	2600	NA	36	NR	NR	NR	NR
41	"	"	"	"	"	"	37	"	"	"	"
45	290	6	301	52	NR	NA	40	2.227	.151	NR	NR
46	"	"	"	"	"	"	38	"	"	"	"
48	270	8	300	50	NR	NA	39	NR	NR	3.76	.70
49	"	"	"	"	"	"	36	"	"	"	"

13:51	258	9	301	NR	NR	NA	38	1.491	.125	NR	NR
13:52	"	"	"	"	"	"	34	"	"	"	"
13:54	265	8	301	NR	NR	NA	33	NR	NR	4.56	.66
13:55	"	"	"	"	"	"	35	"	"	"	"
13:58	288	5	302	60	NR	NA	35	1.462	.124	NR	NR
13:59	"	"	"	"	"	"	36	"	"	"	"
14:06	270	9	302	53	NR	NA	38	NR	NR	NR	NR
14:07	"	"	"	"	"	"	40	"	"	"	"
14:15	275	6	302	55	270	NA	42	1.518	.123	NR	NR
14:16	"	"	"	"	"	"	39	"	"	"	"
14:17	260	8	302	55	NR	NA	41	NR	NR	3.52	.58
14:18	"	"	"	"	"	"	"	"	"	"	"
14:20	275	8	302	NR	NR	NA	40	.968	.100	NR	NR
14:21	"	"	"	"	"	"	42	"	"	"	"
14:23	275	10	302	NR	NR	NA	46	NR	NR	29.20	5.44
14:24	"	"	"	"	"	"	"	"	"	"	"
14:26	280	7	302	50	NR	NA	45	.882	.095	NR	NR
14:27	"	"	"	"	"	"	"	"	"	"	"
14:29	275	4	302	50	NR	NA	45	NR	NR	11.60	5.03
4:30	"	"	"	"	"	"	46	"	"	"	"
4:32	275	8	302	57	NR	NA	48	1.091	.105	NR	NR
4:33	"	"	"	"	"	"	50	"	"	"	"
4:36	280	8	302	56	NR	NA	47	NR	NR	24.40	5.08
4:37	"	"	"	"	"	"	48	"	"	"	"
4:39	250	9	302	NR	NR	NA	47	.721	.087	NR	NR
4:40	"	"	"	"	"	"	"	"	"	"	"
4:42	240	8	302	NR	NR	NA	51	NR	NR	61.60	6.96
4:43	"	"	"	"	"	"	52	"	"	"	"
4:49	275	7	302	50	NR	NA	57	1.338	.116	NR	NR
4:50	"	"	"	"	"	"	59	"	"	"	"
4:52	275	9	302	53	270	NA	57	NR	NR	46.40	6.23
4:53	"	"	"	"	"	"	"	"	"	"	"
4:55	275	7	302	55	NR	NA	56	1.129	.107	NR	NR
4:56	"	"	"	"	"	"	59	"	"	"	"
4:57	275	11	302	NR	NR	NA	55	NR	NR	54.00	6.66
:58	"	"	"	"	"	"	"	"	"	"	"
:01	275	11	302	NR	NR	NA	50	1.252	.112	NR	NR
:02	"	"	"	"	"	"	55	"	"	"	"
:04	274	7	302	52	NR	NA	57	N	NR	75.60	6.84
:05	"	"	"	"	"	"	58	"	"	"	"
:08	275	15	302	54	NR	NA	50	.759	.089	NR	NR
:09	"	"	"	"	"	"	"	"	"	"	"
:14	285	18	302	NR	NR	NA	48	NR	NR	52.80	5.91
:15	"	"	"	"	"	"	46	"	"	"	"
:17	275	15	302	NR	NR	NA	45	.550	.077	NR	NR
:18	"	"	"	"	"	"	46	"	"	"	"
:20	275	17	302	NR	NR	NA	48	NR	NR	45.60	5.66
:21	"	"	"	"	"	"	49	"	"	"	"
:46	266	16	303	55	NR	NA	45	NR	NR	8.40	1.66
47	"	"	"	"	"	"	"	"	"	"	"
50	271	17	303	55	NR	NA	45	.293	.067	NR	NR
51	"	"	"	"	"	"	46	"	"	"	"
53	272	14	303	60	NR	NA	46	NR	NR	11.70	1.84
54	"	"	"	"	"	"	"	"	"	"	"
57	NR	NR	NR	NR	NR	NA	41	NR	NR	NR	NR
08	270	18	303	60	NR	NA	39	NR	NR	NR	NR
19	265	13	303	62	NR	NA	37	NR	NR	17.46	2.10
20	"	"	"	"	"	"	"	"	"	"	"
21	261	12	303	64	NR	NA	37	.349	.071	NR	NR
22	"	"	"	"	"	"	39	"	"	"	"

16:24	265	15	303	65	NR	NA	36	NR	NR	NR	NR
16:25	"	"	"	"	"	"	38	"	"	"	"
16:27	266	14	303	60	NR	NA	38	NR	NR	7.08	1.66
16:28	"	"	"	"	"	"	41	"	"	"	"
16:34	267	11	303	63	NR	NA	39	.372	.073	NR	NR
16:35	240	9	303	50	NR	NA	41	NR	NR	NR	NR
16:36	"	"	"	"	"	"	39	"	"	"	"
16:39	264	11	303	62	NR	NA	37	.248	.063	NR	NR
16:40	"	"	"	"	"	"	"	"	"	"	"
16:42	257	10	303	NR	NR	NA	38	.248	.063	NR	NR
16:43	"	"	"	"	"	"	39	"	"	"	"
16:44	265	9	303	65	NR	NA	39	NR	NR	14.99	1.92
16:45	"	"	"	"	"	"	35	"	"	"	"
16:48	258	9	303	60	NR	NA	38	NR	NR	8.40	1.61
16:49	"	"	"	"	"	"	39	"	"	"	"
16:54	247	10	303	60	NR	NA	38	NR	NR	NR	NR
17:22	251	12	303	60	NR	NA	38	NR	NR	NR	NR
17:23	"	"	"	"	"	"	33	"	"	"	"
17:25	260	12	303	68	NR	NA	35	NR	NR	NR	NR
17:26	"	"	"	"	"	"	33	"	"	"	"
17:28	253	10	302	62	NR	NA	34	NR	NR	NR	NR
17:29	"	"	"	"	"	"	36	"	"	"	"
17:32	271	11	301	70	NR	NA	34	NR	NR	11.37	1.98
7:33	"	"	"	"	"	"	35	"	"	"	"
7:35	273	14	301	60	NR	NA	38	NR	NR	10.71	1.96
7:36	"	"	"	"	"	"	36	"	"	"	"
7:40	276	10	301	68	NR	NA	36	.530	.084	NR	NR
7:41	"	"	"	"	"	"	35	"	"	"	"
7:43	266	12	301	70	NR	NA	32	NR	NR	38.39	2.90
7:44	"	"	"	"	"	"	35	"	"	"	"
7:46	265	11	302	70	NR	NA	32	NR	NR	26.03	2.52
7:47	"	"	"	"	"	"	"	"	"	"	"
7:48	266	15	301	60	NR	NA	33	NR	NR	12.19	2.02
7:49	"	"	"	"	"	"	37	"	"	"	"
7:51	266	13	302	65	NR	NA	35	NR	NR	13.67	1.91
7:52	"	"	"	"	"	"	38	"	"	"	"
7:54	270	16	301	55	NR	NA	35	NR	NR	14.83	1.96
:55	"	"	"	"	"	"	36	"	"	"	"
:57	267	15	301	50	NR	NA	36	NR	NR	14.83	1.96
:58	"	"	"	"	"	"	32	"	"	"	"
:59	273	16	301	70	NR	NA	36	.372	.073	NR	NR
:00	"	"	"	"	"	"	36	"	"	"	"
:02	270	14	301	70	NR	NA	35	.417	.076	NR	NR
:03	"	"	"	"	"	"	36	"	"	"	"
:05	272	16	301	70	NR	NA	36	NR	NR	27.84	2.22

* * *

NR = NOT RECORDED

NA = NOT AVAILABLE

STD = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE

S DATA WAS RECORDED ON 07/13_14/84

IME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	[O$_3$]	[NO]	+/-	[NO$_2$]	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM^2)	(W/M^2)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
2:30	258	12	295	93	NR	NA	23	NR	NR	NR	NR
2:40	NR	NR	NR	NR	NR	NA	21	NR	NR	NR	NR
2:50	NR	NR	NR	NR	NR	NA	21	NR	NR	NR	NR
2:51	NR	NR	NR	NR	NR	NA	0	NR	NR	NR	NR
2:52	NR	NR	NR	NR	NR	NA	6	NR	NR	NR	NR
2:53	NR	NR	NR	NR	NR	NA	5	NR	NR	NR	NR
2:54	NR	NR	NR	NR	NR	NA	3	NR	NR	NR	NR
2:55	NR	NR	NR	NR	NR	NA	19	NR	NR	NR	NR
2:57	NR	NR	NR	NR	NR	NA	0	NR	NR	NR	NR
2:58	NR	NR	NR	NR	NR	NA	6	NR	NR	NR	NR
3:14	NR	NR	NR	NR	NR	NA	7	NR	NR	NR	NR
4:25	NR	NR	NR	NR	NR	NA	14	NR	NR	NR	NR
4:35	NR	NR	NR	NR	NR	NA	11	NR	NR	NR	NR
5:45	266	8	295	86	NR	NA	15	NR	NR	NR	NR
:00	NR	NR	NR	NR	NR	NA	11	NR	NR	14.90	2.80
:04	NR	NR	NR	NR	NR	NA	11	BDL	BDL	NR	NR
:05	"	"	"	"	"	"	13	NR	NR	"	"
:10	NR	NR	NR	NR	NR	NA	12	NR	NR	12.41	2.60
:15	260	10	295	93	NR	NA	14	NR	NR	NR	NR
:18	NR	NR	NR	NR	NR	NA	10	NR	NR	14.64	2.80
:30	NR	NR	NR	NR	NR	NA	13	NR	NR	NR	NR
:36	NR	NR	NR	NR	NR	NA	11	NR	NR	13.15	2.70
:37	"	"	"	"	"	"	12	"	"	NR	NR
:42	NR	NR	294	100	NR	NA	9	BDL	BDL	NR	NR
:46	NR	NR	NR	NR	NR	NA	10	NR	NR	NR	NR
:49	NR	NR	294	100	NR	NA	10	NR	NR	22.58	3.20
:02	NR	NR	NR	NR	NR	NA	8	NR	NR	NR	NR
:05	NR	NR	NR	NR	NR	NA	8	NR	NR	NR	NR
:11	NR	NR	NR	NR	NR	NA	10	NR	NR	17.87	3.70
:14	255	12	295	100	NR	NA	8	1.034	.135	NR	NR
17	NR	NR	NR	NR	NR	NA	7	NR	NR	NR	NR
24	NR	NR	NR	NR	NR	NA	7	NR	NR	15.88	3.60
27	NR	NR	NR	NR	NR	NA	9	1.271	.151	NR	NR
30	NR	NR	NR	NR	NR	NA	7	NR	NR	NR	NR
43	251	13	NR	NR	NR	NA	7	NR	NR	NR	NR
45	"	"	"	"	"	"	9	"	"	"	"
47	"	"	"	"	"	"	6	"	"	"	"
30	217	11	295	87	NR	NA	10	NR	NR	5.46	5.00
31	"	"	"	"	"	"	8	"	"	NR	NR
35	NR	NR	NR	NR	NR	NA	8	5.618	.319	NR	NR
36	"	"	"	"	"	"	6	NR	NR	"	"
45	NR	NR	NR	NR	NR	NA	8	4.618	.289	NR	NR
48	NR	NR	NR	NR	NR	NA	8	NR	NR	BDL	BDL
49	"	"	"	"	"	"	14	"	"	NR	NR
53	NR	NR	NR	NR	NR	NA	10	NR	NR	NR	NR
57	NR	NR	NR	NR	NR	NA	9	NR	NR	BDL	BDL
58	"	"	"	"	"	"	"	"	"	NR	NR
10	NR	NR	NR	NR	NR	NA	8	3.635	.256	NR	NR
11	"	"	"	"	"	"	10	NR	NR	"	"

09:03	254	8	296	77	NR	NA	9	NR	NR	BDL	BDL
09:04	"	"	"	"	"	"	9	NR	NR	NR	NR
09:08	252	8	297	75	NR	NA	"	3.072	.234	"	"
09:09	"	"	"	"	"	"	10	NR	NR	"	"
09:14	NR	NR	NR	NR	NR	NA	9	NR	NR	6.93	.60
09:15	"	"	"	"	"	"	8	"	"	NR	NR
09:18	NR	NR	NR	NR	NR	NA	8	3.072	.234	NR	NR
09:19	"	"	"	"	"	"	9	NR	NR	"	"
09:20	"	"	"	"	"	"	12	"	"	"	"
09:22	NR	NR	NR	NR	NR	NA	9	NR	NR	13.83	.68
09:23	"	"	"	"	"	"	12	"	"	NR	NR
09:25	NR	NR	NR	NR	NR	NA	11	NR	NR	NR	NR
09:26	"	"	"	"	"	"	9	"	"	"	"
09:27	"	"	"	"	"	"	8	"	"	"	"
09:29	NR	NR	NR	NR	NR	NA	7	NR	NR	8.71	.80
09:30	"	"	"	"	"	"	5	"	"	NR	NR
09:31	"	"	"	"	"	"	"	"	"	"	"
09:33	NR	NR	NR	NR	NR	NA	5	6.473	.343	NR	NR
9:34	"	"	"	"	"	"	4	NR	NR	"	"
9:35	"	"	"	"	"	"	5	"	"	"	"
9:36	NR	NR	NR	NR	NR	NA	3	NR	NR	12.57	.83
9:37	"	"	"	"	"	"	4	"	"	NR	NR
0:02	237	13	297	84	NR	9.0	13	NR	NR	12.31	1.20
0:04	"	"	"	"	"	7.2	11	"	"	NR	NR
0:06	"	"	"	"	"	6.6	12	"	"	"	"
0:08	"	"	"	"	"	8.4	15	"	"	"	"
0:10	"	"	"	"	"	7.8	18	"	"	"	"
0:16	246	12	297	80	NR	6.6	17	2.482	.152	NR	NR
0:18	"	"	"	"	"	6.0	18	NR	NR	NR	NR
0:20	"	"	"	"	"	6.6	16	NR	NR	NR	NR
0:22	"	"	"	"	"	7.2	16	NR	NR	NR	NR
:24	"	"	"	"	"	7.8	15	NR	NR	NR	NR
:25	241	12	297	85	NR	7.8	16	NR	NR	NR	NR
:26	"	"	"	"	"	8.4	16	"	"	"	"
:27	"	"	"	"	"	10.8	14	"	"	"	"
:28	"	"	"	"	"	13.3	18	"	"	"	"
:29	"	"	"	"	"	15.1	18	"	"	"	"
:33	229	11	299	72	NR	15.7	19	NR	NR	15.58	1.20
:35	"	"	"	"	"	14.5	18	"	"	NR	NR
:37	"	"	"	"	"	11.4	20	"	"	"	"
39	"	"	"	"	"	12.0	22	"	"	"	"
41	"	"	"	"	"	"	21	"	"	"	"
42	258	5	299	80	2400	12.0	18	NR	NR	NR	NR
49	270	10	299	75	NR	9.6	22	NR	NR	13.30	1.14
51	"	"	"	"	"	10.8	21	"	"	NR	NR
53	"	"	"	"	"	"	24	"	"	"	"
55	"	"	"	"	"	12.0	26	"	"	"	"
57	"	"	"	"	"	"	25	"	"	"	"
09	245	10	300	70	NR	13.3	30	2.845	.163	NR	NR
11	"	"	"	"	"	11.4	29	NR	NR	"	"
13	"	"	"	"	"	13.3	32	"	"	"	"
15	"	"	"	"	"	15.7	28	"	"	"	"
17	"	"	"	"	"	14.5	30	"	"	"	"
19	240	3	301	70	NR	9.6	26	NR	NR	14.64	1.40
21	"	"	"	"	"	12.7	27	"	"	NR	NR
23	"	"	"	"	"	14.5	26	"	"	"	"
25	"	"	"	"	"	13.3	29	"	"	"	"
27	"	"	"	"	"	"	27	"	"	"	"
5	227	8	300	70	NR	11.4	27	3.255	.173	NR	NR
7	"	"	"	"	"	12.0	28	NR	NR	"	"

11:38	"	"	"	"	"	12.7	"	"	"	"	"
11:40	"	"	"	"	"	15.1	"	"	"	"	"
11:42	"	"	"	"	"	16.9	27	"	"	"	"
11:43	246	7	300	62	1200	21.1	34	NR	NR	NR	NR
12:04	237	9	300	63	NR	15.1	39	NR	NR	9.13	1.05
12:06	"	"	"	"	"	19.3	37	"	"	NR	NR
12:08	"	"	"	"	"	22.3	36	"	"	"	"
12:10	"	"	"	"	"	26.5	39	"	"	"	"
2:12	"	"	"	"	"	"	37	"	"	"	"
2:14	261	8	302	54	NR	24.7	38	1.345	.113	NR	NR
2:16	"	"	"	"	"	18.7	40	NR	NR	"	"
2:17	"	"	"	"	"	24.1	38	"	"	"	"
2:19	"	"	"	"	"	25.3	"	"	"	"	"
2:21	"	"	"	"	"	21.1	40	"	"	"	"
2:22	233	12	303	58	NR	31.9	38	NR	NR	13.90	1.12
2:24	"	"	"	"	"	33.1	39	"	"	NR	NR
2:25	"	"	"	"	"	30.7	42	"	"	"	"
2:27	"	"	"	"	"	31.9	40	"	"	"	"
2:29	"	"	"	"	"	33.1	41	"	"	"	"
2:30	307	4	302	52	NR	22.3	44	1.299	.111	NR	NR
2:32	"	"	"	"	"	"	42	NR	NR	"	"
2:34	"	"	"	"	"	20.5	"	"	"	"	"
2:36	"	"	"	"	"	22.3	45	"	"	"	"
2:38	"	"	"	"	"	29.5	41	"	"	"	"
:48	231	9	304	50	NR	24.1	45	STD	STD	–	–
:50	"	"	"	"	"	31.3	47	"	"	NR	NR
:52	"	"	"	"	"	21.7	45	"	"	"	"
:54	"	"	"	"	"	18.7	49	"	"	"	"
:56	"	"	"	"	"	20.5	48	"	"	"	"
:57	258	12	304	50	NR	21.7	49	.708	.084	NR	NR
:59	"	"	"	"	"	28.9	50	NR	NR	"	"
:01	"	"	"	"	"	24.7	49	"	"	"	"
:03	"	"	"	"	"	36.1	48	"	"	"	"
:05	"	"	"	"	"	21.7	51	"	"	"	"
:08	228	8	304	41	NR	16.3	50	STD	STD	–	–
:10	"	"	"	"	"	28.9	49	"	"	NR	NR
:12	"	"	"	"	"	24.7	51	"	"	"	"
:14	"	"	"	"	"	36.1	"	"	"	"	"
16	"	"	"	"	"	21.7	49	"	"	"	"
19	259	13	304	59	NR	19.9	51	.390	.064	NR	NR
21	"	"	"	"	"	22.9	52	NR	NR	"	"
22	"	"	"	"	"	25.3	51	"	"	"	"
24	"	"	"	"	"	30.1	50	"	"	"	"
26	"	"	"	"	"	30.7	52	"	"	"	"
27	247	9	304	50	NR	28.3	52	NR	NR	BDL	BDL
29	"	"	"	"	"	33.1	"	"	"	NR	NR
31	"	"	"	"	"	31.9	54	"	"	"	"
33	"	"	"	"	"	30.1	53	"	"	"	"
35	"	"	"	"	"	18.7	52	"	"	"	"
37	266	14	304	55	NR	16.3	51	1.390	.115	NR	NR
39	"	"	"	"	"	15.7	47	NR	NR	"	"
41	"	"	"	"	"	13.9	49	"	"	"	"
43	"	"	"	"	"	"	45	"	"	"	"
45	"	"	"	"	"	16.9	48	"	"	"	"
53	228	13	303	60	NR	33.1	37	NR	NR	28.24	1.45
55	"	"	"	"	"	30.1	39	"	"	NR	NR
56	"	"	"	"	"	20.5	38	"	"	"	"
58	"	"	"	"	"	30.1	"	"	"	"	"
0	"	"	"	"	"	18.7	"	"	"	"	"
1	222	13	303	60	NR	20.5	43	NR	NR	NR	NR

14:04	219	14	302	58	NR	16.9	38	5.529	.226	NR	NR
14:06	"	"	"	"	"	31.9	37	NR	NR	"	"
14:07	"	"	"	"	"	"	40	"	"	"	"
14:09	"	"	"	"	"	31.3	47	"	"	"	"
14:11	"	"	"	"	"	29.5	"	"	"	"	"
14:12	238	17	302	55	NR	10.8	38	NR	NR	3.52	1.42
4:14	"	"	"	"	"	13.9	36	"	"	NR	NR
4:16	"	"	"	"	"	12.0	35	"	"	"	"
4:18	"	"	"	"	"	10.2	39	"	"	"	"
4:20	"	"	"	"	"	"	38	"	"	"	"
4:22	231	16	300	66	NR	10.8	33	3.846	.189	NR	NR
4:24	"	"	"	"	"	8.4	32	NR	NR	"	"
4:26	"	"	"	"	"	7.8	28	"	"	"	"
4:28	"	"	"	"	"	"	29	"	"	"	"
4:30	"	"	"	"	"	9.0	28	"	"	"	"
4:37	246	12	301	55	3400	19.3	30	NR	NR	NR	NR
4:42	242	12	301	65	NR	15.1	31	NR	NR	15.53	1.57
4:44	"	"	"	"	"	16.9	30	"	"	NR	NR
4:46	"	"	"	"	"	19.3	31	"	"	"	"
4:48	"	"	"	"	"	18.7	30	"	"	"	"
4:50	"	"	"	"	"	"	"	"	"	"	"
:51	257	11	302	55	NR	19.9	34	5.529	.226	NR	NR
:53	"	"	"	"	"	21.7	36	NR	NR	"	"
:54	"	"	"	"	"	"	35	"	"	"	"
:56	"	"	"	"	"	"	37	"	"	"	"
:58	"	"	"	"	"	22.3	"	"	"	"	"
:59	220	10	303	50	NR	26.5	38	NR	NR	26.15	1.72
:01	"	"	"	"	"	"	37	"	"	NR	NR
:02	"	"	"	"	"	28.3	"	"	"	"	"
:04	"	"	"	"	"	28.9	36	"	"	"	"
:06	"	"	"	"	"	"	40	"	"	"	"
:07	247	11	304	60	NR	26.5	34	6.802	.250	NR	NR
:08	"	"	"	"	"	24.7	36	NR	NR	"	"
:09	"	"	"	"	"	25.3	39	"	"	"	"
:11	"	"	"	"	"	26.5	40	"	"	"	"
:13	"	"	"	"	"	24.7	"	"	"	"	"
:14	239	10	304	50	3700	14.5	42	NR	NR	NR	NR
:26	239	6	304	55	NR	27.7	50	NR	NR	BDL	BDL
27	"	"	"	"	"	24.7	48	"	"	NR	NR
28	"	"	"	"	"	24.1	49	"	"	"	"
29	"	"	"	"	"	22.9	"	"	"	"	"
30	"	"	"	"	"	16.9	48	"	"	"	"
33	252	13	304	55	NR	18.7	52	NR	NR	BDL	BDL
35	"	"	"	"	"	24.1	54	"	"	NR	NR
37	"	"	"	"	"	24.7	"	"	"	"	"
39	"	"	"	"	"	22.3	57	"	"	"	"
41	"	"	"	"	"	24.1	"	"	"	"	"
42	218	4	305	58	NR	23.5	68	—	—	STD	STD
44	"	"	"	"	"	"	"	"	"	"	"
46	"	"	"	"	"	25.3	66	"	"	"	"
48	"	"	"	"	"	25.9	68	"	"	"	"
50	"	"	"	"	"	24.1	66	"	"	"	"
51	251	9	305	55	NR	22.3	64	—	—	STD	STD
53	"	"	"	"	"	19.9	68	"	"	"	"
54	"	"	"	"	"	17.5	67	"	"	"	"
55	"	"	"	"	"	16.3	66	"	"	"	"
57	"	"	"	"	"	15.1	63	"	"	"	"
58	238	12	305	55	NR	19.9	63	NR	NR	NR	NR
59	"	"	"	"	"	22.3	53	"	"	"	"
1	"	"	"	"	"	21.7	52	"	"	"	"

16:03	"	"	"	"	"	19.9	53	"	"	"	"
16:05	"	"	"	"	"	14.5	55	"	"	"	"
6:07	221	11	304	55	NR	14.5	68	NR	NR	8.29	.80
6:09	"	"	"	"	"	11.4	66	"	"	NR	NR
6:10	"	"	"	"	"	10.2	68	"	"	"	"
6:12	"	"	"	"	"	"	67	"	"	"	"
6:14	"	"	"	"	"	"	66	"	"	"	"
6:15	224	9	304	50	NR	10.8	65	.634	.105	NR	NR
6:18	232	11	304	50	NR	16.3	67	NR	NR	12.16	2.60
6:23	NR	NR	305	50	NR	19.9	67	NR	NR	NR	NR
6:26	232	11	305	58	NR	4.2	37	NR	NR	NR	NR
6:30	255	11	305	60	NR	14.5	50	NR	NR	15.14	2.40
6:34	267	8	305	60	NR	11.4	69	.234	.062	NR	NR
6:37	260	12	304	58	NR	13.3	57	NR	NR	11.91	2.40
:41	252	11	303	55	NR	8.4	34	NR	NR	3.23	2.50
:44	274	13	303	70	NR	7.8	28	1.071	.138	NR	NR
:47	284	11	301	60	NR	9.0	39	NR	NR	22.08	3.70
:50	290	11	301	65	NR	13.3	43	1.835	.182	NR	NR
:53	289	10	300	70	NR	10.2	40	NR	NR	32.41	3.90
:56	300	15	300	70	NR	9.0	47	1.216	.147	NR	NR
:59	284	15	300	72	NR	9.6	54	NR	NR	24.32	3.60
:03	300	12	299	68	NR	7.2	47	1.198	.146	NR	NR
:06	285	14	299	70	NR	7.2	42	NR	NR	21.59	3.35
:12	293	8	300	70	NR	6.6	38	NR	NR	15.89	3.50
:15	293	12	299	78	NR	6.6	30	1.489	.163	NR	NR
:18	289	11	299	67	NR	7.2	35	NR	NR	16.62	3.30
:21	292	11	299	65	NR	7.2	46	1.416	.159	NR	NR
:25	284	11	299	70	NR	8.4	36	NR	NR	12.41	3.20
:33	276	7	299	62	NR	8.4	31	1.962	.188	NR	NR
:36	281	6	299	70	NR	10.2	17	NR	NR	21.09	3.57
39	285	6	300	68	NR	8.4	32	1.744	.177	NR	NR
43	281	6	301	68	NR	5.4	30	NR	NR	NR	NR
48	297	7	301	70	NR	7.2	9	NR	NR	NR	NR
53	274	8	300	60	NR	8.4	12	NR	NR	15.63	3.40
56	288	7	300	68	NR	8.4	16	1.689	.174	NR	NR
59	278	9	300	68	NR	5.4	6	NR	NR	23.82	3.60
02	NR	NR	NR	NR	NR	7.8	9	NR	NR	NR	NR
11	272	7	303	60	NR	7.8	34	NR	NR	NR	NR
14	275	8	302	65	NR	9.6	36	NR	NR	37.72	4.20
17	277	7	301	70	NR	9.6	40	2.489	.212	NR	NR
20	269	8	302	60	NR	9.0	40	NR	NR	NR	NR
23	268	8	304	68	NR	10.2	47	NR	NR	22.08	3.40
28	280	7	303	60	NR	9.0	44	1.325	.154	NR	NR
40	280	6	301	65	NR	6.6	43	NR	NR	33.50	3.80
43	NR	NR	NR	NR	NR	7.2	44	1.289	.152	NR	NR
6	NR	NR	NR	NR	NR	7.2	44	NR	NR	NR	NR
1	NR	NR	NR	NR	NR	6.6	42	NR	NR	20.80	3.60
5	NR	NR	NR	NR	NR	6.6	42	1.816	.181	NR	NR
8	NR	NR	NR	NR	NR	6.6	39	NR	NR	29.53	3.80
1	NR	NR	NR	NR	NR	6.0	40	1.562	.167	NR	NR
4	NR	NR	NR	NR	NR	4.8	40	NR	NR	14.64	3.15
7	NR	NR	NR	NR	NR	6.6	41	1.325	.154	NR	NR
2	NR	NR	302	65	NR	4.8	42	NR	NR	NR	NR
5	NR	NR	NR	NR	NR	5.4	40	NR	NR	NR	NR
3	NR	NR	NR	NR	NR	4.8	40	NR	NR	29.28	3.69
2	NR	NR	NR	NR	NR	3.6	39	1.107	.140	NR	NR
	243	6	302	65	NR	4.8	44	NR	NR	38.21	4.10
3	NR	NR	NR	NR	NR	3.0	37	NR	NR	47.15	4.15
	NR	NR	NR	NR	NR	3.0	38	.816	.120	NR	NR
	NR	NR	NR	NR	NR	2.4	37	NR	NR	45.91	4.11

20:11	NR	NR	NR	NR	NR	1.8	35	NR	NR	NR	NR
20:19	NR	NR	NR	NR	NR	1.2	27	NR	NR	30.02	3.50
20:22	NR	NR	NR	NR	NR	1.2	33	.379	.080	NR	NR
20:26	NR	NR	NR	NR	NR	1.2	35	NR	NR	35.24	3.57
20:29	NR	NR	NR	NR	NR	0.6	34	.161	.050	NR	NR
20:32	NR	NR	NR	NR	NR	0.6	35	NR	NR	26.80	3.18
20:36	NR	NR	NR	NR	NR	0.6	38	BDL	BDL	NR	NR
20:39	NR	NR	NR	NR	NR	0.6	33	NR	NR	NR	NR
20:43	NR	NR	NR	NR	NR	0.6	36	NR	NR	NR	NR
20:47	260	6	300	65	NR	0.0	32	NR	NR	30.27	3.12
20:50	NR	NR	NR	NR	NR	0.6	38	BDL	BDL	NR	NR
20:53	NR	NR	NR	NR	NR	NR	33	NR	NR	NR	NR
0:56	"	"	"	"	"	0.0	29	"	"	37.72	3.39
0:57	"	"	"	"	"	"	31	"	"	NR	NR
1:07	NR	NR	NR	NR	NR	0.0	30	NR	NR	31.76	3.20
1:13	NR	NR	NR	NR	NR	0.0	30	BDL	BDL	NR	NR
1:38	278	6	300	65	NR	0.0	30	NR	NR	41.19	3.88
1:41	NR	NR	NR	NR	NR	NR	34	.052	.023	NR	NR
1:45	NR	NR	NR	NR	NR	NR	33	NR	NR	25.56	3.24
1:48	280	6	NR	NR	NR	NR	28	NR	NR	NR	NR
1:52	NR	NR	NR	NR	NR	NR	23	NR	NR	27.54	2.62
1:55	NR	NR	NR	NR	NR	NR	30	BDL	BDL	NR	NR
1:58	NR	NR	NR	NR	NR	NR	29	NR	NR	NR	NR
2:15	250	6	299	65	NR	NR	29	NR	NR	NR	NR
2:23	NR	NR	NR	NR	NR	NR	26	BDL	BDL	NR	NR
2:26	NR	NR	NR	NR	NR	NR	22	NR	NR	49.13	4.08
:31	NR	NR	NR	NR	NR	NR	18	BDL	BDL	NR	NR
:34	245	8	NR	NR	NR	NR	18	NR	NR	NR	NR
:06	265	4	NR	NR	NR	NR	11	NR	NR	48.14	3.76
:13	242	2	NR	NR	NR	NR	14	.088	.034	NR	NR
:15	NR	NR	NR	NR	NR	NR	14	NR	NR	NR	NR
:17	260	3	NR	NR	NR	NR	15	NR	NR	45.16	3.64
:22	235	4	NR	NR	NR	NR	14	BDL	BDL	NR	NR
:28	NR	NR	299	75	NR	NR	15	NR	NR	47.15	3.68
:31	238	6	NR	NR	NR	NR	16	NR	NR	NR	NR
:36	241	6	299	75	NR	NR	15	NR	NR	37.72	3.51
:40	254	5	NR	NR	NR	NR	17	BDL	BDL	NR	NR
:26	271	13	NR	NR	NR	NR	20	NR	NR	2.48	2.13
31	NR	NR	NR	NR	NR	NR	31	BDL	BDL	NR	NR
35	NR	NR	296	75	NR	NR	31	NR	NR	17.37	2.30
39	277	9	NR	NR	NR	NR	27	NR	NR	13.90	2.05
43	268	10	NR	NR	NR	NR	26	NR	NR	NR	NR
55	236	9	NR	NR	NR	NR	25	NR	NR	16.63	2.09
01	238	10	NR	NR	NR	NR	25	NR	NR	20.00	2.46
05	215	16	NR	NR	NR	NR	25	NR	NR	NR	NR
08	220	24	NR	NR	NR	NR	25	BDL	BDL	NR	NR
11	228	22	295	80	NR	NR	28	NR	NR	12.41	1.97
16	NR	NR	NR	NR	NR	NR	26	NR	NR	12.16	2.02
19	218	27	NR	NR	NR	NR	27	NR	NR	6.20	1.47
21	212	23	NR	NR	NR	NR	31	NR	NR	7.20	1.59
26	218	32	NR	100	NR	NR	28	NR	NR	7.69	1.61
27	"	"	"	"	"	"	32	"	"	NR	NR
8	NR	NR	NR	NR	NR	NR	27	NR	NR	NR	NR
9	"	"	"	"	"	"	28	"	"	"	"
0	"	"	"	"	"	"	32	"	"	"	"
5	NR	NR	NR	NR	NR	NR	25	NR	NR	4.71	1.31
7	"	"	"	"	"	"	21	"	"	NR	NR
9	NR	NR	NR	NR	NR	NR	32	NR	NR	NR	NR
1	218	29	NR	NR	NR	NR	29	NR	NR	16.63	2.21
2	"	"	"	"	"	"	25	"	"	NR	NR

01:43	"	"	"	"	"	"	24	"	"	"	"
01:44	NR	NR	NR	NR	NR	NR	26	NR	NR	26.05	2.64
01:45	"	"	"	"	"	"	23	"	"	NR	NR
01:48	229	25	292	100	NR	NR	21	NR	NR	28.78	2.84
01:49	"	"	"	"	"	"	20	"	"	NR	NR
01:53	NR	NR	NR	NR	NR	NR	NR	BDL	BDL	NR	NR
01:56	220	20	NR	NR	NR	NR	20	NR	NR	11.91	1.74
01:57	"	"	"	"	"	"	21	"	"	NR	NR
01:59	218	17	NR	NR	NR	NR	22	NR	NR	13.15	1.97
02:00	"	"	"	"	"	"	21	"	"	NR	NR
02:01	"	"	"	"	"	"	27	"	"	"	"
02:03	203	16	NR	NR	NR	NR	21	NR	NR	16.38	2.15
2:04	"	"	"	"	"	"	24	"	"	NR	NR
2:12	316	10	NR	NR	NR	NR	21	NR	NR	14.14	2.06
2:13	"	"	"	"	"	"	23	"	"	NR	NR
2:14	"	"	"	"	"	"	16	"	"	"	"
2:16	317	9	NR	NR	NR	NR	19	NR	NR	18.36	2.31
2:17	"	"	"	"	"	"	"	"	"	NR	NR
2:18	280	7	NR	NR	NR	NR	22	NR	NR	9.43	1.72
2:19	"	"	"	"	"	"	26	"	"	NR	NR
2:22	NR	NR	NR	NR	NR	NR	35	NR	NR	11.66	1.84
2:23	"	"	"	"	"	"	31	"	"	NR	NR
2:26	288	13	NR	100	NR	NR	31	NR	NR	5.21	1.38
2:27	"	"	"	"	"	"	27	"	"	NR	NR
2:32	273	15	293	100	NR	NR	27	NR	NR	5.46	1.29
2:43	281	15	NR	NR	NR	NR	29	NR	NR	9.93	1.72
:44	"	"	"	"	"	"	26	"	"	NR	NR
:45	"	"	"	"	"	"	"	"	"	"	"
:47	NR	NR	NR	NR	NR	NR	25	BDL	BDL	NR	NR
:53	284	17	NR	NR	NR	NR	23	NR	NR	4.22	1.16
:54	"	"	"	"	"	"	27	"	"	NR	NR
:55	"	"	"	"	"	"	29	"	"	"	"
:56	NR	NR	NR	NR	NR	NR	36	NR	NR	NR	NR
:01	278	11	NR	NR	NR	NR	29	NR	NR	NR	NR
:02	"	"	"	"	"	"	34	"	"	"	"
:04	NR	NR	NR	NR	NR	NR	28	NR	NR	NR	NR
:32	284	10	NR	100	NR	NR	26	–	–	STD	STD
:34	NR	NR	NR	NR	NR	NR	28	–	–	STD	STD
37	NR	NR	NR	NR	NR	NR	28	–	–	STD	STD
38	"	"	"	"	"	"	26	NR	NR	"	"
42	NR	NR	NR	NR	NR	NR	23	NR	NR	8.19	1.57
07	236	14	NR	NR	NR	NR	27	NR	NR	8.44	1.55
08	"	"	"	"	"	"	32	"	"	NR	NR
09	"	"	"	"	"	"	31	"	"	"	"
23	220	13	NR	NR	NR	NR	29	NR	NR	NR	NR
30	NR	NR	NR	NR	NR	NR	32	BDL	BDL	NR	NR
05	318	9	293	85	NR	0.6	25	BDL	BDL	NR	NR
06	"	"	"	"	"	"	22	NR	NR	"	"
11	NR	NR	NR	NR	NR	0.6	22	NR	NR	NR	NR
14	NR	NR	NR	NR	NR	NR	23	NR	NR	NR	NR
8	NR	NR	NR	NR	NR	0.6	22	NR	NR	NR	NR
9	NR	NR	NR	NR	NR	NR	30	NR	NR	7.44	1.57
3	NR	NR	NR	NR	NR	1.2	28	NR	NR	6.45	1.47
7	302	6	NR	NR	NR	1.2	29	BDL	BDL	NR	NR
2	NR	NR	NR	NR	NR	1.2	27	BDL	BDL	NR	NR
7	NR	NR	NR	NR	NR	1.2	28	NR	NR	6.45	1.40
0	307	7	NR	NR	NR	NR	29	NR	NR	12.16	1.79
1	"	"	"	"	"	"	31	"	"	NR	NR
2	"	"	"	"	"	"	27	"	"	"	"
1	270	6	NR	NR	NR	2.4	18	NR	NR	26.55	3.85

08:12	"	"	"	"	"	"	19	"	"	NR	NR
08:14	NR	NR	NR	NR	NR	NR	11	NR	NR	47.15	4.43
8:15	"	"	"	"	"	"	12	"	"	NR	NR
08:16	"	"	"	"	"	"	11	"	"	"	"
8:17	NR	NR	NR	NR	NR	3.0	14	1.635	.171	NR	NR
8:18	"	"	"	"	"	"	13	NR	NR	"	"
8:19	"	"	"	"	"	"	10	"	"	"	"
8:20	NR	NR	NR	NR	NR	3.0	16	NR	NR	NR	NR
8:21	NR	NR	NR	NR	NR	3.6	25	NR	NR	15.38	2.98
8:22	"	"	"	"	"	"	22	"	"	NR	NR
8:24	NR	NR	NR	NR	NR	3.6	24	.398	.082	NR	NR
8:25	"	"	"	"	"	"	25	NR	NR	"	"
3:26	"	"	"	"	"	"	24	"	"	"	"
3:27	266	7	NR	NR	NR	3.6	27	NR	NR	19.85	2.86
:28	"	"	"	"	"	"	28	"	"	NR	NR
:29	"	"	"	"	"	"	22	"	"	"	"
:30	NR	NR	NR	NR	NR	4.2	19	NR	NR	27.79	3.45
:31	"	"	"	"	"	"	22	"	"	NR	NR
:32	"	"	"	"	"	"	21	"	"	"	"
:33	"	"	"	"	"	"	23	"	"	"	"
:34	255	6	295	92	NR	4.2	21	NR	NR	24.57	3.50
:35	"	"	"	"	"	"	23	"	"	NR	NR
:36	"	"	"	"	"	"	19	"	"	"	"
:37	NR	NR	NR	NR	NR	4.2	18	NR	NR	NR	NR
:39	NR	NR	NR	NR	NR	4.8	21	1.143	.143	NR	NR
:40	"	"	"	"	"	"	17	NR	NR	"	"
:42	NR	NR	NR	NR	NR	NR	22	NR	NR	NR	NR
:43	"	"	"	"	"	"	21	"	"	"	"
44	NR	NR	NR	NR	NR	4.8	23	NR	NR	NR	NR
47	NR	NR	NR	NR	NR	4.8	24	NR	NR	15.38	3.35
48	"	"	"	"	"	"	26	"	"	NR	NR
50	NR	NR	NR	NR	NR	5.4	18	1.726	.176	NR	NR
51	"	"	"	"	"	"	17	NR	NR	"	"
53	NR	NR	NR	NR	NR	5.4	15	NR	NR	NR	NR
54	NR	NR	NR	NR	NR	NR	18	NR	NR	29.28	3.97
55	"	"	"	"	"	"	10	"	"	NR	NR
56	"	"	"	"	"	"	12	"	"	"	"
57	NR	NR	NR	NR	NR	6.0	17	1.926	.186	NR	NR
58	"	"	"	"	"	"	17	NR	NR	"	"
20	236	7	297	85	NR	6.6	15	3.745	.260	NR	NR
21	"	"	"	"	"	"	15	NR	NR	"	"
23	NR	NR	NR	NR	NR	6.6	22	NR	NR	41.19	4.40
24	"	"	"	"	"	"	21	"	"	NR	NR
26	NR	NR	NR	NR	NR	6.0	0	2.017	.191	NR	NR
7	"	"	"	"	"	"	17	NR	NR	"	"
8	"	"	"	"	"	"	19	"	"	"	"
9	"	"	"	"	"	"	17	"	"	"	"
0	NR	NR	NR	NR	NR	6.6	19	NR	NR	29.78	3.84
1	"	"	"	"	"	"	16	"	"	NR	NR
2	"	"	"	"	"	"	12	"	"	"	"
3	NR	NR	NR	NR	NR	6.6	16	1.689	.174	NR	NR
4	"	"	"	"	"	"	17	NR	NR	"	"
5	"	"	"	"	"	"	19	"	"	"	"
	NR	NR	NR	NR	NR	7.2	24	NR	NR	NR	NR
	"	"	"	"	"	"	25	"	"	"	"
	247	7	NR	NR	NR	7.2	24	NR	NR	21.84	3.33
	"	"	"	"	"	"	25	"	"	NR	NR
	"	"	"	"	"	"	23	"	"	"	"
	NR	NR	NR	NR	NR	7.8	24	.798	.119	NR	NR
	"	"	"	"	"	"	24	NR	NR	"	"

09:47	"	"	"	"	"	"	22	"	"	"	"
09:48	NR	NR	NR	NR	NR	7.8	21	NR	NR	29.78	3.58
09:49	"	"	"	"	"	"	20	"	"	NR	NR
10:05	240	12	NR	100	NR	6.6	15	NR	NR	6.05	2.00
10:06	"	"	"	"	"	"	15	"	"	NR	NR
10:08	NR	NR	NR	NR	NR	5.4	14	NR	NR	13.70	2.10
10:09	"	"	"	"	"	6.0	14	"	"	NR	NR
10:11	NR	NR	NR	NR	NR	6.6	10	4.090	.272	NR	NR
10:12	"	"	"	"	"	"	13	NR	NR	"	"
10:14	NR	NR	NR	NR	NR	7.2	16	NR	NR	17.17	2.20
10:15	"	"	"	"	"	"	17	"	"	NR	NR
10:16	"	"	"	"	"	"	14	"	"	"	"
10:17	NR	NR	NR	NR	NR	6.0	15	NR	NR	NR	NR
10:18	"	"	"	"	"	5.4	15	"	"	"	"
.0:19	"	"	"	"	"	6.0	16	"	"	"	"
.0:20	NR	NR	NR	NR	NR	6.0	16	4.017	.270	NR	NR
.0:21	"	"	"	"	"	8.4	15	NR	NR	"	"
0:23	NR	NR	NR	NR	NR	8.4	15	NR	NR	8.14	2.30
0:24	"	"	"	"	"	"	14	"	"	NR	NR
0:25	"	"	"	"	"	6.6	13	"	"	"	"
0:26	251	11	NR	NR	NR	6.6	13	6.200	.335	NR	NR
0:27	"	"	"	"	"	7.8	13	NR	NR	"	"
0:28	"	"	"	"	"	"	14	"	"	"	"
0:29	253	7	NR	NR	NR	7.8	9	NR	NR	6.15	2.50
0:30	"	"	"	"	"	"	13	"	"	NR	NR
0:31	"	"	"	"	"	8.4	11	"	"	"	"
0:32	NR	NR	NR	NR	NR	9.6	13	8.019	.381	NR	NR
0:33	"	"	"	"	"	9.0	14	NR	NR	"	"
:34	"	"	"	"	"	7.2	13	"	"	"	"
:35	"	"	"	"	"	"	14	"	"	"	"
:36	NR	NR	NR	NR	NR	8.4	NR	NR	NR	11.12	2.50
:39	NR	NR	NR	NR	NR	9.6	16	NR	NR	10.72	2.60
:40	"	"	"	"	"	"	11	"	"	NR	NR
:41	NR	NR	NR	NR	NR	6.6	9	9.675	.419	NR	NR
:42	"	"	"	"	"	7.2	10	NR	NR	"	"
:45	NR	NR	NR	NR	NR	9.6	10	NR	NR	14.00	2.60
:46	"	"	"	"	"	"	9	"	"	NR	NR
:49	NR	NR	NR	NR	NR	9.6	9	8.783	.399	NR	NR
:50	"	"	"	"	"	7.2	10	NR	NR	"	"
:51	"	"	"	"	"	"	13	"	"	"	"
:52	NR	NR	NR	NR	NR	6.0	12	NR	NR	18.06	2.70
:53	"	"	"	"	"	4.8	11	"	"	NR	NR
54	"	"	"	"	"	"	10	"	"	"	"
56	260	7	NR	NR	NR	6.6	15	8.128	.384	NR	NR
57	"	"	"	"	"	9.0	16	NR	NR	"	"
58	NR	NR	NR	NR	NR	7.8	11	NR	NR	NR	NR
02	NR	NR	NR	NR	NR	8.4	11	NR	NR	NR	NR
04	NR	NR	NR	NR	NR	9.6	11	NR	NR	24.91	2.80
05	"	"	"	"	"	12.0	13	"	"	NR	NR
06	"	"	"	"	"	13.8	NR	"	"	"	"
07	NR	NR	NR	NR	NR	14.4	9	8.547	.394	NR	NR
08	"	"	"	"	"	15.0	10	NR	NR	"	"
09	"	"	"	"	"	"	17	"	"	"	"
11	NR	NR	NR	NR	NR	14.4	18	NR	NR	18.26	2.90
20	NR	NR	NR	NR	2500	NR	NR	NR	NR	NR	NR
54	NR	NR	NR	NR	2300	NR	NR	NR	NR	NR	NR
3	220	6	NR	NR	NR	12.6	21	NR	NR	28.39	2.20
4	"	"	"	"	"	"	22	"	"	NR	NR
5	"	"	"	"	"	"	21	"	"	"	"
6	NR	NR	NR	NR	NR	6.6	19	5.618	.319	NR	NR

12:07	"	"	"	"	"	7.2	21	NR	NR	"	"
12:28	NR	NR	NR	NR	NR	19.2	21	8.529	.393	NR	NR
12:29	"	"	"	"	"	17.4	21	NR	NR	"	"
12:31	NR	NR	NR	NR	NR	24.0	26	NR	NR	3.77	2.30
12:32	"	"	"	"	"	20.4	NR	"	"	NR	NR
12:34	NR	NR	NR	NR	NR	23.4	22	6.218	.336	NR	NR
12:35	"	"	"	"	"	24.0	19	NR	NR	"	"
14:19	NR	NR	NR	NR	2100	NR	50	NR	NR	NR	NR
15:50	NR	NR	NR	NR	2800	NR	55	NR	NR	NR	NR

NR = NOT RECORDED

NA = NOT AVAILABLE

STD = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE

BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

S DATA WAS RECORDED ON 07/16_17/84

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	[O_3]	[NO]	+/-	[NO_2]	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM^2)	(W/M^2)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
03:40	260	19	295	85	NR	0.0	5	.019	.008	NA	NA
03:41	"	"	"	"	"	"	8	"	"	"	"
03:42	"	"	"	"	"	"	6	"	"	"	"
03:43	"	"	"	"	"	"	"	"	"	"	"
03:47	NR	NR	NR	NR	NR	NR	2	NR	NR	NA	NA
03:48	"	"	"	"	"	"	1	"	"	"	"
03:49	"	"	"	"	"	"	9	"	"	"	"
3:50	"	"	"	"	"	"	7	"	"	"	"
3:51	"	"	"	"	"	"	13	"	"	"	"
3:54	NR	NR	NR	NR	NR	NR	7	NR	NR	NA	NA
3:55	"	"	"	"	"	"	11	"	"	"	"
3:56	"	"	"	"	"	"	9	"	"	"	"
3:57	"	"	"	"	"	"	7	"	"	"	"
3:58	"	"	"	"	"	"	12	"	"	"	"
4:05	266	16	NR	NR	NR	NR	13	.048	.012	NA	NA
4:06	"	"	"	"	"	"	11	"	"	"	"
4:07	"	"	"	"	"	"	5	"	"	"	"
:08	"	"	"	"	"	"	9	"	"	"	"
:09	"	"	"	"	"	"	11	"	"	"	"
:10	"	"	"	"	"	"	15	"	"	"	"
:11	252	15	295	90	NR	NR	9	NR	NR	NA	NA
:12	"	"	"	"	"	"	"	"	"	"	"
:13	"	"	"	"	"	"	8	"	"	"	"
:14	"	"	"	"	"	"	"	"	"	"	"
:15	"	"	"	"	"	"	13	"	"	"	"
:18	267	17	NR	NR	NR	0.0	14	.029	.010	NA	NA
:19	"	"	"	"	"	"	17	"	"	"	"
:20	"	"	"	"	"	"	16	"	"	"	"
:21	"	"	"	"	"	"	14	"	"	"	"
22	"	"	"	"	"	"	8	"	"	"	"
23	260	17	295	85	NR	0.0	15	NR	NR	NA	NA
24	"	"	"	"	"	"	10	"	"	"	"
25	"	"	"	"	"	"	15	"	"	"	"
26	"	"	"	"	"	"	12	"	"	"	"
27	"	"	"	"	"	"	11	"	"	"	"
28	"	"	"	"	"	"	"	"	"	"	"
29	NR	NR	NR	NR	NR	0.0	11	.042	.012	NA	NA
30	"	"	"	"	"	"	5	"	"	"	"
31	"	"	"	"	"	"	7	"	"	"	"
32	"	"	"	"	"	"	"	"	"	"	"
33	"	"	"	"	"	"	"	"	"	"	"
34	"	"	"	"	"	"	"	"	"	"	"
35	NR	NR	NR	NR	NR	NR	8	NR	NR	NA	NA
6	"	"	"	"	"	"	13	"	"	"	"
7	"	"	"	"	"	"	14	"	"	"	"
8	"	"	"	"	"	"	7	"	"	"	"
9	"	"	"	"	"	"	5	"	"	"	"
1	NR	NR	NR	NR	NR	NR	7	NR	NR	NA	NA

04:42	"	"	"	"	"	"	8	"	"	"	"
04:43	"	"	"	"	"	"	7	"	"	"	"
04:46	NR	NR	NR	NR	NR	NR	7	NR	NR	NA	NA
04:47	"	"	"	"	"	"	5	"	"	"	"
04:48	"	"	"	"	"	"	6	"	"	"	"
04:51	260	18	NR	NR	NR	0.0	4	.067	.015	NA	NA
04:52	"	"	"	"	"	"	5	"	"	"	"
04:53	"	"	"	"	"	"	7	"	"	"	"
04:54	"	"	"	"	"	"	10	"	"	"	"
04:55	"	"	"	"	"	"	6	"	"	"	"
04:57	NR	NR	NR	NR	NR	NR	4	NR	NR	NA	NA
04:58	"	"	"	"	"	"	0	"	"	"	"
04:59	"	"	"	"	"	"	5	"	"	"	"
05:00	"	"	"	"	"	"	3	"	"	"	"
05:01	"	"	"	"	"	"	5	"	"	"	"
05:02	"	"	"	"	"	"	8	"	"	"	"
05:08	251	14	294	75	NR	NR	5	NR	NR	NA	NA
05:09	"	"	"	"	"	"	8	"	"	"	"
05:10	"	"	"	"	"	"	9	"	"	"	"
05:51	256	12	294	98	NR	NR	5	NR	NR	NR	NR
05:52	"	"	"	"	"	"	8	"	"	"	"
06:04	NR	NR	NR	NR	NR	NR	10	BDL	BDL	NR	NR
06:05	"	"	"	"	"	"	5	"	"	"	"
6:09	NR	NR	NR	NR	NR	NR	8	NR	NR	11.90	1.30
6:13	NR	NR	NR	NR	NR	NR	4	NR	NR	NR	NR
6:19	NR	NR	NR	NR	NR	NR	10	–	–	STD	STD
6:20	"	"	"	"	"	"	7	"	"	"	"
6:22	NR	NR	NR	NR	NR	NR	8	–	–	STD	STD
6:23	"	"	"	"	"	"	9	"	"	"	"
6:34	271	14	294	100	NR	NR	9	NR	NR	12.04	1.30
6:35	"	"	"	"	"	"	13	"	"	"	"
6:36	"	"	"	"	"	"	12	"	"	"	"
:43	268	12	NR	NR	NR	NR	14	NR	NR	10.64	1.20
:44	"	"	"	"	"	"	11	"	"	"	"
:46	NR	NR	NR	NR	NR	NR	10	BDL	BDL	NR	NR
:47	"	"	"	"	"	"	12	"	"	"	"
:52	NR	NR	NR	NR	NR	0.6	8	NR	NR	NR	NR
:53	"	"	"	"	"	"	10	"	"	"	"
:57	NR	NR	NR	NR	NR	0.6	10	NR	NR	11.34	1.30
:58	"	"	"	"	"	"	9	"	"	"	"
:01	NR	NR	NR	NR	NR	0.6	17	NR	NR	11.90	1.30
:02	"	"	"	"	"	"	21	"	"	"	"
:03	"	"	"	"	"	"	18	"	"	"	"
:04	NR	NR	NR	NR	NR	1.2	16	.588	.118	NR	NR
:05	"	"	"	"	"	"	15	"	"	"	"
:06	"	"	"	"	"	"	14	"	"	"	"
08	276	12	294	100	NR	1.2	10	NR	NR	19.89	1.70
09	"	"	"	"	"	"	2	"	"	"	"
10	"	"	"	"	"	"	3	"	"	"	"
11	NR	NR	NR	NR	NR	1.2	7	.404	.102	NR	NR
12	"	"	"	"	"	"	6	"	"	"	"
13	"	"	"	"	"	"	3	"	"	"	"
14	NR	NR	NR	NR	NR	1.8	4	NR	NR	21.43	1.70
15	"	"	"	"	"	"	8	"	"	"	"
17	NR	NR	NR	NR	NR	1.8	15	.936	.131	NR	NR
18	"	"	"	"	"	"	10	"	"	"	"
20	NR	NR	NR	NR	NR	1.8	11	NR	NR	32.77	2.10
21	"	"	"	"	"	"	12	"	"	"	"
22	"	"	"	"	"	"	11	"	"	"	"
24	NR	NR	NR	NR	NR	1.8	12	NR	NR	34.73	2.10

07:25	"	"	"	"	"	"	16	"	"	"	"
07:27	NR	NR	NR	NR	NR	2.4	2	NR	NR	NR	NR
07:28	NR	NR	NR	NR	NR	2.4	3	NR	NR	NR	NR
07:29	NR	NR	NR	NR	NR	2.4	6	NR	NR	NR	NR
07:31	NR	NR	NR	NR	NR	2.4	2	4.147	.281	NR	NR
07:32	"	"	"	"	"	"	5	"	"	"	"
07:34	271	9	295	100	NR	2.4	10	NR	NR	31.79	2.10
07:35	"	"	"	"	"	"	"	"	"	"	"
07:36	"	"	"	"	"	"	11	"	"	"	"
07:38	NR	NR	NR	NR	NR	2.4	7	5.028	.304	NR	NR
07:39	"	"	"	"	"	"	9	"	"	"	"
07:40	"	"	"	"	"	"	"	"	"	"	"
07:41	NR	NR	296	100	NR	2.4	10	NR	NR	27.73	2.00
07:42	"	"	"	"	"	"	"	"	"	"	"
07:43	NR	NR	NR	NR	NR	1.8	6	NR	NR	8.00	1.10
07:44	"	"	"	"	"	"	3	"	"	"	"
07:45	"	"	"	"	"	2.4	1	"	"	"	"
07:51	NR	NR	NR	NR	NR	3.0	2	NR	NR	19.00	1.60
07:52	"	"	"	"	"	"	8	"	"	"	"
07:53	"	"	"	"	"	"	11	"	"	"	"
07:54	"	"	"	"	"	"	15	"	"	"	"
07:55	276	12	NR	NR	NR	2.4	11	6.257	.339	NR	NR
07:56	"	"	"	"	"	"	9	"	"	"	"
07:57	"	"	"	"	"	"	10	"	"	"	"
07:58	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
08:12	NR	NR	NR	NR	NR	3.6	10	NR	NR	26.89	1.90
08:13	"	"	"	"	"	"	7	"	"	"	"
8:14	"	"	"	"	"	"	8	"	"	"	"
8:15	256	8	296	100	NR	3.6	5	15.474	1.202	NR	NR
8:16	"	"	"	"	"	"	"	"	"	"	"
8:19	NR	NR	NR	NR	NR	3.6	5	NR	NR	20.87	1.70
8:20	"	"	"	"	"	"	1	"	"	"	"
8:21	NR	NR	NR	NR	NR	3.6	4	18.337	1.308	NR	NR
8:22	"	"	"	"	"	"	2	"	"	"	"
8:23	"	"	"	"	"	"	0	"	"	"	"
8:24	"	"	"	"	"	"	2	"	"	"	"
8:25	NR	NR	NR	NR	NR	4.2	3	19.184	1.338	NR	NR
8:26	"	"	"	"	"	"	7	"	"	"	"
8:27	"	"	"	"	"	4.8	4	"	"	"	"
8:28	268	9	NR	NR	NR	5.4	8	NR	NR	6.70	.97
8:29	"	"	"	"	"	6.0	7	"	"	"	"
8:30	"	"	"	"	"	7.2	9	"	"	"	"
:31	NR	NR	NR	NR	NR	6.6	5	NR	NR	NR	NR
:32	NR	NR	NR	NR	NR	7.2	7	NR	NR	NR	NR
:33	NR	NR	NR	NR	NR	7.2	5	20.026	1.367	NR	NR
:34	"	"	"	"	"	"	8	"	"	"	"
:35	"	"	"	"	"	"	4	"	"	"	"
:36	NR	NR	NR	NR	NR	6.6	2	NR	NR	13.73	1.40
:37	"	"	"	"	"	"	1	"	"	"	"
:38	"	"	"	"	"	"	6	"	"	"	"
:39	"	"	"	"	"	7.2	5	"	"	"	"
:40	274	8	298	100	NR	8.4	8	NR	NR	NR	NR
:43	NR	NR	NR	NR	NR	8.4	7	20.689	1.389	NR	NR
:44	"	"	"	"	"	"	11	"	"	"	"
:45	"	"	"	"	"	"	10	"	"	"	"
46	NR	NR	NR	NR	NR	9.0	9	NR	NR	8.96	1.10
47	"	"	"	"	"	"	10	"	"	"	"
48	"	"	"	"	"	"	9	"	"	"	"
49	NR	NR	NR	NR	NR	8.4	8	19.829	1.360	NR	NR
50	"	"	"	"	"	"	"	"	"	"	"

