United States
Environmental Protection
Agency

Office of Mobile Sources
Emission Control Technology Division
2565 Plymouth Road
Ann Arbor, Michigan 48105

EPA 460/3-85-009a
September 1985

Air

EPA

Outdoor Smog Chamber Experiments: Reactivity of Methanol Exhaust

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Prepared under Subcontract with
Southwest Research Institute
Contract No. 68-03-3162
Work Assignment 30

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Prepared for

U. S. ENVIRONMENTAL PROTECTION AGENCY
Office of Mobile Sources
Emission Control Technology Division
2565 Plymouth Road
Ann Arbor, MI 48105

September 1985

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Abstract

The purpose of this project was to provide an experimental smog chamber database especially designed to test photochemical kinetics mechanisms that would be used to assess the effects of methanol fuel use in automobiles. The mechanisms would be used in urban air quality control models to investigate the advantages of large scale use of methanol fuel in automobiles. The smog chamber experiments were performed during three summer months. They have been added to the existing UNC database for photochemical mechanism validation and testing, bringing the total number of dual-experiments in the database to over 400.

Three different hydrocarbon mixtures were used: a 13-component mixture representing synthetic automobile exhaust; an 18-component mixture representing synthetic urban ambient hydrocarbons; and a 14-component mixture derived from the synthetic automobile exhaust by the addition of n-butane. Three different synthetic methanol exhaust mixtures were used: 80% methanol/20% formaldehyde; 90% methanol/10% formaldehyde; and 100% methanol. All experiments used a target initial concentration of 0.35 ppm oxides of nitrogen, which was 80% nitric oxide. Two basic levels of the hydrocarbon mixture were used: 3 ppmC and 1 ppmC which gave approximately a 9 to 1 and a 3 to 1 hydrocarbon to nitrogen oxide ratio.

In the experiments, a reference mixture of 100% of the hydrocarbon mixture was reacted on one side of the dual chamber while a "substituted" mixture of 67% carbon hydrocarbon mixture, 33% carbon synthetic methanol exhaust (with one of the three levels of formaldehyde) was reacted on the other side of the dual chamber. In this manner, the relative reactivities of the two systems can be directly compared and models must reproduce both sides of the chamber with one set of simulation assumptions.

Twenty-nine dual smog chamber runs were conducted. Eighteen of these experiments are satisfactory for model testing and fourteen are excellent. The other 11 experiments, while having poorer sunlight, which complicates model testing, are still quite useful to support the trends or directional effects of the substitution process.

Synthetic methanol exhaust substitution in these experiments never resulted in an increase in ozone maximum or a shorting of time to events over that of the reference side, even for a synthetic methanol mixture with 20% formaldehyde.

For the highly reactive synthetic automobile exhaust at the 3 ppmC level, there was essential no reduction in ozone when synthetic methanol was substituted. This was primarily because these systems were limited by available oxides of nitrogen and not by the organic reactant. There was a delay in time to events that was reduced to almost no delay in the 20% formaldehyde experiments. At the 1 ppmC level, there was 30–40% reduction in maximum ozone when the synthetic methanol exhaust was substituted, depending upon the level of formaldehyde in the methanol exhaust.

For the less reactive synthetic urban mixture at the 3 ppmC level, there was ≈15% reduction in maximum ozone when the synthetic methanol exhaust was substituted. At the 1 ppmC level, which produced less than 0.15 ppm ozone, there was an 0–80% reduction in ozone maximum depending upon the formaldehyde content of the synthetic methanol exhaust.

A small demonstration modeling exercise suggested that even the newest version of the Carbon Bond mechanism has difficulties correctly simulating the range of conditions in these experiments and further model testing with these data are strongly recommended.

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Acknowledgements

This project was assisted by several university staff and many students. Richard Kamens managed the construction of the methyl nitrate synthesis apparatus and David Benham performed the synthesis work. The site operations were managed by John Suedbeck.

The following students performed data processing tasks: Lynn Clark, Jeffrey Hoffner, Charles McDowell, Jennifer Jeffreys, Greg Yates, and Cindy Stock. The following students performed experiments at the site: Jeff Arnold, David Benham, Lisa McQuay, and Joe Simmeonssen.

1

Introduction

Need for Data

Methanol is an alternative fuel for automobiles. The Environmental Protection Agency,[1] various groups in southern California,[2] The Department of Energy, E.I. DuPont de Nemurs Co., and ARCO Petroleum Co.[3] have been very active in investigating the use of methanol fuel (95% methanol, 5% isopentane or 85% methanol, 15% gasoline) in modified passenger cars.

To assess the effects that large scale use of methanol fuel might have on an urban air shed, complex urban air shed models (UAM) are needed. These models combine the effects of reactive emissions, local transport, vertical mixing, and chemistry to predict the distribution of pollutants (*e.g.* ozone) in the air shed. With these models, the effects of changes in emissions can be predicted and thus the probable effects of a particular control strategy can be assessed before complex and costly policies are promulgated.

A natural question that arises in the application of such models is "How accurate are the predictions?" This can only be answered by testing the model components individually and the model as a whole. Testing usually means comparing the model predictions against measurements made in real situations. One of the most complex components of the urban air shed model is the chemical mechanism that is supposed to describe the urban atmospheric chemistry. This component is often developed independently of the UAM and the same mechanism can be incorporated into models with varying degrees of meterological complexity (*e.g.* trajectory models vs. multi-layer grid models).

Photochemical Reaction Mechanisms For Urban Air shed Models

In an urban air shed model simulation, chemical transformation is only one process affecting pollutant concentrations. Emissions, transport, dilution, dry deposition, and reaction all change the concentrations. In this complex situation, it is not possible to unambigiously determine if the representation of the chemical transformation process is adequate. In addition, the atmosphere contains many hundred chemical species and not all of these can be represented in the chemical model. To keep the UAM model solvable, some generalization processes (*e.g.* treat all aldehydes as if they were acetaldehyde), and some deletion processes (*e.g.* no need to represent acetone), and some distortion processes (*e.g.* apply the same rate constant to all paraffins larger than butane) must be used in constructing mechanisms for use in UAMs. Different choices in implementing these simplifying processes leads to different overall representations of the chemical transformations by different model developers; it is not clear that there is one best mechanism.

To improve the belief that the chemical transformation process is adequately represented, especially in light of the simplifications needed to treat the large number of species, photochemical mechanisms are tested for their ability to represent events in situations where chemistry is the dominant process affecting concentrations. Thus smog chambers are used to create various degrees of chemical complexity and the models are tested for their ability to represent the chemical transformations in these chamber systems.

It is important to recognize, however, that the most dominant factors affecting concentrations in the urban atmosphere are dilution (which can easily be five-fold over the course of a day) and emissions of precursors into small morning mixing heights. Except for a few experiments performed at UNC, smog chamber experiments do not normally include these important factors. Therefore, caution must be used when attempting to extrapolate chamber results to the ambient atmospheric conditions. This is the primary function of the urban air shed model: to combine the effects of all important processes.

The chamber test situation has to be complex enough to include important aspects of the urban situation and yet simple enough to explicitly test the chemical mechanism. Experiments are usually designed to proceed from a simple situation to an approximation of an urban situation in a successive series of increasingly complex experiments. Thus test conditions usually begin with simple one-HC systems in static operating conditions and proceed to simple-HC mixtures and then to complex-HC mixtures. When these systems can be adequately represented by the chemical model, more realistic urban-like operating conditions are added. For example, in addition to using complex HC mixtures, large dilution is used throughout the experiment and reactive emissions are injected continuously. A demonstration that models work for these conditions certainly enhances the belief that these models would give reasonably good predictions in the urban atmosphere simulation. Certainly, one would have to be suspicious of a model that could not adequately simulate the chamber conditions which are clearly simpler than the urban situation.

Previous Methanol Test Data

The University of Santa Clara (USC) conducted a series of indoor smog chamber experiments to investigate the impact that exhaust from cars using methanol fuel might have on urban photochemistry. In these experiments, the effect of a reduction of 33% of the volatile organic compounds (VOC) in a synthetic hydrocarbon mixture was compared with substitution of 33% of the VOC with synthetic methanol exhaust.[3] The experiments were performed at three hydrocarbon (HC) to nitrogen oxides (NO_x) ratios: 3:1, 9:1, and 27:1. Table 1 lists the composition of the surrogate mixtures used in the study. Figure 1 shows an example of the ≈9:1 HC-to-NO_x data that were produced in this study.

System Applications Inc. (SAI) used the chamber results to test the ability of the Carbon Bond III photochemical mechanism to represent the effects of methanol-fuel substitution.[3] Some problems with the mechanism's representation of aromatics were encountered in these tests and the mechanism was expanded to include more detailed aromatics representation. The new mechanism was then used in a series of air shed model simulations to estimate the benefits of large scale use of methanol-fuel in the South Coast Air Basin of Los Angeles.[4,3] Whereas the original air shed simulations with CB3 mechanism suggested ≈22% reduction, the new, expanded CBM suggested ≈18% reduction in the maximum 1-hour ozone (O_3) level when 100% of the mobile source VOC (approximately one-half the total urban VOC) was replaced with 90% methanol and 10% formaldehyde on a per carbon basis. The study also found that the results were very sensitive to the assumption of how much formaldehyde was in the methanol exhaust.

Considering the discussion above, there are some aspects of the USC/SAI study that are troublesome:

1) The experimental conditions of the indoor chamber resulted in very fast experiments and sometimes the initial conditions were not very typical of urban-like conditions (*e.g.* initial NO_x=1.2 ppm). This means that models that were tested with the chamber data must be "extrapolated" significantly when they are applied to urban ambient atmospheric conditions.

Table 1. University of Santa Clara Synthetic HC Mixtures

(Units are fraction of total carbon)

HC Mixture

Compound	Fraction	Adj. Fraction[a]
n-butane	0.150	0.169
n-pentane	0.200	0.225
2,3,4-trimethyl pentane	0.150	0.169
ethylene	0.050	0.056
propylene	0.050	0.056
toluene	0.125	0.141
m-xylene	0.125	0.141
iso-butene	0.150	
(formaldehyde)	(0.038)	(0.042)
(acetone)	(0.112)	
paraffin	0.500	0.563
olefin	0.100	0.113
aromatic	0.250	0.282
aldehydes		0.042
and ketones	0.150	
Total	1.000	1.000

Methanol Mixture

Compound	Fraction	Adj. Fraction
methanol	0.692	0.900
isobutene	0.308	
(formaldehyde)	(0.077)	0.100
(acetone)	(0.231)	
Total	1.000	1.000

[a] USC used iso-butene as a surrogate for formaldehyde. It was assumed that, in a reactive system, iso-butene would be rapidly converted to formaldehyde and acetone by hydroxyl radical attack. It was further assumed that acetone was unreactive and could be omitted in calculating the composition of the mixture. The carbon fractions omitting the acetone are given in the column headed "Adj. Fraction."

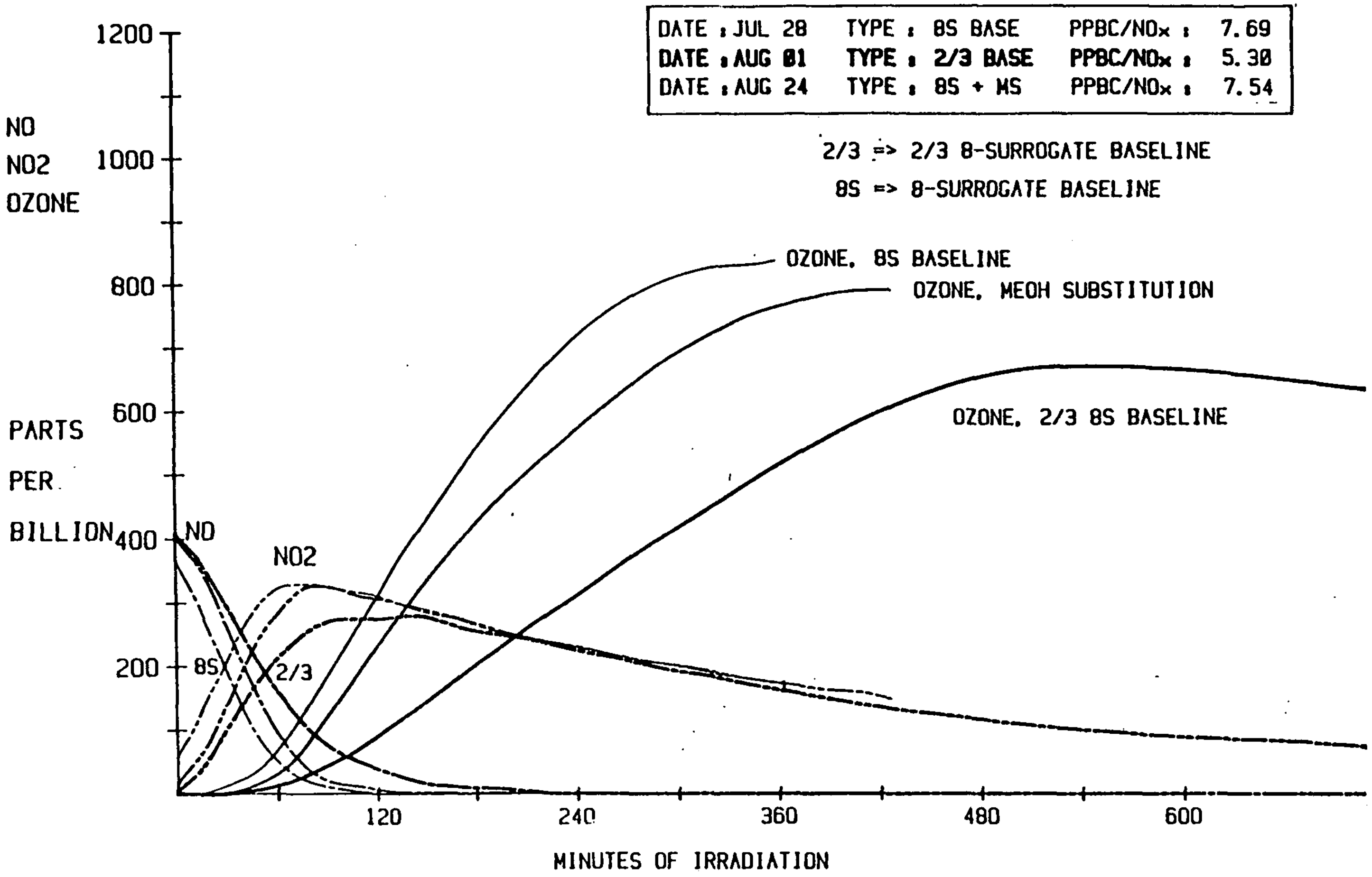


Figure 1. University of Santa Clara Indoor Chamber Experimental Results.

2) The surrogate mixture *did not contain formaldehyde*, but instead used iso-butene as a substitute for formaldehyde in both the urban mixture and in the methanol exhaust. This was based upon the assumption that iso-butene would rapidly react to produce formaldehyde. The $HO^{\cdot}$ reaction with iso-butene, however, produces an $RO_2^{\cdot}$ radical that converts an NO to an NO_2 for each iso-butene, *before making formaldehyde and acetone.* This "extra" reactivity would not occur with formaldehyde. Also the delay in the production of HCHO may not have correctly represented the importance of the role of the formaldehyde from the methanol exhaust, particularly at the low HC-to-NO_x ratio. In addition, acetone is a photolytic species that appears explicitly in the newer CBX mechanism at a non-negligible photolysis rate, contributing additional new radicals. Thus substituting for formaldehyde leads to the need for another "extrapolation" of models tested with these data when used for urban simulations.
3) The CB3 mechanism had difficulty simulating the surrogate HC mixture used; this was attributed to the presence of 12.5% m-xylene in the synthetic HC mixture. The CB3 mechanism was revised to include a new representation for xylenes. The new CB mechanism was not explicitly tested for its ability to represent either m-xylene or other higher aromatics. It predicted a significantly smaller reduction in the air shed simulations. It is not possible with just the USC data to tell if the adjusted model predictions are correct or not.
4) When a model has difficulty simulating aspects of the USC chamber, there is no simpler set of data for this chamber that could be used to test the component parts of mechanisms, and thus, in this chamber, it would be difficult to determine if a problem existed with the mixture chosen, with the chamber characterization, with the operating conditions, or with the chemical mechanism used.

These observations suggested that additional test data were needed to assure that urban air shed simulation models were adequate to assess the effects of large scale methanol fuel use.

Previous UNC Model Testing Data

The University of North Carolina, through an extensive program with EPA, has been producing smog chamber data from a unique large dual outdoor smog chamber for more than 12 years. The primary thrust of this program has been to produce data to test the adequacy of developing photochemical kinetics mechanisms to represent various critical phenomena in the chemical transformation processes. A logical extension of this work was to include methanol-fuel exhaust in the reactivity tests already being conducted. Because of the extensive data set available, this program would be tightly focused on methanol-related phenomena. Yet, because these methanol experiments would not stand alone, they would still have a generality and wide range of applicability in testing mechanisms because they would fit logically into an extensive test series.

Four projects using the UNC Outdoor Smog Chamber have contributed the majority of data for model testing. Although these projects had their own goals and purposes, they were not designed or performed totally independently of each other nor of this project. Instead each project depended upon data from other projects to address specific issues. Thus data from these projects are needed to complete the partial description provided by the specific work performed in this project. These other projects are briefly described below.

Simple Systems Project

Between 1977 and 1981 this project produced 114 dual-experiments designed to test explicit mechanisms for aldehydes, olefins, paraffins, and simple two-component mixtures. These data were described in a final report[5] and a magnetic tape containing the data is available from UNC. Data were sent to several EPA-sponsored model-development groups including SAI. These data were part of the set used to test and develop the CB3 mechanism.[6]

The final report described guidance for modeling the data including recommendations on treatment of light data, dilution rates, wall losses, and use of water vapor and temperature data. These guidelines are also applicable to the data described in this report.

Reactivity Project

Another 70 dual-experiments were produced as part of a 1981–83 EPA grant[7] that investigated how well models could represent reactivity changes in simple and complex HC mixtures. Table 2 lists the composition of some of the mixtures used in these tests. Blends of the mixtures in Table 2, at various ratios, were also used. The best of these experiments have been distributed to the model development groups at SAI and the University of California at Riverside (UCR). UCR is up-dating and revising the Atkinson, Lloyd, and Winges(ALW) mechanism[8] for use in EPA air shed and EKMA models.

Automobile Exhaust Project

Another 31 dual-experiments using automobile exhaust from two vehicles were pro-

Table 2. Composition of Hydrocarbon Mixtures Used in UNC Smog Chamber Experiments.

(units are percent of total carbon)

Compound	SIMMIX	UNCMIX	SIMARO	COMARO	SYNAUTO	P/B	P/B/T	BASMIX
butane	0.4002				0.0391	0.7663	0.5352	0.3140
pentane	0.3183	0.2531						0.1268
isopentane		0.1484			0.0519			
2-methylpentane		0.0996						
2,4-dimethylpentane		0.0864						
2,2,4-trimethylpentane		0.1202			0.1121			
ethylene	0.1631	0.1167			0.2391			0.0650
propylene	0.1184	0.0524			0.0416	0.2337	0.1648	0.0943
1-butene		0.0254			0.0196			
trans-2-butene					0.0196			
cis-2-butene		0.0313						
2-methyl-1-butene		0.0347						
2-methyl-2-butene		0.0317						
benzene					0.0538			
toluene			0.4886	0.2482	0.2115		0.3000	0.2000
m-xylene			0.3880	0.1882	0.1026			0.2000
o-xylene					0.0481			
1,2,4-trimethylbenzene			0.1234	0.2803	0.0564			
n-propylbenzene				0.1371				
sec-butylbenzene				0.1522				
formaldehyde					0.0200			
total paraffin	0.7185	0.7077	0.0000	0.0000	0.2031	0.7663	0.5352	0.4408
total olefin	0.2815	0.2922	0.0000	0.0000	0.3199	0.2337	0.1648	0.1593
total aromatic	0.0000	0.0000	1.0000	1.0000	0.4724	0.0000	0.3000	0.4000

duced as part of a 1982–84 EPA cooperative agreement. These experiments were described in detail in a final report,[9] and the processed data have been sent to SAI and UCR for model testing.

In the automobile exhaust work, an HC-mixture, which imitated the reactivity of automobile exhaust, was produced by direct side-to-side comparison experiments. This mixture was used in the methanol work and will be described in Chapter 2.

Complex Systems Project

This 1981-83 project produced 128 experiments focused on aromatics chemistry, complex mixtures, and dynamic chamber conditions such as large dilution (five-fold) and continuous injection of reactants. The final report[10] for this project presents an organizational scheme for all 346 experiments from all of the projects through the end of 1983. It also discusses three examples of selecting runs to test an explicit toluene mechanism, to test dynamic operating conditions, and to test an EKMA-type mechanism. The best of these experiments have been distributed to the model development groups at SAI and UCR.

Purpose

The purpose of this research was to produce data, using an outdoor smog chamber, that could be used by model developers to test their chemical mechanisms. The mechanisms would then be used in urban air shed simulation models to predict the effects of large scale methanol fuel use in urban areas.

The reaction mechanism's ability to correctly predict the effects of large changes in the composition of the HC mixture caused by substituting methanol and formaldehyde for mixture carbon is the most important factor that was tested in the experiments performed in this project. In addition, a large number of well matched experiments using well characterized and complex HC mixtures that had a range of reactivity and were based on extensive urban field analysis and automobile exhaust analsysis were to be produced.

It was **NOT** the purpose of this project to:

- reproduce the USC work;
- simulate urban air shed conditions;
- simulate the effect of evaporative emissions; and
- validate mechanisms.

Some comparisons of model predictions and chamber data were performed as part of this project. The focus of this exercise was to demonstrate the utility of the data produced and not to validate or test mechanisms. As described in the introduction, such testing would require a much more extensive set of chamber data and thus would have to use information from other projects.

Approach

The basic tests consisted of side-by-side experiments in which the chemistry of a typical synthetic auto-exhaust or synthetic urban hydrocarbon mixture, at typical HC-to-NO_x ratios, was compared with the chemistry of a mixture in which one-third of the original mixture was substituted by a synthetic methanol-exhaust mixture. In these so called "substitution" experiments, the overall reactivity of the original auto-exhaust or urban mixture was compared with the reactivity of the methanol-exhaust substituted mixture.

The first priority was to compare the reactivity of 100% synthetic automobile exhaust (no evaporative emissions) with a mixture of 33%C synthetic methanol exhaust and 67%C synthetic automobile exhaust. This would test the model's ability to represent a very reactive mixture and to correctly represent the replaced fraction of the urban mixture in the air shed simulations.

The second priority was to compare the reactivity of a less reactive, more typical, urban mixture (which included contributions from evaporative emissions, stationary source emissions, and automobile exhaust) with the same methanol exhaust substituted mixture. This would test the model's ability to represent the "typical" mixture and to test that the model had not been "over-tuned" to a single mixture composition (*e.g.* the auto-exhaust mixture).

When new mixtures are used in the UNC chamber, matched side-to-side comparison experiments are needed to demonstrate that both sides do yield the same reactivity when the same material is injected on both sides. In addition, standard chamber characterization experiments and background test experiments must be performed routinely. Thus the first experiments to be performed were various test experiments needed for Quality Assurance (QA) purposes.

Report Audience

This report is primarily written for a technical reader, especially one interested in using the chamber data produced in this project to test mechanisms. We have assumed that this reader has also read:

- the 1982 UNC report[5] "Outdoor Smog Chamber Experiments To Test Photochemical Models" which contains guidance on representing light intensity and other chamber characteristics;
- the 1985 UNC report[10] "Outdoor Smog Chamber Experiments to Test Photochemical Models: Phase II" which contains a complete index to all pre-1984 chamber experiments and suggestions on run selection for model testing;
- the 1985 UNC report[9] "Outdoor Smog Chamber Experiments Using Automobile Exhaust" which contains information on the characteristics of the vehicles used and the results of 31 dual experiments including a series comparing the synthetic mixture used in this project with automobile exhaust.

Much of the layout and information in this report is designed to assist readers in deciding which experiments they should use for their tests. For this reason, the plots and lists of conditions in Chapter 4 are very important.

A second reader is expected to be a technically oriented policy advisor. To aid this reader in understanding a complex subject, we have included expanded explanations of various processes, more definitions, and some interpretation of findings. In spite of the fact that the chamber data can be interpreted in a relative sense, independently of validating models, this reader is cautioned not to simply extrapolate chamber findings to the urban atmosphere. As described above, there are many factors that influence the urban atmosphere other than chemistry and urban air shed simulation models are needed to attempt to deal with all the factors at once.

2

Design

Design of Synthetic HC Mixtures

SynAuto

One of the tasks in the UNC automobile exhaust project was to test the hypothesis that a synthetic mixture of 10–15 compounds could adequately represent the reactivity of dilute automobile exhaust. In this project, four gas chromatographs (GC) covering the range from C_2 to C_{12} were used to determine the composition of both a controlled and an uncontrolled vehicle used in the study. GC/mass spectra analysis was used on cryocondensed samples to identify the species. From the concentration and identity of the compounds in the exhaust, we prepared a 13-component mixture that would mimic the overall reactivity of the exhaust. The mixture, listed in Table 3, contained 3 paraffins, 4 olefins, 5 aromatics, and formaldehyde. Benzene, because of its non-negligible rate constant and its relatively large concentration in exhaust, was included among the aromatics in the synthetic mixture. Acetylene, a "non-reactive" and major HC compound in exhaust, was not included because it would have created analytical problems in our routine GC analysis (the effect of omitting acetylene is minor, mainly affecting how much synthetic exhaust would be "equivalent" to real exhaust in NMHC units). Details on the types of vehicles, comparisons with a large test fleet, and other experimental results are provided in the final report.[9]

In the project, four dual experiments were performed in which exhaust from one of the vehicles was injected into one side of the chamber and an "equivalent" amount of synthetic exhaust was injected into the other chamber. In all experiments, the

Table 3. Composition of Hydrocarbon Mixtures.
(Units are fraction of total carbon)

Compound	UNCMIX	SynAuto	SynUrban
butane		0.0391	0.1000
pentane	0.2531		0.1367
isopentane	0.1484	0.0519	0.0801
2-methylpentane	0.0996		0.0538
2,4-dimethylpentane	0.0864		0.0467
2,2,4-trimethylpentane	0.1202	0.1121	0.1340
ethylene	0.1167	0.2391	0.0630
propylene	0.0524	0.0416	0.0238
1-butene	0.0254	0.0196	0.0137
trans-2-butene		0.0196	
cis-2-butene	0.0313		0.0169
2-methyl-1-butene	0.0347		0.0187
2-methyl-2-butene	0.0317		0.0171
benzene		0.0538	0.0331
toluene		0.2115	0.1304
m-xylene		0.1026	0.0633
o-xylene		0.0481	0.0296
1,2,4-trimethylbenzene		0.0564	0.0347
formaldehyde		0.0200	0.0200
total paraffin	0.7077	0.2031	0.5404
total olefin	0.2922	0.3199	0.1546
total aromatic	0.0000	0.4724	0.2854

two sides were relatively similar in reactivity, but only when the sides were carefully matched in CO, as well as NMHC, were the O_3 concentrations within 10% on the two sides. One example of a well-matched system is shown in Figure 2. In this experiment, 2.6 ppmC of exhaust from a 1972 V8 Dodge Charger and 2.2 ppmC of the synthetic mix (less because of the acetylene which was ≈15% of the exhaust) showed a remarkably similar reactivity (time to NO-to-NO_2 crossover agreed to within 8 minutes and O_3 maxima agreed to within ≈6%).

Thus we believe that the synthetic mixture called SynAuto in Table 3 is a reasonable approximation of automobile exhaust reactivity.

SynUrban

A second mixture, more typical of urban-like conditions, was needed for use in this study. Both emissions inventory and atmospheric hydrocarbon data were the basis for the compositional design of this synthetic urban mixture (SynUrban).

In 1972 Kopczynski investigated ambient HC compositions in both Los Angeles and Cincinnati.[11] Part of these data are shown in Table 4. Kopczynski used these data to design a mix for smog chamber use. His mix was used by UNC in 1973 as a guide to preparing a synthetic urban mixture, called UNCMIX which is also listed in Table 3. UNCMIX has two parts: paraffins and olefins, which are in a pressurized tank, and aromatics, which because of their significantly lower vapor pressures, are stored as liquid mixture. UNCMIX has been used in more than 100 experiments in our chambers; most of these experiments, however, have used only the paraffin and olefin portion of the mixture.

In conducting this study, we wished to use newer ambient data for the mixture design. Killus and Whitten[12] conducted a review of ambient data to provide the basis for their recommended default composition for air quality modeling in cases of insufficient support data. They found that NMHC composition did not vary greatly between cities. Gipson[13] recently completed an analysis of atmospheric data collected for the Northeast Corridor Regional Modeling Project. He also found little variation among the 435 sites for both composition and average carbon number of each HC class fraction.

It was decided to design a synthetic urban mixture which would come close to matching the default composition of Killus and Whitten, once converted to Carbon Bond Units. These values are listed in Table 5.

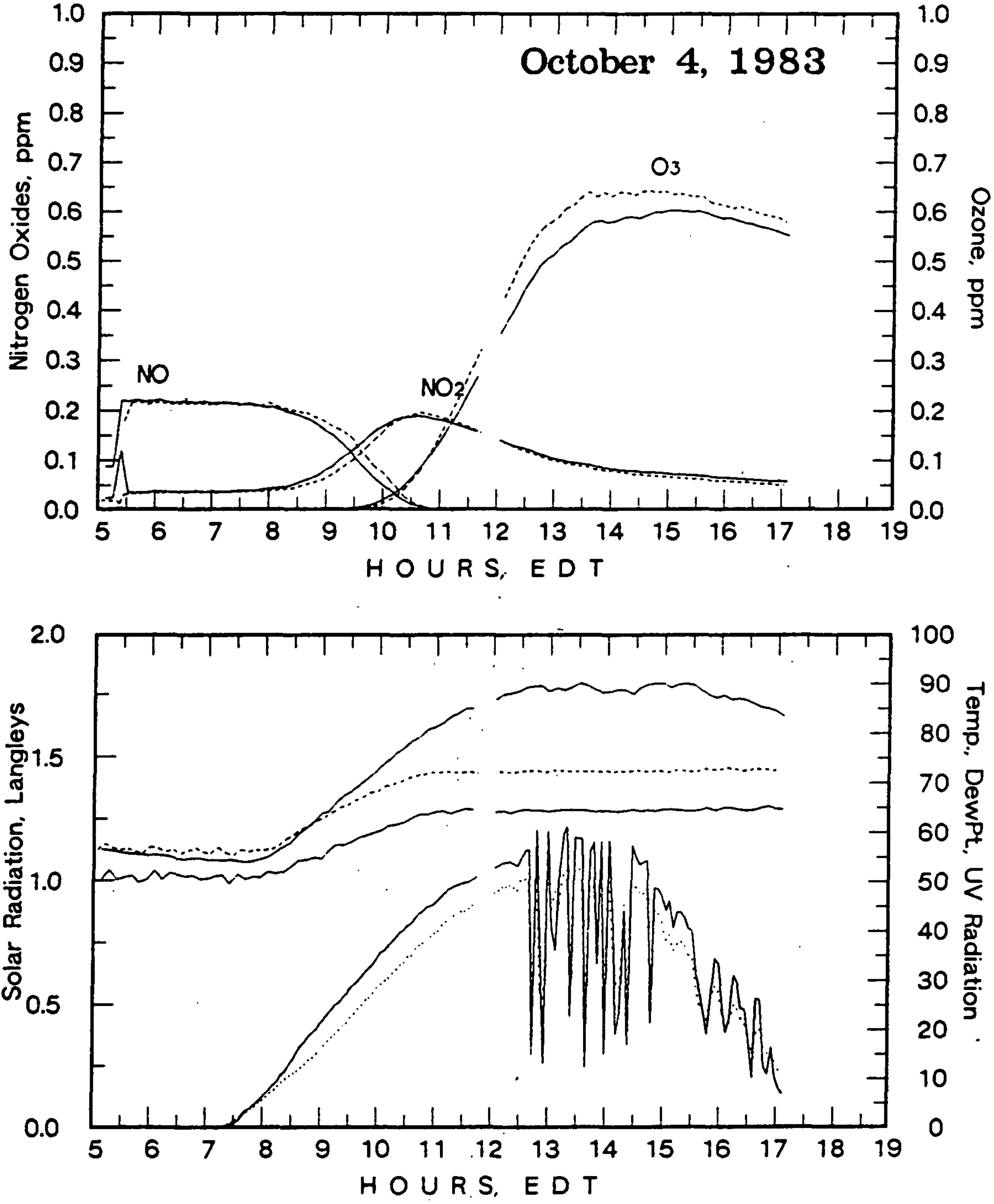


Figure 2.
Top: (Solid) 2.6 ppmC DODGE CHARGER EXHAUST;
(Dashed) 2.2 ppmC SYNAUTO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

Table 4. Analysis of Gas Chromatographic Data Of Los Angeles (Kopczynski) 75% Of Each Major HC Class.

ID NUM.	COMPOUND	CAR. FRACTION
17	ISOPENTANE	0.0917
12	N-BUTANE	0.0840
3	ETHANE	0.0561
19	N-PENTANE	0.0502
6	PROPANE	0.0411
38	2,4-DIMETHYLPENTANE	0.0262
33	N-HEXANE	0.0241
25	CYCLOPENTANE	0.0203
2	ETHYLENE	0.0444
5	PROPYLENE	0.0176
83	2-METHYL-2-BUTENE	0.0085
10	1-BUTENE	0.0069
11	ISOBUTYLENE	0.0069
21	TRANS-2-PENTENE	0.0065
55	TOLUENE	0.0796
68	M-XYLENE	0.0632
67	P-XYLENE	0.0294
71	O-XYLENE	0.0256
78	1,2,4-TRIMETHYLBENZENE	0.0201
79	SEC-BUTYLBENZENE	0.0201
65	ETHYLBENZENE	0.0197
4	ACETYLENE	0.0470

```
 45 COMPOUNDS TOTAL
PAR FRAC 0.5040  PAR CARBON NUM.  4.1363  15 COMPOUNDS
OLE FRAC 0.1131  OLE CARBON NUM.  2.8861  13 COMPOUNDS
ARO FRAC 0.3341  ARO CARBON NUM.  8.2082  15 COMPOUNDS
```

Table 5. Default Carbon Bond Class Fractions as Recommended by Killus and Whitten for CB3[12]

Bond Group	Meaning	Range	Default
PAR	all single bonded carbon	0.50 – 0.70	0.58
ETH	ethylene carbon	0.02 – 0.11	0.04
OLE	all double bonded carbon	0.02 – 0.07	0.03
ARO	all aromatic ring carbon	0.10 – 0.40	0.19
CAR	carbonyl group carbon	0.03 – 0.10	0.05
NR	non-reactive carbon	0.05 – 0.20	0.15

Although these indicate the total class fractions, they do not give the class average carbon numbers and therefore these do not suggest the types of species that should be included in the mixture.

Average carbon numbers, as determined by the Gipson analysis, were used to estimate the species needed in each class (see Table 6).

Table 6. Average Carbon Number at Northeast Corridor Regional Modeling Sites

	Paraffin	Olefin	Aromatic
mean	5.4	2.9	7.7
sd	0.4	0.7	0.02

The average composition of all 435 sampling sites was also used as a guide to designing the synthetic hydrocarbon mixture (see Table 7).

Table 7. Average Composition at Northeast Corridor Regional Modeling Sites (analysis of ambient HC data)

Class	mean %C	s.d.
Paraffin	56.4	9.5
Olefin	10.5	4.9
Aromatic	27.1	8.2
Acetylene	2.7	1.6
Ethane	3.3	2.5

We observed that the paraffin/olefin portion of the UNCMIX was very close to both the class fractions and average carbon number in the Gipson and in the Killus and Whitten studies. The paraffins in the UNCMIX needed a slightly lower average carbon number which could be achieved by the addition of n-butane. The original aromatic portion of UNCMIX, however, had too high an average carbon number (8.3) compared to the new Gipson values. The aromatic portion of the SynAuto mixture, on the other hand, had an average value much closer to the value in Table 6 and was therefore used as part of the SynUrban mixture as well. This aromatics portion in the SynAuto mixture was made up as a liquid in a separate container and thus could be easily used for both mixtures.

A computer program written to analyze hydrocarbon mixtures was utilized to determine the best ratio of the tank portion of UNCMIX, the liquid portion of the SynAuto mixture, and n-butane to achieve the closest agreement with the regular composition and average carbon numbers of Gipson, and the resulting Carbon Bond composition unit default values of Killus and Whitten. The best mixture of UNCMIX, the liquid portion of the synthetic auto exhaust, and n-butane was a 54:36:10 (carbon ratio).

The composition of the designed SynUrban mixture is given in Table 3. It consisted of 18 compounds: 6 paraffins, 6 olefins, 5 aromatics, and formaldehyde. Its composition in terms of the Carbon Bond Mechanism input species is given in Table 8; these can be compared with the default values listed in Table 5 and with the synthetic mixture used in the University of Santa Clara listed in Table 1.

Table 8. Carbon Bond 3 Class Fraction for SynUrban Mixture.
(units are fraction of total carbon)

Class	Carbon %
PAR	0.5498
ETH	0.0533
OLE	0.0281
ARO	0.1710
CARB	0.0299
NR	0.1680

Synthetic Methanol Exhaust

The Emission Control Technology Division of EPA has tested a methanol fueled Ford Escort and a VW Rabbit for emissions using the Federal Test Procedure which employs a dynamometer.[1] The results show that, while the total organic emissions were higher than the gasoline counterparts, the exhaust mostly consisted of unburned methanol (MeOH) and formaldehyde (HCHO), with a small amount of other HCs. In addition, very low levels of methyl nitrite ($MeNO_2$) were detected in the methanol samples, but only under certain testing conditions. $MeNO_2$ formation may be an artifact of the sampling techniques used. The fraction of HCHO in the methanol exhaust can vary from a few percent to nearly 25%.

To simulate the methanol exhaust in our experiments, we used three mixtures of MeOH/HCHO: 80%/20%; 90%/10%; and 100% MeOH. These were called high, mid, and low HCHO exhaust. In a few tests, 1% of the total MeOH was replaced with $MeNO_2$.

Matched, Reduction, and Substitution Experiments

Because the UNC chamber is divided into two side-by-side halves, two experiments are conducted at one time and the same set of instruments are used to measure the reactant and product concentrations on both sides in a timeshared manner. Thus experiments are designed to take advantage of the side-to-side nature of the chamber. In the methanol work, three basic types of side-to-side experiments were used:

- **Matched Conditions**—Both sides of the chamber had exactly the same chemical systems. The primary purpose for this type experiment was to show that the two chamber halves perform identically for the various chemical systems being tested. This allows stronger conclusions about cause-and-effect to be drawn in other experiments with different conditions on the two sides.

- **Reduction Conditions**—The NO_x concentration and the organic reactant mixture being studied were the same on both sides of the chamber, but the HC concentration was reduced by one third on one side of the chamber. These experiments test the model's ability to predict $\Delta O_3/\Delta HC$ correctly with all other conditions being the same.
- **Substitution Conditions**—Conditions on the two sides of the chamber were the same except for the carbon species identity. In the organic mixture on one side, approximately one-third of the carbon was replaced with the same amount of carbon, but with a different species identity. In the methanol substitution experiments, one-third of the SynAuto or SynUrban mixture carbon was replaced with a SynMethanol mixture. The formaldehyde content of the SynMethanol mixture was 0, 10, or 20% of the total SynMethanol mixture. These experiments test the model's ability to correctly predict the effects of composition change in a given mixture at a constant total HC concentration.

In addition to experiments that address the basic questions being asked, experiments were needed for quality assurance and to assess the potentially varying chamber artifact processes such as the magnitude of wall emissions of old reactant material. These experiments are called **Characterization Experiments** and were run routinely.

Time Available for Experiments

Because of the funding starting date (July 1, 1984) and the termination of the funding source on the fiscal year end (September 30, 1984) there was only time for twenty-one scheduled methanol reactivity runs, and nine scheduled chamber test runs (special characterization runs). Based on previous experience and assuming no mechanical or analytical difficulties and 50% good weather, at most about 11 methanol reactivity experiments would be reasonably useful, and maybe 8 of these experiments would be very good. The planning for the experiments also took into account other projects that were scheduled for the chamber.

Not every day could be devoted to making runs; the instruments needed calibrating and chamber characterization runs had to be performed for QA purposes. A series of estimated schedules were used to program the runs for the chamber, but the schedule was change rapidly depending upon meteorological events or instrument status. That is, we may have actually had a calibration day on what was to be a run day, but because it rained, the run was aborted and calibrations were done instead. The planned characterization runs, however, generally were scheduled to occur on the weekends. These runs normally required much less labor because there was no complex sampling and data processing. They were also the slack runs for the week. In other words, if it had been a bad week in terms of successful runs, then the weekend characterization runs were omitted in favor of one of the other runs for that week. This was not done every weekend, however, because of labor costs and the need to have a minimal set of Characterization runs.

Experimental Design

The experimental program had to accomplish a number of objectives:

- demonstrate the reactivity of surrogate exhaust from methanol fueled cars relative to the reactivity of surrogate exhaust from conventional gasoline fueled cars for outdoor conditions at several HC concentrations (NO_X constant);
- provide validation data for models intended to simulate the effects of methanol fuel substitution in control situations;
- investigate the sensitivity of the methanol-VOC mixture reactivity to changes in composition, such as the formaldehyde content of the exhaust, and the detailed composition of the urban mixture.

Initial Experiments

We choose NMHC concentrations based upon previous chamber results and our initial estimates of the relative reactivity of the synthetic mixtures. The HC levels chosen were: 3.0, 2.0, 1.0, 0.66 ppmC. All experiments were to be performed at 0.35 ppm NO_X, which is a reasonable approximation of urban maximum NO_X conditions. Both SynAuto and SynUrban mixtures would be used. The degree of substitution was designed to be 33%, *i.e.*, 33% of the SynAuto or SynUrban mixture carbon was replaced with an equal amount of carbon in the form of MeOH and HCHO.

The *target* conditions for the methanol test experiments are given in Table 9. Experiments for characterization are given in Table 10. These tables describe the purposes of each experiment and predict the outcome. (These predictions were made *before* any experiments were run and have not been changed for this report.)

New Experiments Added In Second Summer

Results from the modeling (reported in Chapter 5) and from the SynUrban experiments, showed that the 1.0 ppmC and 0.66 ppmC SynUrban conditions were too low, and new experiments were required at a higher concentration, but less than the

3.0 ppmC of the August 22, 1984 experiment. We estimated that approximately 2 ppmC SynUrban and 1.4 ppmC SynUrban should give 0.3 and 0.15 ppm O_3. The new target conditions were used in a baseline (*e.g.* no MeOH) experiment, and in a normal MeOH exhaust substitution experiment.

Table 9. Methanol Fuel Reactivity Experiments

(All experiments have 0.35 ppm NO_x)

Num	TYPE	REACTANTS First Side	REACTANTS Second Side	PURPOSE
1	Reduction, 33%	3.00 ppmC SynAuto	2.00 ppmC SynAuto	To determine the effect of 33% reduction in HC in an *auto-exhaust*-like environment at a typical HC-to-NO_x ratio. Expect 30% reduction in ozone maximum.
2	Substitution normal HCHO	3.00 ppmC SynAuto	2.00 ppmC SynAuto 0.89 ppmC MeOH 0.01 ppmC $MeNO_2$ 0.10 ppmC HCHO	To determine the reactivity of the most likely methanol fuel exhaust in an *auto-exhaust*-like environment at a typical HC-to-NO_x ratio. Expect 20% reduction in ozone maximum.
3	Substitution low HCHO	3.00 ppmC SynAuto	2.00 ppmC SynAuto 0.99 ppmC MeOH 0.01 ppmC $MeNO_2$	To determine the reactivity of the lowest reactivity methanol fuel exhaust in an *auto-exhaust*-like environment at a typical HC-to-NO_x ratio. Expect 30% reduction in ozone maximum.
4	Substitution high HCHO	3.00 ppmC SynAuto	2.00 ppmC SynAuto 0.79 ppmC MeOH 0.01 ppmC $MeNO_2$ 0.20 ppmC HCHO	To determine the reactivity of a highly reactive methanol fuel exhaust in an *auto-exhaust*-like environment at a typical HC-to-NO_x ratio. Expect less than 10% reduction in ozone maximum.
5	Reduction, 33%	1.000 ppmC SynAuto	0.666 ppmC SynAuto	To determine the effect of 33% reduction of HC in an *auto-exhaust*-like environment at a *low* HC-to-NO_x ratio. Expect a large reduction in ozone maximum.
6	Substitution normal HCHO	1.000 ppmC SynAuto	0.666 ppmC SynAuto 0.300 ppmC MeOH 0.003 ppmC $MeNO_2$ 0.030 ppmC HCHO	To determine the reactivity of the most likely methanol fuel exhaust in an *auto-exhaust*-like environment at a *low* HC-to-NO_x ratio. Expect a large reduction in ozone maximum.

Table 9, cont'd. Methanol Fuel Reactivity Experiments

(All experiments have 0.35 ppm NO_x)

Num	TYPE	REACTANTS First Side	REACTANTS Second Side	PURPOSE
7	Reduction, 33%	3.00 ppmC SynUrban	2.00 ppmC SynUrban	To determine the effect of 33% reduction in HC in an *urban*-like environment at a typical HC-to-NO_x ratio. Expect 30% reduction in ozone maximum.
8	Substitution normal HCHO	3.00 ppmC SynUrban	2.00 ppmC SynUrban 0.89 ppmC MeOH 0.01 ppmC $MeNO_2$ 0.10 ppmC HCHO	To determine the reactivity of the most likely methanol fuel exhaust in an *urban*-like environment at a typical HC-to-NO_x ratio. Expect 20% reduction in ozone maximum.
9	Substitution high HCHO	3.00 ppmC SynUrban	2.00 ppmC SynUrban 0.79 ppmC MeOH 0.01 ppmC $MeNO_2$ 0.20 ppmC HCHO	To determine the reactivity of a highly reactive methanol fuel exhaust in an *urban*-like environment at a typical HC-to-NO_x ratio. Expect 10% reduction in ozone maximum.
10	Substitution normal HCHO	1.000 ppmC SynUrban	0.666 ppmC SynUrban 0.300 ppmC MeOH 0.003 ppmC $MeNO_2$ 0.030 ppmC HCHO	To determine the reactivity of a typically reactive methanol fuel exhaust in an *urban*-like environment at a low HC-to-NO_x ratio. Expect large reduction in ozone maximum.
11	Substitution normal HCHO	6.00 ppmC SynAuto	4.00 ppmC SynAuto 1.78 ppmC MeOH 0.02 ppmC $MeNO_2$ 0.20 ppmC HCHO	To determine the reactivity of the most likely methanol fuel exhaust in an *auto-exhaust*-like environment at a high HC-to-NO_x ratio. Expect 20% reduction in ozone maximum.
12	Chemistry	1.00 ppmC HCHO	1.00 ppmC HCHO 1.00 ppmC MeOH	To illustrate the chemistry of methanol in a highly reactive environment.

Table 10. Methanol Fuel Characterization Experiments

Num	TYPE	REACTANTS First Side	REACTANTS Second Side	PURPOSE
1C	Character Radical Src.	0.35 ppm NO_x background air	0.35 ppm NO_x 50.0 ppm CO	To test for chamber sources of radicals capable of oxidizing NO to NO_2.
2C	Character Nitrogen Src.	0.0 ppm NO_x 1.0 ppmC RCHO	0.0 ppm NO_x 1.0 ppmC RCHO 50.0 ppm CO	To test for chamber sources of Nitrogen Oxides.
3C	Character Match Test	0.50 ppm NO_x background air	0.50 ppm NO_x background air	To test for matched chamber sources of radicals capable of oxidizing NO to NO_2.
4C	Character Match Test	0.35 ppm NO_x 3.00 ppmC SynAuto	0.35 ppm NO_x 3.00 ppmC SynAuto	To test for matched performance.
5C	Character Match Test	0.35 ppm NO_x 3.00 ppmC UNCMIX	0.35 ppm NO_x 3.00 ppmC UNCMIX	To test for matched performance for comparison with past studies.
6C	Character Photolysis Test	0.50 ppm NO_x 1.00 ppmC HCHO	0.50 ppm NO_x 1.00 ppmC HCHO 50.0 ppm CO	To test photolysis rates in chamber.

3

Methods

Outdoor Chamber and Analytical Facilities

The UNC Outdoor Smog Chamber is located in a rural area away from major pollution sources.[14] The chamber is a 300,000-liter, rigid external A-frame, Teflon film chamber divided into two equal halves by a Teflon film wall. The dual chamber design is used to perform side-by-side comparison experiments. It uses natural sunlight and ambient temperatures and humidity. It is purged overnight with rural ambient air. Instruments are timeshared on the two sides. The chamber and instrument operation and the data acquisition system are controlled by a PDP-11 computer. Complete facilities descriptions are given in Appendix A. Complete analytical system descriptions are given in Appendix B. A complete description of the data processing and quality assurance system is given in a separate volume of this report that also includes a description of the magnetic tape data file format.[15]

Production of Synthetic HC Mixtures

SynAuto Mixture

The synthetic auto-exhaust mixture (SynAuto) used in this study was listed in Table 3. Because of the need to have repeatable injections of this mixture over the course of this program, an injection tank containing ≈10,000 ppm carbon was needed. Ordering such a tank from gas suppliers requires up to three months for delivery and the tank would have cost $1500. In addition, the tank contents would have had to be analyzed by us to check the manufacturer's certification. Because of the time constraint and the need to do the analysis anyway, we elected to make our own injection tank. The time constraint, however, meant that the tank had to be put to use before a complete analysis was finished.

The five aromatic compounds in the mixture would not have remained vaporized in the tank and these compounds, as well as the tri-methyl-pentane, were made up as a liquid mixture. The liquid mixture was injected by microliter syringe. The remaining six compounds were mixed in a high pressure gas tank with N_2. After evacuating the tank, pressure was used to estimate the amount of each compound added to the tank.

A SynAuto injection consists of three parts:

- a timed injection from the tank at a constant flowrate, accounting for 41% of the carbon;
- a microliter syringe injection from the liquid mixture accounting for 57% of the carbon;
- a subliming of a weighted amount of paraformaldehyde into the chamber air, accounting for 2% of the carbon.

The analysis of initial conditions in several experiments and of high concentration injections into the chamber on calibration days were used to determine the tank and liquid composition. The concentrations are based on calibration factors obtained from standard, certified hydrocarbon tanks used to calibrate the gas chromatographs. The "Data Processing and Quality Assurance System Description" document[15] provides details on these calibration factors.

There are two items of concern for these mixtures, especially for the tank: the internal ratios of compounds and the total carbon concentration in each. Table 11 shows both of these items for the desired ideal mixture and for the August 5, supposedly 1.00 ppmC, injection of both the tank and the liquid.

In the injections, ethylene was 1.8% higher and each of the other compounds in the tank were within ±0.6% of their target composition. In the liquid injection, the analysis shows that tri-methyl-pentane was 1% too high, and that the aromatic compounds were all within 0.5% of their target compositions. This is excellent precision and accuracy.

The column marked "design-to-analyzed ratio", however, reveals a problem. The tank had more total carbon than was thought. Likewise, more liquid was injected than was thought. The target tank total concentration was 10,000 ppmC, but

Table 11. Composition of Synthetic Auto Exhaust Mixtures.

Compound	Design ppmC	Design Percent	Analyzed ppmC	Analyzed Percent	Design-to-Analyzed Ratio
Tank Mixture					
ethylene	0.239	58.2	0.389	60.0	0.614
propylene	0.042	10.1	0.066	9.5	0.636
1-butene	0.020	4.8	0.034	5.0	0.588
t-2-butene	0.020	4.8	0.031	4.8	0.645
butane	0.039	9.5	0.056	8.6	0.696
i-pentane	0.052	12.6	0.079	12.0	0.658
sub-total	0.411	100	0.649	100	0.640
Liquid Mixture					
tri-me-pentane	0.112	19.2	0.134	20.0	0.836
benzene	0.054	9.2	0.060	9.0	0.900
toluene	0.212	36.2	0.242	36.2	0.876
m-xylene	0.103	17.6	0.123	18.4	0.837
o-xylene	0.048	8.2	0.045	6.7	1.067
tri-me-benzene	0.056	9.7	0.063	9.5	0.889
sub-total	0.585	100	0.667	100	0.901
Total Tank	0.411	41.3	0.649	49.3	0.640
Total Liquid	0.585	58.7	0.667	50.7	0.901
Total Inj	1.00		1.32		

Table 12. Final SynAuto Mixture Composition

Compound	Composition Design	Composition Actual
butane	0.0391	0.0405
i-pentane	0.0519	0.0552
tri-me-pentane	0.1121	0.1063
ethylene	0.2391	0.2850
propylene	0.0416	0.0433
1-butene	0.0196	0.0258
t-2-butene	0.0196	0.0238
benzene	0.0539	0.0455
toluene	0.2115	0.1942
m-xylene	0.1026	0.0928
o-xylene	0.0481	0.0365
tri-me-benzene	0.0564	0.0510
total	1.0000	1.0000
PAR	0.2031	0.2020
OLE	0.3199	0.3780
ARO	0.4724	0.4200

a quick analysis after it was made suggested that only 8,000 ppmC actually made it into the tank. The 8,000 value was used as the basis for calculating injections for several very good experiments before the preliminary analysis was completed. Table 11 shows that about 20% more tank carbon and about 10% more liquid carbon was injected compared to the targets giving a total concentration of 1.32 ppmC instead of 1.00 ppmC and a 49/51 tank/liquid mixture instead of the 42/58 tank/liquid mixture desired. Because these experiments were so good, we decided to keep the 49/51 mixture for the rest of the work with the SynAuto mixture. This gives a new final composition of the SynAuto Mixture as shown in Table 12.

The total effect of all the errors for the SynAuto mixture was to shift 5% of the carbon from the aromatics class to the olefin class (essentially all in the form of ethylene). The effect of this change on the overall reactivity of the mixture is quite minor. Furthermore, this small variation is well within the variability of exhaust composition as reported in both the UNC automobile study[9] and the EPA 46-Vehicle exhaust study.[16] The exhaust composition, for example, can be greatly affected by the type of gasoline used. Finally, for testing photochemical mechanisms, it is more important that the composition be well known than that the composition exactly fits some target composition: the model must work for a whole range of compositions and a 5% variation is very minor for model performance testing.

The analysis of the initial HC composition and concentrations for both sides of four experiments, two near 3 ppmC and two near 1 ppmC, are shown in Table 13. The HC initial concentrations on one side of each of these days were supposed to be 67% of the HC initial concentration on the other side (*i.e.* a 33% reduction). The table shows that, even though the initial HC concentrations were about 30% too high, the actual side-to-side ratio achieved for these four days was between 64% and 69% compared to the target of 67% side-to-side ratio.

SynUrban Mixture

The SynUrban mixture consists of four parts:

- an injection from the UNCMIX tank, accounting for 54% of the carbon;
- an injection from an n-butane tank, accounting for 10% of the carbon;
- a liquid injection from the aromatic mix portion of SynAuto mix, accounting for 36% of the carbon;
- a formaldehyde injection by subliming a weighted amount of paraformaldehyde directly into the chamber.

Table 13. Initial Conditions in Four Methanol Experiments

Compound	C no.	AUG 5					AUG 7				
		ppmC		ppmC		ratio	ppmC		ppmC		ratio
ethylene	2	0.265	60.08%	0.389	59.98%	0.682	0.251	59.88%	0.381	60.37%	0.658
propylene	3	0.042	9.48%	0.062	9.48%	0.680	0.039	9.41%	0.057	9.06%	0.688
1-butene	4	0.022	5.07%	0.034	5.18%	0.667	0.020	4.82%	0.033	5.19%	0.616
t-2-butene	4	0.021	4.81%	0.031	4.77%	0.686	0.020	4.89%	0.030	4.71%	0.689
butane	4	0.038	8.58%	0.054	8.36%	0.698	0.037	8.73%	0.057	9.04%	0.641
i-pentane	5	0.053	11.98%	0.079	12.23%	0.667	0.051	12.28%	0.073	11.62%	0.701
sub-tot		0.441	48.30%	0.649	49.31%	0.680	0.419	48.47%	0.631	47.83%	0.664
tri-me-pentane	8	0.099	20.90%	0.134	20.06%	0.738	0.095	21.36%	0.138	19.99%	0.691
benzene	6	0.041	8.57%	0.060	9.04%	0.672	0.041	9.29%	0.063	9.15%	0.657
toluene	7	0.172	36.44%	0.242	36.22%	0.713	0.155	34.74%	0.249	36.14%	0.622
m-xylene	8	0.085	18.01%	0.123	18.45%	0.692	0.083	18.58%	0.128	18.53%	0.649
o-xylene	8	0.031	6.51%	0.045	6.71%	0.687	0.031	6.90%	0.046	6.70%	0.667
tri-me-benzene	9	0.045	9.57%	0.063	9.52%	0.713	0.041	9.13%	0.065	9.50%	0.622
sub-tot		0.473	51.70%	0.667	50.69%	0.709	0.446	51.53%	0.689	52.17%	0.647
TOTAL		0.914		1.316		0.695	0.865		1.320		0.655

Compound	C no.	AUG 6					AUG 8				
		ppmC		ppmC		ratio	ppmC		ppmC		ratio
ethylene	2	0.666	60.11%	0.963	60.25%	0.692	0.705	60.11%	1.050	60.25%	0.671
propylene	3	0.104	9.35%	0.149	9.35%	0.693	0.108	9.23%	0.158	9.06%	0.684
1-butene	4	0.059	5.35%	0.085	5.31%	0.698	0.064	5.48%	0.095	5.42%	0.680
t-2-butene	4	0.052	4.69%	0.079	4.94%	0.658	0.058	4.93%	0.089	5.10%	0.650
butane	4	0.095	8.55%	0.136	8.48%	0.698	0.099	8.43%	0.151	8.68%	0.653
i-pentane	5	0.133	11.96%	0.186	11.66%	0.711	0.139	11.82%	0.200	11.48%	0.692
sub-tot		1.108	49.24%	1.599	49.38%	0.693	1.172	47.31%	1.743	47.42%	0.672
tri-me-pentane	8	0.225	19.66%	0.336	20.48%	0.669	0.265	20.29%	0.389	20.11%	0.681
benzene	6	0.088	7.72%	0.122	7.47%	0.721	0.113	8.69%	0.166	8.59%	0.683
toluene	7	0.432	36.92%	0.602	36.75%	0.700	0.480	36.80%	0.715	36.99%	0.672
m-xylene	8	0.212	18.53%	0.301	19.40%	0.702	0.230	17.62%	0.341	17.66%	0.674
o-xylene	8	0.081	7.10%	0.115	7.00%	0.707	0.091	6.94%	0.134	6.94%	0.675
tri-me-benzene	9	0.115	10.06%	0.162	9.89%	0.709	0.126	9.67%	0.188	9.72%	0.672
sub-tot		1.142	50.76%	1.638	50.62%	0.697	1.306	52.69%	1.933	52.58%	0.675
TOTAL		2.250		3.235		0.695	2.478		3.677		0.674

The UNCMIX was a 2% certified tank from the manufacturer; the n-butane tank was a commercial blend of 10,000 ppmC of n-butane in N_2; the liquid analysis was described above. The paraformaldehyde purity was based upon manufacturer assay and was 92% pure.

Synthetic Methanol Exhaust

A synthetic methanol exhaust injection was in three parts:

- a microliter syringe injection of pure MeOH, accounting for 79 to 100% of the substituted carbon;
- an additional formaldehyde injection made by subliming a weighed amount of paraformaldehyde directly into the chamber, accounting for 0 to 20% of the substituted carbon;
- an optional injection of $MeNO_2$ made by flushing a known pressure of pure $MeNO_2$ in a known volume into the chamber, accounting for 0 to 1% of the substituted carbon.

Production of Methyl Nitrite

$MeNO_2$ boils at -12°C and is unstable; it can not be placed in a tank or kept in a bag. It photolyzes readily to produce radicals. $MeNO_2$ must therefore be synthesized and purified in a laboratory and stored in liquid nitrogen. The UNC glass shop produced the needed apparatus. Figure 3 shows the setup for synthesis, storage, and injection. We produced the needed quantities of $MeNO_2$ each week and stored and transported it in liquid N_2.

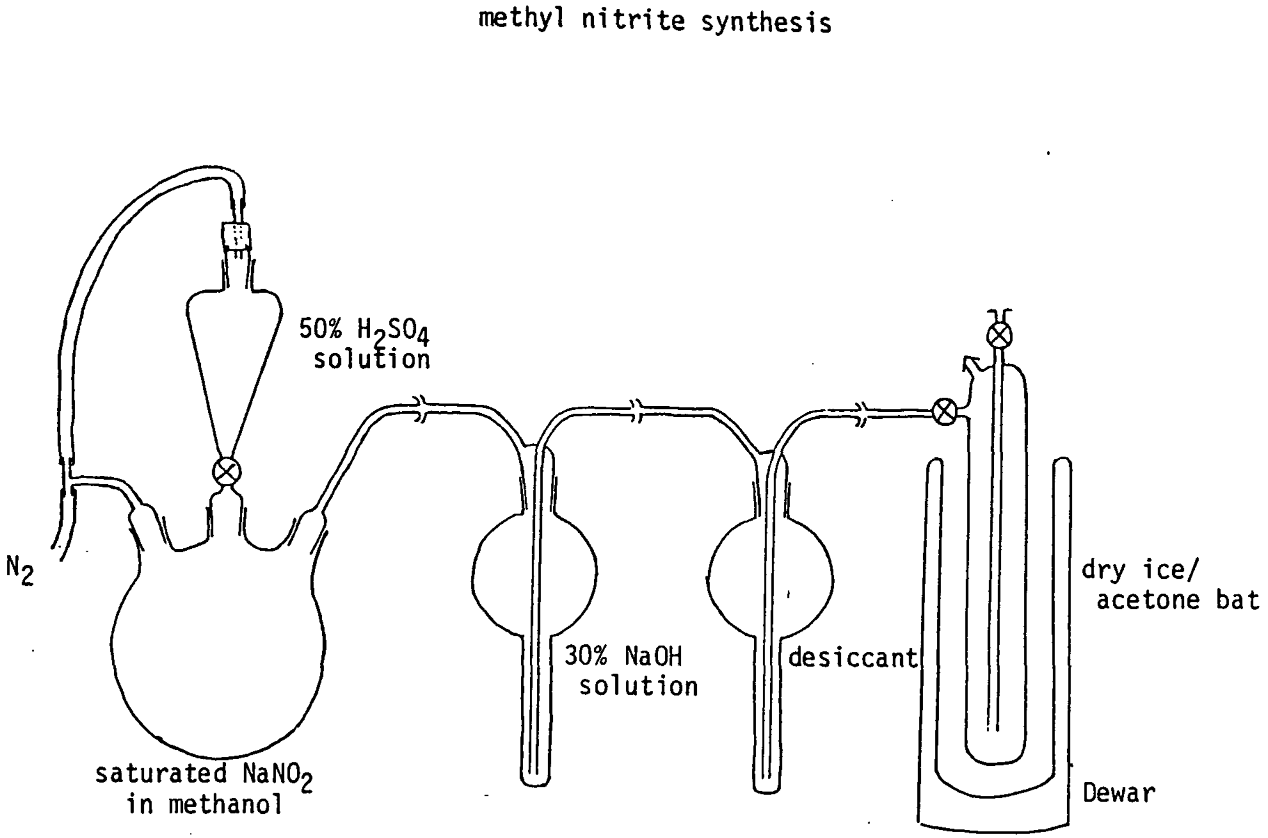


Figure 3. Methyl Nitrite Production Apparatus

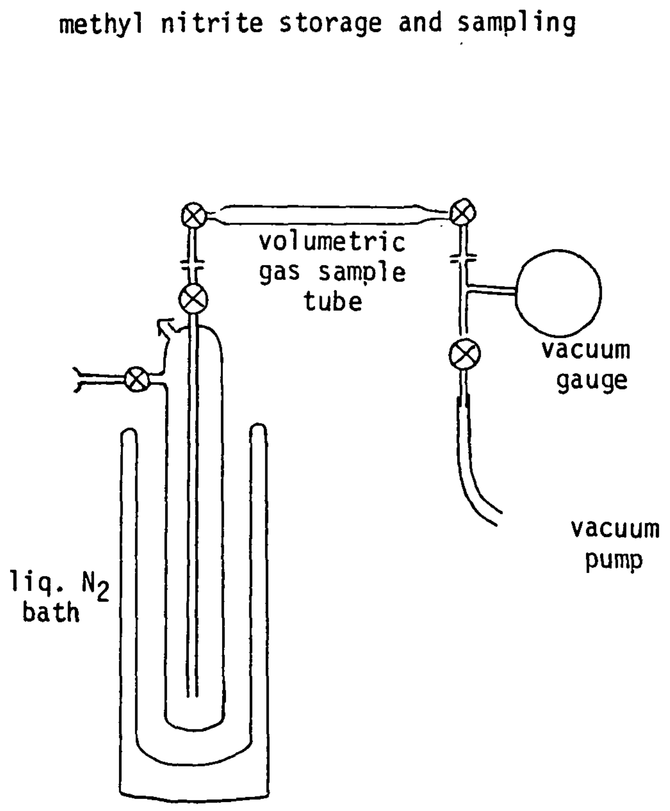


Figure 3. Methyl Nitrite Production Apparatus

4

Results

Overview of Data Set

The experimental work began in mid-July, 1984 and had to end by September 22, 1984. July had 6.22" of rain and the whole year was 12" above the normal rainfall at the beginning of August. August, however, was 2" below normal rainfall for the month. The first part of September had fairly good sun, but Hurricane Diana came to NC for five days in the middle of the month. In addition, the UNCMIX tank was totally exhausted in early September preventing completion of the SynUrban series. In 1985, three experiments were conducted in June with a new UNCMIX tank; two of these were successful, sufficiently completing the SynUrban series for adequate model testing.

The sequence of experimental testing was determined by a set of priorities and by estimates of having successfully completed higher priority runs based upon examination of run results immediately after each run. The priorities were:

- conduct experiments with SynAuto first;
  - ▷ demonstrate matched reactivity in both chambers with SynAuto mix;
  - ▷ demonstrate effects of 33% **reduction** at 3.0 ppmC;
  - ▷ demonstrate effects of 33% **substitution** with normal HCHO methanol exhaust at 3.0 ppmC;
  - ▷ demonstrate effects of 33% **reduction** at 1.0 ppmC;
  - ▷ demonstrate effects of 33% **substitution** with normal HCHO methanol exhaust at 1.0 ppmC;
  - ▷ demonstrate effects of 33% **substitution** with low HCHO methanol exhaust;

  - ▷ demonstrate effects of 33% **substitution** with high HCHO methanol exhaust;
- conduct experiments with SynUrban second;
  - ▷ demonstrate effects of 33% **reduction** at 3.0 ppmC;
  - ▷ demonstrate effects of 33% **substitution** with normal HCHO methanol exhaust at 3.0 ppmC;
  - ▷ demonstrate effects of 33% **reduction** at 1.0 ppmC;
  - ▷ demonstrate effects of 33% **substitution** with normal HCHO methanol exhaust at 1.0 ppmC;
  - ▷ demonstrate effects of 33% **substitution** with low HCHO methanol exhaust;

When a particular experiment was not successful (usually because of bad weather), the run was repeated as soon as possible before proceeding to lower priority runs.

Superimposed upon the experimental goals were the operational needs of providing actual injections for analysis of the blended SynAuto tank composition, of determining abilities to inject a three part mixture in the proper ratios and for testing general chamber performance.

Table 14 is a summary table of the conditions for 29 dual experiments conducted in this program.

In the table, the column headed SegFile gives the name of the experimental data file on the magnetic tape; a blank in this column means that the run was not considered satisfactory for model testing, usually because of poor sunlight, and it was not processed other than to produce the data plots—these runs have approximate initial conditions. There were 11 such runs excluded from the tape. There are 18 runs with completely processed data that are included on the magnetic data tape for distribution to model testers.

The HC Mix column indicates the type of mix used; in addition to the SynAuto, SynUrban, and UNCMIX mixes described in Chapter 2, three other mixtures were used for a few experiments:

- a first version of the SynAuto mixture that had incorrect internal ratios of tank species, designated as SynAuto1 in Table 14; this was discarded after July 22, 1984.
- a SynAutUrb mixture that was used in late September after the UNCMIX tank had been exhausted. This mixture was a blend of 90% SynAuto mixture and 10% n-butane used to establish a more urban-like mixture than SynAuto. This was

used in four experiments; three of these were satisfactory for model testing and are on the magnetic tape. These provide yet a third and related compositional mix to test mechanism responses to compositional changes.

- a mixture called HMWMIX—High Molecular Weight Mixture—was just the liquid portion of the SynAuto and SynUrban mixtures. In this mixture, five aromatics comprised 80% of the carbon and tri-methyl-pentane was the other 20% of the carbon.

Detailed Experimental Data and Plots

This section lists details of the initial conditions and other information for each of the 29 methanol experiments performed in this program. Plots of the NO, NO_2, and O_3 profiles and for the chamber air temperature, dew point and ambient total solar and ultraviolet radiation (TSR and UV) are shown.

Example Description of Information Presented

We will use August 4, 1985 as an example to explain the information presented. The reader should turn to page 64 to examine the information presented for August 4 and to look at the plot on the next page before reading the following description.

The first page of information is a summary of the experimental initial conditions. At the top of this page is the run date and a general description of the run conditions, *e.g.*

SynAuto 1.2 ppmC vs 0.83 ppmC/0.3 ppm MeOH/0.028 ppmC HCHO

This means that the experiment was a substitution experiment with the SynAuto mixture and that the SynMethanol mixture did contain formaldehyde at approximately 10%.

Below the title section is listed information from the run documentation file on the magnetic tape. This information gives the basic results of the run, in this case, the O_3 maximum concentrations produced and the time of the maximum in (). Then the initial conditions are listed for both sides of the chamber. Some of the entries require explanation.

NMHC This value is the sum of all the injected HC. It therefore includes the tank and liquid injections for the SynAuto, the MeOH injection and the HCHO injection. It is the total amount of injected organic carbon available for reaction (it does not include any chamber background organics; see modeling discussion in Chapter 6).

SYN-AUTO	This is the *tank and liquid* portion of the SynAuto mixture injection. It does not include the formaldehyde portion of the SynAuto mixture.
MEOH	This is the amount of MeOH injected. It also does not include any formaldehyde.
HCHO	This is the total HCHO injection. It includes the HCHO component of the SynAuto as well as any HCHO that was part of the surrogate methanol exhaust.
HC species	These are the component HC species of the SynAuto mixture.

An examination of the above values for the August 4, 1984 experiment reveals the following:

- The substituted side had 6% less carbon than the baseline side (1.179 vs. 1.249 ppmC). This was because the SynAuto mixture was reduced on the BLUE side to 0.664 of the RED side concentration by omitting 0.41 ppmC of the SynAuto carbon, but only 0.35 ppmC of SynMethanol was added back, an error of 0.06 ppmC.
- Too little HCHO was injected on both sides. On the RED, baseline side, the actual composition of the SynAuto mixture for this day was 1.52% HCHO rather than the target 2%. Likewise, the amount of the total HCHO injected on the BLUE side was too low; of the 0.041 ppm HCHO injected, 0.013 ppm was for the SynAuto mixture, leaving 0.028 ppm for the SynMethanol. This resulted in the SynMethanol mixture being 8% formaldehyde instead of the target 10% formaldehyde.

This precision for target conditions is typical—it is extremely difficult to achieve much better than 2% overall reproducibility.

In the concentration plot for August 4, the RED chamber data are shown as *solid* lines and the BLUE chamber data are shown as *dashed* lines (this is true for all concentration data plots). The data in these plots are taken every four minutes, but alternate sides so that the data for one side is every eight minutes. In the meterological data plots, TSR is shown as a solid line and UV is shown as a fine dashed line. Dewpoint is shown on both sides of the chamber. The data in these plots are taken every four minutes.

On the August 4, 1984 data plots (Figure 14) there are three "holes," one about 0850–0910 EDT, one about 1150–1330 EDT and one about 1615 EDT. These were periods when the computer data collection was stopped, either because of computer problems (*e.g.* power failure) or because the operator needed to transfer data or perform other required maintenance. On this day, the large hole caused by power problems at the rural site.

In the meteorological data plot of Figure 14, the chamber was initially at saturation (dewpoint = air temperature), but as the sun warmed the chamber, the air temperature rose significantly above the dewpoint, which remained relatively constant at about 80°F. The air temperature rose to 102°F. Small cumulus clouds in the afternoon frequently passed in front of the sun, blocking direct sunlight from the chamber and sensors, causing the "dips" in the TSR and UV data. The sunlight on this day is considered to be "good," approximately an 8 on a scale of 0–10. The sunlight on August 5, 1984 is better and the sunlight on July 17 is "bad," *i.e.* a 0 or 1 on a scale of 0–10. Experiments with such poor light are essentially useless for model testing and no conclusions should be based upon their outcomes. They are included here for completeness.

It should be recalled that the chemiluminscent NO_x meter used in our work responds 100% to PAN as well as to NO_2, but not to HNO_3. Therefore, the data after the NO_2 peak are actually the sum of PAN and NO_2. Processed data sets contain independent data for PAN based upon gas chromatography. In addition, there is a 12–15 second transport time from the chamber to the instruments and thus reaction can occur between O_3 and NO when both are not near zero. This causes O_3 and NO to be lower, and NO_2 to be higher, than the value in the chamber. This process is only important between NO-and-NO_2 crossover and NO_2 maximum and only effects the concentrations by about 10 ppb.

Table 14. Summary of Experimental Initial Concentrations

(units are ppm or ppmC)

(BLUE data on first line, RED data on second line)

Date	SegFile	HC Mix	Type	NO$_X$	NO	NO$_2$	HC	MeOH	HCHO
July 17, 1984		SynAuto1	mid ratio	0.33	0.18	0.15	3.54	0.00	0.00
		SynAuto1	matched	0.33	0.20	0.12	3.54	0.00	0.00
July 19, 1984		SynAuto1	mid ratio	0.30	0.21	0.09	3.54	0.00	0.00
		SynAuto1	matched	0.31	0.22	0.09	3.54	0.00	0.00
July 20, 1984		SynAuto1	mid ratio	0.25	0.20	0.05	3.54	0.00	0.00
		SynAuto1	matched	0.26	0.20	0.05	3.54	0.00	0.00
July 21, 1984		UNCMIX	33% sub. low HCHO	0.26	0.21	0.05	2.36	0.98	0.00
		UNCMIX	mid ratio	0.27	0.22	0.05	3.54	0.00	0.00
July 22, 1984		SynAuto	mid ratio	0.21	0.15	0.05	3.54	0.00	0.00
		SynAuto	33% sub. low HCHO	0.21	0.16	0.06	2.36	0.98	0.00
July 25, 1984	JL2584	SynAuto	33% sub. norm HCHO	0.33	0.25	0.08	2.36	0.90	0.10
		SynAuto	mid ratio	0.33	0.25	0.08	3.54	0.00	0.00
July 26, 1984		SynAuto	mid ratio	0.31	0.24	0.07	3.54	0.00	0.00
		SynAuto	33% sub. low HCHO	0.31	0.24	0.07	2.36	0.99	0.00
July 28, 1984		SynAuto	33% sub. low HCHO	0.30	0.23	0.07	2.36	0.85	0.00
		SynAuto	mid ratio	0.30	0.23	0.07	3.54	0.00	0.00

Table 14. Summary of Experimental Initial Concentrations, cont.

(units are ppm or ppmC)

(BLUE data on first line, RED data on second line)

Date	SegFile	HC Mix	Type	NO_x	NO	NO_2	HC	MeOH	HCHO
Aug. 2, 1984		SynAuto	mid ratio	0.41	0.31	0.09	3.54	0.00	0.00
		SynAuto	33% reduction	0.42	0.32	0.10	2.36	0.00	0.00
Aug. 3, 1984		SynAuto	mid ratio	0.44	0.32	0.12	3.73	0.00	0.06
		SynAuto	33% sub. norm HCHO	0.45	0.32	0.13	2.62	0.90	0.13
Aug. 4, 1984	AU0484	SynAuto	low ratio	0.36	0.28	0.07	0.82	0.32	0.04
		SynAuto	33% sub. norm HCHO	0.37	0.29	0.08	1.23	0.00	0.02
Aug. 5, 1984	AU0584	SynAuto	low ratio	0.35	0.27	0.08	1.32	0.00	0.02
		SynAuto	33% reduction	0.35	0.27	0.08	0.91	0.00	0.01
Aug. 6, 1984	AU0684	SynAuto	mid ratio	0.36	0.28	0.07	3.24	0.00	0.06
		SynAuto	33% reduction	0.35	0.28	0.07	2.25	0.00	0.04
Aug. 7, 1984	AU0784	SynAuto	33% sub. norm HCHO	0.38	0.30	0.08	0.87	0.30	0.06
		SynAuto	low ratio	0.39	0.30	0.08	1.32	0.00	0.04
Aug. 8, 1984	AU0884	SynAuto	mid ratio	0.34	0.26	0.08	3.68	0.00	0.06
		SynAuto	33% sub. high HCHO	0.34	0.26	0.08	2.48	0.79	0.23
Aug. 9, 1984	AU0984	SynAuto	33% sub. high HCHO	0.39	0.30	0.09	0.86	0.26	0.08
		SynAuto	low ratio	0.39	0.30	0.09	1.28	0.00	0.02
Aug. 22, 1984	AU2284	SynUrban	33% sub. norm HCHO	0.32	0.25	0.07	2.04	0.87	0.13
		SynUrban	mid ratio	0.32	0.25	0.07	3.04	0.00	0.06
Aug. 25, 1984	AU2584	SynUrban	low ratio	0.34	0.27	0.07	1.07	0.00	0.02
		SynUrban	33% sub. norm HCHO	0.35	0.27	0.08	0.72	0.29	0.04

Table 14. Summary of Experimental Initial Concentrations, cont.

(units are ppm or ppmC)

(BLUE data on first line, RED data on second line)

Date	SegFile	HC Mix	Type	NO_x	NO	NO_2	HC	MeOH	HCHO
Aug. 28, 1984		SynUrban	low ratio	0.31	0.25	0.06	1.16	0.00	0.02
		SynUrban	33% sub. low HCHO	0.32	0.26	0.07	0.81	0.32	0.01
Sept. 1, 1984	ST0184	SynUrban	mid ratio	0.30	0.24	0.06	3.31	0.00	0.06
		SynUrban	33% sub. low HCHO	0.31	0.25	0.06	2.66	0.97	0.04
Sept. 2, 1984	ST0284	SynUrban	33% reduction	0.32	0.26	0.06	0.76	0.00	0.01
		SynUrban	low ratio	0.34	0.28	0.06	1.10	0.00	0.02
Sept. 3, 1984	ST0384	SynUrban	low ratio	0.35	0.24	0.11	0.78	0.26	0.07
		SynUrban	33% sub. high HCHO	0.35	0.24	0.11	1.10	0.00	0.02
Sept. 8, 1984	ST0884	SynAutUrb	mid ratio	0.33	0.21	0.13	2.79	0.00	0.05
		SynAutUrb	33% reduction	0.33	0.20	0.12	1.84	0.00	0.04
Sept. 9, 1984		SynAutUrb	low-mid ratio	0.34	0.29	0.06	2.14	0.00	0.04
		SynAutUrb	33% reduction	0.35	0.29	0.06	1.42	0.00	0.02
Sept.17, 1984	ST1784	SynAutUrb	30% sub norm HCHO	0.34	0.27	0.07	1.42	0.57	0.08
		SynAutUrb	low-mid ratio	0.34	0.27	0.07	2.14	0.00	0.04
Sept.19, 1984	ST1984	HMWMIX	40% reduction	0.34	0.25	0.09	2.63	0.00	0.00
		HMWMIX		0.34	0.25	0.09	4.43	0.00	0.00
Sept.21, 1984	ST2184	SynAutUrb	low-mid ratio + HCHO	0.36	0.27	0.09	2.42	0.00	0.18
		SynAutUrb	low-mid ratio	0.36	0.28	0.09	2.43	0.00	0.00

Table 14. Summary of Experimental Initial Concentrations, cont.

(units are ppm or ppmC)

(BLUE data on first line, RED data on second line)

Date	SegFile	HC Mix	Type	NO_x	NO	NO_2	HC	MeOH	HCHO
June 26, 1985	JN2685	SynUrban	mid ratio	0.35	0.28	0.07	4.01	0.00	0.06
		SynUrban	33% reduction	0.35	0.28	0.07	2.44	0.00	0.04
June 28, 1985	JN2885	SynUrban	low-mid ratio	0.35	0.28	0.07	1.78	0.58	0.09
		SynUrban	33% sub norm HCHO	0.35	0.28	0.07	2.65	0.00	0.04

July 17, 1984

SynAuto1 Matched 3.5 ppmC (no HCHO)

RESULTS: O3 MAX: BLUE 0.4605 PPM(1720); RED 0.4424 PPM(1724).