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08:51       "    "     "     "    "      "       5         "      "       "      "
08:52      NR   NR    NR    NR   NR    7.8       6    17.224  1.268     NR     NR
08:53       "    "     "     "    "      "       1         "      "       "      "
08:54       "    "     "     "    "      "       3         "      "       "      "
08:55      NR   NR    NR    NR   NR    6.6       7        NR     NR   20.31   1.70
08:56       "    "     "     "    "      "       6         "      "       "      "
08:57       "    "     "     "    "      "       "         "      "       "      "
08:58      NR   NR    NR    NR   NR    7.2       0    17.646  1.283     NR     NR
08:59       "    "     "     "    "      "       3         "      "       "      "
09:00       "    "     "     "    "      "      12         "      "       "      "
09:01      NR   NR    NR    NR   NR    8.4       5        NR     NR   25.49   1.90
09:02       "    "     "     "    "      "       9         "      "       "      "
09:03       "    "     "     "    "    9.0       7         "      "       "      "
10:41     222    6   301    50   NR   17.5      18        NR     NR   38.80   2.30
10:45     230    9   301    60   NR   18.1      19        NR     NR   30.81   2.10
10:53     218   11   301    60   NR   13.9      18     6.440   .344     NR     NR
10:56     240    9   300    60   NR   15.1      19        NR     NR      NR     NR
10:59     230   10   300    60   NR   19.3      21        NR     NR   10.22   1.20
11:05     230   10   301    60   NR   24.7      25     6.440   .344     NR     NR
 1:08     235   11   301    60   NR   24.7      27        NR     NR   14.14   1.40
 1:12     240   11    NR    NR   NR   24.7      23     6.477   .345     NR     NR
 1:15     230    8   301    50   NR   24.0      26        NR     NR   14.85   1.40
 1:21     230   12   301    60   NR   18.0      25     3.193   .242     NR     NR
 1:24     230    8   301    60   NR   19.9      28        NR     NR      NR     NR
 1:29     230   11   301    60   NR   17.5      24        NR     NR      NR     NR
 1:41     250    9   302    50   NR   27.7      31        NR     NR   25.40   3.60
 1:44     250    7   302    50   NR   27.1      31     1.675   .206     NR     NR
 1:48     255    7   302    50   NR   27.7      30        NR     NR    7.36   3.00
 1:51     220   11   302    50   NR   27.7      33     1.548   .198     NR     NR
 1:55     220   11   302    40 1275   28.9      40        NR     NR    8.60   3.00
 1:59     255   11   303    50   NR   24.7      38        NR     NR   14.30   3.00
 2:02     270   11   303    40   NR   25.9      38      .812   .144     NR     NR
 2:06     240   14   303    50   NR   28.3      43        NR     NR      NR     NR
 :12      250   11   303    50 7500   24.7      39        NR     NR      NR     NR
 :16      240   10   303    45   NR   30.1      38      .508   .114     NR     NR
 :19      230   NR   303    45   NR   19.3      41        NR     NR   11.15   2.40
 :25      220   10   303    40   NR   23.5      44         -      -     STD    STD
 :28      260    7    NR    50   NR   15.1      39         -      -     STD    STD
 :31      235   12    NR    50 2800   13.3      41         -      -     STD    STD
 :38      235    9   303    50   NR   21.1      44        NR     NR      NR     NR
 :42      250    9   303    50   NR    6.0      42      .178   .067     NR     NR
 :45      270   11   303    50   NR    4.8      46        NR     NR    7.00   2.00
 :49      250   14    NR    60 2700    6.0      38      .381   .098     NR     NR
  56      260   12   302    60   NR   13.9      49       STD    STD      -      -
  59      245   14   303    50   NR   30.1      46       STD    STD      -      -
  07      240   15   303    60   NR   30.7      46      .609   .124     NR     NR
  11      264   12   305    55   NR   31.9      57        NR     NR   13.67   2.90
  14      245   11   304    42   NR   32.5      48      .660   .129     NR     NR
  17      238   11   304    42   NR   31.9      48        NR     NR   11.82   2.50
  22      235   13   303    50   NR   31.3      48      .482   .111     NR     NR
  25      240   16    NR    50   NR   32.5      50        NR     NR   11.09   2.70
  29      235   15    NR    50 2600   33.1      50      .736   .137     NR     NR
  31      235   16   303    50   NR   33.1      48        NR     NR      NR     NR
  35      235   14   303    55   NR   22.9      48        NR     NR      NR     NR
  38      245    9    NR    50   NR   33.1      48      .635   .127     NR     NR
  41      235   14   303    55   NR   19.9      52        NR     NR    3.75   2.30
  45      240   12   304    55   NR   34.3      53      .761   .139     NR     NR
  48      260   16   304    50   NR   19.9      55        NR     NR   13.75   2.50
  51      264   14   305    50   NR   10.2      49      .254   .080     NR     NR
  54      229   14   305    55   NR   10.2      53        NR     NR    8.00   2.20
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13:58	240	11	304	52	NR	9.0	49	NR	NR	5.40	2.10
14:02	247	16	304	52	NR	9.0	50	.355	.095	NR	NR
14:05	251	11	303	59	NR	8.4	48	NR	NR	4.60	2.10
14:08	265	12	304	58	NR	7.8	49	NR	NR	NR	NR
14:11	235	12	303	54	NR	8.4	49	NR	NR	7.50	2.30
14:14	239	8	303	60	NR	9.6	45	.431	.105	NR	NR
14:18	230	17	303	55	2000	27.7	45	NR	NR	10.05	2.50
14:22	230	15	NR	55	NR	31.3	43	.482	.111	NR	NR
14:25	220	17	303	60	NR	16.9	43	NR	NR	1.90	1.80
14:28	220	16	NR	60	NR	16.3	42	.203	.072	NR	NR
14:33	220	16	303	55	7200	25.9	44	NR	NR	9.20	1.60
14:37	220	20	NR	55	NR	28.9	43	1.193	.174	NR	NR
14:40	230	17	303	60	NR	27.7	45	NR	NR	5.40	3.00
14:43	220	19	303	50	NR	30.1	38	1.802	.214	NR	NR
14:46	230	15	303	60	NR	30.7	43	NR	NR	16.10	3.40
4:50	220	15	303	50	6500	28.9	41	1.624	.203	NR	NR
4:54	212	15	304	55	NR	25.9	47	NR	NR	8.40	2.80
4:58	226	11	304	61	NR	27.1	42	1.269	.179	NR	NR
5:01	213	13	304	58	NR	19.9	44	NR	NR	BDL	BDL
5:15	226	13	303	58	4500	16.3	44	NR	NR	BDL	BDL
5:21	224	16	302	65	NR	6.6	46	NR	NR	BDL	BDL
5:24	225	19	302	60	NR	6.6	42	.025	.025	NR	NR
5:27	220	25	302	65	NR	6.0	44	NR	NR	7.10	1.80
5:31	225	31	300	70	NR	6.6	35	.508	.114	NR	NR
5:34	235	27	299	60	2500	6.0	39	NR	NR	7.50	2.00
5:37	235	23	299	55	2100	5.4	40	NR	NR	5.80	2.00
5:41	235	16	300	60	NR	11.4	44	.660	.129	NR	NR
5:45	245	16	301	50	1400	22.3	42	NR	NR	NR	NR
5:48	235	17	NR	55	NR	24.7	41	NR	NR	9.00	2.30
5:51	240	18	302	55	700	25.3	34	.635	.127	NR	NR
5:54	230	20	303	52	NR	25.9	35	NR	NR	5.00	2.00
5:57	231	18	303	52	NR	25.9	47	.609	.124	NR	NR
:01	222	20	302	50	850	27.7	41	NR	NR	2.80	1.80
:04	214	13	303	50	NR	30.1	42	.660	.129	NR	NR
:07	219	17	303	50	NR	21.1	40	NR	NR	2.40	1.70
:11	216	17	302	50	NR	16.3	39	.279	.084	NR	NR
:14	234	14	301	50	NR	16.9	39	NR	NR	2.90	1.80
:17	232	16	301	60	854	14.5	34	.457	.108	NR	NR
:23	219	16	300	60	NR	11.4	33	.761	.139	NR	NR
:26	234	15	300	60	NR	10.8	29	NR	NR	3.00	2.00
:30	216	23	300	60	NR	15.7	30	NR	NR	NR	NR
:36	255	11	301	50	4500	21.7	35	NR	NR	15.80	3.00
:39	257	5	303	49	NR	22.3	42	1.345	.185	NR	NR
:42	269	4	302	52	NR	6.6	38	NR	NR	12.25	2.80
:45	96	12	299	65	2500	6.0	39	1.015	.161	NR	NR
48	84	14	298	60	NR	4.8	31	NR	NR	5.40	2.20
51	89	12	298	60	2100	4.2	35	.254	.080	NR	NR
54	83	12	297	65	NR	3.0	34	NR	NR	12.00	2.20
57	88	10	297	NR	NR	1.2	38	.203	.072	NR	NR
01	91	7	297	55	1200	3.0	43	NR	NR	4.40	1.70
04	95	6	297	60	NR	1.8	43	.127	.057	NR	NR
07	109	4	297	51	590	1.2	35	NR	NR	BDL	BDL
10	106	2	297	62	NR	1.8	39	NR	NR	NR	NR
13	149	4	297	62	1000	1.8	29	.228	.076	NR	NR
16	155	5	297	65	NR	1.8	34	NR	NR	NR	NR
19	155	7	297	78	NR	1.8	31	NR	NR	NR	NR
22	162	8	297	88	NR	2.4	32	NR	NR	BDL	BDL
25	156	6	296	90	1400	2.4	29	NR	NR	3.80	2.10
28	155	7	296	90	NR	1.2	32	.533	.116	NR	NR
32	165	8	296	90	NR	1.2	32	NR	NR	5.10	2.20

17:34	170	5	296	85	NR	1.2	34	NR	NR	11.10	2.4
17:37	173	7	296	100	1200	0.6	34	.152	.062	NR	NR
17:43	184	7	296	95	NR	0.6	33	NR	NR	6.00	1.90
17:46	209	7	295	100	NR	0.6	32	NR	NR	11.80	2.20
17:49	212	8	295	80	NR	0.0	31	.178	.067	NR	NR
17:52	214	10	295	82	1600	0.6	37	NR	NR	2.00	1.50
17:55	220	11	295	80	NR	0.6	35	NR	NR	7.10	1.80
.7:59	210	12	295	80	NR	0.6	32	.102	.051	NR	NR
.8:03	220	15	295	80	1800	0.6	34	NR	NR	9.90	1.80
8:07	220	12	295	90	NR	0.0	29	NR	NR	8.50	1.70
8:10	220	13	295	100	NR	0.6	32	.228	.076	NR	NR
8:13	220	12	295	85	NR	0.6	24	NR	NR	20.20	2.30
8:16	220	12	295	75	NR	0.6	30	NR	NR	3.20	1.70
8:19	230	9	294	90	1400	0.6	29	.381	.098	NR	NR
8:23	220	9	294	80	NR	0.6	26	NR	NR	10.60	1.80
3:27	220	11	294	90	NR	0.6	27	NR	NR	24.3	1.9
3:30	225	11	294	90	NR	0.6	27	.203	.072	NR	NR
3:33	230	14	294	95	NR	0.6	24	NR	NR	28.50	2.40
3:39	226	17	294	85	NR	0.6	26	NR	NR	18.10	2.60
:42	226	18	295	90	NR	0.6	28	NR	NR	6.80	2.00
:45	223	19	295	85	1450	1.2	28	.279	.084	NR	NR
:48	221	21	295	90	NR	1.2	35	NR	NR	5.40	1.90
:51	222	21	295	84	NR	1.2	33	NR	NR	3.60	1.80
:54	223	24	295	80	1120	1.2	34	.152	.062	NR	NR
:00	224	19	294	86	NR	1.2	34	NR	NR	6.00	1.90
:03	217	10	295	90	NR	1.2	28	NR	NR	2.50	1.70
:06	223	19	295	90	NR	1.8	33	.228	.076	NR	NR
:09	228	18	295	85	NR	1.8	36	NR	NR	9.50	1.80
:12	226	19	295	83	NR	1.8	30	NR	NR	7.10	1.80
:23	230	17	NR	NR	NR	1.8	20	NR	NR	6.60	2.00
:24	"	"	"	"	"	"	25	"	"	"	"
:25	"	"	"	"	"	"	28	"	"	"	"
:26	233	17	NR	NR	NR	NR	29	.838	.146	NR	NR
27	"	"	"	"	"	"	30	"	"	"	"
34	NR	NR	NR	NR	NR	NR	23	NR	NR	NR	NR
35	"	"	"	"	"	"	27	"	"	"	"
36	NR	NR	NR	NR	NR	NR	24	NR	NR	NR	NR
37	"	"	"	"	"	"	26	"	"	"	"
52	231	17	NR	NR	NR	NR	23	NR	NR	NR	NR
53	"	"	"	"	"	"	24	"	"	"	"
43	223	16	295	75	NR	NR	28	NR	NR	3.40	1.10
44	"	"	"	"	"	"	26	"	"	"	"
48	221	15	NR	NR	NR	NR	26	.025	.025	NR	NR
49	"	"	"	"	"	"	25	"	"	"	"
50	NR	NR	NR	NR	NR	NR	28	NR	NR	5.50	1.30
57	221	15	NR	NR	NR	NR	24	NR	NR	8.40	1.50
58	"	"	"	"	"	"	25	"	"	"	"
3	NR	NR	NR	NR	NR	NR	27	NR	NR	10.60	1.80
4	"	"	"	"	"	"	23	"	"	"	"
6	NR	NR	NR	NR	NR	NR	19	.025	.025	NR	NR
0	NR	NR	NR	NR	NR	NR	21	NR	NR	NR	NR
1	"	"	"	"	"	"	22	"	"	"	"
2	NR	NR	NR	NR	NR	NR	21	NR	NR	9.40	1.70
3	"	"	"	"	"	"	22	"	"	"	"
2	221	18	NR	NR	NR	NR	23	NR	NR	8.80	1.60
3	"	"	"	"	"	"	26	"	"	"	"
4	"	"	"	"	"	"	23	"	"	"	"
5	"	"	"	"	"	"	19	"	"	"	"
6	NR	NR	295	80	NR	NR	20	NR	NR	NR	NR
7	"	"	"	"	"	"	22	"	"	"	"

21:28	"	"	"	"	"	"	23	"	"	"	"
21:29	"	"	"	"	"	"	20	"	"	"	"
21:30	"	"	"	"	"	"	17	"	"	"	"
21:33	NR	NR	NR	NR	NR	NR	21	STD	STD	–	–
1:34	"	"	"	"	"	"	19	"	"	"	"
1:36	NR	NR	295	87	NR	NR	21	NR	NR	NR	NR
1:41	NR	NR	NR	NR	NR	NR	22	NR	NR	6.90	1.50
1:42	"	"	"	"	"	"	24	"	"	"	"
1:43	"	"	"	"	"	"	19	"	"	"	"
1:47	NR	NR	NR	NR	NR	NR	20	–	–	STD	STD
1:48	"	"	"	"	"	"	"	"	"	"	"
1:51	NR	NR	NR	NR	NR	NR	20	–	–	STD	STD
1:52	"	"	"	"	"	"	"	"	"	"	"
1:54	NR	NR	NR	NR	NR	NR	23	–	–	STD	STD
1:55	"	"	"	"	"	"	19	"	"	"	"
:01	212	19	NR	NR	NR	NR	19	NR	NR	3.80	1.20
:02	"	"	"	"	"	"	20	"	"	"	"
:03	"	"	"	"	"	"	24	"	"	"	"
:04	NR	NR	NR	NR	NR	NR	26	.051	.036	NR	NR
:05	"	"	"	"	"	"	25	"	"	"	"
:06	"	"	"	"	"	"	21	"	"	"	"
:07	"	"	"	"	"	"	20	"	"	"	"
:11	213	17	295	85	NR	NR	20	NR	NR	2.50	1.30
:12	"	"	"	"	"	"	19	"	"	"	"
:15	NR	NR	NR	NR	NR	NR	22	.102	.051	NR	NR
:16	"	"	"	"	"	"	21	"	"	"	"
:17	"	"	"	"	"	"	23	"	"	"	"
18	NR	NR	NR	NR	NR	NR	19	NR	NR	NR	NR
19	"	"	"	"	"	"	18	"	"	"	"
20	"	"	"	"	"	"	23	"	"	"	"
28	236	16	295	85	NR	NA	12	.034	.011	NA	NA
29	"	"	"	"	"	"	12	"	"	"	"
30	"	"	"	"	"	"	10	"	"	"	"
31	"	"	"	"	"	"	11	"	"	"	"
35	242	17	NR	NR	NR	NA	17	NR	NR	NA	NA
36	"	"	"	"	"	"	16	"	"	"	"
37	"	"	"	"	"	"	13	"	"	"	"
38	"	"	"	"	"	"	11	"	"	"	"
39	"	"	"	"	"	"	8	"	"	"	"
0	"	"	"	"	"	"	11	"	"	"	"
1	NR	NR	NR	NR	NR	NA	13	.034	.011	NA	NA
2	"	"	"	"	"	"	15	"	"	"	"
3	"	"	"	"	"	"	16	"	"	"	"
4	"	"	"	"	"	"	19	"	"	"	"
6	243	20	NR	NR	NR	NA	21	NR	NR	NA	NA
7	"	"	"	"	"	"	16	"	"	"	"
8	"	"	"	"	"	"	21	"	"	"	"
9	240	18	294	95	NR	NA	16	.026	.010	NA	NA
0	"	"	"	"	"	"	12	"	"	"	"
	"	"	"	"	"	"	14	"	"	"	"
	NR	NR	NR	NR	NR	NA	14	NR	NR	NA	NA
	"	"	"	"	"	"	15	"	"	"	"
	"	"	"	"	"	"	13	"	"	"	"
	"	"	"	"	"	"	14	"	"	"	"
	NR	NR	NR	NR	NR	NA	13	.049	.014	NA	NA
	"	"	"	"	"	"	19	"	"	"	"
	"	"	"	"	"	"	13	"	"	"	"
	NR	NR	NR	NR	NR	NA	16	NR	NR	NA	NA
	"	"	"	"	"	"	13	"	"	"	"
	"	"	"	"	"	"	12	"	"	"	"

01:16	NR	NR	NR	NR	NR	NA	NR	NR	NR	NA	NA
01:42	NR	NR	NR	NR	2000	NA	14	NR	NR	NA	NA
01:43	"	"	"	"	"	"	"	"	"	"	"
01:47	NR	NR	NR	NR	NR	NA	12	.026	.010	NA	NA
01:48	"	"	"	"	"	"	20	"	"	"	"
01:55	243	20	294	95	NR	NA	14	NR	NR	NA	NA
01:56	"	"	"	"	"	"	12	"	"	"	"
01:57	"	"	"	"	"	"	12	"	"	"	"
02:00	NR	NR	NR	NR	NR	NA	10	.015	.008	NA	NA
2:01	"	"	"	"	"	"	12	"	"	"	"
2:02	"	"	"	"	"	"	10	"	"	"	"
2:06	NR	NR	NR	NR	NR	NA	10	NR	NR	NA	NA
2:07	"	"	"	"	"	"	11	"	"	"	"
2:25	253	19	294	75	NR	NA	10	NR	NR	NA	NA
2:26	"	"	"	"	"	"	10	"	"	"	"
2:27	"	"	"	"	"	"	11	"	"	"	"
2:30	NR	NR	NR	NR	NR	NA	21	.049	.014	NA	NA
2:31	"	"	"	"	"	"	16	"	"	"	"
2:32	"	"	"	"	"	"	12	"	"	"	"
2:37	NR	NR	294	95	NR	NA	16	NR	NR	NA	NA
2:38	"	"	"	"	"	"	17	"	"	"	"
2:39	"	"	"	"	"	"	11	"	"	"	"
2:40	"	"	"	"	"	"	14	"	"	"	"
:42	NR	NR	294	95	NR	NA	19	.132	.022	NA	NA
:43	"	"	"	"	"	"	15	"	"	"	"
:44	"	"	"	"	"	"	13	"	"	"	"
:45	"	"	"	"	"	"	9	"	"	"	"
:50	NR	NR	NR	NR	NR	NA	13	NR	NR	NA	NA
:51	"	"	"	"	"	"	15	"	"	"	"
:18	259	18	294	90	1700	NA	11	NR	NR	NA	NA
:19	"	"	"	"	"	"	9	"	"	"	"
:23	NR	NR	NR	NR	NR	NA	11	NR	NR	NA	NA
:28	NR	NR	NR	NR	NR	NA	11	NR	NR	NA	NA
:06	258	15	294	91	NR	NA	9	.056	.015	NA	NA
:07	"	"	"	"	"	"	10	"	"	"	"
13	NR	NR	NR	NR	NR	NA	11	NR	NR	NA	NA
14	"	"	"	"	"	"	15	"	"	"	"
15	"	"	"	"	"	"	11	"	"	"	"
18	253	15	294	93	NR	NA	17	.056	.015	NA	NA
19	"	"	"	"	"	"	14	"	"	"	"
20	"	"	"	"	"	"	11		"	"	"
21	"	"	"	"	"		12	"	"	"	"
24	NR	NR	NR	NR	NR	NA	21	NR	NR	NA	NA
25	"	"	"	"	"	"	21	"	"	"	"
26	"	"	"	"	"	"	21	"	"	"	"
29	NR	NR	NR	NR	NR	NA	20	NR	NR	NA	NA
30	"	"	"	"	"	"	9	"	"	"	"
40	240	15	NR	NR	NR	NA	10	.019	.008	NA	NA
41	"	"	"	"	"	"	13	"	"	"	"
42	"	"	"	"	"	"	12	"	"	"	"
43	"	"	"	"	"	"	13	"	"	"	"
4	"	"	"	"	"	"	24	"	"	"	"
6	NR	NR	NR	NR	NR	NA	24	NR	NR	NA	NA
7	"	"	"	"	"	"	22	"	"	"	"
8	"	"	"	"	"	"	23	"	"	"	"
3	NR	NR	NR	NR	700	NA	20	.098	.019	NA	NA
4	"	"	"	"	"	"	15	"	"	"	"
5	"	"	"	"	"	"	10	"	"	"	"
6	"	"	"	"	"	"	9	"	"	"	"
7	237	15	NR	NR	NR	NA	10	NR	NR	NA	NA

05:00	"	"	"	"	"	"	9	"	"	"	"
05:01	"	"	"	"	"	"	12	"	"	"	"
05:02	"	"	"	"	"	"	20	"	"	"	"
05:13	238	14	294	93	NR	NA	13	NR	NR	NA	NA
05:14	"	"	"	"	"	"	9	"	"	"	"
05:15	"	"	"	"	"	"	11	"	"	"	"
05:16	"	"	"	"	"	"	13	"	"	"	"
05:19	NR	NR	NR	NR	NR	NA	11	BDL	BDL	NA	NA
05:20	"	"	"	"	"	"	12	"	"	"	"
05:21	"	"	"	"	"	"	12	"	"	"	"
05:25	NR	NR	NR	NR	NR	NA	15	NR	NR	NA	NA
05:27	"	"	"	"	"	"	12	"	"	"	"
05:32	NR	NR	NR	NR	NR	NA	10	.008	.005	NA	NA
05:33	"	"	"	"	"	"	12	"	"	"	"
05:34	"	"	"	"	"	"	12	"	"	"	"
05:35	"	"	"	"	"	"	9	"	"	"	"
05:37	238	12	NR	NR	NR	NA	17	NR	NR	NA	NA
05:38	"	"	"	"	"	"	19	"	"	"	"
05:43	NR	NR	NR	NR	NR	NA	16	NR	NR	NA	NA
05:44	"	"	"	"	"	"	13	"	"	"	"
5:48	NR	NR	NR	NR	NR	NA	11	NR	NR	NA	NA
5:49	"	"	"	"	"	"	9	"	"	"	"
6:30	242	16	294	100	NR	0.0	9	NR	NR	NA	NA
6:31	"	"	"	"	"	"	10	"	"	"	"
6:37	NR	NR	NR	NR	NR	0.0	8	.107	.053	NA	NA
6:40	NR	NR	NR	NR	NR	0.0	19	NR	NR	6.51	1.30
6:41	"	"	"	"	"	"	18	"	"	"	"
:42	"	"	"	"	"	"	17	"	"	"	"
:46	NR	NR	NR	NR	NR	0.0	10	—	—	STD	STD
:50	236	14	294	100	NR	0.0	10	—	—	STD	STD
:51	"	"	"	"	"	"	11	"	"	"	"
:54	NR	NR	NR	NR	NR	0.0	5	NR	NR	NR	NR
:55	"	"	"	"	"	"	10	"	"	"	"
:58	NR	NR	344	100	NR	0.6	13	NR	NR	5.99	1.30
:59	"	"	"	"	"	0.6	14	"	"	"	"
:00	"	"	"	"	"	"	19	"	"	"	"
:04	230	17	294	100	NR	0.6	11	.160	.065	NR	NR
:05	"	"	"	"	"	"	"	"	"	"	"
:06	NR	NR	NR	NR	NR	0.6	10	NR	NR	NR	NR
08	NR	NR	NR	NR	NR	0.6	12	NR	NR	NR	NR
15	NR	NR	NR	NR	NR	1.2	NR	NR	NR	NR	NR
27	243	14	294	100	NR	1.2	12	NR	NR	3.87	1.30
28	"	"	"	"	"	"	8	"	"	"	"
29	"	"	"	"	"	"	7	"	"	"	"
30	"	"	"	"	"	"	5	"	"	"	"
30	NR	NR	NR	NR	NR	1.2	2	.773	.144	NR	NR
31	"	"	"	"	"	"	6	"	"	"	"
32	"	"	"	"	"	1.8	10	"	"	"	"
33	NR	NR	NR	NR	NR	1.8	12	NR	NR	BDL	BDL
34	"	"	"	"	"	"	11	"	"	"	"
35	"	"	"	"	"	"	8	"	"	"	"
38	NR	NR	294	100	NR	1.8	12	1.173	.177	NR	NR
39	"	"	"	"	"	"	19	"	"	"	"
0	NR	NR	NR	NR	NR	1.8	19	NR	NR	2.20	1.50
1	"	"	"	"	"	"	14	"	"	"	"
4	241	15	294	100	NR	1.8	10	1.147	.175	NR	NR
5	"	"	"	"	"	"	9	"	"	"	"
6	"	"	"	"	"	2.4	7	"	"	"	"
8	NR	NR	NR	NR	NR	1.8	10	NR	NR	BDL	BDL
9	"	"	"	"	"	2.4	"	"	"	"	"

07:53	254	13	NR	NR	NR	2.4	8	1.253	.183	NR	NR
07:54	"	"	"	"	"	3.0	9	"	"	"	"
07:57	NR	NR	294	100	NR	3.6	11	NR	NR	7.6	2.0
07:58	"	"	"	"	"	"	13	"	"	"	"
07:59	"	"	"	"	"	"	17	"	"	"	"
08:00	NR	NR	NR	NR	NR	3.0	16	1.787	.218	NR	NR
08:01	"	"	"	"	"	2.4	13	"	"	"	"
08:02	"	"	"	"	"	"	12	"	"	"	"
8:03	NR	NR	NR	NR	NR	2.4	8	NR	NR	9.70	2.10
8:04	"	"	"	"	"	"	6	"	"	"	"
8:05	"	"	"	"	"	"	8	"	"	"	"
8:06	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
8:17	260	12	294	100	NR	4.8	11	NR	NR	10.90	2.90
8:18	"	"	"	"	"	"	8	"	"	"	"
8:19	"	"	"	"	"	"	12	"	"	"	"
8:20	NR	NR	NR	NR	NR	4.8	15	4.747	.356	NR	NR
8:21	"	"	"	"	"	"	17	"	"	"	"
:24	253	14	NR	NR	NR	NR	NR	NR	NR	NR	NR
:28	NR	NR	295	100	NR	5.4	12	5.893	.396	NR	NR
:29	"	"	"	"	"	"	9	"	"	"	"
:30	"	"	"	"	"	6.6	11	"	"	"	"
:31	NR	NR	NR	NR	NR	4.8	10	NR	NR	13.00	3.10
:32	"	"	"	"	"	"	9	"	"	"	"
:33	"	"	"	"	"	6.0	5	"	"	"	"
:34	NR	NR	NR	NR	NR	5.4	7	7.573	.449	NR	NR
:35	"	"	"	"	"	"	10	"	"	"	"
:37	258	12	295	100	NR	5.4	6	NR	NR	15.30	3.40
:38	"	"	"	"	"	"	16	"	"	"	"
:41	NR	NR	NR	NR	NR	6.6	11	7.093	.435	NR	NR
:42	"	"	"	"	"	4.8	10	"	"	"	"
:43	"	"	"	"	"	6.6	13	"	"	"	"
44	NR	NR	NR	NR	NR	4.8	11	NR	NR	17.80	3.40
45	"	"	"	"	"	6.0	13	"	"	"	"
47	NR	NR	NR	NR	NR	7.2	10	.400	.103	NR	NR
48	"	"	"	"	"	"	12	"	"	"	"
51	NR	NR	NR	NR	NR	7.2	11	NR	NR	15.00	3.10
52	"	"	"	"	"	"	3	"	"	"	"
53	"	"	"	"	"	"	6	"	"	"	"
54	NR	NR	NR	NR	NR	6.0	9	6.853	.427	NR	NR
55	"	"	"	"	"	"	8	"	"	"	"
56	"	"	"	"	"	"	11	"	"	"	"
09	244	12	296	100	NR	4.8	7	NR	NR	7.60	2.90
13	NR	NR	NR	NR	NR	5.4	12	NR	NR	NR	NR
4	"	"	"	"	"	"	"	"	"	"	"
0	255	13	297	70	1000	11.4	17	NR	NR	6.00	2.10
3	255	11	297	80	NR	7.8	12	2.400	.253	NR	NR
7	250	11	297	80	NR	11.4	18	NR	NR	6.50	2.10
9	240	10	297	85	NR	13.3	19	2.773	.272	NR	NR
3	250	13	298	80	1900	17.5	19	NR	NR	2.30	2.10
6	250	10	298	70	NR	17.5	21	NR	NR	NR	NR
0	250	9	298	10	NR	16.9	21	2.853	.276	NR	NR
3	240	10	NR	NR	NR	13.9	18	NR	NR	BDL	BDL
7	260	12	299	70	1900	25.9	21	2.907	.278	NR	NR
5	230	12	299	60	NR	23.5	24	NR	NR	NR	NR
7	230	10	299	55	NR	34.9	18	NR	NR	NR	NR
	240	13	300	60	NR	23.5	14	NR	NR	4.80	2.00
	240	11	300	65	NR	25.3	17	2.027	.232	NR	NR
	230	11	300	65	NR	19.9	15	NR	NR	BDL	BDL
	240	13	300	60	3100	11.4	21	1.280	.185	NR	NR
	220	13	301	65	NR	24.1	19	NR	NR	7.90	1.90

12:19	215	10	301	60	2700	22.3	17	.693	.136	NR	NR
12:20	"	"	"	"	3800	"	"	"	"	"	"
12:22	230	8	301	55	NR	21.7	27	NR	NR	BDL	BDL
12:25	240	10	301	60	NR	19.3	23	.693	.136	NR	NR
12:56	230	14	302	55	NR	36.1	22	NR	NR	BDL	BDL
12:59	220	13	302	55	NR	15.7	24	.427	.107	NR	NR
13:02	210	8	301	55	2400	15.1	26	NR	NR	BDL	BDL
13:06	260	10	301	50	2400	18.1	26	.240	.080	NR	NR
13:21	215	13	301	50	NR	14.5	21	NR	NR	BDL	BDL
13:24	210	12	301	55	2800	16.3	27	.373	.100	NR	NR
13:27	215	11	301	50	NR	19.3	26	NR	NR	BDL	BDL
13:30	215	13	301	60	NR	13.9	21	.240	.080	NR	NR
14:05	224	15	302	55	590	21.7	28	NR	NR	2.20	1.30
4:09	236	9	303	55	NR	19.3	28	1.440	.196	NR	NR
4:12	213	12	303	60	NR	38.0	23	NR	NR	3.30	1.30
4:17	212	9	302	60	2400	16.8	29	1.280	.185	NR	NR
4:36	220	10	302	60	NR	15.1	19	NR	NR	5.30	1.40
4:37	"	"	"	"	"	"	25	"	"	"	"
4:39	230	7	303	NR	NR	36.1	21	1.200	.179	NR	NR
4:55	235	11	303	NR	NR	34.9	23	NR	NR	BDL	BDL
4:56	"	"	"	"	"	"	20	"	"	"	"
5:03	220	10	303	55	1600	17.5	27	.320	.092	NR	NR
5:26	210	12	303	NR	NR	32.5	23	NR	NR	1.50	0.75
5:27	"	"	"	"	"	"	27	"	"	"	"
5:29	210	19	302	NR	NR	13.9	20	.213	.075	NR	NR
5:33	215	23	302	50	450	33.7	23	NR	NR	1.80	0.95
5:37	225	15	302	NR	NR	30.7	25	.587	.125	NR	NR
5:57	255	5	303	50	1600	28.9	28	NR	NR	2.60	0.83
5:58	"	"	"	"	"	"	19	"	"	"	"
:00	210	15	303	60	NR	21.9	28	.213	.075	NR	NR
:01	"	"	"	"	"	"	27	"	"	"	"
:04	215	14	303	55	1400	28.9	19	NR	NR	BDL	BDL
:05	"	"	"	"	"	"	21	"	"	"	"
:10	210	10	303	NR	NR	29.5	21	NR	NR	1.00	0.77
:11	"	"	"	"	"	"	24	"	"	"	"
:14	210	10	304	50	1200	28.9	26	.187	.071	NR	NR
:17	210	15	304	50	NR	16.3	19	NR	NR	1.80	0.86
:18	"	"	"	"	"	28.9	26	"	"	"	"
:21	200	11	303	NR	1400	27.7	20	.293	.088	NR	NR
:22	"	"	"	"	"	"	23	"	"	"	"
:41	205	11	303	50	1200	13.9	19	NR	NR	BDL	BDL
42	"	"	"	"	"	"	20	"	"	"	"
44	210	16	303	50	NR	9.6	24	.107	.053	NR	NR
45	"	"	"	"	"	"	20	"	"	"	"
47	215	17	303	60	NR	10.2	23	NR	NR	0.70	0.66
48	"	"	"	"	"	"	13	"	"	"	"
51	210	15	302	60	1200	10.2	12	.133	.060	NR	NR
52	"	"	"	"	"	"	18	"	"	"	"
56	210	15	302	NR	NR	10.2	23	NR	NR	1.90	0.79
57	"	"	"	"	"	"	25	"	"	"	"
00	210	18	302	50	NR	10.2	23	.240	.080	NR	NR
01	"	"	"	"	"	"	21	"	"	"	"
03	210	15	302	55	1400	9.6	24	NR	NR	1.10	0.79
04	"	"	"	"	"	"	20	"	"	"	"
08	206	17	302	55	NR	5.4	17	NR	NR	2.80	0.77
13	210	16	302	60	1000	12.0	22	BDL	BDL	NR	NR
14	"	"	"	"	"	"	15	"	"	"	"
8	215	13	302	60	NR	13.9	19	NR	NR	BDL	BDL
9	"	"	"	"	"	"	22	"	"	"	"
1	215	15	302	50	1300	12.0	26	.023	.009	NR	NR

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17:22     "    "     "      "     "      "      23        "      "      "      "
17:25   220   14   302     60    NR   12.0      20       NR     NR    BDL    BDL
17:28   210   22   302     50  1900   15.1      16       NR     NR     NR     NR
17:29     "    "     "      "     "      "      23        "      "      "      "
17:31   220   21   302     55    NR   11.4      27       NR     NR   2.20   0.83
17:32     "    "     "      "     "      "      24        "      "      "      "
17:35   210   28   302     70  1500    4.8      21       NR     NR    BDL    BDL
17:39   220   49   298     70    NR    2.4      22      BDL    BDL     NR     NR
17:42   220   45   297     70  1000    2.4      30       NR     NR   1.30   0.66
 7:45   210   42   297     70  1000    3.0      19      BDL    BDL     NR     NR
 7:46     "    "     "      "     "      "      23        "      "      "      "
 7:48   210   38   297     70    NR    1.8      22       NR     NR   2.00   0.75
 7:50   210   47   294     90    NR    1.8      21      BDL    BDL     NR     NR
 7:51     "    "     "      "     "      "      22        "      "      "      "
 7:53   210   34   293     90   700    2.4      24       NR     NR   0.55   0.53
 7:58   210   32   293     90   700    3.0      27       NR     NR   1.30   0.66
 7:59     "    "     "      "     "      "      28        "      "      "      "
 8:01   210   33   293    100    NR    3.6      26     .053   .038     NR     NR
 8:02     "    "     "      "     "      "      21        "      "      "      "
 3:04   210   32   293     90   450    4.8       9       NR     NR    BDL    BDL
 3:07   210   31   293     75    NR    6.0      25     .160   .065     NR     NR
 3:08     "    "     "      "     "      "      27        "      "      "      "
  :11   210   26   294     80   450   10.2      32       NR     NR    BDL    BDL
  :14   210   31   294     75    NR   13.9      23     .213   .075     NR     NR
  :15     "    "     "      "     "      "      26        "      "      "      "
  :17   210   29   295     85    NR   13.3      26       NR     NR     NR     NR
  :18     "    "     "      "     "      "      20        "      "      "      "
  :20   210   25   296     90   700   13.9      22       NR     NR     NR     NR
  :22   215   19   296     90    NR   12.7      23       NR     NR   1.00   0.70
  :23     "    "     "      "     "      "      25        "      "      "      "
  :27   210   22   296     80    NR   11.4      21       NR     NR   2.20   0.90
  :28     "    "     "      "     "      "      24        "      "      "      "
  :31   210   24   295     75    NR    7.2      16     .187   .071     NR     NR
  :32     "    "     "      "     "      "      18        "      "      "      "
  :34   215   27   294     90   450    6.0      24       NR     NR   1.30   0.86
  :35     "    "     "      "     "      "      17        "      "      "      "
  :37   210   21   294     85    NR    5.4      20     .267   .084     NR     NR
   40   210   21   294     90  1000    5.4      25       NR     NR    BDL    BDL
   41     "    "     "      "     "      "      21        "      "      "      "
   43   210   22   294     80    NR    4.8      19       NR     NR     NR     NR
   44     "    "     "      "     "      "      21        "      "      "      "
   47   210   21   294     75  1400    4.8      18       NR     NR   2.00   0.90
   48     "    "     "      "     "      "      17        "      "      "      "
   50   210   20   294     80    NR    4.2      19     .240   .080     NR     NR
   51     "    "     "      "     "      "      23        "      "      "      "
   53   210   22   294     75  1600    4.2      20       NR     NR   1.50   0.84
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NR = NOT RECORDED

NA = NOT AVAILABLE

STD = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE

BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

[illegible] DATA WAS RECORDED ON 07/13/84

TIME	WIND (DEGREES)	(MPH)	TEMP (K)	REL. HUM. (%)	C.C.N. (#/CM²)	UV. FLUX. (W/M²)	[O$_3$] (PPB)	[NO] (PPB)	+/- (PPB)	[NO$_2$] (PPB)	+/- (PPB)
12:06	241	20	295	100	NR	0.0	11	.042	.030	NA	NA
02:07	"	"	"	"	"	"	7	"	"	"	"
12:08	"	"	"	"	"	"	14	"	"	"	"
12:09	NR	NR	NR	NR	NR	NR	16	NR	NR	1.20	.57
12:10	"	"	"	"	"	"	18	"	"	"	"
12:15	NR	NR	NR	NR	NR	NR	19	NR	NR	NR	NR
12:16	"	"	"	"	"	"	24	"	"	"	"
12:18	247	23	NR	NR	NR	NR	14	NR	NR	2.50	.76
12:19	"	"	"	"	"	"	"	"	"	"	"
2:22	NR	NR	NR	NR	NR	NR	14	.042	.030	NR	NR
2:23	"	"	"	"	"	"	24	"	"	"	"
2:24	241	25	NR	NR	NR	NR	17	NR	NR	3.00	.86
2:25	"	"	"	"	"	"	15	"	"	"	"
2:26	"	"	"	"	"	"	11	"	"	"	"
2:28	NR	NR	294	100	NR	NR	15	NR	NR	NR	NR
2:29	"	"	"	"	"	"	14	"	"	"	"
2:32	241	27	NR	NR	NR	NR	17	NR	NR	4.10	1.00
2:33	"	"	"	"	"	"	21	"	"	"	"
2:34	"	"	"	"	"	"	21	"	"	"	"
:46	262	23	NR	NR	NR	NR	19	NR	NR	6.20	1.20
:50	261	27	293	100	NR	NR	23	NR	NR	4.00	1.00
:51	"	"	"	"	"	"	"	"	"	"	"
:53	257	25	NR	NR	NR	NR	26	BDL	BDL	NR	NR
:54	"	"	"	"	"	"	25	"	"	"	"
:55	"	"	"	"	"	"	24	"	"	"	"
:56	NR	NR	NR	NR	NR	NR	28	NR	NR	5.50	1.10
:57	"	"	"	"	"	"	26	"	"	"	"
:58	"	"	"	"	"	"	25	"	"	"	"
:00	254	22	NR	NR	NR	NR	27	NR	NR	3.00	.83
:01	"	"	"	"	"	"	24	"	"	"	"
:02	"	"	"	"	"	"	25	"	"	"	"
:03	NR	NR	NR	NR	NR	NR	21	NR	NR	NR	NR
:05	NR	NR	NR	NR	NR	NR	19	NR	NR	5.50	1.10
08	NR	NR	NR	NR	NR	NR	20	NR	NR	4.00	.97
09	"	"	"	"	"	"	26	"	"	"	"
12	259	15	NR	100	NR	NR	23	NR	NR	3.30	.90
13	"	"	"	"	"	"	"	"	"	"	"
14	"	"	"	"	"	"	22	"	"	"	"
17	256	18	NR	NR	NR	NR	21	NR	NR	3.60	.90
18	"	"	"	"	"	"	22	"	"	"	"
21	NR	NR	NR	NR	NR	NR	22	NR	NR	5.50	1.00
22	"	"	"	"	"	"	23	"	"	"	"
[illegible]	[illegible]	17	NR	NR	NR	NR	27	.042	.030	NR	NR
[illegible]	"	"	"	"	"	"	33	"	"	"	"
[illegible]	"	"	"	"	"	"	24	"	"	"	"
[illegible]	"	"	"	"	"	"	32	"	"	"	"
[illegible]	NR	NR	NR	NR	NR	NR	21	NR	NR	3.30	.76
[illegible]	"	"	"	"	"	"	27	"	"	"	"

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03:52    264   18    292    100    NR      NR     25          NR     NR     5.40     .99
03:53      "    "      "      "     "       "     26           "      "        "       "
03:54      "    "      "      "     "       "     25           "      "        "       "
04:53    263   25     NR     NR    NR      NR     26          NR     NR    10.00    1.30
04:54      "    "      "      "     "       "      "           "      "        "       "
04:56     NR   NR    293    100  1600      NR     19        .106   .047       NR      NR
04:57      "    "      "      "     "       "     16           "      "        "       "
04:58      "    "      "      "     "       "     19           "      "        "       "
04:59    258   21     NR     NR    NR      NR     21          NR     NR    14.10    1.60
05:03     NR   NR     NR     NR    NR      NR     17          NR     NR       NR      NR
05:04      "    "      "      "     "       "     14           "      "        "       "
05:06    260   22     NR     NR    NR      NR     24          NR     NR    11.50    1.40
05:07      "    "      "      "     "       "     25           "      "        "       "
05:08      "    "      "      "     "       "     24           "      "        "       "
05:12    258   25    293    100    NR      NR     23          NR     NR     5.30    1.30
05:13      "    "      "      "     "       "     22           "      "        "       "
05:14      "    "      "      "     "       "     19           "      "        "       "
 5:16     NR   NR     NR     NR    NR      NR     15          NR     NR       NR      NR
 5:17      "    "      "      "     "       "     18           "      "        "       "
 5:20     NR   NR     NR     NR    NR      NR     17          NR     NR     7.30    1.30
 5:21      "    "      "      "     "       "     14           "      "        "       "
 5:24     NR   NR     NR     NR    NR      NR     15         BDL    BDL       NR      NR
 5:25      "    "      "      "     "       "     20           "      "        "       "
 5:28     NR   NR     NR     NR    NR      NR     22          NR     NR     7.30    1.30
 5:32    258   24    293    100    NR      NR     20          NR     NR       NR      NR
 5:41    288   18    293    100    NR      NR     19          NR     NR     5.00    1.10
 5:45    284   18     NR     NR    NR      NR     22          NR     NR       NR      NR
 5:46      "    "      "      "     "       "     18           "      "        "       "
 5:48    291   14     NR     NR    NR      NR     24          NR     NR     3.40    1.00
  :52    272   16     NR     NR    NR      NR     26          NR     NR     4.90    1.20
  :53      "    "      "      "     "       "     23           "      "        "       "
  :55    271   17     NR     NR    NR      NR     22          NR     NR     8.20    1.40
  :56      "    "      "      "     "       "     21           "      "        "       "
  :02    265   17     NR     NR    NR      NR     22          NR     NR     8.30    1.40
  :03      "    "      "      "     "       "     24           "      "        "       "
  :04     NR   NR     NR     NR    NR      NR     21          NR     NR     8.10    1.40
  :05      "    "      "      "     "       "     19           "      "        "       "
  :07    265   20     NR     NR    NR      NR     24          NR     NR       NR      NR
  :08      "    "      "      "     "       "     22           "      "        "
  :10     NR   NR     NR     NR    NR      NR     19        .042   .030       NR      NR
  :15    259   18    293    100    NR     0.0     19          NR     NR     9.80    1.50
  :17     NR   NR     NR     NR    NR      NR     15          NR     NR    13.50    1.70
   18      "    "      "      "     "       "     16           "      "        "       "
   21    260   18     NR     NR    NR      NR     11          NR     NR     9.60    1.50
   24     NR   NR     NR     NR    NR     0.0     21          NR     NR       NR      NR
   29    259   19    293    100    NR     0.0     14          NR     NR    13.40    1.60
   30      "    "      "      "     "       "     19           "      "        "       "
   31      "    "      "      "     "       "     18           "      "        "       "
   38    257   20     NR     NR    NR      NR     19          NR     NR    14.50    1.70
   39      "    "      "      "     "       "      "           "      "        "       "
   40     NR   NR     NR     NR    NR      NR     17          NR     NR    11.90    1.50
   41      "    "      "      "     "       "      "           "      "        "       "
   45     NR   NR     NR     NR    NR     0.0     13         STD    STD        —       —
   46      "    "      "      "     "       "     15           "      "        "       "
   50     NR   NR     NR     NR    NR      NR     15        .085   .042       NR      NR
   51      "    "      "      "     "       "     20           "      "        "       "
   56    265   17    294    100    NR     0.0     15           —      —      STD     STD
   57      "    "      "      "     "     0.4     17           "      "        "       "
   58      "    "      "      "     "       "     19           "      "        "       "
    0     NR   NR     NR     NR    NR     0.6     12           —      —      STD     STD
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07:05      262   18     294     100     NR     0.6      21           NR      NR    8.60     1.60
07:06       NR   NR      NR      NR     NR     0.0      25         .149    .056      NR       NR
07:07        "    "       "       "      "       "      15            "       "       "        "
07:08        "    "       "       "      "       "      16            "       "       "        "
07:12       NR   NR      NR      NR     NR     0.0      14           NR      NR      NR       NR
07:13        "    "       "       "      "       "      20            "       "       "        "
07:16      261   17      NR      NR     NR     0.6      13           NR      NR   16.50     2.20
07:17        "    "       "       "      "     1.2      14            "       "       "        "
07:18        "    "       "       "      "       "      13            "       "       "        "
07:45      269   14     294     100     NR     1.2      12           NR      NR   30.10     2.80
07:46        "    "       "       "      "       "       "            "       "       "        "
07:47        "    "       "       "      "       "      11            "       "       "        "
07:48       NR   NR      NR      NR     NR     0.6      11         .849    .134      NR       NR
07:49        "    "       "       "      "       "      14            "       "       "        "
07:52      276    8     294     100     NR     0.6      15           NR      NR   43.80     3.00
07:56      282   12      NR      NR     NR     0.6      15         .934    .141      NR       NR
07:57        "    "       "       "      "       "       9            "       "       "        "
07:59      280   13      NR      NR     NR     0.6      16           NR      NR   29.20     2.70
08:00        "    "       "       "      "       "      13            "       "       "        "
08:01        "    "       "       "      "     1.2      12            "       "       "        "
08:02      263   15      NR      NR     NR     0.6       7           NR      NR      NR       NR
 8:03        "    "       "       "      "       "       6            "       "       "        "
 8:04       NR   NR      NR      NR     NR     1.2       4           NR      NR      NR       NR
 8:05       NR   NR      NR      NR     NR     1.2       5           NR      NR      NR       NR
 8:06      305   10      NR      NR     NR     0.6       6           NR      NR    4.70     2.40
 8:07        "    "       "       "      "       "       9            "       "       "        "
 8:08        "    "       "       "      "       "      10            "       "       "        "
 8:37      265   15      NR      NR     NR     4.2      11           NR      NR   36.00     3.20
 8:38        "    "       "       "      "       "      10            "       "       "        "
 8:41      234   14      NR      NR     NR     6.0      15        2.611    .235      NR       NR
 8:46       NR   NR      NR      NR     NR     6.0      16           NR      NR   28.70     3.40
 8:48       NR   NR      NR      NR     NR     6.0      12        3.057    .255      NR       NR
 8:49        "    "       "       "      "     7.2      15            "       "       "        "
  :54       NR   NR      NR      NR     NR     3.6      16           NR      NR      NR       NR
  :58      245   14      NR      NR     NR     3.6      16           NR      NR   23.20     3.50
  :59        "    "       "       "      "       "      12            "       "       "        "
  :01      277   14      NR      NR     NR     4.8      13        2.930    .249      NR       NR
  :02        "    "       "       "      "       "      10            "       "       "        "
  :34      267   12      NR      NR     NR     7.8      14        4.692    .316      NR       NR
  :35        "    "       "       "      "       "      16            "       "       "        "
  :36        "    "       "       "      "       "      18            "       "       "        "
  :37       NR   NR     294     100     NR     9.0      15           NR      NR   25.90     4.10
  :38        "    "       "       "      "       "      14            "       "       "        "
  :40      273   13     295     100     NR    10.2      17        6.369    .368      NR       NR
  :44      275   10     295     100     NR     9.6      14           NR      NR      NR       NR
  :46      269   11     295     100     NR    11.4      26           NR      NR      NR       NR

[illegible]

NR = NOT RECORDED

NA = NOT AVAILABLE

STD = A CALIBRATION POINT WAS RUN

" = THE SAME AS THE PRECEDING VALUE
```

BDL = THE SIGNAL IS BELOW THE DETECTION LIMIT

HIS DATA WAS RECORDED ON 07/27/84

TIME	WIND (DEGREES)	(MPH)	TEMP (K)	REL. HUM. (%)	C.C.N. (#/CM^3)	UV. FLUX (W/M^2)	[O_3] (PPB)	[NO] (PPB)	+/- (PPB)	[NO_2] (PPB)	+/- (PPB)
12:45	270	10	299	55	NR	15.1	54	NA	NA	NA	NA
13:35	307	41	298	65	1900	1.8	29	NR	NR	NR	NR
13:39	322	45	296	68	NR	2.4	40	NR	NR	3.20	.83
13:40	"	"	"	"	"	"	44	"	"	"	"
13:42	321	32	291	84	NR	2.4	58	.136	.079	NR	NR
13:43	"	"	"	"	"	"	53	"	"	"	"
13:44	326	22	291	NR	590	2.4	48	NR	NR	NR	NR
13:47	347	22	290	85	NR	3.0	47	NR	NR	4.26	.98
13:48	"	"	"	"	"	"	46	"	"	"	"
13:50	340	19	290	100	NR	3.6	54	.091	.064	NR	NR
13:53	332	20	291	100	NR	3.0	51	NR	NR	.61	.55
13:56	300	19	291	100	150	2.4	43	NR	NR	NR	NR
14:00	272	18	292	100	NR	1.8	41	NR	NR	3.04	.87
4:01	"	"	"	"	"	"	44	"	"	"	"
4:04	275	4	292	100	NR	1.8	55	NR	NR	NR	NR
4:07	262	1	293	100	NR	3.0	55	NR	NR	NR	NR
4:10	26	10	293	100	NR	3.0	47	NR	NR	4.11	1.00
4:13	14	15	291	100	NR	3.0	48	.182	.091	NR	NR
4:16	254	15	292	100	NR	3.6	50	NR	NR	NR	NR
4:17	"	"	"	"	"	"	45	"	"	"	"
4:19	252	13	293	100	450	4.8	48	NR	NR	1.07	.70
4:20	"	"	"	"	"	"	46	"	"	"	"
4:23	235	8	295	100	NR	7.8	49	.182	.091	NR	NR
4:24	"	"	"	"	"	"	48	"	"	"	"
4:27	238	7	295	100	NR	9.0	45	NR	NR	1.07	.70
:28	"	"	"	"	"	"	48	"	"	"	"
:30	217	8	295	95	NR	10.2	56	.273	.111	NR	NR
:31	"	"	"	"	"	"	50	"	"	"	"
:34	215	8	295	90	1000	10.8	54	NR	NR	8.68	1.40
:37	220	8	295	95	NR	10.8	52	.273	.111	NR	NR
:40	240	10	295	95	NR	10.8	57	NR	NR	1.98	.73
:43	255	11	295	95	NR	10.8	52	BDL	BDL	NR	NR
:46	255	10	295	80	NR	11.4	49	NR	NR	BDL	BDL
:52	255	10	296	70	510	17.5	53	.363	.129	NR	NR
:55	255	11	296	80	NR	12.0	53	NR	NR	2.13	.79
:59	250	10	296	85	NR	10.2	55	.136	.079	NR	NR
:05	255	13	296	90	1100	8.4	56	NR	NR	NR	NR
:13	320	11	296	90	NR	3.6	53	.636	.170	NR	NR
17	320	11	296	98	1600	3.6	45	NR	NR	8.68	1.50
20	245	22	296	100	NR	3.6	41	1.363	.249	NR	NR
23	250	25	275	100	NR	3.0	36	NR	NR	14.31	1.90
25	245	25	293	100	NR	3.0	34	1.000	.213	NR	NR
30	240	26	294	100	NR	2.4	36	NR	NR	10.35	1.60
33	235	25	294	95	NR	2.4	35	.727	.182	NR	NR
36	240	25	294	100	NR	1.8	38	NR	NR	3.07	1.40
37	235	20	294	100	NR	1.8	39	NR	NR	NR	NR
45	230	21	294	100	NR	1.8	43	NR	NR	NR	NR
50	230	22	274	85	1400	1.8	15	NR	NR	4.41	1.10

15:56	225	16	294	95	NR	3.0	42	NR	NR	[illegible]	
15:58	240	15	294	90	NR	3.6	46	NR	NR	NR	NR
16:02	250	13	294	95	NR	6.6	49	NR	NR	NR	NR
16:05	255	14	294	NR	NR	9.6	50	NR	NR	NR	NR
16:08	250	18	296	90	NR	15.1	48	NR	NR	6.09	1.20
16:11	260	19	296	75	NR	15.7	50	NR	NR	NR	NR
16:17	255	18	297	80	3000	14.5	50	NR	NR	NR	NR
16:18	"	"	"	"	"	"	41	"	"	"	"
16:19	"	"	"	"	"	"	43	"	"	"	"
16:22	255	24	296	98	NR	11.4	40	NR	NR	NR	NR
16:23	"	"	"	"	"	"	36	"	"	"	"
16:24	"	"	"	"	"	"	35	"	"	"	"
16:25	"	"	"	"	"	"	"	"	"	"	"
16:26	"	"	"	"	"	"	32	"	"	"	"
16:29	265	20	296	95	NR	8.4	35	NR	NR	NR	NR
16:30	"	"	"	"	"	"	"	"	"	"	"
16:31	"	"	"	"	"	"	34	"	"	"	"
16:32	"	"	"	"	"	"	32	"	"	"	"
16:33	"	"	"	"	"	"	"	"	"	"	"
16:38	265	16	295	98	NR	5.4	32	NR	NR	23.90	1.90
6:39	"	"	"	"	"	"	29	"	"	"	"
6:41	265	15	295	100	3000	3.0	29	2.090	.308	NR	NR
6:42	"	"	"	"	"	"	22	"	"	"	"
6:43	265	13	295	100	NR	4.8	27	NR	NR	23.74	2.20
6:44	"	"	"	"	"	"	24	"	"	"	"

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IS DATA WAS RECORDED ON JULY THIRTIETH, NINETEEN HUNDRED

TIME	WIND (DEGREES)	(MPH)	TEMP (K)	REL. HUM. (%)	C.C.N. (#/CM²)	UV. FLUX (W/M²)	$[O_3]$ (PPB)	[NO] (PPB)	+/- (PPB)	$[NO_2]$ (PPB)	+/- (PPB)
10:50	144	15	NR	NR	NR	6.0	NA	NA	NA	NA	NA
11:00	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
12:00	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
13:26	143	15	290	100	NR	3.0	27	NR	NR	NR	NR
13:29	145	15	290	100	NR	2.4	31	.825	.229	NR	NR
13:33	131	15	290	100	NR	6.6	26	NR	NR	NR	NR
13:36	134	13	291	100	NR	6.6	28	NR	NR	NR	NR
3:39	138	17	291	100	NR	6.6	28	.317	.142	NR	NR
3:43	141	16	291	100	NR	6.0	29	NR	NR	NR	NR
3:46	142	16	291	100	NR	6.0	29	.317	.142	NR	NR
3:49	140	19	291	100	NR	7.2	29	NR	NR	NR	NR
3:52	143	17	291	100	NR	11.4	35	NR	NR	NR	NR
3:55	146	23	291	100	NR	9.6	31	NR	NR	NR	NR
3:58	142	21	291	100	NR	10.8	31	.762	.220	NR	NR
4:01	147	17	291	100	NR	10.8	28	NR	NR	NR	NR
4:06	152	20	291	100	NR	9.0	30	.825	.229	NR	NR
4:09	146	17	291	100	NR	9.6	33	NR	NR	NR	NR
4:12	151	21	291	100	NR	7.2	28	NR	NR	NR	NR
4:18	146	14	291	100	NR	7.2	25	.508	.180	NR	NR
4:21	144	20	291	100	NR	12.0	32	NR	NR	NR	NR
4:26	145	17	291	100	NR	12.6	26	NR	NR	NR	NR
:29	139	18	291	100	NR	12.0	26	1.016	.254	NR	NR
:33	141	20	291	100	NR	9.0	23	.762	.220	NR	NR
:37	141	15	291	100	NR	9.6	25	NR	NR	NR	NR
:40	144	19	291	100	NR	7.2	28	.254	.127	NR	NR
:43	134	15	291	100	NR	8.4	26	NR	NR	NR	NR
:47	144	19	291	100	NR	7.8	27	.317	.142	NR	NR
:50	136	21	291	100	NR	9.6	27	NR	NR	NR	NR
:53	142	25	291	100	NR	15.7	26	NR	NR	NR	NR
:57	147	20	291	100	NR	6.0	28	.698	.211	NR	NR
:01	156	23	291	100	NR	4.2	29	NR	NR	NR	NR
:05	145	20	291	100	NR	4.2	26	NR	NR	NR	NR
:10	141	16	291	100	NR	4.2	26	NR	NR	NR	NR
:14	141	15	291	100	NR	3.6	29	NR	NR	NR	NR
20	142	20	291	100	NR	4.2	26	NR	NR	NR	NR
24	155	19	291	100	NR	7.8	29	.444	.168	NR	NR
27	150	21	291	100	NR	9.6	28	NR	NR	NR	NR
30	145	21	291	100	580	9.6	28	.317	.142	NR	NR
33	145	19	291	100	NR	10.2	27	NR	NR	6.40	2.40
37	140	18	291	100	NR	9.0	27	.381	.156	NR	NR
41	145	16	291	100	NR	9.0	29	NR	NR	2.96	1.90
44	140	20	291	100	NR	8.4	29	.254	.127	NR	NR
47	140	20	291	100	NR	6.6	27	NR	NR	BDL	BDL
50	140	18	291	100	NR	6.0	29	.127	.090	NR	NR
53	140	23	291	100	NR	7.8	27	NR	NR	NR	NR
56	145	19	291	100	470	6.0	26	NR	NR	NR	NR
59	145	18	291	100	NR	7.8	29	NR	NR	3.45	1.70
02	135	20	291	100	NR	7.2	27	BDL	BDL	NR	NR

16:05	140	19	291	100	NR	7.2	31	NR	NR	3.45	2.00
16:08	145	19	291	100	NR	8.4	29	.254	.127	NR	NR
16:12	145	19	291	100	NR	6.6	26	NR	NR	BDL	BDL
16:16	140	19	291	100	NR	6.0	29	.190	.110	NR	NR
16:18	150	16	291	100	NR	6.6	27	NR	NR	1.97	1.80
16:22	135	16	291	100	NR	4.8	28	.190	.110	NR	NR
16:25	150	19	291	100	NR	4.8	27	NR	NR	8.87	3.00
16:28	145	16	291	100	450	4.8	29	.254	.127	NR	NR
16:32	139	22	291	100	580	5.4	31	NR	NR	2.46	1.70
16:35	140	18	291	100	NR	4.8	28	NR	NR	NR	NR
16:41	139	23	291	100	NR	6.0	29	NR	NR	6.40	2.10
16:44	146	18	291	100	NR	4.8	31	.190	.110	NR	NR
16:47	144	22	291	100	NR	5.4	29	NR	NR	3.94	1.90
16:51	146	18	291	100	NR	5.4	28	NR	NR	3.94	1.80
16:54	144	15	291	100	NR	4.8	30	.127	.090	NR	NR
16:57	139	22	291	100	NR	3.6	31	NR	NR	5.91	2.00
17:00	143	18	291	100	NR	4.8	29	BDL	BDL	NR	NR
17:03	151	18	291	100	NR	5.4	28	NR	NR	6.40	2.00
7:19	145	15	290	100	NR	4.2	28	BDL	BDL	NR	NR
7:22	145	19	290	100	580	2.4	29	NR	NR	3.94	1.60
7:25	140	17	290	100	NR	1.8	27	.127	.090	NR	NR
7:28	145	17	290	100	NR	3.0	23	NR	NR	9.85	2.50

* * *

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IS DATA WAS RECORDED ON JULY THIRTYFIRST,NINETEEN HUNDRE

TIME	WIND		TEMP	REL. HUM.	C.C.N.	UV. FLUX	[O$_3$]	[NO]	+/-	[NO$_2$]	+/-
	(DEGREES)	(MPH)	(K)	(%)	(#/CM^2)	(W/M^2)	(PPB)	(PPB)	(PPB)	(PPB)	(PPB)
14:30	160	13	297	100	NR	22.3	25	NA	NA	NA	NA
14:36	NR	NR	297	100	NR	13.9	27	NR	NR	NR	NR
14:39	160	14	297	100	NR	15.1	24	.281	.140	NR	NR
14:42	160	12	297	100	NR	20.5	27	NR	NR	NR	NR
14:45	165	10	297	100	NR	12.0	21	NR	NR	NR	NR
14:47	160	15	296	100	NR	13.3	22	.281	.140	NR	NR
14:50	160	14	296	100	NR	7.2	25	NR	NR	NR	NR
4:53	160	13	296	100	NR	8.4	24	NR	NR	NR	NR
4:55	160	13	296	100	NR	12.7	19	NR	NR	NR	NR
5:00	160	14	296	100	450	13.9	20	.351	.157	NR	NR
5:03	160	14	296	100	NR	15.1	24	NR	NR	NR	NR
5:06	155	11	296	100	NR	14.5	23	.140	.099	NR	NR
5:09	155	9	296	100	NR	13.3	22	NR	NR	NR	NR
5:12	160	13	296	100	NR	10.8	25	.140	.099	NR	NR
5:18	150	11	296	100	580	10.8	28	NR	NR	NR	NR
5:19	"	"	"	"	"	"	19	"	"	"	"
5:21	155	12	296	100	NR	10.2	26	NR	NR	NR	NR
5:26	155	12	296	100	NR	14.5	25	.632	.211	NR	NR
5:29	155	10	296	100	NR	13.3	25	NR	NR	NR	NR
5:34	155	9	296	100	1000	12.0	26	NR	NR	NR	NR
5:39	155	8	296	100	NR	9.6	26	NR	NR	NR	NR
5:42	165	11	296	100	NR	7.8	28	NR	NR	NR	NR
5:45	155	10	296	100	NR	6.6	25	NR	NR	NR	NR
5:51	155	10	295	100	1200	4.8	22	NR	NR	NR	NR
5:54	170	8	294	100	NR	4.8	30	.421	.172	NR	NR
:57	160	7	294	100	NR	7.2	19	NR	NR	NR	NR
:00	150	8	294	100	NR	9.0	26	.281	.140	NR	NR
:03	140	11	294	100	NR	14.5	25	NR	NR	NR	NR
:07	155	12	294	100	NR	15.1	30	.351	.157	NR	NR
:10	155	11	295	100	NR	10.2	24	NR	NR	NR	NR
:13	155	11	294	100	1000	10.2	26	NR	NR	NR	NR
:16	150	12	294	100	NR	7.2	29	NR	NR	NR	NR
:19	155	11	294	100	NR	3.6	23	.351	.157	NR	NR
:22	150	8	294	100	NR	4.8	25	NR	NR	NR	NR
:25	145	9	294	100	NR	7.8	25	.281	.140	NR	NR
:28	140	10	294	100	880	9.0	28	NR	NR	NR	NR
31	145	10	294	100	NR	12.7	31	NR	NR	NR	NR
35	145	8	294	100	NR	12.7	29	NR	NR	NR	NR
38	140	9	294	100	NR	7.2	30	BDL	BDL	NR	NR

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[illegible]

TIME	WIND (DEGREES)	(MPH)	TEMP (K)	REL. HUM. (%)	C.C.N. (#/CM^3)	UV. FLUX (W/M^2)	[O$_3$] (PPB)	[NO] (PPB)	+/- (PPB)	[NO$_2$] (PPB)	+/- (PPB)
11:22	180	7	294	100	460	4.8	25	NR	NR	BDL	BDL
11:26	170	6	294	100	NR	4.2	19	2.800	.374	NR	NR
11:28	170	7	294	100	NR	4.8	23	NR	NR	NR	NR
11:32	160	8	294	100	NR	4.8	21	NR	NR	BDL	BDL
11:35	160	8	294	100	NR	4.2	6	.700	.187	NR	NR
11:38	160	9	294	100	NR	3.0	13	NR	NR	NR	NR
11:46	175	9	294	100	NR	4.2	29	NR	NR	NR	NR
11:51	175	9	294	100	NR	6.0	17	NR	NR	NR	NR
11:55	170	10	295	100	NR	13.3	16	NR	NR	NR	NR
11:58	180	10	295	100	580	13.9	13	NR	NR	NR	NR
12:01	185	9	295	100	NR	10.2	21	NR	NR	4.70	2.50
12:04	175	11	295	100	NR	8.4	21	.150	.870	NR	NR
.2:07	175	10	295	100	NR	10.8	23	NR	NR	BDL	BDL
.2:10	160	10	295	100	NR	6.6	22	.500	.158	NR	NR
2:13	172	9	295	100	NR	7.8	19	NR	NR	BDL	BDL
2:17	161	12	295	100	NR	7.2	9	NR	NR	NR	NR
2:20	163	11	295	100	NR	7.2	19	NR	NR	BDL	BDL
2:23	166	7	295	100	NR	11.4	15	.650	.180	NR	NR
2:27	173	10	295	100	NR	12.0	17	1.800	.300	NR	NR
2:30	181	7	295	100	NR	11.4	19	NR	NR	6.80	4.40
2:33	164	10	296	100	NR	14.5	19	2.100	.324	NR	NR
2:36	174	8	296	100	NR	13.3	21	NR	NR	BDL	BDL
2:40	165	9	296	100	NR	18.1	20	2.000	.316	NR	NR
2:45	163	6	295	100	NR	13.9	20	1.250	.250	NR	NR
2:48	162	6	295	100	NR	13.3	20	NR	NR	7.30	5.00
:52	163	7	296	100	NR	18.1	23	2.300	.339	NR	NR
:55	160	7	296	00	NR	28.9	23	NR	NR	9.40	5.20
:58	162	7	296	100	NR	24.1	20	NR	NR	NR	NR
:01	NR	NR	NR	NR	NR	26.5	20	NR	NR	NR	NR
:39	156	4	297	77	NR	33.1	27	NR	NR	NR	NR
:42	144	6	298	70	NR	36.1	26	NR	NR	BDL	BDL
:45	128	5	297	80	NR	25.3	25	1.000	.224	NR	NR
:48	138	5	297	85	NR	26.5	26	NR	NR	NR	NR
:51	133	6	297	80	NR	31.9	26	NR	NR	NR	NR
:54	140	8	297	90	NR	24.1	26	NR	NR	7.30	2.80
:57	125	6	297	85	1600	25.9	27	.150	.087	NR	NR
:03	145	6	297	90	NR	15.1	21	NR	NR	NR	NR
:17	110	4	297	82	NR	19.9	27	NR	NR	NR	NR
:27	140	6	299	80	NR	41.6	26	.100	.071	NR	NR
35	140	8	298	85	1000	30.1	26	NR	NR	5.20	2.20
39	155	5	298	90	NR	17.5	25	BDL	BDL	NR	NR
41	140	5	299	90	NR	16.9	26	NR	NR	BDL	BDL
44	145	6	298	95	NR	16.3	25	BDL	BDL	NR	NR
49	140	5	298	90	NR	14.5	26	NR	NR	3.70	1.70
51	145	4	298	95	NR	12.0	29	NR	NR	NR	NR
55	160	6	298	95	NR	13.3	30	NR	NR	BDL	BDL
03	160	8	298	100	NR	12.7	24	BDL	BDL	NR	NR
06	150	8	298	100	1200	12.7	30	NR	NR	7.10	1.50
14	155	9	298	100	NR	9.4	22	–	–	STD	STD

15:18	"	"	"	"	"	"	20	"	"	"	"
15:19	"	"	"	"	"	"	25	"	"	"	"
15:20	"	"	"	"	"	"	23	"	"	"	"
15:21	"	"	"	"	"	"	18	"	"	"	"
15:24	160	8	297	100	1200	7.8	25	-	-	STD	STD
15:25	"	"	"	"	"	"	"	"	"	"	"
15:26	"	"	"	"	"	"	26	"	"	"	"
15:27	"	"	"	"	"	"	24	"	"	"	"

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ATMOSPHERIC NITROGEN OXIDES: THEIR DETECTION AND CHEMISTRY

SECOND YEAR REPORT

TIME PERIOD Aug. 1, 1984 → Aug. 31, 1985

Prepared for:

Coordinating Research Council, Inc.
219 Perimeter Center Parkway
Atlanta, Georgia, 30346.

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PROJECT SUMMARY

Instrument Development

The CRC supported instrument development effort at Georgia Tech has been tailored to interface with the major scientific goal of our program: the comprehensive investigation of the atmospheric chemistry of the nitrogen oxide family. Available laboratory and field data, in conjunction with model calculations, suggest that this family of compounds may impact on air quality in at least three significant ways:

(1) Produce one of the major atmospheric acidic compounds, HNO_3

(2) Lead to major increases in the concentration levels of potentially harmful oxidants such as O_3 and PAN (peroxyacetylnitrate) type compounds.

(3) Control the levels of still other more reactive atmospheric oxidants such as OH and HO_2. The former species, OH, is believed to be the critical oxidant acting to control the atmospheric lifetimes of numerous trace gases released into the atmosphere.

During the second year of our proposed three year program, nearly 50% of our effort was devoted to instrument development activities. Specific species for which measurement technology was explored include: NO_2, NO_3, and HNO_2. Our instrument development efforts on the first of these trace gases, NO_2, represent an extension of the effort initiated in the first year, during which time a prototype PF/TP-LIF (photofragmentation/two photon laser-induced fluorescence) system was tested. This first generation system had a detection limit of 700 to 1000 pptv for a 5 minute integration. By contrast, the improved 2nd generation PF/TP-LIF NO_2 sensor has a detection limit of ~ 100 ppt per 5 minute integration. (Typical ambient NO_2 levels over continental areas range from 30 pptv up to several ppbv, depending on the elevation and the proximity to large urban areas.) With the addition of an excimer laser as the photofragmentation source, the limit of detection of the 2nd generation system is estimated to be 5 - 7 pptv. Of equal importance is the fact that the 2nd generation PF/TP-LIF NO_2 sensor is fully integrated into the TP-LIF NO instrument such that a common set of laser and electronic hardware is now used in the detection of both species. Finally, we believe it is noteworthy that the cycling time between an NO and NO_2 measurement has now been reduced from 300s for the original prototype system to .1s for the 2nd generation instrument. The latter NO_2 instrument has been used in all nighttime N_xO_y field studies by our group as of May 1985.

Feasibility studies oriented toward developing NO_3 and HNO_2 atmospheric detectors also followed the PF-LIF approach; however, in both of the latter cases the photofragment to be detected was the NO species formed in the v"=2 or 3 level. Much to our initial surprise, the results from the study on NO_3 indicated that negligible amounts of NO are generated at the optimum photolysis wavelength of 589 nm (e.g. $NO_3 + h\nu_1 \xrightarrow{\lambda=589nm} NO(v''=2,1,0) + O_2$). The latter results are contrary to those reported by Magnotta and Johnston (1980); but, further study of this system has now provided what we believe is the answer to these conflicting observations. For high laser power densities, NO_2, which is nearly always present when NO_3 is generated, also produces NO with reasonably good efficiency as a result of the two photon process: $NO_2 + h\nu_1 \xrightarrow{\lambda=598nm} NO_2^* \xrightarrow{\lambda=589nm} NO + O$. Magnotta and Johnston's experiment, like ours, was performed with a high energy pulsed dye laser. Tests in our case showed that the NO produced from an NO_2/NO_3 gas mixture is quadratically dependent on the laser energy density, as would be expected for a sequential two photon absorption process as shown above for NO_2.

As a result of our discovering that the quantum yield for the production of NO from NO_3 is for all practical purposes zero, we are now actively pursuing the use of a multi-pass long path differential absorption technique for measuring nighttime NO_3 levels.

The HNO_2 PF-LIF feasibility tests showed far more promise than the NO_3 system in that NO was clearly shown to be produced in the v"=2 level when using a photolysis wavelength of 355 nm. During this investigation, however, we also found that the photolysis of NO_2 produced a finite amount of NO in the v"=2 level. By calculating the product of the cross-section and the quantum yield for production of NO(v"=2) for both HNO_2 and NO_2, we have tentatively concluded that the NO(v"=2) interference from NO_2 would greatly compromise the use of the PF-LIF detection scheme for monitoring nighttime levels of HNO_2. For this reason we have initiated a second study of HNO_2 that is designed to look at an alternative PF-LIF approach for detecting HNO_2, i.e. that involving the OH radical. The OH radical can be detected using a laser probe wavelength of 282 nm. The LIF detection of OH at this wavelength has been extensively employed by several investigators (including the Georgia Tech group) in an effort to measure ambient levels of tropospheric OH. Although the latter study is still in progress, calculations on this system suggest a nighttime detection limit for HNO_2 of ~ 20 pptv.

Field Studies

Much of our field sampling effort during the second year has been centered on the nighttime chemistry of the nitrogen oxides, with a special emphasis being placed on observations of NO. Our interest in nighttime NO levels was catalyzed by the 1982 and 1983 nighttime NO measurements recorded during our participation in NASA's Chemical Instrumentation Test and Evaluation (CITE) program. (During the Wallops Island ground based intercomparison, average NO levels of 12pptv were observed; in the airborne studies over the Pacific .8 to 2.8pptv NO was found.) These unexpected levels of NO were quite intriguing since our conventional scientific wisdom tells us that the reaction of O_3 with NO after sunset should result in negligible levels of NO being present throughout the night.

With CRC support, extensive nighttime measurements of NO were initiated at Stone Mountain starting in the fall of 1984. One of the early goals of this field sampling effort was that of investigating the potential problems of "laser-generated artifacts" and "sampling integrity" in the Georgia Tech TP-LIF

NO system. These tests encompassed variations in: UV laser energy, IR laser energy, laser rep-rate, sampling flow rates, type of sampling line, location of the sampling inlet, and length of sampling line. Thus far, the results from these tests have revealed no anomalous characteristics in the TP-LIF NO field system.

The values of nighttime NO observed at Stone Mountain have typically ranged from 3 to 20 pptv (with the average value being ~11pptv) as measured during the spring 1985 sampling period. Earlier observations in the fall of 1984 showed levels nearly 2 to 2½ times higher. These very high NO values were later (e.g. during the fall of 1985) shown to be due to local contamination on the mountain resulting from a gas heater in one of 4 buildings on the mountain. During the spring sampling period extensive data were also recorded for the key variables NO_2, O_3, CO, Relative Humidity, T, Wind Direction and Wind Speed. More limited in number were measurements of HNO_3 (gas phase) and NO_3^- in the aerosol phase. Also of considerable importance were meteorological observations near the base of Stone Mountain. The latter information, in conjunction with the field station MET data, strongly suggests that the field sampling site itself is almost always above the nocturnal boundary layer, thus minimizing the transport of surface released NO_x to the sampling location.

The unexpected high values of nighttime NO at Stone Mountain have resulted in our exploring both dynamic as well as possible chemical explanations. The chemical mechanisms examined have encompassed reactions that would act to slow down the loss of NO via the NO + O_3 reaction as well as reactions that at night might generate NO. A tentative mechanism that seems to qualitatively possess the right characteristics is that summarized below:

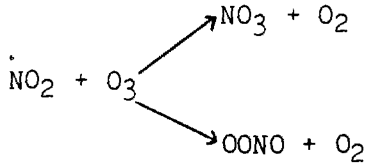
(a) $NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + O_2$

(a') $NO + O_3 \xrightleftharpoons{M} OOONO$

(b) $OOONO + NO \rightarrow NO_2 + OONO$

(c) $OONO \rightarrow O_2 + NO$

(d)



(c) $OONO \rightarrow O_2 + NO$

However, inspite of both laboratory as well as ambient air experiments that have provided additional evidence supporting the basic features of this mechanism, the results from BAC-MP4 calculations (calculations designed to ascertain whether an intermediate such as OOONO or other possible intermediates could have a sufficient long lifetime to serve as an inhibitor species in the conversion of NO to NO_2 via its reaction with O_3) have not been encouraging. We also find that when using the above mechanism to predict the values of nighttime NO (using simultaneous field measurements of NO_2, O_3, T, and Rel. Humid.) that the levels calculated are lower than those observed at our Stone Mountain sampling site. For the spring sampling period, the predicted value is too low by ~a factor of 1½ to 2.

During July 1985, additional field studies were carried out using Georgia Tech's Convair 240 aircraft. These airborne field sampling operations were primarily focused on the Stone Mountain area, involving a grid ~ 40 by 40miles in size and involving sampling elevations of 1000, 2000, and 4000 feet above the surface terrain. (Note, the top of the Stone Mt. tower is ~ 900' above the surface terrain.) Results from these flights showed average levels of NO to be in the 2.5 to 5.2 pptv range, with no significant dependence on altitude. Thus, these data would appear to be in reasonable agreement with other tests indicating that the top of Stone Mountain is not itself a significant source of NO_x. Nevertheless, considering the low values of NO being measured and the fact that an acceptable mechanism has yet to be developed to explain these observations, the authors must conclude that there remain at least three possible explanations: (1) that there are other yet undefined chemical processes that permit low levels of NO to persist at night even when excess O_3 is present; (2) that the NO levels observed are a result of yet unidentified transport processes operating between the nocturnal boundary layer and the free air stream immediately above this boundary layer (low probability); or (3) that the NO levels observed are a result of some yet poorly understood artifact in the sampling of NO using the in-situ TP-LIF system. Suffice it to say, additional work on this research topic is still needed.

The potential chemical ramifications of persistent nighttime levels of NO are numerous but certainly one of the most significant of these is that, at the levels observed, NO could serve as one of the major controlling species for NO_3. Given the very large rate coefficient for the reaction of NO with NO_3 (3×10^{-11} cm^3/molec/sec), only a few pptv of NO is required to dominate the loss of NO_3 in the nighttime atmosphere. For very clean tropospheric air masses like those occurring over the Pacific Ocean only a fraction of a pptv of NO would be required. In both of the above cases, the reaction of NO with NO_3 would return NO_3 to NO_2 and thus decrease the nighttime rate of production of HNO_3.

I. INTRODUCTION

The primary objectives of the Georgia Tech program under CRC sponsorship have been two fold: (1) the development of new instrument capability for measuring nitrogen oxide species; and (2) studies of the chemistry of the nitrogen oxide family, under clear air and cloud conditions. The rationale for pursuing the first area of activity is based on the fact that there are no less than 8 different nitrogen oxide species in the nitrogen oxide family. And, if the organic nitrogen oxide forms were to be included we could perhaps increase the above number by another 4 to 8 species. Thus, in our judgement, quantum jumps in our understanding of the complex chemistry encompassed by this mix of species will be dictated by the rate at which we add reliable new instruments to measure these compounds.

As a further illustration of the above point, we might want to examine what our current state-of-knowledge is as related to the nitrogen oxides. Such an examination might quickly lead us to making the statement: after nearly 15 to 20 years of study most of the major scientific questions related to the nitrogen oxide family still remain partially or totally unanswered. For example, although clear air measurements of NO, NO_2 and O_3 have been reported for many years, one of the fundamental questions involving these three species, e.g. NO, NO_2, O_3 photochemical equilibrium, has yet to be unequivocally demonstrated over a wide range of atmospheric conditions.

$$\frac{J_{NO_2}[NO_2]}{k[NO][O_3]} = 1 \qquad \text{eq. A}$$

The available evidence points to eq. A being incomplete in that NO is converted to NO_2 not only via reaction with O_3 but to some extent also by reaction with HO_2 and RO_2 species. Even so, at the present time the possibility that the NO_2 measurements used in these photochemical calculations might be in error must be seriously examined. NASA's GTE program will be addressing this problem in the summer of 1986, during which time four different NO_2 sensors will be intercompared over a wide range of atmospheric conditions. (Georgia Tech's PF/TP-LIF NO_2 sensor will be one of those instruments intercompared). Once we can convince ourselves that reliable measurements of NO_2 can be made, and new experiments still show departures from the simple photochemical expression shown in equation A (which is quite likely), reactions (1) and (2) will define yet a new instrumental barrier.

(1) $HO_2 + NO \rightarrow NO_2 + OH$

(2) $RO_2 + NO \rightarrow NO_2 + RO$

At this time there are no proven HO_2 or RO_2 sensors which permit a quantitative assessment of the importance of reactions (1) and (2).

On a quite different front, one may question how well we understand one of the major sink reactions for the nitrogen oxides i.e., the process,

(3) $OH + NO_2 + M \rightarrow HNO_3 + M$

The controlling species in this case is the OH radical and thus reliable measurements must also be made of this species. However, because of the extremely low levels of this radical in the daytime atmosphere, the necessary techniques for its measurement are still in the development stage. At this time, therefore, we must conclude that our ability to quantitatively assess the rate of production of HNO_3 under widely different atmospheric conditions is subject to considerable uncertainty.

The two scientific issues raised in the above text are but representative of a broader spectrum of questions related to daytime N_xO_y chemistry. At the same time, it must be recognized that a still quite different chemistry prevails for the nitrogen oxides at night; and, there are nearly an equal number of unanswered questions concerned with this unique chemistry. Conventional wisdom suggests that this nighttime N_xO_y chemistry should follow the reaction sequence (4) → (8):

Sunset $\underline{(4)\ NO + O_3 \rightarrow NO_2 + O_2}$

(5) $NO_2 + O_3 \rightarrow NO_3 + O_2$

(6) $NO_3 + NO_2 + M \rightarrow N_2O_5 + M$

(7) $N_2O_5 + H_2O \rightarrow$ Heterog. $\rightarrow 2HNO_3$

(8) NO_3 + Org. $\rightarrow$ HNO_3 + Org. Radical (Atkinson et al.1984)

Thus, one would predict that NO disappears virtually instantaneously at sunset; that NO_2 over the course of several hours slowly decreases in level via conversion to NO_3; and that the NO_3 species is converted into HNO_3 either by direct reaction with organics (e.g. olefinic compounds and/or aldehydes) or via reaction with NO_2 to form N_2O_5 which undergoes further reaction with H_2O to form HNO_3. The testing of this nighttime chemistry has consisted of measurements of NO_2, NO_3, O_3, and H_2O. However, under no set of atmospheric conditions has there been observed any systematic decrease of NO_2 at night, and in no case has there been observed a systematic increase in HNO_3 or NO_3^- at night. Surprising also are the recent studies by the Georgia Tech group which suggest that the NO concentration, under nighttime conditions, may not be zero as suggested by reaction (4). These recent nighttime measurements indicate persistent NO levels typically 3 to 20 pptv in a rural/urban environment even when the observations are made above the noctural boundary layer. These data, as well as other aspects of nighttime N_xO_y chemistry, will be discussed more fully in Section III of this document.

From the above discussion, we may conclude that much work remains to be done on both daytime and nighttime N_xO_y chemistry. However, other aspects of nitrogen oxide chemistry are also in need of further investigation. These include our acquiring a more comprehensive understanding of the role of clouds in the nitrogen oxide cycle and also of better defining the global sources of NO_x. For example, at the present time the single largest uncertainty in our assessment of the global source strength of NO_x is that involving the production of NO_x from lightning. According to the recent National Academy of Sciences report, "Global Tropospheric Chemistry: A Plan for Action" (1984), the estimated production of NO_x from lightning ranges from 2 to 20 Tg (N)/yr. At the upper end of this scale, the lightning flux is nearly equivalent to the NO_x production from industrial activities and thus would suggest that the global NO_x source budget is still somewhat weighted in favor of natural global sources. Obviously, given the lower estimate for lightning production, the anthropogenic NO_x source would emerge as the dominant global source of NO_x. Which of these estimates is actually correct is likely to have a impact on our long range planning for NO_x controls in the U.S.A. as well as other heavily industrialized nations.

In the discussion that follows, several of the above issues (plus others) will be examined in greater detail. In most cases, this will reflect results obtained during the first two years of our ongoing CRC program. However, where appropriate, we will also present some of our thinking on possible tasks to be pursued during the third year of our program.

II INSTRUMENT DEVELOPMENT

During the time period (Aug. 1984 → Aug. 1985), research proceeded on the development of LIF detection methods for the nitrogen oxide species NO, NO_2, HNO_2, and NO_3. Details concerning each of these systems are provided in the text that follows.

A. NO and NO_2 LIF Sensor

During the first contract year of our CRC program, the authors outlined a new approach to measuring both the NO and NO_2 species using a common set of lasers and detection hardware. At the time of our report on this new development, however, two shortcomings in this system were noted. The first of these involved the problem of cycling the system between the NO and NO_2 measuring modes. (At that time the required cycling time was on the order of 5 minutes.) The second problem area identified was concerned with the sensitivity of the modified NO/NO_2 sensor. For example, in the first generation NO/NO_2 system, the detection limit of the NO TP-LIF sensor was 5 to 8 pptv (5 min. integration) and that for the PF-TP-LIF (photofragmentation - two photon/laser-induced fluorescence) NO_2 detector was in the 700 to 1000 pptv range.

The newly modified NO/NO_2 detection system is shown in Figs. 1a and 1b. In this configuration, the NO sensor uses the frequency doubled output from a dye laser (e.g. that near 574 nm) which is frequency mixed with the 1.06μ fundamental of the Nd:YAG laser to generate 226 nm radiation which corresponds to the γ,(0,0) NO optical transition. The same dye laser fundamental, however, is also H_2 Raman shifted (2nd Stokes) to yield 1.08μ radiation, the latter wavelength can be used to pump NO from the $A^2\Sigma$ to the $D^2\Sigma$ state. Recall, that in our first generation NO/NO_2 system the YAG fundamental at 1.06μ was used to pump the A to D transition. The cross-section at the 1.06μ is nearly 100 times weaker than that at 1.08μ (see Bradshaw et al. 1985). The generation of 1.08μ radiation in conjunction with other modest changes in the collection optics

AP - APERTURE; AMP - AMPLIFIER DYE CELL; BS - BEAM SPLITTER; BC - BEAM COMBINER; HGI - 2ND & 3RD
M - RMAX MIRROR; P- AR COATED 90° TIR PRISM; H_2RS - HYDROGEN RAMAN SHIFTER; PDL- PULSED DYE LASER;
PBP - PELLIN BROCA PRISM; OSC - DYE LASER OSCILLATOR CAVITY; SHG - 2ND HARMONIC CRYSTAL;
SFM - SUM FREQUENCY MIXING CRYSTAL; OB_1 - OPTICAL BLOCK 355 NM; OB_2 - OPTICAL BLOCK 574 NM;

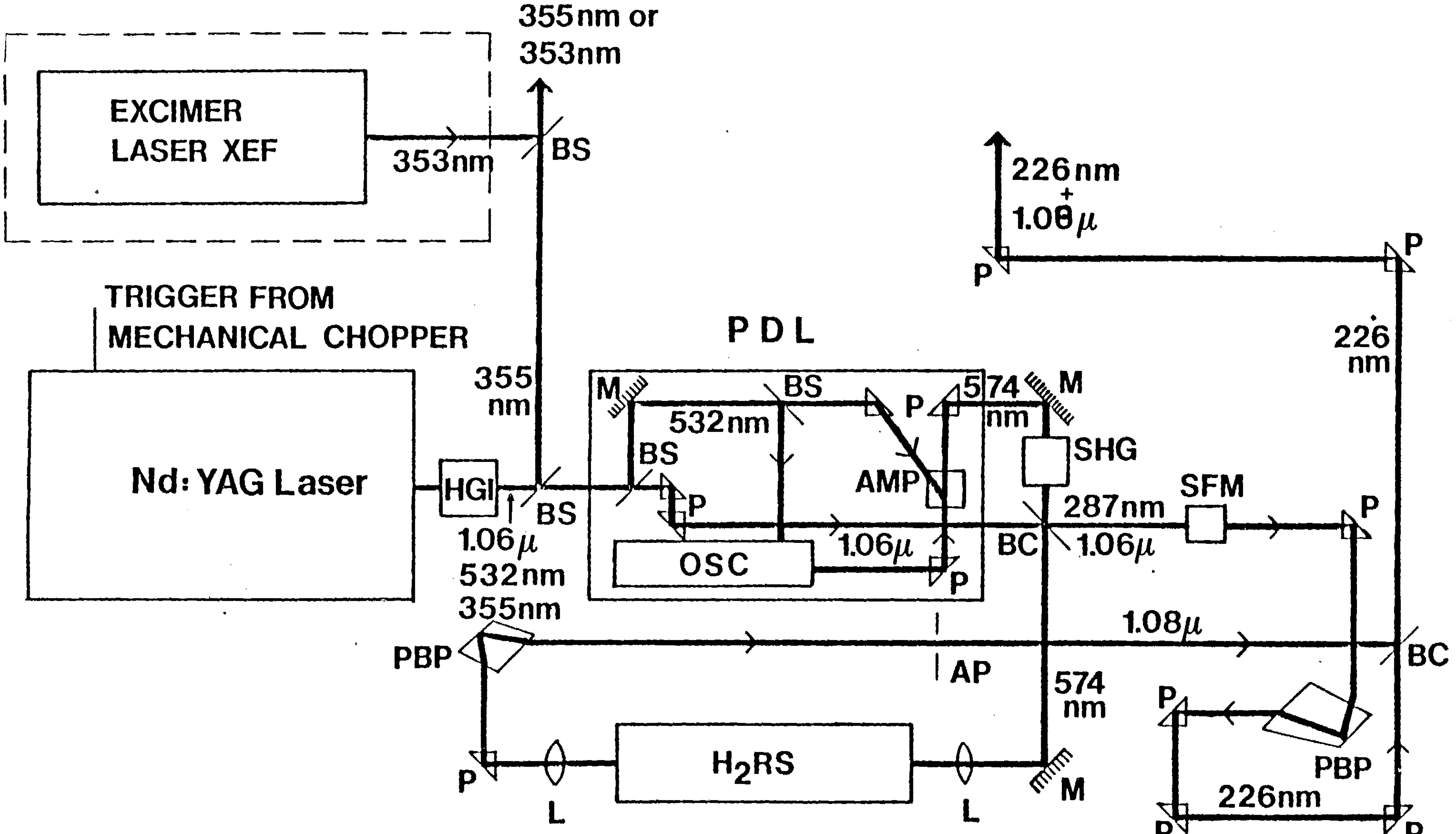


FIG. 1A - **PF -TP/LIF NO_2 SYSTEM**

AFC - AMBIENT FLUORESCENCE CHAMBER; EMD - ENERGY MONITORING DIODE; F - FILTER PACK; PMT - COI PHOTOMULTIPLIER TUBE
P - PRISM; RC - REFERENCE CELL; MC - MECHANICAL CHOPPER; MMC - MIRRORED MECHANICAL CHOPPER

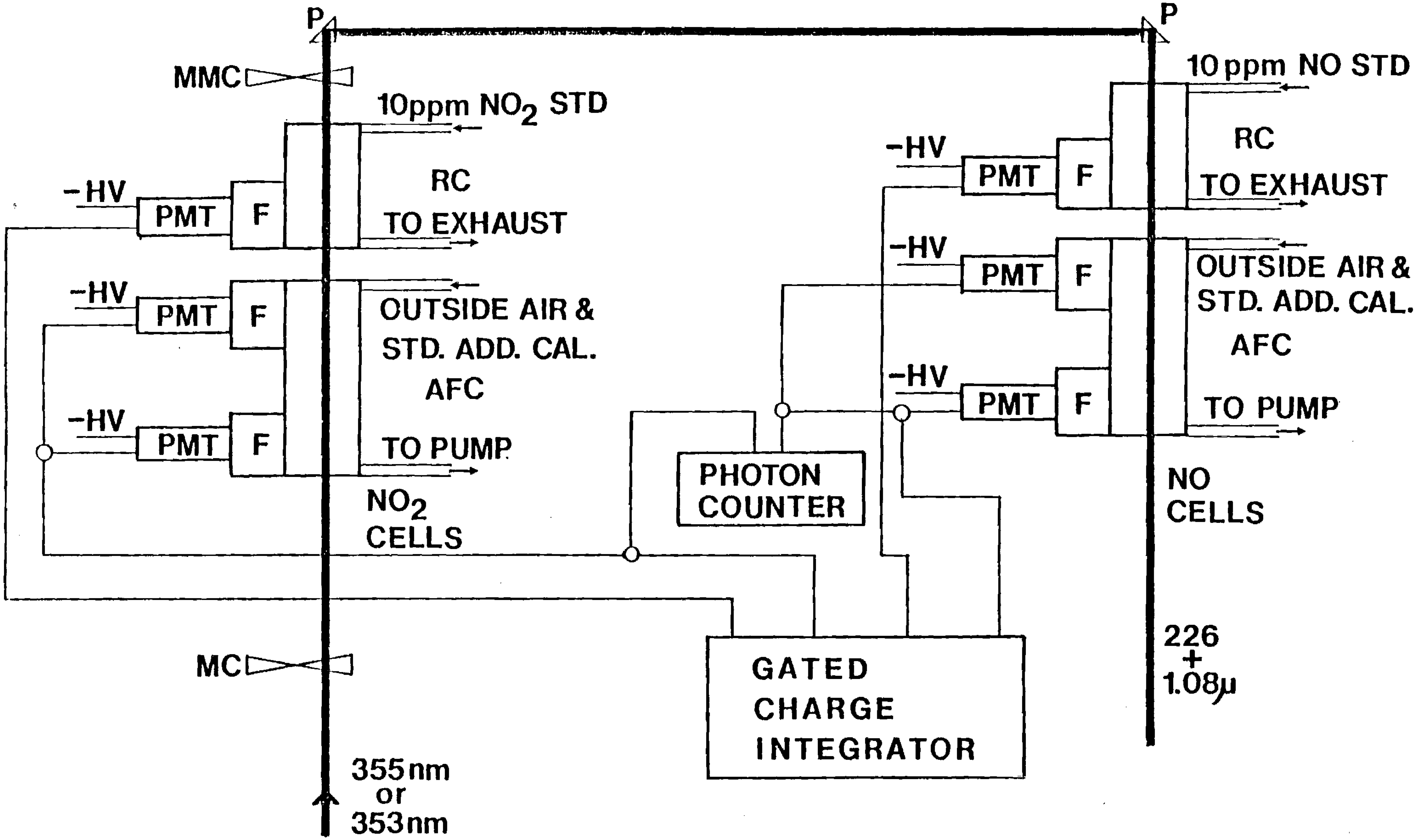


FIG. 1B - **TP/LIF NO// PF-TP/LIF NO_2 SYSTEMS** (which include the addition of two more PMTs) have resulted in an NO TP-LIF detection limit of 1 to 2 pptv per 5 minutes.

At the same time that these improvements were being incorporated into the NO detection component of the NO/NO_2 system, we also were working on making several significant alterations in the NO_2 detection scheme. Among these changes was the insertion of a second fluorescence chamber and a set of optical chopping wheels which permit the near simultaneous measurement of NO and NO_2, e.g. measurements within 100 ms. As shown in Figs. 1a and 1b, the NO fluorescence chamber receives only the 1.08μ and 226 nm beams; thus, it detects only the ambient NO level. The NO_2 chamber, on the other hand, receives the 1.08μ and 226 nm beams and, in addition, the 3rd harmonic from the Nd:YAG laser, i.e. 355 nm radiation. The synchronized chopping wheels serve to first block the 1.08/226 beams, allowing the photolysis of NO_2 at 355 nm, and then on a subsequent laser firing they block the 355 nm radiation and thus permit the 1.08/226 beams to enter the cell to detect the photo generated NO from NO_2

This new NO_2 system can be operated in either one of two modes. In the first mode, one has the option of measuring the sum of the ambient NO plus that NO generated from the photofragmentation of NO_2. The level of NO_2 can then be obtained by subtracting away the natural ambient NO level as measured independently in the NO fluorescence chamber. Alternatively, O_3 can be added to the gas stream going into the NO_2 chamber (in advance of its reaching the fluorescence chamber) in which case virtually all NO_x entering the NO_2 detection cell is in the form of NO_2. The NO detected from the photofragmentation of this NO_2 is again the sum of NO_2 generated from the titration of ambient NO plus ambient NO_2. The independent measurement of ambient NO in the NO fluorescence chamber thus allows one to caluclate the level of ambient NO_2 in the second chamber.

With the above improvements, the detection limit for NO_2 for a 5 minute integration time is now ~100 pptv. This value can be compared with the 700 to

1000 pptv detection for the first generation PF-TP-LIF NO_2 system used during the first year. Even so, as shown in Fig. 1a, still further improvement in the NO_2 system is possible with the use of an excimer laser as the photolysis source for photofragmentating NO_2. The detection limit for this excimer based system is estimated to be 5 to 7 pptv per 5 min. integration period. The latter improvement is the result of the enhanced rep-rate of the eximer versus the YAG laser system, e.g. 200Hz vs. 10Hz. Thus, in the case of the excimer based system multiple photolysis shots can be used during the 100 ms between the YAG laser firings. By this means, upwards of 40% of the NO_2 can be converted into NO. Note, that this 3nd generation NO/NO_2 LIF detection system, like its predecessor, also will use a common set of lasers to measure both NO and NO_2.

B. NO_3 PF-LIF Sensor

In our original proposal, we suggested that the NO_3 species could be detected via the sequence (9) → (11)

(9) $NO_3 + h\nu_1 \rightarrow NO\ (v''=2 \text{ or } 3) + O_2$ $\quad \lambda_1 = 589$ nm

(10) $NO\ (v''=2 \text{ or } 3) + h\nu_2 \rightarrow NO^*(v'=0)$ $\quad \lambda_2 = 248$ or 259 nm

(11) $NO^*(v'=0) \rightarrow NO\ (v''=0) + h\nu_3\ (\lambda=226\text{nm})$

The above approach was predicated on the photofragmentation step, (9), having a measurable quantum yield as reported by Magnotta and Johnston (1980). Our efforts to observe NO formation from NO_3 showed that the NO produced from the photolysis of the gas mixture (i.e. $NO_2 + NO_3$) did not correlate with the concentration level of NO_3. Subsequent tests, in fact, showed that nearly all of the NO produced near the photolysis wavelength of 589 nm was the result of a two photon process involving NO_2, e.g.

(12) $NO_2 + h\nu_1 \rightarrow NO_2^*$

(13) $NO_2^* + h\nu_1 \rightarrow NO + O$

Although Magnotta and Johnston (1980) were somewhat sketchy in providing details on the laser flux in their experiments, an examination of the specifications on their flash pumped dye laser strongly suggests that their laser power and energy density was comparable to that used in our experiments. In our experiments, it was clearly established that the NO production was quadratically dependent on the laser energy density, as would be the case if the above mechanism were the principal source of NO.

The above results are perhaps not as unexpected as one might first think in view of the discrepancy that currently exists in the literature concerning the primary quantum yields, $\Phi_9 + \Phi_{14}$, for the photodecomposition of NO_3 relative to the NO_3 absorption cross section reported by Graham and Johnston (1978). Here Φ_9 and Φ_{14} refer to the primary processes:

(14) $NO_3 + h\nu \rightarrow NO_2 + O \quad \Phi_{14}$

(9) $NO_3 + h\nu \rightarrow NO + O_2 \quad \Phi_9$.

Using the latter authors' values of $\sigma(NO_3)$, one finds that for wavelengths < 610 nm, the calculated $\Phi_9 + \Phi_{14}$ value is greater than unity which, of course, is impossible. Our results indicate that the cross sections are probably correct, but the measured production of NO from process (9) is too high due to its formation from the independent pathway

$$NO_2 + h\nu_1 \rightarrow NO_2^* \xrightarrow{h\nu_1} NO + O.$$

In Magnotta and Johnston's experiment, as is true for most studies involving NO_3, appreciable amounts of NO_2 were present in their photolysis cell.

As a side issue, we have attempted to assess the above NO_3 photochemical findings in terms of their atmospheric significance and have found that they will not have any major impact on N_xO_y chemistry in the troposphere but could have a calculable influence on the chemistry in the stratosphere. The latter effect will be to decrease the impact of nitrogen oxides on the destruction of stratospheric O_3.

Concerning our future plans on nighttime NO_3 measurements, as outlined in our 3rd year proposal to CRC, we now are of the opinion that the most productive approach to measuring NO_3 at our Stone Mountain site will be to use a multi-pass long-path differential absorption method.

C. HNO_2 PF-LIF Sensor

Our proposed method for detecting HNO_2 was similar to that discussed above for NO_3, namely,

(15) $HNO_2 + h\nu_1 \xrightarrow{\lambda=355 \text{ or } 353nm} OH + NO\ (v''=2 \text{ or } 3)$

(10) $NO(v''=2 \text{ or } 3) + h\nu_2 \xrightarrow{\lambda=248 \text{ or } 259nm} NO^*(v'=0)$

(11) $NO^*(v'=0) \rightarrow NO(v''=0) + h\nu_3\ (\lambda_3= 226nm)$

The results from our early experiments have indeed shown that vibrationally excited NO is generated from the photolysis of HNO_2 at 355 nm. Even so, back-to-back tests with NO_2 also have shown that the ratio $\frac{HNO_2(NO,v''=2)}{NO_2(NO,v''=2)}$ is only 20:1 at 355 nm. (The production of $v''=2$ from NO_2 is now believed to be the result of absorption of 355 nm radiation by rotationally hot NO_2 and/or two-photon NO_2 processes as discussed earlier.) By changing the photolysis wavelength to 353 nm, the above ratio could be increased to ~ 40:1 due to an increase in $\sigma(HNO_2)$ and a decrease in $\sigma(NO_2)$. However, the data of Platt et al. (1980, 1981), indicate that nighttime levels of NO_2 typically exceed those of HNO_2 by factors of 40 to 200.

At this time, therefore, two alternatives have been considered: (1) use of the 368 nm band of HNO_2, and (2) the detection of OH rather than NO, e.g.

(15) $HNO_2 + h\nu_1 \xrightarrow{\lambda=353 \text{ or } 355nm} OH + NO$

(16) $OH + h\nu_2 \xrightarrow{\lambda=282\ nm} OH^*$

(17) $OH^* \rightarrow OH + h\nu_3\ (\lambda_2 = 309nm)$

The major disadvantage of the first approach is that there are no strong laser lines in the vicinity of 368 nm; thus, even if a somewhat more favorable ratio of $\frac{HNO_2(NO,v=2)}{NO_2(NO,v''=2)}$ is found, the sensitivity of the HNO_2 PF-LIF system via NO ($v''=2$) detection is likely to be quite poor. For this reason we have opted to focus on the second approach, involving the detection of the OH radical. Obviously, the advantages of this approach are that intense laser sources at 353 and/or 355 nm can again be used, and there is also the experience base at Georgia Tech in OH detection schemes.

Although the high concentration levels of both H_2O_2 and HNO_3 might initially be considered a possible source of interference using 353 or 355 nm photolysis, the very low cross sections values for these species, in comparison to HNO_2, suggest a negligible effect down to HNO_2 levels of a few pptv. What must be looked at more carefully, however, is the production of OH from these species, as well as from O_3, due to the OH probe laser which is positioned at a wavelength of 282 nm.* Even so, calculations suggest that by using low to moderate energies at 282 nm, the interference problem from H_2O_2, HNO_3, and O_3/H_2O can easily be controlled. In fact, detection limits for HNO_2 of 10 to 20 pptv now seem tractable for an integration time of one to two minutes.

With the completion of our 3rd generation TP-LIF OH sensor which utilizes the wavelengths of 350 nm and 2.8μ, there will be even far less interference and levels of 1 to 2 pptv of HNO_2 would appear possible.

The PF-LIF HNO_2 system using OH detection is now being actively worked on, and we are cautiously optimistic that a field operational system will be ready by mid-January 1986.

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* The Hydroxyl radical can be generated and detected from the sequential absorptions of 282 nm radiation according to reactions (a) → (d)

(a) $O_3 + h\nu_1 \xrightarrow{\lambda_1 = 282nm} O(^1D) + O_2$
(b) $O(^1D) + H_2O \rightarrow 2OH$
(c) $OH + h\nu_1 \xrightarrow{\lambda_1 = 282nm} OH^*$
(d) $OH^* \rightarrow OH + h\nu_2$ (λ= 310nm)