INITIAL CONDITIONS:	BLUE	RED
NO	0.181	0.201
NO2	0.147	0.124
NMHC	3.540	3.540
SYN-AUTO(TANK&LIQUID)	3.540	3.540

RUN NOT PROCESSED

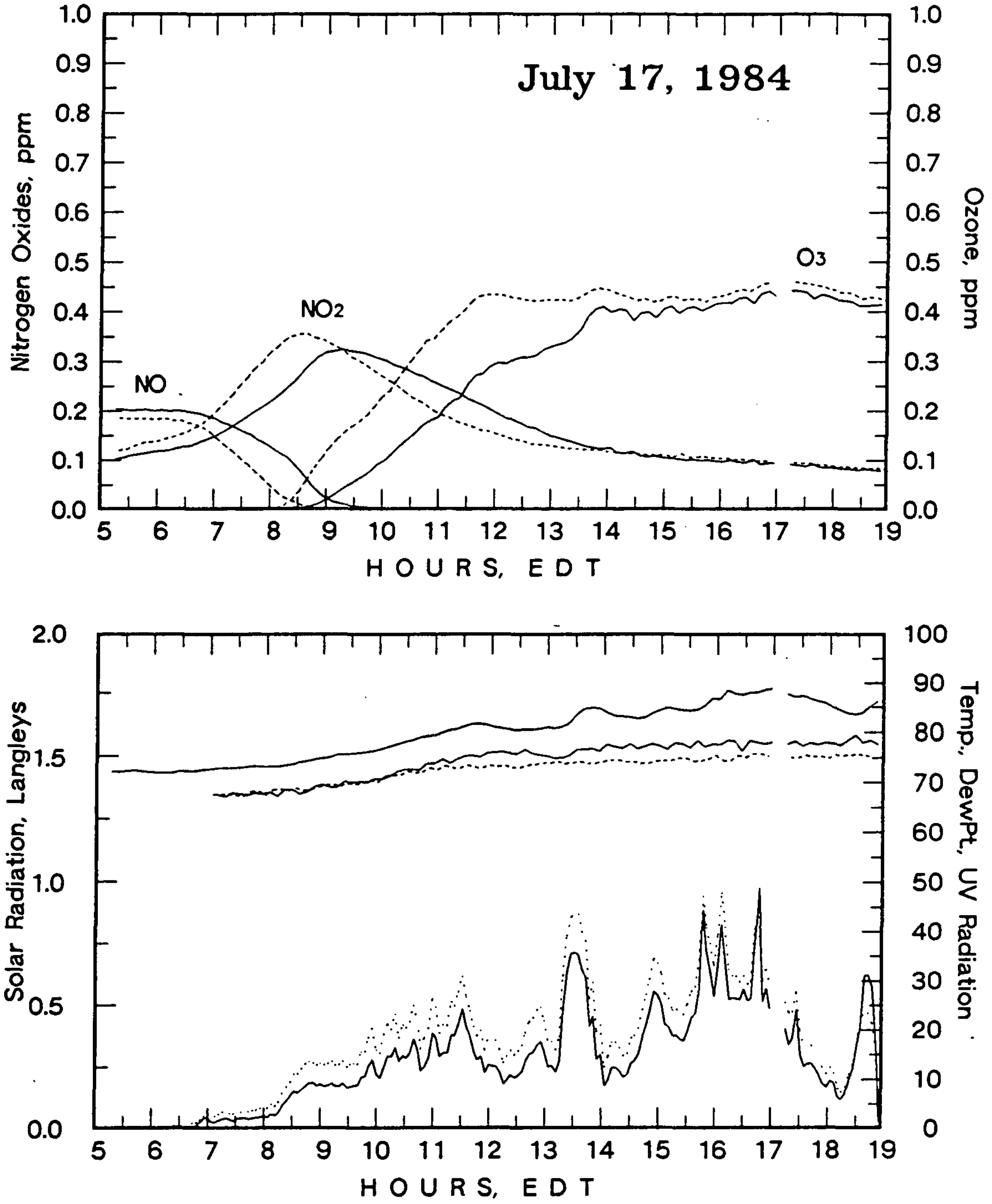


Figure 4.
Top: (Solid) 3.54 ppmc SYNAUTO (FIRST), no HCHO, no MeOH;
(Dashed) 3.54 ppmC SYNAUTO (FIRST), no HCHO, no MeOH;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

July 19, 1984

SynAuto1 Matched 3.5 ppmC (no HCHO and MeOH)

RESULTS: O3 MAX: BLUE 0.8058 PPM(1304); RED 0.7889 PPM(1300).

INITIAL CONDITIONS:	BLUE	RED
NO	0.214	0.224
NO2	0.090	0.085
NMHC	3.540	3.540
SYN-AUTO(TANK&LIQUID)	3.540	3.540
ETHYLENE		
PROPYLENE		
1-BUTENE	0.068	0.071
N-BUTANE	0.130	0.135
TRANS-2-BUTENE	0.074	0.075
ISOPENTANE	0.173	0.155
2,2,4-TRIMETHYLPENTANE		
BENZENE	0.157	0.160
TOLUENE	0.683	0.728
M-XYLENE	0.347	0.353
O-XYLENE	0.133	0.165

RUN NOT PROCESSED

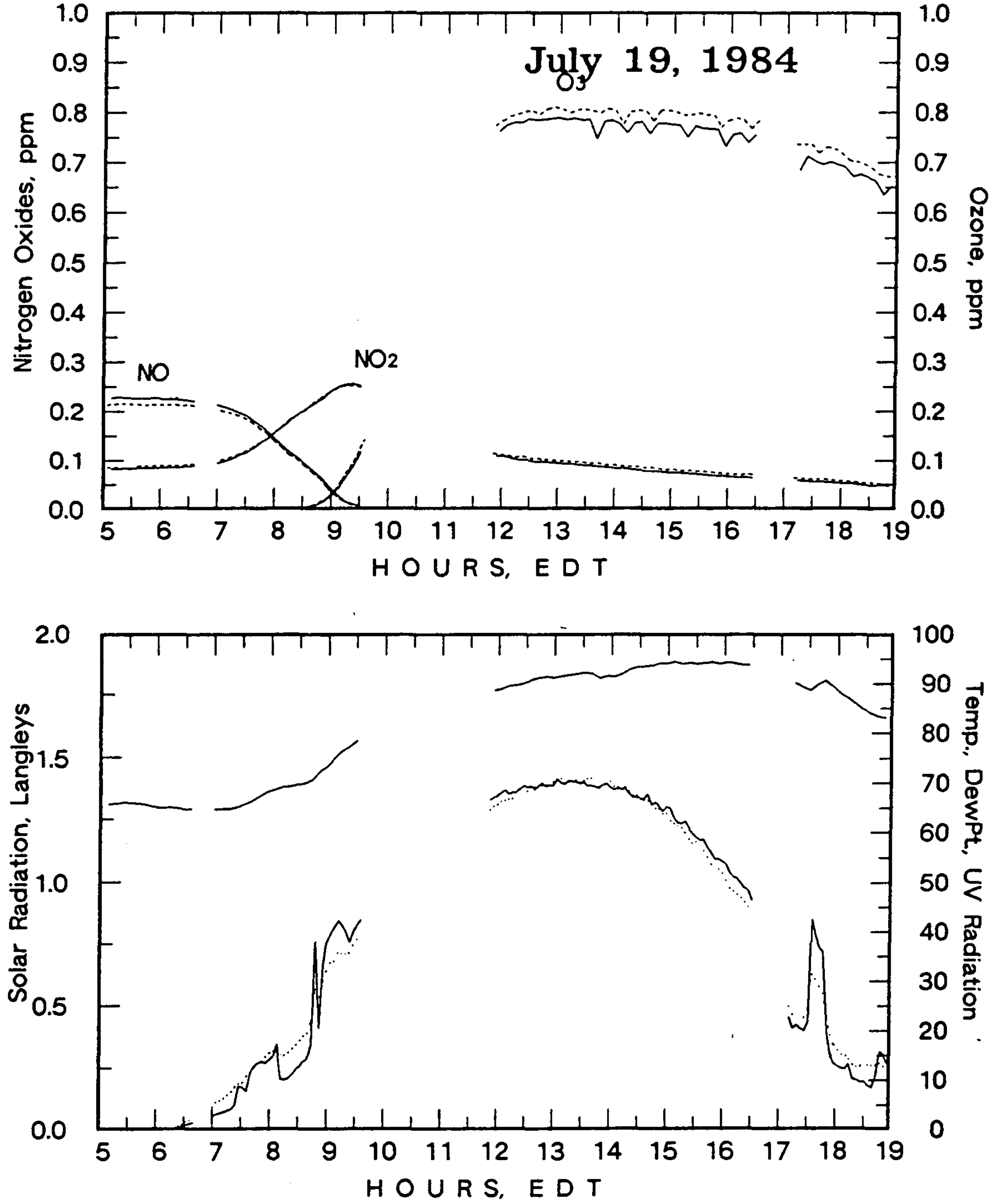


Figure 5.
Top: (Solid) 3.54 ppmC SYNAUTO (FIRST), no HCHO, no MeOH;
(Dashed) 3.54 ppmC SYNAUTO (FIRST), no HCHO, no MeOH;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

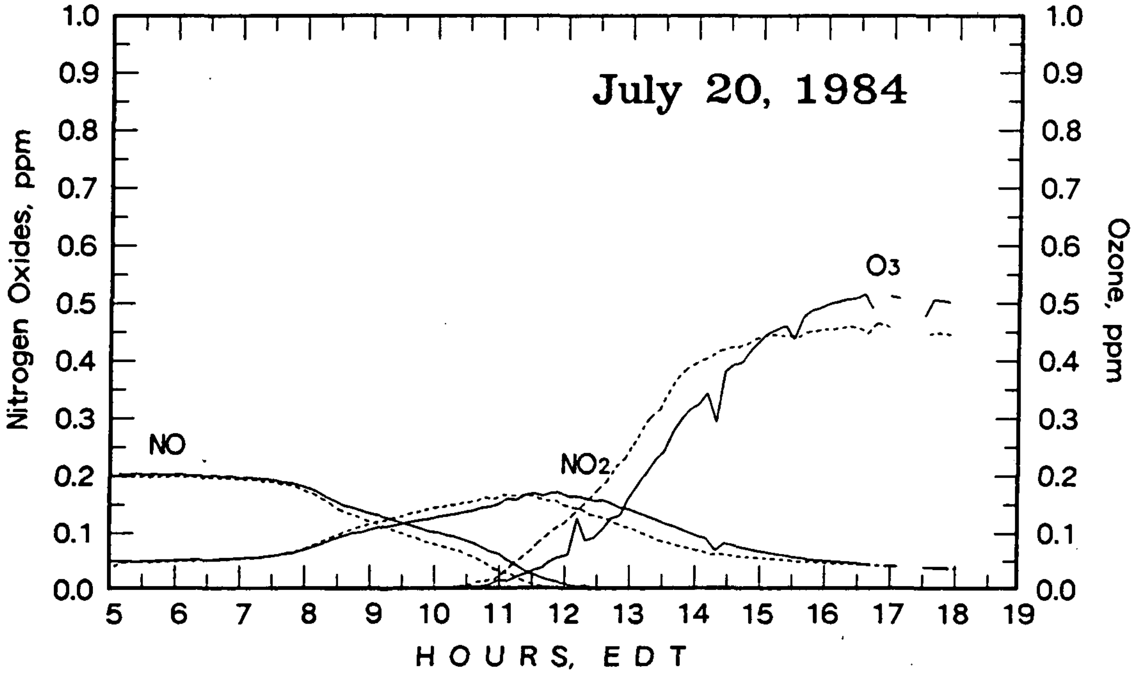
July 20, 1984

SynAutol Matched 3.5 ppmC (no HCHO and MeOH)

RESULTS: O3 MAX: BLUE 0.4649 PPM(1648); RED 0.5157 PPM(1636).

INITIAL CONDITIONS:	BLUE	RED
NO	0.199	0.202
NO2	0.050	0.053
NMHC	3.540	3.540
SYN-AUTO(TANK&LIQUID)	3.540	3.540
ETHYLENE		
2,2,4-TRIMETHYLPENTANE		
BENZENE	0.152	0.103
TOLUENE	0.665	0.459
M-XYLENE	0.356	0.242
O-XYLENE	0.124	0.103

RUN NOT PROCESSED



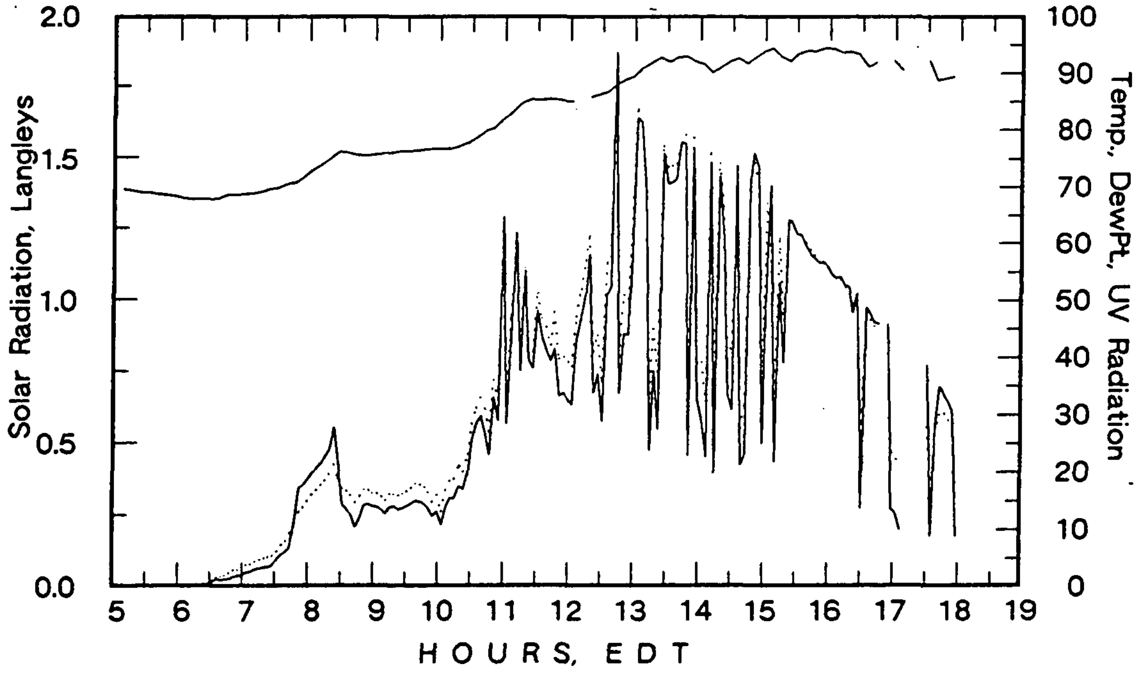


Figure 6.
Top: (Solid lines) 3.54 ppmC SYNAUTO (FIRST), no HCHO, no MeOH;
(Dashed lines) 3.54 ppmC SYNAUTO (FIRST), no HCHO, no MeOH;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

July 21, 1984

UNCMIX, subst., 3.0 ppmC vs 2.0 ppmC and 1 ppm MeOH (no HCHO)

RESULTS: O3 MAX: BLUE 0.4250 PPM(1712); RED 0.6060 PPM(1700).

INITIAL CONDITIONS:	BLUE	RED
NO	0.210	0.218
NO2	0.047	0.050
UNCMIX	2.360	3.540
MEOH	0.980	0.000
ETHYLENE		
PROPYLENE	0.086	0.127
1-BUTENE	0.055	0.080
TRANS-2-BUTENE	0.058	0.071
ISOPENTANE	0.274	0.402
N-PENTANE	0.457	0.694

RUN NOT PROCESSED

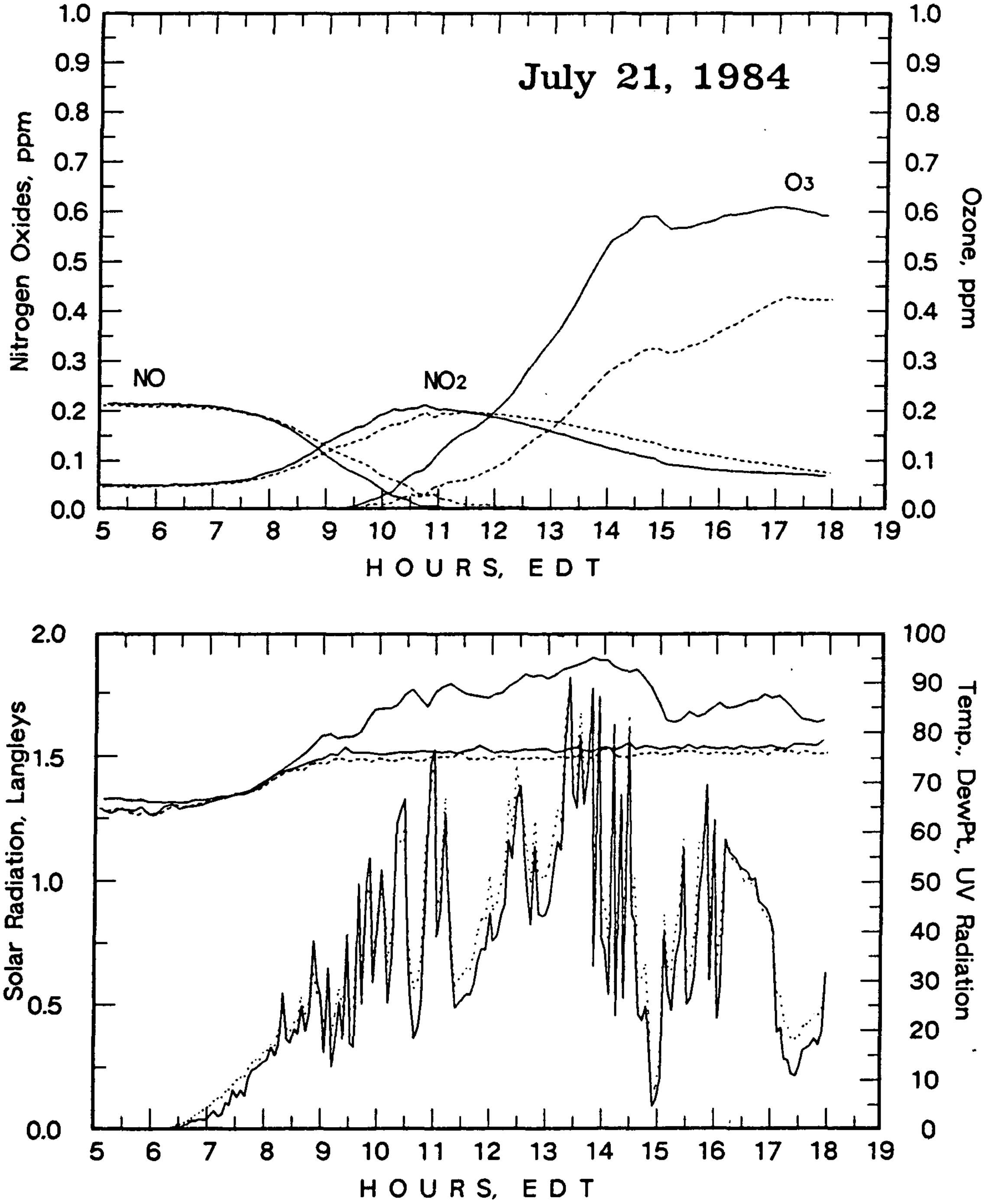


Figure 7.
Top: (Solid) 3.54 ppmC UNCMIX, no MeOH, no HCHO;
(Dashed) 2.36 ppmC UNCMIX, 0.98 ppm MeOH, no HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

July 22, 1984

SynAuto 3.5 ppmC vs 2.0 ppmC/1.0 ppm MeOH (no HCHO)

RESULTS: O3 MAX: BLUE 0.3843 PPM(1736); RED 0.3359 PPM(1756).

INITIAL CONDITIONS:	BLUE	RED
NO	0.153	0.155
NO2	0.054	0.057
NMHC	3.540	3.340
SYN-URBAN(TANK&LIQUID)	3.540	2.360
MEOH	0.000	0.980
ETHYLENE		
PROPYLENE	0.035	0.028
ISOPENTANE	0.115	0.097
N-PENTANE	0.195	0.146
2,2,4-TRIMETHYLPENTANE	0.319	0.235
BENZENE	0.131	0.101
TOLUENE	0.645	0.457
M-XYLENE	0.310	0.226
O-XYLENE	0.135	0.123
1,2,4-TRIMETHYLBENZENE	0.236	0.193

RUN NOT PROCESSED

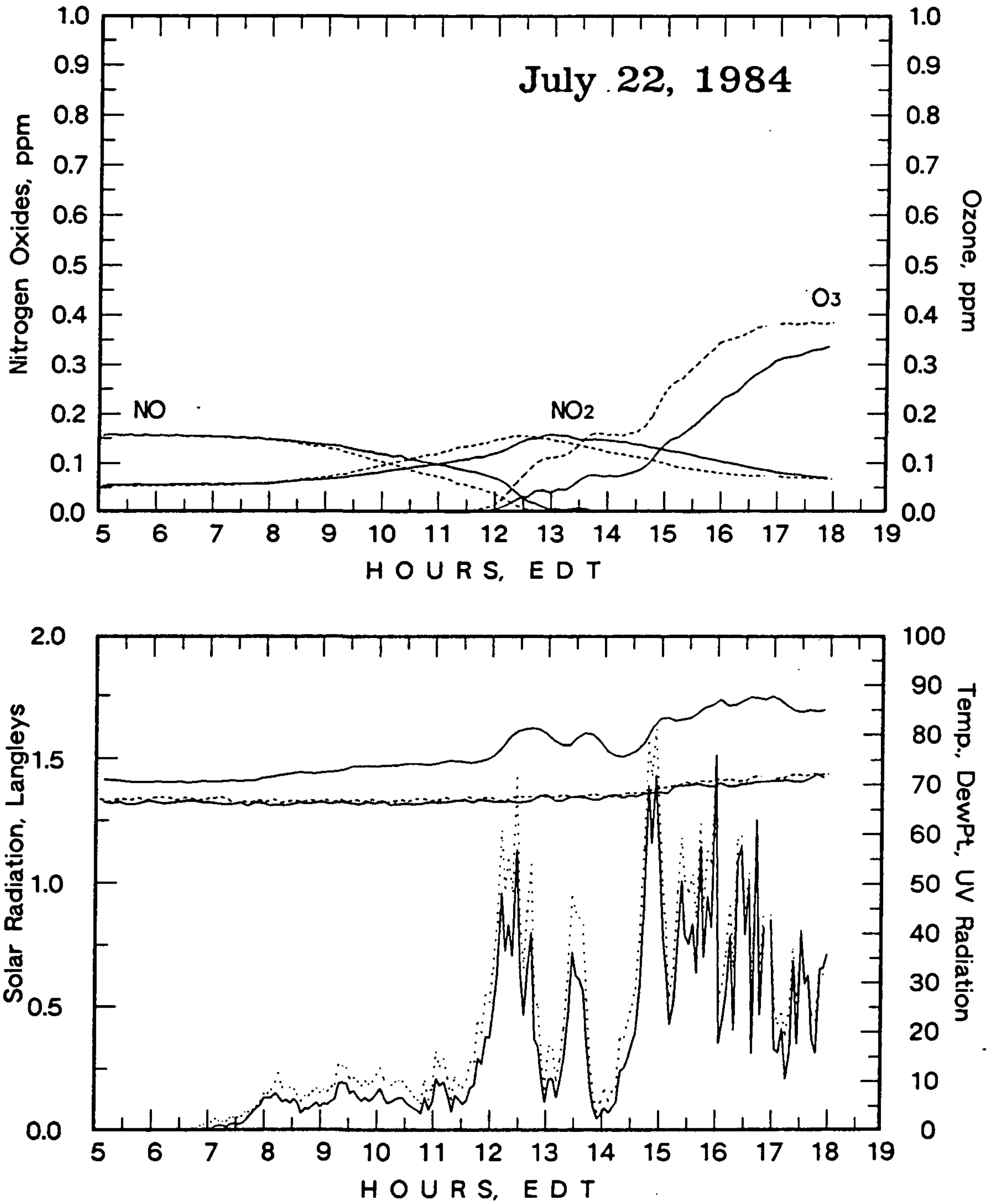


Figure 8.
Top: (Solid) 2.36 ppmC SYNAUTO (FIRST), 0.98 ppm MeOH, no HCHO;
(Dashed) 3.54 ppmC SYNAUTO (FIRST), no MeOH, no HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

July 25, 1984

SynAuto 3.5 ppmC vs 2.0 ppmC plus 0.9 ppm MeOH and 0.1 HCHO

RESULTS: 03 MAX: BLUE 0.7711 PPM(1352); RED 0.7655 PPM(1332).

INITIAL CONDITIONS:	BLUE	RED
NO	0.249	0.254
NO2	0.076	0.076
NMHC	3.540	3.540
SYN-URBAN(TANK&LIQUID)	2.360	3.540
MEOH	0.900	0.000
HCHO	0.100	0.000

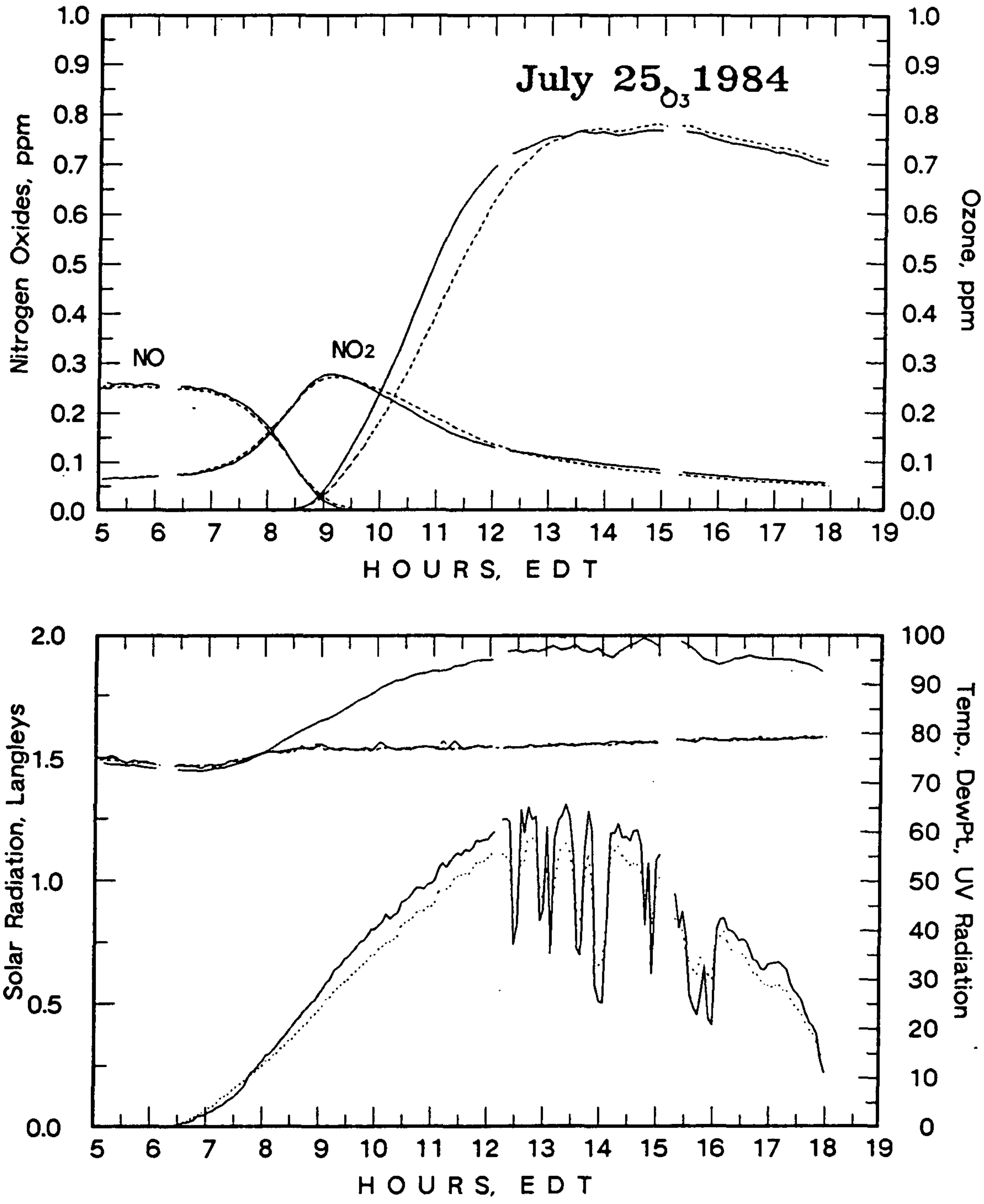


Figure 9.
Top: (Solid) 3.54 ppmC SYNAUTO, no MeOH, no HCHO;
(Dashed) 2.36 ppmC SYNAUTO, 0.9 ppm MeOH, 0.1 HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

July 26, 1984

SunAuto 3.5 ppmC vs 2.4 ppmC plus 1.0 ppm MeOH (no HCHO)

RESULTS: O3 MAX: BLUE 0.7050 PPM(1520); RED 0.7211 PPM(1524).

INITIAL CONDITIONS:	BLUE	RED
NO	0.238	0.241
NO2	0.071	0.071
NMHC	3.540	3.350
SYN-URBAN(TANK&LIQUID)	3.540	2.360
MEOH	0.000	0.990

RUN NOT PROCESSED

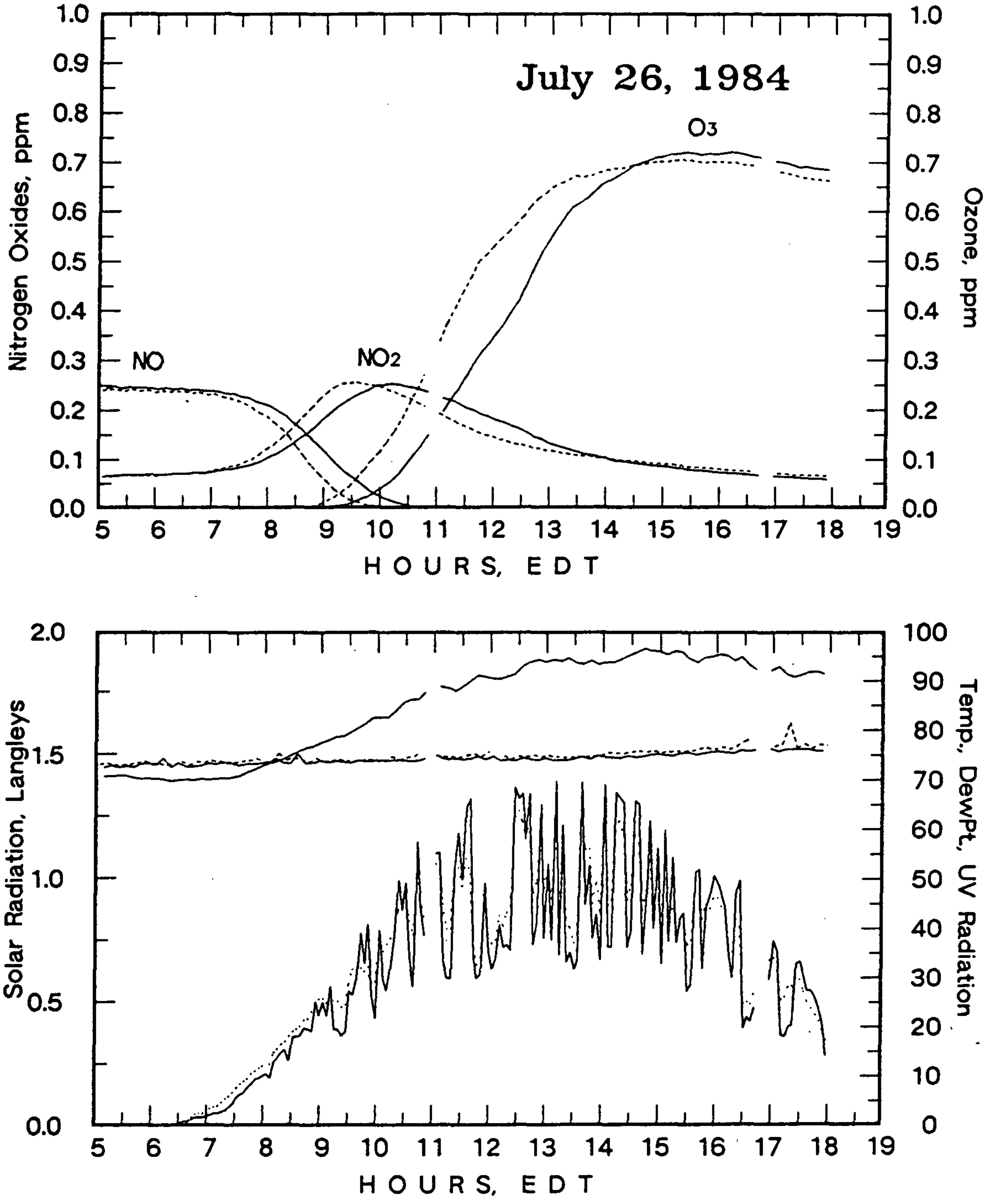


Figure 10.
Top: (Solid) 2.36 ppmC SYNAUTO, 0.99 ppm MeOH, no HCHO;
(Dashed) 3.54 ppmC SYNAUTO, no MeOH, no HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

July 28, 1984

SynAuto 3.5 ppmC vs 2.4 ppmC plus 0.8 ppm MeOH (no HCHO)

RESULTS: 03 MAX: BLUE 0.5050 PPM(1440); RED 0.4867 PPM(1436).

INITIAL CONDITIONS:	BLUE	RED
NO	0.229	0.231
NO2	0.067	0.070
NMHC	3.210	3.540
SYN-AUTO(TANK&LIQUID)	2.360	3.540
MEOH	0.850	0.000

RUN NOT PROCESSED

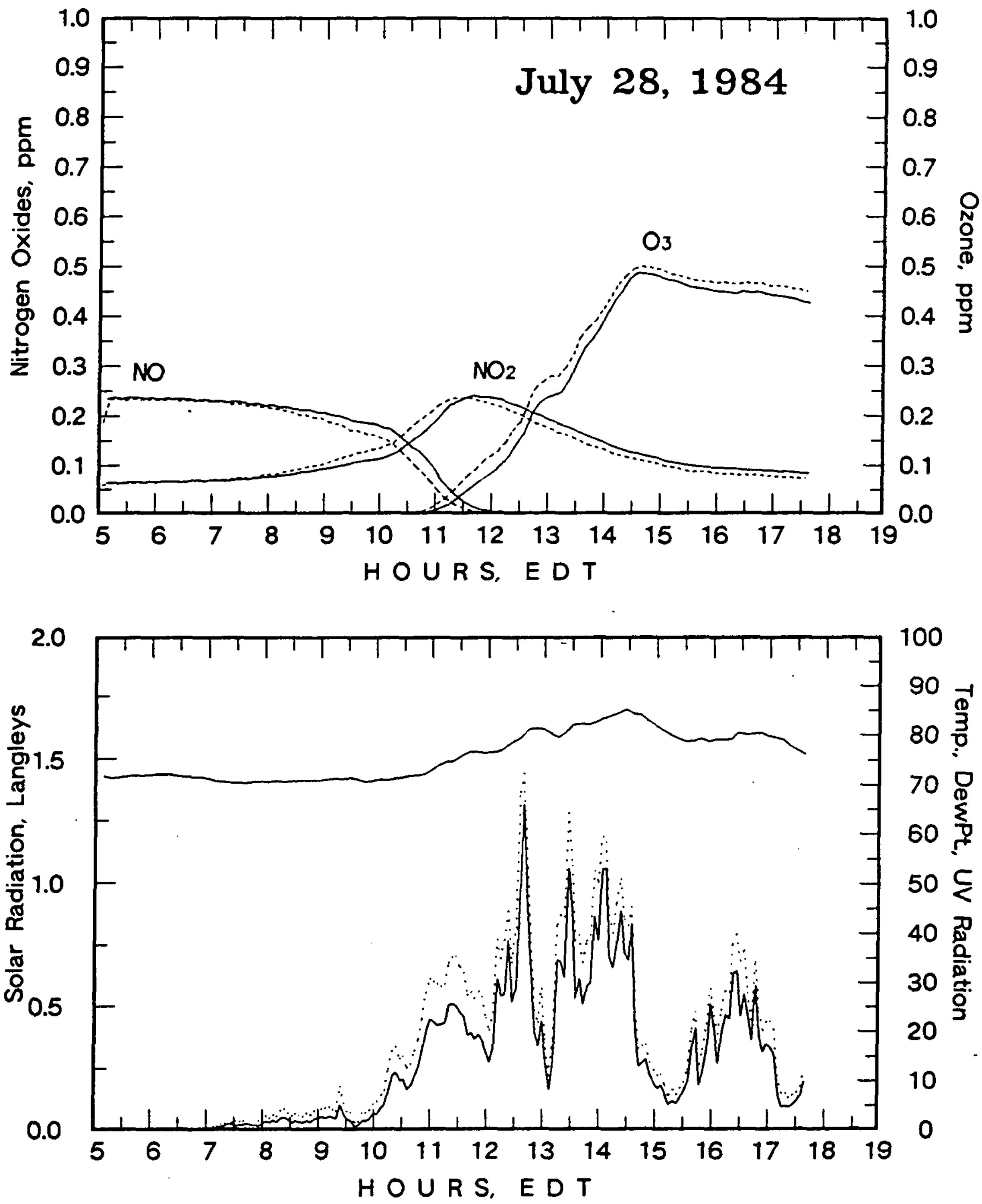


Figure 11.
Top: (Solid) 3.54 ppmC SYNAUTO, NO MeOH, no HCHO;
(Dashed) 2.36 ppmC SYNAUTO, 0.85 ppm MeOH, no HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

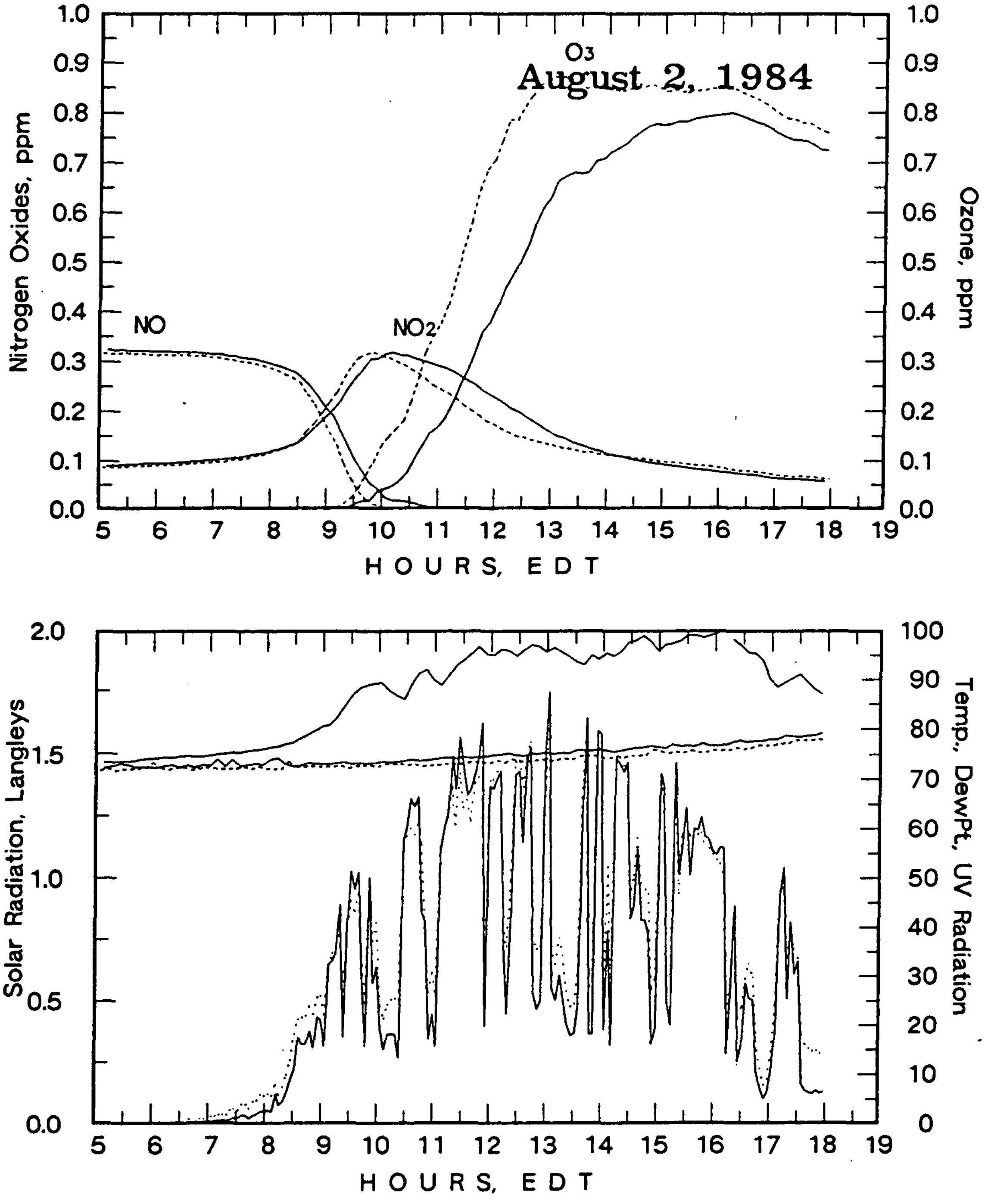
August 2, 1984

SynAuto Reduction 3.5 to 2.4 ppmC (no HCHO)

INITIAL CONDITIONS:	BLUE	RED
NO	0.312	0.318
NO2	0.094	0.099
NMHC	3.540	2.360
SYN-AUTO(TANK&LIQUID)	3.540	2.360
ETHYLENE	@0730 1.099	0.776
PROPYLENE	@0730 0.177	@0700 0.122
1-BUTENE	@0730 0.117	@0700 0.081
N-BUTANE	@0730 0.173	@0700 0.121
TRANS-2-BUTENE	@0730 0.082	@0700 0.060
ISOPENTANE	@0730 0.194	@0700 0.145
2,2,4-TRIMETHYLPENTANE	@0730 0.344	@0700 0.238
BENZENE	@0730 0.126	@0700 0.091
TOLUENE	@0730 0.695	@0700 0.490
M-XYLENE	@0730 0.345	@0700 0.265
O-XYLENE	@0730 0.143	@0700 0.099

RESULTS: O3 MAX: BLUE 0.8712 PPM(1312); RED 0.7996 PPM(1612).