III. FIELD STUDIES

The second year of our proposed CRC program encompassed both field sampling at our Stone Mountain site as well as sampling on Georgia Tech's Convair 240 aircraft.

A. Stone Mountain Field Studies

1. Overview of Previous Studies

As noted in the "Introduction", our conventional wisdom on the nighttime chemistry of the nitrogen oxides holds that the following sequence of reactions should occur:

$$\underline{(4)\ NO + O_3 \rightarrow NO_2 + O_2} \quad \text{sunset}$$

followed by:

$$(5)\ NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$(6)\ NO_2 + NO_3 + M \rightarrow N_2O_5 + M$$

$$(7)\ N_2O_5 + H_2O \xrightarrow[\text{homog.?}]{\text{heterog.}} 2HNO_3$$

$$(8)\ NO_3 + Org. \rightarrow HNO_3 + Org.\bullet$$

The lifetime of NO at sunset is dictated by the level of O_3, and for typical levels of O_3 of 40 ppbv and a temperature of 300°K it is ~ one minute. Thus, in an environment where excess O_3 prevails, one expects to find unmeasurably low levels of NO. By contrast, the NO_2 present in the nighttime atmosphere undergoes a much slower reaction with O_3, the $^1/e$ folding time being ~ 8 hours.

At least one of the reaction products from the NO_2/O_3 reaction has been shown to be NO_3. The NO_3 radical is known to disappear both via its reaction with NO_2 to form N_2O_5 and its reaction with organics (e.g. aldehydes and olefinic compounds) to give, among other products, HNO_3. The N_2O_5 species is indicated to be in equilibrium with NO_3 and NO_2 and to be removed from the atmosphere by heterogeneous reactions involving H_2O, thereby forming another source of nighttime HNO_3. The possibility of a gas phase homogeneous N_2O_5 + H_2O reaction remains uncertain.

Thus, the overall chemical picture for the N_xO_y system at night suggests that NO is virtually instantaneously converted to NO_2; that NO_2 over 8 to 10 hours is converted into NO_3; that NO_3 is converted into HNO_3 and N_2O_5; and that some fraction of this N_2O_5 decomposes back to NO_3 and/or is converted to HNO_3. However, not until 1979 was there a serious effort to examine this proposed N_xO_y chemistry, a chemistry which had been deduced predominantly from modelling exercises based on laboratory rate coefficient measurements of the appropriate elementary reactions. Then in 1979/1980 both a German group (under the direction of Ehhalt) and a U.S. group (under the direction of Noxon) succeeded in measuring nighttime tropospheric levels of NO_3 using the method of long-path differential absorption (Platt et al., 1981; Platt et al., 1984; Platt and Perner, 1980; Noxon et al., 1980; Noxon, 1983). These early measurements of NO_3 as well as subsequent observations have indicated that the NO_3 species displays tropospheric lifetimes as short as a fraction of a minute to as long as a few hours . In general, however, the lifetime of NO_3 is found to be far shorter than that predicted. In some cases this has been explained by the importance of reactions (7) and (8). In other cases, however, investigators have invoked the presence of a yet unidentified reactant, "X" (Noxon, 1980; Noxon, 1984) to explain the observed lifetime of NO_3.

Our group's interest in nighttime N_xO_y chemistry was catalyzed as a result of our participation in NASA's GTE/CITE program during the summer of 1983. The GTE/CITE program had as one of its major objectives the intercomparison of different types of NO sensors at concentration levels believed to be present in the natural global troposphere. The nighttime results from the CITE I field experiments are summarized in Table I. From these summary data, it is seen that on the nights of July 28 and July 29 (1983) the average level of NO ranged from 12 to 14 pptv. (On both days the measurement time period was 20:00 to 24:00 hours). Quite significant, in our estimation, these TP-LIF NO measurements were found to be in good agreement (i.e. ± 20%) with concurrent measurements from two independently modified chemiluminescence NO sensors (Torres, 1985; and Ridley and Carrol, 1985).

TABLE I: NASA GTE/CITE I NIGHTTIME NO OBSERVATIONS

LOCATION/DATE	SAMPLING TIME PERIOD	ALTITUDE	$\overline{O_3}$	$\overline{\text{NO}}$ LEVEL	S/N
WALLOPS ISL. VA., JULY 28(1983)	20:00 → 24:00	GRD.	44	14 PPTV	15/1
WALLOPS ISL. VA., JULY 29(1983)	20:00 → 24:00	GRD.	31	12 PPTV	15/1
EASTERN N. PACIFIC, NOV.6(1983)	20:15 → 21:00	880'	26	2.8 PPTV	5/1
EASTERN N. PACIFIC, NOV.6(1983)	18:15 → 19:15	21,000'	22	1.6 PPTV	7/1
EASTERN N. PACIFIC, NOV.26(1983)	17:50 → 18:01	32,000'	25	.8 PPTV	3/1
EASTERN N. PACIFIC, NOV.26(1983)	18:01 → 18:08	20,000'	25	1.2 PPTV	2/1

Another set of nighttime NO data was that collected during the 1983 fall GTE/CITE field sampling program. This field sampling effort involved the use of NASA's Convair 990 as a sampling platform. These nighttime airborne sampled NO data are again shown in Table I. From these data, it can be seen that on both Nov. 6 and Nov. 26, the average values observed over the Eastern Pacific were .8 to 2.8 pptv. These nighttime levels are much lower than those at Wallops Is.,Va.; however, considering the very low NO values observed in the Eastern Pacific during the daytime (e.g. 10 → 60 pptv versus 300 to 1000 pptv at Wallops Is.), the values of 2.8 to .8 pptv still appear to be quite high based on the observed nighttime ambient O_3 levels of 20 → 40 ppbv.

The chemilumenscence NO sensors were also aboard the Convair 990 during the fall 1983 mission, but the detection limit on these instruments was limited to 2 to 3 pptv. Thus, definitive measurements from the chemiluminescence instruments were not possible under nighttime conditions, i.e. within the precision of the measurements a value of zero could be assigned.

If one accepts these early measurements of nocturnal NO at face value, two questions immediately surface:

(A) How does the presence of NO at night alter the overall N_xO_y chemistry and the chemistries of other families of compounds?

and (B) What mechanism or mechanisms could account for the persistence of NO at night under conditions where O_3 is in large excess?

But however intriguing both these questions might be, the most obvious first task is that of trying to assess the integrity of the measurements themselves. For example, were these observations of finite levels of NO under nighttime conditions plagued by instrumental artifacts; or alternatively, could they simply have been the result of unknown localized sources of NO.

Although the time available to investigate these questions during the GTE/CITE I field operations was minimal, the post analyses of these data have provided some insight as to the possible magnitude of the aforementioned problems. Concerning the Wallops Island data, for example, the intercomparison of three independent data sets derived from three different instruments (two different instrument types), clearly indicates that within each instrument's stated precision all were measuring the same value of nighttime NO, i.e. ~ 12 pptv. This finding would tend to dispel the hypothesis that the NO observations were an instrumental artifact, but one still cannot argue that it is decisive. Concerning the local source question, it can be pointed out that considerable effort was made by NASA to insure that the site at Wallops Island was free of any major contamination sources. The fact that over several hours of running time on two separate evenings the observed NO levels were reasonably constant would tend to support the idea that the NO was not being generated by the investigators' activities; but again, it cannot be argued that some other localized source could not have contributed to the observed NO levels. Neither can we rule out the possibility that the NO was generated in the common manifold from which all three groups sampled from. The manifold, however, was constructed entirely from pyrex glass with the exception of one mass flow meter head that was constructed from stainless steel and located near the intake of the manifold. Obviously, another potential localized NO source could have been biogenic emissions. In the latter case, though, the effect should have been minimized due to the intake of manifold being 18 feet above the ground. If this source had been the dominant NO source at the site, one might also have expected to see much more variability in the levels of NO due to highly variable nighttime winds.

Concerning the airborne GTE NO measurements, it is more difficult to provide answers to all the questions that may be raised. For example, it can be asked if aircraft emissions could not have been the cause of the levels of NO observed. An argument against this possibility is that if the latter contamination source were important why wouldn't the levels of NO have been constant. Recall, the Georgia Tech results showed NO levels as low as .8 pptv and as high as 2.8 pptv. Equally important, is the fact that the Georgia Tech instrument was the most forward positioned instrument on the aircraft,the intake being 10 to 15 feet in front of the intakes of the Convair 990 jet engines. (The inlet location also extended well beyond the aircraft boundary layer.)

A second potential problem in the NO measurements that might be considered involves that of cabin contamination of our sample inlet line. This problem, however, can be more convincingly dismissed since during each nighttime as well as daytime flight once the TP-LIF NO sensor was placed in an operational mode all connections in the sample inlet line were exposed to a gas mixture containing ~ 10 ppmv of NO. Only in one case was there any evidence of leakage and in that case the connector was tightened and the problem was eliminated. Based on the exposure level of 10 ppmv and the integration times employed, we have estimated that cabin leakage was <u>significantly</u> less than 1 pptv. A problem area that cannot be eliminated as easily involves the possibility that there was decomposition of some nitrogen oxide species in the sampling line which generated NO, e.g. NO_2, PAN, etc. In this case, it must be noted that of the ~ 10 feet of sampling line, 8 $^1/_2$ feet was fabricated from teflon tubing but that the first 1 $^1/_2$ feet was made from stainless steel. Thus, we cannot totally rule out decomposition, however, controlled tests at our Stone Mountain field station suggest that decomposition on stainless steel should not have been a problem under non-cloud sampling conditions.

Two final areas that have not been discussed in our analysis of the reliability of the GTE NO measurements relate to the questions: (1) how certain can one be that NO was the only species detected? And (2), to what extent could laser generated interferences been a problem? Both of these issues were discussed in our first year CRC Annual Report and thus only a brief overview will be given here. The unequivocal detection of NO is ensured in the TP-LIF system due to the requirement that two spectroscopically specific transitions must be pumped. Numerous checks on this system, including the tuning to several different NO transitions, have consistently demonstrated that the TP-LIF NO system is the most selective/specific instrument available today for measuring NO. However, specificity in measuring NO cannot be equated to there being no interference of any type. Processes of the type:

(18) $Y - NO + h\nu_1 \rightarrow Y + NO$

(19) $NO + h\nu_1 \rightarrow NO\ (A^2\Sigma)$

(20) $NO(A^2\Sigma) + h\nu_2 \rightarrow NO(D^2\Sigma)$

(21) $NO(D^2\Sigma) \rightarrow NO\ (X^2\Pi) + h\nu_3$

must be critically examined. As discussed in our yearly report and also in the scientific publication by Bradshaw et al. (1985), numerous tests and calculations indicate that interferences of the above type are of negligible importance. At Wallops Island, where we employed the highest UV energies (e.g. 3 mJ), we have calculated that the interference from NO_2 could have been as high as 1 to 1.5 pptv. For the GTE airborne study where the 226 nm energy was typically equal to or less than 1mJ, the interference is estimated to be <u>far less than 1 pptv</u>. In both cases, the net effect on the observed NO signal is inconsequential.

2. Ambient Nighttime NO Observations and Quality Control Tests

Given the above nighttime NO observations from the NASA GTE program, we might conclude that these data are very intriguing, but that the absence of extensive testing for instrumental and sampling artifacts still can leave one with an element of doubt as to their reliability. It was with this somewhat pessimistic point of view that the Georgia Tech group took the TP-LIF NO system to Stone Mountain to determine the credibility of these earlier nighttime NO observations.

The data collected at Stone Mountain have been summarized in Table II. Also shown in summary form in Table III are the numerous test results that were performed at different times during the ambient NO measurement time period. We believe that the latter results demonstrate that the ambient NO data base is free from any glaring instrumental and sampling artifacts. In all, some 60 independent experiments were carried out involving seven test categories. The seven test categories included variations in: UV laser energy, laser rep-rate, the energy and wavelength of the IR laser, NO transitions pumped, the type and length of sampling line used, location of sampling line, and the NO sampling flow rate. As indicated in Table III, these tests addressed three basic issues: (1) laser generated NO formation, (2) the NO detection specificity of the TP-LIF system, and (3) sampling integrity. From the data collected, we found that only in one test was a result obtained that was significantly different from a back-to-back control experiment. Significant in this case means that the results could not be explained in terms of the natural variability of ambient NO, typically 20 to 35%, over a 20 to 30 minute integration period. This outlying result involved NO measurements recorded using a stainless steel sampling line versus that from teflon tubing under heavy cloud conditions. In the latter experiment, we found that the stainless steel sampling line gave nearly a factor of two higher NO signal than did teflon tubing.* We now believe that this increase was due to the decomposition of HNO_2 on the stainless steel sampling line, however, this conclusion is still speculation on our part.

The UV laser energy experiments are of special significance since it is here that we believe instrumental artifacts would most likely surface. As can be seen from the reaction sequence (18) → (20), if the UV laser were generating NO, the signal from this self-generated NO would scale quadratically with laser energy density. Thus, if the NO signal were totally due to laser photolysis, when reducing the energy by a factor of five the observed signal should drop by 25 as compared to a factor of five if the NO signal were generated from ambient NO. In all cases tested, we found that the NO signal level scaled linearly with laser energy within the natural variability of the ambient NO level. Nevertheless, because this laser interference problem is one that could be strongly dependent on the chemical composition of the atmosphere, this test was routinely performed throughout both the fall and spring sampling periods. From some 18 independent experiments of this type performed, the deviation observed in the full energy versus reduced energy never exceeded a level that was outside that which could be ascribed to the natural variability of NO (e.g. 20 to 35%). The precision on these experiments was controlled by the integration time chosen and typically was held to the ±10 to 15% level although in some cases it was as good as ±5% and in a very few cases as poor as ± 25%.

Another type of experiment that was performed less often than the energy variation one but relates to UV laser generated NO, is that labelled in Table III as "rep-rate" variation. In performing this experiment, we wanted to determine the possible effects of multiple laser shots being injected into the fluorescence cell before the cell contents could be displaced. For our experimental set up, the typical residence time in the .6 liter fluorescence

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* Recent laboratory tests using the PF-LIF HNO_2 sensor indicate that HNO_2 does not decompose on teflon tubing.

TABLE II: SPRING 1985 NIGHTTIME NO OBSERVATIONS
AT STONE MOUNTAIN, GEORGIA

DATE	T(OK)	HUMIDITY (%)	WIND DIR.	WIND SPEED (M/S)	$[\overline{NO_2}]$ PPBV	$[\overline{O_3}]$ PPBV	$[\overline{NO}]$(a) PPTV
MAY 21 (00:30 → 3:15)	294	58	210^0	7	---	65	31 ± 8(b)
JUNE 1 (23:00 → 3:30)	301	40	330^0	2	.7	93	3.6±1.5(b)
JUNE 3 (2:50 → 5:30)	300	68	280^0	11	4.5	63	7.5±2.0(b)
JUNE 4 (1:18 → 6:00)	301	55	305^0	7	3.0	68	8.8± 4(b)
JUNE 6 (1:30 → 4:50)	299	70	350^0	5	6	70	15 ± 4(b)
JUNE 11 (00:00 → 4:30)	296	63	260^0	8	15 ± 10	45 ± 15	20 ± 9
JUNE 13 (3:40 →)	292	73	230^0	10	8 ± 6	10 ± 5	11 ± 2

(a) Precision: ± 5% or better for nightly average.

(b) Uncertainties shown reflect the natural variability in [NO] over the measured time period.

TABLE III : NIGHTTIME NO TESTS TO EXAMINE FOR LASER GENERATED ARTIFACTS AND SAMPLING INTEGRITY IN AMBIENT AIR

	TYPE OF TEST	NUMBER OF INDEP. TESTS	OBSERVED DEVIATION
*	SEVEN FOLD FLOW INCREASE	10	≦ ± 25%
*	THREE FOLD FLOW DECREASE	2	≦ ± 30%
†	226 NM ENERGY REDUCTION OF TWO TO FIVE FOLD	18	≦ ± 25%
	ROOF TOP INLET VS. WINDOW INLET	10	≦ ± 20%
**	ALL TEFLON VS. TEFLON/STAINLESS INLET	8	≦ ± 20%
	HEATED VS. UNHEATED TEFLON INLET	2	≦ ± 30%
	LENGTH OF TEFLON TUBING 8, 30, 100 FT.	6	≦ ± 25%
	IR WAVELENGTH CHECKS 1.06μ (~ 70 mJ) 1.08μ (~ 1 mJ)	1	≦ ± 30%
	LASER REP-RATE 10 Hz vs. 1 Hz	2	≦ ± 35%

* STD. FLOW 18 L/MIN.

† TYPICAL 226 NM ENERGY .9 mJ, BEAM DIAMETER 5 mm

** In one test run in the presence of heavy clouds, the Teflon/stainless sampling line gave a factor of two higher NO signal.

chamber was ~ 2 sec. Thus, at a laser rep-rate of 10Hz, typically 10 to 20 laser shots were injected into the fluorescence chamber during the time that a given air parcel was in the chamber. Since the volume element defined by the beam passing through the cell is only ~ 6 cm^3, this means that the dilution factor was ~ a factor of 100. Such a large dilution factor would suggest that the build up of laser generated NO between laser shots should have been small. However, to test this hypothesis, experiments were carried out that involved varying the laser rep-rate from 10 to 1Hz. As shown in Table III, no statistically significant deviation was seen in the 1Hz versus 10Hz experiments. These results, like the UV laser energy variations, again argue against the importance of UV laser generated NO interference.

The IR wavelength variation shown in Table III represents yet a final test to establish the absence of laser generated NO. As discussed by Bradshaw et al. (1985), the two laser approaches that have been used in the TP-LIF system have involved 226 nm/1.06μ and 226 nm/1.08μ pumping. The first approach involving 1.06μ radiation corresponds to a very weak transition between the A and D states of NO, i.e. $\Delta J = 5$. Thus, very high energies must be used to achieve high sensitivity, e.g. ≳ 70 mJ/pulse. The tunable 1.08μ wavelength, on the other hand, corresponds to one of the stronger transitions between the A and D states and thus equal or greater sensitivity can be achieved with only ~ 1 mJ/pulse of this radiation. The above test, involving a back-to-back comparison of the NO signal from each laser configuration, was designed to show that the system utilizing 70 mJ/pulse of 1.06 did not result in laser generated NO. As seen in Table III, no evidence of interference was found.

As cited earlier in the text, a second potential problem area where extensive testing was performed involved checks on "sampling integrity". In this case, areas of concern ranged from contamination at sampling locations outside the observation tower, to contamination inside the building, to decomposition of trace constituents within the sampling line. (As was true for the UV laser interference tests, since the sampling decomposition problem was seen as one which could be strongly dependent on atmospheric composition, tests related to this problem were performed numerous times during both the Fall and Spring.)

The sample line decomposition tests were peformed using passivated stainless steel and teflon. Although only in one case was a difference observed, that involving sampling in heavy clouds, all future sampling was restricted to teflon lines. Following the decision to use only teflon, tests were carried out to determine if the length of teflon sampling line might influence the measured levels of NO. In these tests, teflon sampling lines of 8, 30, and 100 feet were intercompared: result - no effect observed.

Flow rate variations, which test both for the presence of sample line decomposition and for NO build up in the fluorescence chamber, were routinely performed throughout the sampling period. In these tests, flow rates were varied from ~ 5 l/min up to ~ 120 l/min. Within the signal fluctuations resulting from the natural variability of the ambient NO levels, no effect on the measured NO signal was observed.

The question of whether the lab itself could be a source of contamination (due to leaking joints in the sampling line) was routinely checked by exposing each connection as well as the fluorescence cell with a gas mixture containing 10 ppmv NO. This type of test was routinely performed before any outside ambient air sampling was initiated. To check for outgassing from the tower building itself, sampling intakes were located near the second floor of the tower (~ 25 feet above the surface rock), at the 6th floor (~ 85 feet above the surface) which is the floor the field station is located, and approximately 5 feet above the roof of the tower (~ 112 feet above the surface rock). All three sampling locations again were found to give the same NO level within the natural variability of the ambient NO levels. In all of the above tests, the potential problem of lab-light photolysis of NO_2 within the sampling line was avoided with the use of black teflon tubing and operating the lab in a mode not requiring overhead lights.

Based on all of the test results discussed above, as summarized in Table III, it can be stated that the authors have uncovered no evidence indicating that the measured ambient nighttime NO levels reported in Table II are not representative of the true background NO levels present on top of Stone Mountain at the times indicated. It must be added, however, that only those ambient data collected after May 21, 1985 can be labelled as free of any localized NO sources on top of the mountain. Earlier observations (e.g. late fall, 1984) were discovered to be influenced by the presence of a natural gas heater in one of four buildings atop the mountain. We had originally been informed by the Park Service that only electric heat was used on top of the mountain. The latter discovery was made by us in the fall of 1985 and the problem was quickly circumvented by having the Park Service install a timer switch on the gas burner. This timer switch kept the burner in the off position from 6 p.m. at night until 6 a.m. in the morning.

An examination of several ambient nighttime NO data sets from the fall of 1984 showed average NO levels to be ~ 2 to 2½ times higher than those observed in the spring of 1985. They were also nearly a factor of two higher than a still more recent nighttime NO data set collected in the fall of 1985*, a data set collected after the deactivation of the gas burner.

Given the absence of any identified sources of error in the NO data set presented in Table II and the newer data set from the fall of 1985, the authors have attempted to explore both dynamic and possible chemical explanations for these nighttime NO observations. The search for new chemical reaction mechanisms to explain the observations has involved both an examination of reactions that generate NO and those that might decrease the efficiency with

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* This data set will be reported in our 3rd year report.

which NO is converted to NO_2. Summarized below is the current status of our efforts to develop one such mechanism. (The authors emphasize that this mechanism must be considered tentative in nature and further adjustments are likely to be needed.)

(22) $NO + O_3 + M \rightleftarrows OOONO + M$

(23) $OOONO + NO \rightarrow NO_2 + OONO$

(24) $OONO \rightarrow O_2 + NO$

(25) $OONO + NO \rightarrow 2\ NO_2$ (guestimated to be unlikely)

(26a) $NO_2 + O_3 \rightarrow NO_3 + O_2$

(26b) " " $\rightarrow OONO + O_2$

(24) $OONO \rightarrow O_2 + NO$

(25) $OONO + NO \rightarrow 2\ NO_2$ (guestimated to be unlikely)

In this modified mechanism for the reaction of NO with O_3, we have postulated that the major channel of this reaction* proceeds through the intermediate OOONO. This intermediate is shown as reacting via two channels. The first of these is the back reaction, k_{-22}, which returns the OOONO species to the initial reactants NO and NO_3. The second channel involves the further reaction with a second molecule of NO to form NO_2 and another intermediate, OONO. The latter species is the same intermediate that has been hypothesized for the termolecular reaction of NO with O_2, i.e.

$$NO + O_2 \rightarrow OONO$$

$$OONO + NO \rightarrow 2\ NO_2 \cdot$$

Knowing that the termolecular reaction is quadratically dependent on NO, due to the reaction of OONO with NO being very slow, we have postulated that under atmospheric conditions the fate of OONO in the NO/O_3 reaction sequence is very likely to be that of decomposition to reform NO and O_2. Thus, a steady-state treatment of the proposed NO/O_3 mechanism results in the expression

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* The authors note that a minor channel of rx. 22 involves the direct formation of electronically excited NO_2^*. This appears to have only a very modest effect on the kinetic analysis that is presented in the subsequent text.

$$[\mathrm{OOONO}] = \frac{k_{22}[\mathrm{NO}][\mathrm{O_3}]}{k_{-22} + k_{23}\,[\mathrm{NO}]} \; .$$

And, the rate of loss of NO is given by:

$$-\frac{d[\mathrm{NO}]}{dt} = k_{22}\,[\mathrm{OOONO}][\mathrm{NO}] \cdot$$

Thus, if one postulates that under normal daytime conditions the levels of NO are sufficiently high that $k_{23}[\mathrm{NO}] >> k_{-22}$, the expression for the loss of NO due to reaction with O_3 becomes:

$$\text{CASE A} \quad -\frac{d[\mathrm{NO}]}{dt} = k_{22}\,[\mathrm{NO}][\mathrm{O_3}]$$

which is the currently accepted loss expression for NO in the atmosphere based on its reaction with O_3. However, one may argue that at very low NO levels (e.g. those present at night over continental areas or those that are present during the daytime over remote marine areas) $k_{23}\,[\mathrm{NO}] << k_{-22}$ in which case the loss of NO via reaction with O_3 becomes:

$$\text{CASE B} \quad -\frac{d[\mathrm{NO}]}{dt} = \frac{k_{22}}{k_{-22}}\;k_{23}\,[\mathrm{NO}]^2[\mathrm{O_3}]$$

That is, the loss process becomes quadratically dependent on the concentration of NO.

3. Controlled Laboratory O_3 Titration Tests

In an attempt to test the above hypothesis, the authors carried out several controlled laboratory studies in which the extent to which O_3 was added to a gas stream containing varying levels of NO to determine the degree of titration of NO by O_3 as a function of the level of NO. These experiments were performed using ultra zero air with NO added to the gas stream from a two stage dynamic dilution system that was connected to an NO calibration standard. The reactor for these experiments was either an extended length of $^{3}/_{8}$" O.D. Teflon tubing; or alternatively, a 3.5 liter all glass reactor equipped with a coarse fritted disk at its entrance to assure uniform mixing throughout the reactor volume. Both types of reactor gave similar results. Those shown in Fig. 2 are from the all glass reactor. The conditions for this experiment involved the addition of 141 ppbv of O_3 which according to CASE A would have corresponded to 2.2 $^{1}/e$ folding times for the NO/O_3 reaction. The latter also corresponds to a reduction in the initial NO level of a factor of 9. The dotted line in Fig. 2 corresponds, to the predicted titration level based on CASE A conditions, i.e. $k_{23}[NO] >> k_{-22}$, or to what may be referred to as the accepted mechanism for the NO + O_3 reaction which gives directly the products NO_2 and O_2. As can be seen from Fig. 2, this indeed is found to be the case for the highest levels of NO employed. As ~ 30 pptv of initial NO is approached, however, non-negligible deviation is seen between the predicted and observed titration levels. This deviation becomes very marked for initial levels of NO below 10 pptv. Below this level the rate of loss of NO approaches quadratic dependence on NO as predicted by CASE B. (Note, that the numbers in parenthesis give the signal/noise ratio for the measurement of the residue NO level.) Using mechanism (22) → (24), we have computer fit the data in Fig. 2, shown as a solid line, and thus have been able to evaluate the ratio of rate coefficients k_{-22}/k_{23}. This fit gave a value for the above ratio of 1.5 x 10^{8}. By taking the value of k_{23} to be similar to that for the reactions HO_2 + NO and CH_3OO + NO, k_{-22} is evaluated to be 1.5 x 10^{-3} s^{-1}, which suggests a natural lifetime for OOONO in the absence of NO of ~660 s.*

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* With the addition of the rx. step $NO + O_3 \rightarrow NO_2{}^* + O_2$, the lifetime of OOONO is found to be closer to 200s.

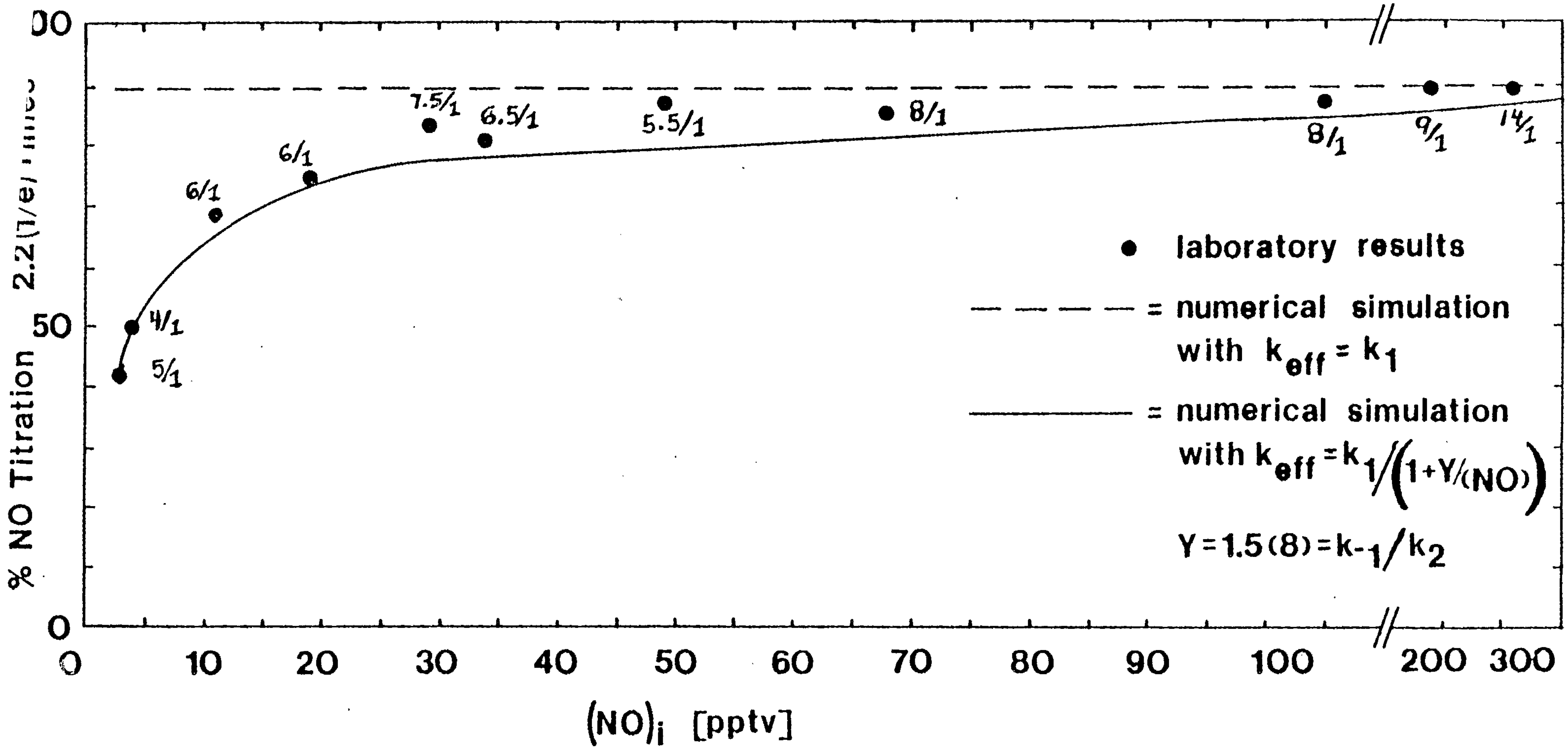


FIG. 2 LABORATORY TITRATION OF NO WITH O_3 AS A FUNCTION OF INITIAL NO LEVEL: 1 ATM. AIR AND 141 PPBV OF O_3.

Other evidence supporting the proposed O_3 + NO reaction mechanism can be found in the matrix isolation study by Bhatia and Hall (1980). In this study, NO and O_3 were allowed to react in the gas phase and the products were then subsequently trapped in an Argon matrix at 10^0K. One of the reported products isolated in the matrix was OONO. This same species was also isolated at still higher levels in a study of the NO + NO + O_2 reaction.

Although the proposed mechanism for the NO + O_3 reaction would appear to explain the substantial decrease in the rate of conversion of NO to NO_2 at night (for low levels of NO), it cannot by itself explain the persistence of NO throughout the night at the levels observed at Stone Mountain or those observed during the NASA GTE/CITE I field sampling program. If, therefore, there is to be a chemical explanation for these levels a reaction (or reactions) is needed that converts one of the prevalent nighttime nitrogen oxide species back to NO. One such possibility is that shown here as reaction (26b). In this case $NO_2$is shown as reacting with O_3 to form peroxy NO_3 (OONO). As was true for the modified NO/O_3 mechanism, our speculation is that OONO undergoes decomposition to form O_2 and NO. (Note, we are not the first group to propose that NO_2 reacts with O_3 to form NO. Stedman and Niki (1973) and Wu, Morris, and Niki (1973) have also suggested this possibility but no direct evidence was available to support the hypothesis.)

To test the proposed NO formation hypothesis via the reaction sequence 26b followed by 25, we once again resorted to performing a set of controlled laboratory experiments. (In this study we used the previously described 3.5 liter glass reactor.) In run #1 the gas mixture consisted of NO and O_3 in zero air. In this case the resulting residue NO was measured at a level of .8 ± .5 pptv. In runs #2 and #3 a large amount of NO_2 was added to the above mixture of NO and O_3 and the resulting residual NO was again measured. The exact conditions for all experiments are shown in Table IV.

TABLE IV: Evaluation of the Rx.: $NO_2 + O_3 \rightarrow NO + 2O_2$

	Initial [NO] pptv.	Initial $[NO_2]$ ppbv.	$[O_3]$ ppmv.	T ^0K	1/e Rx. Times $(NO + O_3)$	Final [NO] pptv.
Run # 1	237	< .1	1.09	300	15.8	.8 ± .5
Run # 2	220	4.42	1.09	300	15.8	3.5 ± .5
Run # 3	220	4.42	1.09	300	15.8	5.0 ± 1.4

The results from these limited experiments suggest two things. First, we see that even though ~ 16 1/e folding times have been used to titrate NO with O_3, there remains a measurable level of NO. Second, with the addition of 4.4 ppbv of NO_2 to the NO/O_3 gas mixture, we find that the final level of NO is 4 to 6 times higher than in the absence of NO_2. We interpret these results, as providing at least indirect evidence that there is a branching in the $NO_2 + O_3$ reaction which generates NO as a product.

Applying our mechanism for the NO/O_3 reaction and the laboratory evaluated ratio k_{-22}/k_{23}, we have modelled run #1 to determine the final value of NO. The value calculated was .6 pptv. This can be compared to the measured value of .8 ± .5. Likewise, we have modelled Runs #2 and #3 with the objective of evaluating the branching ratio of 26a and 26b. In the latter exercise, the value of k_{25} was taken to be the accepted value for this reaction, i.e. 3×10^{-17} cm^3/molec/s. The results from these modelling calculations were as follows:

Branching Ratio k_{26a}/k_{26b}	Predicted Residual NO (pptv)
1	11
.5	6.7
.4	5.7
.3	4.6
.2	3.6
.1	2.3

From these results, we estimate an average branching ratio of ~ .3 for the reaction of NO_2 with O_3.

4. Ambient Air O_3 Titration Tests

Using the estimated value of k_{-22}/k_{23} and the branching ratio k_{26a}/k_{26b}, we have also examined the results of several O_3 titration experiments involving ambient nighttime air. A summary of these observations and the model calculated NO residuals is shown in Table V.

From these results we see that the observed residual NO level and that calculated from mechanism (22) → (26) are in reasonably good agreement. With the June 13 observation showing the largest discrepancy, i.e. a factor 1½.

Collectively, we see these results as lending an element of support to the new mechanism which encompasses both a decrease in the rate at which NO is converted to NO_2 via reaction with O_3 and a nighttime source of NO via the reaction of NO_2 with O_3.

5. Comparison of Proposed Mechanism with Ambient NO Levels

In yet another test of the proposed $NO/NO_2/O_3$ mechanism we have also compared observed nighttime NO values with those calculated from a model based on the reaction scheme (22)→(26). This comparison is shown in Table VI. From the observed versus calculated values of NO, it is apparent that the proposed mechanism cannot fully account for the observed high values of NO. The disagreement being approximately a factor of two.

TABLE V : O_3 TITRATION OF AMBIENT NIGHTTIME NO AT STONE MOUNTAIN, GEORGIA

DATE/ TIME PERIOD	TEMP (OK)	HUMIDITY (%)	O_3 ADDED PPBV	1/e RX TIMES (NO + O_3)	BK. GRD [NO_2]PPBV	INITIAL(b) [NO] PPTV	FINAL(b) [NO] PPTV	MODEL CALC. FINAL [NO]
JUNE 3	300	68	1450	5.4	4.5	7.5 ± 2.0(a)	5.5 ± 2.0(a)	4.0
JUNE 4	298	67	2600	3.9	2.5	7.3 ± 2.5(a)	4.3 ± 2.1(a)	3.8
JUNE 6	299	70	650	3.4	4.0	15.0 ± 3.1(a)	6.0 ± 3.0(a)	5.4
JUNE 11	296	63	670	4.6	15	13.5 ± 3.0(a)	7.0 ± 2.5(a)	11
JUNE 13	292	73	670	4.6	8	22 ± 8(a)	11 ± 3.1(a)	7.1

(a) uncertainty shown represents natural variability over sampling period

(b) precision on initial [NO] was typically ±10% and on final [NO] ±15%

TABLE VI: Comparison of Model Predicted Nighttime NO levels with those observed during the Spring 1985

Date	Obs. [NO] (pptv)	Calc. [NO] (pptv)
June 1	3.6	1.7
June 3	7.5	5.3
June 4	8.8	4.1
June 6	15	6.0
June 11	20	11
June 13	11	7.2

Although the agreement between theory and observation is not all that bad, it is somewhat discouraging to find that according to BMP-MP4 calculations, the intermediate hypothesized, OOONO, would not be expected to have a lifetime anywhere approaching 200 sec.. In fact, thus far efforts to find any intermediate, cyclic or linear, that would have the characteristics required of the mechanism have met with little success. Based on the Stone Mountain results, therefore, we see the discrepancy between predicted results versus observations as having four possible explanations: (1) the mechanism is incomplete in its assessment of the rate of conversion of NO to NO_2; (2) the proposed mechanism is incomplete in that there may exist more efficient reactions that produce NO from either NO_2 or other nitrogen oxides present in the nighttime atmosphere; (3) the field observations themselves are incorrect; and (4) the transport of NO from the nocturnal boundary layer to the field sampling site on top of Stone Mountain is more efficient than originally thought. Of these four possibilities, we believe that the observations being in error is the least likely; but, we still see the need for further tests in conjunction with further ambient measurements to be totally convinced of this fact. Of the remaining three explanations we believe that unidentified chemical reactions being a source of NO and the "transport" hypothesis as the two most likely ones.

B. Airborne Studies of Nighttime N_xO_y Chemistry

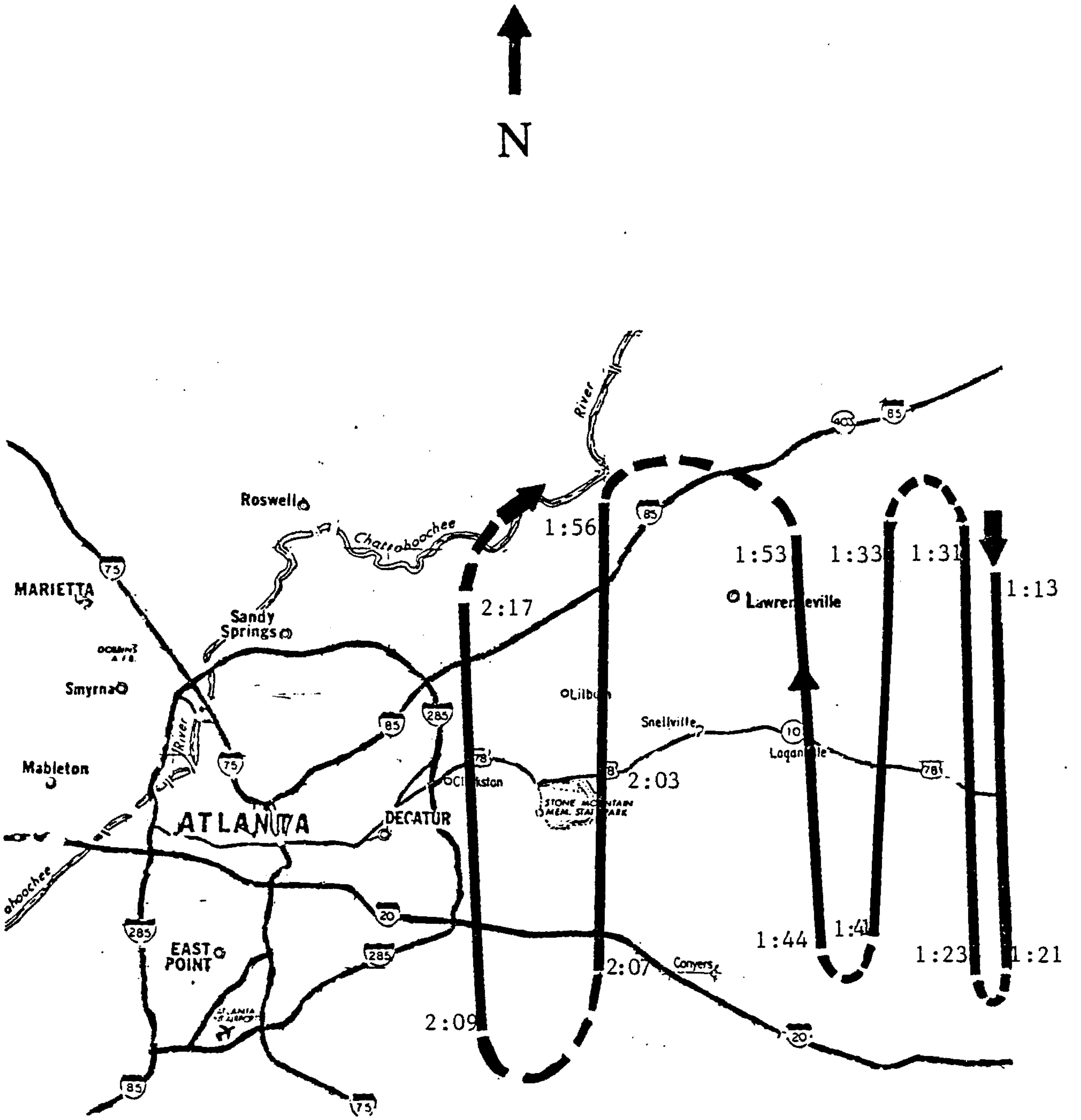
(1) Overview

A major objective in carrying out the Georgia Tech airborne study was that of establishing that the measurements of nighttime NO, which have been focused thus far on our Stone Mountain field sampling station, did not suffer from still unidentified localized NO sources or other artifacts related to a fixed site sampling scenario. We also hoped that the airborne study might provide further insight as to the importance of transport processes in influencing our nighttime NO observations.

Aircraft Sampling:

To assess each of the above issues, the authors have used Georgia Tech's Convair 240 as a sampling platform. In these experiments two sampling modes were selected: (1) that of sampling NO at an altitude close to that of the Stone Mountain tower and in the immediate vicinity of Stone Mountain as well as over an expanded region that included urban Atlanta and rural areas of Georgia; and (2) that of sampling NO as a function of altitude, again with the same geographical areas being covered as under sampling scenaio (1). Given these boundary conditions, a sampling region was chosen which was approximately 40 miles by 40 miles with Stone Mountain being located in the central western part of the sampling grid (see Fig. 3A). The same geographical region was examined on both July 21 and July 22. However, an additional feature of the July 21 flight was our adding in a sampling dog-leg that ran nearly due west of the city of Atlanta (see Fig. 3C). In the latter case, we flew approximately 75 miles west of the city at an altitude of 4000' and then returned to the Charlie Brown airport at an altitude of 1500'.

The altitude variations (scenario 2) included sampling at 1000', 2000', and 4000' (see Figs. 3A, B and C and Figs. 4A, B and C). Of considerable interest in these multiple altitude runs was examining the ratios $NO/NO_2/HNO_3$ to assess the role of transport on the observed levels of NO.



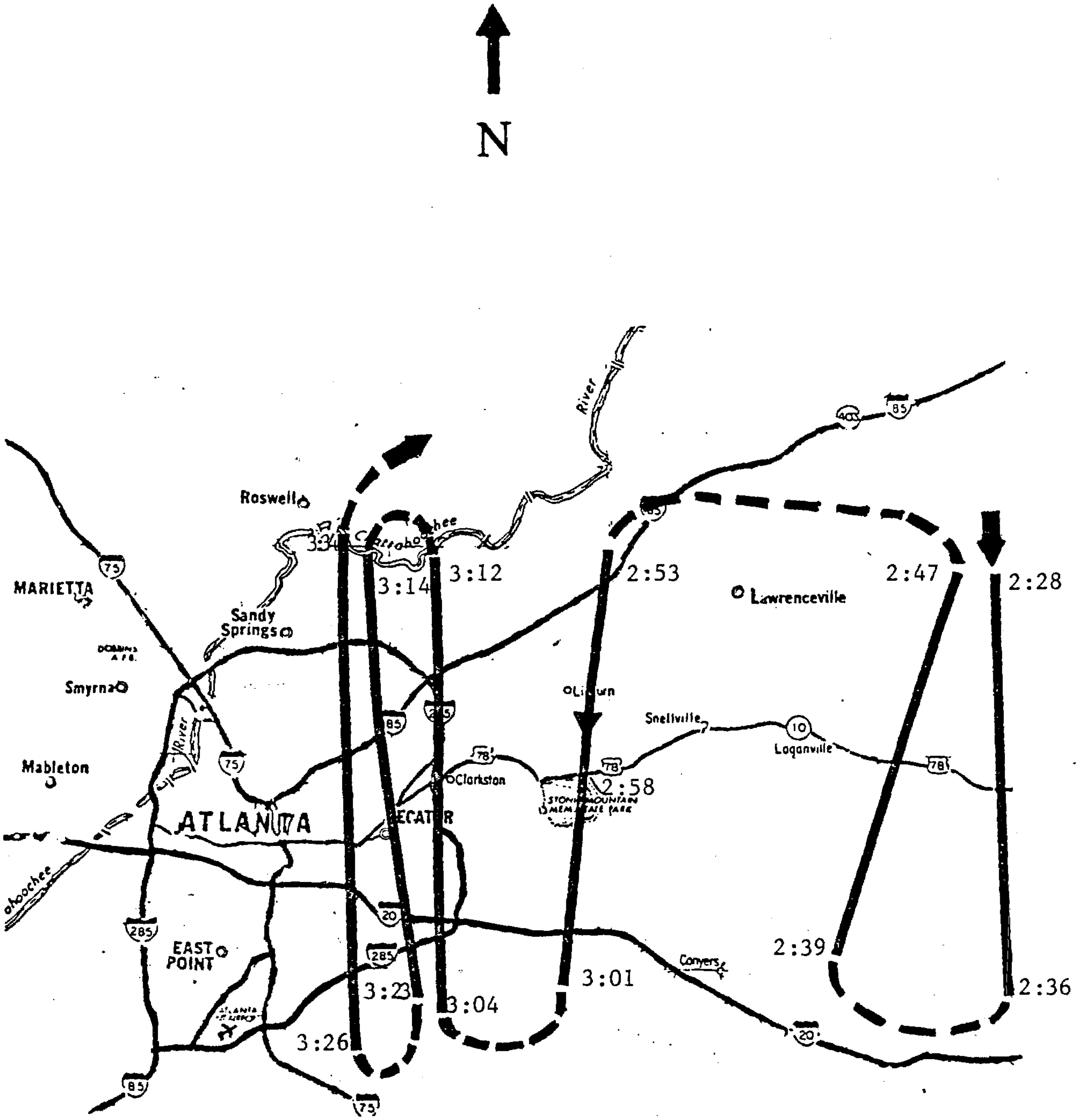
.g. 3A: FLIGHT #3 Scale 1" ≈ 10 miles

July 21, 1985

2000 ft. M.S.L.

(1000 ft. geometric)

ROKEN LINE - indicates that on each turn the exact geographical location of the aircraft was not recorded

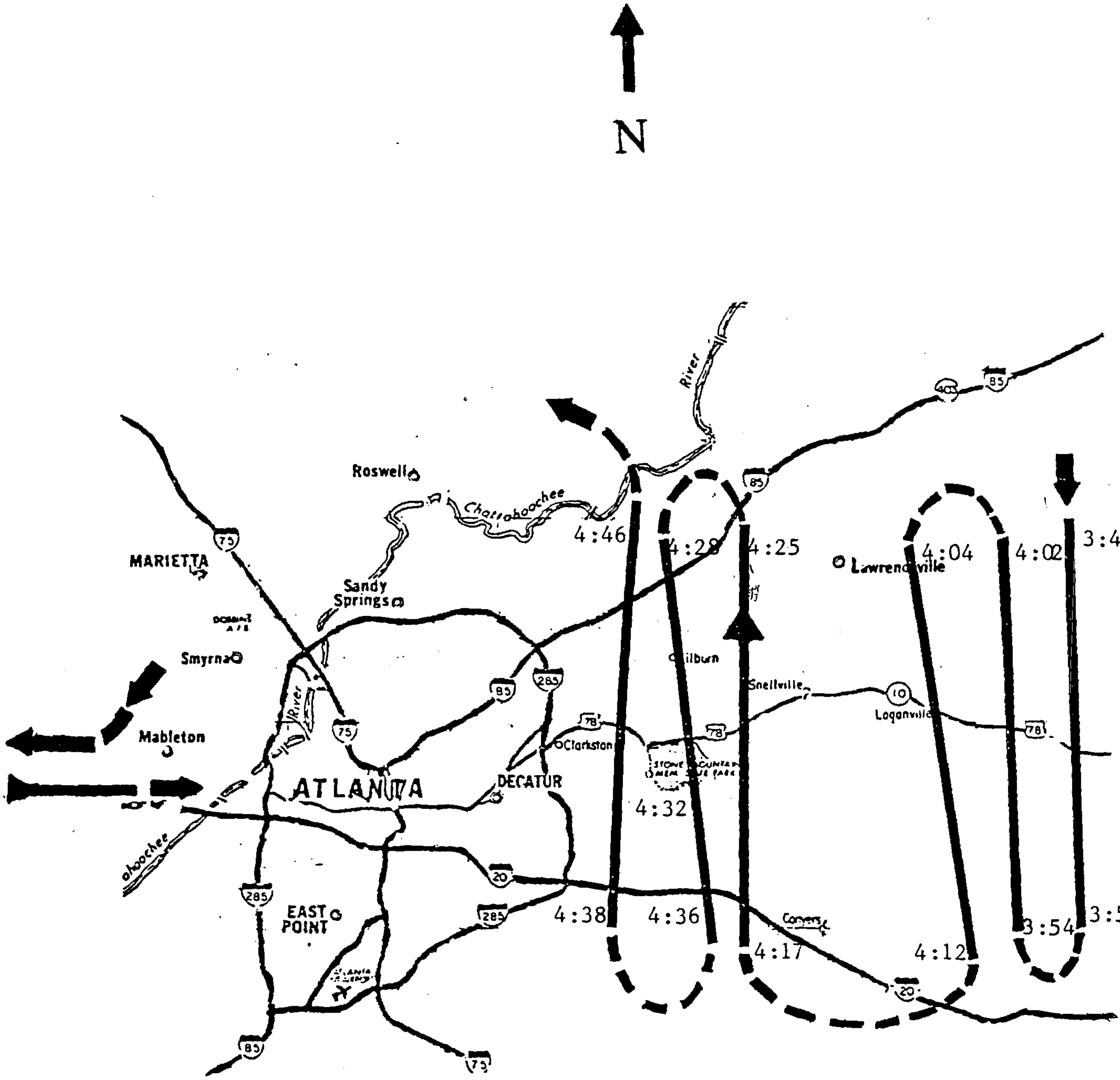


ig. 3B : FLIGHT #3 Scale 1" ≈ 10 miles

July 21, 1985

3000 ft. M.S.L.
(2000 ft. geometric)

ROKEN LINE - indicates that on each turn the exact geographical location of the aircraft was not recorded



FLIGHT # 3 Scale 1" ≈ 10 miles

July 21, 1985

5000 ft. M.S.L.

(4000 ft. geometric)

ROKEN LINE - indicates that on each turn the exact geographical location of the aircraft was not recorded

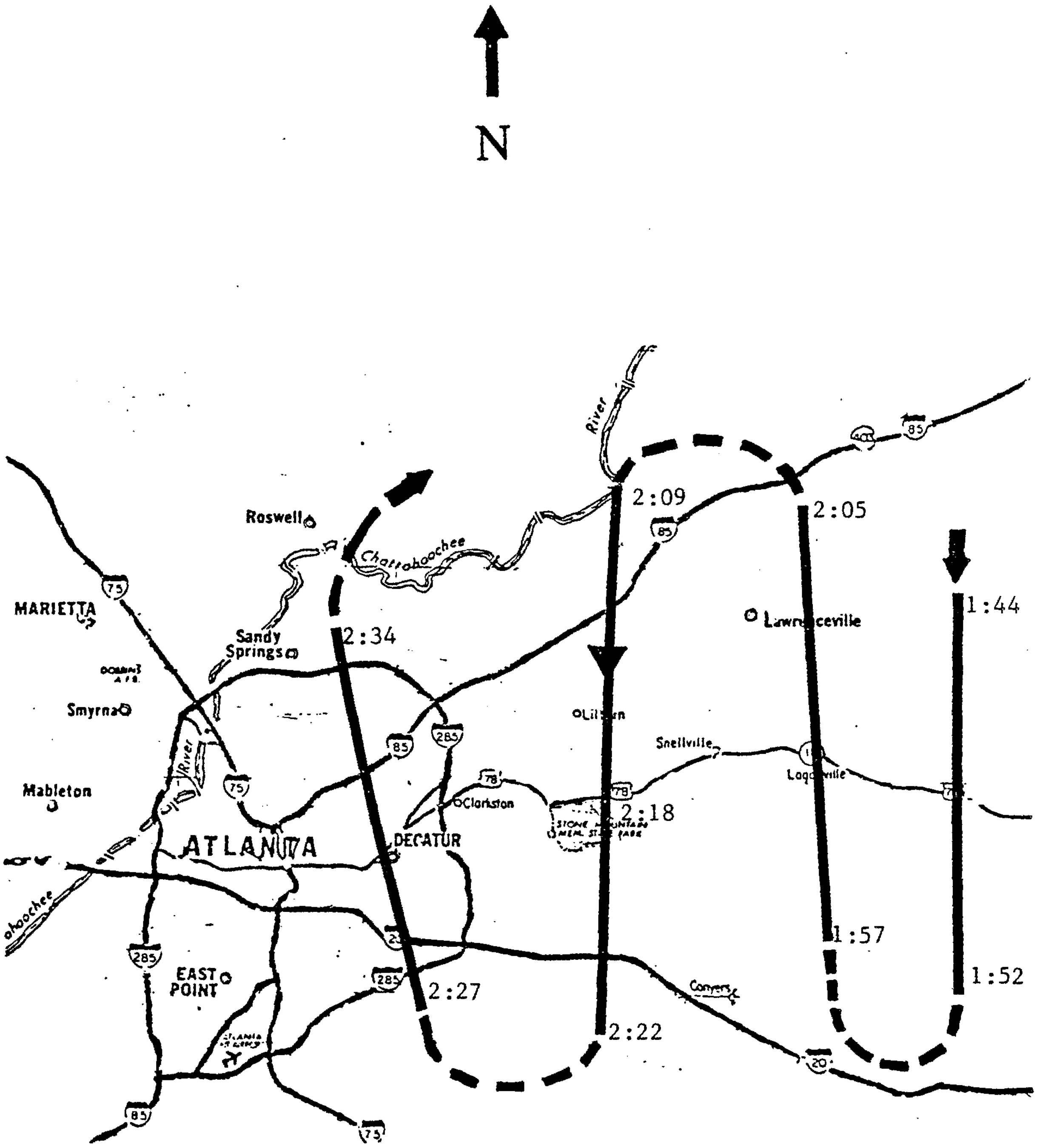


Fig. 4A: FLIGHT # 4 Scale 1" ≈ 10 miles

July 22, 1985

2000 ft. M.S.L.

(1000 ft. geometric)

ROKEN LINE - indicates that on each turn the exact geographical location of the aircraf
was not recorded

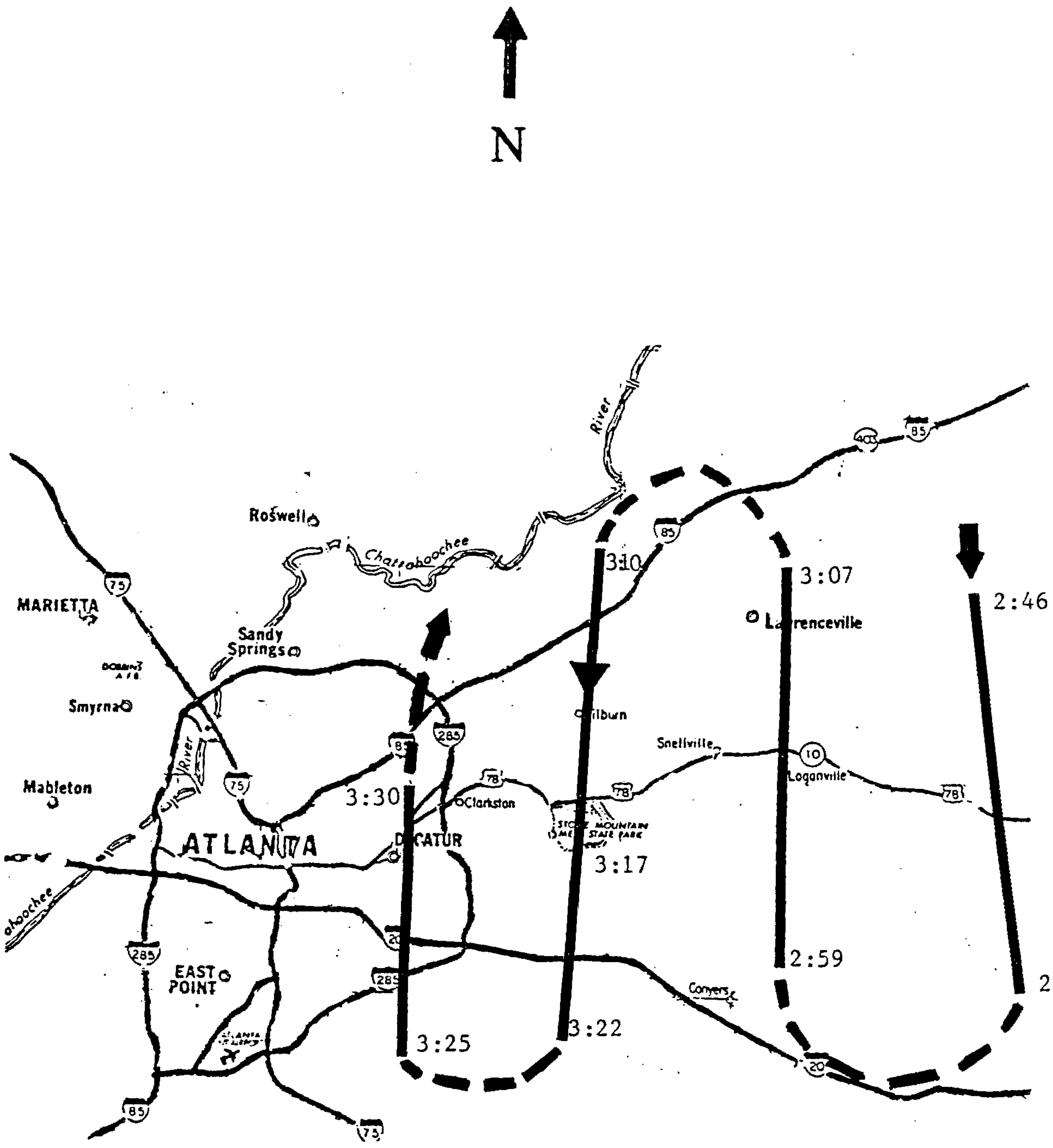


Fig. 4B: FLIGHT # 4   Scale 1" ≃ 10 miles
July 22, 1985
3000 ft. M.S.L.
(2000 ft. geometric)

BROKEN LINE - indicates that on each turn the exact geographical location of the aircraft was not recorded

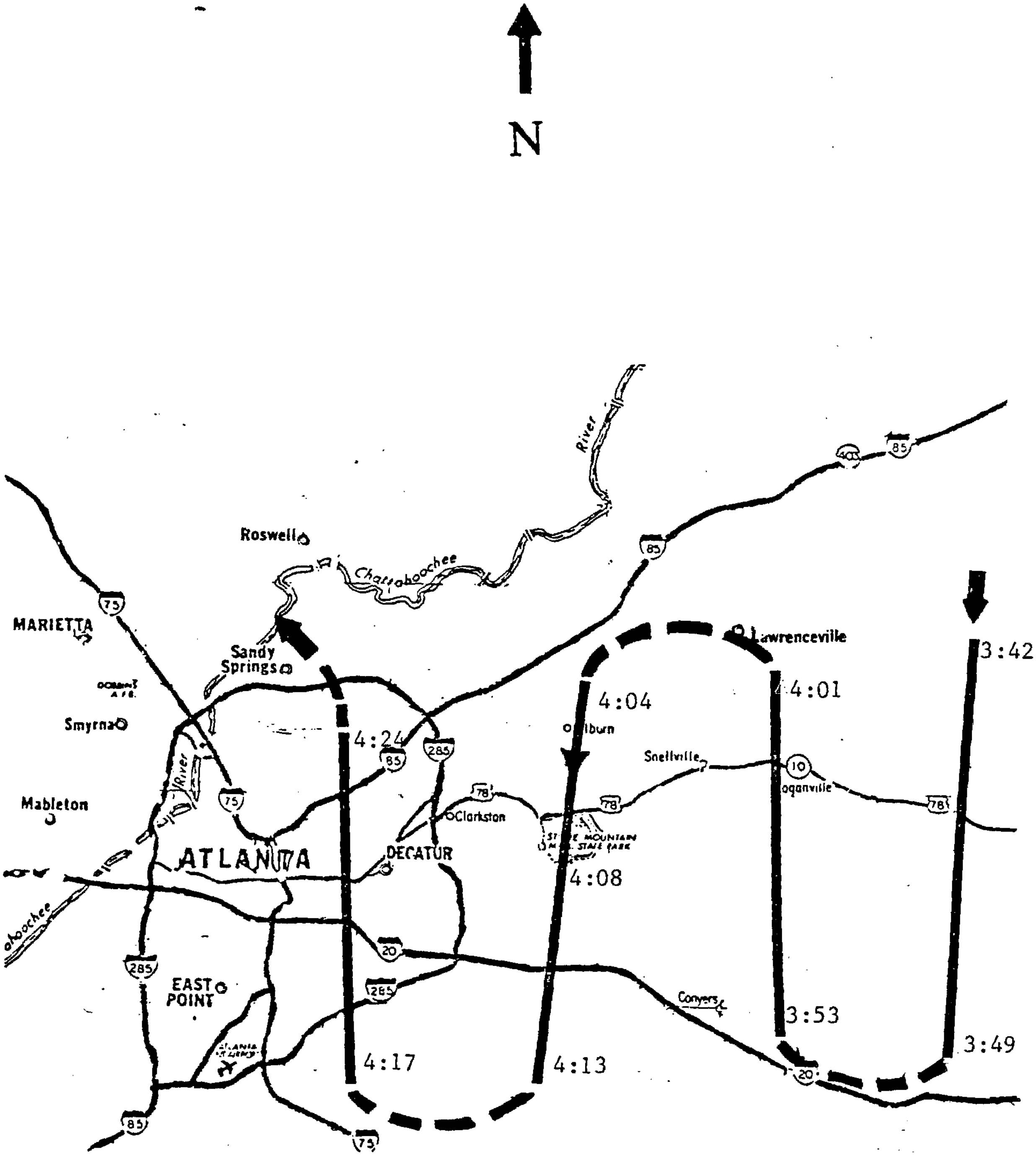


Fig. 4C: FLIGHT #4 Scale 1" ≈ 10 miles
July 22, 1985
5000 ft. M.S.L.
(4000 ft. geometric)

BROKEN LINE - indicates that on each turn the exact geographical location of the aircraft was not recorded

It can be seen (Figs.3 and 4) that the airborne sampling path followed on the nights of July 21 and 22 was vectored north to south with the eastern leg being flown first and the western leg last. This sampling profile was dictated by the prevailing wind field from 1000' to 6000'. On both nights, the winds were from the southwest to west direction. Thus, the sampling path followed served to minimize the possibility of our straying into our own aircraft plume. In fact, there was no indication from the NO or NO_2 data that this ever occurred.

The chemical variables measured included NO*, NO_2, O_3, HNO_3, and aerosol composition (e.g. NO_3^-, SO_4^{-2}, NH_4^+, etc.) Recorded on-board meteorological data included pressure, temperature and dew point. Sampling of the gases NO and NO_2 was carried out using the PF-TP-LIF NO/NO_2 sensor, whereas that for O_3 involved an airborne Dasibi ozone analyzer. (In-flight calibrations for NO and NO_2 were carried out on both July 21 and July 22). The HNO_3 and aerosol samples were collected using one of Dr. Huebert's high-vol samplers and each sample collected was sealed in a teflon bag and subsequently analyzed in Dr. Huebert's laboratory at Colorado College by ion-chromatography.

To eliminate the possibility of contamination from aircraft exhaust, independent sample inlets for NO, NO_2, and O_3 were located in the ceiling over the aircraft cockpit. Each intake was positioned so as to point 180^0 out of phase to the direction of motion of the aircraft, thereby minimizing contamination on takeoffs. Each inlet extended ~ 8" above the aircraft skin; and thus, being only ~ 4 feet behind the nose of the aircraft, each inlet was at least 6" above the turbulent boundary layer of the aircraft.

In the case of the NO sampling line, as an additional precaution against the photolysis of ambient NO_2 (which would have resulted in an artifact NO

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* Due to a sample inlet problem, NO data were collected only during the last one hour of flight #3. There was a complete NO data set on Flight #4.

signal), black teflon tubing was employed, and as still a final safeguard all aircraft cabin lights were turned off. Only small wattage red lamps were permitted throughout the flight operation. To establish that no aircraft cabin gases were leaking into the NO sampling system, all connections from the cockpit back to the fluorescence cell were sequentially bagged and then filled with a 10 ppmv NO gas mixture. The absence of any change in the NO signal rate (under flight conditions) with and without the bagged gas mixture was taken as convincing evidence that aircraft cabin contamination was negligibly small.

The gas phase HNO_3 and aerosol high-vol sampler was designed following Huebert's airborne specifications (isokinetic sampler) and was located ~ 20' back from the nose of the aircraft. Since this system was not forward of the prop line, it was mounted in the ceiling of the aircraft, approximately on the aircraft centerline. The intake of the high-vol sample extended ~ 18" above the aircraft skin, and thus was again well above the aircraft skin boundary layer.

Meteorology

Meteorological conditions in the greater Atlanta area, as well as all of central Georgia, were found to be distinctly different on the nights of July 20/21 and July 21/22. Our meteorological analysis of conditions during these two flights has been based on local weather radar echoes, discussions with pilots flying into Stone Mountain and Charlie Brown airports, our own airborne observations, surface and 850 mb pressure maps for Eastern U.S.A., and radiosonde readings from Athens, Georgia (approximately 50 miles east of Stone Mountain), Nashville, Tennessee, and Centerville, Alabama.

On July 21 (00:30 to 06:00 hrs.), the entire Atlanta area and most of central Georgia was under the influence of a low pressure system centered close to Tampa, Florida but over the Gulf of Mexico. Winds from the surface to ~ 6000' were < 5 knots. The entire central Georgia area, as well as much of the southeastern U.S.A. experienced stagnating air conditions with the visibility between 1000 and 6000' being reported by pilots to be no more than 2 to 3 miles.

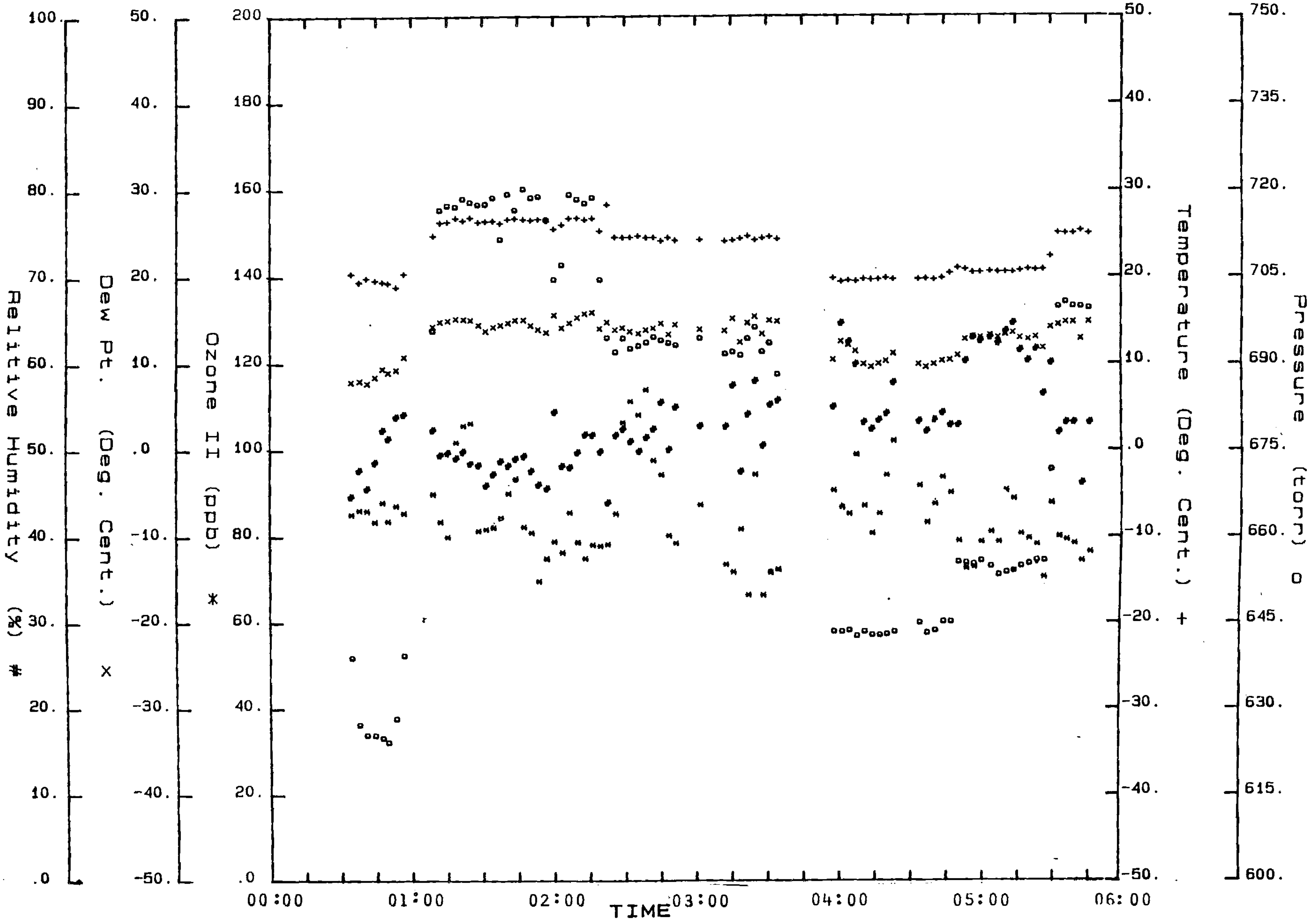
Our own airborne observations confirmed these poor visibility conditions. Radar echoes before and during the July 21 flight showed no major convective activity within a 150 mile radius of Atlanta.

In sharp contrast to the flight of July 21, atmospheric conditions for the flight on July 22 (00:30 to 05:30 hrs.) can be characterized as being highly improved with visibility over the altitude range of 1000' to 6000' being 10 to 15 miles. During the ~ 24 hour period between these two flights, the low pressure system in the Gulf of Mexico moved farther south and central Georgia came under the influence of a weak high pressure system to the north/northwest of Georgia. The 08:00 hr. radiosonde data from Nashville and Athens further indicated that during the night a low level nocturnal jet set up over the altitudes of 2000' to 4000' with wind speeds in the 11 to 12 knots range; thus accounting for the highly improved visibility conditions. Although radar echoes in the Atlanta area showed some thunderstorm activity early in the evening, these small cells had virtually all dissipated by the time of take-off (~ 00:45 hrs. on July 22).

The chemical observations recorded on July 21 (Flight #3) and July 22 (Flight 4) are discussed in the text that follows. (The authors note that flights #1 and #2, each of which was less than 2 hours in duration, were designated as shakedown/test flights and no NO or NO_2 data were collected).

(2) Flight #3 (July 21, 1985)

As shown in Figs. 3A, B, and C, the primary data collection periods for flight #3 were 01:13 → 02:17 (1000'), 02:28 → 03:34 (2000'), 03:44 → 04:46 (4000'), 5:02 → 5:24 (4000') and 05:34 → 06:00 (1500'). As noted earlier in the text, the flight legs 05:02 → 05:24 and 5:34 → 06:00 were not in the vicinity of Stone Mountain but rather west of the greater Atlanta metropolitan region. During each of the above time periods, the variables pressure, temperature, dew point, and O_3 were continuously recorded. These data are shown in Fig. 5. Representative values of temperature, dew point, and O_3 for those flight legs in


Relitive Humidity (%) #
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04:00
05:00
06:00
TIME

the vicinity of Stone Mountain were: (1000' T = 27^0, D.P.= 15^0C, O_3= 80 ppbv; (2000') T= 24^0C, D.P.= 14^0C, O_3= highly variable with an average of ~ 93 ppbv; and (4000') T= 20^0C, D.P.= 11^0C, O_3= 90 ppbv. On the two flight legs west of Atlanta, representative values for the above variables include: (4000') T= 21^0C, D.P.=13^0C, O_3= 85 ppbv; and (1500') T= 25^0C, D.P.= 15^0C, O_3= 80 ppbv.

Gas phase HNO_3 levels as well as the concentration levels of SO_4^{-2}, NO_3^-, NH_4^+, Na^+, and Cl^- in the aerosol phase are shown in Table VII. For the latter variables, due to the need for long integration times on high-vol filter samplers, no more than two independent measurements were available at each altitude. As shown in Table VII, both gas phase HNO_3 and the major constituents in the aerosol phase show a consistent trend of decreasing levels with increasing altitude. Nitric acid varied from a high of 2.7 ppbv to a low of .93 ppbv over an altitude range of 1000' to 4000' for the Stone Mountain sampling grid. Similarly, the major aerosol species SO_4^{-2} and NH_4^+ ranged from 47.5 and 18.0 $\mu g/m^3$ at 1000' to lows of 10.6 and 2.8 $\mu g/m^3$ at 4000'. It is also interesting to note from Table VIII that of the total atmospheric nitrate burden, approximately twenty times more nitrate was found in the gaseous form than in the aerosol phase. This ratio of 20 to 1 for NO_3(gas)/NO_3(aerosol) was observed for both low and high altitude runs.

As cited earlier in the text, for flight #3 no NO observations were available during the Stone Mountain grid sampling period due to a sample inlet problem. The latter problem, however, was resolved late in the flight and NO values were measured on the sampling legs that were flown to the west of the city of Atlanta. For the time period 5:02 → 5:24 (~ 4000') the average NO value was 5.2 ± 1.5 pptv and that measured on the return leg 5:34 → 06:00 (~ 1500') was 3.9 ± 1.5 pptv. The corresponding average NO_2 levels for each of these sampling legs were 2.4 ± .5 ppbv (~ 4000') and 1.8 ± .4 ppbv (~ 1500').

For the Stone Mountain sampling grid, the NO_2 levels at 1000' (radar altitude) can be subdivided into two distinct time periods, reflecting

TABLE VII. GAS PHASE HNO_3 AND AEROSOL COMPOSITION FROM STONE MOUNTAIN FLIGHT #3, JULY 21, (01:13 - 06:00).

Altitude (Radar Alt., ft.)	Sampling Time Period	$[HNO_3]$ pptv	SO_4^{-2} $\mu g/m^3$	NO_3^- $\mu g/m^3$	NH_4^+ $\mu g/n^3$	Cl^- $\mu g/m^3$	Na^+ $\mu g/m^3$
1000	01:15→01:35	2720±55	47.5±1.0	1.15±.07	11.5±.2	1.31±.02	.10±.02
1000	01:48→02:08	2080±40	49.3±1.0	1.38±.07	18.0±.4	.04±.02	.05±.02
2000	02:29→02:49	1040±20	12.5± .3	0.12±.07	3.52±.07	< .02	.01±.02
4000	03:00→03:20	930±80	10.6± .2	0.25±.07	2.79±.06	< .02	.02±.02
4000	05:05→05:25	650±40	12.3± .2	0.18±.07	2.72±.05	.02±.02	< .01

significantly different NO_2 concentration levels. From 01:13 to 01:52 the average NO_2 level was 2.6 ± .4 ppbv, whereas from 01:52 → 2:17 the average value for NO_2 was 5.3 ± .5 ppbv. From the flight profiles shown in Figs. 3A, it can be seen that the increase in NO_2 correlates reasonably well with flight legs involving three separate passes over Interstate I-85. Although the above time periods do not exactly overlap those on the high-vol sampler, it still can be clearly seen in Table VII that for the high-vol samples collected over the time period 1:48 → 2:08, significant increases in the major ions SO_4^{-2}, NO_3^-, and NH_4^+ are observed relative to those measured from 1:15 → 1:35. The absence of a significant increase in the HNO_3 levels for these two time periods is understandable since one would not expect NO_x released from automobiles to be quickly converted into HNO_3.

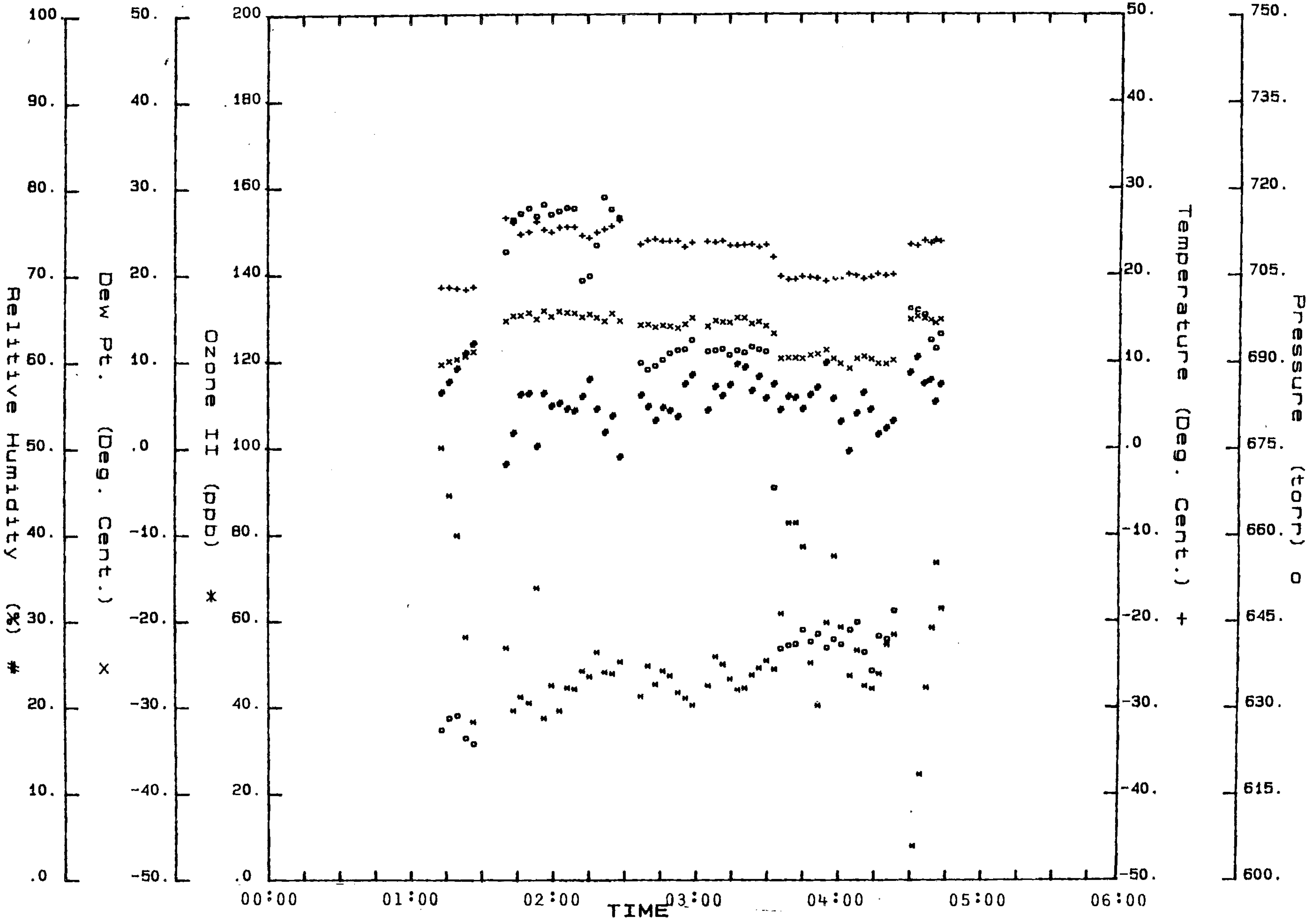
The NO_2 levels at the altitudes of 2000' and 4000' were both in the range of 3.0 ± .4 ppbv.

3. Flight # 4 (July 22, 1985)

On the night (early morning) of July 22, rather dramatic changes were observed in a meteorological conditions relative to those encountered on the previous night. This dramatic change in meteorological conditions is readily reflected in equally dramatic changes in the levels of most of the measured chemical variables.

The primary data collection periods for flight #4 are shown in Figs. 4A, B, and C. These include: 01:44 → 02:34 (1000'), 02:46 → 03:30 (2000') and 03:42 → 04:24 (4000'). The data for the variables pressure, temperature, dew point, and O_3 (collected continuously and reported as 3 min. averages) are shown in Fig. 6. Representative values of these variables for the Stone Mountain airborne sampling grid were: (1000') $T = 25^{o}C$, $D.P. = 15^{o}C$, $O_3 = 45$ ppbv; (2000') $T = 24^{o}C$, $D.P. = 14^{o}C$, $O_3 = 48$ ppbv; and (4000') $T = 20^{o}C$, $D.P. = 10^{o}C$, $O_3 =$ highly variable with an average of 55 ppbv. Thus, it can be seen that between flights #3 and #4

FLIGHT - FOUR



Relitive Humidity (%) *
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Dew Pt. (Deg. Cent.) x
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Ozone II (ppb) *
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the most significant change in the above variables involved a drop in the average level of O_3 of nearly a factor of two.

Gas phase HNO_3 levels as well as the concentration levels for several aerosol chemical constituents are shown in Table VIII. In sharp contrast to the observations of flight #3, there is seen to be no significant trend with altitude for most of the species measured. A possible exception to the above statement involves the 4000' leg where both SO_4^{-2} and NH_4^+ appear to drop significantly at the latter altitude relative to the values measured at 1000' and 2000'. The average level of HNO_3 for all altitudes was .28 ppbv with only a 20% change being seen over 1000 to 4000'. (Quite significant here is the fact that the levels of HNO_3 at 1000' for flights 3 and 4 differed by nearly a factor of 9, flight #4 being lower.) The major aerosol species SO_4^{-2} and NH_4^+ were found in flight #4 to average ~ 3 and 1.5 $\mu g/m^3$, respectively for the altitudes of 1000 and 2000'. These levels are again significantly lower than those observed on flight #3. As was true of flight #3, however, the distribution of nitrate between the gas and aerosol phases favors the gas phase by a factor of $\geq$ 10.

Due to the low levels of NO present during flight #4, we have in most cases reported only the average value for this species for each altitude sampled in the Stone Mountain grid. The one exception to this involves the flight leg at 1000'. During a 7 minute period (~ 2:05 → 2:12) while over Interstate I-85, NO levels were observed of 13 ± 3 pptv with correspondingly high levels of NO_2 of 13.5 ppbv. By contrast, for the remainder of the flight legs at 1000', the average NO level was 2.4 ± 1 pptv and that for NO_2 was 1.0 ± .2 ppbv. (The authors note that the higher NO and NO_2 levels over the time period of 02:05 → 02:12 are also seen reflected in increases in the levels of SO_4^{-2} and NH_4^+ for the high-vol integration period of 02:00 → 02:20.) For the altitudes of 2000' and 4000' very little change was observed in the levels of NO or NO_2 and furthermore the levels at these two higher alttitudes (e.g. NO = 2.5 ± 1 pptv

TABLE VIII. GAS PHASE HNO_3 AND AEROSOL COMPOSITION FROM STONE MOUNTAIN FLIGHT #4, JULY 22 (01:44 → 04:30)

Altitude (Radar Alt.,ft.)	Sampling Time Period	$[HNO_3]$ pptv	SO_4^{-2} $\mu g/m^3$	NO_3^- $\mu g/m^3$	NH_4^+ $\mu g/m^3$	Cl^- $\mu g/m^3$	Na^+ $\mu g/m^3$
1000	01:33→01:53	260±60	2.42±.08	<.07	1.18±.03	.37±.02	< .02
1000	02:00→02:20	320±40	4.55±.09	.05±.07	2.00±.04	2.27±.05	.23±.02
2000	02:37→02:57	290±50	2.68±.08	0.3±.07	1.20±.03	.04±.02	< .02
2000	03:09→03:29	210±40	3.78±.08	0.2±.07	1.58±.03	.06±.02	.01±.02
4000	03:40→04:00	250±110	.08 ±.08	.03±.07	0.40±.03	< .02	<.02

and NO_2 = .75 ± .15 ppbv) were, within the uncertainty of the measurements the same as those observed at 1000', excluding the hot spot over I-85.

Summary/Conclusions on Nighttime Airborne Data

The flights on July 21 and July 22 encompassed two uniquely different chemical environments which reflect major changes in meteorological conditions over central Georgia during a 24 hour period. On July 21, the atmospheric environment up to altitudes of 6000' was one involving stagnant air conditions, whereas that on July 22 was one involving a moderately well-ventilated lower atmosphere. The levels of virtually all chemical variables measured reflect this major change in meteorological conditions.

The levels of NO measured during the two flight operations (ranging from 5.2 to 2.4 pptv) are viewed by the authors as falling well within the range of NO values reported at the Stone Mountain field sampling station for spring and summertime conditions and are also in good agreement with those observed in the fall of 1985. These results suggest that there are no unique NO sources at the mountain top site itself and further suggest that the measurements at the field station are representative of the average levels of NO that might be found over a much larger geographical area around Stone Mountain for the same altitude.

Also quite significant are the results from the July 22 flight which show the levels of NO, NO_2, and HNO_3 to be nearly constant at altitudes ranging from 1000 to 4000'. This observation would tend to argue against the hypothesis that the NO levels observed were a result of some unique transport mechanism, since NO_2 and HNO_3 are known to be much longer lived species at night than NO (e.g. minutes vs. hours). Even so, we recognize that the S/N ratios for the NO data were only 2.5 to 1 and thus one could argue that we cannot categorically eliminate the question of the role of transport. Also, we would reemphasize the point that the above arguments are being made only in the context of late spring/summer conditions, i.e. for those cases where NO levels are observed to be quite low.

Finally, as with the earlier collected Stone Mountain $NO/NO_2/O_3$ data, it was of considerable interest to us to see the comparison between the airborne NO levels and those predicted by our proposed $NO/NO_2/O_3$ nighttime chemistry mechanism as outlined in Section IIIA. These results are summarized below in Table IX.

TABLE IX: COMPARISON OF NIGHTTIME AIRBORNE NO OBSERVATIONS WITH NEW N_xO_y MODEL PREDICTIONS.

Flight#	Sampling Time Period	Radar Altitude (Ft.)	[$\bar{O}_3$] ppbv	[$\overline{NO_2}$] ppbv	Obs. [NO] pptv.	Model Calc.[NO] pptv
3	05:02→05:24	4000'	85	2.4±.5	5.2±1.5	3.4
3	05:34→06:00	1500'	80	1.8±.4	3.9±1.5	2.9
4	01:44→02:34	1000'	45	1.0±.2	2.4± 1	1.7
4	02:46→-3:30	2000'	48	.75±.15	2.5± 1	1.6
4	03:42→04:24	4000'	55	.76±.15	2.5± 1	1.6

From this comparison, it can be seen that the field observations appear to be systematically higher than the model predictions by a factor of ~ 1.5. Thus, the airborne database is found to be similarly close in its comparison with the modelling results as was the late spring Stone Mountain NO data. Recall, in the latter case, the agreement ranged from a factor of 1.5 to 2.

C. Summary/Conclusions on Nighttime NO Field Observations:

At this time we still cannot provide a comprehensive explanation for the observed levels of ambient nighttime NO in the presence of excess O_3. We believe, however, that it is unlikely that further studies will find major flaws in these data due to laser generated artifacts. But, we cannot rule out some esoteric "sampling integrity" problem. On the other hand, the NO results from the July airborne experiments are quite significant in that these data provide strong evidence that the top of Stone Mountain does not itself represent a localized source of NO. They furthermore have shown that on a given night the ratios of NO to NO_2 and NO to HNO_3 can be found that do not vary significantly over the altitude range of 1000' to 4000', altitudes well above the nocturnal boundary layer. Thus, the low but persistent levels of NO observed during these flights would seem to suggest either the presence of an atmospheric in-situ source of NO, or alternatively, a yet unidentified flaw in the measurements.

Furthermore, even though reaction schemes have been proposed by the authors, that seemingly provide a chemical basis for the nighttime presence of NO, there remain major questions concerning the validity of some of the proposed elementary reactions, especially as they related to postulated intermediates such as OOONO. Other reactions may have to be added to those already proposed and the possibility also exists that some of those proposed may not stand up to critical testing. We must conclude, therefore, that considerable work still remains to be done on this important research topic.

Recognizing the caveats expressed in the previous text, one is still tempted to explore what the possible scientific ramifications might be based on the current evidence which shows measurable levels of NO in the nighttime atmosphere. These have been summarized below.

(1) The number of species acting to control the nighttime level of NO_3, which extrapolates to controlling the nighttime production of HNO_3,

will have to be expanded to include NO. The controlling reactions would then become:

NO_3 + organics → HNO_3 + Org. •

$NO_3 + NO_2 + M \rightarrow N_2O_5 \xrightarrow{\text{heterog.}} 2HNO_3$

and $NO_3 + NO \rightarrow 2NO_2$

(2) To the extent that the NO + NO_3 reaction might dominate the nighttime levels of NO_3, one would not expect to see significant decreases in the nighttime levels of NO_2. It seems possible, in fact, that the observations of Noxon (1980 and 1984) may represent a case where NO was the controlling species for NO_3, i.e. NO was Noxon's unknown reactant "X". In the 1984 experiments, only .8 pptv of NO would have been required to explain Noxon's results.

(3) In remote areas, like the eastern and central Pacific Ocean, where the natural daytime level of NO is in the sub 10 pptv, the <u>simple photochemical expression</u> previously used to relate NO, NO_2, and O_3, e.g.

$$\frac{J_{(NO_2)}[NO_2]}{k[NO][O_3]} = 1$$

may require modification if the NO/O_3 reaction is indeed non-linear in NO at low levels of NO.

(4) To the extent that NO_3 reacts with aldehydes and/or O_3 reacts with olefins at night to produce HO_2 radicals, the presence of NO at night could result in the production of finite levels of nighttime OH via the reaction,

$HO_2 + NO \rightarrow NO_2 + OH$

and (5) At levels below 10 pptv, it is quite possible that chemiluminescence NO sensors, which rely on the NO + O_3 reaction, may display significant non-linear behavior and thus will require very careful calibrations if they are to be used at these low levels.

IV. OTHER CRC RELATED ACTIVITIES

Although instrument development tasks and the Stone Mountain field sampling studies have been the central focus of the second year Georgia Tech program, two related activities are deserving of some discussion. The first of these is concerned with the progress that has been made in establishing the Stone Mountain field sampling station as an efficient atmospheric chemistry data collection site; the second involves the progress that has been made in interpreting some of the earlier NO_x lightning data.

A. Stone Mountain Facility Development

During the early phases of the Stone Mountain operation most of the data recording was handled by means of stripchart recorders or was entered by hand into research notebooks. We can now report that this cumbersome operation has been replaced with a fully interfaced data logging computer. The variables: wind speed, wind direction, dew point, temperature, pressure, visible flux, UV flux, O_3, CO, NO, and NO_2 can be routinely and systematically recorded. In addition to the aforementioned data storage capability, we also have added a Hewlett Packard graphics recorder to enable the plotting of any six of the above variables at one time. The latter piece of equipment thus allows us to examine new data in a quick look-see mode and therefore forms the basis for real-time decision making during a field sampling operation.

Chemical variables that still involve manual operations include: gaseous nitric acid, aerosol chemical composition and rain/cloud water composition.

Future additions to the array of variables now being measured at Stone Mountain include NO_3 and HNO_2. The necessary instrumentation for measuring the latter two species will be developed as part of our proposed third year CRC program.

B. Analysis of NO Lightning Data

As briefly discussed in the "Introduction", the uncertainty in the global production of NO_x from lightning currently stands as the largest uncertainty in the evaluation of global sources of NO_x. The recent National Academy of Sciences document, "Global Tropospheric Chemistry: A Plan for Action" (1984) gives the range of 2 to 20 Tg(N)/yr. Other sources have suggested that the upper limit could be as high as 30 Tg(N)/yr, Drapcho et al. (1983).

The idea that lightning could be a significant source of atmospheric-fixed nitrogen is generally attributed to von Liebig, who apparently first suggested in 1857 that NO_3^- formed in rain water was originally produced from lightning induced reactions between N_2 and O_2. In the middle 1900s von Liebig's hypothesis was tested by numerous investigators who searched for a correlation between dissolved NO_3^- in precipitation and lightning intensity (e.g. Hutchinson, 1954; Viemeister, 1960; and Visser, 1961). Finding little or no correlation, these investigators concluded that lightning represented a small or negligible source of atmospheric-fixed nitrogen.

Our current understanding of the chemistry of atmospheric nitrogen oxides suggests that the lack of correlation between dissolved NO_3^- and lightning intensity does not necessarily mean that lightning is a small source of global NO_x. While the high temperatures in and around the lightning channel produced fixed nitrogen in the form of NO and N_2O, most of the NO_3^- in precipitation appears to arise from the dissolution of gaseous HNO_3 (Chameides, 1984). For lightning produced NO to be incorporated in rain, it must first be chemically oxidized to HNO_3. This oxidation can proceed by two pathways:

Daytime:
$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + OH + M \rightarrow HNO_3$

Nighttime:
$NO_2 + O_3 \rightarrow NO_3 + O_2$
$NO_3 + \text{org.} \rightarrow HNO_3 + \text{org. radical}$
$NO_2 + NO_3 + M \rightarrow N_2O_5$
$N_2O_5 + H_2O \rightarrow HNO_3$

These reactions generally require 4 to 15 hours to go to completion (e.g. one $^1/_e$ folding time). Since this oxidation time is much longer than the 1 hour lifetime of a typical cloud, one would not expect NO production by lightning to lead to an immediate enhancement of NO_3^- in the rain water collected during a given storm.

In more recent years, investigators have taken a more direct approach to estimating the nitrogen fixation rate by lightning. This has involved attempting to determine through direct field observation or theoretical modelling the amount of NO produced by a single flash of lightning and then extrapolating to a global production rate by multiplying by the global flash rate. Nevertheless, one must deal with several significant uncertainties associated with these approaches. In the case of the theoretical calculations, not only must the global flash rate be known (which with satellite observations is now becoming one of the better established parameters) but also required are the average number of strokes per flash, the average energy of a stroke, the average length of a stroke, and the average yield of NO per Joule of energy dissipated.

Efforts to experimentally determine the production of NO_x from lightning suffer from the problem of identifying the proper sampling strategy. Where does one measure NO_x in a cloud to properly assess the production of NO_x? For example, during the summer of 1984 the Georgia Tech group on several occasions made NO and NO_2 measurements at their Stone Mountain field site during electrical storms. However, only approximately half of the time did we observe significant increases in the levels of these nitrogen oxides.

Previous to the Georgia Tech measurements, only two case studies have been reported in the literature where NO_x measurements were made in the immediate vicinity of electrically active clouds, Noxon (1976) and Drapcho et al (1983). In the first study, (Noxon 1976), a measurement of NO_2 was made directly below the base of an active cumulonimbus cloud using a long-path absorption technique. Not surprisingly, in analyzing this type of data a very large uncertainty is encountered in determining the efficiency with which lightning generated NO_x was advected out of the cloud base. The second reported field observation by Drapco et al. (1983) is perhaps even more shaky than the first in that a cloud-to-ground lightning strike occurred some distance away from the sampling site . Again, some very major assumptions had to be made concerning the transport of this lightning generated NO_x to the actual site where the measurement was recorded.

In the fall of 1984, during the NASA GTE CITE I project, several flights were staged out of Honolulu, Hawaii. During one of these flights, two bands of cumulonimbus were intersected. Each of these bands had ~ 5 well defined cells. The aircraft was flying at ~ 32,000' and at that altitude the anvils of two cells were penetrated. During both of these penetrations, the levels of NO were observed to change from background levels of ~ 20 pptv to levels approaching nearly 1 ppbv. Thus, we see these observations as providing strong circumstantial evidence for electrified clouds being a significant source of NO_x. However, we now believe that these in-cloud measurements can also be used in a more quantitative manner to make estimates of the global nitrogen fixation rate by lightning. Unlike the theoretical estimates which must first evaluate the NO_x produced by a single flash, our proposed new approach allows one to directly estimate the amount of NO_x advected out of the top of a cumulonimbus cell. It therefore has the advantage of providing an independent means of evaluating the NO_x production from not only bolt lightning but all other possible sources of cloud generated NO_x, e.g. that from corona processes.

The approach that we have taken in using the airborne NO measurements over the Pacific is as follows: The average NO measured from both clouds is computed and then an estimate is made of the fraction of the original NO produced by the lightning that was converted into NO_2 at the time of sampling. (The latter conversion takes place due to the reaction $O_3 + NO \rightarrow NO_2 + O_2$ where the O_3 level is that measured on the aircraft, e.g. in this case 40 ppbv). Taking this approach, we find that the average NO level in crossing through two anvils was 440 pptv. We estimate that ~ half of the original NO was converted into NO_2 at the time of sampling and therefore the total $NO_x = NO + NO_2$ is 880 pptv. (We estimate that the uncertainty in this quantity is ± a factor of two.) This value for the NO_x level is combined with the amount of mass of air advected out of the top of a typical cumulonimbus cell, Φ_c, and the total number of cumulonimbus cells that are occurring at any instant in time over the entire globe. The appropriate equation is therefore:

$$P_{(NO_x)} = [NO_x] \times \Phi_c \times S \times 3 \times 10^7 \text{ s/yr} \times 10^{-3} \frac{\text{tons}}{\text{kg}} \times \frac{14\text{g N/mole}}{29\text{g air/mole}}$$

where $P(NO_x)$ is the global NO_x fixation rate from lightning in units of tons (N)/yr, Φ_c is the average rate at which air is advected out of the cloud top in units of kg/s, and S is the number of cumulonimbus cells that are at any instant occurring over the entire planet. Cloud dynamic studies indicate that the average value of Φ_c is 2×10^8 kg/s [Navarra, 1979; Kropfli and Miller, 1976; Anc and Marwitz, 1968] with upper and lower values typically being within ± a factor of 2. The value of S has been estimated by Chalmer (1967) and Navarra (1979) as being between 1400 and 3000 cells and for our initial calculations we have therefore taken the average value of 2200. Using these values for $[NO_x]$, Φ_c, and S, the resulting average global production of NO_x is calculated to be 7×10^6 $\text{tons}^{(N)}$/yr or ~ 7 Tg (N)/yr. (See JGR, 92, p2153, 1987).

A comparison of the average global NO_x production estimated from our calculations with those reported in the literature, based strictly on theoretical considerations, shows nearly a factor of two higher value for the experimentally derived production rate. We believe that by making measurements of both NO and NO_2 in numerous cumulonimbus cells, in conjunction with more detailed meterological observations of each cloud examined, one should be able to obtain a far more reliable value for the global nitrogen fixation rate by electrified clouds. This approach, however, does have one major drawback. It requires the use of a jet aircraft to reach the high elevations for penetrating into the anvil of a cumulonimbus cell. At the present time the authors know of only one large jet that is available to the atmospheric sciences community, the DC-8 owned and operated by NASA Ames.

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ATMOSPHERIC NITROGEN OXIDES THEIR DETECTION AND CHEMISTRY

THIRD YEAR REPORT

TIME PERIOD: SEPT. 1985 - DEC. 1986

Prepared for:

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Atlanta, GA 30346

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PROJECT SUMMARY

Instrument Development

The CRC supported instrument development effort at Georgia Tech has been tailored to interface with the major scientific goal of our program: the comprehensive investigation of the atmospheric chemistry of the nitrogen oxide family. Our current knowledge about this family of atmospheric compounds suggests that it impacts on air quality in at least four significant ways:

(1) it leads to the production of one of the atmosphere's major acidic compounds, HNO_3;
(2) it is responsible for major increases in the concentration levels of potentially harmful oxidants such as O_3 and PAN type compounds;
(3) it provides an instantaneous source of reactive OH radicals during early morning hours which can initiate smog formation chemistry;
(4) throughout daylight hours it acts to control highly reactive HO_2 and OH radicals, the latter species being one of those oxidants that controls the lifetime of numerous other trace gases released into the atmosphere.

During the third year of our CRC program ~ 50% of our time was devoted to instrument development and 50% to field sampling and data interpretation. As during our second year, our instrument development activity was focused on the detection of three species: NO_2, HNO_2, and NO_3. However, in the case of NO_2, our efforts were directed at developing a third generation NO_2/NO sensor. The goal, therefore, was that of measuring NO and NO_2 simultaneously, using one common set of lasers and electronic hardware, and at the same time greatly improving on the detection sensitivity of this LIF system. This goal has been very convincingly achieved as evidenced from the fact that the photofragmentation/ laser-induced fluorescence (PF-LIF) instrument now has a detection limit for NO and NO_2 that is at the sub 10 pptv level. Additionally, this 3rd generation system has been fully tested both for ground-based and airborne field-sampling operations.

Nearing the end of the 2nd year of our CRC program, we were just beginning the development of a UV photofragmentation/laser-induced fluorescence (PF-LIF) HNO_2 instrument, based not on the detection of NO as originally planned, but rather on detecting the photofragment OH. This new system capitalized on the fact that a very high quantum yield (i.e. $\geq .8$) has been found by several investigators for the primary process: $HONO + h\nu\ (\lambda = 355\ nm) \rightarrow OH + NO$. With the 3rd year of our CRC program now ended, it can be reported that the development of the PF-LIF HNO_2 instrument is complete, and this new system has been used to collect the first ever HNO_2 data base for urban Atlanta. This in-situ measuring instrument has a detection limit of 20 to 50 pptv, depending on the background noise level of the atmosphere, and has been calibrated at HNO_2 levels as low as 185 pptv. However, it also has been shown to be linear in signal response over five orders of magnitude change in the HNO_2 concentration.

The third area of instrument development, involving NO_3, has again progressed very nicely; but as of this writing, we are still three or four months away from having an operational system. Recall, at the end of our 2nd year CRC program, we had established that the original approach proposed for detecting NO_3, i.e. PF-LIF, was not successful since the primary process:

$$NO_3 + h\nu\ (589\ nm) \rightarrow NO + O_2$$

was found to have a quantum yield approaching zero. Thus, in the 3rd year of our program, we made the decision to use the established technique of "long-path differential absorption". As of this writing, all hardware required for the NO_3 differential absorption system has been purchased and extensive testing of this equipment has been underway for several months. Unique to the Georgia Tech system is the fact that a folded .2 to .5 km optical path will be used rather than the single pass 3 to 10 km absorption path used by previous invetigators. Thus, one of the critical features of our new system, in comparison to previously developed LPDA systems, is that the NO_3 measurement made by the Georgia Tech system will take place in the immediate vicinity of the Georgia Tech field-sampling station. Under these conditions, NO_3 measurements atop Stone Mountain can be confidently combined with the numerous in-situ measurements of other variables being made at the on-site field-station for purposes of performing comprehensive modelling calculations. Test results now completed suggest that a detection limit of $\leq$ 10 pptv of NO_3 should be achievable with our first generation NO_3 sensor.

Field and Lab Studies

There have been three major field studies and one major laboratory investigation completed during the 3rd year. These investigations involved: (1) additional nighttime NO measurements at our Stone Mt. field-station; (2) field measurements of HNO_2 and supporting variables in urban Atlanta as measured on the Georgia Tech campus; (3) airborne measurements of NO/NO_2 over marine and continental terrain at both high altitudes and within the boundary layer; and (4) laboratory measurements to establish the potential importance of corona discharge in the generation of NO_x within electrified clouds. The results from these investigations produced the following findings.

The nighttime NO measurements, during the early and late fall of 1985, have demonstrated that our earlier measurements in the fall of 1984 were influenced by the operation of a gas heating unit in one of four buildings atop Stone Mt. The 1985 fall measurements are quite consistent with those recorded in the spring of 1985 and show average nighttime NO levels (in the presence of excess O_3) to be in the range of 12 pptv. The problem created by the winter operation of the gas heater atop Stone Mt. has now been circumvented by the installation of a timer switch on the gas burner. (Under normal winter weather conditions this timer prevents the heater operating during the hours of 6 p.m. to 6 a.m.)

The scientific explanation for low but persistent nighttime levels of NO is still being actively explored. Our latest hypothesis involves the possible role of nighttime HNO_2 as related to its decomposition within liquid or on solid particulate aerosols. However, some aspects of our earlier hypothesized mechanism for explaining nighttime NO may also be required.

The urban measurements of HNO_2 near downtown Atlanta have been most revealing. Over a period of nearly three months, spanning the time of 12/23/85 to 3/28/86, maximum nighttime HNO_2 values of ~ 6 ppbv and minimum nighttime values of < 10 pptv were observed. The average nighttime level of HNO_2 was ~ 2 ppbv. As observed by other investigators, measureable levels of HNO_2 were only recorded after sunset and typically the HNO_2 level dropped to below our detection limit of, ~ 20 pptv, within approximately 1 hour following sunrise. Although there is still considerable speculation as to the major mechanism(s) of formation for this species, correlations between automobile traffic through downtown Atlanta (in conjunction with wind direction) strongly suggest that automobiles may be the major source of this nighttime species. In fact, controlled tests involving a single automobile fitted with a catalytic converter suggest that the major source of HNO_2 may be emissions directly from the tail pipe of automobiles - new tests are being planned to prove or disprove this hypothesis. What does now appear to be clear is that for an urban area such as the city of Atlanta, the integrated production of OH from the early morning photolysis of HNO_2 exceeds that from the primary photolysis of O_3 up to mid to late morning. These results would suggest that OH driven-smog chemistry, in a city such as Atlanta, may be principally driven during morning hours by the photolysis of nighttime generated HNO_2. Furthermore, if HNO_2 is directly coupled to the emissions from automobiles, photolytic generated OH from HNO_2 might become an extremely important forcing function for smog formation over a significant fraction of each day.

Our involvement in a NASA sponsored airborne N_xO_y experiment represented a target of opportunity in which we found that several of the goals of the NASA airborne N_xO_y program overlaped those of our CRC program. A critical one of these involved fast photochemical theory as related to testing the daytime coupling of NO with NO_2. As part of this effort, an extensive double-blind intercomparison was carried out in which four different NO_2 sensors were tested, one of those being the Georgia Tech PF/TP-LIF NO_2 instrument. In short, the Georgia Tech system performed very well, delivering reliable results on not only NO_2 but also NO. What did become obvious after each investigator's NO_2 results were submitted to NASA was that NO_2 catalytic converter instruments proved to be quite unreliable for determining NO_2 levels under most environmental conditions encountered during this airborne field-sampling operation. Quite important also was the preliminary finding that the very high NO_2 readings recorded onthe catalytic converter instrument did not appear to be correlated in any systematic way with real-time measurements of PAN, HNO_3 or total NO_y. Photochemical equilibrium calculation relating Georgia Tech's measured NO_2/NO ratios with experimentally measured levels of H_2O, O_3, UV, flux, T, and P and model calculated levels of HO_2, CH_3,O_2, and RO_2, are now in progress and will be reported to CRC at a latter date. Computations completed todate, however, indicate good aggreement between theory and experiment (within 1 σ error bars) for the case of the clean marine troposphere. In all of the above cases, RO_2 radicals played only a minor role in influencing the NO_2/NO ratio.

The final area of science activity for our group during the third year encompassed a study of corona discharge. The specific goal here was that of trying to unequivocally demonstrate that corona discharge in the atmosphere, particularly in electrified clouds, represents a major, unrecognized natural source of global NO_x. Our study, which has endeavored to use applied fields and corona current levels similar to those measured in the atmosphere, has convincingly demonstrated that corona discharges under these simulated atmospheric conditions does represent a significant source of NO_x. These tests have been performed using a variety of hardware configurations, ranging from those that had very well defined field strengths and corona onset voltages to those that made use of more real-world configurations involving, for example, small pine trees.

As related to electrified clouds, some estimates indicate that of the total electrical energy dissipation within an electrified cloud the energy associated with corona discharges dominates that from stroke lightning. It is thus possible that corona effects within thunderstorms could result in a global production of NO_x that is equal to or even exceeds that from bolt lightning. If so, virtually all past efforts to evaluate the global production of NO_x via electrified clouds have significantly underestimated the global yield of NO_x from this source since all are based on bolt lightning alone.

I. INTRODUCTION

The CRC supported program at Georgia Tech has been designed around the development of state-of-the-art N_xO_y atmospheric sensors with the ultimate goal of completing a comprehensive investigation of the atmospheric chemistry of the N_xO_y family of compounds. As noted in numerous documents, this family of compounds impacts on air quality in at least three significant ways:

(1) it encompasses one of the atmosphere's major acidic compounds, HNO_3;

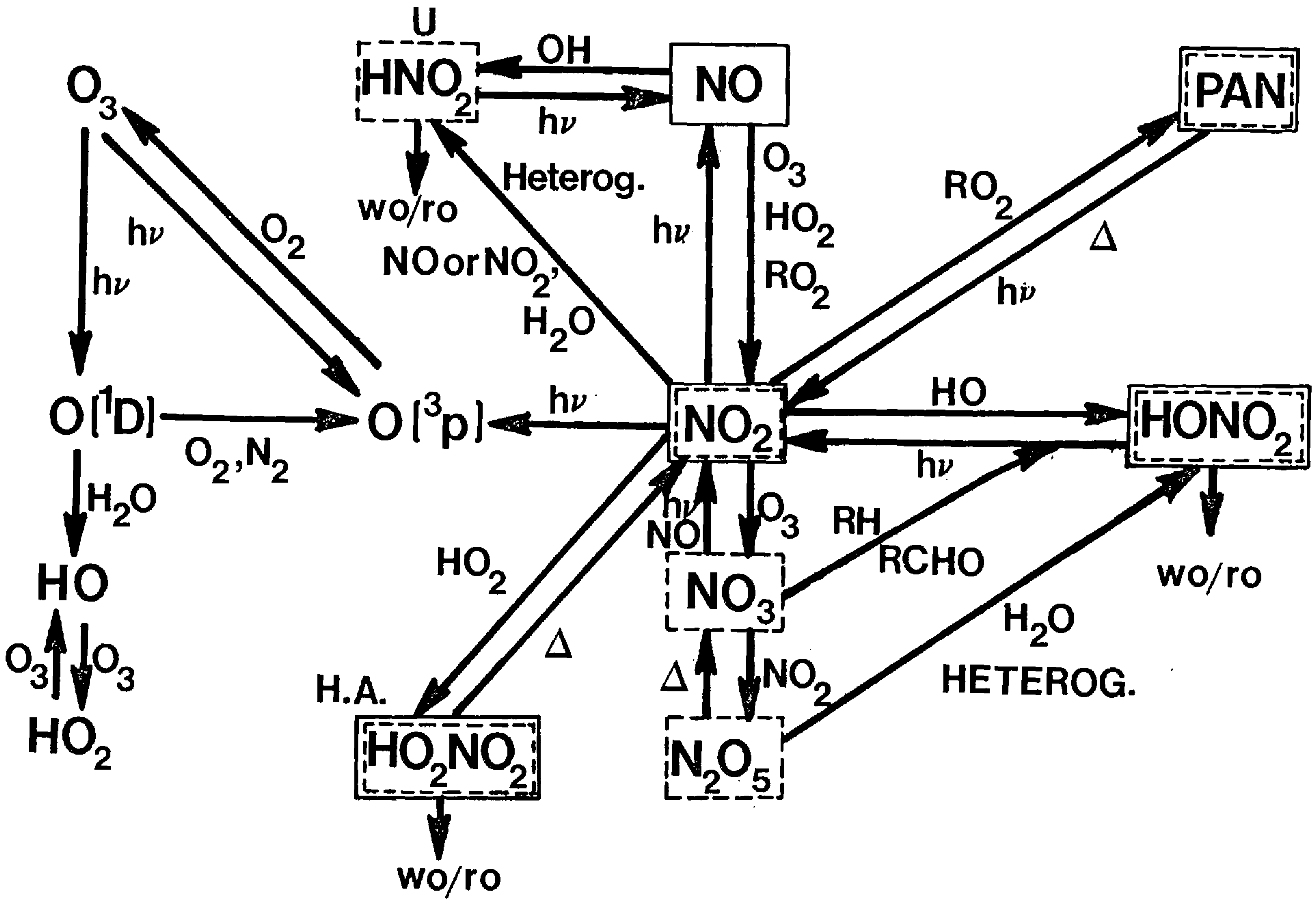
(2) it is responsible for major increases in the concentration levels of potentially harmful oxidants such as O_3 and PAN;

(3) it serves to control the levels of still other more reactive atmospheric oxidants such as OH and HO_2.