RUN NOT PROCESSED



August 2, 1984

Figure 12.

Top: (Solid) 2.36 ppmC SYNAUTO, no MeOH, no HCHO;
(Dashed) 3.54 ppmC SYNAUTO, no MeOH, no HCHO;

Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

August 3, 1984

SynAuto 3.79 ppmC vs 2.67 ppmC plus 0.9 ppm MeOH and 0.09 HCHO

RESULTS: 03 MAX: BLUE 0.8927 PPM(1416); RED 0.8900 PPM(1412).

INITIAL CONDITIONS:	BLUE	RED
NO	0.317	0.324
NO2	0.120	0.129
NMHC	3.785	3.656
SYN-AUTO(TANK&LIQUID)	3.728	2.625
MEOH	0.000	0.897
HCHO	0.057	0.134
ETHYLENE	1.055	0.718
PROPYLENE	0.210	0.149
1-BUTENE	0.111	0.077
TRANS-2-BUTENE	0.098	0.070
N-BUTANE	0.176	0.116
ISOPENTANE	0.278	0.193
2,2,4-TRIMETHYLPENTANE	0.363	0.260
BENZENE	0.162	0.119
TOLUENE	0.667	0.484
M-XYLENE	0.311	0.220
O-XYLENE	0.122	0.093
1,2,4-TRIMETHYLBENZENE	0.175	0.127

RUN NOT PROCESSED

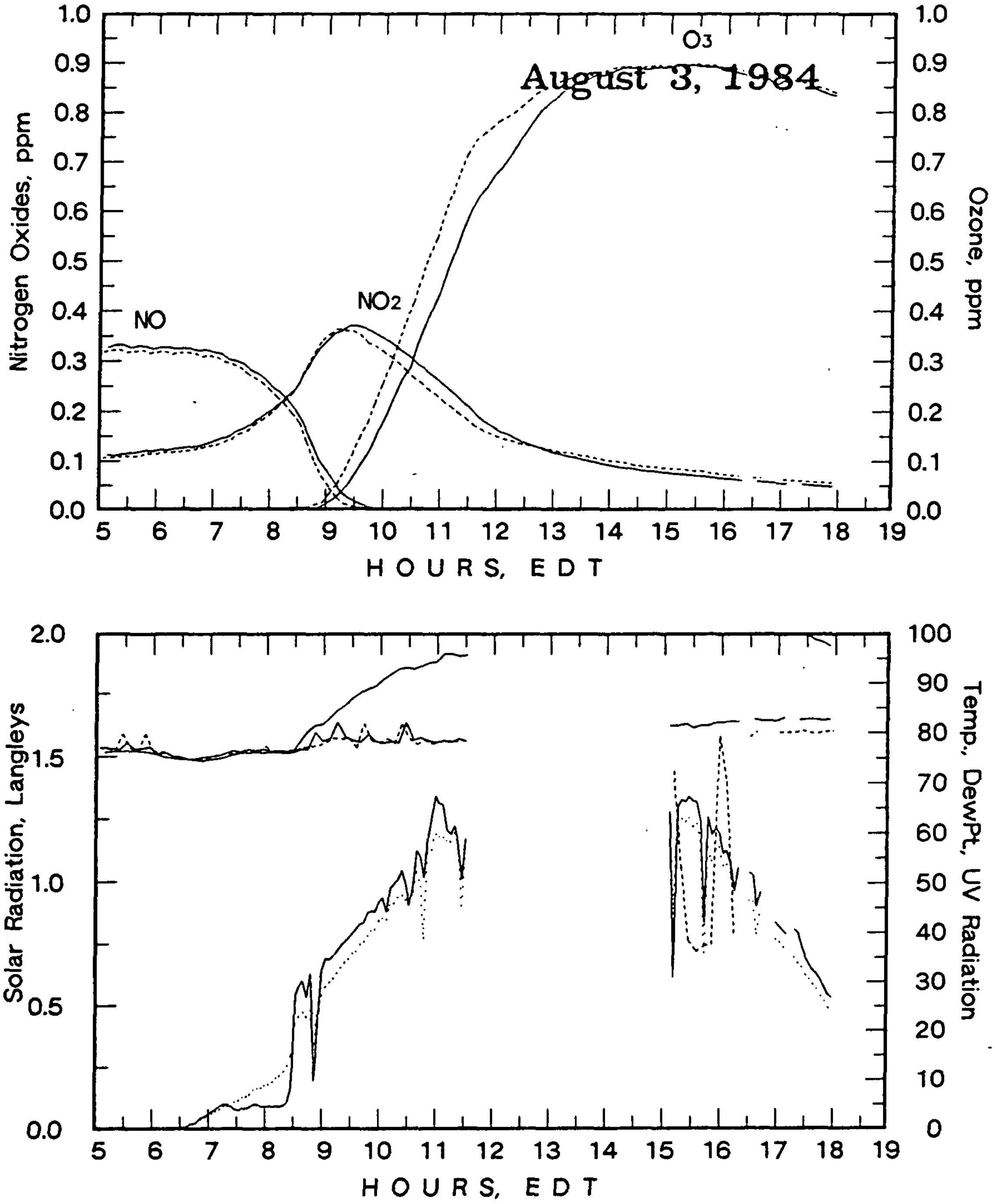


Figure 13.
Top: (Solid) 2.62 ppmC SYNAUTO, 0.9 ppm MeOH + 0.13 ppm HCHO;
(Dashed) 3.73 ppmC SYNAUTO, no MeOH, 0.06 ppm HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

August 4, 1984

SynAuto 1.25 ppmC vs 0.83 ppmC/0.3 ppm MeOH/0.028 ppmC HCHO

RESULTS: O3 MAX: BLUE 0.3284 PPM(1744); RED 0.5154 PPM(1732).

INITIAL CONDITIONS:	BLUE	RED
NO	0.284	0.293
NO2	0.071	0.077
NMHC	1.178	1.250
SYN-AUTO(TANK&LIQUID)	0.817	1.231
MEOH	0.320	0.000
HCHO	0.041	0.019
ETHYLENE	0.244	0.365
PROPYLENE	0.034	0.053
1-BUTENE	0.021	0.031
TRANS-2-BUTENE	0.019	0.029
N-BUTANE	0.031	0.046
ISOPENTANE	0.047	0.067
2,2,4-TRIMETHYLPENTANE	0.085	0.127
BENZENE	0.036	0.055
TOLUENE	0.154	0.236
M-XYLENE	0.076	0.115
O-XYLENE	0.029	0.045
1,2,4-TRIMETHYLBENZENE	0.041	0.062

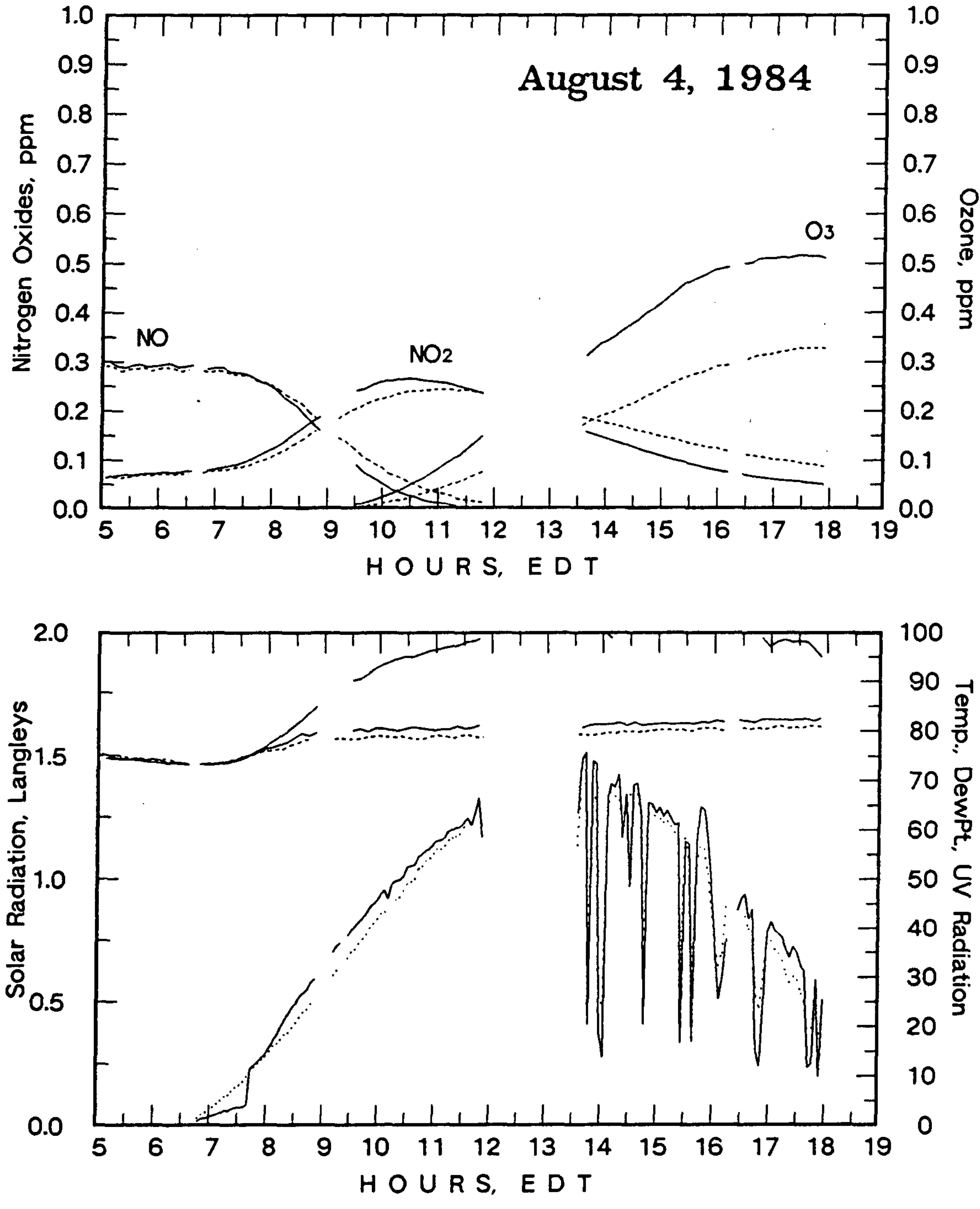


Figure 14.
Top: (Solid) 1.23 ppmC SYNAUTO, no MeOH, 0.02 ppm HCHO;
(Dashed) 0.82 ppmC SYNAUTO, 0.32 ppm MeOH + 0.04 ppmC HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

August 5, 1984

SynAuto 1.3 ppmC vs 0.93 ppmC

RESULTS: O3 MAX: BLUE 0.5946 PPM(1728); RED 0.3352 PPM(1756).

INITIAL CONDITIONS:	BLUE	RED
NO	0.268	0.272
NO2	0.077	0.079
NMHC	1.335	0.926
SYN-AUTO(TANK&LIQUID)	1.316	0.914
HCHO	0.019	0.012
ETHYLENE	0.389	0.265
PROPYLENE	0.062	0.042
1-BUTENE	0.034	0.022
TRANS-2-BUTENE	0.031	0.021
N-BUTANE	0.054	0.038
ISOPENTANE	0.079	0.053
2,2,4-TRIMETHYLPENTANE	0.134	0.099
BENZENE	0.060	0.041
TOLUENE	0.242	0.172
M-XYLENE	0.123	0.085
O-XYLENE	0.045	0.031
1,2,4-TRIMETHYLBENZENE	0.064	0.045

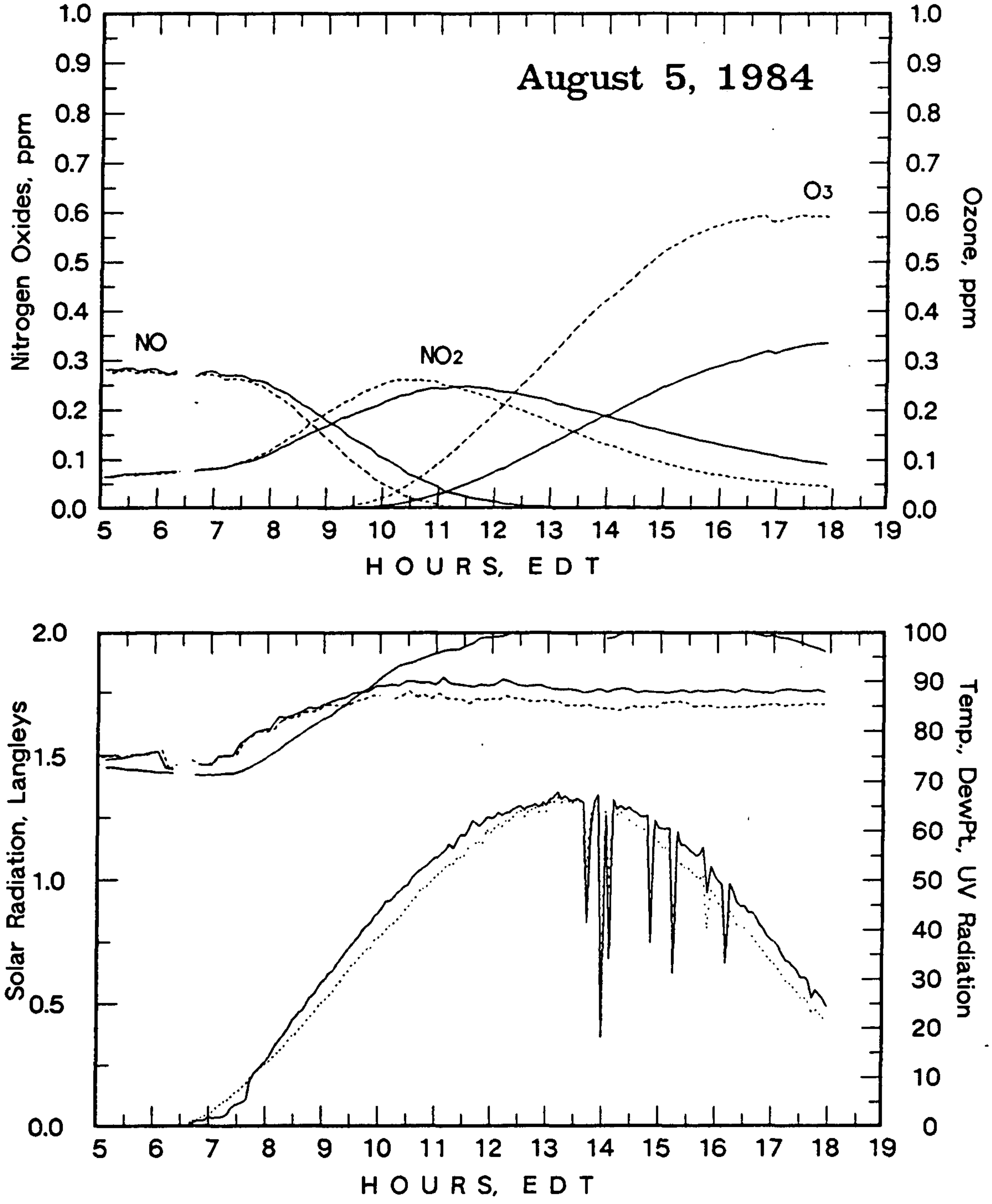


Figure 15.
Top: (Solid) 0.91 ppmC SYNAUTO, no MeOH, 0.01 ppm HCHO;
(Dashed) 1.32 ppmC SYNAUTO, no MeOH, 0.02 ppm HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

August 6, 1984

SynAuto 3.2 vs 2.3 ppmC (no HCHO or MeOH)

RESULTS: O3 MAX: BLUE 0.9398 PPM(1408); RED 0.8874 PPM(1420).

INITIAL CONDITIONS:	BLUE	RED
NO	0.283	0.279
NO2	0.072	0.072
NMHC	3.293	2.289
SYN-AUTO(TANK&LIQUID)	3.236	2.250
HCHO	0.057	0.039
ETHYLENE	0.963	0.666
PROPYLENE	0.149	0.104
1-BUTENE	0.085	0.059
TRANS-2-BUTENE	0.079	0.052
N-BUTANE	0.136	0.095
ISOPENTANE	0.186	0.133
2,2,4-TRIMETHYLPENTANE	0.336	0.225
BENZENE	0.122	0.088
TOLUENE	0.602	0.422
M-XYLENE	0.301	0.212
O-XYLENE	0.115	0.081
1,2,4-TRIMETHYLBENZENE	0.162	0.115

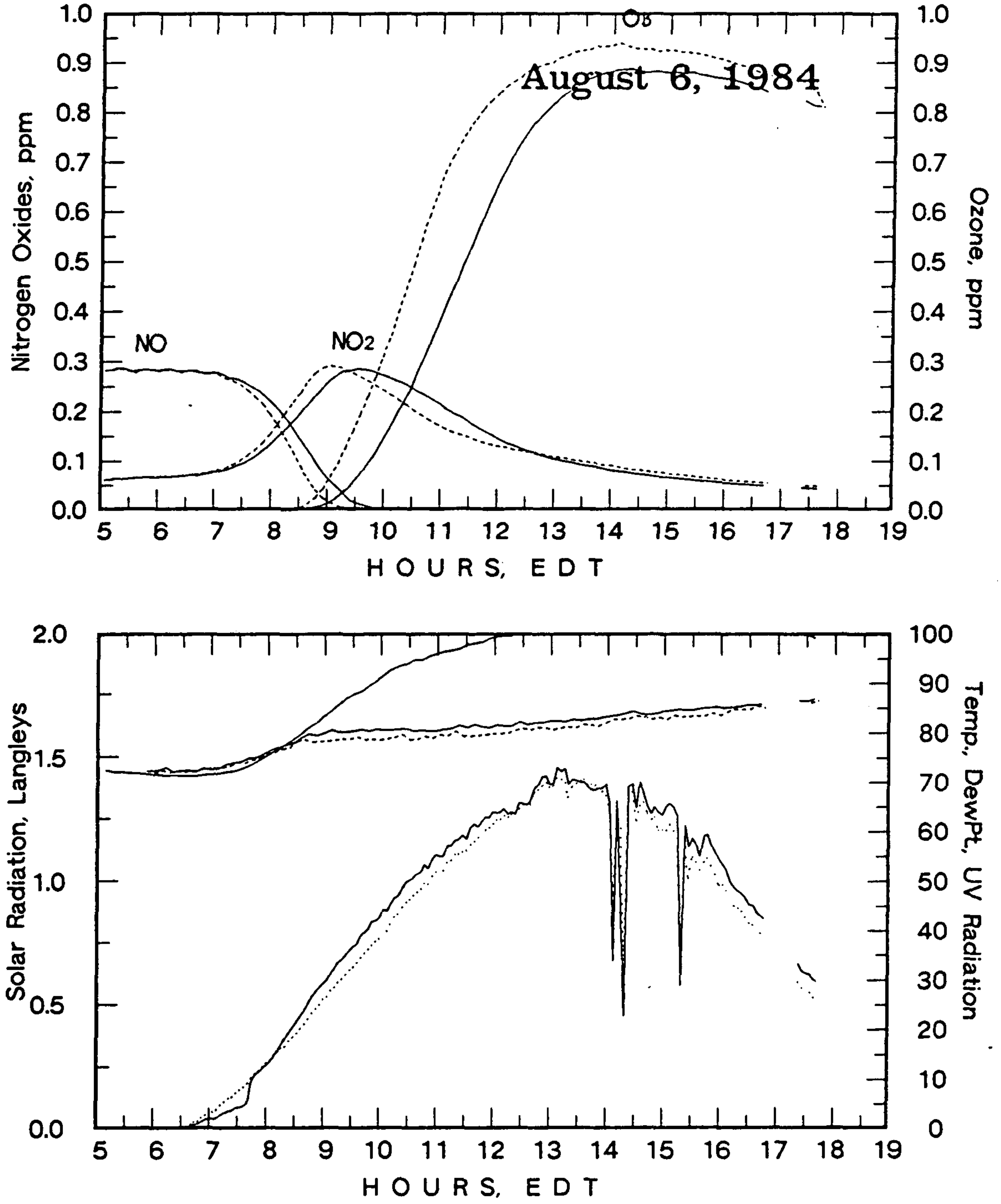


Figure 16.
Top: (Solid) 2.25 ppmC SYNAUTO, no MeOH, 0.04 ppm HCHO;
(Dashed) 3.24 ppmC SYNAUTO, no MeOH, 0.06 ppm HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

August 7, 1984

SynAuto 1.36 ppmC vs 0.89 ppmC/0.3 ppm MeOH/0.029 ppm HCHO

RESULTS: O3 MAX: BLUE 0.4109 PPM(1749); RED 0.6012 PPM(1737).

INITIAL CONDITIONS:	BLUE	RED
NO	0.296	0.302
NO2	0.084	0.083
NMHC	1.220	1.361
SYN-AUTO(TANK&LIQUID)	0.865	1.320
HCHO	0.056	0.041
MEOH	0.299	0.000
ETHYLENE	0.251	0.381
PROPYLENE	0.040	0.057
1-BUTENE	0.020	0.033
TRANS-2-BUTENE	0.021	0.030
N-BUTANE	0.037	0.057
ISOPENTANE	0.052	0.073
2,2,4-TRIMETHYLPENTANE	0.095	0.138
BENZENE	0.041	0.063
TOLUENE	0.155	0.249
M-XYLENE	0.083	0.128
O-XYLENE	0.031	0.046
1,2,4-TRIMETHYLBENZENE	0.041	0.065

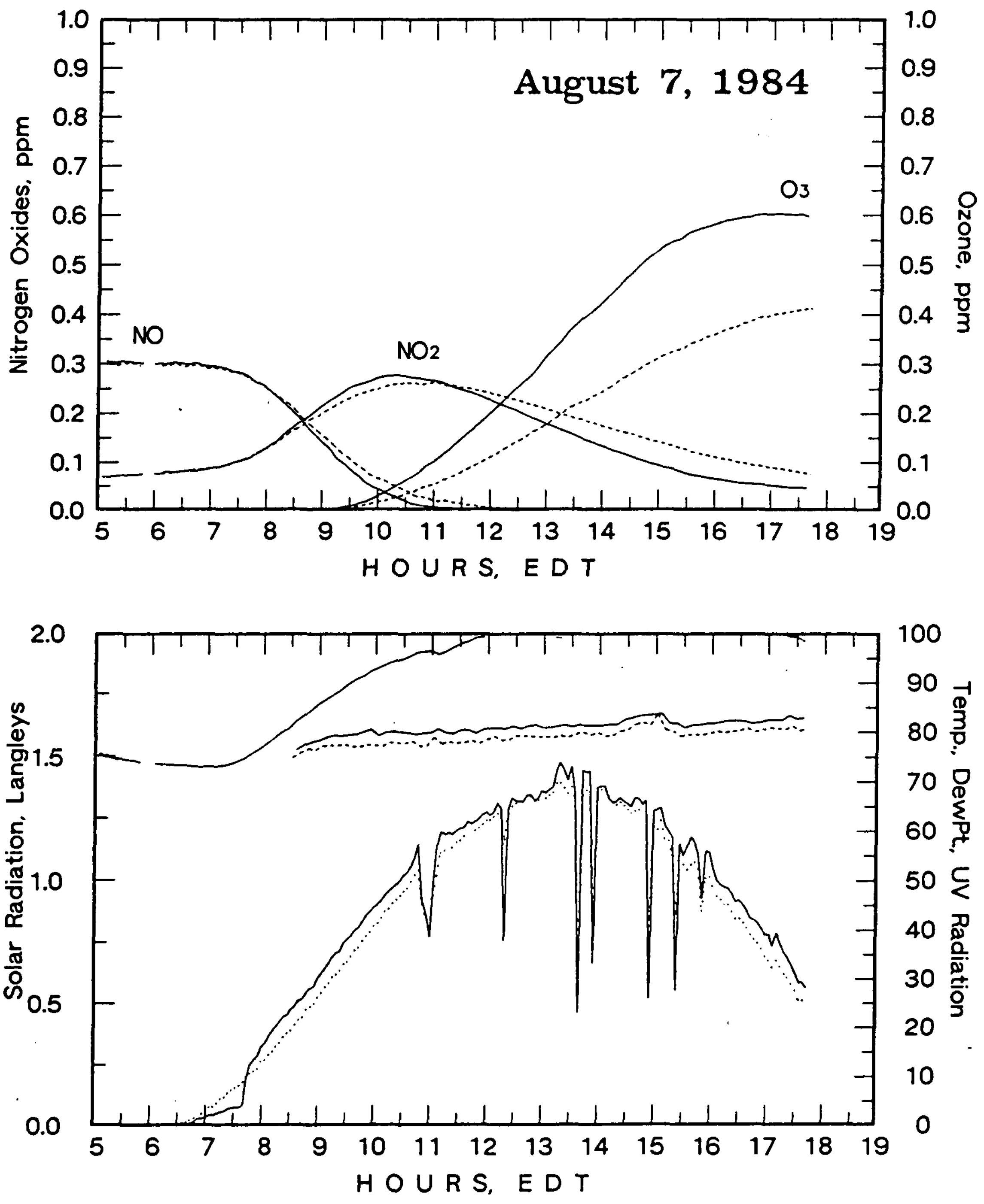


Figure 17.
Top: (Solid) 1.32 ppmC SYNAUTO, no MeOH, 0.04 HCHO, no MeNO2;
(Dashed) 0.87 ppmC SYNAUTO, 0.3 MeOH, 0.06 HCHO, 3 ppb MeNO2;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

August 8, 1984

SynAuto 3.7 ppmC vs 2.5 ppmC/0.79 ppm MeOH/0.19 ppm HCHO

RESULTS: 03 MAX: BLUE 0.8329 PPM(1432); RED 0.8364 PPM(1428).

INITIAL CONDITIONS:	BLUE	RED
NO	0.264	0.262
NO2	0.078	0.076
NMHC	3.734	3.491
SYN-AUTO(TANK&LIQUID)	3.677	2.478
MEOH	0.000	0.785
HCHO	0.057	0.228
ETHYLENE	1.050	0.705
PROPYLENE	0.158	0.108
1-BUTENE	0.095	0.064
TRANS-2-BUTENE	0.089	0.058
N-BUTANE	0.151	0.099
ISOPENTANE	0.200	0.139
2,2,4-TRIMETHYLPENTANE	0.389	0.265
BENZENE	0.166	0.113
TOLUENE	0.715	0.481
M-XYLENE	0.341	0.230
O-XYLENE	0.134	0.096
1,2,4-TRIMETHYLBENZENE	0.188	0.126

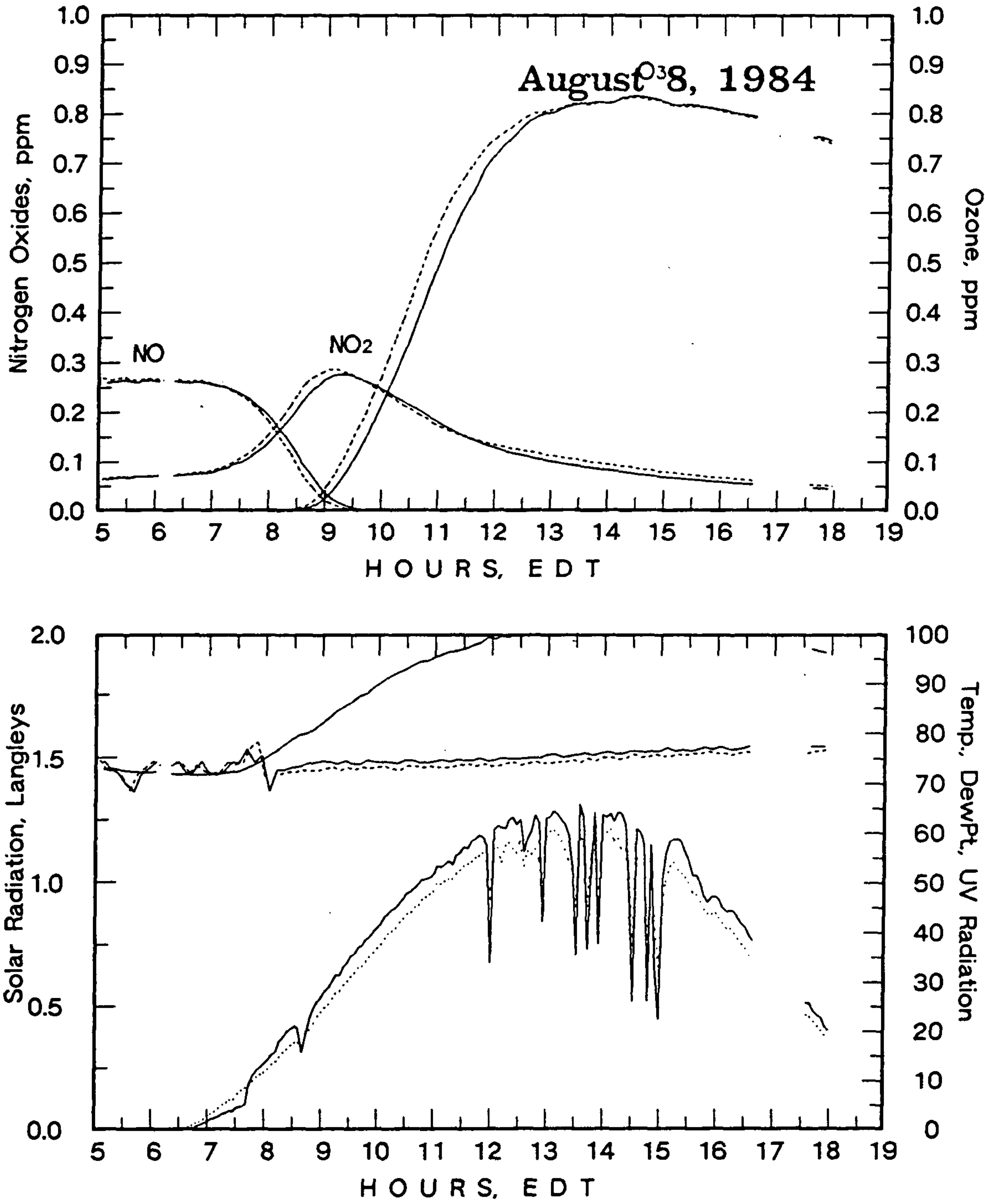


Figure 18.
Top: (Solid) 2.48 ppmC SYNAUTO, 0.79 MeOH, 0.23 HCHO, 10 ppb MeNO2;
(Dashed) 3.68 ppmC SYNAUTO, no MeOH, 0.06 HCHO, no MeNO2;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

August 9, 1984

SynAuto 1.3 ppmC vs 0.87 ppmC/0.26 ppm MeOH/0.06 ppm HCHO

RESULTS: O3 MAX: BLUE 0.3213 PPM(1616); RED 0.5205 PPM(1612).

INITIAL CONDITIONS:	BLUE	RED
NO	0.298	0.302
NO2	0.089	0.087
NMHC	1.196	1.303
SYN-AUTO(TANK&LIQUID)	0.858	1.284
MEOH	0.262	0.000
HCHO	0.076	0.019
ETHYLENE	0.238	0.345
PROPYLENE	0.038	0.056
1-BUTENE	0.021	0.032
TRANS-2-BUTENE	0.019	0.029
N-BUTANE	0.036	0.052
ISOPENTANE	0.049	0.070
2,2,4-TRIMETHYLPENTANE	0.101	0.146
BENZENE	0.039	0.059
TOLUENE	0.165	0.256
M-XYLENE	0.081	0.122
O-XYLENE	0.031	0.049
1,2,4-TRIMETHYLBENZENE	0.043	0.067

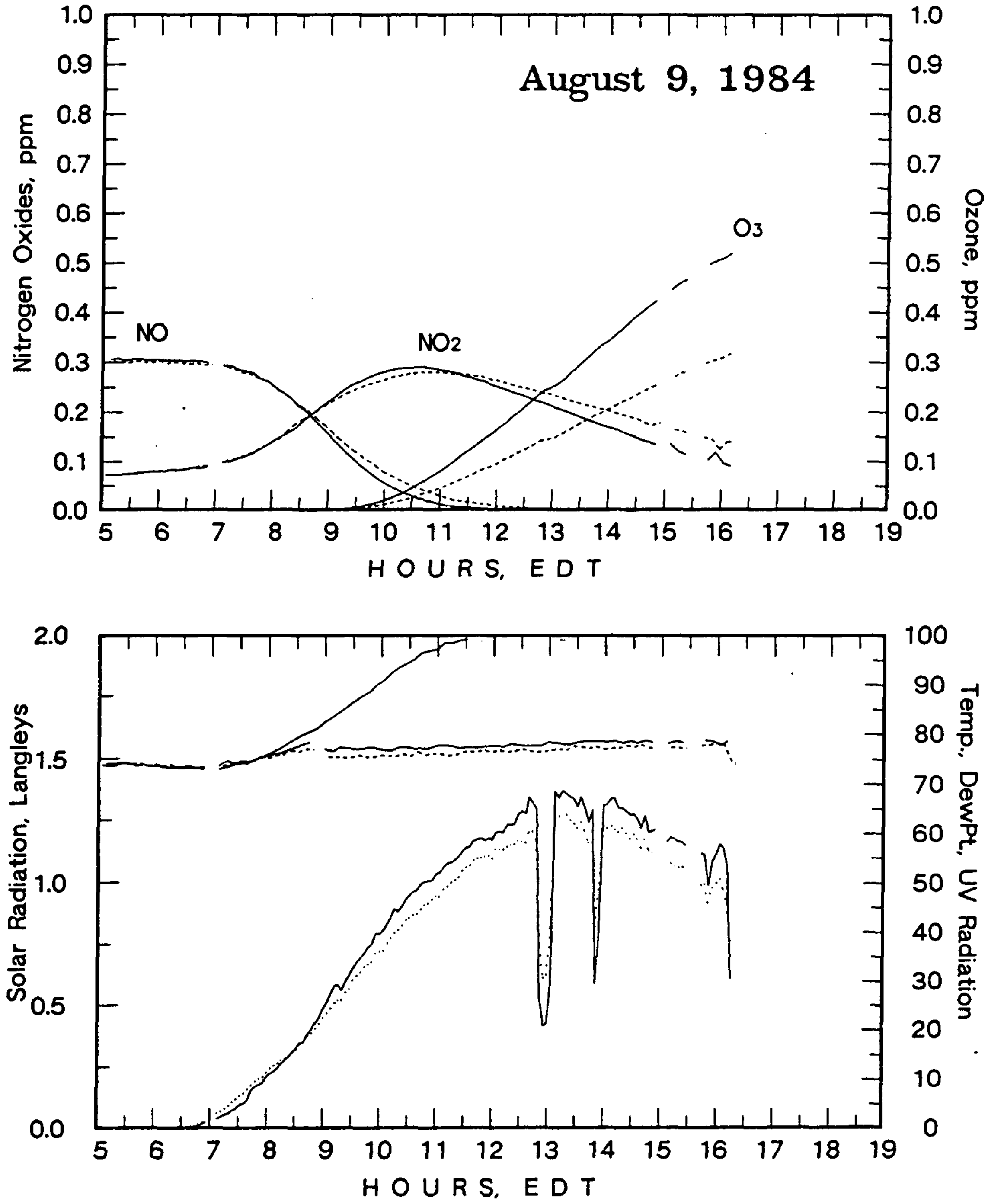


Figure 19.
Top: (Solid) 1.28 ppmC SYNAUTO, no MeOH, 0.02 ppm HCHO, no MeNO2;
(Dashed) 0.86 ppmC SYNAUTO, 0.26 MeOH, 0.08 HCHO, 3 ppb MeNO2;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

August 22, 1984

SynUrban 3.1 ppmC vs 2.1 ppmC/0.87 ppm MeOH/0.092 ppm HCHO

RESULTS: O3 MAX: BLUE 0.6345 PPM(1624); RED 0.6572 PPM(1628).

INITIAL CONDITIONS:	BLUE	RED
NO	0.247	0.254
NO2	0.068	0.070
NMHC	3.039	3.097
SYN-URBAN(TANK&LIQUID)	2.042	3.041
MEOH	0.867	0.000
HCHO	0.130	0.056
ETHYLENE	0.148	0.231
PROPYLENE	0.056	0.091
1-BUTENE	0.033	0.054
TRANS-2-BUTENE	0.034	0.047
N-BUTANE	0.167	0.253
ISOPENTANE	0.176	0.266
2-METHYL-1-BUTENE	0.059	0.082
2-METHYL-2-BUTENE	0.030	0.047
N-PENTANE	0.263	0.386
2-METHYLPENTANE	0.100	0.154
2,4-DIMETHYLPENTANE	0.144	0.221
2,2,4-TRIMETHYLPENTANE	0.185	0.275
BENZENE	0.053	0.079
TOLUENE	0.278	0.403
M-XYLENE	0.145	0.203
O-XYLENE	0.065	0.088
1,2,4-TRIMETHYLBENZENE	0.108	0.160

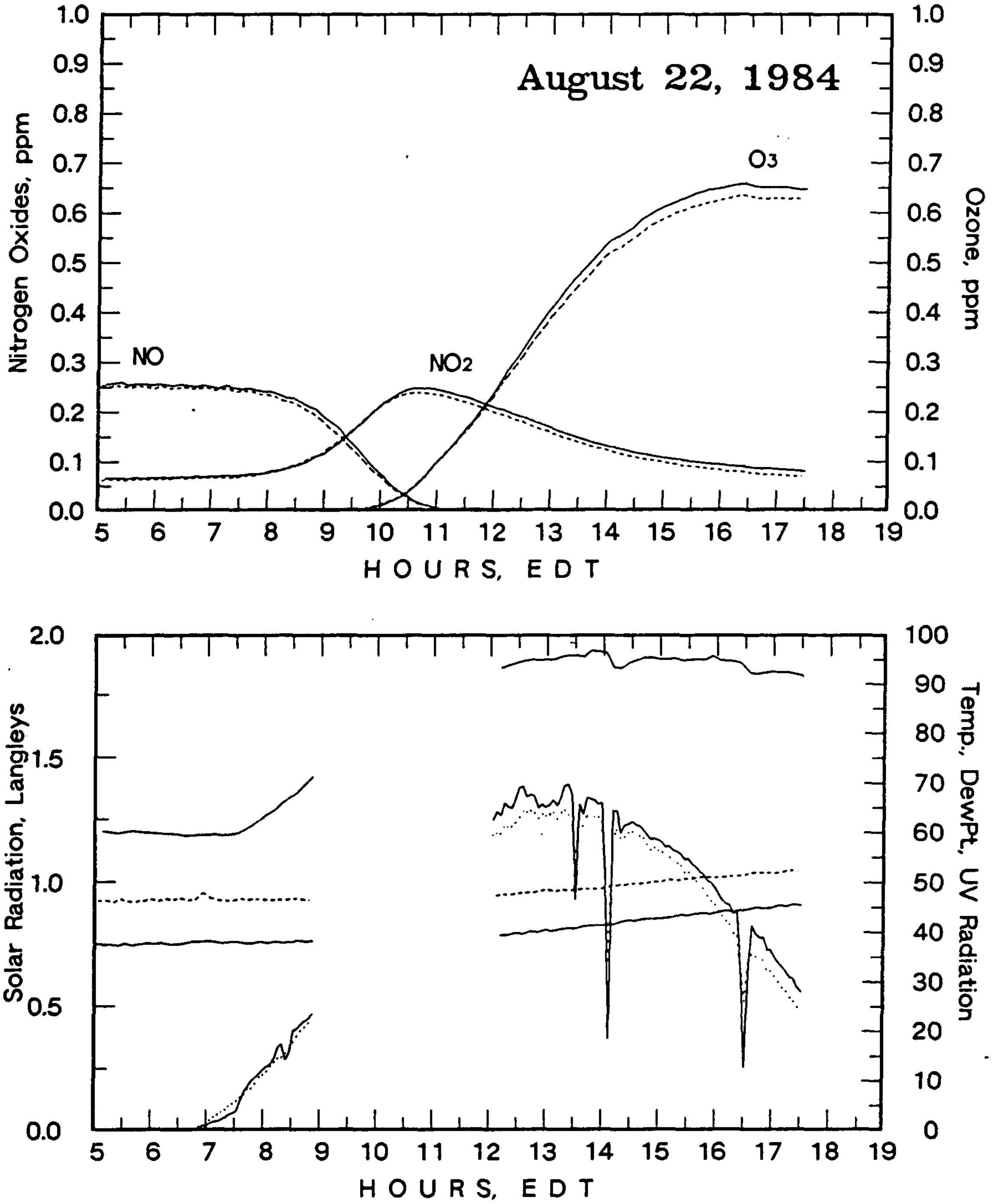


Figure 20.
Top: (Solid) 3.04 ppmC SYNURBAN, no MeOH, 0.06 ppm HCHO, no MeNO2;
(Dashed) 2.04 ppmC SYNURBAN, 0.87 MeOH, 0.13 HCHO, 10 ppb MeN
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

August 25, 1984

SynUrban 1.09 ppmC vs 0.73 ppmC/0.29 ppm MeOH/0.03 ppm HCHO

RESULTS: O3 MAX: BLUE 0.0963 PPM(1744); RED 0.0744 PPM(1732).