This three fold chemical impact on the chemistry of the atmosphere, together with the many complex chemical pathways coupling this family of compounds to other key atmospheric species is shown here in the form of Fig. 1. Also illustrated in this figure are several other unique characteristics of this chemical family, among these are: different day versus nighttime chemistry, different low altitude versus high altitude chemistry and a different chemistry in urban areas versus that in the clean troposphere. Not surprisingly, therefore, one is lead to the conclusion that a successful understanding of the chemistry of the nitrogen oxide family is central to our understanding of all of atmospheric chemistry.

During the third year of our proposed three year program to CRC, significant progress was made on both instrument development and in the collection of N_xO_y field data. Concerning our instrument development activities, our #1 priority was given to the successful completion of an in-situ photofragmentation LIF HNO_2 sensor. Our #2 and #3 priorities were the

FIG. 1 MAJOR ATMOSPHERIC REACTIONS OF N_xO_y SPECIES: SOLID LINE BOXES INDICATE MAJOR DAYTIME NITROGEN SPECIES: BROKEN LINE BOXES INDICATE SIGNIFICANT NIGHT-TIME NITROGEN SPECIES. WO/RO = WASHOUT/RAINOUT; Δ = THERMAL DECOMPOSITION; Hν = ABSORPTION OF LIGHT; U = IMPORTANCE IS MAINLY IN URBAN ATMOSPHERE; AND H.A. = IMPORTANCE MAINLY AT HIGH ALTITUDE.



completion of the NO_3 (long path differential absorption) instrument and the completion of a 3rd generation high sensitivity NO_2/NO LIF detector. Our field study programs, on the other hand, have encompassed: (1) HNO_2 measurements in urban Atlanta; (2) further nighttime measurements of NO at our Stone Mountain field station; and (3) an airborne study to examine the photochemical equilibrium of the NO, NO_2, O_3, system.

A final area of activity has involved a laboratory investigation of the potential impact of corona discharge as a natural source of NO_x in the troposphere. Details on the latter investigation as well as those-involving instrument development activities and field study results are provided in sections II and III of this report.

II. INSTRUMENT DEVELOPMENT

A. NO/NO_2 PF-LIF System

The development of a common instrument to measure both NO and NO_2 has been on our CRC list of objectives almost from the beginning of the program. In fact, during the first program year, the first generation PF-TP-LIF NO/NO_2 sensor was put into service. However, this 1st generation system suffered from two short commings: (1) it required cycling between NO and NO_2, i.e. these two species could not be measured simultaneously; and (2) the detection limit of this system for NO_2 was only 700 to 1000 pptv. In the second generation system (covered in our 2nd year CRC report), major improvements were made in both areas mentioned above. As in the 1st generation system, this new NO/NO_2 sensor used the frequency doubled output from a dye laser (e.g. that at 287 nm) to frequency mix with the 1.06μ fundamental from the Nd:YAG laser to generate 226 nm radiation . The latter wavelength corresponds to the γ (0,0) NO optical transition. In the 2nd generation system, however, ~ 50% of the dye laser fundamental (centered at 574 nm and used to generate the frequency doubled 287 nm beam) was passed through a H_2 Raman shifter where the 2nd Stokes output yielded 1.08μ radiation. This wavelength is ideally suited to pump NO from the $A^2\Sigma$ to the $D^2\Sigma$ state, the absorption cross section being over two orders of magnitude greater at 1.08μ versus 1.06μ. Other changes made in the 2nd generation system included the addition of a second fluorescence chamber and a set of optical chopping wheels to the system. The latter two changes were primarily responsible for the 2nd generation system having the capability of simultaneous detection of NO and NO_2. As shown in Fig. 2, with this hardware configuration, the NO fluorescence chamber receives only the 1.08μ and 226 nm beams and thus detects only ambient NO. The NO_2 chamber, on the other hand, receives the 1.08μ and 226 nm beams and, in addition, the 3rd harmonic from the Nd:YAG laser, i.e. 355 nm radiation. The synchronized chopping wheels serve to

PDL- PULSED DYE LASER;
PELLIN BROCA PRISM; OSC - DYE LASER OSCILLATOR CAVITY; SHG - 2ND HARMONIC CRYSTAL;
SFM - SUM FREQUENCY MIXING CRYSTAL; OB_1 - OPTICAL BLOCK 355 NM; OB_2 - OPTICAL BLOCK 574 NM; (Not shown are two mechanical choppers)

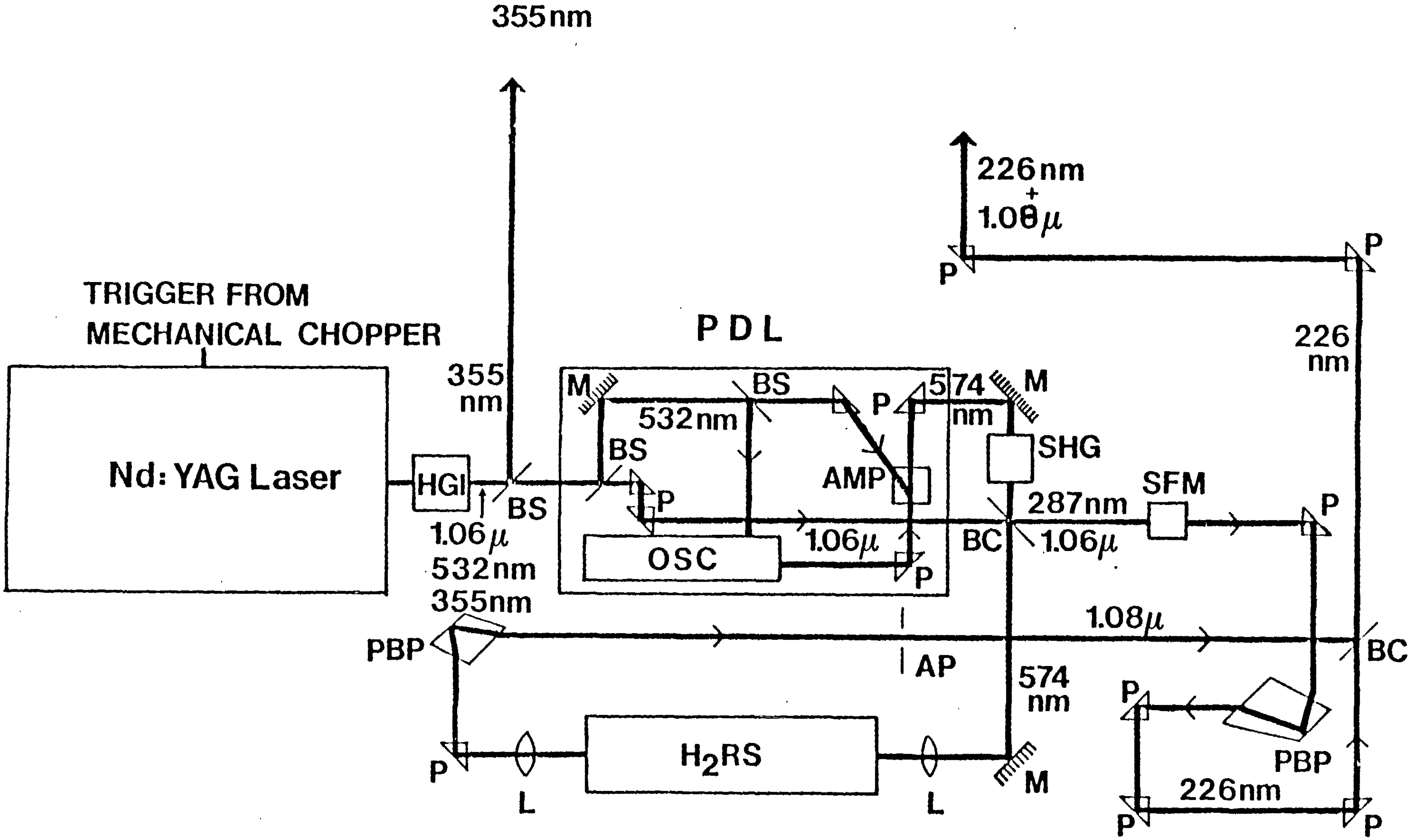


FIG. 2 - PF -TP/LIF NO_2/ NO SYSTEM

first block the 1.08/226 beams, allowing the photolysis of NO_2 at 355 nm, and then on a subsequent laser firing they block the 355 nm beam and permit the 1.08/226 beams to enter the NO_2 fluorescence chamber, thus detecting ambient NO plus photo-generated NO from NO_2. Since the ambient NO is independently measured in the first cell, the level of NO_2 can be obtained by subtracting away the ambient NO level from the signal measured in cell #2 (ambient NO + photo-generated NO from NO_2).

With the above improvements, the 2nd generation NO/NO_2 LIF sensor was able to make simultaneous measurements of NO and NO_2 (e.g. within 100 ms of each other), and the NO_2 detection limit of this system was 100 pptv for an integration period of 5 min. This performance can be compared to the 1st generation system that had a detection limit of ~ 1000 pptv for the same integration time.

In the 3rd generation NO/NO_2 PF/TP-LIF system, two major changes have been implemented: (1) the NO_2 photolysis efficiency has been greatly improved with the use of a XeF excimer laser whose output is centered at 353 nm; and (2) there have been further improvements in the beam processing optics as well as in the detection efficiency of the 190 nm fluorescence from the $D^2\Sigma$ state of NO (see Fig. 3). The three wavelengths used in this sytem are seen to be: (1) 226 nm, used to excite ground state NO into the $A^2\Sigma^+$ level; (2) 1080 nm, used to pump NO from the $A^2\Sigma^+$ level to the $D^2\Sigma$ state; and (3) 353 nm, used to photodecompose NO_2. Of the three wavelengths required, only the 353 nm XeF excimer line is available as a fundamental output wavelength from a laser. In the 3rd generation system, the required tunable laser wavelengths at 1080 and 226 nm are developed in the same way as in the 2nd generation system. In this case, the output of a pulsed Nd:YAG laser (DCR), frequency doubled to produce an intense beam of 532 nm laser radiation, is used to pump a dye laser (PDL) that is tuned to operate at 574 nm. This 574 nm beam is then frequency doubled, using a KD^*P type II crystal (XTAL), to produce tunable laser radiation centered at 287 nm. After separation of the 575 and 287 nm beams using dichioic mirror (DM), the 287 nm beam is then

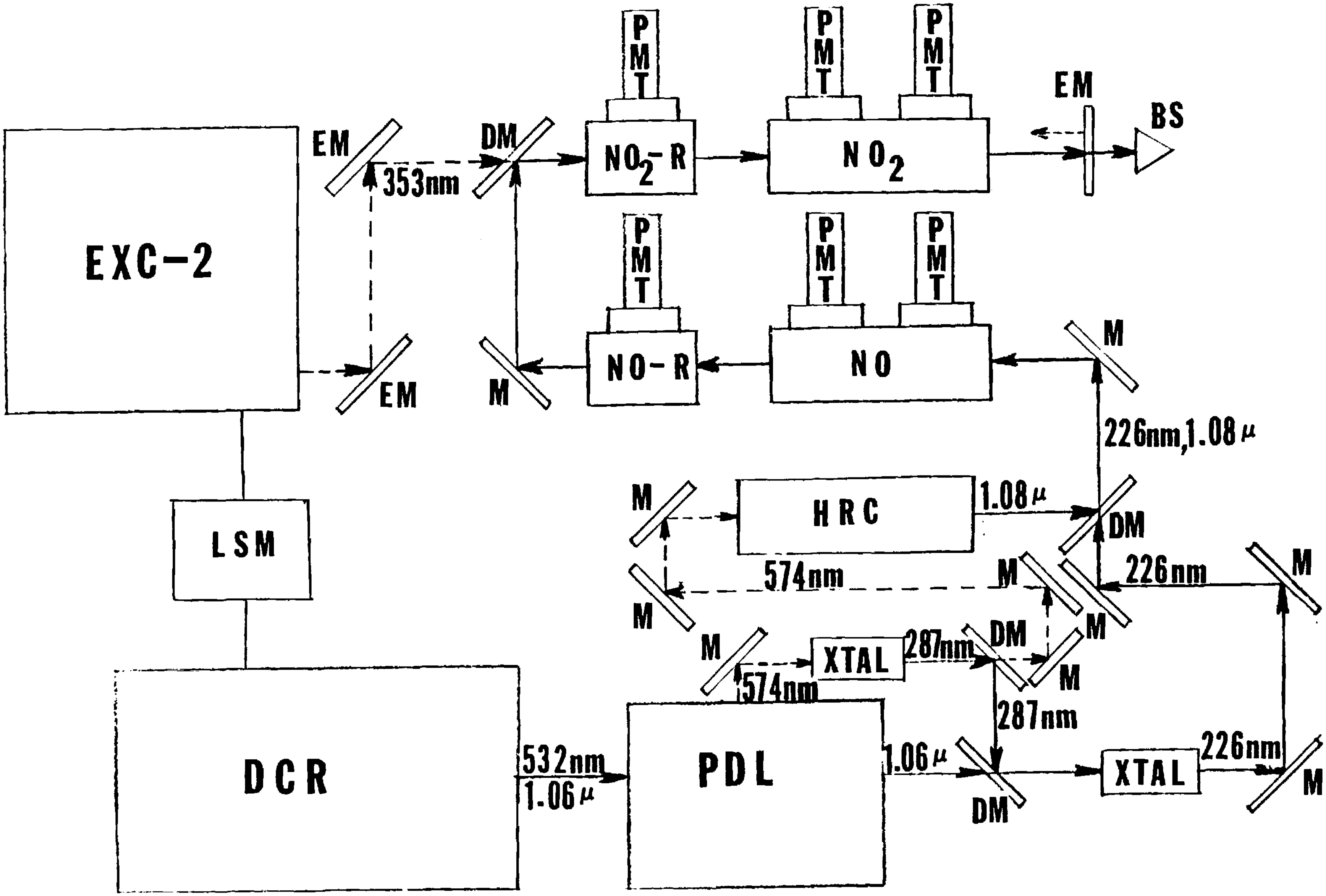


FIG. 3 TP-LIF/PF-TP-LIF NO/NO_2 DETECTION SYSTEM

(BS) Beam Stop; (DM) Dichroic Mirror; (EM) Excimer Mirror; (HRC) H_2 Raman Cell; (M) Mirror; (NO) NO Sample Cell; (NO-R) NO Reference Cell; (NO_2) NO_2 Sample Cell; (NO_2-R) NO_2 Reference Cell; (PMT) Photomultiplier Tube; (XTAL) Frequency Conversion Crystal; (LSM) Laser Synchronization Module injected into a frequency up-converter (a KD^*P DR cut crystal) where the 287 nm beam is mixed with residual 1064 nm radiation from the YAG laser. The latter operation produces tunable laser radiation centered around 226 nm. The remaining wavelength at 1080 nm, used to pump NO from the $A^2\Sigma$ to the $D^2\Sigma$ state, is generated by frequency down converting the residual 547 nm dye laser output using a H_2 Raman cell.

Typical laser energies at 353, 226, and 1080 nm are 38, 1.0, and 4 mJ, respectively. The XeF excimer laser in the PF/TP-LIF system is operated in the range of 100 to 200 Hz, depending on the sampling flow rate; whereas the YAG laser is run at 10 Hz. The rep-rate of the excimer laser, during a field experiment, is selected such that ~ 50% of the available NO_2 is photolyzed.

System Calibration - As was the case in our earlier STP-LIF NO sensor, the PF/TP-LIF NO_2/NO sensor is calibrated using the "standard addition" method. This procedure has been described in detail by Bradshaw et al. 1985. One modification in our calibration procedure for the PF/TP-LIF system involves the calibration of the NO_2 fluorescence cell with both NO_2 and NO calibration sources. Thus, the exact relationship in the detection efficiency for NO in the NO fluorescence cell and the NO_2 fluorescence cell is continually checked. The NO_2 calibration source consists of 44 ppmv of NO_2 in bottled zero air.

This standard has been systematically checked over a three year period using long path UV absorption, at Georgia Tech, and more recently, by a diode laser system at the National Bureau of Standards. During this time period, the concentration has been observed to change by only 16% from its original value, most of which occurred during the first year. This loss is speculated to have been caused by the reaction of NO_2 with the walls of the gas cylinder.

Interferences - Previously (see, e.g. Bradshaw et al., 1985) we have mentioned the possibility of photolytic interferences in the detection of NO via the TP-LIF technique. Recall, however, that for the NO detection system no interference species was identified, a result that is in good agreement with our experimental field observations. In the case of NO_2, we have examined several categories of potential interfering chemical species. The first category considered involves molecules that could be photolyzed at λ=353 nm (the NO_2 photolysis wavelength). Based upon our estimates of each species abundance in the clean troposphere as well as the species absorption cross sections, one may conclude from Table I that the most likely interference might come from CH_3ONO; however, even this source results in a signal level only 4% of that from NO_2.

Table I

Production of Interference NO from Photolysis at λ=353 nm

Species	Relative Absorption Cross Section NO_2=1	Relative Species Abundance (Daytime)	NO Quantum Yield	Interference Ratio (NO_2=1)
HONO	0.9	0.02	0.7	0.0013
CH_3ONO	8.5	0.01	0.5	0.04

A second type of photolytic interference that was explored involved molecules that might undergo photolysis at either λ=353 nm or 226 nm, thereby producing NO_2. This NO_2 could subsequently be photolyzed by the 353 nm photolysis beam to produce detectable NO. The latter process, though, is 5 to 10 times less efficient than the process discussed earlier since it requires three photons instead of two to generate NO. Table II presents estimates of the interference that might be expected from the production of NO_2 by the photolysis of several different NO_2 containing atmospheric nitrogen compounds.

Table II

Estimated Interference due to NO_2 Production by Various Atmospheric Species due to Photolysis at λ=353 nm

Species	Effective Fractional Photolysis (E_{355}=40 mJ/pulse	Relative Species Abundance (Daytime), NO_2=1)	Quantum Yield for NO_2	Interference Ratio
HO_2NO_2	$\leqq 1x10^{-4}$	4	~ 1	$\leqq 5x10^{-4}$
HNO_3	$\leqq 1x10^{-6}$	10	1	$\leqq 1x10^{-5}$
CH_3ONO_2	$\leqq 1x10^{-6}$	0.1	1	$\leqq 1x10^{-7}$
N_2O_5	$\leqq 1x10^{-5}$	1	1	$\leqq 1x10^{-5}$

Table III, on the other hand, gives the results of the estimated interference arising from photolysis at λ=226 nm.

Table III

Estimated Interference due to NO_2 Production by Various Molecules due to Photolysis at λ=226 nm

Species	Effective* Fractional Photolysis (E_{226}=2mJ)	Relative Species Abundance (Daytime), NO_2=1)	Quantum Yield for NO_2	Interference Ratio
HNO_3	$\sim 1.4x10^{-5}$	10	1	$\sim 1.4x10^{-4}$
HO_2NO_2	$1.6x10^{-4}$	4	1	$6.4x10^{-4}$
N_2O_5	$3.6x10^{-4}$	1	1	$3.6x10^{-4}$

*Includes an estiamted 10x reduction factor due to cell dilution in the 100 ms between 226 nm laser pulse.

As can be seen from the above tables, photolytic interferences are not predicted to cause a measurable interference in the detection of NO_2. However, yet another type of interference that must be considered in the detection of NO_2 is thermal decomposition in the sampling line. This interference could arise from either gas phase or surface-catalyzed decomposition of nitrogen oxide species containing an NO_2 grouping. Table IV shows our estimated level of interference from thermal decomposition for those molecules believed most likely to produce measurable interference when sampling at high altitudes for conditions where the sampling line temperature is held at 280 K.

Table IV

Estimated Interference from Thermal Decomposition of N_xO_y Species at 5 km

Species	Lifetime at 280 K*	Relative Species Abundance at 5 km (Daytime), NO_2=1)	Interference Ratio (NO_2=1) 400 ms Sample Time
HO_2NO_2	~ 50 Sec.	4	<.1
N_2O_5	~ 100 Sec.	.5	<.02

*Approximate temperature of sampling line.

From the above data, it would not appear that either HO_2NO_2 or N_2O_5 should not present any problems to our achieving reliable measurements of NO_2 at 5 km or at higher altitudes. At low altitudes, the HO_2NO_2 and N_2O_5 are nearly completely dissociated and thus represent evel less of a problem. As discussed in the text that follows, as well as in section IIIB, the results from the NASA CITE II program confirm the above statements and/or conclusions.

PF/TP-LIF NO_2/NO System Performance - As of this writing, the PF/TP-LIF NO_2/NO system is now fully operational and has been extensively tested on the NASA L-188C turboprop Electra. In fact, it was this system that was used by our group during the NASA GTE CITE II program. One of the major objectives of the latter program was the intercomparison of four different types of NO_2 sensors, i.e. a chemiluminescence instrument having a catalytic NO_2 to NO converter, a chemiluminescence instrument equipped with a photolytic NO_2 to NO converter, a tunable diode laser system, and the Georgia Tech PF/TP-LIF NO/NO_2 sensor.

During the CITE II mission extensive NO_2 and NO data were collected by the Georgia Tech group on eight consecutive missions. The detection limit of the Georgia Tech PF/TP-LIF NO/NO_2 system (2/1 S/N) was ~3 pptv and 12 pptv, respectively, for a two minute integration time. However, since the PF/TP-LIF system is a signal limited system, we were able to further improve on the above stated detection limit for both NO and NO_2 with further increases in the integration time. The S/N ratio, in this case, improved as the square root of the integration time for times well in excess of 1 hour. Thus, NO_2 detection limits of 3 pptv were achieved by blocking individual two minute integration times.

Currently, we can collect signal data every 30 seconds, and if needed still faster collection rates can be achieved with minor computer program modifications. Still further improvements of a factor of 2 to 3 in the sensitivity of the 3rd generation system are expected to come in the form of higher performance PMT's and higher efficiency beam processing optics for combining the UV and IR laser beams.

B. HNO_2 PF-LIF DETECTION SYSTEM

Development and preliminary field testing of an in-situ PF-LIF detection system for atmospheric nitrous acid, HNO_2, represented a major area of activity during the third year of our CRC program.

Few direct atmospheric measurements of HNO_2 have been reported in the literature. The colormetically based measurements by Nash (1974) are now believed to be unreliable due to interferences by other atmospheric species, most likely PAN. Likewise the recent denuder tube measurements by Sjodin and Ferm (1985) exhibit very little diurnal variation in the measured HNO_2 concentration and may therefore be considered suspect in light of our understanding of HNO_2 loss processes. The most reliable HNO_2 observations are the spectroscopically based measurements made by long path optical differential absorption (Perner and Platt (1979); Platt et al. (1981); Harris et al. (1982, 1983)). Albeit, while this latter technique offers spectroscopic selectivity, it suffers from a number of limitations. The long optical paths required for high sensitivity (on the order of kilometers) makes both correlation with other controlling parameters difficult and precludes the use of the sensor on mobile sampling platforms (e.g. aircraft). Additionally, the "open air" nature of this technique significantly complicates any controlled tests of system performance, such as interference tests, as well as limiting measurements to periods of good visibility. These limitations provided the rationale for our development of an in-situ type atmospheric HNO_2 sensor that addresses these limitations while retaining spectroscopic selectivity for HNO_2.

(1) Experimental Approach

The photofragmentation/laser-induced fluorescence (PF-LIF) technique allows for the detection of polyatomic molecules that possess excited states that do not fluoresce or, at best, do so only poorly. In this approach, originally described theoretically by Rodgers, et al. (1980), the molecule of interest is photolyzed to produce one or more photofragments that can be detected by laser-induced fluorescence. The spectra and photochemistry of HNO_2 make it an excellent candidate for detection by the PF-LIF technique since HNO_2 itself is non-fluorescent, and it also possesses a strong near-ultraviolet absorption spectrum (see Fig. 4). Previous studies by Cox (1974a,b) have shown a near unity primary quantum yield in this spectral region for the process:

(1) $HONO + h\nu \longrightarrow OH + NO.$

Both of these photofragments, OH and NO, may readily be detected by laser-induced fluorescence. The approach originally proposed for the detection of HNO_2 by the PF-LIF technique was aimed at detection of the NO photofragment (see, for example, CRC 2nd year report). More specifically:

(2) $HONO + h\nu_1$ (355 NM) $\longrightarrow OH(X) + NO(X,v''= 0,1,2)$

(3) $NO(X,v''=2) + h\nu 2$ (248 nm) $\longrightarrow NO(A,v'= 0)$

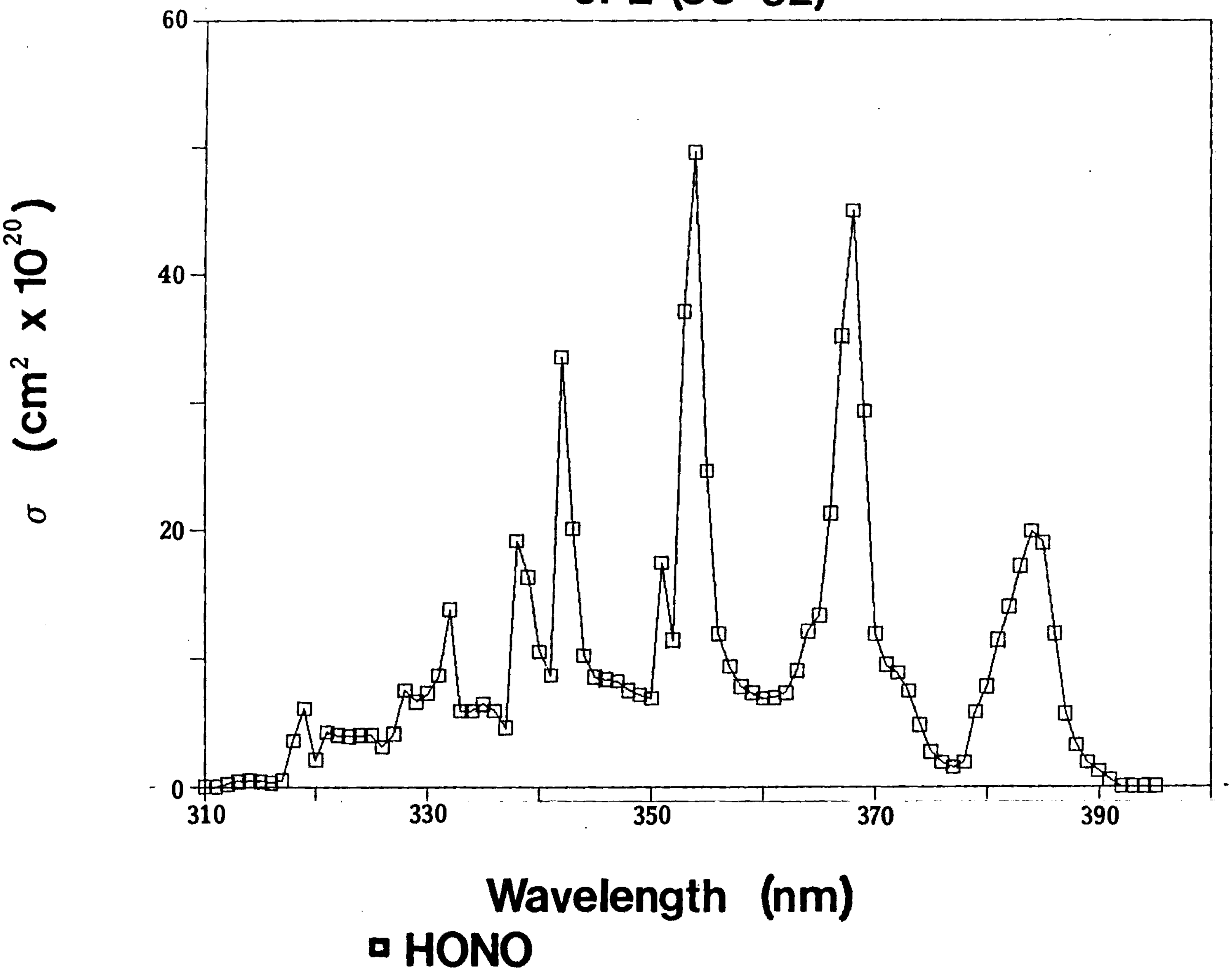
(4) $NO(A,v'=0) \longrightarrow NO(X,v''=2) + h\nu_3$ (226 nm).

This proposed detection system, which sought to detect vibrationally excited photofragments, offered the very substantial advantage of being noise background-free. However, a critical assumption in this proposed detection scheme was that NO_2 would represent a negligable interference for $NO(X,v'' = 2)$ detection since the production of this fragment from the photolysis of NO_2 at 355 nm is, on average, slightly endothermic. As was discussed in our second year CRC report, this assumption proved to be invalid. We found, in fact, that NO_2 represented a non-negligible interference in the PF-LIF detection of HNO_2 when sampling the NO photofragment.

As a result of these observations, efforts during this last year were aimed at developing a PF-LIF sensor based on detection of the OH photofragment, again with HNO_2 being photolyzed at 355 nm. That is:

FIG. 4

Absorption Cross Section
JPL (83-62)



(5) $HONO + h\nu_1$ (355 nm) $\xrightarrow{\quad}$ OH(A,v'=1)

(6) OH(X,v"=0) + $h\nu_2$ (282 nm) $\xrightarrow{\quad}$ OH(A,v'=1)

(7) OH(A,v'=1) + M $\xrightarrow{\quad}$ OH(A,v'=0) + M^+

(8) OH(A,v'=0,1) $\xrightarrow{\quad}$ OH(X) + $h\nu_3$ (~309 nm).

This approach, while not background free, nevertheless builds upon the already established technique of single-photon laser-induced fluorescence (SP-LIF), a technique that at the levels of OH expected from the photolysis of HNO_2 has excellent sensitivity (Rodgers, et al. (1985)). The latter approach is limited principally by the interference resulting from photolysis of atmospheric ozone when exciting the X→A transition in OH at 282 nm. Ozone photolysis at this wavelength results in the production of metastable atomic oxygen, $O(^1D)$, which rapidly reacts with ambient water vapor to produce a laser generated OH inteference signal. The control of this interference is therefore an important consideration in the overall design of an SP-LIF OH detection system.

The simplest, and one of the most effective, methods of controlling this interference involves limiting the magnitude of the 282 nm laser energy (Davis, et al. (1981a,b)). This approach limits the OH interference signal since production of this signal is proportional to the square of the 282 nm laser energy while the OH signal due to photolysis of HNO_2 is linear in laser energy (ambient OH levels are too low to produce any measureble interference). Rodgers (1986) has presented detailed calculations for both the expected signal strength for a typical PF-LIF HNO_2 detection system and the ratio of the O_3/H_2O interference signal strength to the expected HNO_2 signal. The estimated PF-LIF HNO_2 signal strength was found to be:

(I) $S_{HONO} = 86 * C_1 E_2(mJ) * [HONOppbv)]$

where E_2 is the 282 nm laser energy in mJ/pulse and C_1 is the water vapor quenching correction factor given by:

(II) $C_1 = (1 + 1.74 \times 10^{-2} * [H_2O(Torr)])^{-1}$.

The fractional interference signal was estimated to be:

(III) $S_1/S_{HONO} = 4.9 \times 10^{-4} * E_2(mJ/pulse) * [H_2O(Torr)] * [O_3]/[HONO]$.

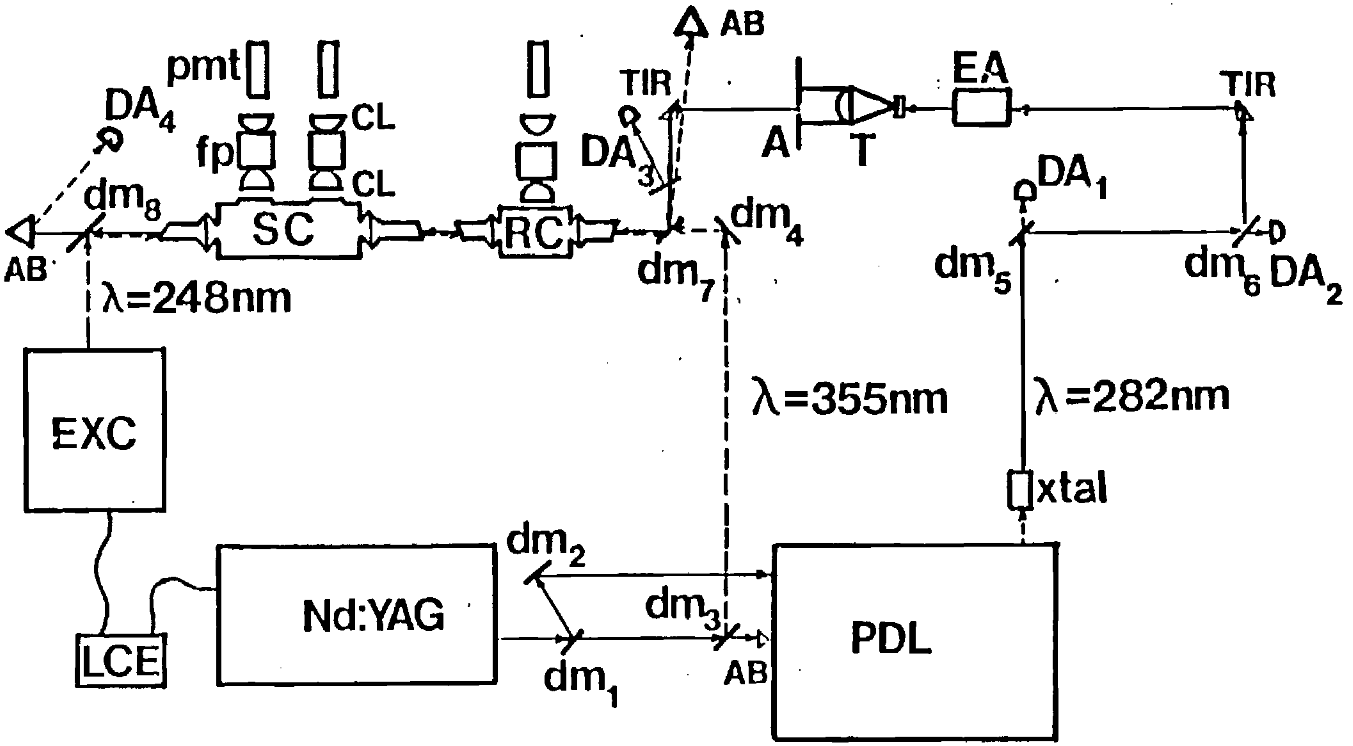
As can be seen from equation (III), for typical nighttime measurement conditions of $[H_2O]$=10 Torr, $[O_3]$=20 ppbv, E_2 = 0.2 mJ/pulse and [HONO] =1 ppbv, the expected interference is of the order of 2% of the total signal level.

(2) Experimental Hardware

The PF-LIF HNO_2 system is composed of five basic subsystems: (1) a Nd:YAG-driven dye laser system with its accompanying non-linear crystals and beam processing optics that produce the needed photolysis and probe frequencies; (2) an air sampling system that serves to collect outside air and deliver it to the sampling chamber; (3) a sampling chamber, equipped with fluorescence collection optics and photomultiplier tube assemblies; (4) an electronic detection system and (5) a dynamic dilution flow calibration system. Each of these subsystems has been discussed in detail by Rodgers (1986), and therefore, only a brief description is given here.

Laser Systems - Figure 5 gives a schematic illustration of the optical layout used in the PF-LIF HNO_2 detection system. Central to this system is a Nd:YAG driver laser (Quanta Ray DCR IIa). The resulting second and third harmonic output wavelengths from this laser at 532 nm and 355 nm respectively, are separated from the Nd:YAG fundamental at 1.06µ by a series of dichroic mirrors (DM_1 - DM_4). Mirrors DM_1 and DM_2 served to separate out the 532 nm second harmonic, while mirrors DM_3 and DM_4 isolated the 355 nm third harmonic. After mirror DM_4, the energy of the 355 nm HNO_2 photolysis beam was nominally 100 ± 10 mJ/pulse.

PF-LIF HONO DETECTION SYSTEM OPTICAL LAYOUT



A= Aperture
AB= Absorption Beam Dump
CL= Fluorescence Collection Lens
DA= Laser Diode
DM= Dichroic Mirror
EA= Laser Energy Attenuator

EXC= Excimer Laser
FP= Optical Filter Pack
LCE= Laser Coupling Electronics
PMT= Photomultiplier Tube
PDL= Pulse Dye Laser

RC= Reference Cell
SC= Sampling Chamber
T= Telescope
TIR= Beam Steering Prism
XTAL= Frequency Doubling Crystal

Fig 5 : Optical Layout for PF-LIF HONO Detection System

The 532 nm beam served as the optical pump for a Quanta Ray model PDL-1a dye laser used to generate the tunable 282 nm radiation for detection of the OH photofragment.

With an intracavity etalon installed, the dye laser energy conversion efficiency ranged from 18 to 24 per cent. This resulted in a typical 564 nm energy output of ~30 mJ/pulse for an average input pump energy of 150 mJ/pulse. The output linewidth of the dye laser was 0.06 ± 0.015 cm^{-1}. The dye laser output was frequency-doubled to 282 nm using an angle tuned $KD^{*}P$ crystal as shown in Fig. 5, producing on the average 2.5 to 3 mJ/pulse of tunable ultraviolet radiation.

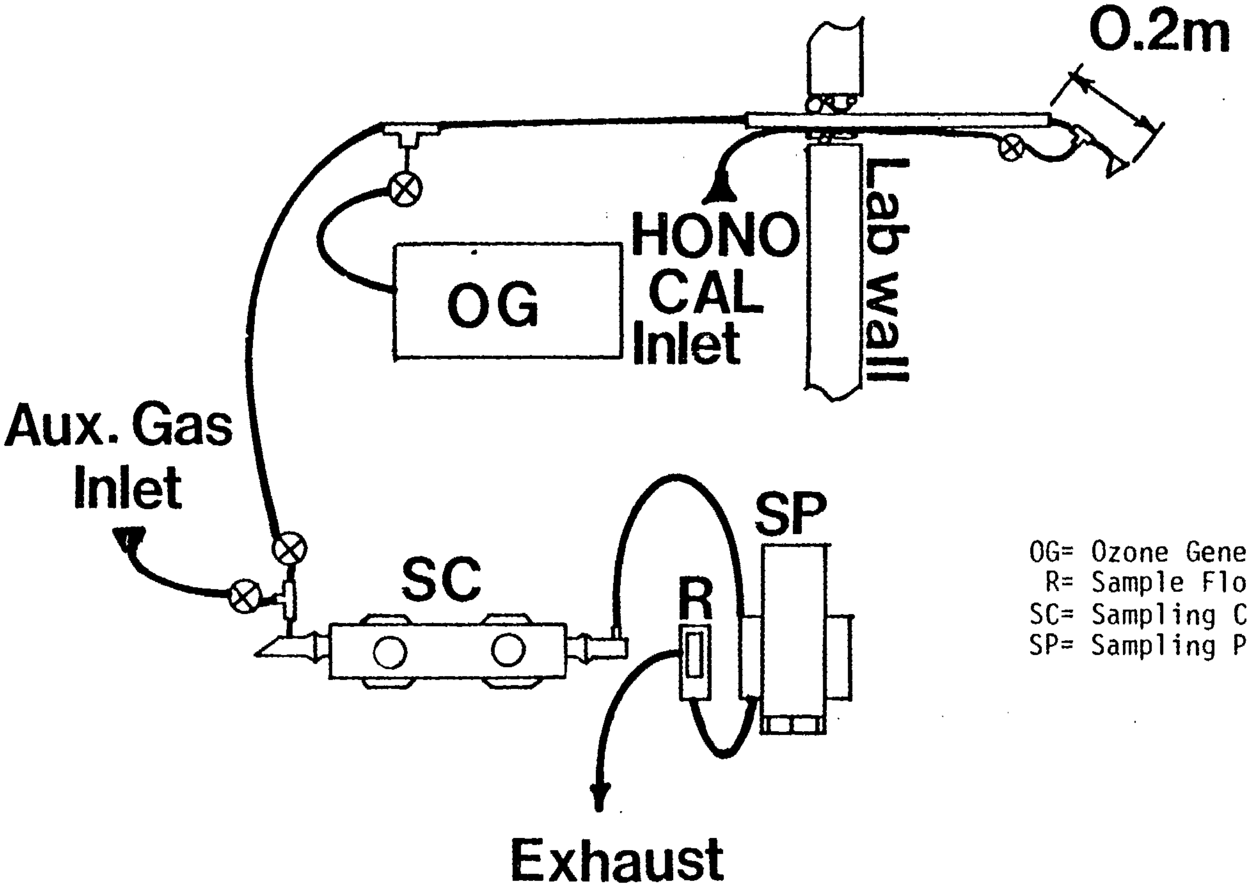
The frequency-doubled dye laser output was separated from the fundamental wavelength using dichroic mirrors DM_5 and DM_6. Since the optical path between DM_5 and DM_6 was traversed only by the probe beam and not by the 355 nm photolysis beam, variations in the effective pathlength could be used to adjust the relative time of arrival of the photolysis and probe beams at the sampling cell. For our experiments, the distance between DM_5 and DM_6, and to a lesser extent the separations between other components, resulted in a delay in the arrival of the probe laser beam at the sampling region by ~ 14 ns, relative to the photolysis pulse. Since the width of both pulses was nearly one-half of the latter value (6-7 ns FWHM), the photolysis of HNO_2 was over 90% complete before the arrival of the OH probe beam.

The UV beam steering prism located after mirror DM_6 was used to steer the 282 nm beam through a variable optical attenuator that served to provide the desired input laser energy at the OH/HNO_2 sampling cell. (Under typical measurement conditions approximately o.2 mJ/pulse of 282 nm laser energy entered the sampling cell.) After adjustment of the UV laser energy, the beam was further processed by expansion in a 5x Galilean-type telescope and then passed through a 1.0 cm aperture positioned approximately 5 cm behind the telescope. This optical processing sequence served to both create a more homogenous 282 nm beam as well as to match the 282 nm beam diameter to that of the 355 nm photolysis beam. The enlarged beam diameter had the dual advantage of both reducing the 282 nm beam divergence and further reduced the O_3/H_2O interference problem. At mirror DM_7 the reflected 282 nm OH/HONO sampling beam was combined with the transmitted ($T \cong 85-90\%$) 355 nm photolysis beam, and the combined beams were then directed through two optical cells. The first of these cells was used as a calibration/reference system, the second as the ambient air monitoring chamber.

Air Sampling System - In making in-situ measurements of HNO_2 an important consideration in setting up the sample inlet line to the fluorescence chamber was the alteration of the ambient level of HNO_2 due to surface reactions, either through reduction of HNO_2 concentrations due to surface decomposition, or to system generated artifacts due to surface catalyzed HNO_2 production. Recognizing these potential problems, the HNO_2 sampling system, illustrated schematically in Fig. 6, was constructed of materials (principally teflon) that were found to be relatively inert to surface reactions involving HNO_2. In particular, no parts were used that would bring the sampled air stream in contact with metal surfaces. Details of the tests performed on this system to demonstrate the absence of system generated artifacts are discussed later in the text under the section (2), "System Performance", and are further elaborated on in the work by Rodgers (1986).

As illustrated in Fig. 6, the main sampling line consisted of a 0.95 cm i.d. diameter black teflon tubing, having an overall length of approximately nine meters. (Black tubing was selected over conventional translucent teflon to eliminate the possibility of HNO_2 photolysis within the sampling line by

PF-LIF-HONO AIR SAMPLING SYSTEM



OG= Ozone Generator
R= Sample Flow Rotamter
SC= Sampling Chamber
SP= Sampling Pump

Fig 6 : PF-LIF HONO Air Sampling System

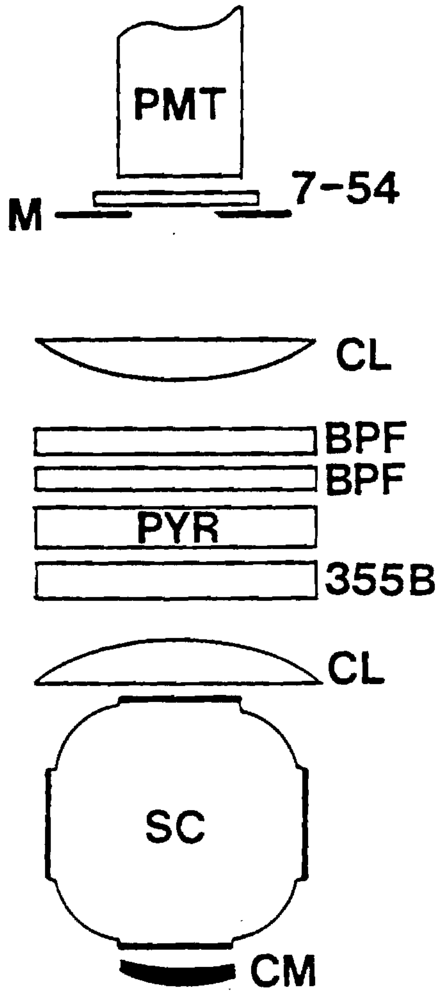
fluorescent lights used to illuminate the laboratory.) The ambient air intake for this system was located three meters beyond a brick and mortar laboratory wall located on the eastern side of the Baker Research Building on the Georgia Tech campus. The inlet was approximately 10 meters above ground level, and its location was such that it bordered a lightly travelled street on the Georgia Tech campus.

At two locations along the teflon sampling line, 0.3 and 4.0 m from the inlet, were located teflon "tee" assemblies that permitted injection of other gases, e.g. ozone/air or HNO_2 calibration mixtures into the ambient air stream.

The fluorescence chamber connected to the teflon sampling line consisted of a 0.8 l all quartz cell containing 8 viewing ports. The average residence time of HNO_2 in the sampling system was 1.8 seconds, with a worst case time of approximately 2.5 seconds. Using the results of Rogers et al. (1985), the maximum HNO_2 sampling loss was estimated to be ~4% for the conditions employed in our system.

Fluorescence Detection System - The fluorescence detection optics and optical filter pack assembly, shown in Fig. 7, was a derivative of an earlier system described by Davis et al. (1979). It is also identical in its optical configuration to the system previously described by Bradshaw et al. (1984) and Rodgers et al. (1985) except for the addition of a 355 nm chemical blocking filter (described by Bradshaw et al. (1984)).

Electronic Detection System - The detection electronics employed in the HNO_2 detection system were similar to those used in other single-photon LIF systems by our group such as those previously discussed by Davis et al. (1979); Bradshaw et al. (1982) and Rodgers (1985). The data collection system used in this investigation consisted of a small data-logging microcomputer system (Creative Micro Systems, Inc., model 9687), an interactive terminal and a printer. This system was essentially equivalent to the one described by Rodgers et al. (1985) and was used to collect and store the information from both a gated-charge


PF-LIF
HONO Detection Optics and Filter Pack

7-54= Colored Glass Filter
355B= 355 nm Blocking Filter
BPF= Band Pass Filter (309 nm)
CL= Fluorescence Collection Lens
CM= Fluorescence Collection Mirror

M= PMT Mask
PMT= Photomultiplier Tube
PYR= Pyridine Filter
SC= Sampling Chamber

Fig. 7 : Detection Optics and Filter Pack for PF-LIF HONO Detection System

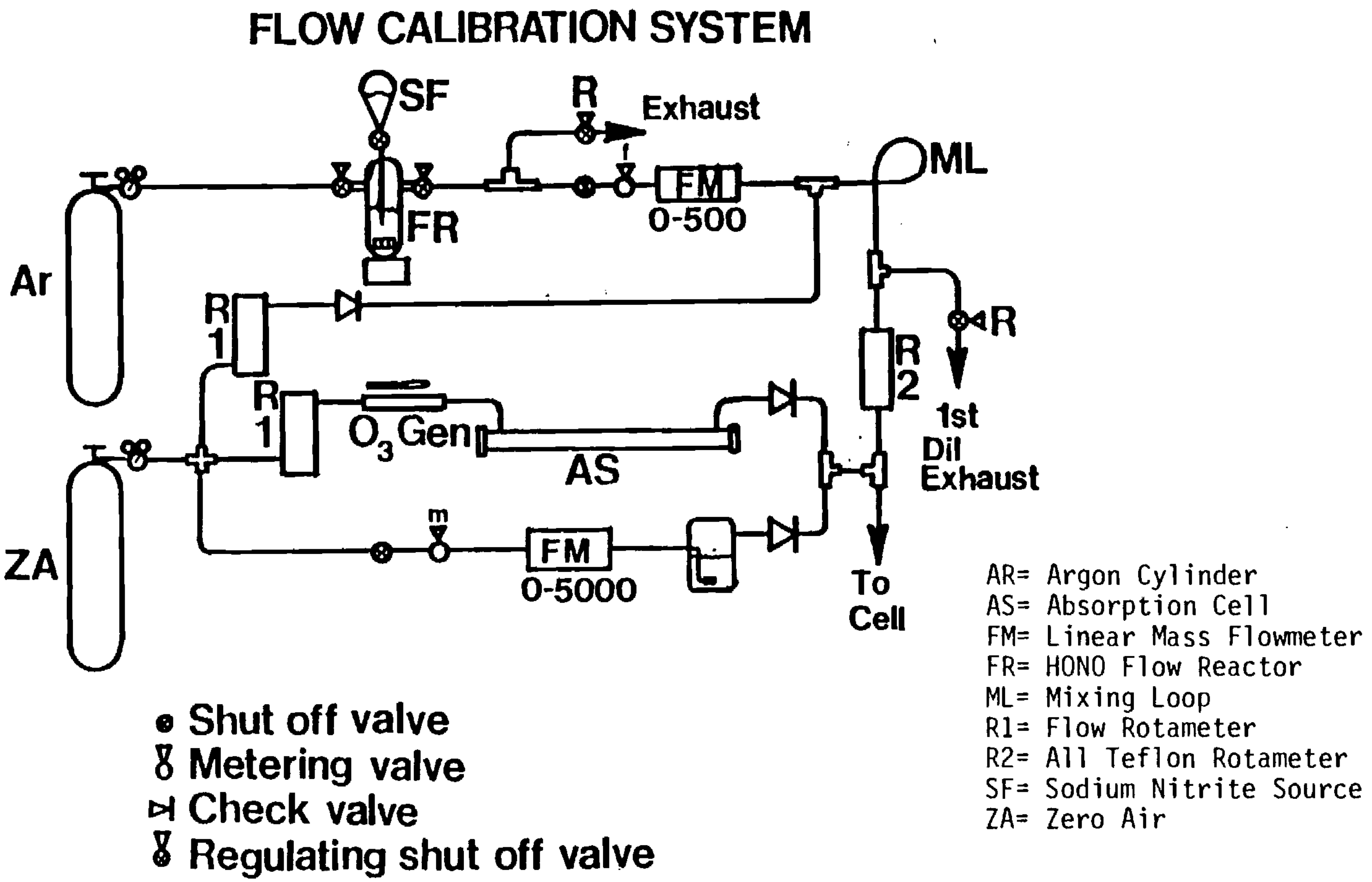
integrator and an array of other instruments that provided ancillary measurements of other atmospheric parameters.

Flow Calibration System - Figure 8 provides a schematic diagram of the flow calibration system used in this study. This system was of the dynamic dilution type and was designed to allow either HNO_2/air or O_3/H_2O/air mixtures to be introduced into the sampling chamber. The flow system was constructed entirely of glass, quartz, stainless-steel, and teflon (with small areas of contact with Viton O-rings and seals). Those portions of the system in contact HNO_2 gas mixtures consisted of teflon, except for one stainless-steel flowmeter and a small length of pyrex glass used in the rotameters and the HNO_2 generator.

Nitrous acid was produced by the method of Cox (1947a,b) which involves the reaction of sodium nitrite with H_2SO_4 acid. This method produces HNO_2 via the reaction of nitrite ion with H_3O^+. However, side reactions involving the nitrite ion and impurities also result in the simultaneous production of some NO_2. For the conditions used in this study, the ratio of HNO_2 to NO_2 was normally found to lie between 1.5 and 2.0.

The HNO_2 content from the first dilution stage was determined by near-ultraviolet absorption spectroscopy (The estimated accuracy of the HNO_2 cross section is ±15%). This concentration level was used in conjunction with the final dilution factor to calculate the HNO_2 concentration in the sampling cell. Using a two stage dilution system, the HNO_2 concentration limits were 2 ppbv for ambient air calibrations and 10 ppbv for laboratory tests; whereas, by adding a third stage of dilution HNO_2 levels as low as 100 pptv could be achieved in the fluorescence sampling chamber.

The calibration system shown in Fig. 8 could also be operated as an OH calibration system using the O_3/H_2O calibration technique described by Rodgers et al. (1982, 1985). In this system, known concentrations of hydroxyl radicals are produced by the UV photolysis of ozone and the subsequent reaction of $O(^1D)$



AR= Argon Cylinder
AS= Absorption Cell
FM= Linear Mass Flowmeter
FR= HONO Flow Reactor
ML= Mixing Loop
R1= Flow Rotameter
R2= All Teflon Rotameter
SF= Sodium Nitrite Source
ZA= Zero Air

Fig 8 : Schematic Diagram of HONO Flow Calibration System with water vapor to produce two hydroxyl radicals. Rodgers et al. (1985) have shown that this technique is in excellent agreement with an alternate calibration approach using photolysis of hydrogen peroxide as the OH radical source.

(3) System Performance

Laser Null Experiments - To demonstrate that neither the probe laser tuning sequence nor the photolysis laser on/off sequencing resulted in the production of artifact signals, a series of laser null experiments were performed in conjunction with the HNO_2 measurement program. In these tests the complete detection system, including the air sampling sub-system, was used as an actual HNO_2 measurement except that the probe laser was tuned to a nearby spectral region devoid of OH absorption. In this case, the signal due to OH fluorescence should be zero and statistically significant deviations from this result would indicate the prescence of artifacts.

Ths first laser null experiment performed on the system (12/11/85) did, in fact, indicate such a result. Subsequent examination of several system components revealed that an energy monitoring diode was operating at a level that was above its linear response range. After this problem was corrected, none of the remaining eleven laser null experiments were more than two standard deviations away from a null (zero) result. Thus, to the limit of the experimental resolution (normally about 1 part in 150), no system generated artifacts were identified.

System Linearity Tests - While the laser null experiments provided evidence that system-generated artifacts were, at most, a small portion of the total signal, since they produce no signal they do not provide information on the expected accuracy of scaling the recovered fluorescence signal to standard conditions.

The linearity of the PF-LIF signal with 355 nm laser energy was demonstrated both for the case of laboratory mixtures of HNO_2 in air, generated by the flow calibration system, and for measurements made with ambient air. Fig. 9 shows the results of a laboratory 355 nm energy scaling test. This test was performed at relatively high concentrations of HNO_2 (86 ppbv) and therefore shows a strong linear dependence of the fluorescence signal on 355 nm laser energy with relatively little scatter. Unfortunately, fluorescence scaling experiments using outside air are more difficult due to the changing atmospheric concentration of the species and can only be accomplished successfully under stable conditions. Figure 10 shows the results of a 355 nm energy scaling tests performed on the night of February 3, 1986. The much lower ambient concentration of HNO_2 and the natural variability of the concentration of HNO_2 made the scatter in these data somewhat higher than the laboratory tests. Even so, the slope of the regression line indicates a linear dependence of the PF-LIF fluorescence signal on 355 nm laser energy.

Figures 11 and 12 give the results of similar scaling tests performed with the 282 nm beam. In this case, the laboratory test was performed at a reduced HNO_2 concentration (22 ppbv) relative to the 355 nm test. In contrast, the ambient air scaling test (conducted on 2/11/86) was conducted at high (~3x) concentrations of HNO_2 than the similar tests for the 355 nm beam. This higher concentration permitted a series of tests where both the 355 and 282 nm energies were varied. The results of these tests are shown in Fig. 13. All of these tests indicated that within the experimental error, the PF-LIF fluorescence signal depended linearly upon both the 355 and 282 nm energies.

<u>Calibrations</u> - A number of system calibrations, using both the O_3/H_2O and the HNO_2 standard addition technique, were performed during the HNO_2 ambient measurement program. The HNO_2 calibration system was used to demonstrate the

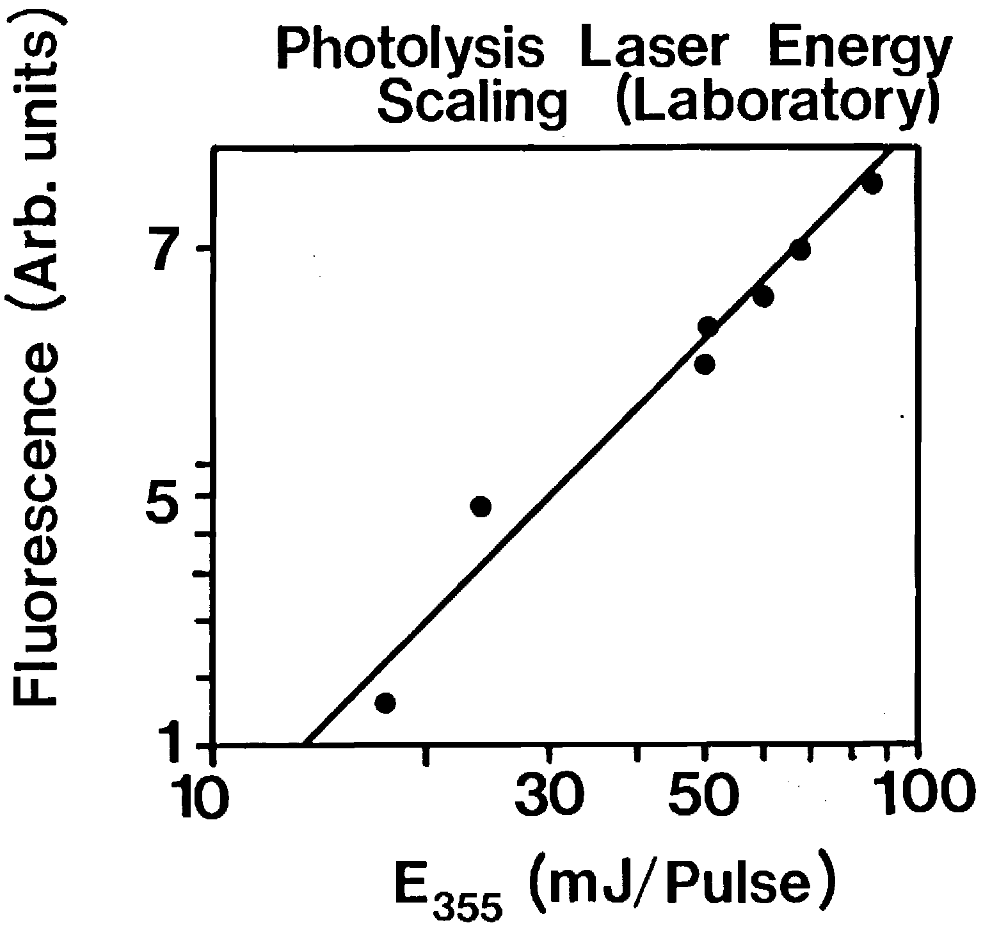


Fig. 9 : Photolysis Laser Energy Scaling of PF-LIF HONO Fluorescence Signal (Laboratory Results)

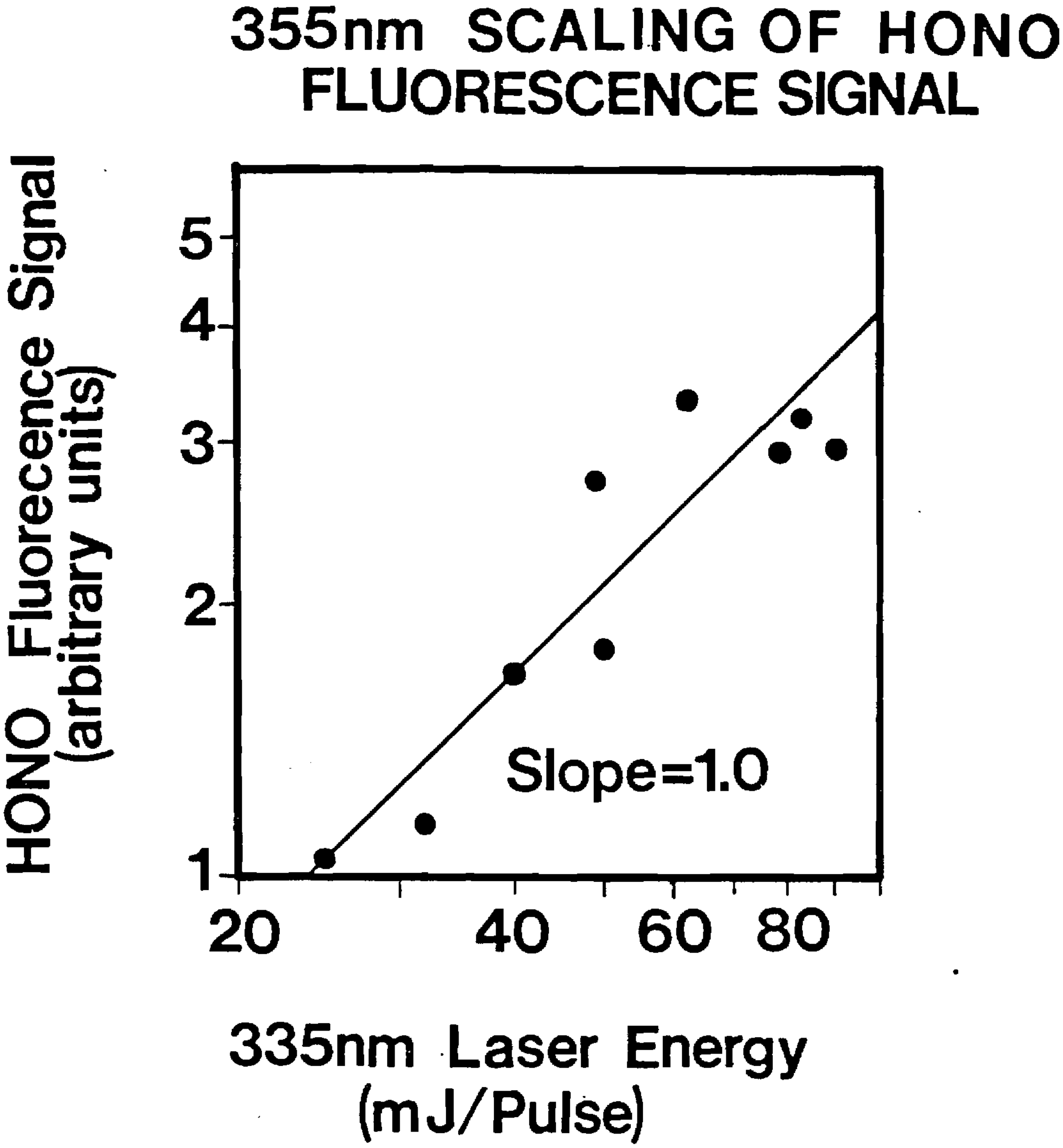


Fig. 10 : Photolysis Laser Energy Scaling of PF-LIF HONO Fluorescence (Outside Air Measurements)

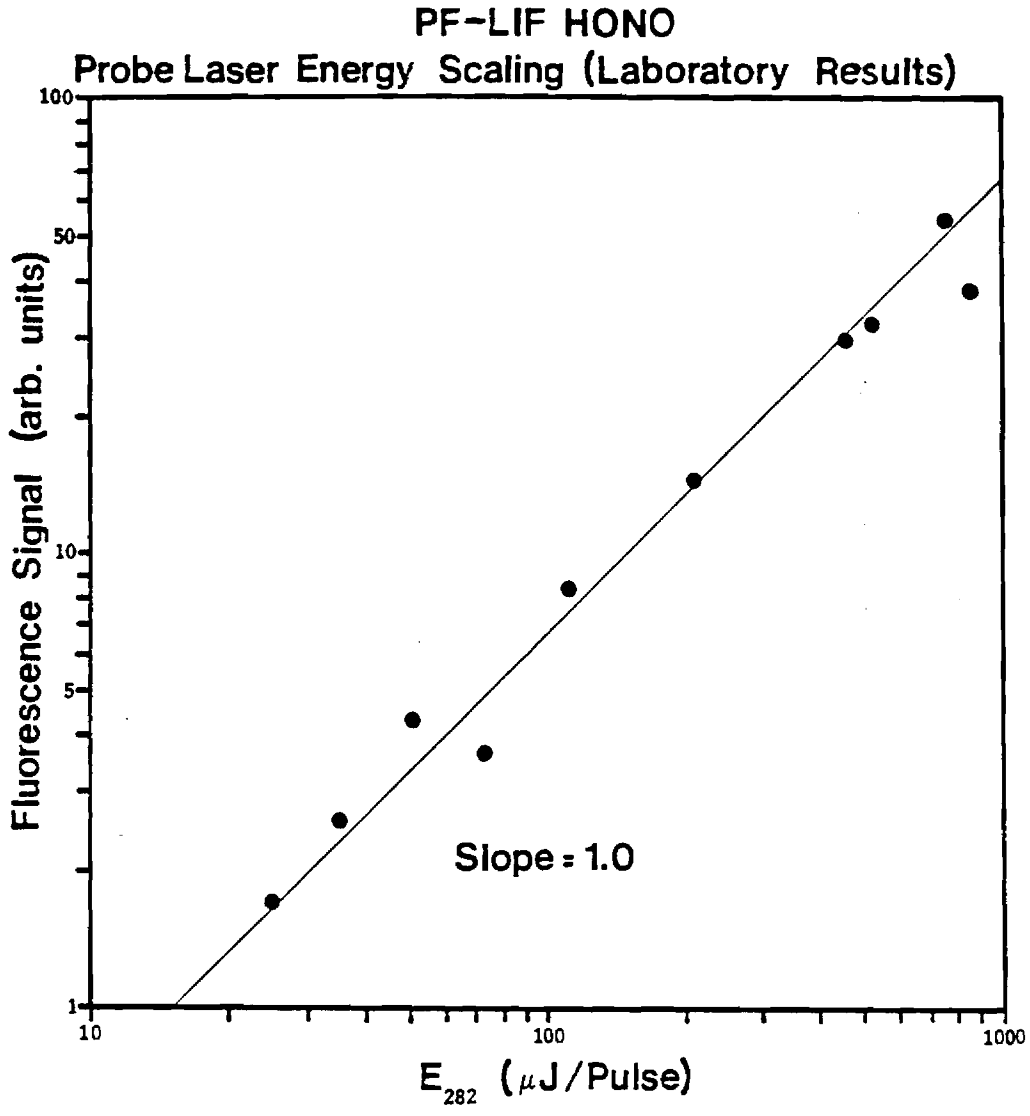


Fig. 11 : Probe Laser Energy Scaling of PF-LIF HONO Fluorescence Signal (Laboratory Results)

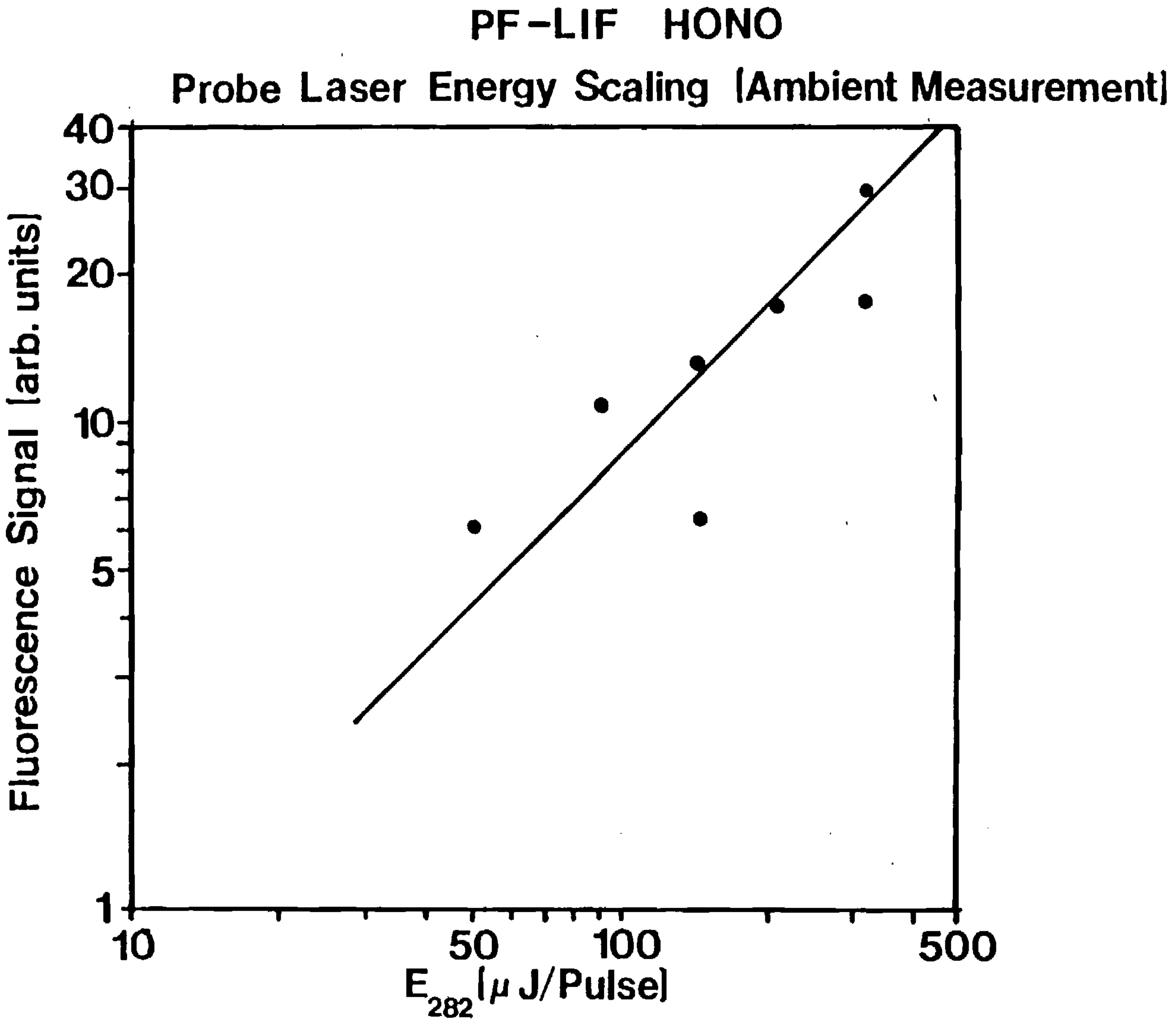


Fig. 12 : Probe Laser Energy Scaling of PF-LIF HONO Fluorescence (Outside Air Measurements)

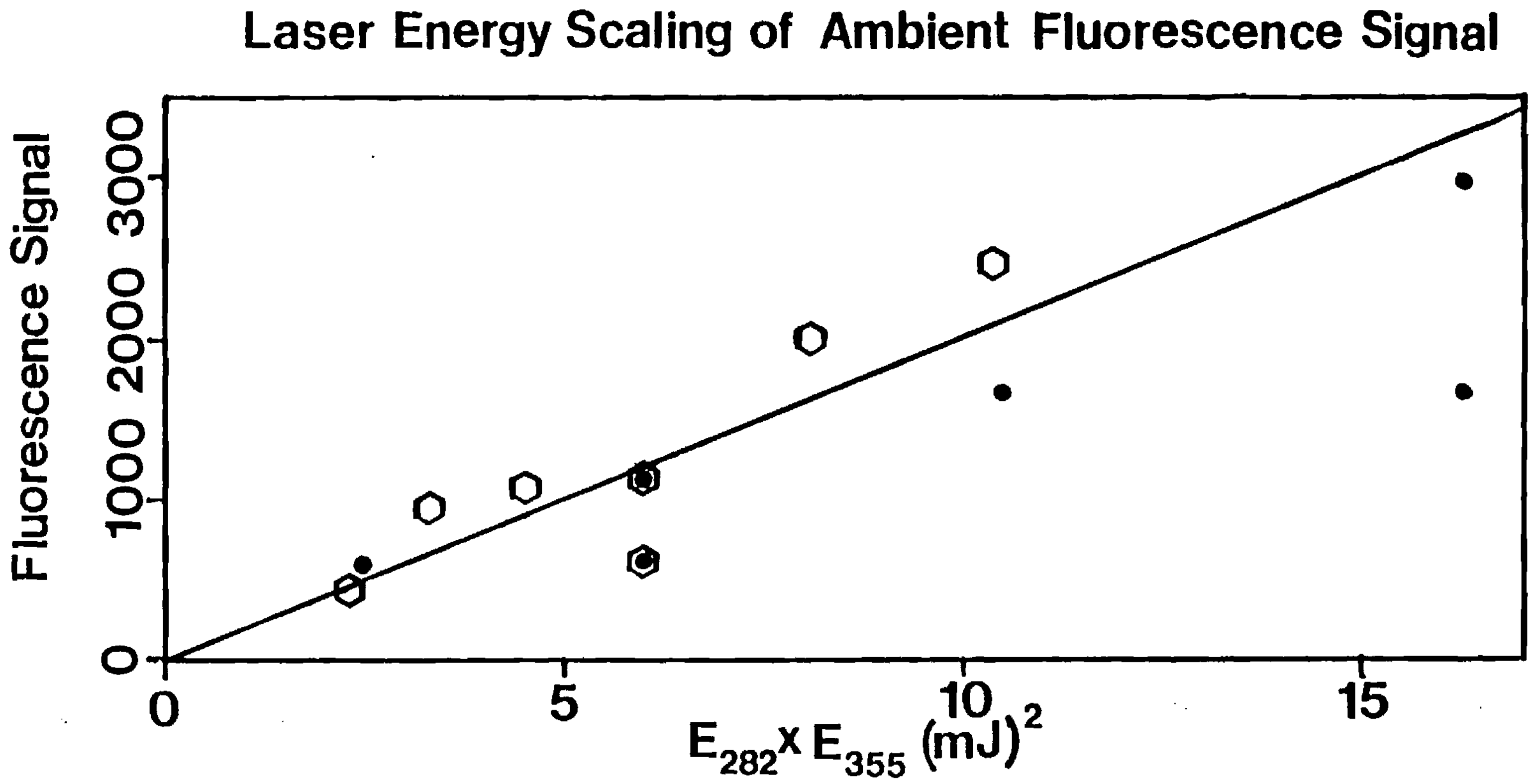


Fig. 13 : Photolysis/Probe Laser Energy Scaling of PF-LIF HONO Signal (Outside Air Measurements); Measurements made with constant 355 nm energy;

• Measurements made with constant 282 nm energy.

linear response of the PF-LIF technique for the detection of HNO_2. The latter results are shown in Fig. 14. This figure demonstrates the linear response of the PF-LIF system over a HNO_2 concentration range of 185 pptv to 150 ppbv. The upper limit on the signal linearity was set, in this case, by photomultiplier tube saturation. Tests at reduced photomultiplier tube gain indicated a linear response over the concentration range from 60 ppbv to 10 ppmv. These results indicate an available dynamic range for the system of at least five orders of magnitude. The lower limit of 185 pptv was, once again, not a fundamental system limitation but rather the lowest concentration of HNO_2 that could be reliably generated by the existing three stage dynamic dilution system.

Ambient air calibrations were performed using both the O_3/H_2O and the HNO_2 standard addition approaches. The results of these calibrations are given in table V. In each case the calibration numbers have been normalized to a set of "standard" conditions in order to facilitate comparison between the different measurements. The standard conditions selected involved an integration time of 30 sec, (300 lasershots), 100 mJ/pulse of 355 nm energy, and 0.1 mJ/pulse of 282 nm laser energy. In addition, all measurements were recorded using a two photomultiplier tube sample cell configuration. Finally, all measurements were referenced to atmospheric dry conditions.

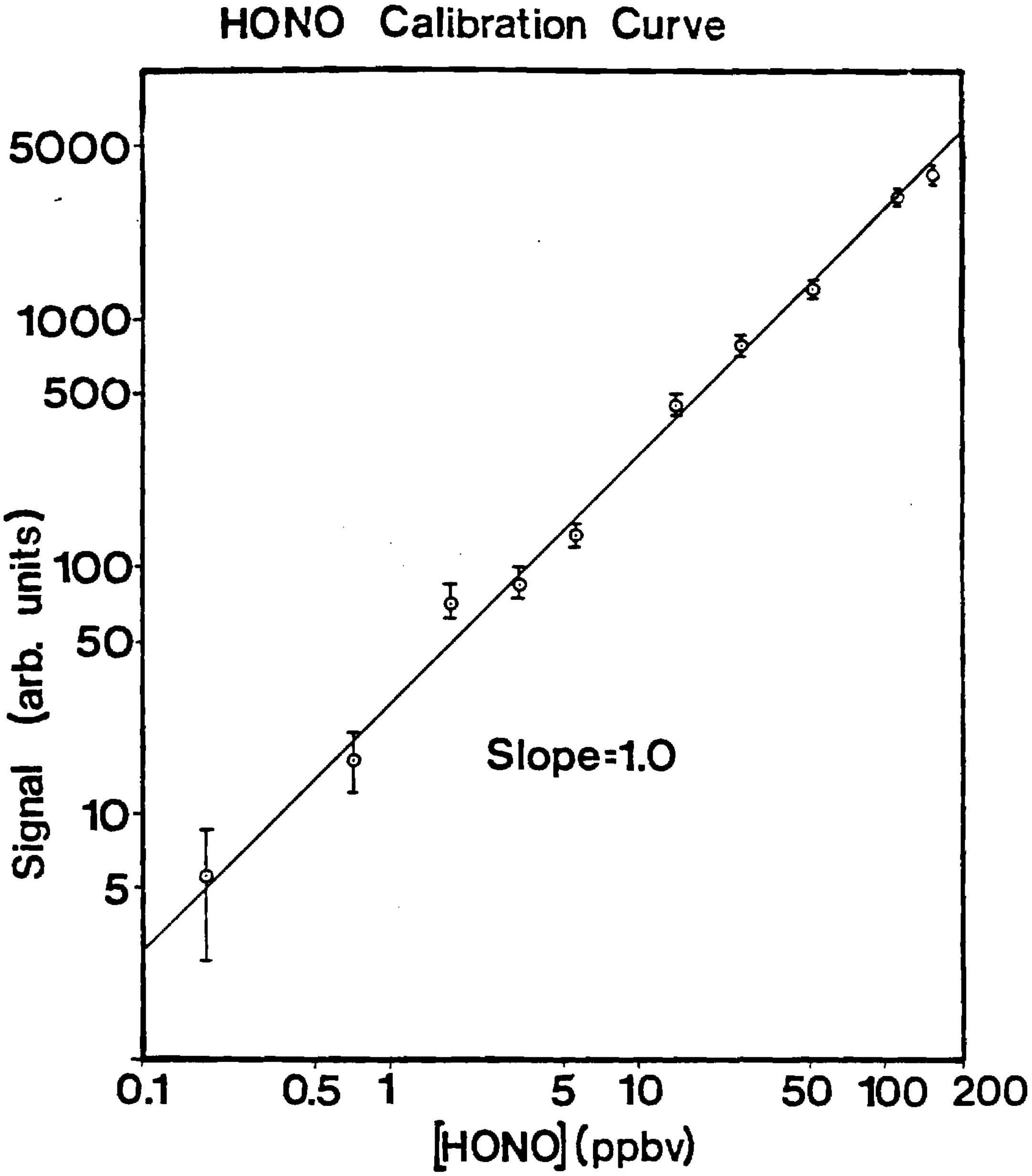


Fig. 14 : Calibration Curve for PF-LIF HONO Detection System (Laboratory Results)

Table V

Normalized Ambient Air System Calibration Numbers

Date	HONO standard addition	O_3/H_2O type calibration
12/23/85***	----	1740*
12/24/85***	1603**	----
1/18/86***	2002	----
2/2/86	----	1909
2/3/86	----	2466
2/5/86	2970	2525
2/9/86	----	2145
2/11/86	----	1844
2/16/86	1953	----
2/28/86	2116	----
3/9/86	2306	----
3/16/86	----	1699
3/20/86	2064	----
3/21/86	2125	1936
3/23/86	2613	----
3/29/86	----	2080
average	2195 ± 374 (1σ)	2038 ± 279 (1σ)

*All O_3/H_2O calibration numbers are based on a value for E_1 of 0.048.
**Units on calibration numbers are photons/300 laser shots/100 mJ (355 nm)/0.1 mJ (282 nm)/dry conditions/ppbv HONO
***These calibration numbers also required scaling for a change in optical filter pack transmission (~1.7x).

As can be seen from Table V, the good agreement between the two calibration approaches (agreement to within about seven percent) can be taken as at least qualitative evidence that any systematic errors present in our calibration procedures are small.

Interference and Sample Loss Tests - As mentioned previously, two of the most important considerations in testing any in-situ type of detection system are establishing that the system is free from interferences and that sampling losses are equally insignificant. In this regard the results of the tests described above place upper limits on certain types of interferences. For example, the observation that the observed fluorescence signal was linear in both 355 and 282 nm laser energy preclude any significant contribution from two photon processes involving either beam, including the well documented O_3/H_2O interference problem. Additional interference tests performed on the PF-LIF HNO_2 detection system have been discussed by Rodgers (1986) and will not be further discussed here except to note that no evidence of interference from any other atmospheric species could be identified.

Sample losses of HNO_2 were evaluated on two occasions as part of the HNO_2 standard addition calibrations. As shown in Fig. 6, the PF-LIF HNO_2 air sampling system was equipped with three gas injection points. The first was located 0.3 m from the inlet, the second port was located 4.0 m from the inlet, and the last injection point was positioned just before the sampling cell inlet. In these sample loss tests a calibration gas mixture was sequentially injected at each point and the resulting fluorescence signals recorded. The results of these tests are summarized in table VI.

Table VI

Sample Loss Tests

Date	1/18/86	3/20/86
Position #1 (0.3 m from inlet)	1861 ± 303(2σ)*	2064 ± 103
Position #2 (4.0 m from inlet)	2002 ± 245	2121 ± 109
Postion #3 (at sampling chamber)	2289 ± 277	1965 ± 144

*Calibration numbers in photons /300 laser shots/ 100 mJ (355 nm)/ 0.1 mJ (282 nm)/ dry conditions/ ppbv HONO.

The 1/18/86 measurements were made under worst case conditions of misty rain and near 100 percent relative humidity, while the 3/20/86 measurements were made under clear conditions. These tests indicate that, in agreement with theoretical estimates, sampling losses in our system were small.

Comparison with Theory - In assessing the performance of a detection system, it is often useful to compare observed system performance with that which might have been expected theoretically. Substituting the standard conditions used for normalization of the system calibration numbers: (i.e. a 282 nm laser energy of 0.1 mJ/pulse, dry conditions , and an integration period of 300 laser shots) into equation II, a "theoretical" calibration number of 2580 was calculated. This value may be compared to those of the HNO_2 standard addition approach (2195 ± 374) and the O_3/H_2O calibration method (2038 ± 279). The experimentally derived values were therefore about twenty percent lower than the theoretical estimate. Considering the combined uncertainties of the theoretical estimate and the experimental measurements, we view this level of agreement to be excellent.

C. NO_3 Long-Path Differential Absorption

The measurement of tropospheric nitrate radical has been reported by at least three groups using the long-path differential absorption technique (Burrows et al., 1985). In all these cases, single ended optical path lengths in excess of 4 km have been used with minimum detectable absorbances of $\leq 10^{-4}$ (base "*e*"). As suggested in Fig. 1 (Section I), for purposes of understanding the nighttime chemistry of NO_3 these long-path length studies raise serious questions concerning the homogenity of the atmosphere over the extended distance of the measurement. The objective of our research effort has therefore been to develop a moderate path length instrument ($\leq$ 0.5 km) using a folded path geometry such that the measurement of NO_3 could be made simultaneously with the measurement of other key species within the ~150m x 150m confines of the sampling site atop Stone Mtn.

Initial evaluation of the instrument design was based on detailed discussions with individuals at the NOAA Boulder, Colo. Aeronomy lab and individuals in Germany working under Dieter Ehhalt. The major concern of these investigators was the ability to utilize commercially available diode array detector systems. These concerns focused on the commercial systems inability to reduce diode array dark count to sufficiently low levels and the need for a higher dynamic range 16 bit data acquistion system rather than the 14 bit system available in commercial systems. Our approach to this potential problem was to carry out a series of tests involving commercially available diode array detectors prior to initiating the ~1 1/2 man year development task associated with construction of a custom diode array detector. After reviewing the specifications of the system that was commercially available, it was decided that at least two systems were worthy of further testing (EG&G-PARC and Tracor Northern). Arrangements were then made to obtain both of these detector systems for evaluation. (It should be noted that neither manufacturer would guarantee performance of their detectors in the $\leq 10^{-4}$ absorbance range of interest.)

Tests carried out at our Stone Mountain field sampling facility demonstrated that the EGG-PARC system was considerably superior (>20 fold) in performance over the Tracor Northern system. The detector noise limit of the PARC system was found to be quivalent to 5×10^{-6} abs (base *e*) for detector array scan times of <100 ms, using back-to-back signal-background measurements. However, it was found that the long term drift component of the light source could raise this limit to $\sim1\times10^{-3}$ abs (base *e*). Subsequent tests have demonstrated that the long term drift in the light source can be minimized by the incorporation of a paired signal/reference spectra measurement. The necessity to cool the diode array below the limits obtainable with the thermoelectric cooling system commercially provided was also evaluated. The dark count noise was found to be linearly proportional to the optical integration time (time between scans) of the diode array. This integration time is dependent on the lamp flux reeaching the detector. Groups operating at long path length (4-10 km) have had to utilize optical integration times on the order of 3 - 15 seconds in order to optimally utilize the full scale output range of the detector. For such long integrations times it is necessary to cool the diode array assembly to dry ice temperatures. However, at the moderate path lengths associated with our system it has been found that sufficient light intensity can be achieved to provide full scale diode array output in <16 ms. On this time scale the need for dry ice cooling appears to be unnecessary. The cross over point now seems to occur around 200 ms. Further tests carried out by our group have also demonstrated that the need for a 16 bit data acquisition system is only required when operating below 5×10^{-6} abs (base *e*).

Thus, based on these test results, we believe that a moderate path length differential absorption spectrometer using a commercially available diode array detector can be constructed for the measurement of tropospheric NO_3. The final system which we have now acquired consists of:

i) 0.125m Crossed Czerny Turner Polychromator with 600 g/mm grating having resolution of 0.3nm/channel.

ii) 150W Quartz hologen light source with an integral 6" spherical reflector.

iii) 10" diameter f=4.5 Telescope

iv) PARC 1024 element diode array detector

v) Hewlett Packard series 300 computer for data reduction

and vi) Vincent associate dual shutter control system for background and reference spectrum acquisition.

Further tests on the above system have demonstrated two limitations which have kept the system from performing below the 3×10^{-4} abs level (base *e*). These being (1) intermittent radio frequency interference from a 300W 30 MHz transmitter located within 20ft of the instrument, and (2) long term drift in the source lamp color temperature. The radio transmitter is scheduled to be relocated in the spring 1987 and current work is underway to construct an optical feedback control for the lamp power supply which will maintain the lamp color temperature to $< \pm 1°$ K.

Based on the tests carried out to date, the final system should be capable of detecting tropospheric NO_3 at levels below 10pptv. Detailed performance specifications are given in Table VII. This level of performance will provide a unique instrumental measurement system capable of monitoring ambient NO_3 levels in the immediate vicinity of the Stone Mountain field sampling station. This capability should provide a powerful tool in the assessment nighttime N_xO_y

TABLE VII

NO_3 ABS. Band	Spectral Resolution	NO_3 Peak Cross Section	Path Length	Minimum Detect. Abs (base *e*)	Integ. Time	Minimum Detect.Conc.
663 nm	0.6 nm	$1.8x10^{-17}cm^2$	250m	$\leq 1x10^{-4}$†	16min	≦ 10ppt
663 nm	0.6 nm	$1.8x10^{-17}$	500m	$\leq 1x10^{-4}$†	16min	≦ 50ppt
626 nm	0.6 nm	$1.2x10^{-17}$	250m	$\leq 1x10^{-4}$†	16min	≦ 15ppt
626 nm	0.6 nm	$1.2x10^{-17}$	500m	$\leq 1x10^{-4}$†	16min	≦ 8ppt
663 nm	0.6 nm	$1.8x10^{-17}$	500m	$2x10^{-5}$‡	30min	1pptv

† nominal sensitivity limit projected for current system

‡ instrumental limit of sensitivity projected for current system

chemistry, devoid of the problems associated with conventional long path (4-10km) measurement systems.

Although funds from our CRC contract are now totally expended, we believe the NO_3 detection system is critical to our long term goals of elucidating nighttime N_xO_y chemistry. For this reason, we are continuing this development effort at a somewhat reduced pace using research funds provided by Georgia Tech. It is our expectation that within the year CRC can once again provide support for what is shaping up to be one of the most comprehensive arrays of N_xO_y instrumentation anywhere in the U.S.A. for purposes of studying nighttime and daytime N_xO_y chemistry.

III. FIELD STUDY RESULTS

A. Stone Mountain Nighttime NO Studies

As discussed in our 2nd year CRC annual report, our effort at Georgia Tech to understand the presence of low levels of NO in the nighttime atmosphere dates back to the summer of 1983. At that time, NO levels in the 10-12 pptv range were measured at Wallops Is., Va. over several nights of sampling as part of our involvement in NASA's CITE I (Chemical Instrumentation Test and Evaluation) Program. Recall, that these NO observations were reported by three different scientific teams (Torres, NASA Wallops Is.; M. McFarland/M. Carrol/ B. Ridley, NOAA and NCAR; and D.Davis, J. Bradshaw, M. Rodgers, and S. Sandholm, Ga. Tech.), using three different instruments involving two different techniques, i.e. two chemiluminescence systems and Georgia Tech's two-photon laser-induced fluorescence (TP-LIF) instrument. Still later, in November of 1983, nighttime observations of NO in the concentration range of ~ 1 pptv were recorded by the Georgia Tech group at middle free-tropospheric altitudes (i.e. 5-9 km) aboard NASA's Convair 990. However, in the latter case even though there were again three NO instruments aboard the aircraft (two chemiluminescence systems and Ga. Tech's TP-LIF instrument) only the TP-LIF system had the necessary detection sensitivity to measure NO at the 1 pptv level with an S/N ratio significantly greater than 2/1.

These early nighttime NO results, derived from the NASA GTE/CITE program, suggested to us that there may, in fact, be chemical processes taking place at night that were still not well understood. In particular, we raised the question whether or not there might not be nighttime N_xO_y chemical processes operating that were capable of maintaining low but persistent steady-state levels of NO, even in the presence of excess O_3.

It was with this information base, then, that our group began pursuing the nighttime NO chemistry question at Georgia Tech's Stone Mt. field-sampling station.

The results from these experiments, starting in the fall of 1984, have proven to be intriguing. In short, the results from the spring 1985 sampling period showed average nighttime NO levels to be ~ 11 pptv, with a typical NO concentration range of 3 to 20 pptv. To our surprise, however, the average NO value from the spring of 1985 was nearly a factor of 2 to 2.5 times higher than that recorded during the fall of 1984. Subsequently, during the summer of 1985, it was discovered that one of four buildings atop Stone Mountain was heated by a natural gas burner that was typically activated during late October. It was not until the late fall of 1985, therefore, that we were able to initiate a new sampling effort to determine the effect of this potential source of NO contamination. At that time, we arranged with the Stone Mt. park service to have a timer switch installed on the gas heater such that between the hours of 6 p.m. and 6 a.m. the unit was shut down. Only in the event of freezing temperatures would an overriding relay (connected to an outdoor temperature sensor) activate the gas heater and at the same time transmit a warning signal to our data-logging computer at the field-sampling station.

The results from the fall 1985 experiments showed that over a period of time lasting ~ 1½ weeks (a time period preceding the activation of the gas heater), the average nighttime NO level was within 20% of that observed during the spring of 1985, i.e. approximately a factor of two lower than that observed in the fall of 1984. Upon activating the gas heater in early November, without the timer switch on, the average level of nighttime NO was again observed to climb to levels similar to those in the fall of 1984, however considerable variability in levels was observed. The variability observed could be most easily understood in terms of the wind direction as related to: (1) the position on top of the mountain of the Georgia Tech sampling tower building relative to the "theater building" which housed the gas heater; and (2) in terms of the sampled air coming from a wind direction that would have brought it in contact with the city of Atlanta, i.e. the Atlanta city plume. In fact, on at least two nights during which time the wind was directly out of the east and thus moved the exhaust plume from the "theater building" directly to the Georgia Tech sampling Tower building (a worst case contamination scenario), controlled tests were performed in which the gas heater was pulsed "on" and "off". In these experiments buring periods of 5 minutes were used with approximately 15 minutes between burns. The results from these tests (again representing a worst case wind direction scenario) showed that the "on" versus "off" NO levels varied by ~ one order of magnitude, with the "on" cycle being the highest.

Upon activating the timer switch, which as stated earlier was designed to keep the gas heater in the "off" configuration between the hours of 6 p.m. and 6 a.m., a new set of nighttime NO measurements was recorded. In this case, the NO results were in good agreement with those collected earlier in the Fall, preceeding the activation of the heater. It follows, therefore, that they were also in generally good agreement with the nighttime NO levels observed in the spring of 1985.

In summary, although the discovery of the gas heater in the "theater building" atop Stone Mt. resulted in the rejection of the Fall 1984 nighttime ambient NO data base, we now have demonstrated that consistent nighttime NO data exists for both the spring of 1985 and early/late Fall 1985. The average nighttime value of NO for these measurement periods was ~ 10 pptv while the O_3 level typically ranged between 15 to 40 ppbv. In addition, as reported in our 2nd year CRC report, two aircraft flight operations over Stone Mt. and the surrounding countryside during the summer of 1985 revealed NO levels ranging from 2.5 to 5 pptv over the geometric altitudes of 1000, 2000, and 4000 ft. These values are well within the range of NO levels observed at the Stone Mt. station itself. Finally, as again reported in our Year 2 CRC report, extensive tests were performed at our Stone Mt. sampling station to establish the absence of any problems as related to: (1) laser generated NO formation, (2) the NO detection specificity of the TP-LIF system, and (3) the sampling integrity of our sample inlet lines. All of these test results, within the observed natural variability of ambient NO (typically ± 25%), were found to support the validity of our observed ambient levels of nighttime NO. Thus, as of this writing, we have no evidence that suggests that the Stone Mt. nighttime observations are not representative of the true background nighttime levels of NO. However, as pointed out in our 2nd Year report, our efforts to develop a mechanism(s) to explain the presence of this NO (in the presence of excess O_3) have been only partially successful. On a more optimistic note, though, recently a totally new look has been taken in examining the nighttime NO question and this involves the possible role of HNO_2 in the nighttime atmosphere. We are speculating, for example, that reactions of HNO_2 in liquid aerosols (under nighttime conditions) could serve as a steady source of NO. Suffice it to say, more work still remains to be done on the nighttime NO question.

B. Airborne $NO/NO_2/O_3$/UV Flux Photoequilibrium Studies

Although clear air measurements of NO and NO_2 have been reported on for nearly a decade now, the fundamental question whether the observed atmospheric ratio for these two key species is in agreement with that predicted from fast photochemical theory has yet to be answered when examined in the context of a wide range of environmental conditions.

The simplest photochemical scenario involves the three reaction sequence (9)-(11):

$$(9) \quad NO + O_3 \rightarrow NO_2 + O_2$$

$$(10) \quad NO_2 + h\nu \rightarrow NO + O$$

$$(11) \quad O + O_2 \xrightarrow{M} O_3$$

Photostationary-state conditions would then require that equation IV be satisfied:

$$\text{IV} \qquad \frac{J_{10}\ [NO_2]}{k_9[NO]\ [O_3]} = 1$$

In fact, except for some cases involving urban plumes or urban environmental conditions, the experimentally determined numerical value of equation IV has typically been found to exceed the assigned value of 1. In some cases, experimental values have been measured as high as 9 or 10, although values of 2 to 5 appear to be more common. Explanations for the departure from the photoequilibrium state as defined by eq. IV have ranged from systematic errors in the measurement of the levels of NO and NO_2 to the possibility that reactions such as (12), (13), and (14) were critical in establishing the photostationary state ratio of NO_2/NO.

$$(12) \quad HO_2 + NO \rightarrow NO_2 + OH$$

$$(13) \quad CH_3O_2 + NO \rightarrow NO_2 + CH_3O$$

$$(14) \quad RO_2 + NO \rightarrow NO_2 + RO$$

where "R" represents all other possible organic groupings beyond CH_3. Assuming reactions (12) → (14) do contribute significantly to the conversion of NO to NO_2, the photostationary state equation IV must be modified according to:

$$V \qquad \frac{J_{10}\ [NO_2]}{[NO]\ (k_9\ [O_3] + k_{12}\ [HO_2] + k_{13}\ [CH_3O_2] + k_{14}\ [RO_2])} = 1$$

However, to test equation V rigorously, one must be able to experimentally measure the concentrations of the independent variables: HO_2, CH_3O_2, and RO_2. As of this writing, this is an experimental feat that is still beyond the community's instrumental capability. In lieu of this instrumental capability, one must depend heavily upon current photochemical models to evaluate the stationary state values of HO_2, CH_3O_2, and RO_2. Although the latter calculations can be handled, if they are to actually be used to compare against experimental measurements of NO_2/NOI, several additional atmospheric variables must be measured simultaneously with those already listed (NO, NO_2, O_3, UV flux, T, P), namely: CO, H_2O, and NMHC (non-methane hydrocarbons).

It was in the context of the above setting that the Georgia Tech group saw an opportunity in 1986 to make what we believed would be a significant contribution to the CRC N_xO_y chemistry program. The contribution, in this case, would involve improving our understanding of the fast photochemical cycling of daytime NO and NO_2. The opportunity made available to us came in the form of our participate in NASA's GTE/CITE II field experiment.* This airborne field study provided an opportunity to address the NO/NO_2 photostationary state question from several unique points of view, for example: as part of this field

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* Our involvement in these experiments was made possible by the joint funding of our program by NASA and CRC; thus, our final results will acknowledge financial assistance from both organization.

study four totally different NO_2 sensors were intercompared, i.e. NASA Wallops Island's ferrous sulfate NO_2 catalytic converter with chemiluminescence NO detection; NOAA/NCAR's CW NO_2 photoconverter with chemiluminescence NO detection; York University's tunable diode laser NO_2 detection system; and Ga. Tech's photofragmentation two-photon laser-induced fluorescence NO_2 sensor. Additionally, both the NOAA/NCAR and Georgia Tech instruments were designed to simultaneously measure NO and NO_2. Finally, the sampling profiles laid out for the CITE II study included measurements under both marine and continental (heavily polluted to slightly polluted) environmental conditions as well as boundary layer and free tropospheric sampling. In all cases the critical variables required to support modelling calculations, (e.g. O_3, UV flux, CO, H_2O, PAN, HNO_3, NO_y, Temp., and Pressure) were continuously monitored by either NASA personnel or other scientific investigators.

For the readers convenience, a listing of the various flight missions carried out during the CITE II program has been provided here in the form of Table VIII.

TABLE VIII: CITE II FLIGHT MISSIONS
(Aug. 15 → Sept. 4, 1986)

Flight #	Date	Scene	Altitude Profile	Air Mass Type
1	Aug.15	Oceanic, daytime	All sampling at 16,000 ft.	non-tropical maritime
2	Aug.19	Oceanic, daytime	50% at 16,000 ft. 50% at 500 ft.	tropical maritime
3	Aug.21	Oceanic, daytime	85% at 16,000 ft. 15% at 500 ft.	non-tropical maritime
4	Aug.23/24	Continental, nighttime	All sampling at 16,000 ft.	tropical maritime to moderately polluted continental
5	Aug.26	Oceanic, daytime	50% at 16,000 ft. 30% at 2,500 ft. 20% at 500 ft.	Mixed Continental and Maritime
6	Aug.28	Continental, daytime	40% at 16,000 ft. 25% at 12,500 ft. 20% at 8,500 ft. 15% at 500 ft.	TBD*
7	Aug.30	Oceanic, daytime	50% at 16,000 ft. 25% at 7,500 ft. 25% at 500 ft.	non-tropical maritime
8	Aug.31	Continental, daytime	All sampling at 16,000 ft.	TBD*
9	Sept.2	Continental, daytime	50% 20,000 ft. 50% 8,000 ft.	TBD*
10	Sept.4	Continental, daytime	100% at 16,000 ft.	TBD*
11	Sept.4	Continental, daytime/nighttime	100% at 16,000 ft.	TBD*

TBD* - To Be Determined from air trajectory analysis.

Although the data from CITE II is still being analyzed, at least three preliminary findings are worth mentioning even at this early date. (The entire data analysis from Georgia Tech's involvement in the CITE II program will be provided to CRC at a later date.) (1) It has been clearly demonstrated that NO_2 catalytic converters result in excessively high readings of NO_2 (relative to the tunable diode laser, the CW NO_2 photoconverter, and Georgia Tech's PF/TP-LIF NO_2 system) under nearly all atmospheric conditions sampled during the CITE II program. Although previous investigators have provided data that has suggested that there could be chemical interferences in the use of catalytic converters to measure NO_2, there seems to have persisted a general feeling in the community that with proper corrections the catalytic converter system could still be used to make reliable measurements of NO_2. In fact, this may still be true for a very limited set of environmental conditions (e.g. an urban smog environment). On average, however, all efforts to explain the deviation between the catalytic system and the three other NO_2 sensors in terms of the levels of PAN, HNO_3, and NO_y failed to show any systematic trend. (2) Georgia Tech's PF/TP-LIF NO_2 sensor was shown to be free of any apparent chemical interferences (including those from HO_2NO_2 and N_2O_5). Furthermore, a regression analysis of Georgia Tech's NO_2 data versus the average NO_2 value, as defined by the York Univ., NOAA/NCAR, and Ga. Tech NO_2 measurements, resulted in a slope of 1.05 with an intercept of only 9 pptv. (3) Preliminary modelling calculations, as related to NO_2/NO ratios measured in clean maritime air, indicate good agreement between experiment and theory within the 1σ error bars of the measurements and the theoretical calculations. These calculations also indicate that only the NO to NO_2 conversion reactions (9), (12) and (13) are required to achieve agreement between theory and experiments, i.e. there was no indication of RO_2 radicals playing a significant role in this conversion.

C. Urban Atlanta HNO_2 Studies

(1) Introduction

The HNO_2 measurements reported here were made on the campus of Georgia Institute of Technology between mid-December, 1985 and the end of March, 1986. Georgia Tech is located in Atlanta, a city of approximately two million persons (SMSA), situated in north-central Georgia in the foothills of the southern Appalachians. The terrain in and around Atlanta is generally hilly and has a mean altitude of 300 m (MSL). As seen from Fig. 15, Georgia Tech is located approximately four kilometers north of the central business district near the intersection of two major interstate highways (I-75 and I-85). The Baker building, the site of the measurements, borders a lightly travelled street near the northwest boundary of the campus. The peachtree ridge, the major north-south geographical feature of the area, is located about two kilometers toward the east.

<u>Traffic Patterns</u> - Most of the high-rise buildings which comprise the Atlanta skyline are located either in the central business district or along the peachtree ridge. Substantial development has also occurred in the northern portion of the city along I-285, principally between its intersection with I-75 and I-85. Automobile traffic in Atlanta is dominated by movement of commuters between their homes and these developed areas. In the vicinity of Georgia Tech, this commuter traffic is channeled largely through the interstate highway system and the major streets which are located on, or adjacent to, the peachtree ridge. During peak hours, the traffic loading on the downtown

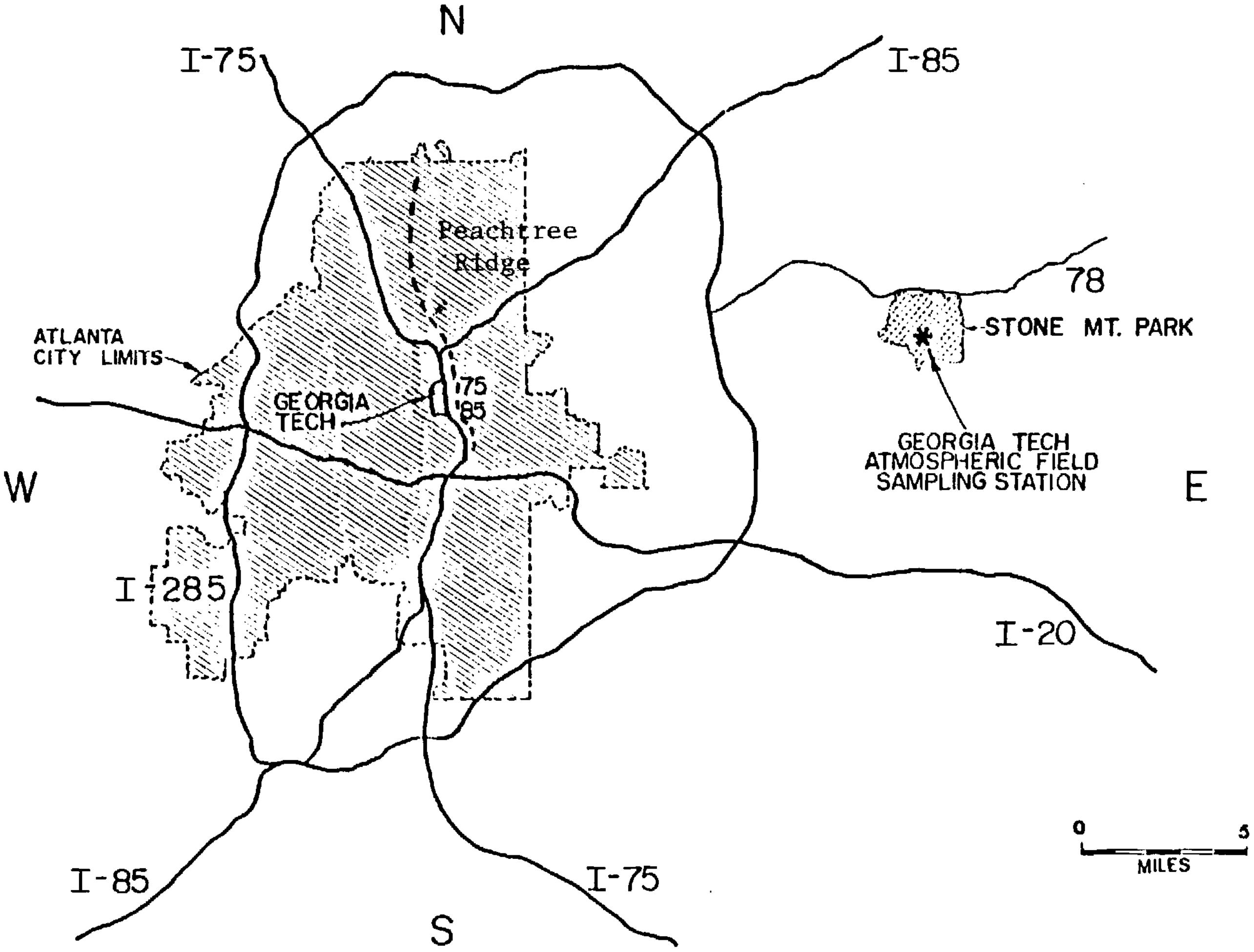

Figure 3-1: Map of Georgia Tech Sampling Location within Atlanta, Georgia

interstate connector is very heavy (~ 10,000 cars/hr.) and therefore provides a major source of atmospheric pollutants, including HNO_2 precursors and/or HNO_2 itself. However, despite its urban setting, traffic within the boundaries of the Georgia Tech campus is relatively light.

Late in the evening, traffic both on the campus and along the service streets in the vicinity is very light. In contrast, the interstate highways maintain a significant traffic volume until well after midnight.

Meteorological Patterns - During the winter and early spring in Atlanta, the time period for these measurements, the winds are predominantly from the northwest and average about five meters per second (NOAA (1983)). Temperatures in the area are rather mild, due in part to the proximity of both the gulf of Mexico and the Atlantic Ocean (about 400 km to the south and southwest, respectively). Normal daytime highs range from about 10° Cin January to nearly 20° C by late March (NOAA (1984)). Nighttime lows are approximately 10° C cooler. During these months, ground fogs are common, occuring about one day in three (NOAA (1985, 1986a,b,c)). Normal precipitation during this period (December-March) is nearly 50 cm. During the period of these measurements, a severe drought was underway in the region and actual precipitation was less than 25 cm.

Chemical Variables - In addition to measuring atmospheric HNO_2 concentration levels, a number of ancillary parameters were recorded to provide information on the prevailing meteorological and chemical environment. Table IX lists the chemical sensors used in conjunction with this study.

Table IX

Ancillary Chemical Measurements

Species	Methodology	Operator
O_3	UV absorption	Ga. Tech
NO	chemilumenescence	DNR[1]
NO_2	chemilumenescence + convertor	DNR
NO_x	chemilumenescence + convertor	DNR
SO_2	pulsed fluorescence	DNR
HNO_3	nylon filter	Ga. Tech[2]
aerosol ammonium	filter matte	Ga. Tech[2]
aerosol sulfate	filter matte	Ga. Tech[2]
aerosol nitrate	filter matte	Ga. Tech[2]
UV solar flux	Eppley filter radiometer	Ga. Tech
short wave solar	Eppley pyranometer	Ga. Tech

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[1] Georgia Department of Natural Resources, NAMS site at Georgia Tech

[2] Filter collection by Georgia Tech and analysis by Dr. Barry Huebert of Department of Chemistry, Colorado College, Colorado Springs, CO.

Meteorological Variables - The meteorological instrumentation available for this investigation was less extensive than that available for the chemical parameters. On site data collection was limited to twice hourly measurements (during sampling periods) of temperature and dew point made with a sling psychrometer and visual observations of cloud cover. In addition, the barometric pressure and tendency as well as wind speed and direction were recorded from the hourly updates provided by the N.O.A.A. weather radio station at Hartsfield International Airport located some 16 kilometers south of Georgia Tech.

(2) Summary of Measurements

Measurements of atmospheric HNO_2 were made from the Baker building site at Georgia Tech during twenty-seven evenings between mid-December, 1985 and the end of March, 1986. Of these measurement periods, eight were dedicated to various types of system tests (e.g., tests with aerosol filters to try to establish the source of the background fluorescence noise) with the remainder involving ambient measurements. Nitrous acid concentration measurements were successfully made during fifteen of these nineteen opportunities. Of the four non-successful runs, for two measurement periods, which included one during midday, only upper limits values of HNO_2 could be determined. The remaining two measurement efforts had to be halted due to equipment failures. Of the fifteen periods in which measurements were made, each included at least one system calibration. These HNO_2 data are summarized in Table X. Complete tabulated data for these measurement periods, including the available ancillary measurements, are given in Appendix A. In addition to these data tables, data from several of the measurement periods have been plotted along with some of the controlling variables in the accompanying figures.

Table X

Summary of Ambient HONO Measurements made on the Georgia Tech Campus in Atlanta, Georgia

Starting Date	Measurement Period (EST)	Wind Direction	Ancillary Measurements	Max [HONO] (ppbv)	Min [HONO] (ppbv)
12/23/85	2005-2115	SW	M1*	0.32	0.26
12/24/85	1410-1535	SW	M1	<0.24	
1/18/86	2106-2137	SW	M1	<0.12	
2/2/86	2030-2210	SW	M1	0.35	0.18
2/3/86	2055-2215	SSW	M1	0.41	0.34
2/5/86	2335-0320	SE	M1,M2	0.24	<0.10
2/9/86	2025-2250	SE	M1,M2,O3,NA	1.8	0.36
2/11/86	2020-2255	NW	M1,M2,O3	2.1	0.49
2/16/86	1800-0918	S	M1,M2,O3,D,NA	3.1	<0.03
2/28/86	1910-0145	NW	M1,M2	3.9	0.11
3/9/86	1850-2055	S	M1,M2,M3	0.63	<0.15
3/16/86	1600-2250	NW	M1,M2,O3,D,S	0.92	0.07
3/20/86	2010-2305	NW	M1,D,O3	0.95	0.64
3/21/86	2025-0926	NW	M1,M2,O3,NA,D,S	1.9	<0.05
3/23/86	2216-0134	NW	M1,D	2.6	1.4
3/28/86	2046-0335	E	M1,O3	6.4	1.6

*For ancillary measurements:
M1 = National Weather Service data
M2 = Temperature and dew point
M3 = Wind Speed and direction
O3 = Ozone Concentration data
NA = Nitric acid and aerosols
D = NO, NO$_2$, NO$_x$ and SO$_2$ (Ga. Dept. of Natural Resources)
S = UV/visible solar flux

Figure 16 shows a diurnal plot of the measured HNO$_2$ and O$_3$ levels recorded on 2/16-17/86. Figure 17 presents averaged nitrogen oxide concentrations (along with SO$_2$) provided by the Georgia Department of Natural Resources from their NAMS site at Georgia Tech during the same

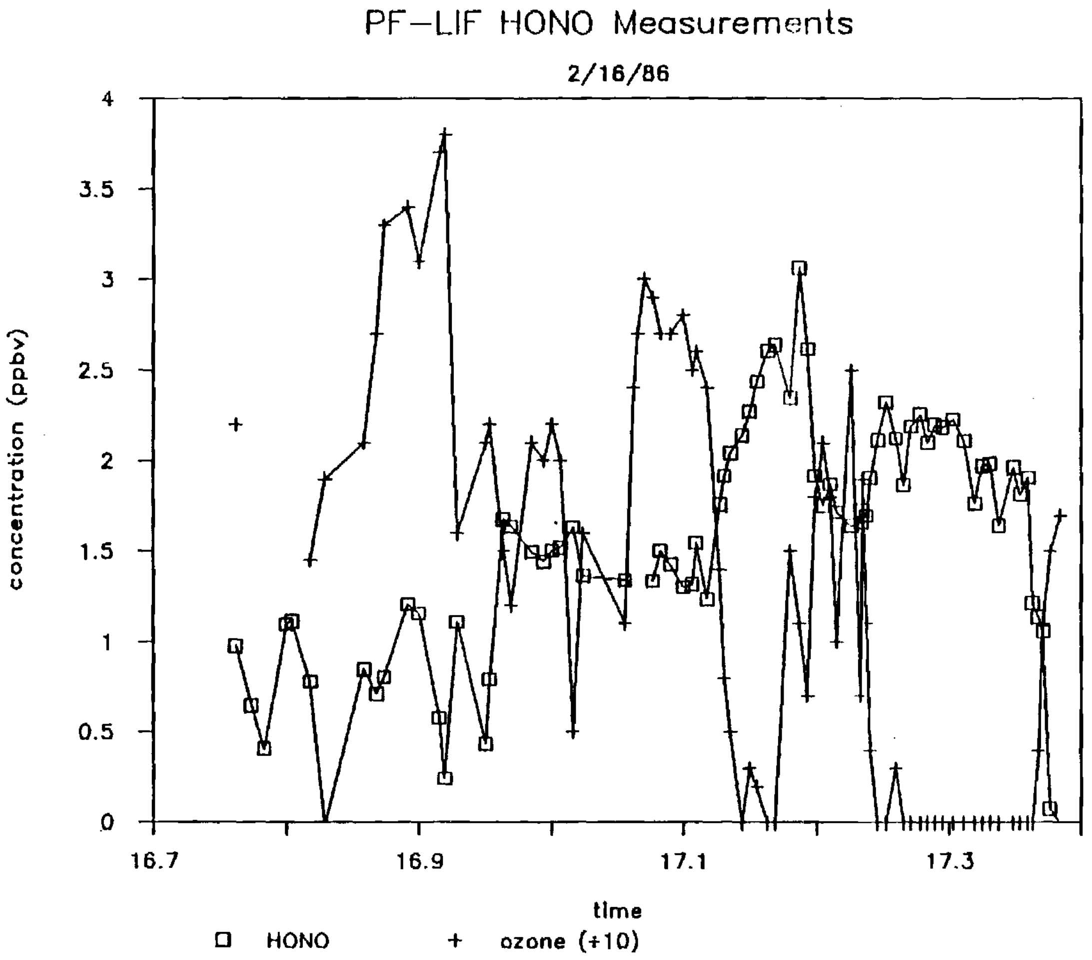


Figure 16 : PF-LIF HONO/O_3 Measurements for 2/16/86, Time is Given in Decimal Days

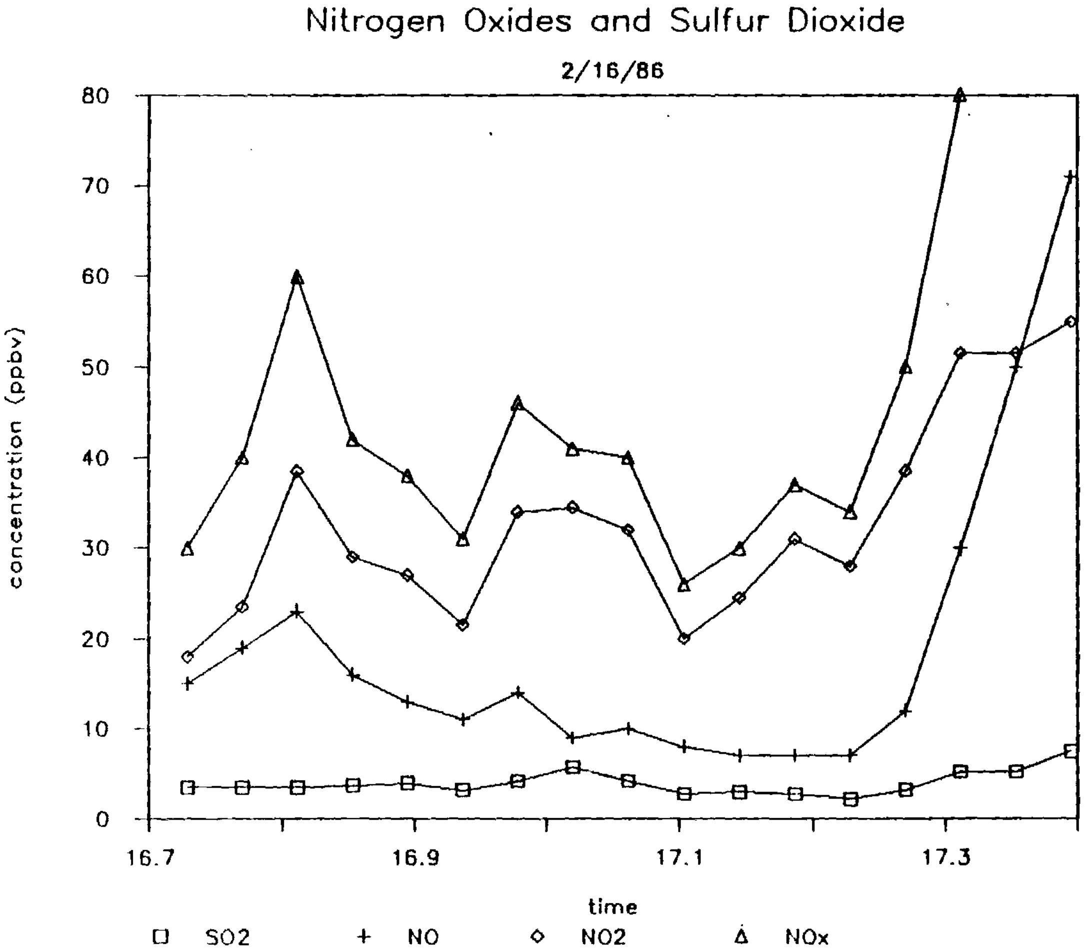


Figure 17 : Nitrogen Oxides and Sulfur Dioxide for 2/16/86, Time is Given in Decimal Days

time period. Note that in figure 17, the NO values plotted include an offset of approximately 5 ppbv and therefore the NO concentration between midnight and shortly before 3 a.m. is not statistically different from zero. The temporal profiles of the meteorological variables for the 2/16/86 diurnal run are given in figure 18.

The data for the second HNO_2 diurnal run (3/21-22/86), including UV solar flux and nitric acid data, are shown in figure 19. The nitrogen oxide concentrations and chemical analysis of ambient aerosols are given in figures 20 and 21, respectively. Figure 22 plots the observed ozone concentration against UV solar flux. The meteorological variables for this measurement period are shown in figure 23.

Three other data sets which indicate the influence of the meteorological environment on the observed HNO_2 concentrations are given in figures 24 through 26. Figure 24 illustrates the effect of fog formation on HNO_2 concentrations observed during the evening of the fifth of February. Figure 25 shows the close correlation between wind speed and observed HNO_2 concentrations for the night of March 9, 1986. The effect of local sources is demonstrated in figure 26. This figure shows the very high concentrations of HNO_2 that were observed due to a rare easterly wind which brought air from the heavily travelled I-75/85 interstate highway.

The early evening buildup of HNO_2 from its low daytime values is shown in figure 27 where HNO_2 concentrations are plotted along with the UV solar flux. The simultaneously observed NO and NO_2 concentrations are shown in figure 28 and the meteorological variables observed at the site are given in figure 29.

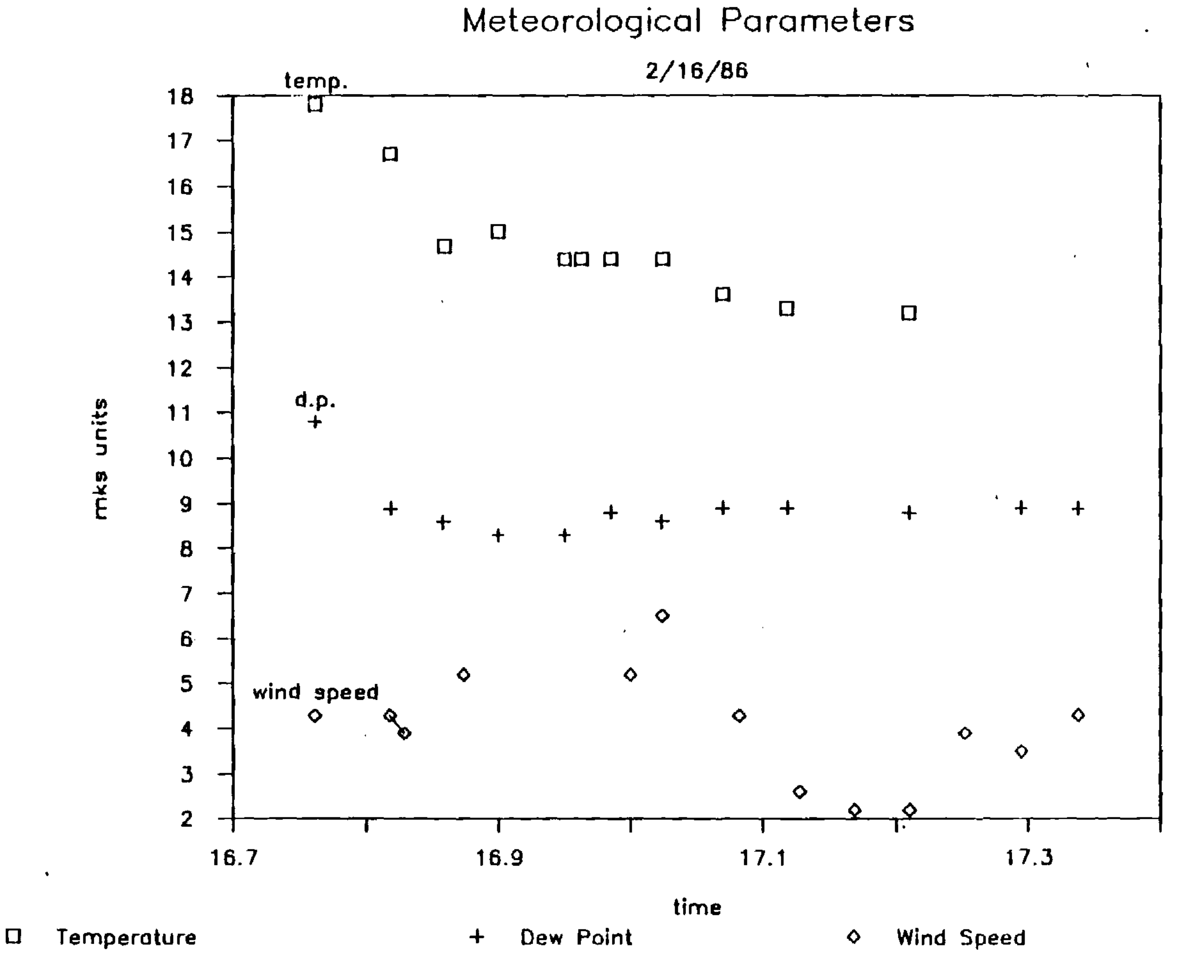


Figure 18 : Meteorological Parameters for Atlanta, Georgia for 2/16/86, Time is Given in Decimal Days

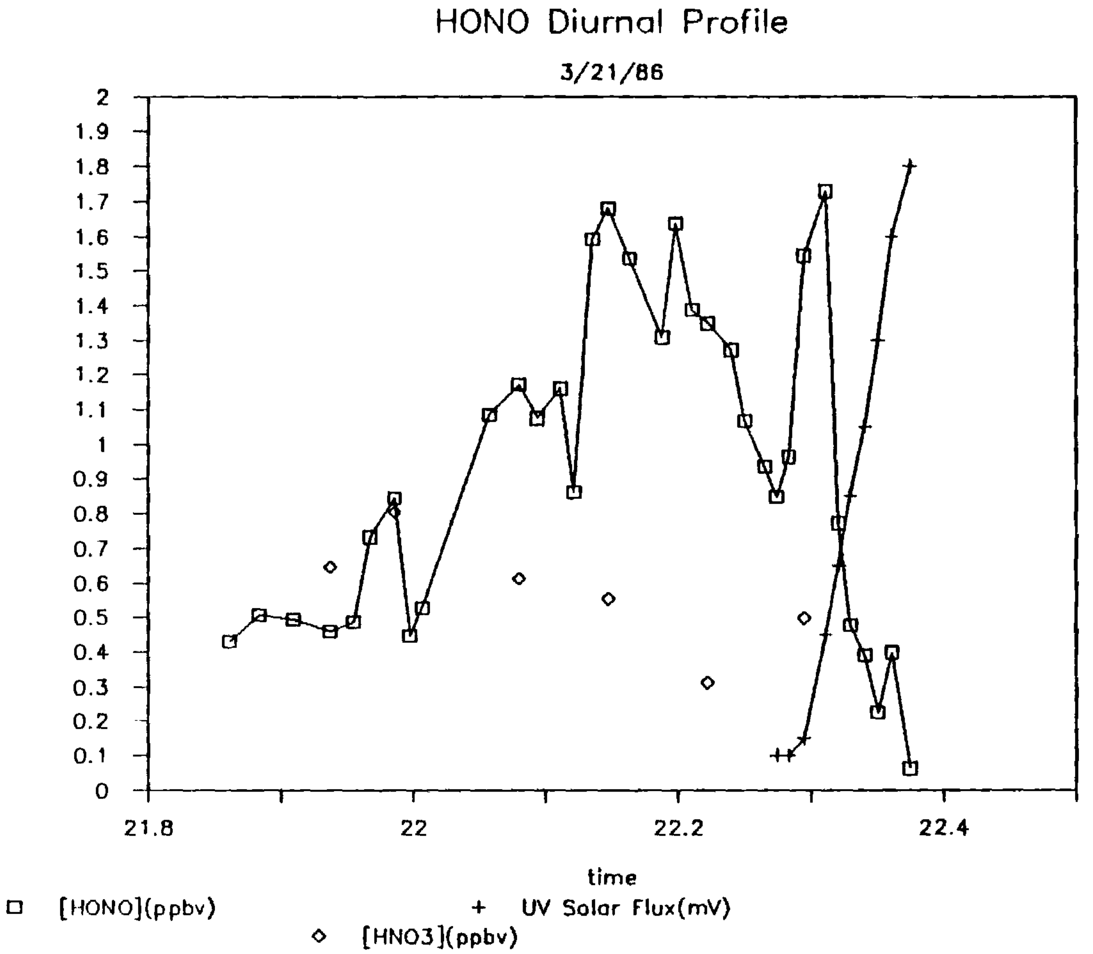


Figure 19 : HONO Diurnal Profile for 3/21/86, Time is Given in Decimal Days

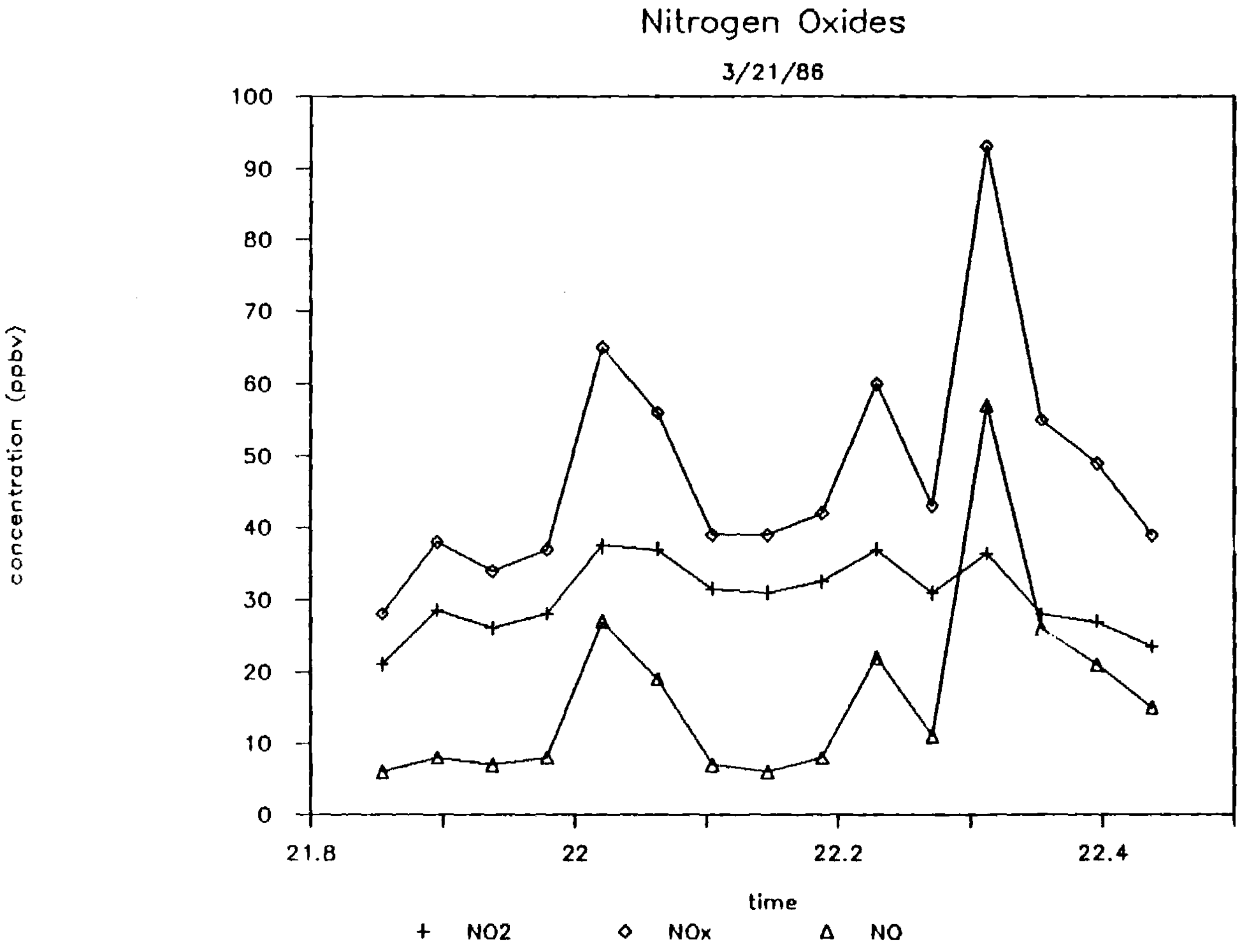


Figure 20 : Nitrogen Oxides for 3/21/86, Time is Given in Decimal Days

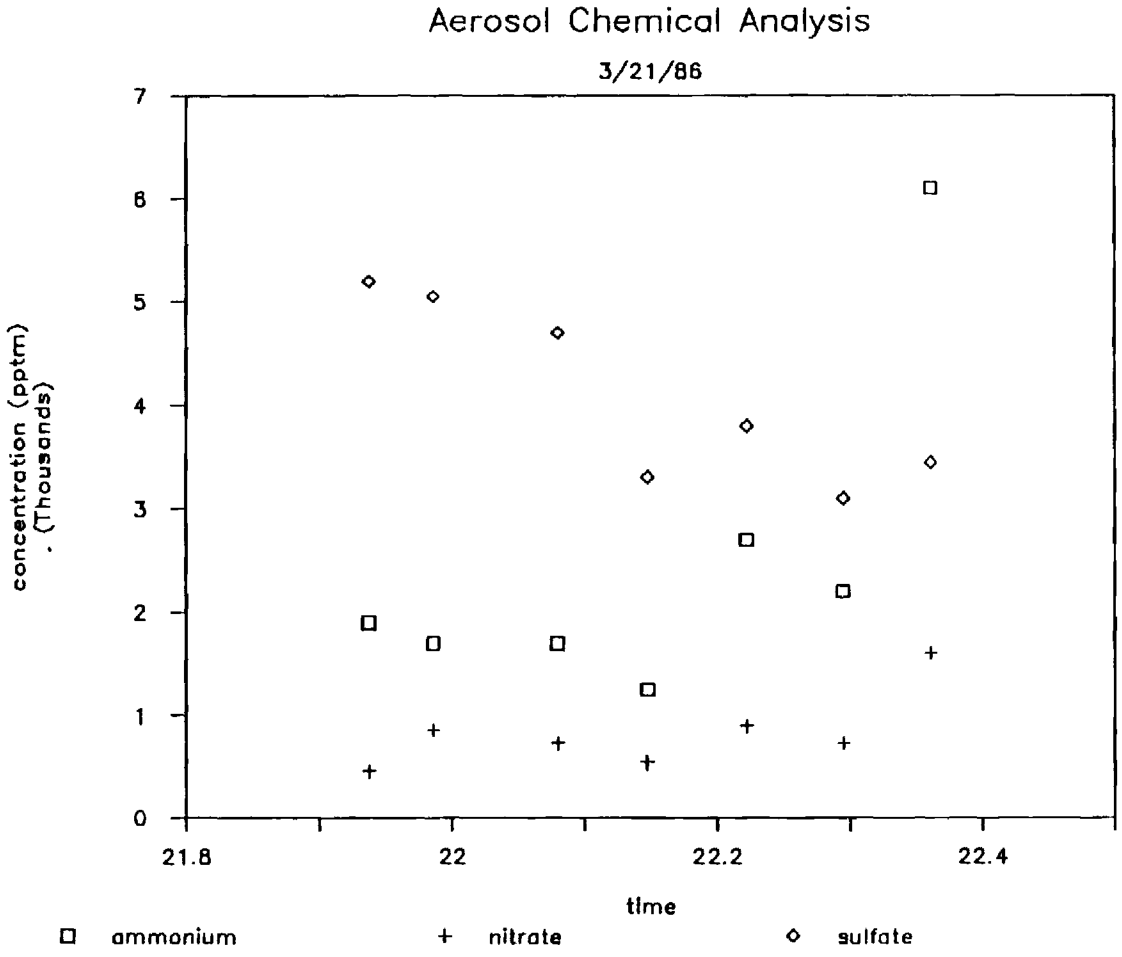


Figure 21 : Aerosol Chemical Analysis for 3/21/86, Time is Given in Decimal Days

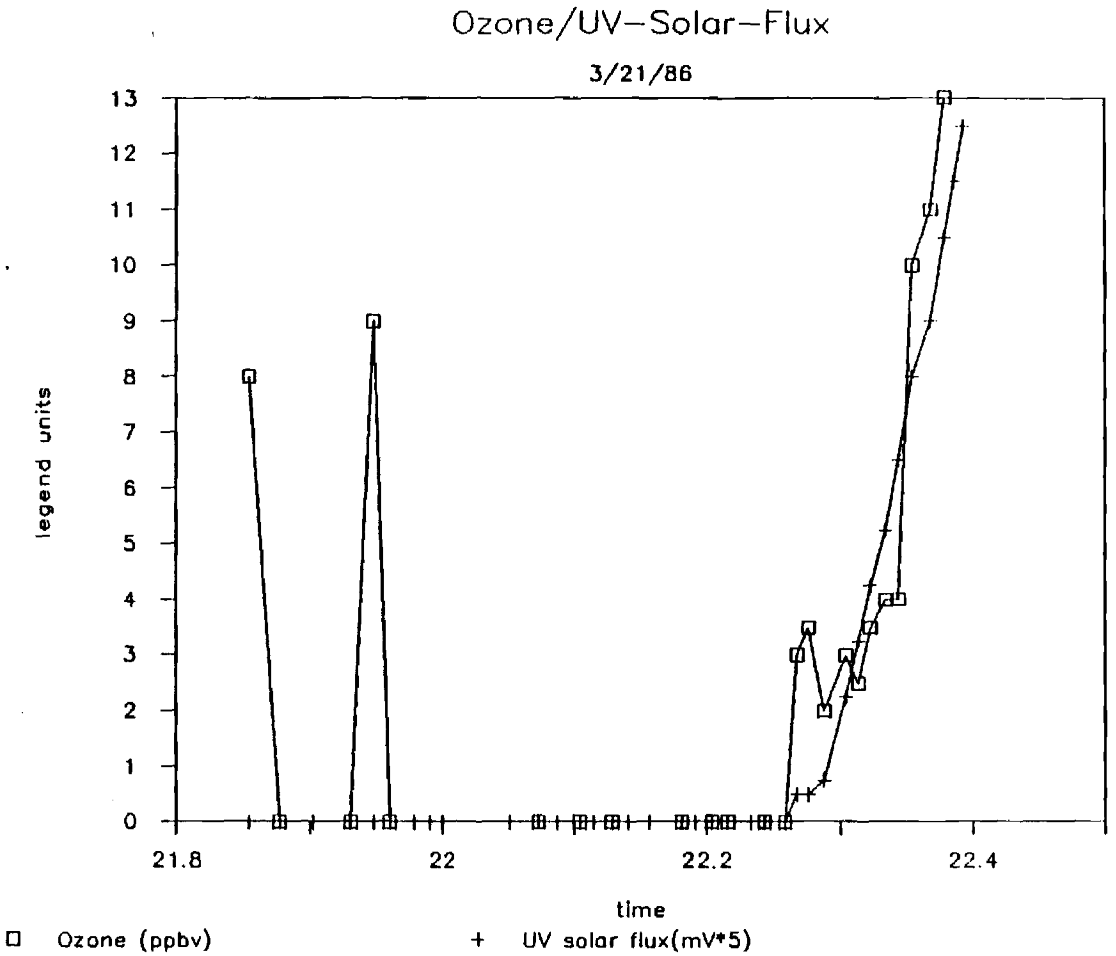


Figure 22 : Ozone/Ultraviolet Solar Flux for 3/21/86, Time is Given in Decimal Days

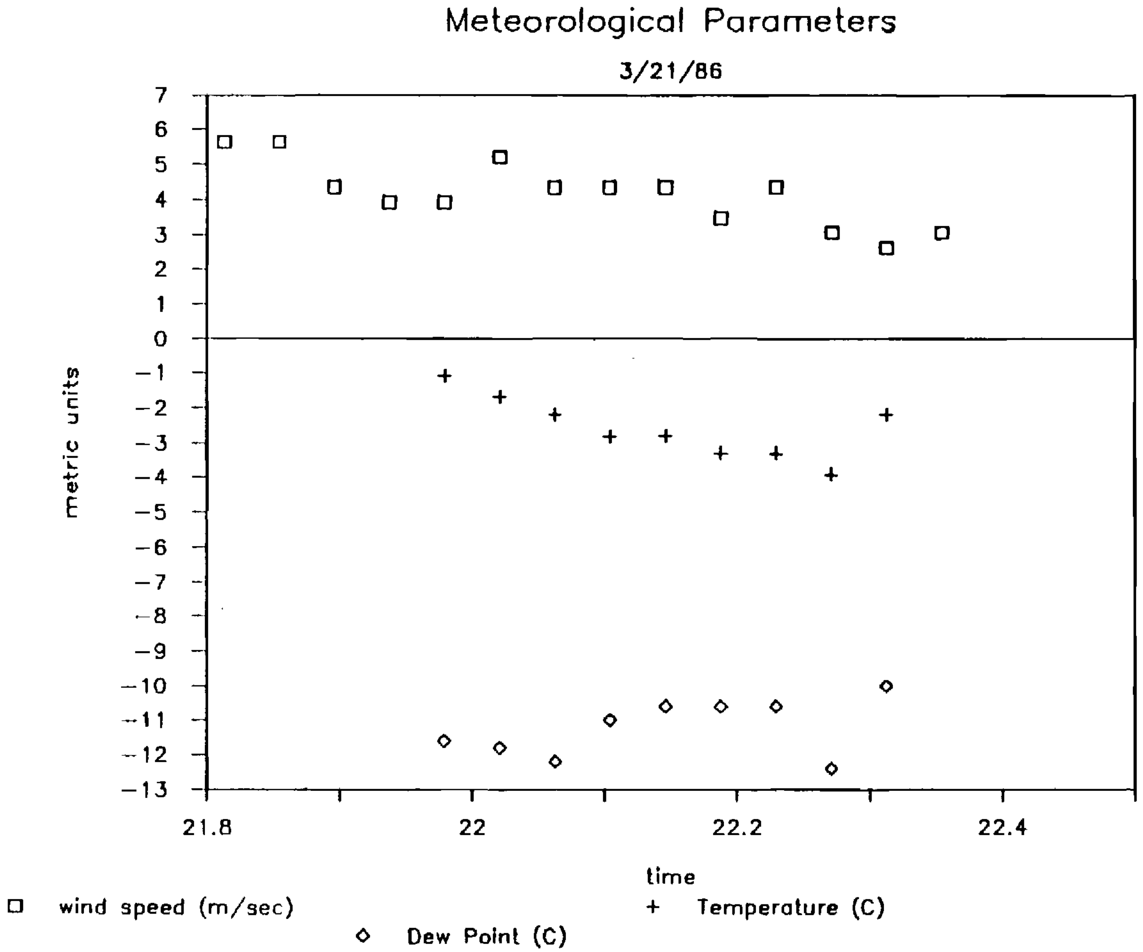


Figure 23 : Meteorological Parameters for 3/21/86, Time is Given in Decimal Days

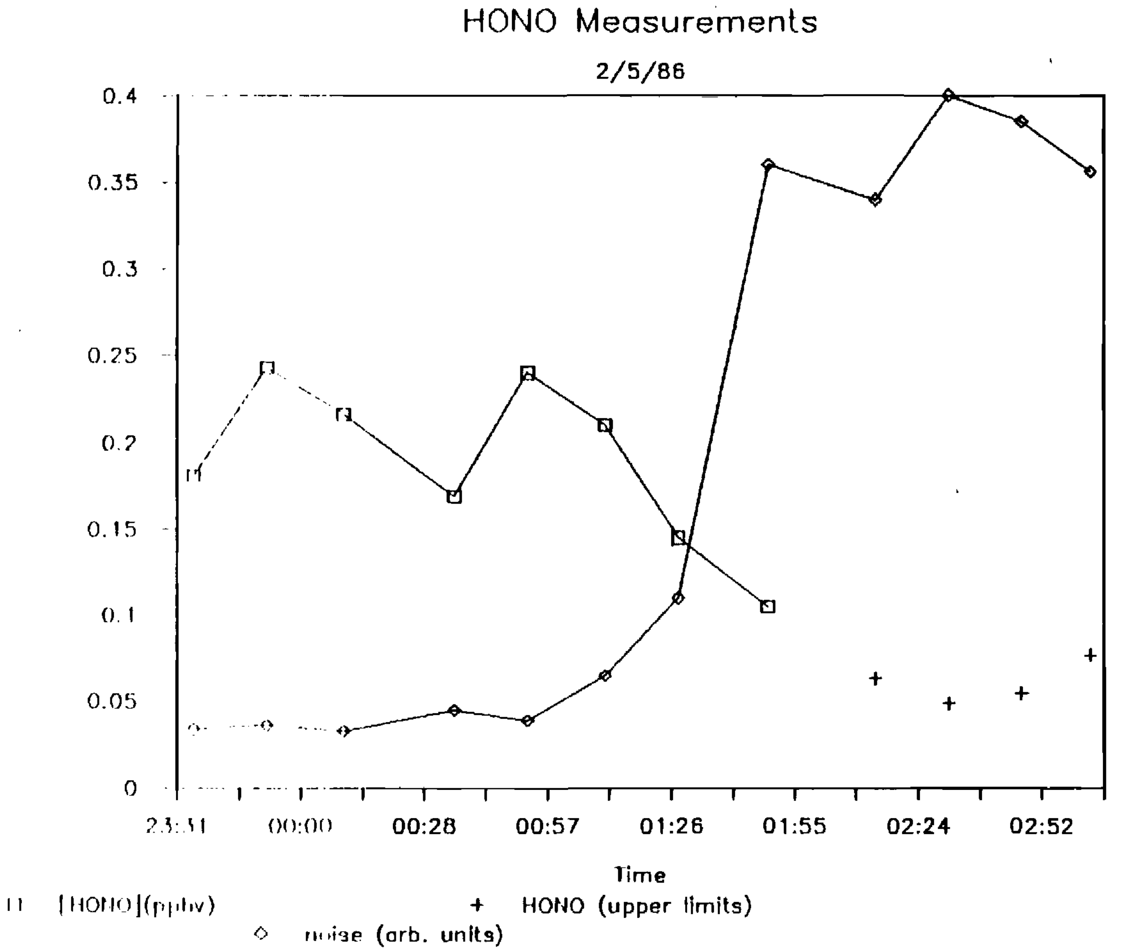


Figure 24 : Effect of Fog on HONO Concentration Level (2/5/86)
(Laser Noise Correlates with Presence of Fog)

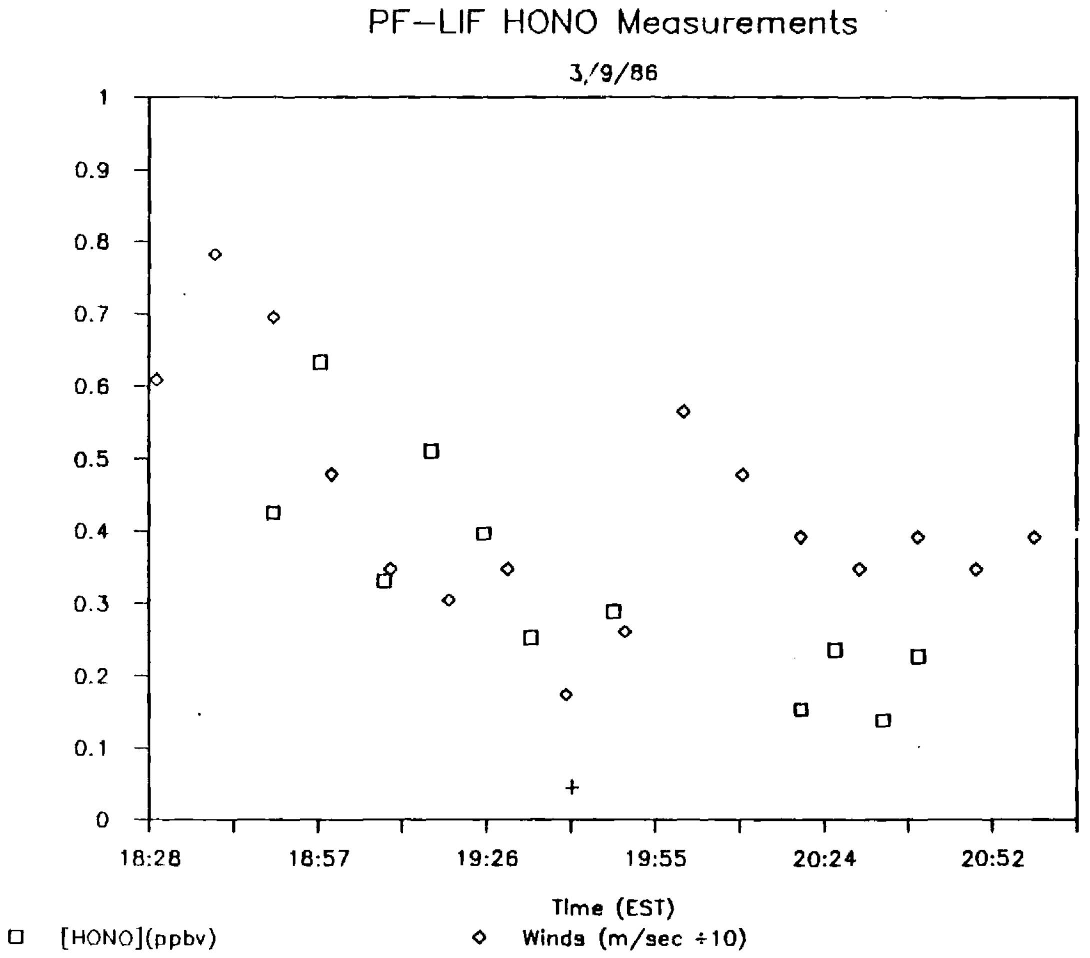


Figure 25 : HONO/Wind-Speed Correlation for 3/9/86

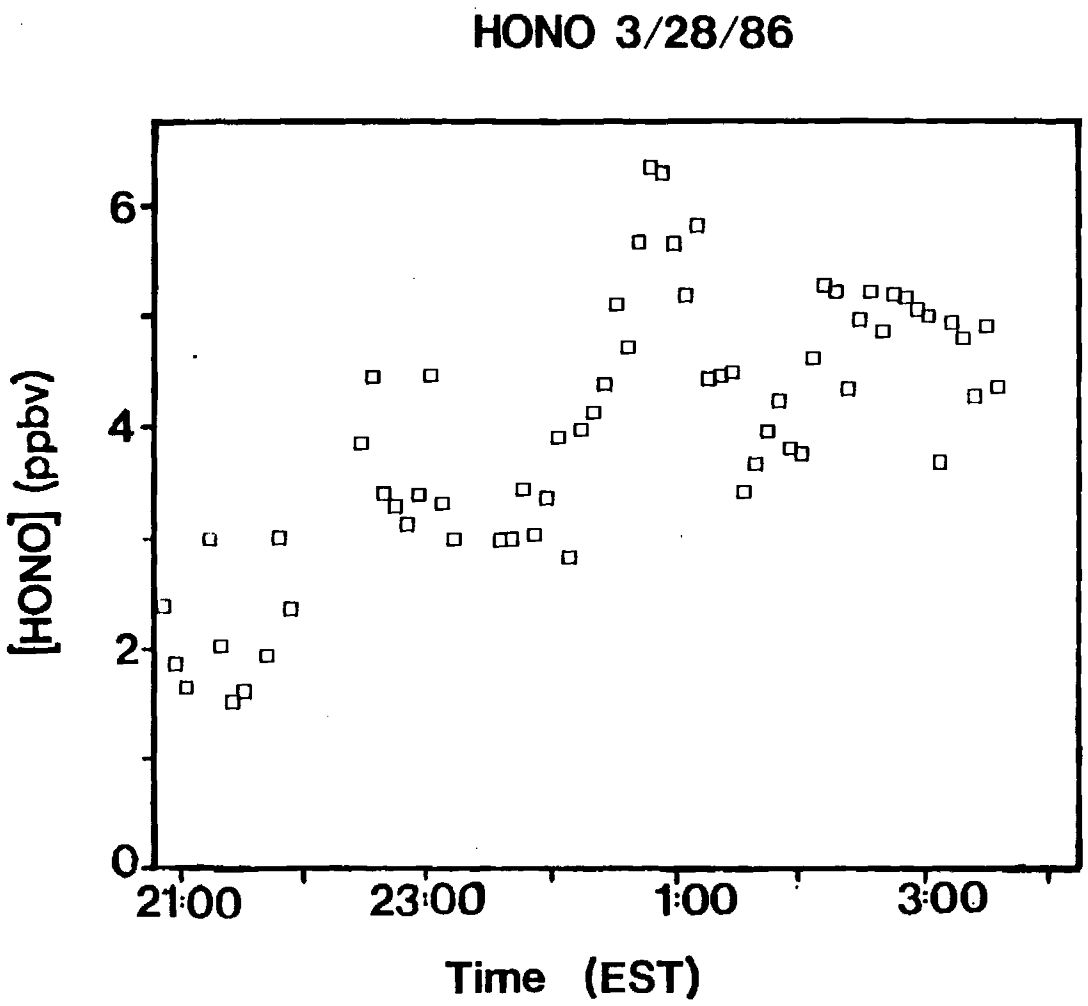


Figure 26 : HONO Measurements for 3/28/86

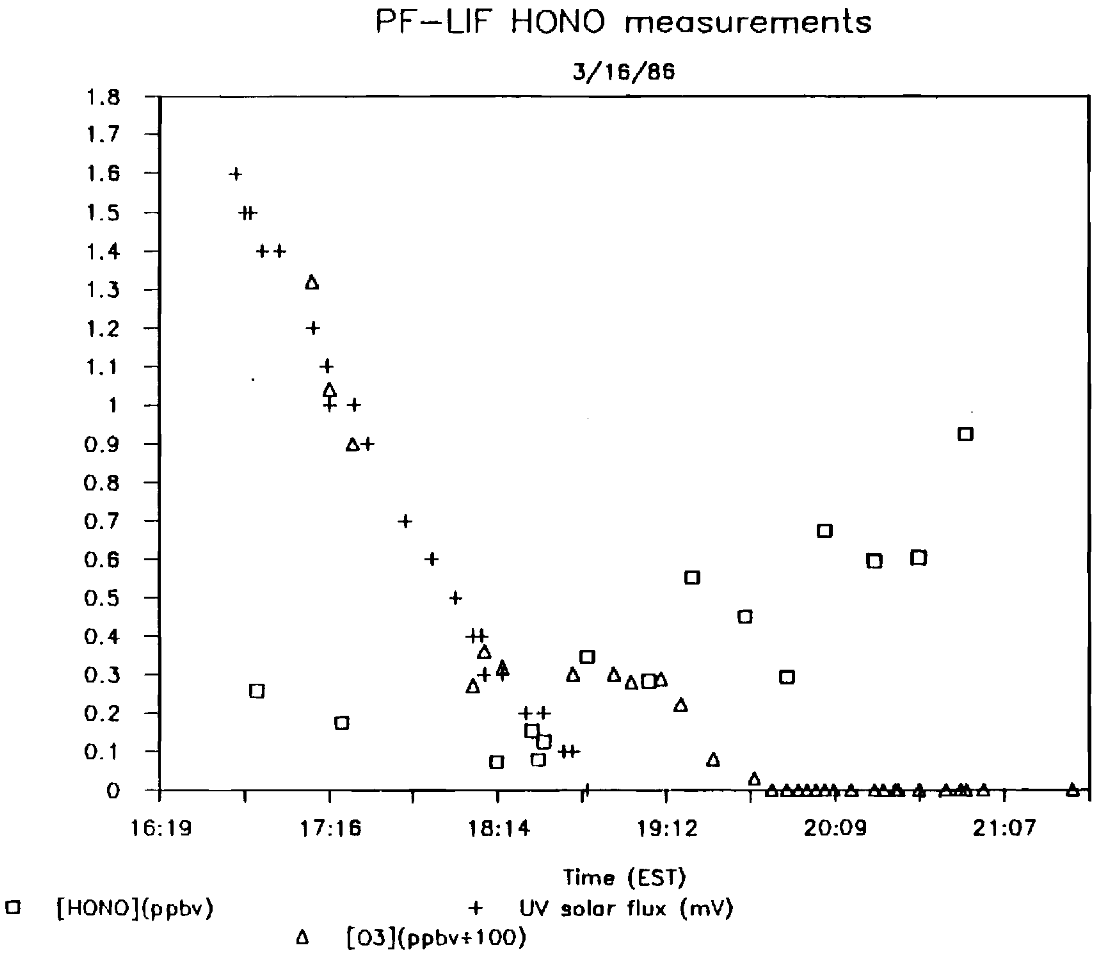


Figure 27 : Early Evening HONO Production for 3/16/86

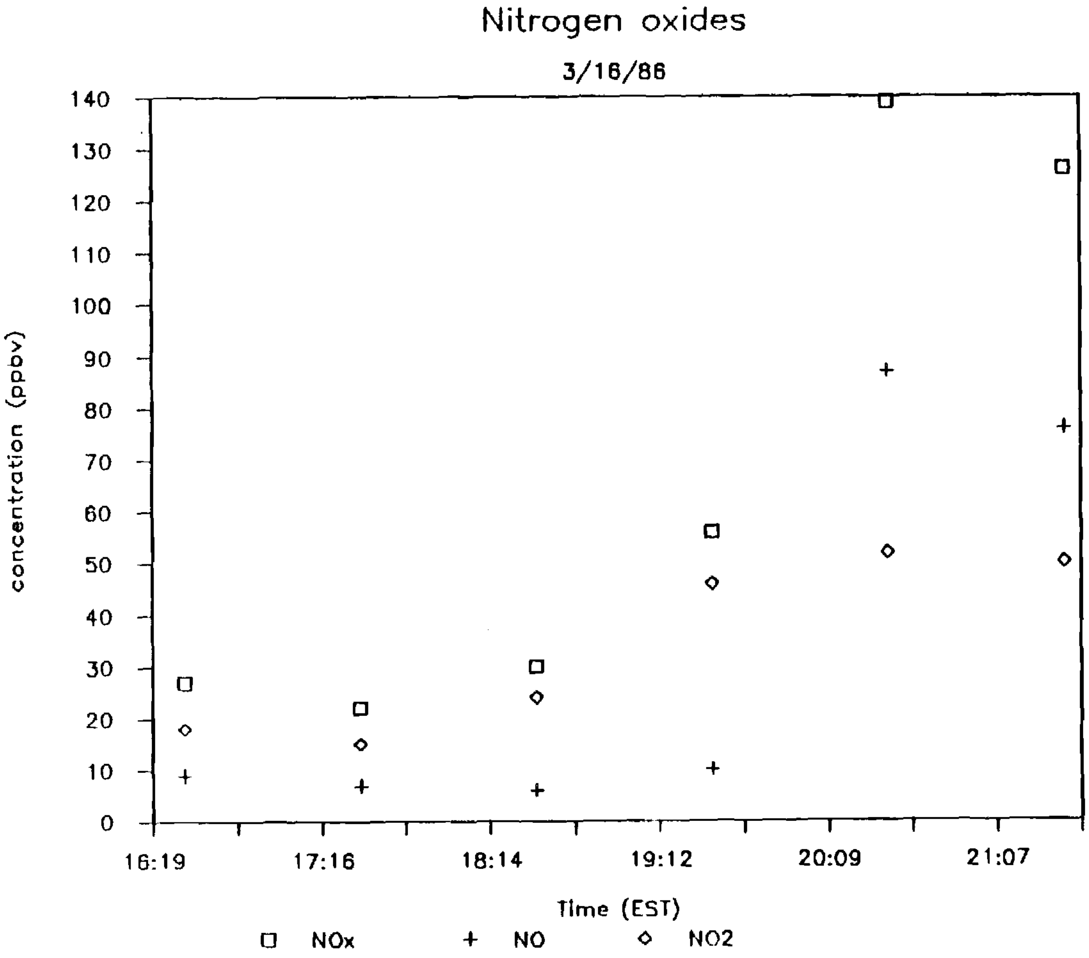


Figure 28 : Nitrogen Oxides for 3/16/86

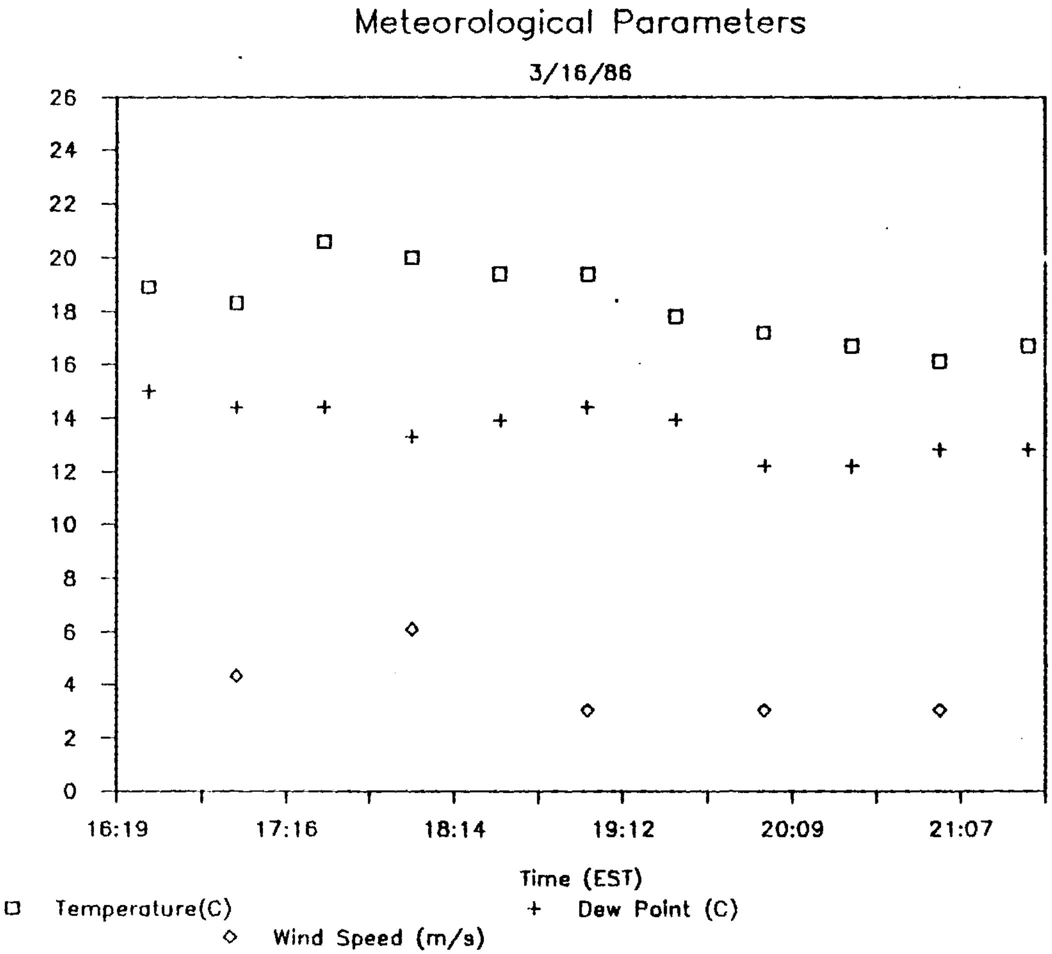


Figure 29 : Meteorological Variables for 3/16/86

(3) Discussion of HNO_2 Atlanta Field Results

Diurnal Variation of HNO_2 Concentrations - The HNO_2 concentrations measured in Atlanta, Georgia, as summarized in the preceding text and as shown in detail in Appendix A, are in qualitative agreement with previous observations made in the vicinity of Los Angeles, California by the long-path differential-absorption technique (Platt et al. (1980); Harris et al. (1982,1983)). Both data sets indicate a strong diurnal variation in the concentration of HNO_2 with midday levels always at or below the instrumental detection limit (typically in the range of 20 to 60 pptv for the PF-LIF technique) and nighttime levels reaching the parts-per-billion range.

HNO_2 Loss Proceses - Perhaps the most striking difference between the chemical and the spectroscopic measurements of atmospheric HNO_2 are seen in the reported diurnal profiles. Measurements made by the PF-LIF detection system, illustrated in figures 16 and 19, show a rapid decay of HNO_2 levels after sunrise. Conversely, the level of HNO_2 was observed to markedly increase after sunset (figure 27). Since none of the likely HNO_2 production mechanisms are expected to be inoperative during daylight hours, these measurements imply that the dominate sink of atmospheric HNO_2 is probably photolysis by sunlight. This observation is in agreement with both photochemical theory and previous spectroscopic measurements of HNO_2.

Although the data are limited, the results from this study also suggest that HNO_2 may be lost via incorporation into fog droplets (e.g. see figure 24). While not unexpected, due to the high solubility of

HNO_2 in water (H=50), these measurements indicate that nocturnal fog and haze may define major sinks for HNO_2.

HNO₂ Production Processes - The measurements made by the PF-LIF technique have indicated, as have the previous spectroscopically-based methods (Perner and Platt (1979); Platt et al. (1980); Harris et al. (1982,1983)), that in polluted areas nighttime HNO_2 production rates are substantial. In some instances, the observed net production rate for HNO_2 has exceeded 1 ppbv/hour (7×10^6 molec/cm^3/sec), though more typical values are perhaps one fourth this large. As discussed earlier, a number of different chemical production mechanisms have been proposed to explain this nighttime production. The mechanisms currently believed to be most likely entail heterogeneous reactions involving NO_2 (and perhaps NO) and H_2O.

$$NO + NO_2 + H_2O \xrightarrow{\text{heterog.}} 2\ HNO_2$$

$$NO + \text{olefin} \rightarrow HNO_2 + \text{products}$$

$$CH_3C(O)OONO_2(PAN) \rightarrow HNO_2 + \text{products}$$

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

$$NO_2 + H_2O + \text{reactant} \rightarrow HNO_2 + \text{products}$$

$$NO + HNO_3 \rightarrow NO_2 + HNO_2$$

$$HNO_3 + 2NO + H_2O \rightarrow HNO_2 + \text{product}$$

Since these reactions are most rapid at high NO_x concentrations, there is some evidence that these, or some other set of reactions, occur within automobile exhaust systems (Pitts et al. 1984b). If this is the case, then the observed nighttime atmospheric HNO_2 concentration growth may involve accumulation of nocturnal HNO_2 emissions from primary sources.

The current series of HNO_2 measurements provides some evidence as to the possible sources of atmospheric HNO_2. For example, we have examined the correlations between HNO_2 concentration levels and those of other chemical variables. This approach must be used with some caution, however, as different sources may vary significantly in their relative contributions to the total production rate depending upon the meteorological conditions and the background chemical environment. Several of these correlations have been summarized in the previous text.

Following the UV solar flux, the atmospheric variable that might be identified as the most likely to show a significant correlation with HNO_2 would be the concentration levels of nitrogen oxides. (The latter species are believed to be HNO_2 precursors). In addition, a correlation might also be expected between HNO_2 and ozone since ozone is strongly coupled to urban N_xO_y chemistry. The existence of a correlation between the levels of two species does not mean, however, that a causal link exists between them. This latter situation appears to exist for the HNO_2 profile recorded on the evening of 3/16/86 (see figure 27). This figure shows a strong positive correlation between HNO_2 and NO but a significant anticorrelation between these two species and O_3. For this event, however, it appears that all three of the above variables are strongly dependent on yet a fourth variable, the UV solar flux. Thus, the actual relationship between the levels of HNO_2, NO and O_3 is masked by the early evening variation in the UV flux.

During the night, the actual interdependence between HNO_2, NO, and NO_2 can be examined with fewer complications. The 2/16/86 diurnal profile (figure 16), for example, shows a complex relationship between the observed levels of HNO_2 and ozone. In this case, however, a comparison of the chemical profiles with the wind speed shown in Fig. 18 shows that HNO_2 levels are observed to vary inversely with the speed of a southerly wind, with the time period of largest increase in HNO_2 levels corresponding closely with near calm conditions. This observation would tend to suggest that the sampling site is located in the vicinity of a strong HNO_2 source and the observed HNO_2 levels are controlled by the source strength and the extent of ventilation provided by the winds. A similar pattern of behavior appeared in the data taken on 3/9/86 (Fig. 25) with winds also occurring from the south.

Some support of this hypothesis is provided by the measurements made under easterly wind conditions on 3/28/86. These measurements, which yielded the highest recorded HNO_2 concentrations, were made in air parcels that were in recent contact with the heavily travelled interstate highway east of Georgia Tech. Thus, they provide at least an inferential link that automobile traffic in general, and interstate highway 85/75, in particular, represents the major source of HNO_2 observed in this study. This conclusion is consistent with that reached by Harris et al. (1983) who made measurements near a heavily travelled interstate highway in Los Angeles.

If automobile traffic is taken to be the major source of urban HNO_2, the question remains whether this source is derived from chemical transformations in the environment due to the release of precursor species (e.g. NO_x) from automobiles or from the direct release of HNO_2 from automobile exhausts. Seemingly, one possibile way of finding the answer to this question would involve correlating the observed HNO_2 production rate with relative humidity. In the free atmosphere, humidity is controlled by dynamic processes whereas automobile exhaust systems have an independent source of water vapor due to the combustion process. Since the reactions which form HNO_2 are believed to be heterogeneous and involve surface layers of water, the production rate would be a function of the relative humidity and NO_x concentration level, if environmental production is dominant. On the other hand, if the dominant source is direct release, then traffic volume would be the only controlling factor. Unfortunately, relative humidity in the Atlanta area varies comparitively little (50% ± 10%, NOAA (1983)) for clear conditions during the winter months. Higher relative humidity values are normally associated with the production of ground fogs which may serve as a strong sink for atmospheric HNO_2 (as shown in Fig. 24) and thereby make interpretation difficult.

Definitive correlations between atmospheric HNO_2 production and humidity will require a much larger data set over a wider range of conditions than that provided by this investigation. However, to provide some information regarding the direct release versus environmental production hypotheses, tests involving controlled driving of an automobile down the street bordering the Baker building were performed on two separate occasions, e.g. 2/16/86 and 3/21/86. In both cases, a late model catalytic-converter equipped automobile was periodically driven along the street during a single integration period

(10 minutes). This measurement was compared to ambient values measured both before and after the test period to establish whether any concentration enhancement was observed. On both nights, our observations indicate that a single automobile resulted in an enhancement in the measured HNO_2 level of between 100 and 150 pptv. This represents an 11 to 17% increase over the nominal background level before and after the car experiment. Since the time period between the passage of the car and sampling by the PF-LIF system was short (i.e. $\leq$ 10 min.), these results would suggest that the HNO_2 must either be directly emitted by the automobile or the production rate within the environment was extremely rapid. This result also suggests that the observed enhanced HNO_2 levels occurring just before sunset during the 3/16/86 measurement event may have been due to local traffic on the Georgia Tech campus rather than reflecting the production of HNO_2 from large scale sources of NO_x.

(4) Estimate of OH Production Due to Photolysis of HNO_2