INITIAL CONDITIONS:	BLUE	RED
NO	0.262	0.272
NO2	0.068	0.076
NMHC	1.089	1.058
SYN-URBAN(TANK&LIQUID)	1.070	0.720
MEOH	0.000	0.295
HCHO	0.019	0.043
ETHYLENE	0.129	0.098
PROPYLENE	0.040	0.031
1-BUTENE	0.023	0.016
N-BUTANE	0.027	0.017
CIS-2-BUTENE	0.021	0.012
ISOPENTANE	0.095	0.066
N-PENTANE	0.120	0.097
2,2,4-TRIMETHYLPENTANE	0.117	0.086
BENZENE	0.030	0.025
TOLUENE	0.141	0.103
M-XYLENE	0.069	0.053
O-XYLENE	0.031	0.024

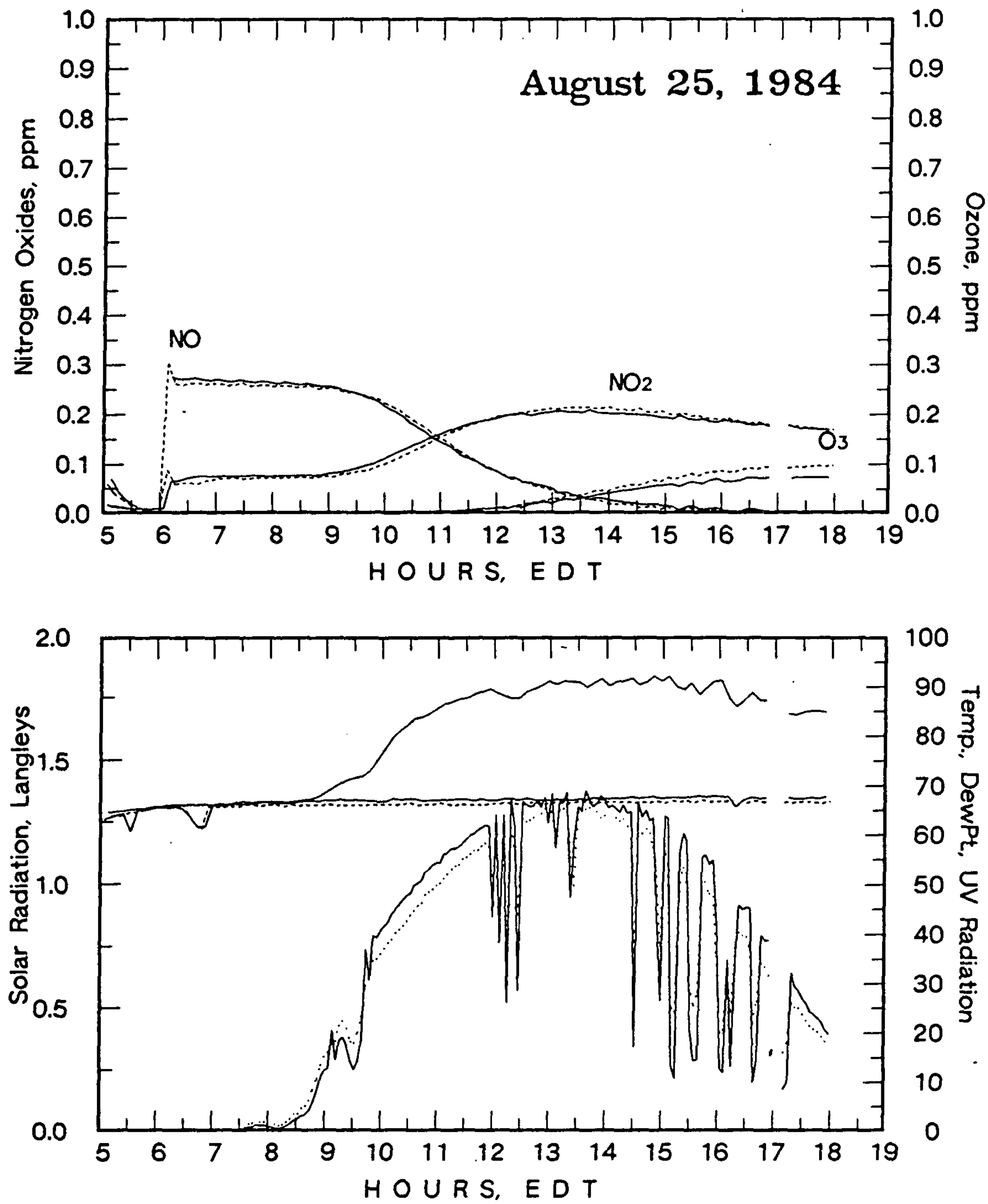


Figure 21.
Top: (Solid) 0.72 ppmC SYNURBAN, 0.29 ppm MeOH, 0.04 ppm HCHO;
(Dashed) 1.07 ppmC SYNURBAN, no MeOH;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

August 28, 1984

SynUrban 1.18 ppmC vs 0.82 ppmC/0.33 ppm MeOH

RESULTS: 03 MAX: BLUE 0.0560 PPM(1456); RED 0.0307 PPM(1452).

INITIAL CONDITIONS:	BLUE	RED
NO	0.250	0.256
NO2	0.062	0.068
NMHC	1.176	1.149
SYN-URBAN(TANK&LIQUID)	1.157	0.809
MEOH	0.000	0.327
HCHO	0.019	0.013
ETHYLENE	0.142	0.123
PROPYLENE	0.031	0.020
1-BUTENE	0.020	0.010
TRANS-2-BUTENE	0.015	0.013
N-BUTANE	0.118	0.088
ISOPENTANE	0.080	0.053
2-METHYL-1-BUTENE	0.022	0.013
2-METHYL-2-BUTENE	0.016	0.009
N-PENTANE	0.137	0.086
2-METHYLPENTANE	0.053	0.031
2,4-DIMETHYLPENTANE	0.076	0.045
2,2,4-TRIMETHYLPENTANE	0.109	0.074
BENZENE	0.022	0.022
TOLUENE	0.158	0.094
M-XYLENE	0.145	0.052
O-XYLENE	0.035	0.030
1,2,4-TRIMETHYLBENZENE	0.048	0.045

RUN NOT PROCESSED

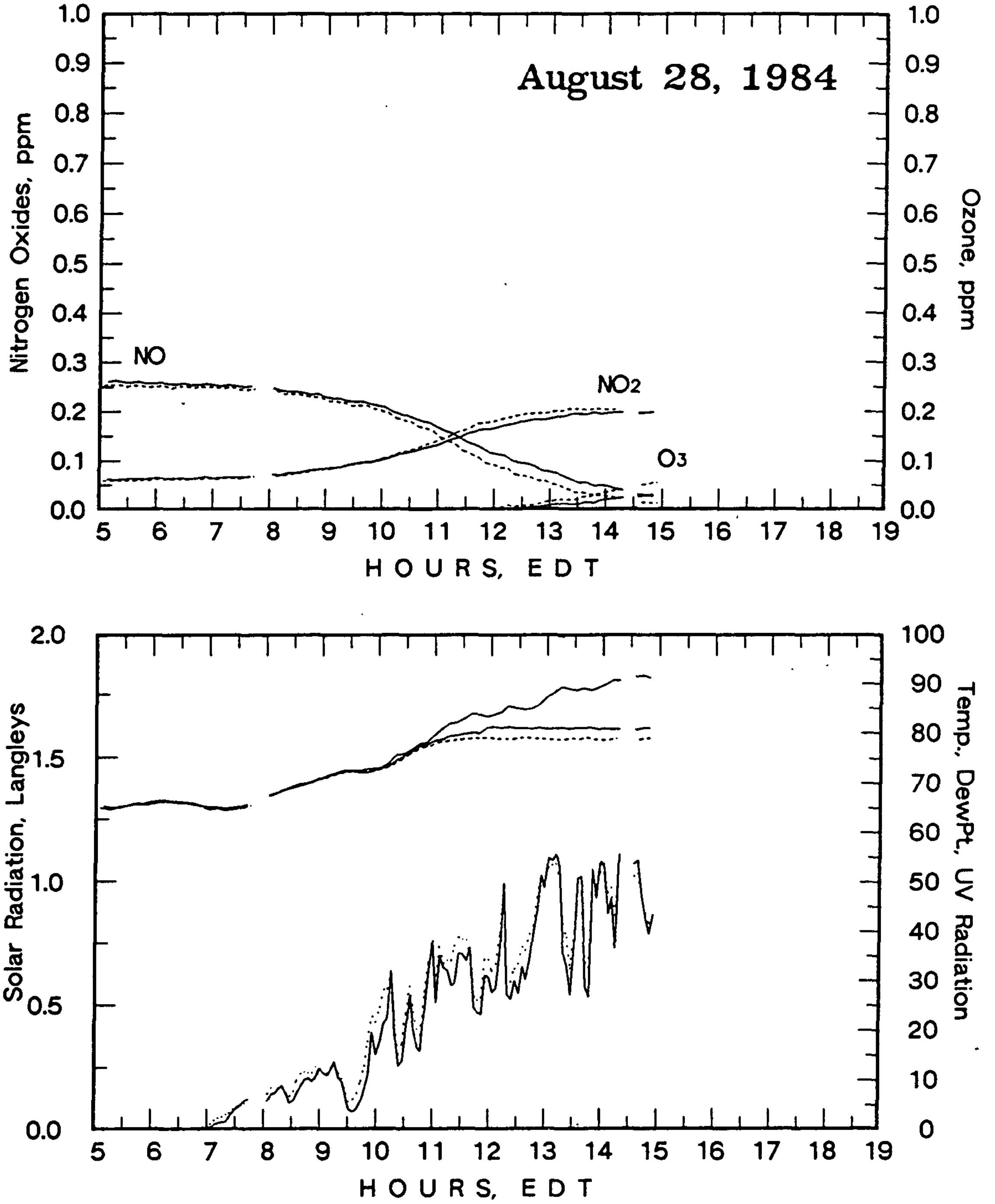


Figure 22.

Top: (Solid) 0.81 ppmC SYNURBAN, 0.32 ppm MeOH, 0.01 ppm HCHO;
(Dashed) 1.16 ppmC SYNURBAN, no MeOH, 0.02 ppm HCHO;

Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

September 1, 1984

SynUrban 3.37 ppmC vs 2.70 ppmC/.97 ppm MeOH

RESULTS: O3 MAX: BLUE 0.6457 PPM(1608); RED 0.5459 PPM(1708).

INITIAL CONDITIONS:	BLUE	RED
NO	0.243	0.252
NO2	0.059	0.062
NMHC	3.365	3.663
SYN-URBAN(TANK&LIQUID)	3.310	2.660
MEOH	0.000	0.966
HCHO	0.055	0.037
ETHYLENE	0.200	0.164
PROPYLENE	0.092	0.061
1-BUTENE	0.048	0.033
N-BUTANE	0.380	0.678
CIS-2-BUTENE	0.042	0.028
ISOPENTANE	0.242	0.167
N-PENTANE	0.420	0.310
2,2,4-TRIMETHYLPENTANE	0.289	0.189
BENZENE	0.076	0.049
TOLUENE	0.408	0.275
M-XYLENE	0.204	0.152
O-XYLENE	0.087	0.076

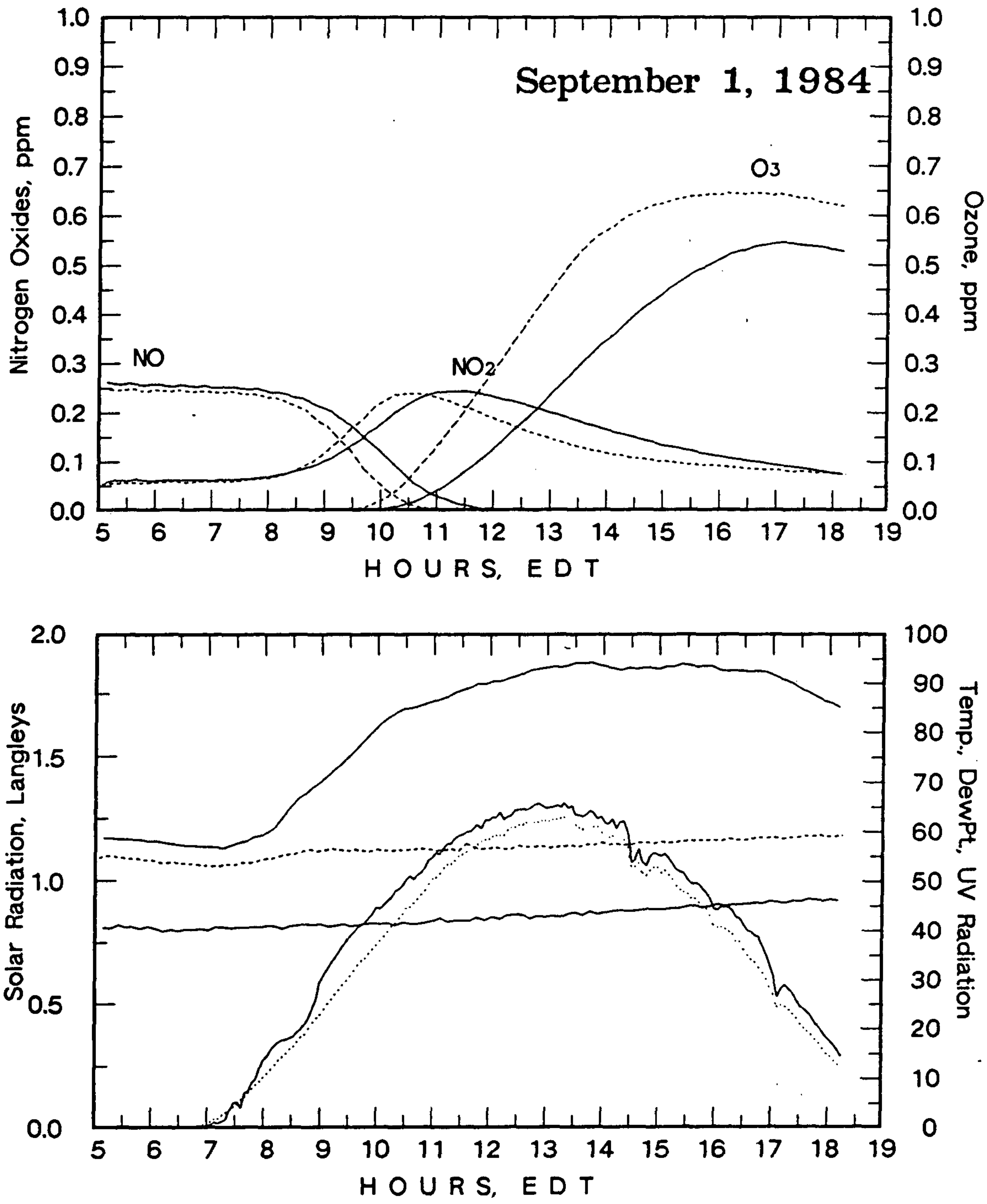


Figure 23.
Top: (Solid) 2.66 ppmC SYNURBAN, 0.97 ppm MeOH;
(Dashed) 3.31 ppmC SYNURBAN, no MeOH;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

September 2, 1984

SynUrban 1.12 ppmC vs 0.77 ppmC

RESULTS: O3 MAX: BLUE 0.0199 PPM(1656); RED 0.1193 PPM(1732).

INITIAL CONDITIONS:	BLUE	RED
NO	0.259	0.284
NO2	0.063	0.060
NMHC	0.768	1.118
SYN-URBAN(TANK&LIQUID)	0.756	1.099
HCHO	0.012	0.019
ETHYLENE	0.056	0.089
PROPYLENE	0.028	0.036
1-BUTENE	0.014	0.019
TRANS-2-BUTENE	0.010	0.016
N-BUTANE	0.100	0.130
ISOPENTANE	0.054	0.079
2-METHYL-1-BUTENE	0.015	0.019
2-METHYL-2-BUTENE	0.011	0.014
N-PENTANE	0.090	0.090
2-METHYLPENTANE	0.036	0.046
2,4-DIMETHYLPENTANE	0.051	0.066
2,2,4-TRIMETHYLPENTANE	0.096	0.157
BENZENE	0.020	0.028
TOLUENE	0.083	0.130
M-XYLENE	0.044	0.063
O-XYLENE	0.028	0.033
1,2,4-TRIMETHYLBENZENE	0.000	0.000

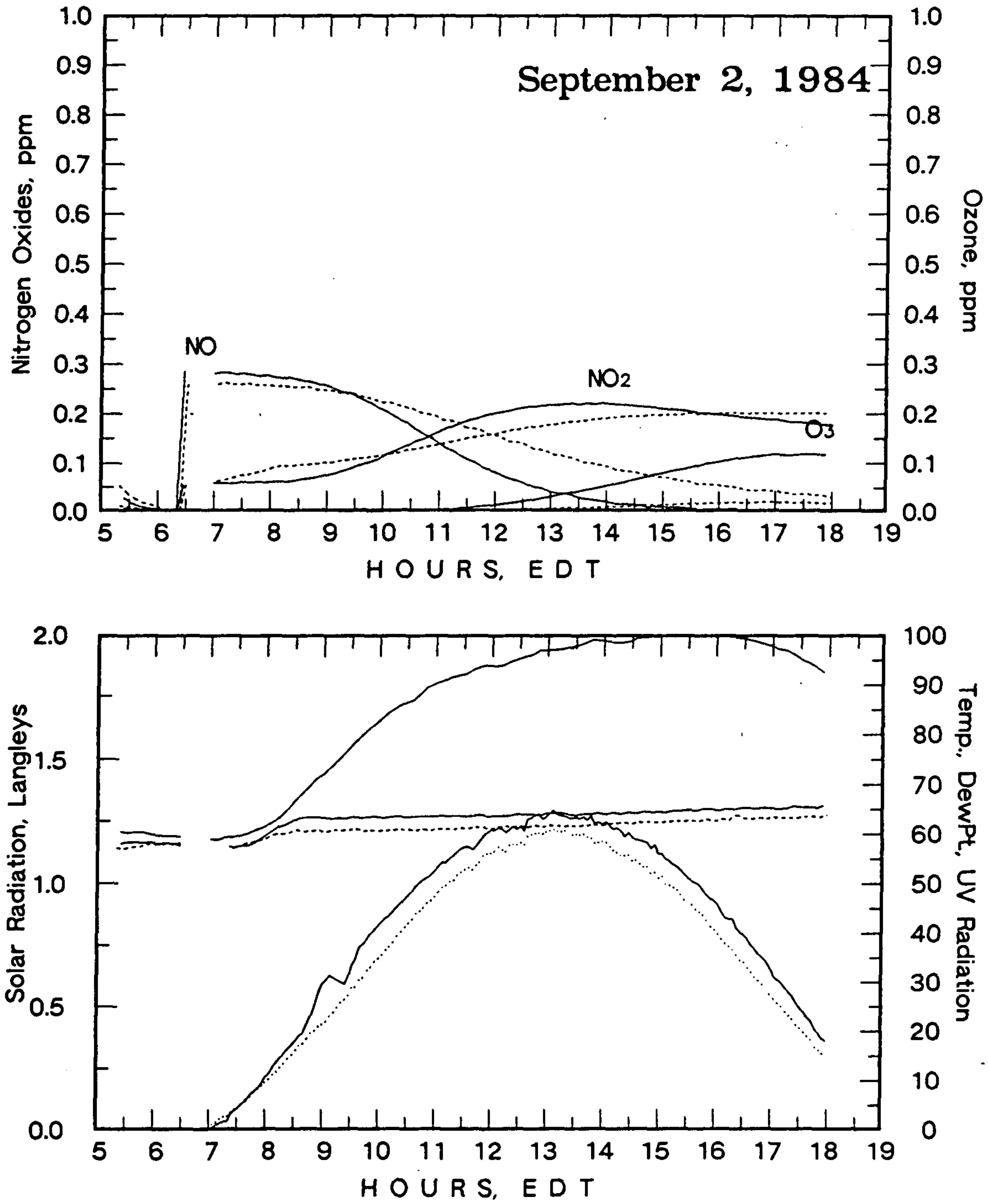


Figure 24.
Top: (Solid) 1.10 ppmC SYNURBAN, no MeOH, 0.02 ppm HCHO;
(Dashed) 0.76 ppmC SYNURBAN, no MeOH, 0.01 ppm HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

September 3, 1984

SynUrban 1.03 ppmC vs 0.79 ppmC/0.26 ppm MeOH/0.06 ppm HCHO

RESULTS: O3 MAX: BLUE 0.0578 PPM(1728); RED 0.0479 PPM(1724).

INITIAL CONDITIONS:	BLUE	RED
NO	0.240	0.241
NO2	0.112	0.111
NMHC	1.116	1.033
SYN-URBAN(TANK&LIQUID)	0.778	1.014
MEOH	0.264	0.000
HCHO	0.074	0.019
ETHYLENE	0.067	0.089
PROPYLENE	0.021	0.024
1-BUTENE	0.015	0.016
TRANS-2-BUTENE	0.012	0.014
N-BUTANE	0.082	0.118
ISOPENTANE	0.051	0.078
2-METHYL-1-BUTENE	0.016	0.018
2-METHYL-2-BUTENE	0.011	0.013
N-PENTANE	0.095	0.095
2-METHYLPENTANE	0.037	0.043
2,4-DIMETHYLPENTANE	0.053	0.062
2,2,4-TRIMETHYLPENTANE	0.083	0.114
BENZENE	0.027	0.031
TOLUENE	0.098	0.136
M-XYLENE	0.047	0.065
O-XYLENE	0.027	0.038
1,2,4-TRIMETHYLBENZENE	0.035	0.058

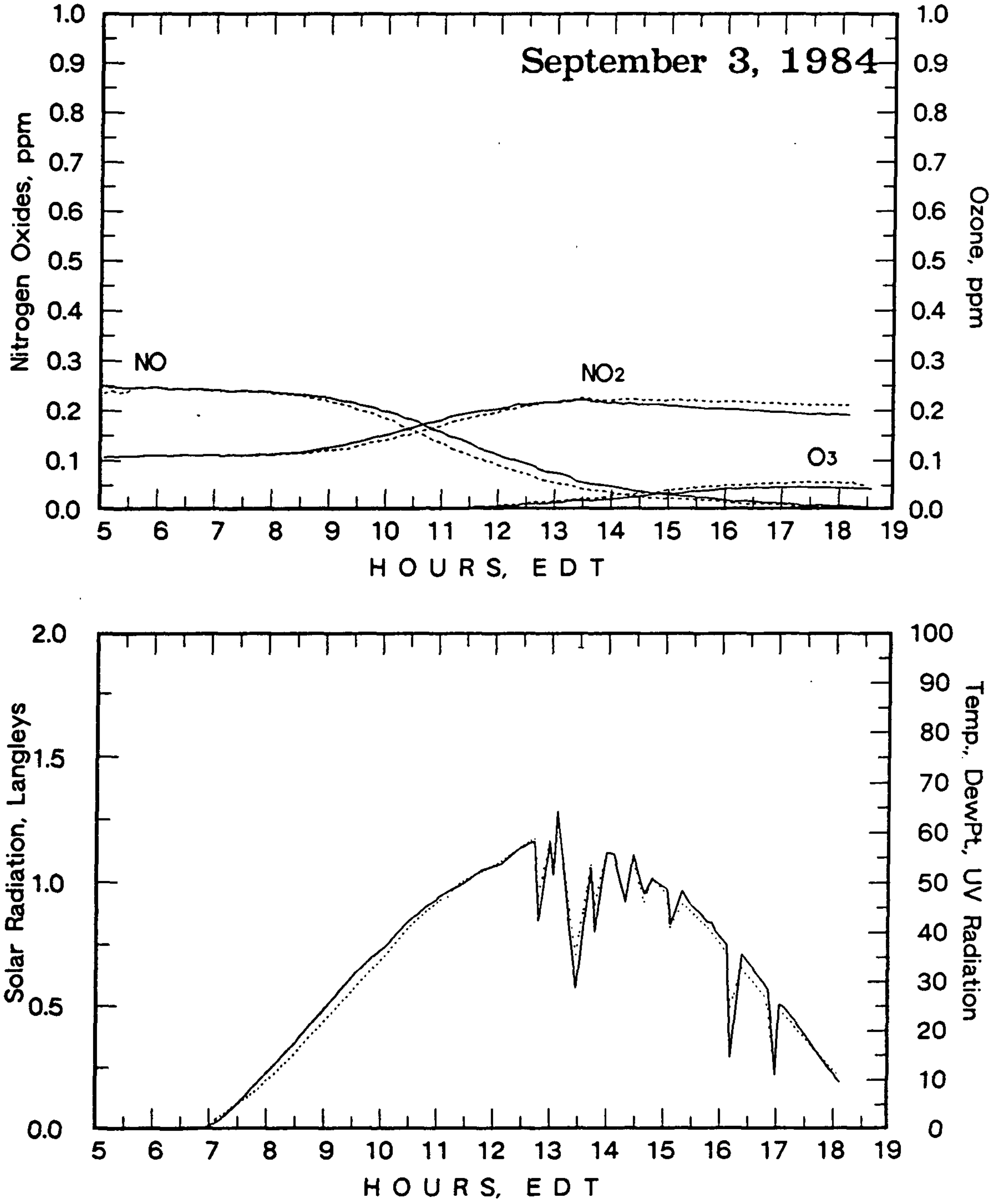


Figure 25.
Top: (Solid) 1.01 ppmC SYNURBAN, no MeOH, 0.02 ppm HCHO;
(Dashed) 0.78 ppmC SYNURBAN, 0.26 ppm MeOH, 0.07 ppm HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

September 8, 1984

SynAuto 2.8 vs 1.8 ppmC (no MeOH)

RESULTS: O3 MAX: BLUE 0.7472 PPM(1456); RED 0.5659 PPM(1708).

INITIAL CONDITIONS:	BLUE	RED
NO	0.205	0.204
NO2	0.126	0.121
NMHC	2.840	1.880
SYN-AUTO(TANK&LIQUID)	2.790	1.840
HCHO	0.050	0.040
ETHYLENE	0.979	0.641
PROPYLENE	@0702 0.134	@0732 0.088
1-BUTENE	@0702 0.075	@0732 0.044
N-BUTANE	@0702 0.446	@0732 0.321
CIS-2-BUTENE	@0702 0.053	@0732 0.053
ISOPENTANE	@0702 0.215	@0732 0.122
N-PENTANE	@0702 0.128	@0732 0.000
2,2,4-TRIMETHYLPENTANE	@0702 0.218	@0832 0.126
BENZENE	@0702 0.047	@0832 0.036
TOLUENE	@0702 0.088	@0832 0.229
M-XYLENE	@0702 0.044	@0832 0.125
O-XYLENE	@0702 0.079	@0832 0.062
1,2,4-TRIMETHYLBENZENE	@0702 0.053	@0832 0.096

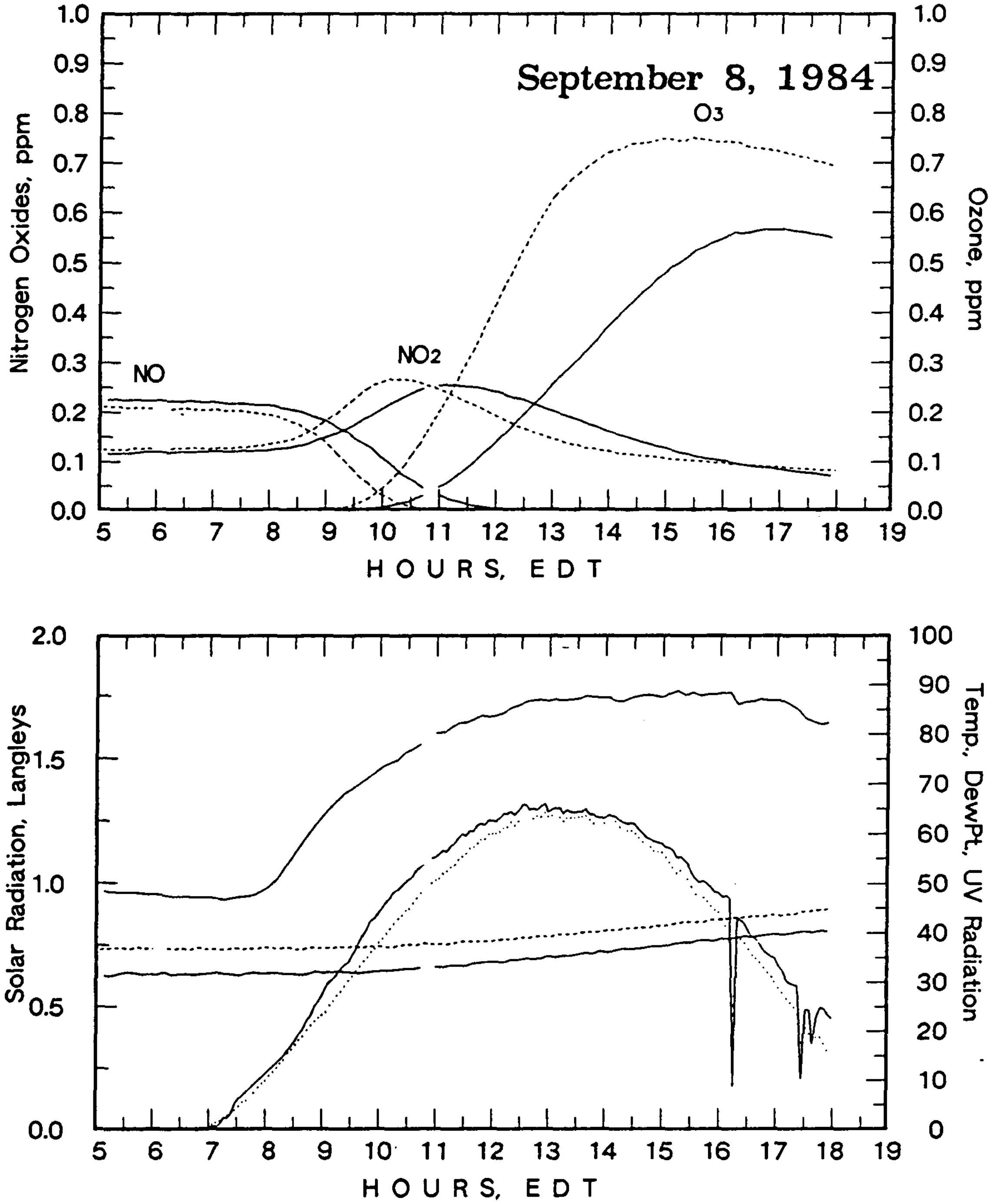


Figure 26.
Top: (Solid) 1.8 ppmC SYNAUTO, 0.2 ppmC Butane, no MeOH;
(Dashed) 2.7 ppmC SYNAUTO, 0.3 ppmC Butane, no MeOH;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

September 9, 1984

SynAuto 2.1 vs 1.4 ppmC (no MeOH)

RESULTS: O3 MAX: BLUE 0.6062 PPM(1600); RED 0.4203 PPM(1636).

INITIAL CONDITIONS:	BLUE	RED
NO	0.285	0.294
NO2	0.055	0.060
NMHC	2.180	1.440
SYN-AUTO(TANK&LIQUID)	2.140	1.420
HCHO	0.040	0.020
ETHYLENE	0.554	0.392
PROPYLENE	0.110	0.075
1-BUTENE	0.052	0.030
N-BUTANE	0.094	0.066
TRANS-2-BUTENE	0.054	0.037
ISOPENTANE	0.135	0.103
2,2,4-TRIMETHYLPENTANE	0.187	0.133
BENZENE	0.056	0.038
TOLUENE	0.373	0.284
M-XYLENE	0.188	0.145
O-XYLENE	0.084	0.057
1,2,4-TRIMETHYLBENZENE	0.093	0.060

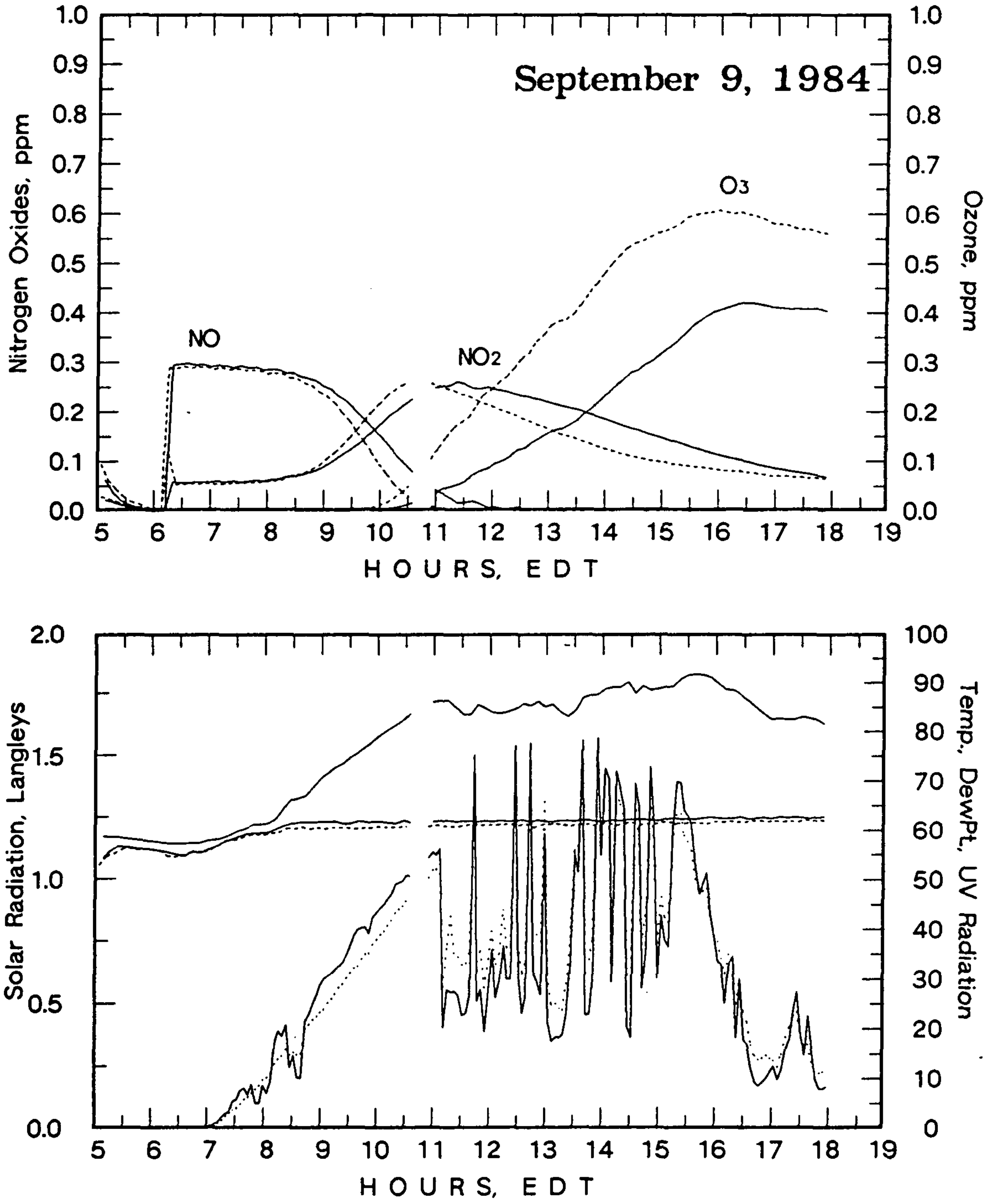


Figure 27.

Top: (Solid) 1.42 ppmC SYNAUTO, 0.13 ppmC Butane, no MeOH;
(Dashed) 2.14 ppmC SYNAUTO, 0.2 ppmC Butane, no MeOH;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

September 17, 1984

SynAuto 2.18 vs 1.45 ppmC/0.57 ppm MeOH

RESULTS: O3 MAX: BLUE 0.4836 PPM(1632); RED 0.5389 PPM(1524).