As discussed earlier in the text, one of the principle reasons for studying the chemistry of HNO_2 is its potential importance as a source for atmospheric OH. The potential importance of HNO_2 can readily be seen by considering the peak midday value for the primary production of OH from ozone photolysis. During the time period of the HNO_2 measurements, typical midday values of ozone ranged between 40 and 50 ppbv (although occasional values in excess of 100 ppbv were recorded) and water vapor concentrations were normally about 6 torr (50% relative humidity at a temperature of 14° C). Using a photochemical rate for $O(^1D)$ production from photolysis of ozone of 3×10^{-5} sec^{-1} as typical for midday conditions in Atlanta during the winter months, an OH production rate of 4.5×10^6 molec/cm^3/sec was estimated. This value for the OH production level may be compared to that estimated from early morning photolysis of 2 ppbv of HNO_2 over a two hour period, i.e. 6.9×10^6 molec/cm^3/sec. Although the non-HNO_2 OH production estimate neglects the influence of secondary OH production via reaction of NO with HO_2, these results still point toward the early morning photolysis of HNO_2 as potentially playing a very important role in urban smog formation. As discussed by Harris et al. (1984), this early morning initiation of OH radical driven chemistry may have a profound influence on the total oxidant dosage (concentration*time) experienced in urban environments. Figure 30 shows the estimated OH production due to HNO_2 photolysis for the morning of March 22, 1986. For each of the three cases considered here, it was assumed that the observed HNO_2 decay was due entirely to photolytic destruction. For case (1), the lower curve, a lower bound on the estimated OH production was calculated by assuming that no HNO_2 was produced after sunrise. For case (2), the middle curve, a constant post-sunrise source of HNO_2 was assumed that was equal to the average value of the HNO_2 production rate observed during the night. Finally, in case (3), the upper curve, it was assumed that the HNO_2 production followed the profile of NO, with the peak value being 1.8 ppbv/hour. As can be seen from Fig. 30, the peak value for OH as well as the integrated production are both moderately sensitive to assumptions regarding the post-sunrise HNO_2 production rate. In all cases, however, the estimated OH production rate during this period dominates over production from ozone photolysis.

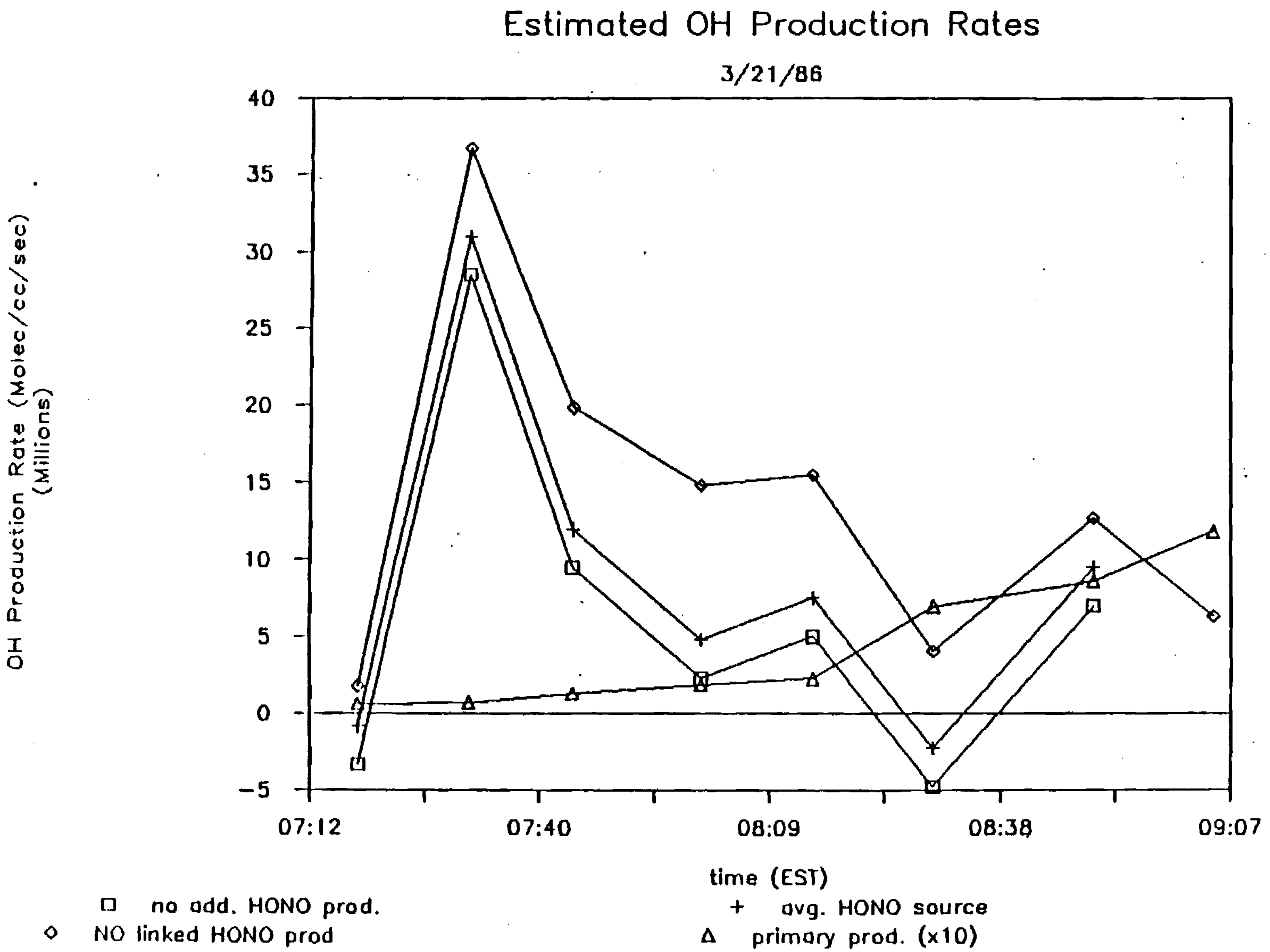


Figure 30 : Estimated OH Production Rates via HONO versus Primary Production from O_3 Photolysis

As noted earlier in the text, taken together these results suggest that the early morning photolysis of HNO_2, accumulated during the night, may serve as the principle means by which OH radical-driven chemistry is initiated in the morning in the Atlanta area, and probably in most other large urban centers. Furthermore, if the source of HNO_2 is directly coupled to the emissions from automobiles, photolytic generated OH from HNO_2 would then become an extremely important driving force for smog formation over a significant fraction of each day. Further tests to prove or disprove the latter hypothesis are being planned for the immediate future.

IV. LABORATORY STUDY RESULTS

A. Corona Discharge Experiments - Production of NO_x and O_3

(1) Introduction

The electrical parameters associated with the phenomenon known as coronal discharge have been extensively studied for over half a century (Crooker (1916), Whitehead (1910), and Harding and McEachron (1920)). However, the question of whether or not the generic chemical species NO_x is generated in significant amounts remains, as yet, unclear. As related to atmospheric chemical processes, recent studies (Rahim (1984), Coucouvinus (1983) and Donohoe et al. (1977)) have been carried out which have attempted to characterize the bulk coronal production of species such as O_3, N_2O, and NO. However, these studies were carried out with minimal concern about the electrical characteristics of coronal discharge as they might relate to the atmosphere. These studies have utilized high frequency, high current corona plasmas, which have no natural counterpart. In addition to this problem, the general lack of instrument sensitivity used by these investigators (i.e. $[NO_x] \geq 5$ppbv,$[O_3] > 100$ppbv) have also limited their ability to work at typical atmospheric field strengths, subsequently preventing the direct observation of NO_x production.

Our research efforts have been aimed at assessing the chemical source strengths for NO and O_3 under conditions applicable to the lower atmosphere. This corresponds to using dc potentials at significantly lower currents than those involved in previously reported work, which has necessitated the use of instrumentation possessing far greater detection sensitivity. In our case, a high sensitivity NO chemiluminescence sensor was constructed in order to fulfill the measurement requirements for NO and NO_2; whereas, for O_3 a commercial Dasibi UV absorption O_3 analyzer was employed.

(2) Experimental

The expermental hardware employed in our corona discharge study is shown in Fig.31. From this figure, it is seen that a two-stage dynamic dilution system was used both to provide various gas mixtures (e.g. N_2/O_2/Ar/etc.) to the corona cell and at other times to provide calibration gas to the NO/NO_x chemiluminescence instrument. A water bubbler was also employed in order to study the effects of varying relative humidity on the coronal production of NO_x and O_3. To detect NO_2 with the NO chemiluminescent detector, a photolysis cell was built that consisted of a 150 W Xenon arc lamp fitted with a UV filter. The measured photolysis efficiency for the process $NO_2 + h\nu \longrightarrow NO + O$ was typically 45%. However, a significant problem that developed in the present coronal study was the observation that odd nitrogen production in our system was always accompanied by a significantly greater production of ozone. Thus, prior to the chemiluminescnence NO measurement, the rate of the reaction $NO + O_3 \longrightarrow NO_2 + O_2$ ($k = 1.8 \times 10^{-14}$ mole cm^3/sec) was sufficiently fast to back titrate all the NO produced from the photo-converter to NO_2. This necessitated the use of a system that would destroy the ozone generated within the coronal discharge without perturbing the measurement of coronal generated NO/NO_x. The ozone destruction system consisted of a quartz tube heated to approximately 500°C. This system was found to destroy > 95% of the ozone and thus allowed the NO_2 photo-converter cell to quantitatively convert NO_2 to NO.

The chemiluminescent NO instrument used in this study was similar in design to the instrument developed by Kley and McFarland (1980). Our instrument had a detection limit of 20 pptv NO and 50 pptv NO_2. By contrast, commercial NO/NO_x instruments have detection limits of approximately 2 and 5 ppbv, respectively. The enhanced sensitivity relative to commercial instruments has been realized by the utilization of: i) a larger, gold-coated reaction chamber, allowing for

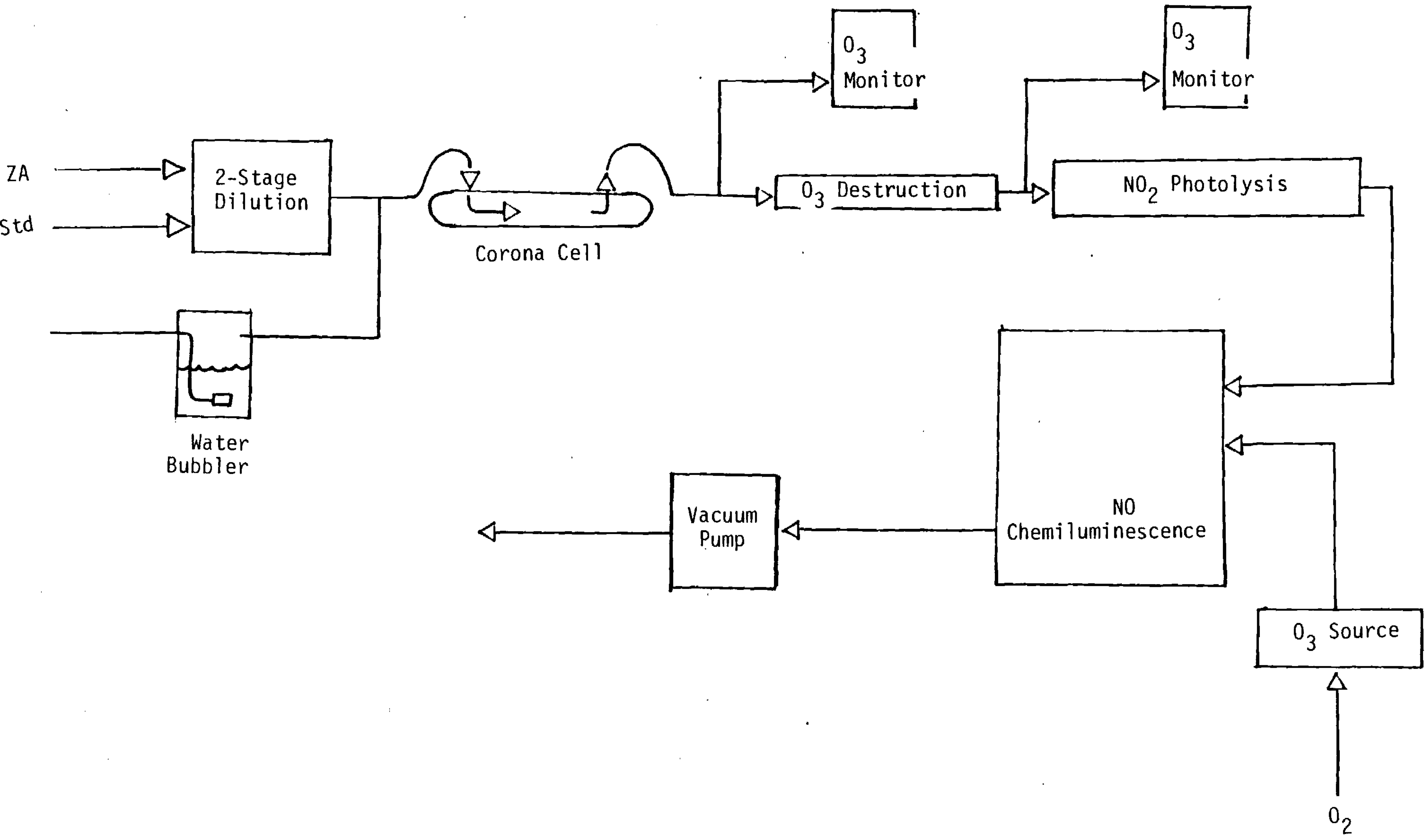


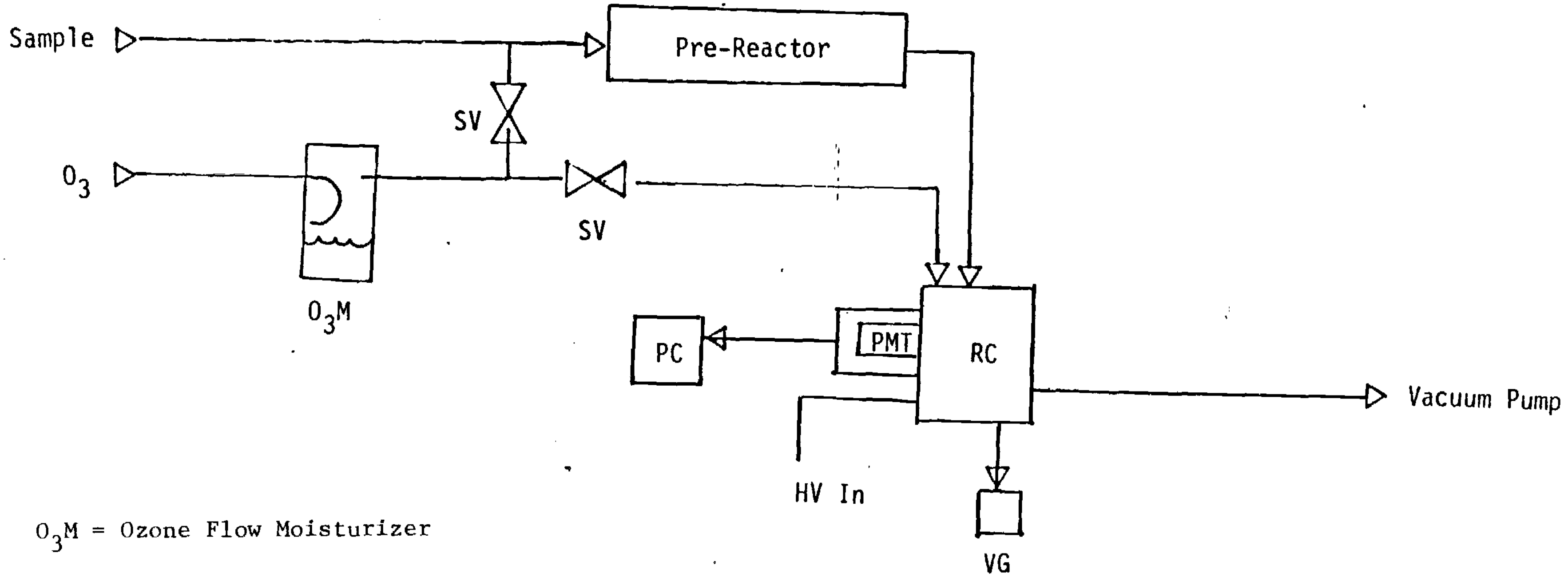
Figure 31: Schematic layout of Corona Discharge Experimental Hardware

significant increases in sample through put; ii) photon counting electronics; iii) a pre-reactor for obtaining the instrument background and; iv) a higher capacity ozone source. A water bubbler was also inserted into the ozone flow stream in order to reduce the background count rate; however, our test results have shown that there is no need to bubble the O_3 flow through water in order to reduce the background count rate. Instead, the ozone flow was "passed" over the water. The reason for this background reduction by H_2O has been demonstrated to be due to water vapor quenching of the long-lived luminescence occurring at the reaction chamber walls. The detailed layout of the NO/NO_x chemiluminescent instrument is shown is Fig. 32.

As noted earlier, ozone was measured using UV absorption in the form of a commercial Dasibi instrument. The sensitivity of this instrument permitted the collection of statistically significant results above ~10 ppbv, thus enabling us to measure coronal ozone production at applied fields relevant to the troposphere.

Our laboratory investigation of coronal discharges utilized two basic cell geometries. The first of these was a coaxial designed cell as shown in Fig. 33. This system, consisted of a stainless steel cylindrical outer electrode and a concentric wire inner electrode. This design was chosen for the majority of the experiments performed during this study since the associated field strength can be well characterized, and the resulting field distribution is symmetric with respect to the inner electrode. (This electrode geometry has been extensively characterized (see for example the recent review by Loeb (1984)). The corona chamber itself consisted of a 5 cm diameter pyrex glass tube having an inner electrode made from different types of wire whose diameters were varied from 12μm to 600μm.

Figure 32 : NO Chemiluminescence Detection System



O_3M = Ozone Flow Moisturizer

SV = Solenoid Valve

PC = Photon Counting Equipment

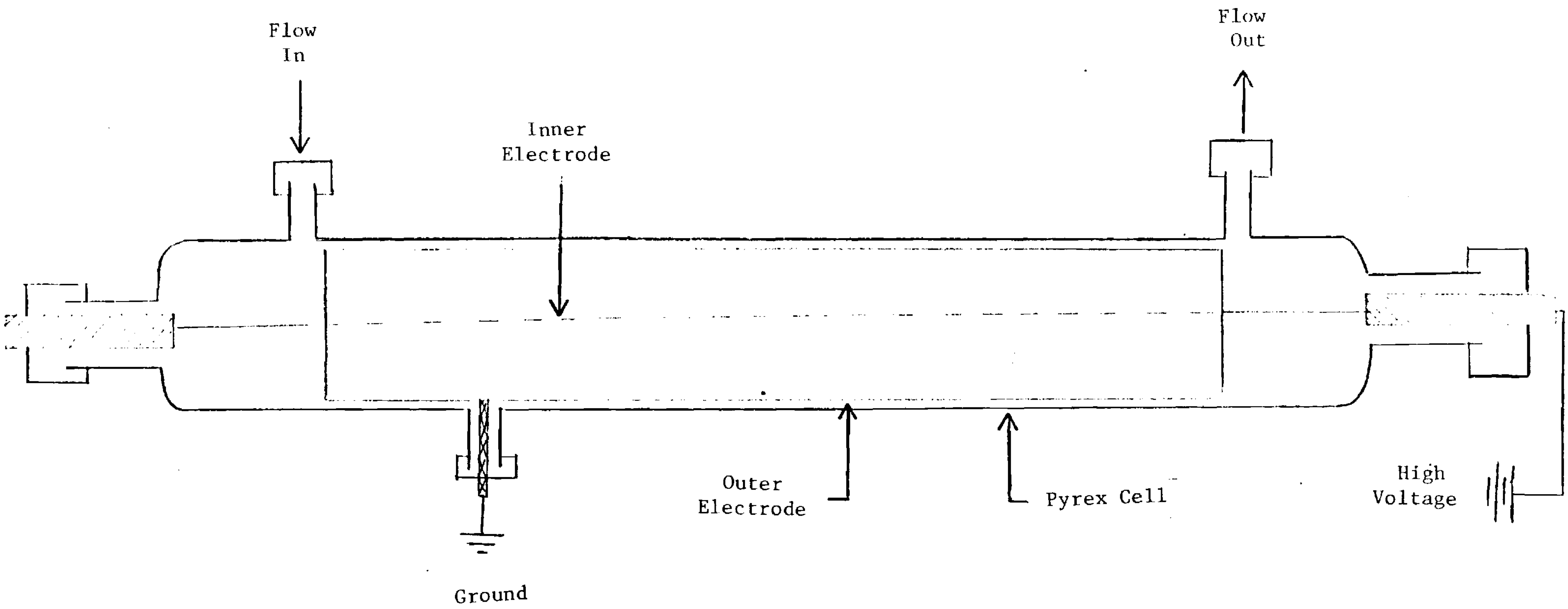
HV = High Voltage

PMT = Photo Multiplier Tube

RC = Reaction Chamber

VG = Vacuum Guage

Figure 33: Coaxial Design Coronal Discharge Chamber



The second corona chamber was of the point-to-plane geometry design. One version of the latter cell is that shown in Fig. 34. This chamber, like the coaxial design, was fabricated from pyrex. The point-to-plane design permitted tests using metal needles, pine needles, juniper sprigs, and ice crystals.

(3) Experimental Results

A representative voltage-current curve for the coaxial designed cell is shown in Fig. 35. It can be seen from this plot that the coaxial cell configuration has a well defined onset corona voltage. This onset voltage, at which point stable coronal discharge occurs, was found to be inversely proportional to the radius of the inner wire electrode. Suffice it to say, coronal discharges present in nature are generated from a variety of different points (viz., pine needles, ice crystals) having a complex distribution of point radii. This distinction between the characteristics of a single point source versus poly-disperse multi-point sources has been demonstrated using spruce trees (Ette (1966) and Jhawar and Chalmers (1967)). An example of the behavior of a multi-point coated coaxial wire having a poly-disperse point distribution is shown in Fig. 36. From this plot it is immediately obvious that for the multi-point source, as compared to a fixed radius source, the onset of corona is significantly lowered. In fact, it is reduced to a level where the onset of corona no longer exhibits a well defined "threshold" voltage effect. Thus, in this system stable corona currents were measurable down to 500 pA.

It has been hypothesized that any NO_x produced via coronal discharge would originate from the primary production of NO. However, the direct measurement of NO produced in coronal discharge has not been previously observed due to the aforementioned rapid titration of $NO + O_3 \longrightarrow NO_2 + O_2$. We have been able to directly measure NO production at low applied fields for both 12μm and 25μm diameter wires where ozone production was less than 40 ppbv. These direct

Figure 34: Point-to-Plane Coronal Discharge Chamber

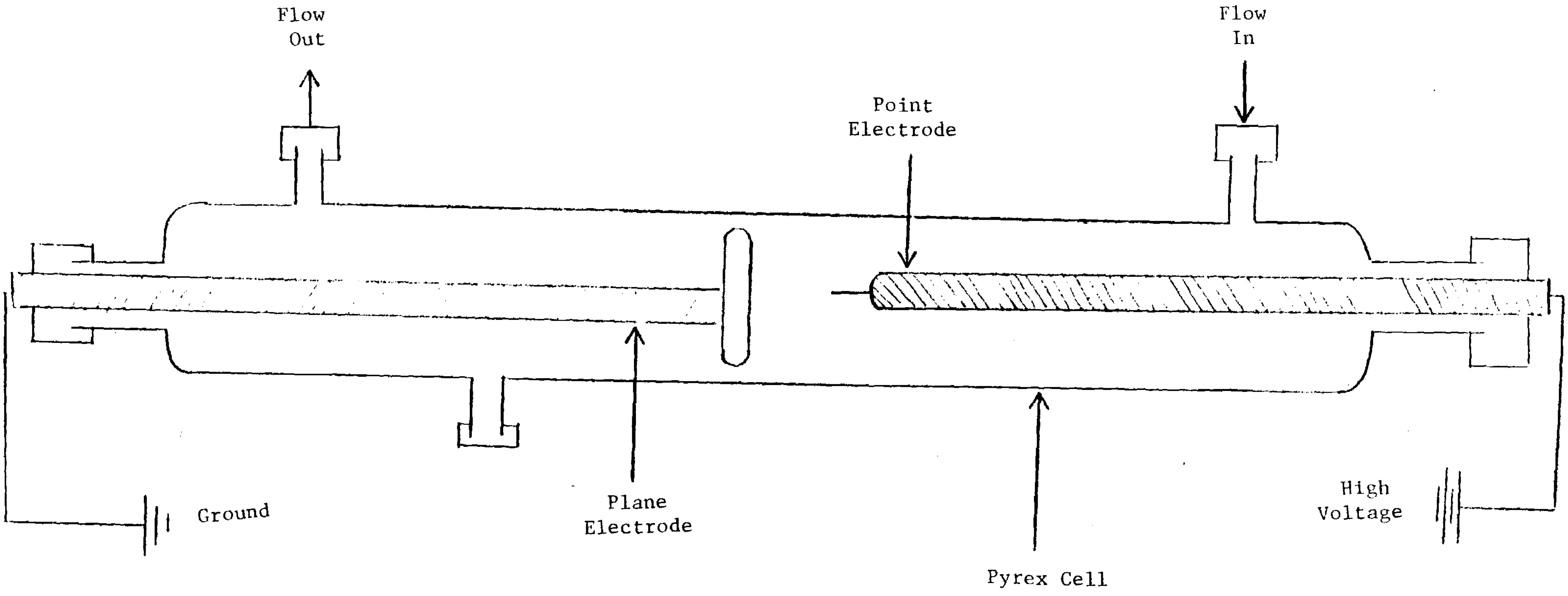


Figure 35:

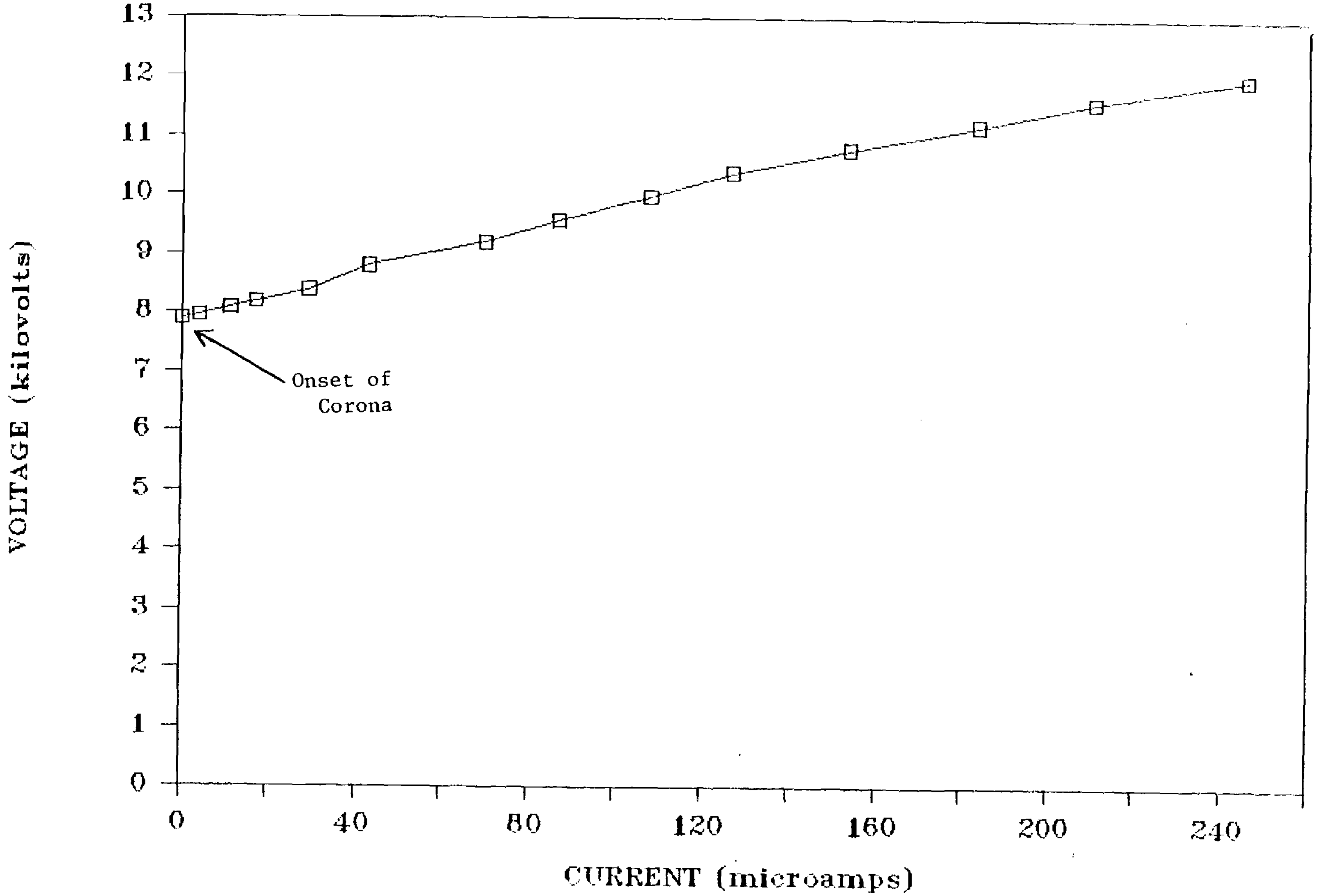
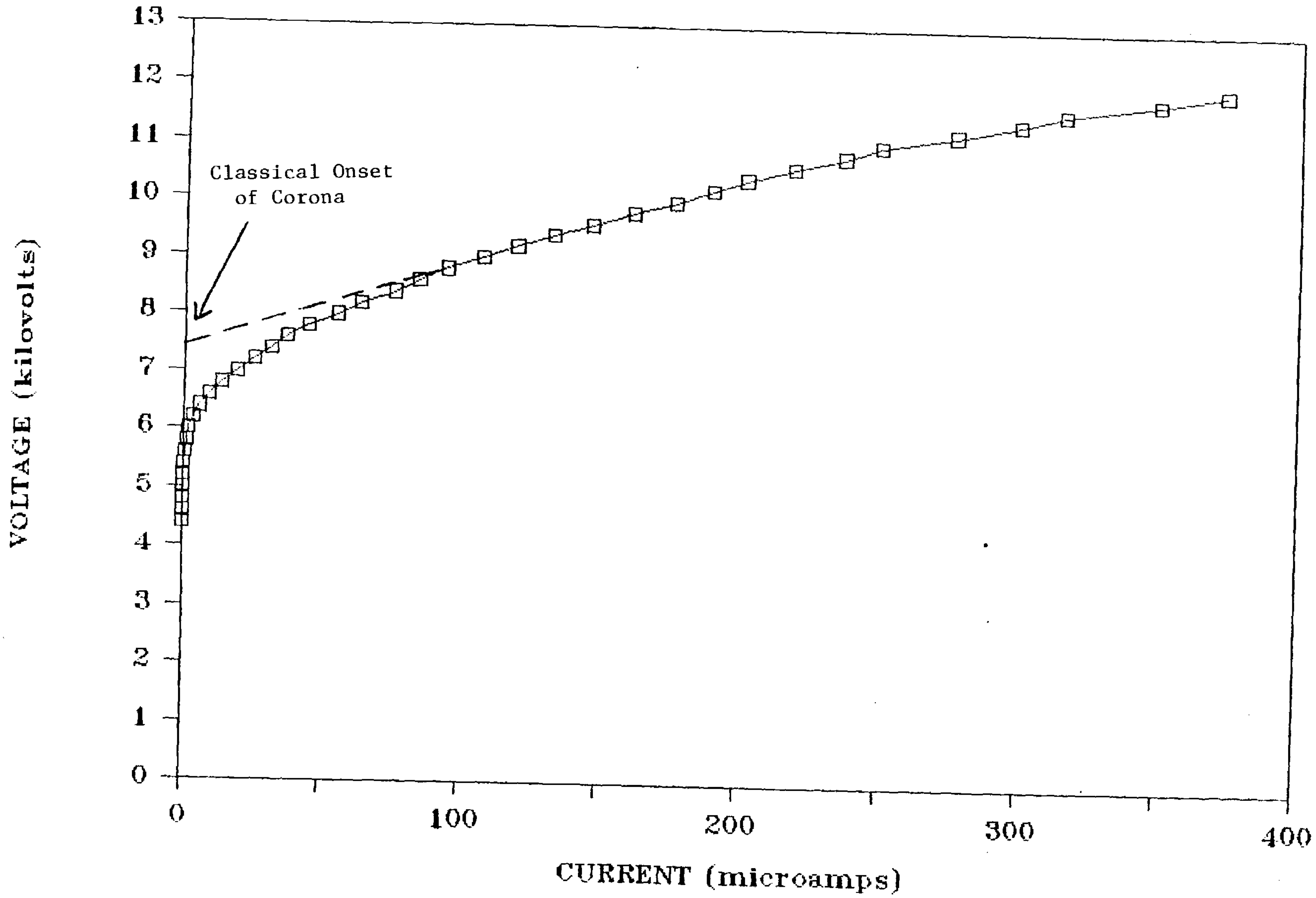

VOLTAGE (kilovolts)
CURRENT (microamps)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
0
40
80
120
160
200
240
Onset of Corona

Figure 36:


13
12
11
10
9
8
7
6
5
4
3
2
1
0
VOLTAGE (kilovolts)
0
100
200
300
400
CURRENT (microamps)
Classical Onset of Corona

measurements of NO were possible because of the sub-ppbv detection capabilities of the modified chemiluminescence NO instrument.

Our measurements of NO_x have shown that, unlike ozone, NO_x is not dependent on the wire radius, but its production is dependent only on the corona current. NO_x also appears to be independent of the type of metal inner electrode. The one exception to this was a stainless steel wire passed through a flame to provide an oxide layer on the wire. Table XI shows representative NO_x production for a fixed current using various wire source materials. These results show that we have achieved NO/NO_x measurements over a current range of 200 nA to 250 μA for applied fields that have been varied from 2.7 kV/m to 25 kV/m. In addition, the inner radius of the wire electrode has been varied from 6 μm to 300 μm.

Atmospheric Significance - Observations of atmospheric corona discharge near the surface are well documented. (Jacobson and Krider (1976), Livingston and Krider (1978), Standler and Winn (1979).) For example, several groups have measured the voltage field near the earth's surface in the vicinity of thunderstorms as well as under fair weather conditions. These measured fields are in the 5 to 20 kV/m and 100 V/m range, respectively. Coronal currents have also been measured from objects such as pine trees where peak values have been recorded of 100 nA/m^2 and average estimated yearly values have been estimated to be in the 1 nA/m^2 range. Our investigations have now shown that both O_3 and NO can be generated from coronal discharges involving pine needle surfaces.

The production of NO and O_3 from the terrestrial sources can be estimated using existing peak surface corona current measurements. For example, by combining the latter type measurements with our laboratory generated O_3/NO production efficiencies, overall source strengths for both O_3 and NO near thunderstorm activity can be obtained. The results from these calculations

Table XI

Surface Type	Diameter (μm)	Current (μA)	[NO_x] (molec/sec) ($\times 10^{15}$)	V_a (kV/m)
		POSITIVE CORONA		
Chromel	254	11	6.3	12.9
Aluminum	250	11	7.2	12.1
Tungsten	250	11	6.7	11.7
Copper	508	11	7.2	16.7
Stainless Steel	406	10	5.6	17.3
Stainless Steel (oxide)	406	10	35.	14.4
Multi-point	n/a	10	17.	n/a
		NEGATIVE CORONA		
Chromel	254	9	5.0	14.3
Aluminum	250	9	3.4	12.0
Tungsten	250	9	4.4	14.7
Copper	508	9	3.0	15.3
Stainless Steel (oxide)	406	10	3.2	12.5
Multi-point	n/a	10	2.9	n/a

suggest that localized high levels of O_3 and NO_x could be generated by corona discharge from pine needles (e.g. O_3 levels of $\gg$ 100 ppbv) and thus could result in deleterious effects to trees of this type. However, it appears that this surface source of O_3 and NO_x is unlikely to have a significant impact on the global budgets of either species. On the other hand, it has been hypothesized that corona discharges could dominate over stroke lightning in the electrical power dissipation within thunderstorms. In this context, it is of some interest that direct observations of x-ray fluxes within thunderstorm cells track measured corona currents. Both the corona currents and x-ray flux exhibit a maximum just prior to stroke activity and their values go to zero at the time of stroke occurence.

The applied fields within thunderstorms have been measured in the 40 kV/m to greater than 400 kV/m range. Coronal discharges under these high field conditions could thus produce positive ions with energies > 20 eV. It is therefore not unreasonable that corona effects within thunderstorms could result in the production of NO_x equal to or even exceeding that of bolt lightning. If so, virtually all past efforts to evaluate the global production of NO_x via electrified clouds have significantly underestimated the global yield of NO_x from this source since all are based on bolt lightning.

Our future research efforts in this area will be directed at characterizing the production of both NO and O_3 under high field conditions using ice crystal surfaces. This will involve the use of existing measurements of in-cloud coronal currents and x-ray fluxes, combined with laboratory generated O_3/NO production efficiencies. By so doing, we hope to ascertain the overall source strength for both O_3 and NO_x generated by coronal currents within thunderstorms.

VI. SUMMARY OF PAST ACTIVITIES AND PROPOSED FUTURE RESEARCH

A. Introduction

The first three year program funded at Georgia Tech by CRC was entitled "Atmospheric Nitrogen Oxides: Their Detection and Chemistry". As the title suggests, this program has consisted of two major components: the development of new instrument capability for measuring nitrogen oxide species; and studies of the chemistry of the nitrogen oxide family under clear air and cloud conditions as well as studies of this Family of compounds under day and nighttime conditions.

The field study component of our program was focused on measurements made at Georgia Tech's Stone Mountain Field station, complemented whenever possible with airborne measurements using the Georgia Tech Convair 340 or NASA's Convair 990 aircraft and Turbo-prop Electra.

From our vantage point, our three year program with CRC has been very successful as evidenced by several reviewed scientific papers now in print or in press and with at least five other papers now in various stages of being written. The latter papers will be submitted for publication over a time period of 2 to 8 months.

As of this writing, laser-induced fluorescence (LIF) instruments have been successfully developed and extensively field tested for detecting NO, NO_2, and HNO_2. In all three cases, multi-photon LIF techniques have been used, thus making these new detection systems not only the most sensitive available anywhere but also the most selective. Our group also has taken the initiative in making critical engineering modifications to the original designs of some of these new systems. In so doing, we have established a detection capability for more than one species using the same basic laser hardware and supporting optical elements. This new generation of technology has been highly successful in the simultaneous detection of NO and NO_2 at levels in the sub 10 pptv range. Finally, in addition to the successful development of LIF NO, NO_2, and HNO_2 sensors, we are now completing the final phase of a folded long-path differential absorption system for the detection of NO_3. This system should be fully operational at our Stone Mountain Field station by late 1987.

Our group's field studies have been programmed to keep pace with the rate at which new instruments have been developed. For example, due to instrument developments within the last ten months, we have been able to pursue scientific areas such as detailed nighttime HNO_2 studies and detailed examinations of the photochemical equilibrium relationship between NO, NO_2, O_3, and UV flux. Since one of the earliest instruments developed was the TP-LIF NO sensor, our early N_xO_y field studies involved measurements of NO. This early work involving NO measurements (together with ancillary measurements) resulted in significant new findings about the vertical distribution of NO in the troposphere as well as its variability over large horizontal spatial scales.In our case this ranged from industrialized sections of the U.S.A. to remote regions of the Eastern and Central Pacific. These same measurements also permitted for the first time a comprehensive evaluation of the ozone photo production tendency in regions of the troposphere nominally labelled "remote clean troposphere." These evaluations have clearly shown that even in these clean regions significant O_3 photo production can occur and that this production is predominantly driven by the levels of NO, even at mixing ratios of 30 pptv or less.

Another of our stated scientific objectives in our original proposal to CRC was that of assessing natural sources of NO/NO_x. Here again, the NO data base collected thus far has been quite revealing. For example, in the specific case involving remote regions of the North Pacific Ocean, we have found strong evidence showing that two of the major sources of NO are stratospheric/

tropospheric exchange and lightning, with the ocean itself being a negligibily small source. Concerning the evaluation of lightning sources of NO, we have succeeded in developing a totally new approach to estimating the global flux of lightning generated NO_x. This has involved direct measurements of NO from the outflow region (anvil) of cumulonimbus clouds. Following this approach, we have been able to estimate the global production rate of NO_x from lightning at 7 Mt(N)/year. This value is nearly 3 1/2 times larger than that estimated from recent evaluations based strictly on theoretical grounds. Currently, our NO data base from cummulonimbus clouds is still far too small for us to have a high degree of confidence in this early evaluation. However, this first-of-its-kind experimental approach to the problem has been well received by the scientific community and with an expansion in our data base over the next several years, it appears that the global production of NO_x from electrified clouds could become a well defined quantity.

On yet another front, there have been some potentially very important new measurements of NO under nighttime conditions at our Stone Mountain Field station. The levels observed are quite low, typically 10pptv or less, and can only be reliably measured using the TP-LIF NO sensor. Although a full understanding of the chemistry that might be responsible for these nighttime NO levels is still not at hand, the fact that NO is present has very important implications to our understanding of the entire N_xO_y chemical scheme at night, and thus, to the conversion of NO_x to HNO_3 at night.

More recently, within the last 10 months, with the completion of the HNO_2 sensor and the development of an LIF sensor that simultaneously measures NO and NO_2, we have been able to pursue still other scientific goals stated in our original proposal. As shown earlier in this text, with new measurements of HNO_2 and related variables we are now able to examine the role of HNO_2 in producing

OH radicals in the early and mid-morning hours. Such studies should lead to an improved understanding of the role of HNO_2 in inducing photochemical smog formation in urban/suburban areas of the U.S.A. Concerning the NO/NO_2 measurements, together with concurrent measurements of O_3 and UV flux (etc.), extensive measurements have now been completed in air masses over clean regions of the Pacific Ocean as well as over Southwestern U.S.A., under varying degrees of pollution. Thus, we believe in the coming months our data analysis/modelling activities should lead to a critical assessment of the photochemical equilibrium question involving the $NO/NO_2/O_3$ chemical system for a wide range of environmental conditions. Central to this assessment, we believe, will be the availability for the first time of highly reliable measurements of both NO and NO_2 over a very wide range of concentrations.

B. Proposed Future Work for CRC

Our first 3 year program with CRC can be broken down to time commitments of ~ 60% in the area of instrument development and 40% in pursuing science questions. We anticipate that with the success had in developing several new instruments during this three year program, any new program with CRC the balance between science studies and instrument development will be significantly shifted toward the former. Our current appraisal of this balance is 80% science oriented and 20% instrument development.

We are indicating a 20% time commitment to instrument development based on the assumption that one of our major science goals in any new program will involve the continuation of our investigation of nitrogen oxide chemistry. As summarized in Fig. 1 (Section I), the number of nitrogen oxide compounds and co-reactant species is indeed quite large. With regards to such critical co-reactant species as OH and HO_2, instrumental development programs are already well underway under the sponsorship of NSF and NASA. Completion of ground based operational field instruments is expected to occur within the next 1½ years. Yet another on-going program should result in the completion of an LIF sensor for measuring CH_2O also within the next 1 1/2 years.

One new instrument that we are now interested in installing at our Stone Mountain facility is a gas chromatograph. This system will be used in measurements of PAN and certain other hydrocarbons. It is recognized that the latter system does not, in the strict sense of the word, represent an instrument development effort since the methodology for making measurements of these species already exists. However, time will be required to set-up this hardware and to properly train personnel to ensure the collection of reliable data.

A key nitrogen species for which instrumental development will be required is N_2O_5. A knowledge of the concentration levels of the latter nitrogen oxide species may prove to be pivotal to our attaining a full understanding of nighttime N_xO_y chemistry, especially as it relates to assessing the relative importance of nighttime generated HNO_3 from NO_x. Several approaches are currently being evaluated; and when we submit a formal proposal to CRC, we hope to be putting forward recommendations on a preferred approach.

A final area where instrumental activity may be proposed is that of further upgrading our TP-LIF NO detection technology. In this case, however, we are not proposing to up-grade the system in terms of new laser hardware or even a reconfiguration of old laser hardware. Rather, it involves upgrading our fluorescence signal collection efficiency. Presently, although there is no problem in collecting an adequate signal for reliable NO concentration measurements (e.g., with 1 to 2 min. time resolution), the signal collection rate available with the current system is too low to permit NO/NO_2 flux measurements via the eddy correlation method. Use of the latter method for flux determinations typically requires a data collection rate of 5 to 10 Hz, with signal/noise ratios of $\geqq 10/1$. (Recall in the TP-LIF, the noise is normally defined by the photon statistical uncertainty in the signal itself.) Such an improvement in the TP-LIF system becomes possible if one can improve upon the fraction of the total fluorescence sampled. At present, it is significantly less than one percent. Within the last year, however, we have been working with a Japanese firm to develop a new type of photomultiplier tube that will have an increase in photocathode surface area of nearly a factor of 500. This suggests that the signal level per laser shot (the rep-rate being 10 Hz) should increase by nearly 500. If so, eddy-correlation flux measurements should become possible even from an airborne platform. Such measurements would make possible the evaluation of NO_x fluxes from soil exhalation. The latter NO source, together with lightning, are now considered to have the largest uncertainties in their values as related to estimating global and regional NO source fluxes.

In our pursuit of fundamental science questions, many of the questions for which answers will be sought are similar to those raised in our earlier program. For example, as noted in the previous text on "instrumental development", there is still much work to be done in documenting the magnitude of natural NO_x sources. This is a very sensitive issue since a critical question now being asked is: Have man's industrial activities overtaken the planets' natural NO_x sources? The extent to which this is occurring on regional and global scales will very likely have a major impact on the need--or lack of need-- to implement stronger NO_x emission controls. Thus, we believe that there should be a continuation of our lightning investigations, with this activity very likely being carried out in conjunction with one of our NASA programs. We are also interested in examining the other major natural NO_x source, soil exhalation. As noted above, this would most likely involve the use of the eddy correlation method, provided our proposed PMT signal enhancement scheme is successful.

A second area of study will again involve investigations of nighttime N_xO_y chemistry as delineated in Fig. 1 (Section I). With the completion of our initial program in instrumental development, we will be in a position to carry out one of the most comprehensive studies of nighttime N_xO_y chemistry of any group in the U.S.A. or Europe. For example, as related to nighttime HNO_3 production, the species HNO_2, NO, NO_2, NO_3, and HNO_3 will be measured along with numerous other interactive non-nitrogen species. Of continuing interest in our nighttime N_xO_y studies will also be more extensive investigations of the chemistry surrounding HNO_2. Far more information is needed about the sources of this species in an urban/suburban environment as well as its possible non-photolytic loss processes. In both of the above proposed studies, comprehensive modelling of the data will continue to be carried out under the direction of our distinguished colleague, Dr. William Chameides.

Daytime studies of fast photochemical cycling N_xO_y species define yet a third area of investigation. In this case, the addition of new field instruments to measure the reactive coupling species OH and HO_2 should provide a major impetus to these investigations. Of special interest here will be tests to determine if photochemical equilibrium is indeed reached for many of nitrogen oxide species shown in Fig. 1. Of equal importance will be our quantitative evaluation of the daytime production rate of HNO_3 via the $OH + NO_2 \xrightarrow{M} HNO_3$ reaction, thus enabling us to make quantitative comparisons of the day vs. nighttime production of HNO_3, a heretofore impossible experimental goal.

Although not explicitly stated, nearly all of the nighttime and daytime studies of N_xO_y chemistry will occur at our Stone Mountain Field sampling station. However, in the HNO_2 studies, some experimental investigations are also expected to occur on the Georgia Tech campus, near downtown Atlanta. Still a third sampling option that will be available in any future CRC program will be a mobile van. The Georgia Department of Natural Resources (DNR) has provided funds for our group to develop a 48 ft. mobile laboratory (including a considerable amount of new support measurement equipment). The lab will be used to carry out acid rain and photochemical oxidant studies at several different sites in the state of Georgia. This is projected to be a long term (e.g., 6 to 8 years) program. Much of the data collected should be of considerable interest to CRC in terms of its contrast and/or agreement with the more comprehensive data set to be collected at Stone Mountain.

In line with the DNR program now underway, it would be of considerable interest to us to expand our CRC program to include studies on sulfur chemistry, particularly as it might relate to the acid rain question. We are now routinely doing H_2O_2 analysis in rain and cloud water (when the latter is available); and within the next year to 1½ years, plan on adding gas phase H_2O_2 to our list of measurements. With the completion of the TP-LIF OH sensor, the use of an already developed LIF detector for SO_2, ion-chromatographic analysis of SO_4^{-2} as well as other aerosol and rain water ion analysis, we believe within 1½ years time we will be in a strong position to carry out highly informative investigations of atmospheric sulfur chemistry.

In concluding this brief overview of where we have been and where we are headed in our research at Georgia Tech, it seems appropriate to provide you with some estimate of the cost for any future program that might be proposed to CRC. Obviously, all the details in our planning are still not available; however, we believe that because of the complementing programs involving NSF, NASA, and the Gerogia Department of Natural Resources, research of considerable value to CRC could be completed for a very modest cost. Thus, our current estimates to maintain a highly productive research program range from $150,000 to $185,000 per year for each of three years.

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APPENDIX A

AMBIENT MEASUREMENT DATA TABLES

This appendix presents, in tabular form, the HONO measurements summarized in Table 3-2 along with the available ancillary measurements. Each date is separately tabulated. The measurements are coded as:

Time = measurement time (EST) for a point measurement or start time of a HONO measurement cycle (normally ~16 minutes in duration)

[HONO] = concentration of HONO in parts-per-billion (10^{-19}) by volume

SNR = signal-to-noise ratio for the HONO measurement or confidence limit (normally 90%) for upper limit estimate

DP_1, T_1 = dew point and temperature in degrees Celcuis based on National Weather Service data

WS_1, WD_1 = wind speed (m/sec) and wind direction recorded by the National Weather Service at Hartsfield International Airport

T_2, DP_2, WS_2, WD_2 = similiar to above except recorded on site

$[O_3]$ = concentration of ozone in ppbv

[NO], $[NO_2]$, $[NO_x]$ = concentration of NO, NO_2, and NO_x (molybdenum converter) in ppbv as recorded by Georgia Department of Natural Resources NAMS site at Georgia Tech (NO measurement normally contains offset of -5 ppbv)

$[HNO_3]$ = concentration of HNO_3 in ppbv.

UV, VIS = UV and visible solar flux (mV)

Aerosol composition data is not tabulated in this appendix.

Table D-1
12/23/85

Time	[HONO]	SNR	T_1	DP_1	WS_1	WD_1
19:00			10	5.6	4.6	SW
20:05	0.29	2.8				
20:24	0.32	3.4				
20:42	0.26	3.0				
20:59	0.31	3.2				
22:00			7.8	5.0	4.0	SW

Table D-2
12/24/85

Time	[HONO]	SNR	T_1	DP_1	WS_1	WD_1
13:00			13.3	2.2	7.5	SW
14:10	≤0.19	(90%)				
14:40	≤0.18	(90%)				
15:01	≤0.24	(90%)				
15:18	≤0.23	(90%)				
16:00			13.3	-0.5	8.1	NW

Table D-3
1/18/86

Time	[HONO]	SNR	T_1	DP_1	WS_1	WD_1
19:00			14.4	13.3 (rain)	2.9	SSE
21:06	≤0.12	(90%)				
21:22	≤0.11	(90%)				
22:00			14.4	13.3 (rain)	5.8	SW

Table D-4
2/2/86

Time	[HONO]	SNR	T_1	DP_1	WS_1	WD_1
19:00			18.3	7.2	4.6	SW
20:30	0.23	3.4				
20:44	0.18	2.9				
20:59	0.24	4.0				
21:21	0.28	4.2				
21:37	0.35	5.2				
21:55	0.35	5.1				
22:00			15.0	8.3	3.5	SW

Table D-5
2/3/86

Time	[HONO]	SNR	T_1	DP_1	WS_1	WD_1
19:00			17.6	6.1	2.9	SW
20:55	0.34	5.6				
21:11	0.41	6.2				
21:31	0.38	5.8				
21:59	0.34	5.7				
22:00			15.6	7.2	4.6	SSW

Table D-6

2/5/86

Time	[HONO]	SNR	T_2	DP_2	WS_1	WD_1
23:35	0.181	6.4				
23:52	0.243	>10				
00:00			14.5	13	2.3	ESE
00:10	0.216	>10				
00:30			14.5	13		
00:36	0.169	6.0				
00:53	0.24	>10				
1:00			14	13		
1:11	0.21	9.5				
1:28	0.145	5.8				
1:30			14	13.5 (fog)		
1:49	0.105	3.7				
2:00			14.5	13.5 (fog)		
2:14	≤0.064	(90%)				
2:30			13.5	13.5 (fog)		
2:31	≤0.049	(90%)				
2:48	≤0.055	(90%)				
3:00			13.5	13.5		
3:04	≤0.077	(90%)				
4:00					2.3	ESE

Table D-7

2/9/86

Time	[HONO]	SNR	[HNO_3]	[O_3]	T_1	T_2	DP_1	DP_2	WS_1	WD_1
19:00					14.4		6.7		4.0	SE
20:25	0.36	6.4		20						
20:40	0.51	9.4		33						
20:55	0.78	>10	0.68	8		14		9.0		
21:17	0.89	>10		7						
21:36	0.94	>10		9						
21:52	1.29			0						
22:00					12.2		13.3		4.6	SE
22:08	1.46	>10		0						
22:35	1.82	>10		0						

Table D-8

2/11/86

Time	[HONO]	SNR	[O_3]	T_1	T_2	DP_1	WS_1	WD_1
19:00				-1.7		-6.1	8.6	NW
20:20	0.51	>10	5					
20:35	0.49	>10						
20:50	0.72	>10	5					
21:10	1.05	>10						
21:25	1.39	>10	14					
21:41	1.77	>10	4					
22:00	2.12	>10	8	-2.8		-6.1	8.6	NW
22:15	1.46	>10	31		-3			
22:40	2.02	>10						

Table D-9a
2/16-17/86

Time	[HONO]	SNR	$[O_3]$	T_2	DP_2	WS_1	WD_1
18:17	0.98	>10	22	17.8	10.8	4.3	S
18:34	0.65	>10					
18:48	0.41	>10					
19:12	1.09	>10					
19:18	1.11	>10					
19:38	0.78	>10	14.5	16.7	8.9	4.3	S
19:54	≤0.036	(90%)	19			3.9	S
20:36	0.85	>10	21	14.7	8.6		
20:50	0.71	>10	27				
20:58	0.80	>10	33			5.2	S
21:24	1.21	>10	34				
21:36	1.15	>10	31	15	8.3		
21:58	0.58	>10	37				
22:04	0.24	>10	38				
22:17	1.11	>10	16				
22:48	0.44	>10	21	14.4	8.3		
22:52	0.79	>10	22				
23:07	1.67	>10	15	14.4			
23:15	1.64	>10	12				
23:38	1.50	>10	21	14.4	8.8		
23:51	1.44	>10	20				
00:00	1.50	>10	22			5.2	S
00:09	1.52	>10	20				
00:23	1.63	>10	5				
00:34	1.36	>10	16	14.4	8.6		
01:19	1.34	>10	11				
01:50	1.34	>10	29	13.6	8.9		
01:58	1.50	>10	27			4.3	S
02:09	1.43	>10	27				
02:23	1.30	>10	28				
02:33	1.32	>10	25				
02:37	1.55	>10	26				
02:49	1.24	>10	24	13.3	8.9		
03:03	1.76	>10	14			2.6	S
03:08	1.92	>10	8				
03:15	2.04	>10	5				
03:27	2.14	>10	0				
03:35	2.27	>10	3				
03:43	2.43	>10	2				
03:55	2.61	>10	0				
04:03	2.64	>10	0			2.2	S
04:19	2.35	>10	15				
04:29	3.06	>10	11				
04:38	2.61	>10	7				

Table D-9a continued

2/16-17/86

Time	[HONO]	SNR	[O$_3$]	T$_2$	DP$_2$	WS$_1$	WD$_1$
04:46	1.92	>10	18				
04:55	1.75	>10	21				
05:03	1.87	>10	18	13.2	8.8	2.2	S
05:10	1.72	>10	10				
05:26	1.64	>10	25				
05:36	1.66	>10	7				
05:38	1.73	>10	19				
05:42	1.70	>10	11				
05:46	1.91	>10	4				
05:54	2.11	>10	0				
06:03	2.32	>10	0			3.9	S
06:14	2.12	>10	3				
06:22	1.87	>10	0				
06:30	2.19	>10	0				
06:40	2.25	>10	0				
06:48	2.10	>10	0				
06:56	2.20	>10	0				
07:05	2.18	>10	0		8.9	3.5	S
07:16	2.23	>10	0				
07:28	2.11	>10	0				
07:40	1.77	>10	0				
07:48	1.97	>10	0				
07:56	1.98	>10	0				
08:06	1.64	>10	0		8.9	4.3	S
08:22	1.96	>10	0				
08:30	1.82	>10	0				
08:38	1.91	>10	0				
08:43	1.22	>10	0				
08:49	1.14	>10	4				
08:54	1.06	>10	11				
09:02	0.077	2.6	15				
09:13	≤0.032	(90%)	17				

Table D-9b
2/16-17/86

Time	SO_2	NO_2	NOx	NO
17:00	3.5	18	30	15
18:00	3.5	23.5	40	19
19:00	3.5	38.5	60	23
20:00	3.75	29	42	16
21:00	4	27	38	13
22:00	3.25	21.5	31	11
23:00	4.25	34	46	14
00:00	5.75	34.5	41	9
01:00	4.25	32	40	10
02:00	2.75	20	26	8
03:00	3	24.5	30	7
04:00	2.75	31	37	7
05:00	2.25	28	34	7
06:00	3.25	38.5	50	12
07:00	5.25	51.5	80	30
08:00	5.25	51.5	100	50
09:00	7.5	55	124	71
10:00	4.5	44.5	78	35

Table D-10

2/28/86

Time	[HONO]	SNR	T_1	T_2	DP_1	WS_1	WD_1
19:00			+0.5	2	-8.9	4.6	NW
19:10	0.11	4.5					
19:26	0.26	9.7					
19:35	0.24	>10					
19:52	0.47	>10					
20:14	0.63	>10					
20:32	0.51	>10					
20:51	0.93	>10					
21:07	1.22	>10					
22:00			-0.5		-10.0	5.2	NW
22:06	1.66	>10					
22:18	1.17	>10					
22:31	1.76	>10					
22:47	1.93	>10					
23:04	1.49	>10		-1			
23:20	1.44	>10					
23:36	2.01	>10					
23:51	2.66	>10					
00:00				-1.5			
00:10	2.08	>10					
00:31	3.92	>10					
00:47	3.46	>10					
01:00			-2.2		-11.7	6.9	NW
01:01	3.68	>10					
01:16	2.94	>10					
01:31	3.16	>10					

Table D-11

3/9/86

Time	[HONO]	SNR	T_1	T_2	DP_1	DP_2	WS_2	WD_2
18:00				19.4		9.4	6.1	S
18:30				20.6		9.4	6.1	S
18:40							7.8	S
18:50	0.43	6.4					7.0	S
18:58	0.63	9.6						
19:00			19.4	20.8	6.7	7.7	4.8	S
19:09	0.33	5.3						
19:10							3.5	S
19:17	0.51	8.0						
19:20							3.0	S
19:26	0.40	6.3						
19:30				20.0		7.7	3.5	S
19:34	0.25	4.0						
19:40							1.7	S
19:41	≤0.15	(90%)						
19:48	0.29	4.5						
19:50							2.6	S
20:00				20.0		7.0	5.7	S
20:10							4.8	S
20:20	0.15	2.4					3.9	S
20:26	0.24	3.8						
20:30				20.0		7.9	3.5	S
20:34	0.14	2.2						
20:40	0.23	3.7					3.9	S
20:50							3.5	S
21:00				19.7		7.7	3.9	S

Table D-12

3/16/86

Time	[HONO]	$[O_3]$	NO	NO_2	NOx	UV	VIS	T_1	DP_1	WS_1	WD_1
16:00										3.0	W
16:30			9	18	27			18.9	15		
16:42						1.6	3.4				
16:45						1.5	3.3				
16:48						1.5	3.2				
16:50	0.26										
16:52						1.4	3.0				
16:57						1.4	2.9				
17:00								18.3	14.4	4.3	W
17:08		132				1.2	2.5				
17:11						1.1	2.4				
17:16		104				1.0	2.3				
17:17	0.18										
17:21		90				1.0	2.1				
17:25						0.9	2.0				
17:30			7	15	22			20.6	14.4		
17:35						0.7	1.6				
17:43						0.6	1.4				
17:52						0.5	1.1				
18:00								20	13.3	6.1	NW
18:03		27				0.4	0.8				
18:06						0.4	0.7				
18:09		36				0.3	0.6				
18:10	0.07										
18:14		32				0.3	0.5				
18:23						0.2	0.3				
18:24	0.15										
18:26	0.08										
18:28	0.12					0.2	0.2				
18:30			6	24	30			19.4	13.9		
18:32						0.1	0.2				
18:37		30				0.1	0.1				
18:40	0.34					0.0	0.1				
18:45		30					0.0				
18:57		28									
19:00	0.28							19.4	14.4	3.0	NW
19:06		29									
19:10		22									
19:17	0.55										
19:21		8									
19:30			10	46	56			17.8	13.9		
19:34	0.45										
19:39		3									
19:48	0.29										
21:00								19.7	7.7	3.9	S

Table D-12 Continued

3/16/86

Time	[HONO]	[O_3]	NO	NO_2	NOx	UV	VIS	T_1	DP_1	WS_1	WD_1
19:53		0									
19:57		0									
20:00								17.2	12.2	3.0	NW
20:03	0.67										
20:09		0									
20:15	0.59										
20:23		0									
20:30			87	52	139						
20:31	0.60	0									
20:52	0.92	0									
20:54		0									
21:00								16.1	12.8	3.0	N
21:30			76	50	126			16.7	12.8		
22:00								15.6	12.2	2.0	NW

Table D-13

3/20/86

Time	[HONO]	SNR	$[O_3]$	NO	NO_2	SO_2	T_1	DP_1	WS_1	WD_1
20:00				10	24	30				
20:10	0.66	>10								
20:28	0.64	>10								
20:46	0.78	>10								
21:00				9	24	29				
21:19	0.64	>10								
21:34	0.81	>10	36							
21:51	0.93	>10	28							
22:00				6	19	30	3.9	-4.4	5.2	NW
22:09	0.91	>10								
22:29	0.95	>10	36							
22:50	0.88	>10								
23:00				6	17	31				

Table D-14a

3/21-22/86

Time	[HONO]	SNR	$[O_3]$	$[HNO_3]$	UV	VIS
20:30	0.43	>10	8			
21:03	0.51	>10	0			
21:40	0.49	>10				
22:20	0.46	>10	0	0.646		
22:45	0.49	>10	9			
23:03	0.73	>10	0			
23:30	0.84	>10		0.804		
23:47	0.45	>10				
00:00	0.53	>10				
01:13	1.08	>10				
01:45	1.17	>10	0	0.612		
02:05	1.08	>10				
02:30	1.16	>10	0			
02:45	0.86	>10				
03:05	1.59	>10	0			
03:22	1.68	>10		0.544		
03:45	1.53	>10				
04:20	1.31	>10	0			
04:35	1.64	>10				
04:53	1.39	>10	0			
05:10	1.35	>10	0	0.311		
05:35	1.27	>10				
05:50	1.07	>10	0			
06:12	0.94	>10	0			
06:25	0.85	>10	3		0.1	0
06:38	0.96	>10	3.5		0.1	0.1
06:55	1.54	>10	2	0.499	0.15	0.3
07:18	1.73	>10	3		0.45	0.9
07:32	0.77	>10	2.5		0.65	1.3
07:45	0.48	7.5	3.5		0.85	1.8
08:01	0.39	7.1	4		1.05	2.25
08:15	0.22	4.6	4		1.3	2.65
08:30	0.40	5.1	10		1.6	3.2
08:50	≤.06	(90%)	11		1.8	3.65
09:05			13		2.1	4.3
09:15					2.3	4.6
09:25					2.5	4.9

Table D-14b

3/21-22/86

Time	NO	NO_2	SO_2	T_1	DP_1	WS_1	WD_1
20:00	6	21	33			6.5	NW
21:00	6	21	35			5.7	NW
22:00	8	29	35			5.7	NW
23:00	7	26	32			3.9	NW
00:00	8	28	31	-1.1	-11.6	3.9	NW
01:00	27	38	33	-1.7	-11.8	5.2	NW
02:00	19	37	34	-2.2	-12.2	4.3	NW
03:00	7	32	31	-2.8	-11	4.3	NW
04:00	6	31	31	-2.8	-10.6	4.3	N
05:00	8	33	31	-3.3	-10.6	3.5	NW
06:00	22	37	32	-3.3	-10.6	4.3	N
07:00	11	31	32	-3.9	-12.4	3.0	NW
08:00	57	37	34	-2.2	-10	2.7	N
09:00	26	28	31			3.0	NW

Table D-15

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Time	[HONO]	SNR	NO	NO_2	SO_2	T_1	DP_1	WS_1	WD_1
22:00			74	69	43	11.7	-4.4	3.0	W
22:16	2.22	>10							
22:45	2.63	>10							
23:00			20	53	36				
23:01	1.53	>10							
23:28	1.42	>10							
23:45	2.01	>10							
00:00			52	61	35	8.3	-2.2	4.0	NW
00:19	1.90	>10							
00:36	1.47	>10							
01:02	1.59	>10							
01:19	2.17	>10							