INITIAL CONDITIONS:		BLUE	RED
NO		0.269	0.270
NO2		0.067	0.070
NMHC		2.070	2.180
SYN-AUTO(TANK&LIQUID)		1.420	2.140
MEOH		0.570	0.000
HCHO		0.080	0.040
ETHYLENE		0.767	1.142
PROPYLENE	@0730	0.164	0.219
1-BUTENE	@0730	0.076	0.112
N-BUTANE	@0730	0.114	0.213
TRANS-2-BUTENE	@0730	0.073	0.122
ISOPENTANE		0.167	0.283
2,2,4-TRIMETHYLPENTANE		0.302	0.429
BENZENE		0.102	0.124
TOLUENE		0.577	0.845
M-XYLENE		0.302	0.435
O-XYLENE		0.177	0.169
1,2,4-TRIMETHYLBENZENE		0.000	0.000

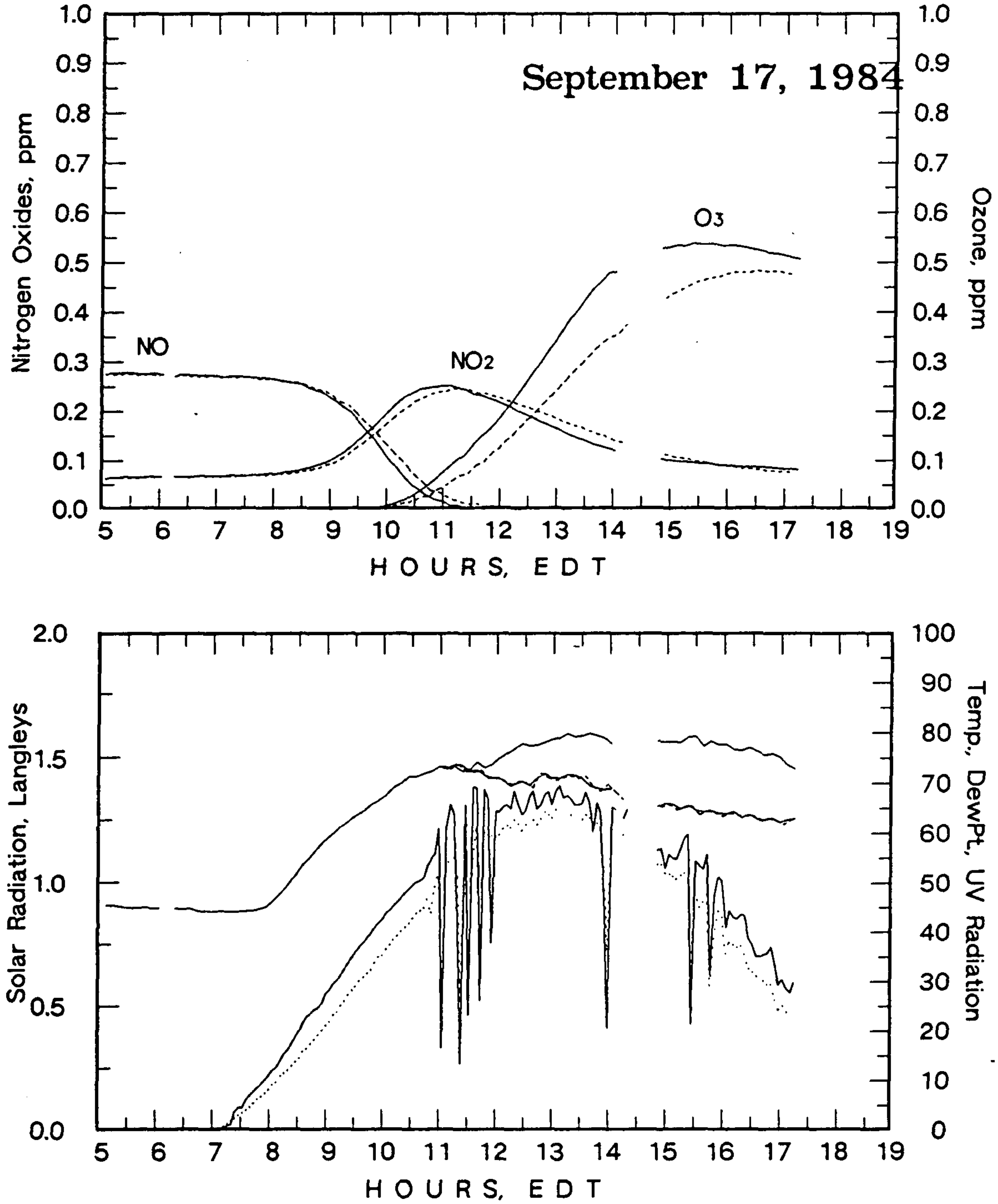


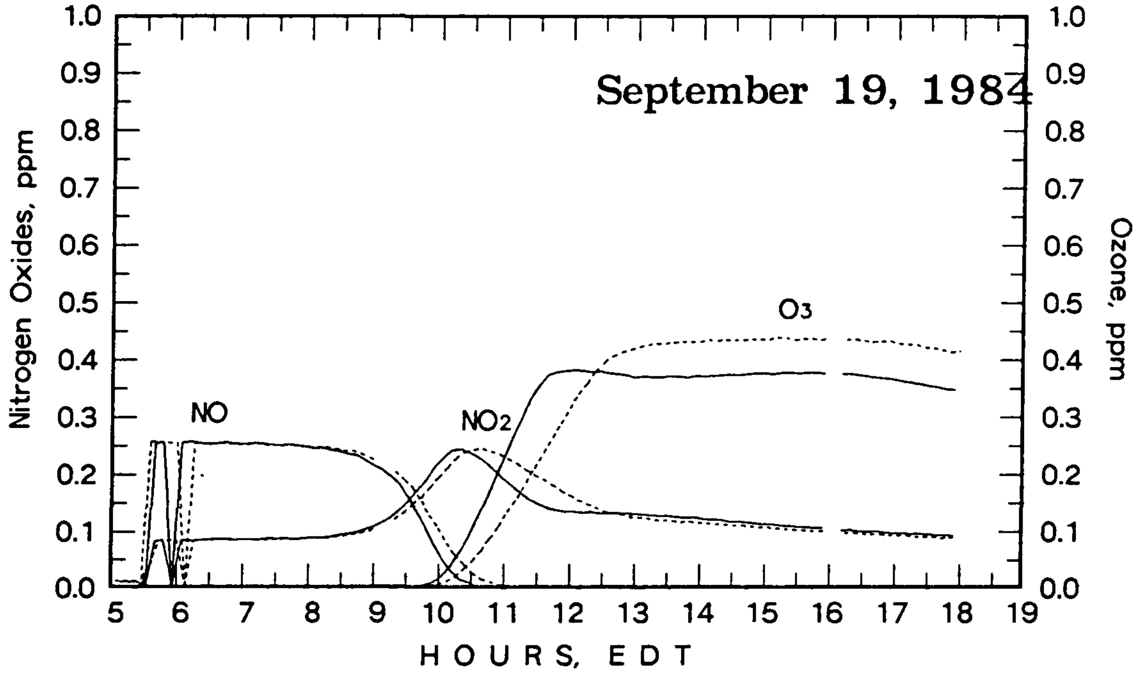
Figure 28.
Top: (Solid) 2.14 ppmC SYNAUTO, 0.2 ppmC Butane, no MeOH, 0.04 HCHO;
(Dashed) 1.42 ppmC SYNAUTO, 0.13 Butane, 0.57 MeOH, 0.08 HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

September 19, 1984

SynAuto HMW 2.6 vs 4.4 ppmC

RESULTS: O3 MAX: BLUE 0.4386 PPM(1512); RED 0.3828 PPM(1204).

INITIAL CONDITIONS:	BLUE	RED
NO	0.252	0.253
NO2	0.086	0.086
2,2,4-TRIMETHYLPENTANE	0.520	0.841
BENZENE	0.147	0.229
TOLUENE	1.011	1.645
M-XYLENE	0.489	0.825
O-XYLENE	0.190	0.337
1,2,4-TRIMETHYLBENZENE	0.269	0.550
NMHC	2.633	4.426
	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	9.8/10	9.8/10
TEMPERATURE F:	45	83
EXPERIMENT STARTS:		0700 (SUNRISE)
INITIAL CONDITIONS ESTABLISHED:		0600
EXPERIMENTS ENDS:		1800



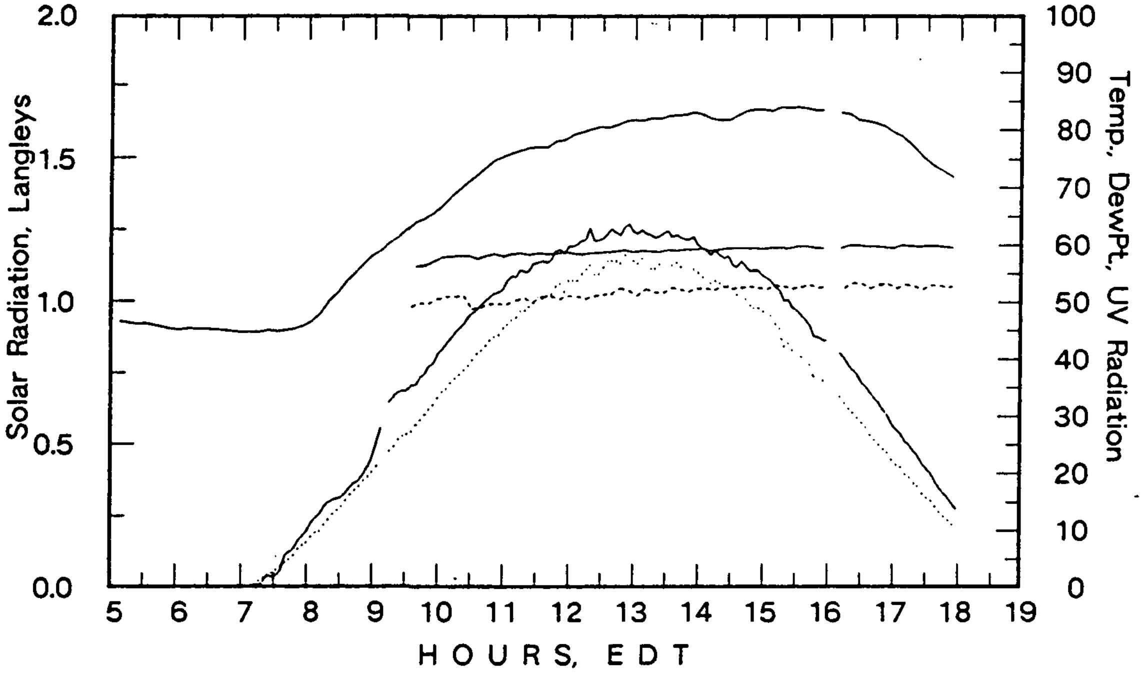


Figure 29.
Top: (Solid) 4.43 ppmC HI MW (liquid) of SYNAUTO and SYNURBAN;
(Dashed) 2.63 ppmC HI MW (liquid) of SYNAUTO and SYNURBAN;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

September 21, 1984

SynAutUrb 2.43 ppmC vs 2.42 ppmC/0.18 ppm HCHO

RESULTS: 03 MAX: BLUE 0.7212 PPM(1448); RED 0.6706 PPM(1556).

INITIAL CONDITIONS:	BLUE		RED
NO	0.273		0.275
NO2	0.086		0.088
NMHC	2.600		2.430
SYN-AUTO(TANK&LIQUID)	2.420		2.430
HCHO	0.180		0.000
ETHYLENE	0.596	@0715	0.602
PROPYLENE	0.119	@0715	0.119
1-BUTENE	0.062	@0715	0.062
N-BUTANE	0.105	@0715	0.101
TRANS-2-BUTENE	0.066	@0715	0.071
ISOPENTANE	0.145	@0715	0.151
2,2,4-TRIMETHYLPENTANE	0.233	@0715	0.228
BENZENE	0.082	@0715	0.081
TOLUENE	0.460	@0715	0.465
M-XYLENE	0.259	@0715	0.266
O-XYLENE	0.118	@0715	0.103
1,2,4-TRIMETHYLBENZENE	0.177	@0715	0.182

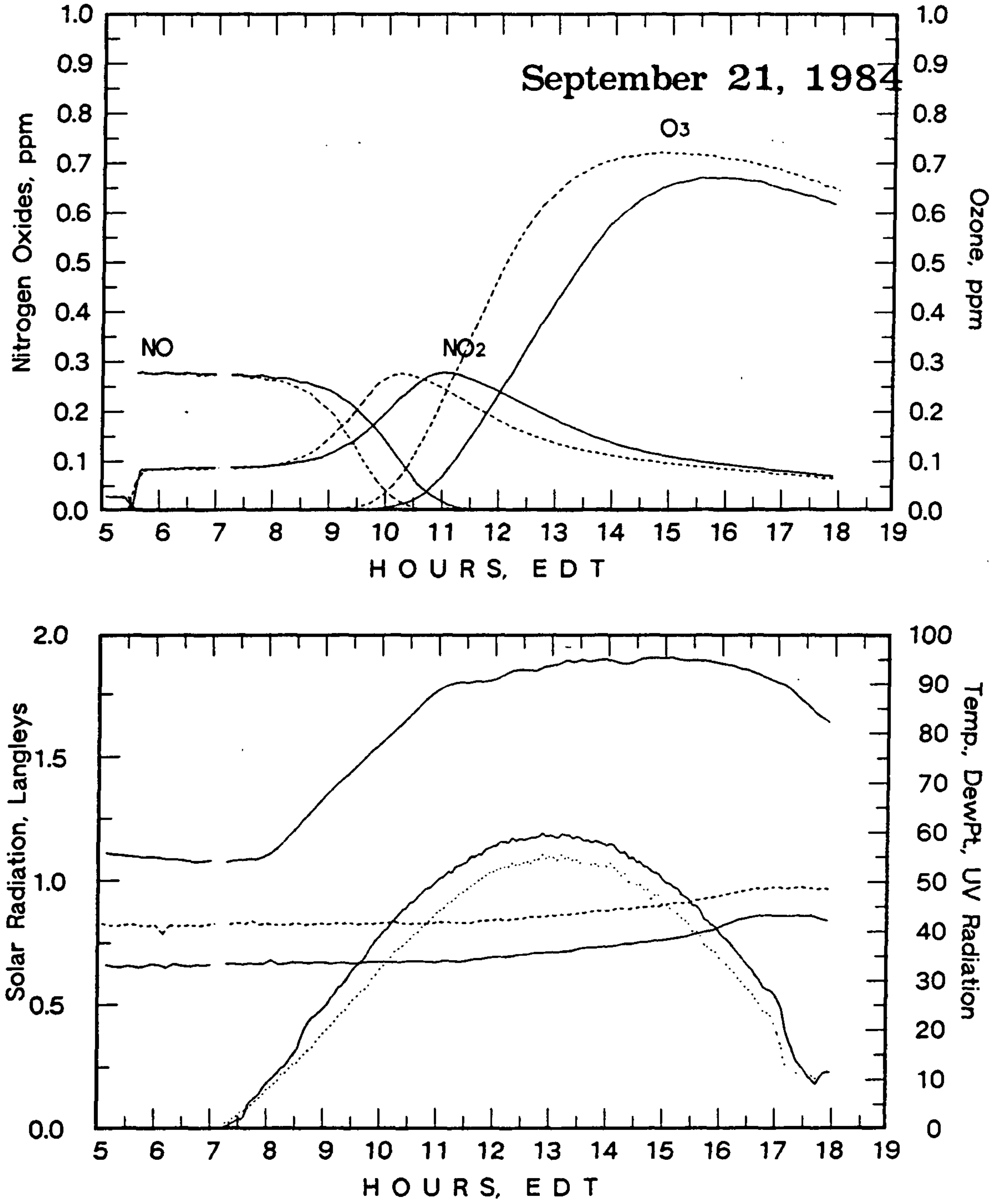


Figure 30.
Top: (Solid) 2.43 ppmC SYNAUTO, no MeOH, no HCHO;
(Dashed) 2.42 ppmC SYNAUTO, no MeOH, 0.18 ppm HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

June 26, 1985

SynUrban 4.07 ppmC vs 2.48 ppmC

RESULTS: O3 MAX: BLUE 0.79 PPM(1505); RED 0.63 PPM(1700).

INITIAL CONDITIONS:	BLUE	RED
NO	0.266	0.264
NO2	0.034	0.035
NMHC	4.072	2.483
SYN-URBAN(TANK&LIQUID)	4.012	2.443
MEOH	0.000	0.000
HCHO	0.060	0.040
ETHYLENE	0.220	0.157
PROPYLENE	0.093	0.062
1-BUTENE	0.050	0.036
TRANS-2-BUTENE	0.047	0.036
N-BUTANE	0.278	0.201
ISOPENTANE	0.285	0.196
2-METHYL-1-BUTENE	0.178	0.063
2-METHYL-2-BUTENE	0.127	0.045
N-PENTANE	0.445	0.324
2-METHYLPENTANE	0.423	0.149
2,4-DIMETHYLPENTANE	0.605	0.213
2,2,4-TRIMETHYLPENTANE	0.385	0.269
BENZENE	0.107	0.079
TOLUENE	0.384	0.293
M-XYLENE	0.179	0.140
O-XYLENE	0.077	0.061
1,2,4-TRIMETHYLBENZENE	0.130	0.119

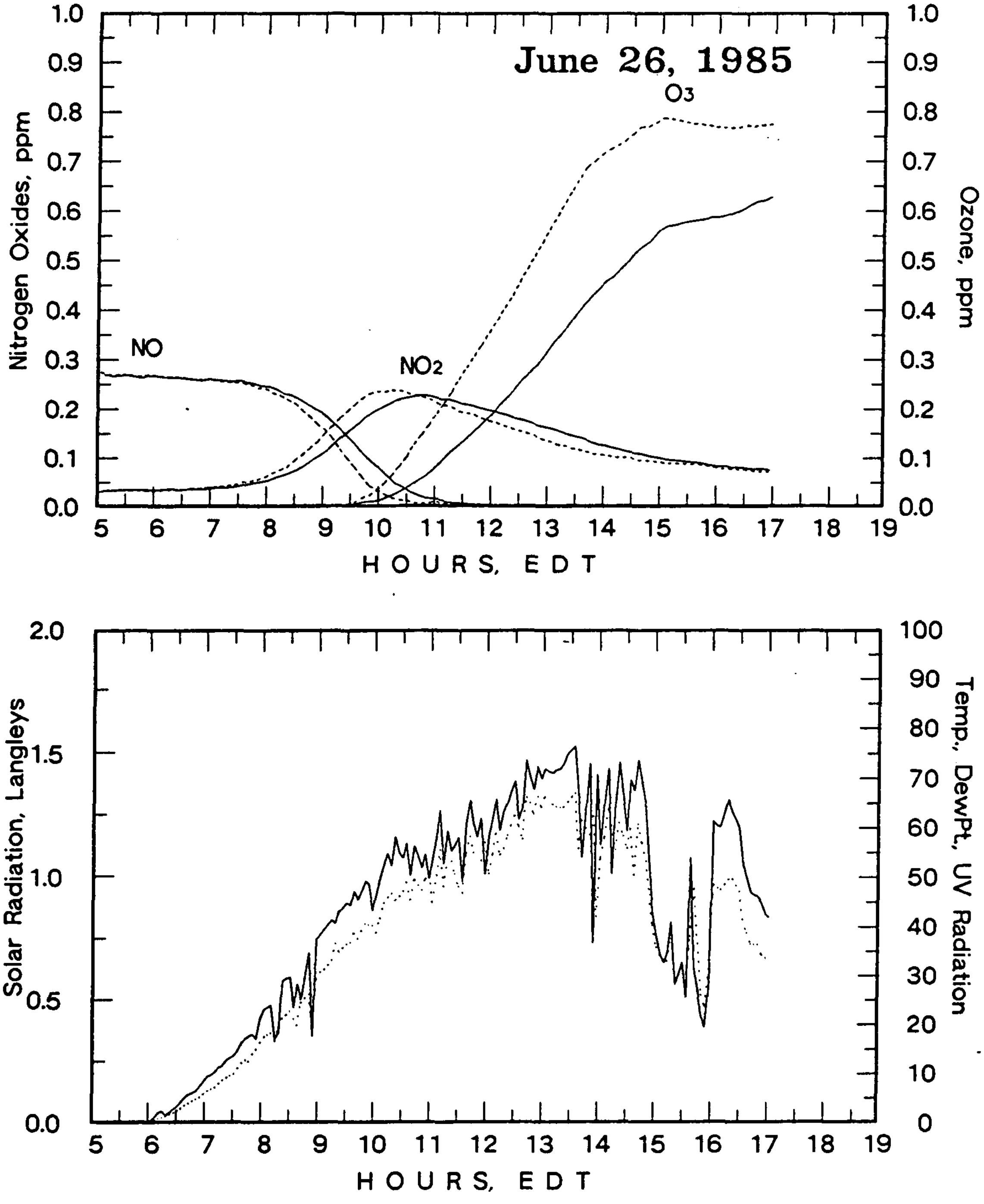


Figure 31.
Top: (Solid) 4.01 ppmC SYNURBAN;
(Dashed) 2.44 ppmC SYNURBAN;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

June 28, 1985

SynUrban 2.69 ppmC vs 1.81 ppmC/0.58 ppm MeOH/0.07 HCHO

RESULTS: O3 MAX: BLUE 0.27 PPM(1655); RED 0.24 PPM(1655).

INITIAL CONDITIONS:	BLUE	RED
NO	0.275	0.273
NO2	0.112	0.107
NMHC	2.452	2.690
SYN-URBAN(TANK&LIQUID)	1.779	2.650
MEOH	0.580	0.000
HCHO	0.093	0.040
ETHYLENE	0.090	0.144
PROPYLENE	0.031	0.056
1-BUTENE	0.018	0.030
N-BUTANE	0.090	0.409
CIS-2-BUTENE	0.017	0.036
ISOPENTANE	0.113	0.184
2-METHYL-1-BUTENE	0.071	0.058
2-METHYL-2-BUTENE	0.051	0.042
N-PENTANE	0.176	0.230
2-METHYLPENTANE	0.168	0.138
2,4-DIMETHYLPENTANE	0.240	0.197
2,2,4-TRIMETHYLPENTANE	0.283	0.425
BENZENE	0.046	0.073
TOLUENE	0.178	0.270
M-XYLENE	0.085	0.127
O-XYLENE	0.037	0.054
1,2,4-TRIMETHYLBENZENE	0.087	0.108

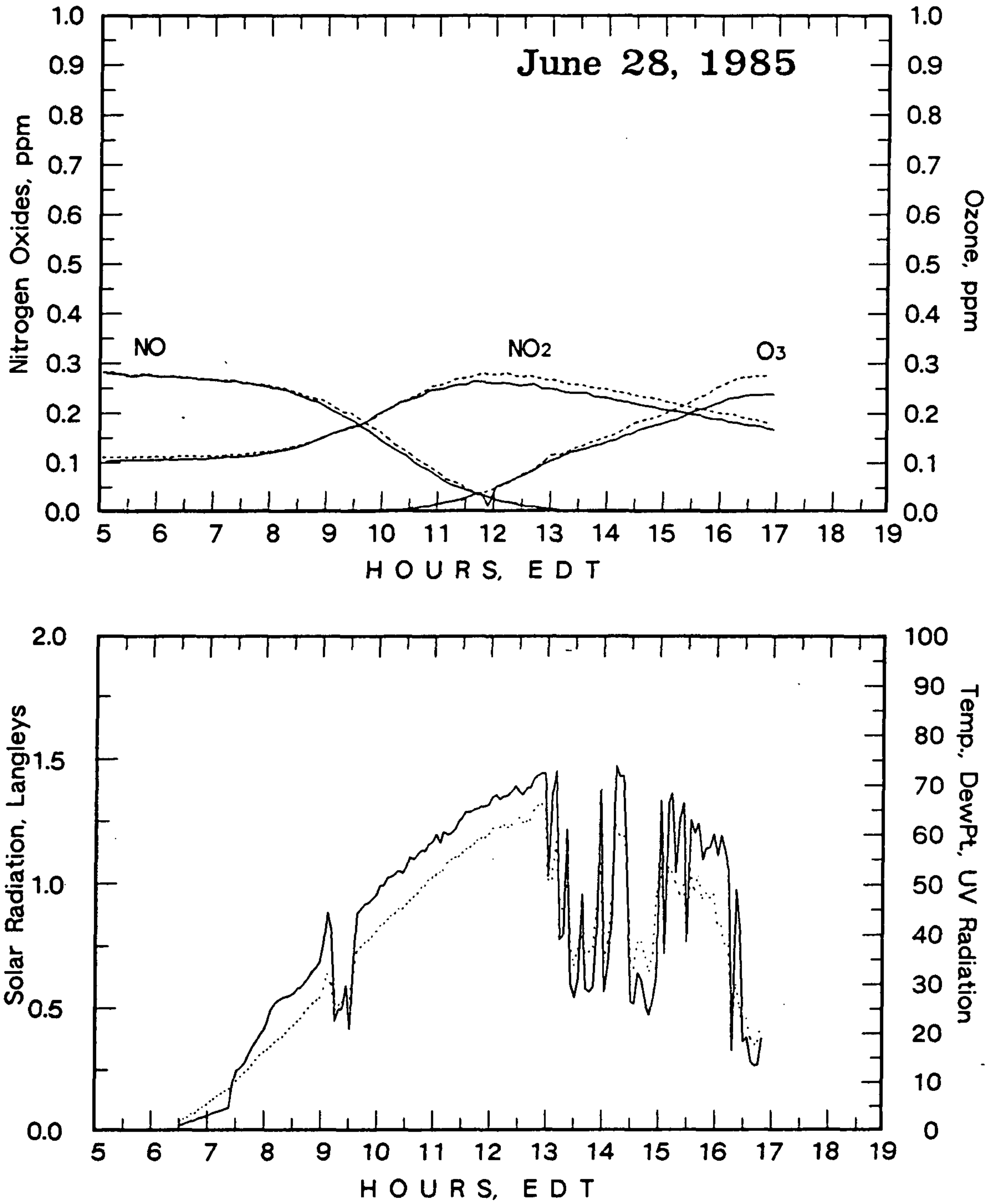


Figure 32.
Top: (Solid) 2.65 ppmC SYNURBAN 0.04 ppm HCHO;
(Dashed) 1.78 ppmC SYNURBAN, 0.58 ppm MeOH, 0.09 ppm HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radaiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line,mcal-cm^{-2}-sec^{-1}).

5

Discussion

This chapter will discuss the results of the experiments from two different viewpoints. In the first part, plots of the primary experimental data will be compared for different conditions to illustrate the effects of MeOH substitution. In the second part, three photochemical mechanism models will be used to simulate selected experiments. This will illustrate the usefulness of the data in testing some current mechanisms that might be used to predict the effects of MeOH substitution.

Meaning of Reactivity

The term reactivity has been used to mean many things relative to smog chamber work. Reactivity scales were created by researchers attempting to quantify smog chamber results. These scales have essentially fallen from use because they over-simplify the understanding of complex smog chamber results and are therefore misleading. The simple reactivity concepts have been replaced by the photochemical kinetics mechanism models that have the potential to represent all the aspects of the situation that impact on "reactivity." Kinetics models, however, are complex representations that have to be manipulated by computers and many people prefer the simpler description provided by "this system is more reactive than that system."

The application of the term "reactivity" to experimental results, however, implies that there is a "scale" that can be used to judge experimental outcomes and that particular experiments can be assigned a location on this scale and thus various experiments can be compared. The units that have been used to calibrate this scale, however, are varied: *e.g.*

- maximum O_3 produced
- rate of NO oxidation
- time to NO-to-NO_2 crossover
- rate of HC consumption
- $HO^{\cdot}$ rate constant for the HC species
- rate of O_3 production
- $\Delta O_3/\Delta HC$ is an important measure for control calculations

A big problem with these scales is that they are not linear, not absolute, and not monotonic (*i.e.* system A may be simultaneously rated lower than system B on one scale and rated higher than system B on another scale), that is, they lack in all the things people readily understand. It is easy to forget these limitations, however, and in this mapping of results on convenient scales, the reader is cautioned not to confuse the simple representations with the complex realities of the chamber results.

In the present situation, relative comparisons of the plots of the NO, NO_2, and O_3 are certainly preferred to a table giving maximum O_3. Even this comparison of plots is dangerous because the weather conditions were often significantly different for different runs, and so conclusions drawn by comparing runs on different days must be checked by examining the TSR and temperature profiles for the different days to see if they are similar. Visual comparison of TSR data can also be misleading. The day may appear clear, but a careful overlay comparison of the plots can, for example, show that a thin overcast might have attenuated the light intensity for the whole day. Other atmospheric factors can change the UV-to-TSR ratio. Likewise, there can be day-to-day variations in the injections and in the compositions of the mixtures and these too must be examined. Models of these days would, of course, use individual detail data for each day and would, therefore, take these important factors into account.

We have selected days for comparison and modeling. We have examined the conditions and data for these days in detail and are comfortable making day-to-day direct comparisons of the experimental data using these selected days. In describing the outcomes in these experiments, we sometimes say that a certain system is "more reactive" or "less reactive" than another system and in doing so we have made a subjective judgment. In this process we intuitively applied weighting factors to the various aspects of the experiments to produce a single scale. An example of such a judgment is saying that the substitution side (RED) of July 26, 1984 is "less reactive" than the baseline side (BLUE) of July 26 because, although both sides eventually made the same amount of O_3, the baseline side made it significantly faster, and the whole baseline experiment was faster as shown by a shorter time to reach NO-to-NO_2 crossover and NO_2 maximum. In many cases, relative timing to events is as important as the magnitudes of the secondary products produced in the chamber. In the outdoor chamber, something that delays the progress of a system can result in later events occurring under decreasing light intensity and thus can affect the magnitude of the later process. That is, systems can be "light-limited" as well as reactant limited.

Experimental Findings

SynAuto Experiments

The basic experimental plan called for 3 ppmC, mid-ratio (*e.g.* 9:1 HC-to-NO_X ratio) experiments to be performed first, and to investigate the effect of the HCHO fraction in the methanol exhaust. These HCHO fractions were called *low* for 0% HCHO, *normal* for 10% HCHO, and *high* for 20% HCHO. Note that these are percentages of the methanol exhaust component, not of the total NMHC. Also recall that the SynAuto mixture itself contains 2% HCHO, so that even in the HC reduction experiments, HCHO was present initially on both sides of the chamber.

After satisfactory experimental results were obtained at the 3 ppmC level, the experimental plan called for the 1 ppmC, low-ratio, *e.g.* 3:1 HC-to-NO_X ratio experiments to be performed with the SynAuto mixture. The completion of the full set of combinations of HCHO fractions at this level, however, was not possible because of time restrictions.

SynAuto Experiments at 3 ppmC

Figure 33 shows the NO_X and O_3 profiles for six 3-ppmC experiments. The top row of plots are for solar radiation conditions that would be somewhat difficult for most models, while the bottom row of plots are for days that had excellent solar radiation conditions.

On the left side of Figure 33 are the ≈33% *reduction* experiments, *i.e.* no methanol-exhaust was added. This shows the effect of direct HC reduction at this HC level and for this particular mixture. This system was NO_X-limited. That is, the system consumed all the NO_X, converting it to HNO_3 and PAN. The downward sloping NO_2 line after 1400 LDT actually is 100% PAN. Because of the high thermal decomposition rate for PAN, the PAN was in equilibrium with a very low concentration of NO_2. The high O_3 concentration was a good source of $HO^\cdot$ radicals (from photolysis) and thus even the small amount of NO_2 produced from the PAN decomposition was

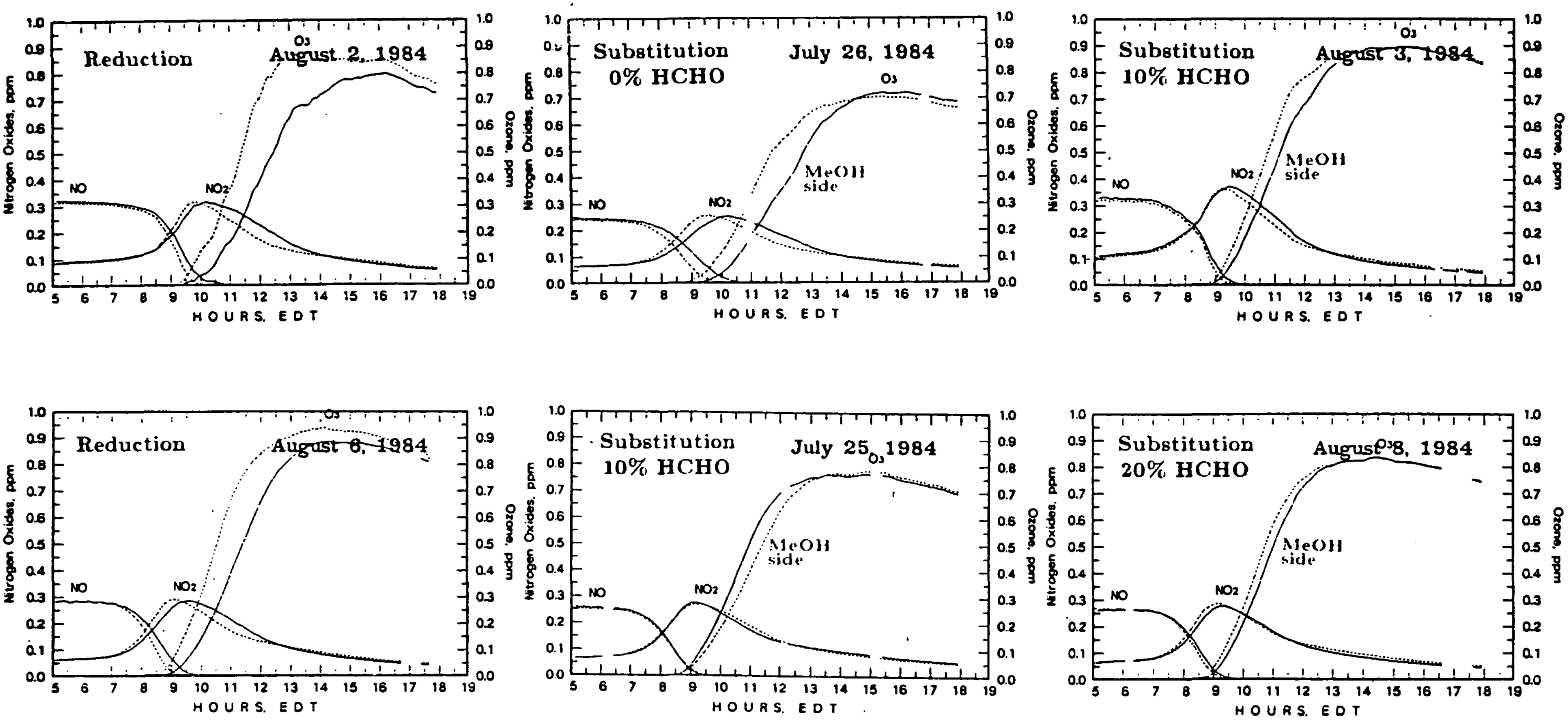


Figure 33.

Comparison of high ratio SynAuto experiments.
Top row: Poorer sunlight conditions.
Bottom row: Good sunlight conditions.

converted to HNO_3 by

$$HO^{\cdot} + NO_2 = HNO_3$$

Since we do not measure HNO_3, it appeared that nitrogen was being lost.

In an NO_x-limited system, the maximum O_3 is essentially determined by the availability of NO_x and not by the HC in the system. Picture the initial location as being on the right and below the O_3 maximum ridge line on an O_3 isopleth diagram. In this area, O_3 maximum concentrations are not very dependent upon HC. The time to reach O_3 maximum, however, is dependent upon the reactivity and concentration of the HC.

The side with less HC was about one hour slower in O_3 production, but produced almost the same O_3 eventually ($\approx$6% less). This is in contrast to the University of Santa Clara results at this ratio (see Figure 1), which showed about the same O_3 production as our experiments at the "basecase," but showed a greater effect for HC-reduction, giving about 25% reduction in O_3 for a 33% reduction in HC. This may be in part due to differences in the basic compositions of the two mixtures. Also note that there was a more rapid loss of NO_x in the slightly slower runs in the USC chamber that lead to less NO_x at the end of the run (see the difference in NO_2 maxima in Figure 1 compared to those in Figure 33). A system that removes NO_x more rapidly will generally make less O_3.

Without modeling both the USC and the UNC chamber with the same kinetics mechanism model and then comparing the two mixtures under the same set of photolytic conditions, it is not possible to determine how consistent the two datasets might be.

The top middle plot in Figure 33 (July 26) shows the effect of adding $\approx$1.0 ppm MeOH, *with no additional* HCHO*—the low formaldehyde condition.* Although the sun was not totally clear on this day, the effect adding only MeOH was almost not detectable when compared to the effect of merely reducing the HC, as shown in the two reduction runs on the left of the figure. That is, MeOH by itself is not very reactive under these conditions (less than a 6% effect on the O_3 maximum and no effect on the timing of events).

The bottom middle plot in Figure 33 (July 25) shows the effect of adding synthetic methanol exhaust with the expected normal amount of HCHO, 10%. Compared to the "baseline" case, there was no difference in the initial timing of events in the two halves, the delay in the formation of O_3 was decreased, and the maximum amount of O_3 produced was identical on the two sides. Although the sun was not as good on the August 3 experiment, it confirms the July 25 experimental results. Even 10% HCHO had a significant effect on the relative reactivity of the system. That is, the two sides on the July 25 experiment with HCHO included in the substitution were much more similar than the two sides on the July 26 experiments without HCHO included in the substitution.

The August 8 experiment in Figure 33 shows the effect of adding SynMethanol with 20% HCHO. There was only a small delay in O_3 formation in the side with MeOH/HCHO. Relative to their baseline sides, the 20% HCHO case was only slightly more reactive than the 10% HCHO case and both of these cases were much more reactive than was the MeOH-only case. That is there was less difference between the two chamber sides for the experiment with 20% HCHO substituted (Aug. 8) than for the experiment with 10% HCHO substituted (July 25) but not nearly as much difference as between the experiments with 10% HCHO substituted (July 25) and the experiment with 0% HCHO substituted (Aug. 6).

Although the SynAuto mix is quite reactive at the 3 ppmC (9:1 HC-to-NO_x ratio) level, the effect of 10% or 20% HCHO in the SynMethanol mixture produces a system as equally reactive as the original HC it replaced. This is different from the results obtained by USC and shown in Figure 1. It should be recalled that the USC study did not use HCHO but substituted iso-butylene.

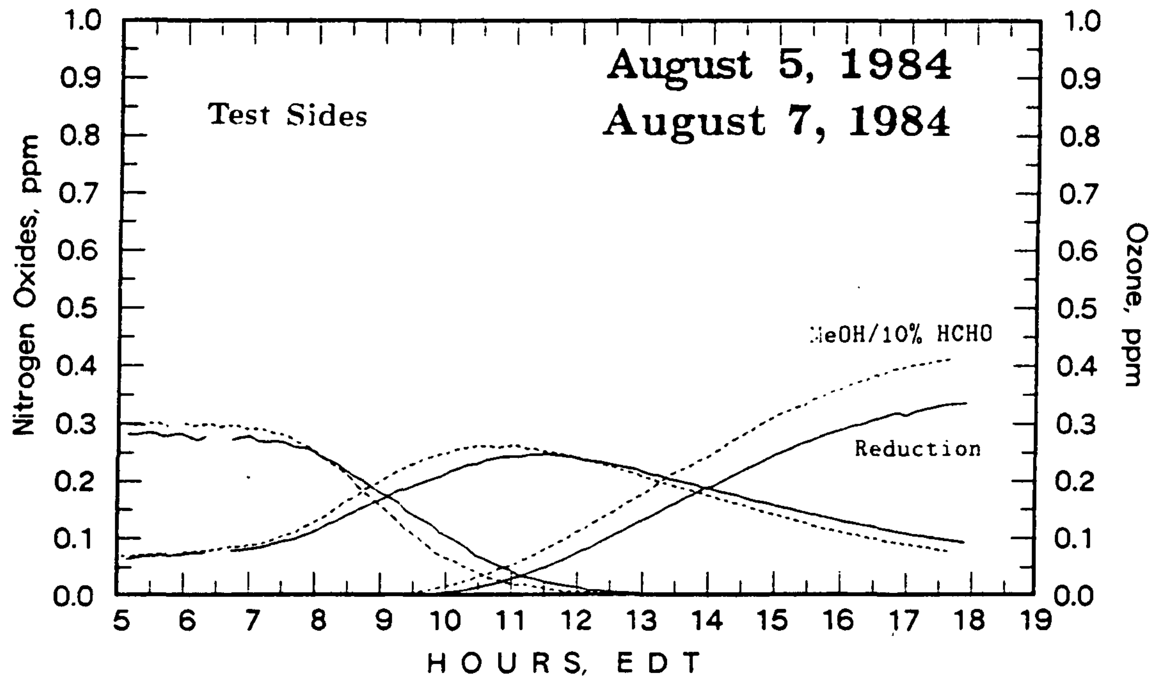
SynAuto Experiments at 1 ppmC

The August 5, 1984 experiment was the baseline reduction experiment for this series. In this experiment, reducing the initial HC from 1.31 ppmC to 0.91 ppmC, a 31% reduction, reduced the maximum O_3 from 0.60 ppm to 0.34 ppm, a 43% reduction.

The August 7, 1984 experiment was the SynMethanol (*normal* HCHO) substitution experiment. Figure 34 shows both the August 5 and the August 7 experimental plots "overlaid" on two plots. The bottom plot of Figure 34 compares the two "reference" sides of the experiments, which were well matched. The top plot shows the effect of the added SynMethanol+10% HCHO. Instead of a 43% reduction in O_3, there was only a 32% reduction in O_3. The total effect is better illustrated in Figure 35 in which both sides of the August 5 and the substituted side of August 7 are shown in one plot.

SynUrban Experiments

Fewer SynUrban experiments were performed, because they were assigned a lower priority than the direct comparison of gasoline exhaust and methanol exhaust (*e.g.*



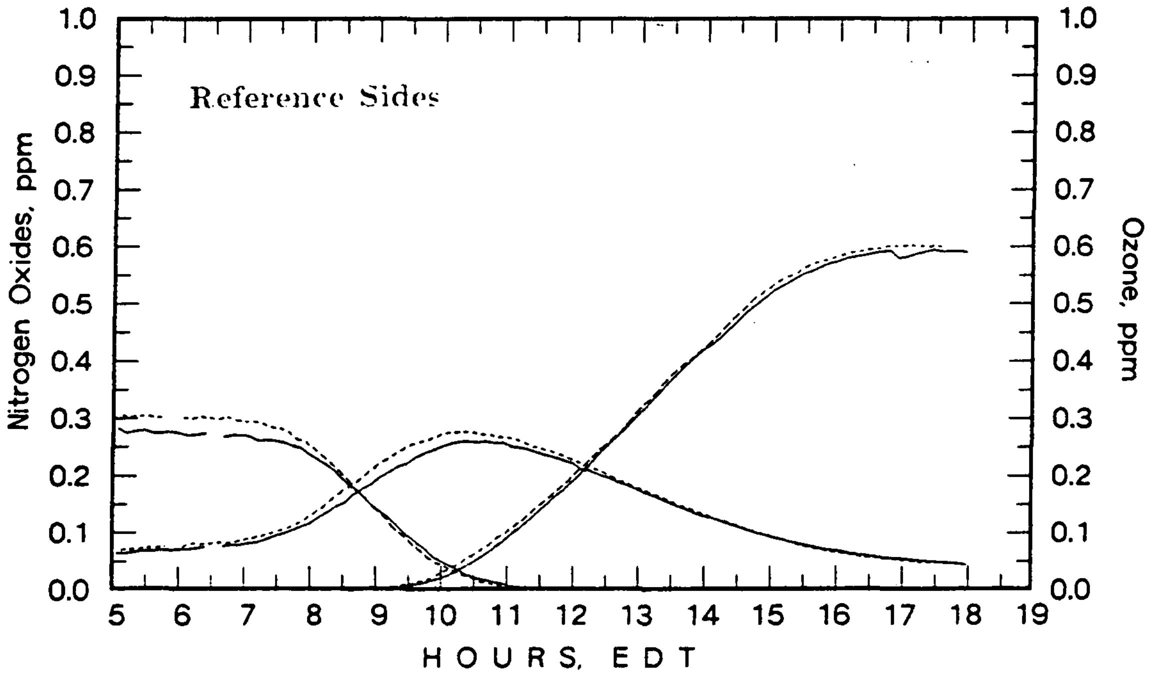


Figure 34.

Comparison of two low ratio SynAuto experiments.
Top: Effect of MeOH/10%HCHO substitution vs. reduction.
Bottom: Reference sides for both days. *i.e.* 100% SynAuto with no reduction or substitution.

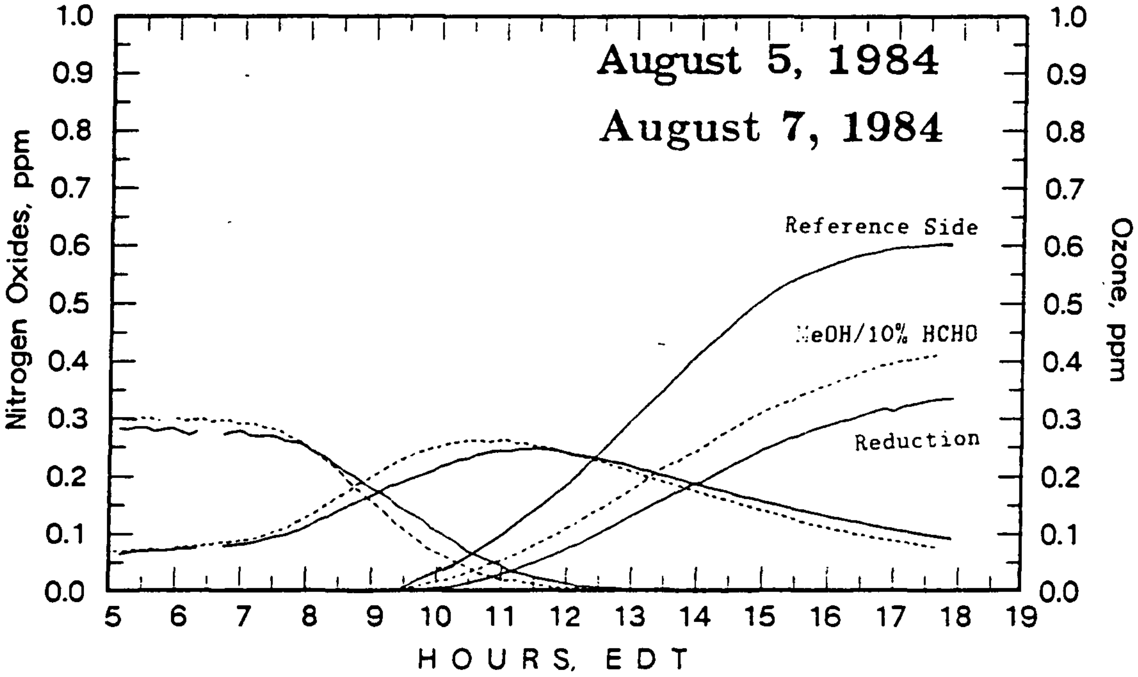


Figure 35.

Comparison of low high ratio SynAuto experiments. Effect of MeOH 10%HCHO substitution vs. reduction.

the SynAuto/SynMethanol experiments) and the poor weather conditions in July forced the SynUrban experiments into the last month of the project. In addition, the high concentration experiments consumed the UNCMIX tank in early September, terminating the SynUrban experiments that depended upon the UNCMIX mixture. In 1985, three SynUrban experiments were performed with a new UNCMIX tank. Two of these experiments are included in this report.

SynUrban Experiments at 3 ppmC

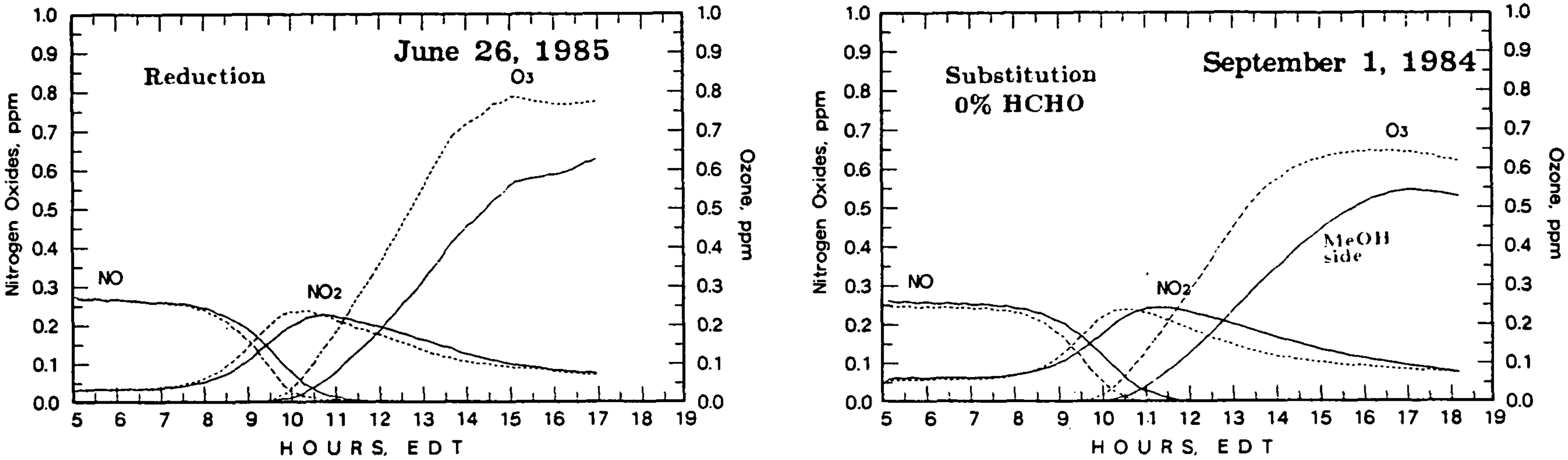
Figure 36 shows the three basic conditions for the 3 ppmC (9:1 HC-to-NO_X ratio) SynUrban experiments. The June 26, 1985 HC reduction experiment occurred under higher solar radiation than the August and September experiments and therefore produced more ozone. The *relative* outcome in the June 26 experiment is in good agreement with that in the September 1 experiment, which only had MeOH substituted and had no additional HCHO other than the 2% HCHO included in the SynUrban mix. The September 1 and August 22 experiments were in excellent agreement as shown by the "overlay" plot in Figure 37.

As would be expected, at the same total HC, the SynUrban mix was less reactive than the SynAuto mix because the SynUrban mix design took into account all urban sources, many of which are much less reactive than automobile exhaust. Furthermore, as shown in the June 26 run, there was a much larger $\Delta O_3/\Delta HC$ for the SynUrban mix than for the SynAuto mix, another reflection of its lower overall reactivity.

As in the SynAuto case, substitution of 100% MeOH for 1/3 of the carbon, resulted in essentially the same outcome as a reduction of 33% of the SynUrban carbon.

Substitution of the most reactive version of the SynMethanol mix (20% HCHO/80% MeOH) for 1/3 of the SynUrban mix, however, results in essentially no reduction of ozone production. In the top plot of Figure 37, the difference between the two O_3 lines was the difference between 0.14 ppm of total HCHO and 0.04 ppm of total HCHO in a mixture of about 3 ppmC! In terms of the methanol exhaust fraction, it is the difference between about 15% HCHO emissions and essentially no HCHO emissions (some of the HCHO in the experiment was part of the SynUrban mixture). This too is in agreement with the results of the SynAuto mixture.

These results suggest that HCHO is the dominant factor in the reactivity of the MeOH-exhaust system in both a reactive background such as the SynAuto mixture, as well as in the less reactive, and more typical, SynUrban mixture.



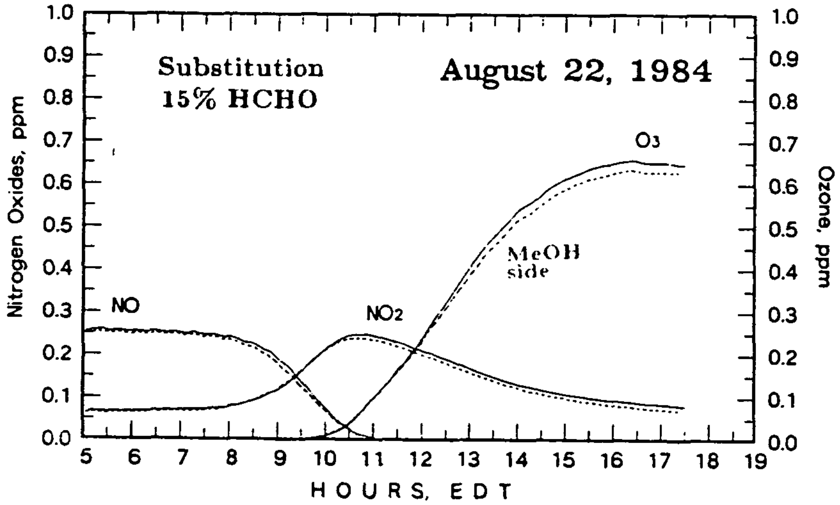


Figure 36.

Comparison of high ratio SynUrban experiments.
Top left: reduction;
Top right: substitution with no HCHO;
Bottom: substitution with 15% HCHO.

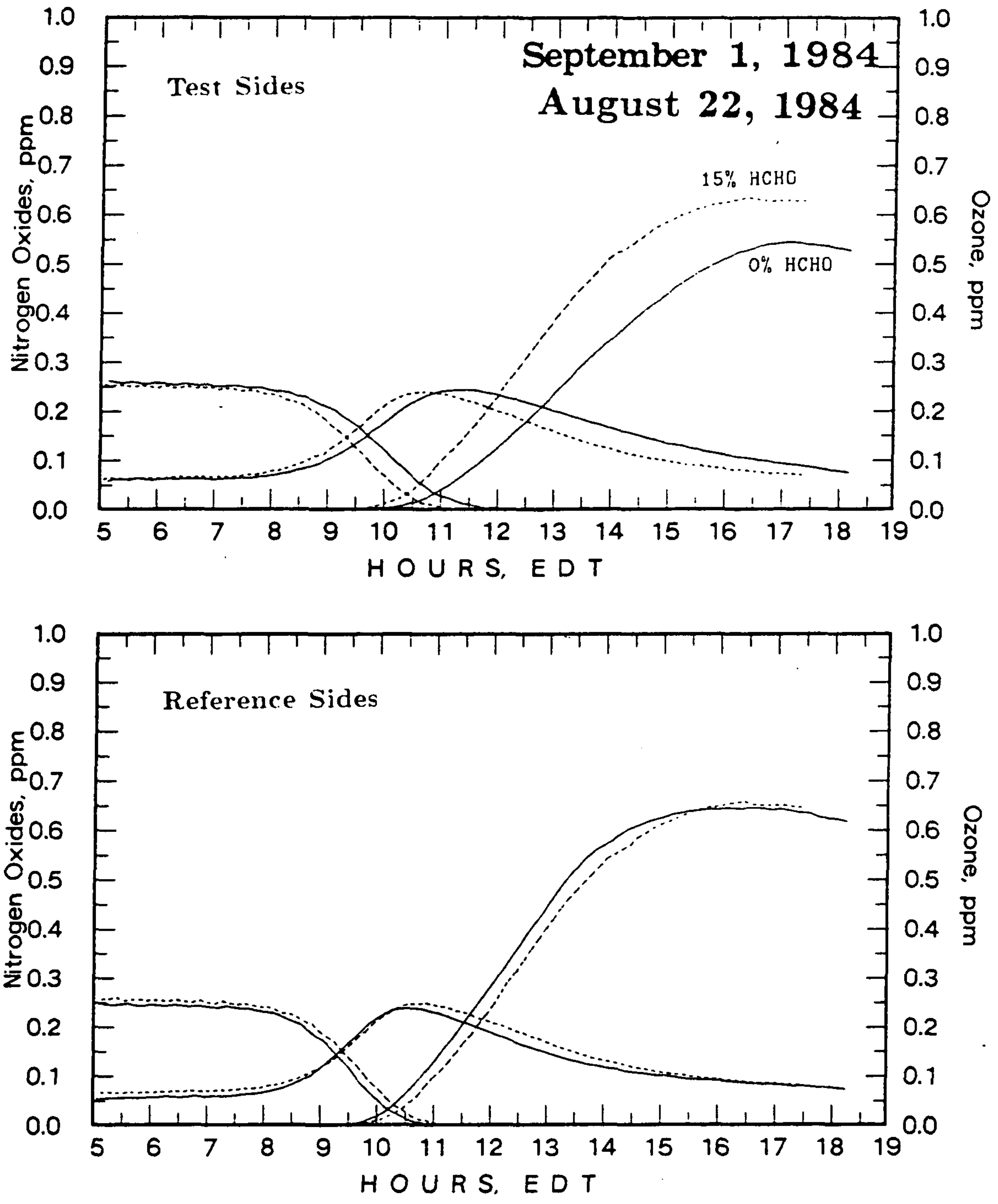


Figure 37.

Comparison of two high ratio SynUrban experiments.

Top: Effect of MeOH/15%HCHO substitution vs. MeOH/0%HCHO substitution.

Bottom: Reference sides for both days, *i.e.* 100% SynUrban with no reduction or substitution.

SynUrban Experiments at 1 ppmC

There were three experiments performed at these conditions, one under poor sun. These were sufficient to confirm that the reactivity of the SynUrban mixture at the 1.0 ppmC level was quite low. The September 2 experiment showed that the system was very sensitive to HC concentration, in that 1.1 ppmC of SynUrban made about 0.12 ppm O_3 and 0.8 ppmC of SynUrban made only 0.02 ppm O_3. The September 3 experiment showed, however, that even in a system as sensitive to HC as this one, MeOH substitution gave results similar to those at higher level of HC, *i.e.* SynMethanol with 20% HCHO had a reactivity similar to the SynUrban mixture itself.

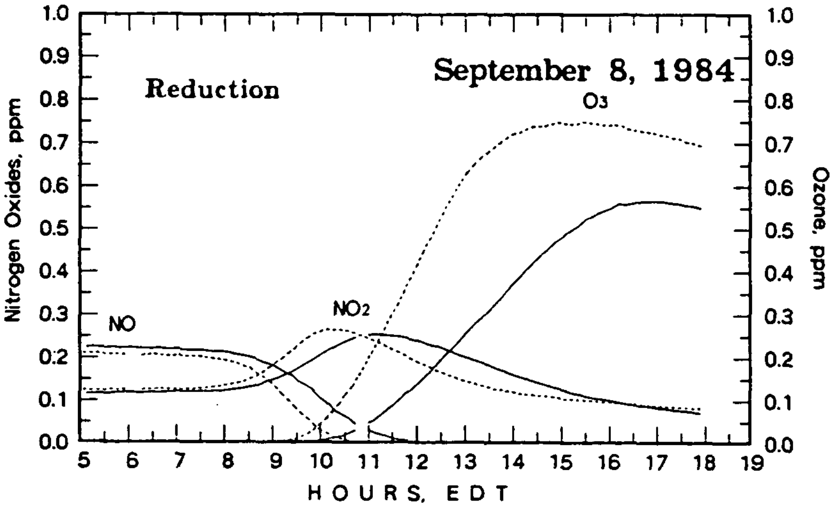
Based on the outcome of these experiments, we selected a higher HC concentration for the 1985 substitution experiments with SynUrban. These were 2 and 1.5 ppmC of HC. One experiment, June 28, was performed at the 2 ppmC level and it produced about 0.3 ppm O_3 under poor sunlight conditions. The substitution of the normal level (actually 11% in this case) HCHO SynMethanol mixture for about 1/3 of the carbon resulted in only a small difference in ozone production, however, the side with the MeOH/HCHO produced slightly more O_3. The sunlight conditions were very poor during the O_3 production and the significantly different levels of HCHO may have had an unusual influence upon the outcome. Because of the poor sunlight, this experiment must be treated as questionable.

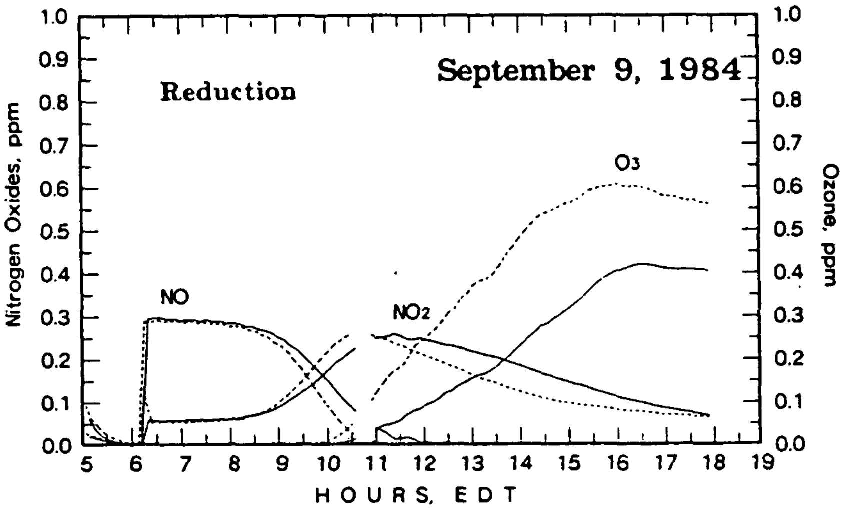
SynAutUrb Experiments at 3 ppmC

When the UNCMIX tank was exhausted in the 1984 SynUrban experiments, we switched to a mixture inbetween SynAuto and SynUrban that was produced by blending the SynAuto mixture with n-butane that was used in the SynUrban mixture. Because the SynUrban mixture already used the aromatic portion of the SynAuto mixture and because the SynUrban mixture already had n-butane at the same level, this new SynAutUrb mixture was equivalent to varying the paraffin and olefin fractions and specific species. This type of experiment would ideally complement the SynUrban and SynAuto experiments to see if the models could accurately track the changes in basic composition of the mixtures.

Figure 38 shows three 3-ppmC (9:1 HC-to-NO_X ratio) experiments with the SynAutUrb mixture. The top two plots show the effects of 1/3 reduction, while the bottom plot shows the effect of 1/3 substitution with a SynMethanol mixture (10% HCHO).

The basic reactivity of this mixture is intermediate between the SynAuto and the SynUrban mixture, being closer to the SynAuto at higher concentrations, and closer to





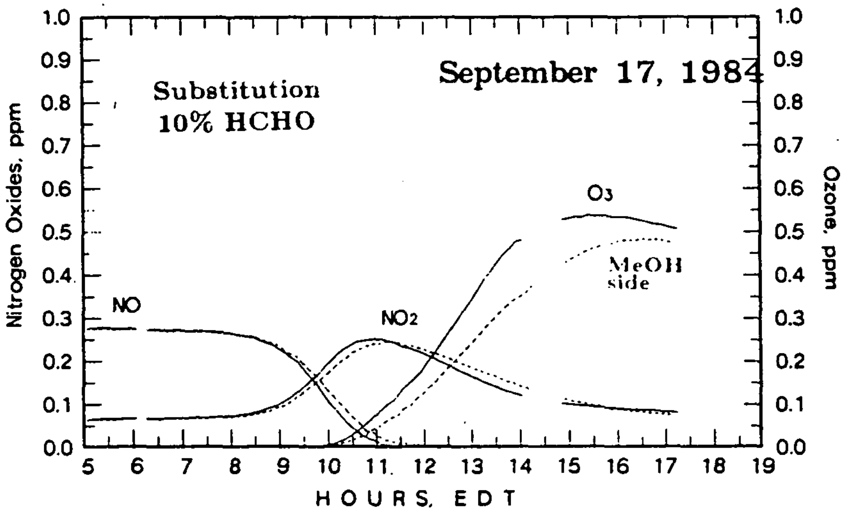


Figure 38.

Comparison of 3 ppmC SynAutUrb experiments.
Top left: reduction;
Top right: reduction (poor sun);
Bottom: substitution with 10% HCHO.

the SynUrban at lower concentrations. The effect of substitution is also intermediate between the effects shown in Figure 33 and in Figure 36. The lower 10% fraction of HCHO in the September 17 experiment resulted in an intermediate response between that for the September 1 and the August 22 SynUrban experiments.

Modeling of Selected Experiments

A primary purpose for producing this new data was to use it to test models for their correct representation of the effects of methanol substitution. To confirm that the data were useful for such model testing, we selected six days for *demonstration modeling*. We say demonstration modeling because actual testing of the models would involve a significant effort and would require the use of chamber data from the 400 run UNC database to test parts of the mechanism that must be assumed to be correct for the purposes of this demonstration.

The days that were selected were two 1-ppmC SynAuto runs, two 3-ppmC SynAuto runs, and two 3-ppmCSynUrban runs. The two 1-ppmC SynAuto runs were the reduction experiment, August 5, and the normal-HCHO, MeOH-substituted experiment, August 7. The two 3-ppmC SynAuto runs were the reduction experiment, August 6, and the high-HCHO, MeOH-substituted experiment, August 8. The two 3-ppmC SynUrban runs were the MeOH-substituted experiment with no HCHO, September 1, and the MeOH-substituted experiment with 20% HCHO, August 22.

The Mechanisms Selected

The mechanism recommended by EPA for EKMA control strategy simulations is the Carbon Bond III (CB3). This mechanism was also used by SAI in the air shed simulations to test the effects of MeOH fuel substitution described in Chapter 1.[2] SAI has been developing a newer, and more complex, version of the CB3 called the Carbon Bond Extended (CBX) mechanism. An early version of the CBX was used in the air shed simulations described in Chapter 1 and it predicted a small benefit for MeOH fuel substitution than did the CB3. The CB3 mechanism used in this work is listed in Table 15. The CBX mechanism used in this work is listed in Table 16.

The CB3 mechanism uses a single species, CARB, to represent all aldehydes and the composition of CARB has been built-in to the structure and rate constants of the mechanism. CB3 therefore is not very suitable to model chamber runs with high HCHO concentrations without extensive modification of the mechanism. We used the CB3 only to model the "baseline" and HC reduction experiments (two days, two sides).

Table 15.

```
CARBON BOND MECHANISM III PER APPENDIX A OF DRAFT REPORT OF GUIDELINES
FOR USE OF CARBON-BOND MECHANISM IN OZIPM/EKMA JULY 1983 (ORIG NUMS)
RESTRUCTURED TO PKSS INPUT CONVENTIONS. LAST REVISED 5/22/84

(1)      NO2  = NO + O                    # 1.0 /L1 ; (1)
(2)        O  = O3                        # 4.4E+06 ; (2)
(3) O3 + NO   = NO2                       # 3.452E+03  @-1450. ;(3)

(4)  O + NO2 = NO                         # 1.30E+04;(5)

(5) O3 + NO2 = NO3                        # 178.6 @ -2450. ;(4)
(6) NO + NO3 = 2.0 * NO2                  # 2.8E+04 ; (11)
(7) NO3+ NO2 = 2.0 * WHNO3                # 4.63E-19 @ 10600. /W ;(12)

(8)        O3 = O                         # 0.0584 /L1; (76)
(9)        O3 = O1D                       # 0.004 /L1;  (73)
(10)       O1D = O                         # 4.44E10;    (74)
(11)       O1D = 2.0 * OH                  # 3.4E5 /W ;  (75)

(12) O3 + OH  = HO2                        # 2.867E+03 @-1000.0 ;(6)
(13) O3 + HO2 = OH                         # 4.006E+02 @-1525. ; (7)

(14) NO + NO  = 2.0 * NO2                  # 1.5E-04 ; (10)
(15) OH + NO  = HONO                       # 9770.;    (72)
(16)      HONO = OH + NO                   #0.179 /L1; (71)

(17) NO + HO2 = OH  + NO2                  # 1.2E+04 ; (13)

(18) OH + NO2 = HNO3                       # 1.6E+04 ; (8)

(19) OH + CO   = HO2                        # 440. ;    (9)
(20) OH (+CH4) = MEO2                       # 28.0;     (NONE)

(21) HO2 + HO2 = H2O2                      # 1.5E+04 ; (14)
```

Table 15. cont.

```
 ( CARBONYL CHEMISTRY )

(22)        CARB = CO                          # 0.00248 /L1; (37)
(23)        CARB = 1.773 * HO2 + 0.227 * MEO2 +
                 0.227 * X + CO              # 0.00220 /L1; (38A-D)

(24) OH   + CARB = CRO2 + X                    # 100.;   (34)
(25) OH   + CARB = HO2  + CO                   # 9.0E+3; (35)
(26) OH   + CARB =   X  + ACO3                 # 8.20E+3;(36)

(27) CRO2 +   NO = NO2  + CARB + ACO3 + X      # 1.2E4;  (69)
 ( DICARBONLY CHEMISTRY )

(28)        DCRB = HO2 + ACO3 + CO            # 0.02 /L1; (67)
(29)  OH  + DCRB = ACO3 + CO                  # 2.5E+04;  (70)

 ( PAN CHEMISTRY )

(30) NO   + ACO3 = NO2 + MEO2 + CO2           # 1.04E+04; (26)
(31) NO2  + ACO3 = PAN                        # 7000.;    (39)
(32)         PAN = ACO3 + NO2                 # 1.040E+18 @ -13500.; (40)
(33) HO2  + ACO3 =                            # 1.5E+04;  (41)

 ( MEO2 CHEMISTRY )

(34) NO   + MEO2 = NO2 + CARB + HO2           # 7400.; (30)
(35) NO   + MEO2 = NO2 + CARB + MEO2 +  X     # 3700.; (29)
(36) NO   + MEO2 = NRAT                       # 900.;  (31)
(37) HO2  + MEO2 =                            # 9000.; (42)

 ( PARRAFFIN CHEMISTRY )
(38) OH   + PARC = MEO2                       # 5559. @ -560. ; (16)
(39) PARC + X =                               # 1.0E+05 ;       (15)
```

Table 15. cont.

```
 ( ETHYLENE CHEMISTRY )

(40) O     + ETHC = 0.5 * MEO2 + 0.5 * HO2 + 0.5 * CO +
                   0.5 * CARB + 0.5 * PARC    # 17582. @ -800 ; (22,23)
(41) OH    + ETHC = RBO2                      # 3330. @ 382.;   (24)
(42) NO    + RBO2 = NO2 + 2.0 * CARB + HO2    # 1.2E+04;        (27)
(43) O3    + RBO2 = 2.0 * CARB + HO2          # 5.00;           (32)

(44) O3    + ETHC = CARB + CRIG               # 12.91 @ -2560.; (25)

 ( OLEFIN CHEMISTRY )

(45) O     + OLEC = 0.5 * ACO3 + 0.5 * MEO2 + 0.5 * X +
                   0.5 * CARB + 0.5 * PARC    # 16070. @ -325;  (17,18)
(46) OH    + OLEC = RAO2                      # 6042.6 @ 540. ; (19)
(47) NO    + RAO2 = NO2 + 2.0 * CARB + HO2    # 1.2E+04;        (28)
(48) O3    + RAO2 = 2.0 * CARB + HO2          # 20.0;           (33)

(49) O3    + OLEC = CARB + 0.5 * CRIG + 0.5 * MCRG +
                             0.5 * X          # 9.4 @ -1900. ; (20,21)

(50) NO    + CRIG = NO2 + CARB                # 1.2E+04; (43)
(51) NO2   + CRIG = NO3 + CARB                # 8000.;   (44)
(52) CARB  + CRIG = ( OZD )                   # 2000.;   (45)

(53) NO    + MCRG = NO2 + CARB + PARC         # 1.2E+04; (46)
(54) NO2   + MCRG = NO3 + CARB + PARC         # 8000.;   (47)
(55) CARB  + MCRG = ( OZD )                   # 2000.;   (48)

(56)         CRIG = 0.76 * CO + 0.18 * HO2    # 1000.; (49,50,51)

(57)         MCRG = 0.765 * MEO2 + 0.340 * OH + 0.510 * HO2 +
               0.085 * CARB + 0.425 * CO # 1000.; (52,53,54,55)
```

Table 15. cont.

```
 ( AROMATIC CHEMISTRY )

(58) OH    + AROC = RARO                            # 26211. @ -600.; (56)
(59) NO    + RARO = NO2 + PHEN + HO2                # 4000.; (58)
(60) OH    + PHEN = HO2 + PARC + 2.5 * CARB +
                    0.5 * DCRB + 1.5 * CO   +
                    0.5 * X                       # 3.E4; (66,60,61)
(61) OH    + PHEN = PHO                             #1.0E4; (68)
(62) NO3   + PHEN = PHO   + HNO3                    # 5000.; (62)
(63) NO2   + PHO  = NPHN                            # 4000.; (63)
(64) HO2   + PHO  = PHEN                            # 5.00E4; (64)

(65) OH    + AROC = HO2 + OPEN                      # 13397. @ -400.; (57)
(66) OPEN + NO    = NO2 + 1.5 * DCRB + 1.5 * X +
                          1.5 * CARB + 1.5 * CO     # 6000.;  (59,60,61)
(67) OPEN + O3    =         1.5 * DCRB + 1.5 * X +
                          1.5 * CARB + 1.5 * CO     # 40.; (65,60,61)

 ( NO METHANOL CHEMISTRY ADDED BECAUSE OF CARB )

 (WALL PROCESSES )
    NOWALL = NO2                                  # 0.01/L1;
  FORMWALL = CARB                                 # 0.02/L1;
```

Table 16.

```
CARBON BOND MECHANISM CBM-X PER APPENDIX C OF DRAFT REPORT "USING THE
EXPANDED CARBON-BOND MECHANISM (CBM-X) IN EKMA WITH COMPUTER CODE
OZIPM-3, SYSAPP-85/194, 23 APR 1985 (ORIGINAL NUMBERS IN PARENS AT END)
RESTRUCTURED TO PKSS INPUT CONVENTIONS. [O2]=210000 PPM [M]=1000000 PPM

L1:NO2 L2:O3=O1D L3:HCHO=HO2 L4:HCHO=H2 L5:RCHO=RAD

(*********** INORGANIC CHEMISTRY **********)

(  1)              NO2   = NO    + O        # 1.0/L1                ;(1)
(  2)              O     = O3               # 4.60247E+05 @ 690.   ;(2)
(  3)      O3    + NO    = NO2              # 3.2278E+03  @-1430.  ;(3)
(  4)      O     + NO2   = NO               # 1.38E+04              ;(4)
(  5)      O     + NO2   = NO3              # 309.8 @ 600           ;(5)
(  6)      O     + NO    = NO2              # 785.6 @ 411           ;(6)

(  7)      O3    + NO2   = NO3              # 176.3 @-2450.     ;(7)
(  8)      NO3   = 0.85*NO2 + 0.85*O + 0.15*NO # 30.6 /L1       ;(30-1)
(  9)      NO3   + NO    = 2.0*NO2          # 1.2144E+04 @ 250 ;(14)
( 10)      NO3   + NO2   = NO    + NO2      # 36.6 @-1230       ;(15)
( 11)      NO3   + NO2   = N2O5             # 831.9 @ 226       ;(16)
( 12)              N2O5  = NO3   + NO2      # 1.96E+16 @-10840 ;(18)
( 13)              N2O5  = 2.0*HNO3         # 1.9E-6 /W         ;(17)

( 14)              O3    = O                # 0.042  /L1        ;(9)
( 15)              O3    = 0.868*O + 0.2644*OH # 1.0E-3/L2      ;(8,10,11)

( 16)      O3    + OH    = HO2              # 2343.8 @-940 ;( 12)
( 17)      O3    + HO2   = OH               # 21.0 @-580   ;( 13)

( 18)      NO    + NO    = 2.0*NO2          # 2.6E-5 @ 530 ;( 25)
( 19)      NO    + NO2   = 2.0*HONO         # 1.6E-11 /W   ;( 19)
( 20)      OH    + NO    = HONO             # 2331.3 @ 427 ;( 23)
( 21)      OH    + HONO  = NO2              # 9770.        ;( 28)
( 22)      HONO + HONO   = NO    + NO2      # 1.5E-5       ;( 20)
( 23)              HONO  = OH    + NO       # 0.18 /L1     ;( 21)

( 24)      HO2   + NO    = OH    + NO2      # 5497.2 @ 240 ;( 24)
```

Table 16. cont.

```
( 25)      HO2  + NO2  = PNA              # 205.6    @ 617   ;( 34)
( 26)           PNA    = HO2   + NO2      # 7.85E+15 @-10420 ;( 35)

( 27)      OH   + NO2  = HNO3             # 2489.2 @ 560 ;( 22)
( 28)      OH   + HNO3 = NO3              # 14.11 @ 778  ;( 29)

( 29)      HO2  + HO2  = H2O2             # 87.39 @ 1150     ;( 32)
( 30)      HO2  + HO2  = H2O2             # 7.69E-10 @ 5800/W;(33)
( 31)           H2O2   = 2.0 * OH         # 0.0014 /L1       ;(26)
( 32)      OH   + H2O2 = HO2              # 4719.8 @-187     ;(27)

( 33)      OH   + CO   = HO2              # 400.0 ;(36)

(*************** FORMALDEHYDE CHEMISTRY ***************)

( 34)           HCHO   = 2.0 * HO2 + CO # 1.0E-3/L3       ;(39)
( 35)           HCHO   = CO             # 1.0E-3/L4       ;(40)

( 36)      OH   + HCHO = HO2   + CO         # 15000. ;(38)

( 37)      HO2  + HCHO = FROX               # 14.8   ;(37)
( 38)           FROX   = HO2   + HCHO       # 90.0   ;(44)
( 39)      FROX + NO   = (FACID)+ NO2 + HO2 # 10400  ;(43)

( 40)      O    + HCHO = OH    + HO2  + CO  # 43019.2@-1550 ;(41)
( 41)      NO3  + HCHO = HNO3 + HO2   + CO  # 0.93   ;(42)

(********** HIGHER CARBONYL CHEMISTRY *********)

( 42)           RCHO   = MEO2 + HO2   + CO  # 1.0E-3/L5     ;(48)

( 43)      MEO2 + NO   = MEO   + NO2        # 6012.7  @ 180   ;(55)
( 44)      MEO (+ O2)  = HCHO + HO2         # 3.235E+7@-1313  ;(59)

( 45)      MEO  + NO   = HCHO + HO2   + NO    # 1920.0          ;(57)
( 46)      MEO  + NO   = MENO2                # 22694.0 @ 200   ;(56)
( 47)           MENO2 = MEO   + NO            # 0.3/L1          ;(62)
( 48)      MEO  + NO2  = MENO3                # 22200.0         ;(58)
```

Table 16. cont.

```
( 49)       MEO2 + NO2    = MPNA              # 503.32  @ 735   ;(53)
( 50)              MPNA   = MEO2 + NO2        # 1.32E+17@-10400 ;(54)

( 51)       OH   + RCHO   = RCO3              # 10372.  @ 250 ;(46)

( 52)       RCO3 + NO     = NO2  + MEO2       # 7130.9  @ 250   ;(50)
( 53)       RCO3 + NO2    = PAN               # 3889.6  @ 250   ;(51)
( 54)              PAN    = RCO3 + NO2        # 5.62E+18@-14000 ;(52)

( 55)       HO2  + RCHO   = MEO2 + HCHO       # 5.0             ;(49)
( 56)       NO3  + RCHO   = RCO3 + HNO3       # 3.7             ;( 47)
( 57)       O    + RCHO   = RCO3 + OH         # 17394.7 @-986 ;( 45)

( 58)       OH   + MENO3   = HCHO + NO2        # 7430.3  @-360 ;(60)
( 59)       OH   + MENO2   = HCHO + NO         # 7417.4  @-340 ;(61)

( 60)       MEO2 + MEO2   = 0.696*MEO + 0.652*HCHO (+ 0.652*MEOH)
                                              # 240.44 @220 ;(63-4)
( 61)       MEO2 + RCO3   = MEO  + MEO2       # 4400.0         ;(65)
( 62)       RCO3 + RCO3   = 2.0 * MEO2        # 3700.0         ;(66)
( 63)       MEO2 + HO2    = (ROOH)            # 113.45 @ 1300 ;(67)
( 64)       RCO3 + HO2    = (ROOH)            # 9600.0         ;(68)
(********** DICARBONLY CHEMISTRY **********)
( 65)              GLY    = 1.785*CO + 0.213*HCHO + 0.186*HO2
                                              # 0.0075/L1    ;(72-4)
( 66)       OH   +  GLY   = HO2  + 2.0*CO     # 15000.0      ;(75)
( 67)              MGLY   = RCO3 + HO2  + CO  # 0.02/L1      ;(76)
( 68)       OH   +  MGLY  = MGPX              # 26000.0      ;(77)
( 69)       MGPX + NO     = RCO3 + NO2        # 12000.0      ;(78)

(*************** BACKGROUND METHANE ***************)

( 70)       OH   (+ CH4)   = MEO2              # 21.0         ;(79)
```

Table 16. cont.

```
(*************** PARAFIN CHEMISTRY ***************)

( 71)     OH     + PAR = 0.13*PARO2 + 0.87*PARO2R # 1150.0 ;(80-1)

( 72)     PARO2  + NO  = NO2  + HO2  + RCHO + X   # 12000.0 ;(82)
( 73)     PARO2R + NO  = 0.923*NO2 + 0.923*PAROR (+ 0.077*PARNO3)
                                                  # 13000.0 ;(83-4)

( 74)           PAROR  = RCHO + D + X   # 1.43E+15 @-7000 ;( 87)
( 75)           PAROR  = 0.385*KETONE + 0.385*HO2 + 0.615*ACTONE
                         + 0.615*D + 1.23*X # 390000.0   ;(86,88)
( 76)     PAROR + NO2  = (PARNO3)             # 22000.0    ;(85)

( 77)     D     + PAR  = 0.30*PARO2 + 0.70*AO2 + 1.40*X  # 10000.0;(90-1)
( 78)     AO2   + NO   = NO2   + HO2   + ACTONE  # 12000.0  ;(93)

( 79)     D     + KETONE = RCO3 + X            # 10000.0  ;( 92)

( 80)     X     + PAR  =        # 10000.0 ;(89)

(*************** KETONE/ACETONE CHEMISTRY ***************)

( 81)            ACTONE  = MEO2 + RCO3   # 0.00004/L1 ;(69)
( 82)     OH   + ACTONE  = ACOCO2        # 580.0      ;(70)
( 83)     ACOCO2 + NO    = NO2   + HCHO + RCO3 # 12000.0 ;(71)
( 84)           KETONE   = RCO3 + PARO2 + 2.0*X  # 0.0003/L1 ;(94)
```

Table 16. cont.

```
(*************** ETHYLENE CHEMISTRY ***************)

( 85)      O    + ETH   = MEO2 + HO2  + CO # 15824.0@-800 ;(104)
( 86)      OH   + ETH   = MEO2 + HCHO      # 3330.2 @ 382 ;(105)

( 87)      O3   + ETH   = HCHO + 0.37*CRIG + 0.3654*CO +
                            0.1260*HO2 (+ 0.0441*FACID)
                                           # 37.18@-2840  ;(106-7,108-11)

(*************** OLEFIN CHEMISTRY ***************)
( 88)      O    + OLE   = 0.80*RCHO + 0.15*PARO2 + 0.15*HO2 + 0.15*CO
                          + 0.05*MEO2 + 0.05*RCO3 + 0.20*X
                                                  # 17560.0 @-324;(95-7)

( 89)      OH   + OLE   = MEO2 + RCHO + X # 6928.6 @ 537 ;(98)
( 90)      O3   + OLE   = X + 0.50*RCHO + 0.50*HCHO + 0.30*CRIG
                        + 0.30*MCRG +  0.116*CO + 0.04*HO2 (+ 0.014*FACID)
                        + 0.144*MEO2 + 0.096*CO + 0.096*HO2 + 0.016*HCHO
                        + 0.080*OH        # 10.46 @-1897 ;(99-102,108-15)

( 91)      CRIG + NO    = HCHO + NO2      # 10000.0     ;(116)
( 92)      CRIG + NO2   = HCHO + NO3      # 1000.0      ;(117)
( 93)             CRIG  = (FACID)         # 0.006   /W  ;(118)
( 94)      CRIG + HCHO  = (OZD)           # 30.0        ;(119)
( 95)      CRIG + RCHO  = (OZD)           # 30.0        ;(120)
( 96)      MCRG + NO    = RCHO + NO2      # 10000.0     ;(121)
( 97)      MCRG + NO2   = RCHO + NO3      # 1000.0      ;(122)
( 98)             MCRG  = (AACID)        # 0.006   /W  ;(123)
( 99)      MCRG + HCHO  = (OZD)           # 30.0        ;(124)
(100)      MCRG + RCHO  = (OZD)           # 30.0        ;(125)
(101)      NO3    + OLE  = NO2RO2         # 11.4        ;(103)
(102)      NO2RO2 + NO   = (0.091*DINO2) + (0.909*PARNO2)
                          + 0.909*HO2 + 0.909*NO2  # 11000.0 ;(126-7)
```

Table 16. cont.

```
(*************** AROMATIC CHEMISTRY ***************)
(103)        TOL  + OH    = 0.564*OPEN + 0.564*GLY + 0.359*PHEN
                          + 0.359*HO2  + 0.359*PAR + 0.077*BO2
                                                     # 9750.0    ;(128-30)
(104)        OPEN + NO    = NO2  + HO2  + MGLY + GLY  # 10000.0   ;(131)
(105)        BO2  + NO    = NO2  + HO2  + BZA         # 12000.0   ;(136)
(106)               BZA   = (PROD)                    # 0.004/L1   ;(138)
(107)        OH   + BZA   = BZO2                      # 20000.0   ;(133)
(108)        BZO2 + NO    = NO2  + PHO2 + CO          # 3700.0    ;(135)
(109)        BZO2 + NO2   = PBZN                      # 2500.0    ;(134)
(110)               PBZN  = BZO2 + NO2          # 5.57E+18 @-14000 ;(137)
(111)        PHO2 + NO    = NO2  + PHO                # 12000.0    ;(140)
(112)        PHO  + NO2   = NPHN                      # 20000.0    ;(139)
(113)        PHEN + NO3   = PHO  + HNO3               # 14000.0   ;(132)
(114)        XYL  + OH    = 0.056*XYLO + 0.278*HO2 + 0.278*PHEN
                          + 0.556*PAR + 0.666*OPEN + 0.666*MGLY
                                                   # 36000.0   ;(145-7)
(115)        XYLO + NO    = NO2  + HO2  + TLA      # 12000.0   ;(142)
(116)        TLA  + OH    = TLO2                   # 20000.0   ;(143)
(117)        TLO2 + NO    = NO2  + PHO  + 2.0 * PAR # 4000.0    ;(144)



(METHANOL CHEMISTRY )
             OH + MEOH    = HCHO + HO2             # 1550 ;
     MEONO                = HCHO + HO2 + NO        # 0.2/L1 ;

( WALL CHEMISTRY )
                  NOWALL = NO2                     # 0.1/L1 ;
                FORMWALL = HCHO                    # 0.2/L1 ;
```

A popular alternative to the Carbon Bond approach for constructing mechanisms has been the the Atkinson, Lloyd, and Winges (ALW) reaction mechanisms. This mechanism is currently undergoing significant up-dating and testing under EPA contract using data from our chamber as well as from the UCR indoor chamber. The original ALW mechanism as used in this study is listed in Table 17.

The ALW and CBX mechanisms are much more complex than the CB3 mechanism, and are much more expensive to use, but they provide explicit representation of HCHO as well as many of the other species in the SynAuto mixture. The ALW mechanism was used to model four SynAuto days and the CBX mechanism was used to model the four SynAuto days and two SynUrban days.

Table 17.

THE ATKINSON ET AL. REACTION MECHANISM AS PRESENTED IN
TABLE A.2 OF THE LEONE AND SEINFELD REPORT PART 2
RENUMBERED AND RE-ORGANIZED BY JEFFRIES

```
(      INORGANIC REACTIONS      )

( 1) NO2 = NO + O3                                #1.0 /L;
( 2) NO + O3 = NO2                                #3355.7 @-1450;

( 3) NO2 + O3  = NO3                              #177.9 @-2450;
( 4) NO  + NO3 = 2.00*NO2                         #28188;
( 5)       NO3 = 0.30*NO + 0.70*NO2 + 0.70*O3 #15.5 /L;
( 6) NO2 + NO3 = N2O5                             #104027 @-1100;
( 7)      N2O5 = NO2 + NO3                        #3.5E18 @-12280;
( 8)      N2O5 = 2.00*HNO3                        #4.46E-6 /W;

( 9)      O3 = 2.00*OH                            #2.3E-8 /W /L;

(10) OH  + NO = HONO                              #9796.9;
(11)     HONO = OH + NO                           #0.17 /L;

(12) OH  + NO2 = HNO3                             #16891;

(13) HO2 + NO  = OH + NO2                         #12416;

(14) HO2 + NO2 = HO2NO2                           #1689;
(15)    HO2NO2 = HO2 + NO2                        #7.8E15 @-10420;

(16) HO2 + HO2 = H2O2                             #114.09 @1100;
(17) HO2 + HO2 = H2O2                             #6.53E-10 @5800 /W;
(18)      H2O2 = 2.00*OH                          #7.1E-4 /L;

(19) OH  + O3 = HO2                               #2349 @-940;
(20) HO2 + O3 = OH                                #16.11 @-580;

(21) OH  + CO = HO2                               #436.2;
```

Table 17. cont.

```
( FORMALDEHYDE CHEMISTRY  )

(22) HCHO = 2.00*HO2 + CO                  #3.1E-3 /L;
(23) HCHO = CO                             #3E-3 /L;

(24) OH + HCHO = HO2 + CO                  #14765;

( ACETALDEHYDE CHEMISTRY )

(25)        CCHO = COO + HO2 + CO          #6E-4 /L;

(26) OH  + CCHO = CCO3                     #10067 @250;
(27) CCO3 + NO  = NO2 + COO                #10403;
(28) CCO3 + NO2 = PAN                      #7047;
(29)         PAN = CCO3 + NO2              #1.2E18 @-13543;

(30) COO + NO = HCHO + HO2 + NO2           #10403;
(31)        RC2CHO = CCO2 + CO + HO2       #8.4E-4 /L1;

(32) OH + RC2CHO  = RC2CO3                 #30872;
(33) RC2CO3 + NO  = CCO2 + NO2             #10403;

(34) RC2CO3 + NO2 = HIGHPANS               #7047;
(35)     HIGHPANS = RC2CO3 + NO2           #1.2E18 @-13543;

(36) CCO2   + NO  = CCHO + HO2 + NO2       #10403;

(  DICARBONYL CHEMISTRY )

(37)        GLY = HCHO + CO                #1E-10 /L1;
(38) OH   + GLY = HO2 + CO                 #29530;

(39)       MGLY = CCO3 + HO2 + CO          #0.15 /L1;
(40) OH + MGLY = CCO3 + CO                 #22148;
```

Table 17. cont.

```
( KETONE CHEMISTRY )
(41)        ACETONE = CCO3 + COO              #1.7E-3 /L1;
(42)      ETHMEKET = CCO3 + CCO2              #1.7E-3 /L1;

(43) OH + ETHMEKET = RRRCO2                   #14765 @-330;
(44) RRRCO2 + NO    = NO2 + CCHO + CCO3       #10403;

( ALKANE CHEMISTRY )

(45) OH  + PROPANE = PROPACO2                 #22148 @-680;
(46) PROPACO2 + NO = HO2 + NO2 + ACETONE      #10403;

(47) OH + ALKANES = RC3CO2                    #22148 @-400;
                  (R=H,CH3,ETH,PRO, . . . )
(48) RC3CO2  + NO = -0.80*NO + 1.70*NO2 + 0.9*HO2 + 0.15*HCHO +0.30*CCHO
                  + 0.10*RC2CHO + 0.30*ACETONE + 0.45*ETHMEKET
                                              #10403;

( OLEFIN CHEMISTRY )

(49) OH + ETHENE   = -1.00*NO + NO2 + HO2 + 2.00*HCHO          #3255 @380;
(50) OH + PROPENE  = -1.00*NO + NO2 + HO2 + HCHO + CCHO        #6040 @540;

(52) O3 + ETHENE   = HCHO + 0.40*CH2DIOX + 0.40*CO + 0.12*HO2
                                                            #14.09 @-2560;
(53) O3 + PROPENE  = 0.50*HCHO + 0.50*CCHO + 0.20*CH2DIOX + 0.20*ETHDIOX
                   + 0.30*CO + 0.20*HO2 + 0.10*OH + 0.20*COO
                                                            #10.40 @-1900;
(55) CH2DIOX + NO  = HCHO + NO2               #10403;
(56) CH2DIOX + NO2 = HCHO + NO3               #1040;
(57)       CH2DIOX = (PRODUCT1)               #5.03E-3 /W;
(58) ETHDIOX + NO  = CCHO + NO2               #10403;
(59) ETHDIOX + NO2 = CCHO + NO3               #1040;
(60)       ETHDIOX = (PRODUCT2)               #5.03E-3 /W;
```

Table 17. cont.

```
( AROMATIC CHEMISTRY )

(61) OH + BENZENE  = 0.25*CRESOL + 0.25*HO2    + 0.75*AROADDO1 #1778.5;
(62) OH + TOLUENE  = 0.20*CRESOL + 0.20*HO2    + 0.65*AROADDO1
                                   + 0.15*AROCO2            #9060.4;
(63) OH + RRRC8ARO = 0.25*CRESOL + 0.25*HO2    + 0.75*AROADDO1 #33557;

(64) AROADDO1 + NO = 0.75*NO2 + 0.75*HO2 + 0.75*GAMDIALS + 0.75*MGLY #10403;
(65) AROCO2   + NO = 0.75*NO2 + 0.75*HO2 + 0.75*BENZALD               #10403;

(66) OH    + GAMDIALS = GRADICAL #43624;
(67) GRADICAL  +  NO = -2.00*NO + 3.00*NO2 + 0.55*HO2 + 0.55*GLY + 0.45*CCO3
                      + 0.45*MGLY + 0.55*CO                           #10403;
(68) GRADICAL  + NO2 = GRADNO2                              #7047;
(69)         GRADNO2 = GRADICAL + NO2                       #1.2E18 @-13543;

(70) OH   +  CRESOL = AROADDO2                              #63758;
(71) AROADDO2 + NO = 0.75*NO2 + 0.75*HO2 + 0.75*GAMDIALS #10403;
(72) NO3 +  CRESOL = HNO3 + PHENOXY                        #22148;

(73)       BENZALD = (PRODUCT4)                             #4.5E-3 /L1;
(74) OH +  BENZALD = BZCO3                                  #19128;
(75) BZCO3  +  NO  = NO2  + BZO2                            #10403;
(76) BZCO3  +  NO2 = PBZN                                   #7047;
(77)          PBZN = NO2 + BZCO3                            #1E17 @-13025;

(78) BZO2   +  NO  = PHENOXY + NO2                          #10403;
(79) PHENOXY + NO2 = (PRODUCT3)                             #22148;

(80) OH   + (CH4)  = COO                                    # 28. ;
```

Table 17. cont.

```
( METHANOL CHEMISTRY )

        OH + MEOH = HCHO + HO2                          #1550 ;
     MEONO        = HCHO + HO2 + NO                     #0.2/L1;

( WALL PROCESSES )

        NOWALL  = NO2                                   #0.01/L1;
      FORMWALL  = HCHO                                  #0.02/L1;

( DILUTION ENTRAINMENT )

  ( CONTINENTIAL BACKGROUND AIR )
  = 0.30*CO + 0.04*O3 + 0.0005*NO2 +
    0.005* HCHO + 0.0025 * CCHO +
    0.001*ETHENE + 0.0005*PROPENE + 0.0008*TOLUENE     #1.0/E;


KEY ::
        #  -- rate constant at 300 deg K or A-factor
        @  -- activation energy
        /L -- reaction depends upon light
        /W -- reaction depends upon water
        ;  -- end of reaction
       ( ) -- comments

UNITS :: PPM and MINS
```

Modifications and Assumptions

The chemistry of $HO^{\cdot} + MeOH$ was added to ALW and CBX in the form of explicit chemistry for MeOH. See the end of each mechanism's listing for the reactions that were added.

All chambers have some wall artifact processes that can potentially affect the experimental results. We have investigated these processes in a number of chamber characterization experiments. The major observed chamber processes are the slow appearance of gas phase NO_X in experiments in which no NO_X was added to the chamber and the more rapid oxidation of significant NO concentrations in the absence of injected organics. The appearance of NO_X in the chambers is believed to be from the release of nitrogen material that was adsorbed on the chamber walls in previous experiments. For example, nitric acid is a major nitrogen end product in most chamber experiments and it has a high affinity for chamber walls. The rapid oxidation of NO in the absence of injected organics is an indication of a radical source associated with the chamber itself. This too is believe to be from material adsorbed on the chamber walls in previous experiments.

Modeling studies of the UNC chamber have suggested[17] that an adequate representation for the NO_X process was

$$wall.NO_X = NO_2$$

at a rate proportional to the light intensity. The amount of *wall*.NO_X needed to account for the gas phase appearance was a function of the chamber history. Typical values were between 5–20 ppb of *wall*.NO_X; this amount was introduced into the chamber over a 10 hour period. Likewise, an adequate representation of the NO oxidation processes was found to be represented by introduction of HCHO, also from the walls by

$$wall.HCHO = HCHO$$

at a rate proportional to the light intensity. The amount of *wall*.HCHO needed to account for the NO oxidation was also a function of the chamber history. Typical values were between 5–35 ppb of *wall*.HCHO.

In addition to these processes, injected gas-phase NO_2 may react with the chamber walls to produce HONO, a powerful radical source, at a rate dependent upon the surface conditions. Further, some HONO may be present initially as a result of high concentrations of NO_X occurring during chamber injections. We believe that the most common chamber initial condition is 0.0 ppb of initial HONO. Sometimes we have found that simulations require 1–2 ppb initial HONO.

The additional reactions for chamber processes are clearly indicated at the bottom of each of the mechanism listings.

Reactions that add continental background HC in the dilution air were also added to the mechanism. In addition, 38 ppbC of continental background HC was added to the chamber injections, as well as background CO (0.3 ppm) and CH_4.

Several potential refinements, such as a zenith angle dependence of the ratio of formaldehyde photolysis to NO_2 photolysis and optimally adjusting the photolysis rates for the UVR-to-TSR ratio for specific days were not included in these simulations.

The ALW mechanism was designed for conditions in which the NO concentration would never be below 10^{-4} ppm. Although this may be true in urban simulations, it certainly was not true in reactive smog chamber simulations such as those of August 6 and 8. In these simulations, the simulation program had to be stopped after about 400 minutes when the NO concentration fell below 0.1 ppb so these model plots are short compared to the data and the lower concentration simulations.

In comparing the data and model profiles, remember that the NO_2 experimental data also includes PAN and at the end of the fast runs this data is almost 100% PAN. The plotted model data includes both PAN and HNO_3 profiles; these are labeled on the plots.

A Caution

As in the reactivity issue, there is no single adequate measure for model-experiment comparison. The best understanding comes from a direct comparison of the species profiles from the experiment and the simulation and model-to-model comparison when different assumptions have been made. Simple measures such as the maximum O_3 prediction error are misleading. In some of the cases described below, different assumptions have been used to force a better fit for the purpose of illustrating the magnitude of model-data disagreement. For these cases, reporting errors for O_3 maximum predictions is meaningless.

The Simulations

We performed 40 simulations. Entries in columns and rows of Table 18 indicate which conditions were simulated. The columns of Table 18 represent the mechanisms and wall assumptions used. The entries in the table body are the difference in minutes between the experiment and simulation NO-to-NO_2-crossovers (which is a measure of the model's initial reactivity), and the magnitude of the model's O_3 maximum relative to the experiment (which is a measure of the model's final reactivity). A ↑ means the model over- predicted and a ↓ means that the model underpredicted the ozone; an = means that the model and data O_3 maximum agreed.

Table 19 describes the wall assumption terms used in Table 18.

Figure 39, and following figures, show the model and data profiles for NO, NO_2, and O_3 and the model profiles for PAN and HNO_3. The top plot in each figure is RED chamber data, and the bottom plot is BLUE chamber data; the *solid* lines are experimental data and the *dashed* lines are model predictions.

Discussion of Model Results

Overall Results

The large majority of all the simulation results were slower than the experiments, even with extreme assumptions of wall processes. For example,

- CBX simulations without any wall assumptions (the minimal case) for the basic SynAuto mixture (*i.e.* no SynMethanol added) experiments were 70 to 125 minutes slow (plots of these simulations are not shown);
- CBX simulations with *high* wall assumptions for the basic SynAuto mixture experiments were still 40 to 100 minutes slow;
- CBX simulations with *extreme* wall assumptions for the basic SynAuto mixture were slow by 15 to 45 minutes;
- for CBX, in these SynAuto simulations, there was a direct inverse relationship between the initial HC concentration and the lateness of the crossover time;
- CB3 simulations were also slow relative to the data, but these underpredicted the O_3 because of higher NO_2 losses at the end of the simulations (*i.e.* the predicted PAN exceeds the NO_2 measurement, which includes PAN);
- CB3 was less sensitive to wall radical sources than was CBX;
- ALW simulations were very similar to the CBX simulations; in fact, overlaying the two mechanism's simulations for August 5 shows essentially a perfect match in all species profiles predicted by the two mechanisms;

A general trend, is that all three mechanisms appear to have too little reactivity in the beginning of SynAuto simulations and too much reactivity in the end. When the initial reactivity is *artificially* increased by the use of extremely high wall assumptions and radical sources, the models tend to do better, but now tend to overpredict the latter stages of the experiments.

Table 18. Model Simulations General Performance

(numbers are data - model times to NO-to-NO_2-crossover)
(↑ is over prediction of ozone, ↓ is under prediction of ozone)

Date	HC/SynMeOH	CB3 high	CB3 extra	ALW high	CBX none	CBX high	CBX extra
SynAuto Experiments							
AU05	0.91	−100 ↓	−50 ↑	−100 ↓	−125 ↓	−105 ↓	−45 =
	1.31	−60 ↑	−30 ↑	−90 ↓	−80 ↓	−80 ↓	−30 ↑
AU06	2.25	−30 ↓	−10 ↓	−60 ↑	−85 =	−50 ↑	−20 =
	3.23	−20 ↓	0 ↓	−40 ↑	−70 ↑	−38 ↑	−15 ↑
AU07	1.32			−75 ↓		−85 ↓	−40 ↑
	0.87/0.36			−75 ↓		−65 ↓	−40 ↑
AU08	2.48/1.02			−35 ↑		+25 ↑	−32 ↑
	3.68			−20 ↑		−35 ↑	−8 ↑
SynUrban Experiments							
AU22	3.04					+25 ↑↑	
	2.04/1.00					+30 ↑↑	
ST01	3.31					+8 ↑↑	
	2.66/1.04					+8 ↑↑	

Table 19. Model Simulation Wall Assumptions

(ppb of initial material on walls or reaction rate)

Condition	*wall*.NO_X	*wall*.HCHO	HONO	NO_2+ walls
none	0	0	0	0
typical	10	25	0	0
high	25	50	0	0
extra	25	50	5	1.6×10^{-4}

It was not the purpose of this work to test the mechanisms. We modeled a few experiments in the UNC database to gain insight into what might be causing the problems; these simulations are not shown here. CBX was used to model an experiment with UNCMIX that had m-xylene added to one side and tri-methylbenzene added to the other side. The experiment produced essentially matched results for the two sides. With high wall sources necessary to have the initial timing of the simulation agree with the experiment, the CBX simulation likewise produced matched results for the two sides, but over predicted the O_3 production in both sides by about 40%.

In another experiment a four component simple mix (n-butane, pentane, ethylene, propylene) was compared with UNCMIX; both mixtures had the same total carbon fraction in the paraffin and olefin classes (0.70/0.30) and neither mix had aromatics. In the experiment, the simple mix was slightly more reactive than the UNCMIX. In the CBX simulation with high wall sources, the UNCMIX side was simulated reasonably well, but the simple mix side was underpredicted by nearly 50%! Because all the paraffin carbon is treated the same way in the CBX, the difficulties between the simple mix and the UNCMIX side (which had the same amount of paraffin carbon) must be in the treatment of the olefins. The simple mix had 20%C as ethylene, as did the SynAuto experiments in which CBX also performed poorly. On the other side, UNCMIX only had 10%C as ethylene and the SynUrban, for which the CBX performed better, had only 6%C as ethylene. This suggests that the new explicit chemistry for ethylene in CBX needs to be tested.

It appears that the CBX mechanism has too little reactivity in the simplest paraffin/olefin portion of the mechanism and too much reactivity in the aromatics portion of the mechanism.

We recommend that the mechanism be further tested before it is used in air shed simulations for methanol fuel scenarios.

Analysis of Substitution Effects

An analysis technique described by Jeffries[18] in which integrated reaction rates are used to compute a process mass balance and a pathway flowchart was used to investigate the relative effects of the SynMethanol substitution for the August 8, 3-ppmC 9:1 HC-to-NO_x ratio experiment with ≈33% substitution using 20% HCHO. The ALW model simulation was used as the source of the data. Although ALW was somewhat slow on this day, it did approximate the side-to-side differences in the data reasonably well.

Analysis of the model predictions after 600 minutes showed that although there was less concentration of each species in the SynAuto/SM side, the high methanol and formaldehyde resulted in 16% higher HO˙ and $HO_2^{\cdot}$-production. Thus, in spite of the concentration differences in the "reactive" HCs, there was nearly the same total HC consumption in both simulations due to the higher HO˙ in the MeOH-substituted side.

The 100% SynAuto side consumed a total of 0.60 ppmV of 0.90 ppmV initial HC (66%) and the methanol substituted side consumed 0.39 ppmV of 0.58 ppmV initial HC (67%). In addition, the methanol side consumed 0.15 ppmV of MeOH bringing the total consumption to 0.54 ppmV, in relatively close agreement with that on the higher HC, 100% SynAuto side.

A major difference was that the 100% SynAuto side formed a total of 1.04 ppmV of aldehydes and reacted 0.70 ppmV, giving a net formation of 0.34 ppmV aldehydes (0.308 ppmV HCHO). On the MeOH-substituted side, only 0.77 ppmV was formed and 0.80 ppmV was reacted (the difference was taken from the initial aldehyde) giving no net aldehyde formation. Because there was an initial 0.24 ppmV of HCHO, however, a final concentration of 0.22 ppmV aldehyde (0.148 ppmV HCHO) resulted on the MeOH-substituted side. The amount of HCHO formed from MeOH was 0.15 ppmV.

Taken altogether, the 100% SynAuto side reacted 1.30 ppmV of HC and aldehydes and the 33% SynMethanol substituted side reacted 1.34 ppmV of HC and aldehydes. There was 1.41 ppm NO_2 created per ppm HO˙ reacted in the 100% SynAuto side and 1.23 ppm NO_2 created per ppm HO˙ reacted in the SynMethanol-substituted side, a reflection of shorter organic oxidation pathways in the methanol side. As indicated above, however, 16% more HO˙ was produced in the methanol side, which essentially made up for the difference in NO_2-production. That is there were more short cycles on the substituted side, resulting in approximately the same conversion of NO.

This model suggests a clear explanation as to why the two systems would produce the same O_3 in this case. In the actual data for the August 8 experiment, the 100% SynAuto side did make more HCHO (peak value was 0.32 ppm at 1000 EDT) than the MeOH-substituted side (peak value about 0.30 ppm at 1200 EDT). Note, however, that the values discussed above were the sums and differences of total throughputs of various reactions at the end of the 10-hour simulation and thus should not be directly compared with maximum concentration measured in the experiment. This analysis also shows the complexity of the chemical situation and illustrates why photochemical kinetics models are needed to understand the effects of major compositional changes. Improved model fits are needed, however, before more extensive analysis would be worthwhile.

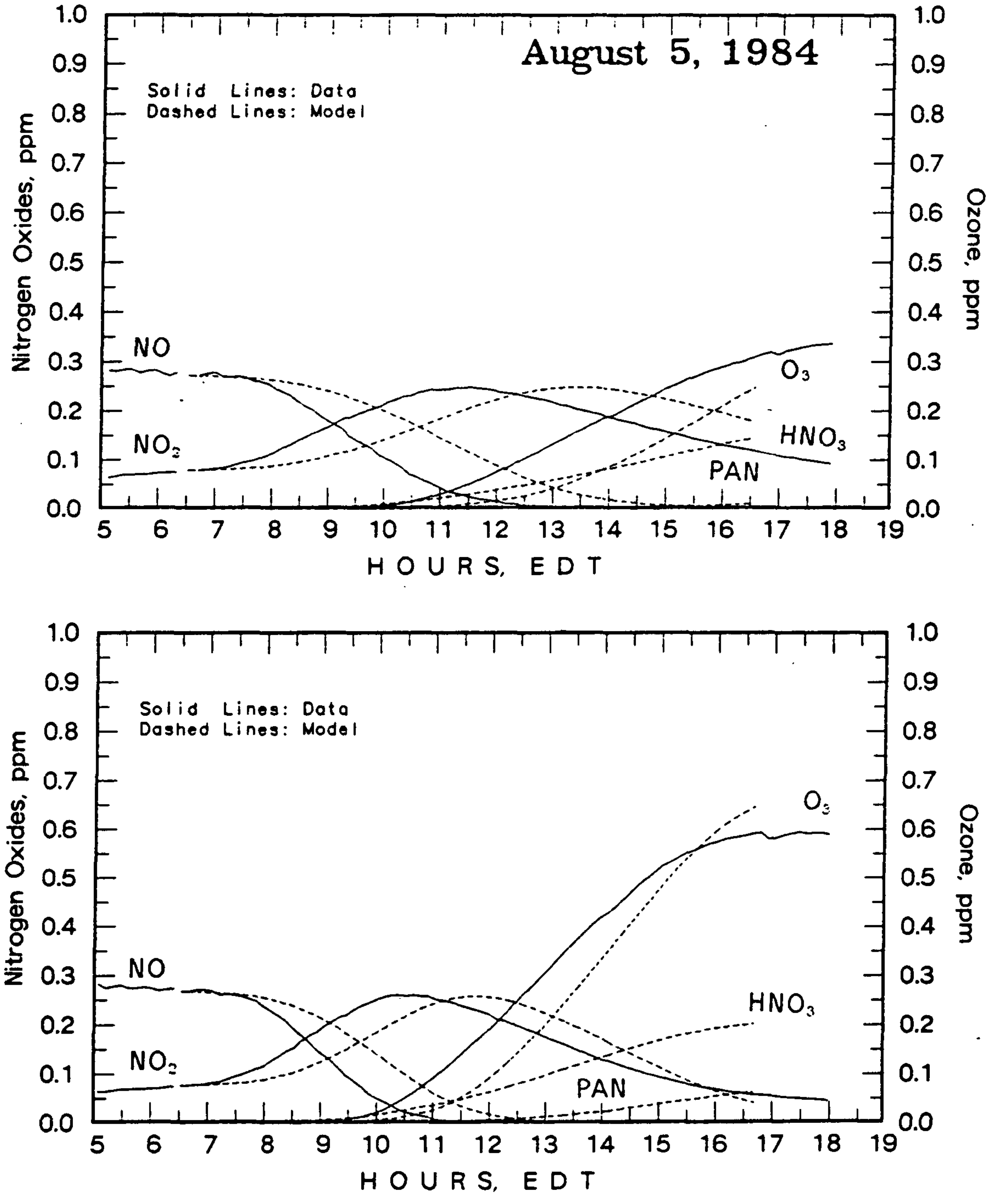


Figure 39. Only High NOx Wall Conditions.
CB3 model; 0 ppb Wall HCHO, 25 ppb Wall NOx, 0 ppb initial HONO; no formation of HONO on walls.
Top: 0.91 ppmC SYNAUTO, no MeOH, 0.01 ppm HCHO
Bottom: 1.31 ppmC SYNAUTO, no MeOH, 0.02 ppm HCHO

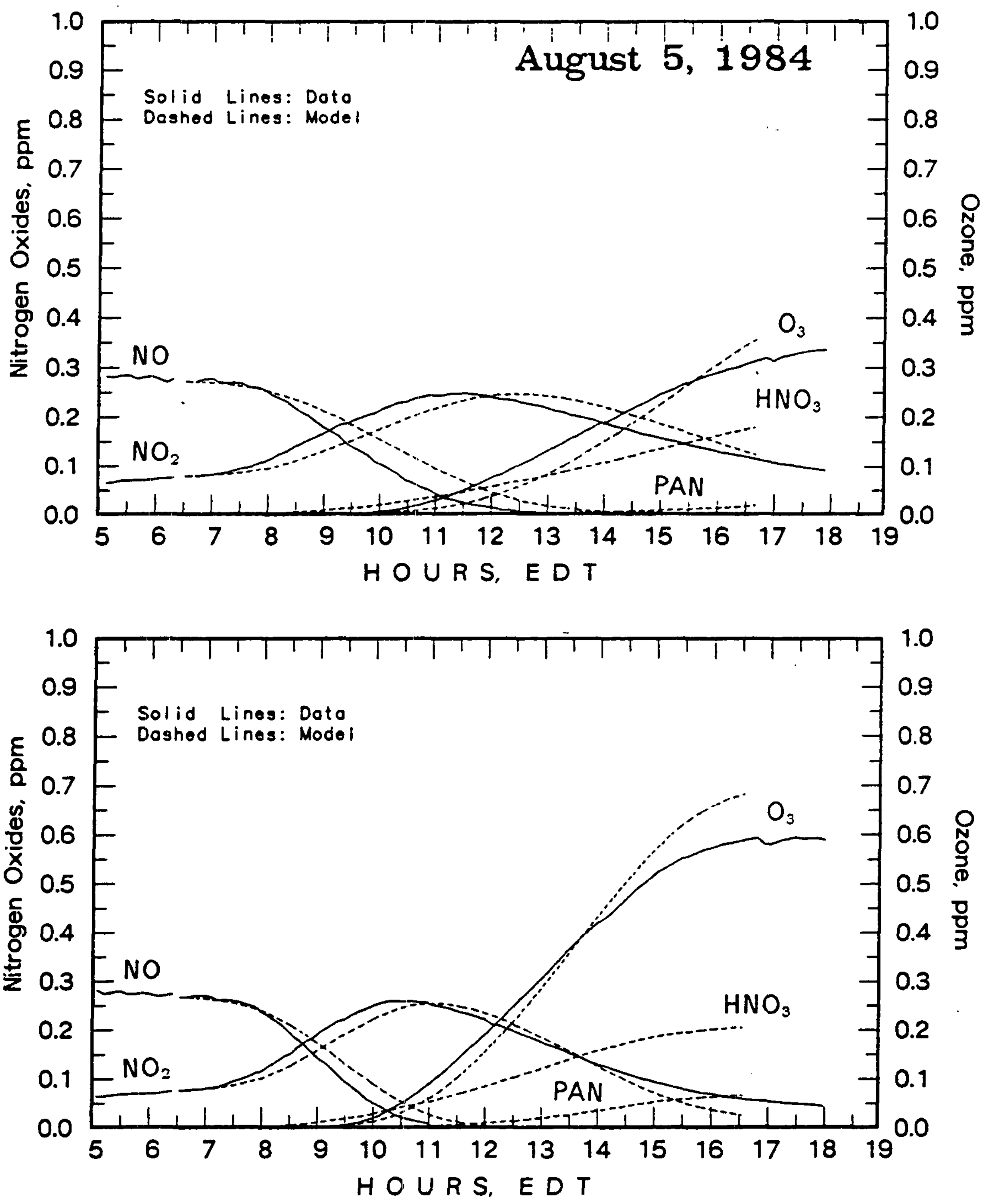


Figure 40. NO Wall HCHO Wall Conditions.
CB3 model; 0 ppb Wall HCHO, 25 ppb Wall NOx, 5 ppb initial HONO; normal formation of HONO on walls.
Top: 0.91 ppmC SYNAUTO, no MeOH, 0.01 ppm HCHO
Bottom: 1.31 ppmC SYNAUTO, no MeOH, 0.02 ppm HCHO

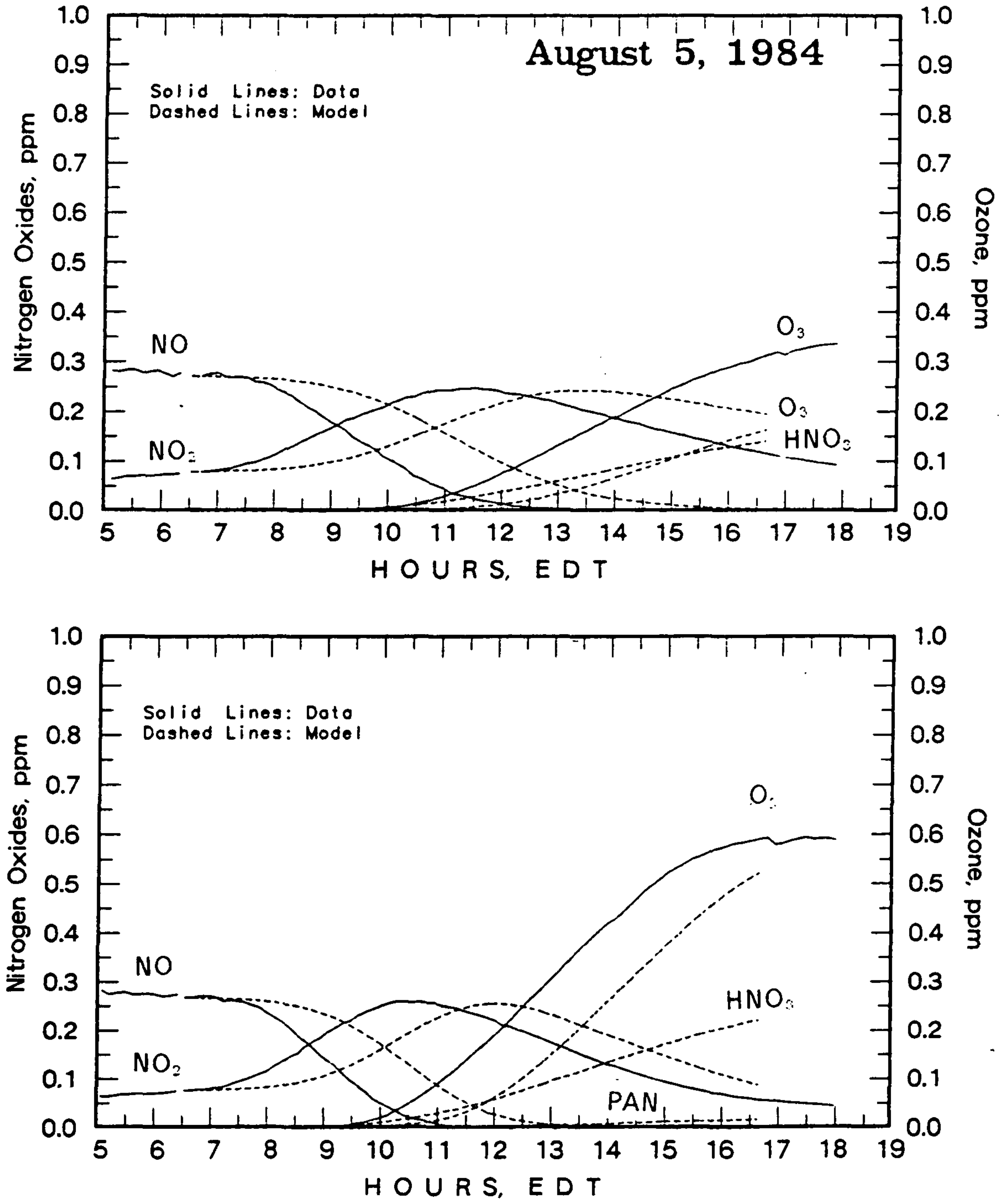


Figure 41. High Wall Conditions.
CBX model; 50 ppb Wall HCHO, 25 ppb Wall NOx, 0 ppb initial HONO; no formation of HONO on walls.
Top: 0.91 ppmC SYNAUTO, no MeOH, 0.01 ppm HCHO
Bottom: 1.31 ppmC SYNAUTO, no MeOH, 0.02 ppm HCHO

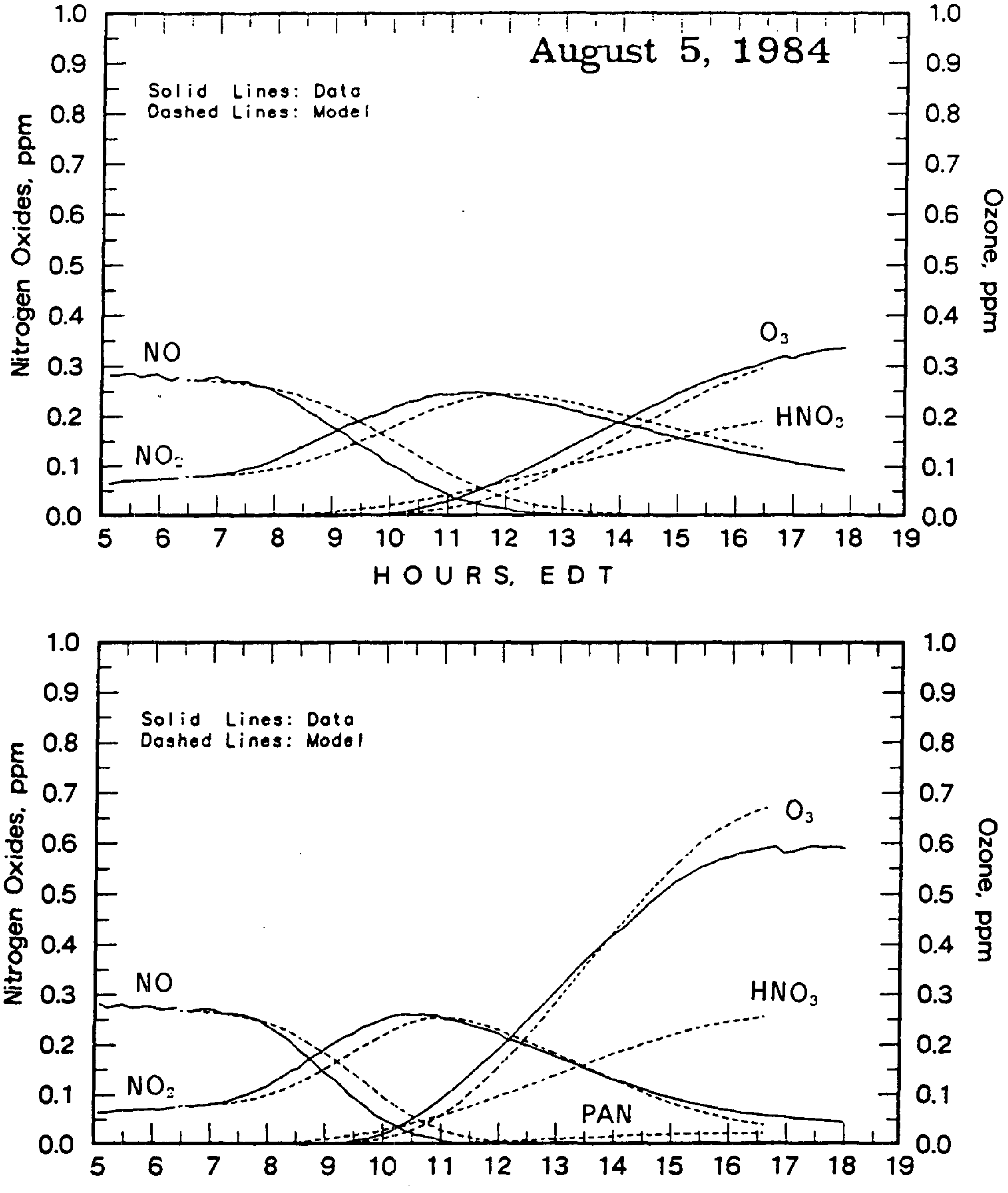


Figure 42. Extra Wall Conditions.
CBX model; 100 ppb Wall HCHO, 25 ppb Wall NOx, 5 ppb initial HONO; normal formation of HONO on walls.
Top: 0.91 ppmC SYNAUTO, no MeOH, 0.01 ppm HCHO
Bottom: 1.31 ppmC SYNAUTO, no MeOH, 0.02 ppm HCHO

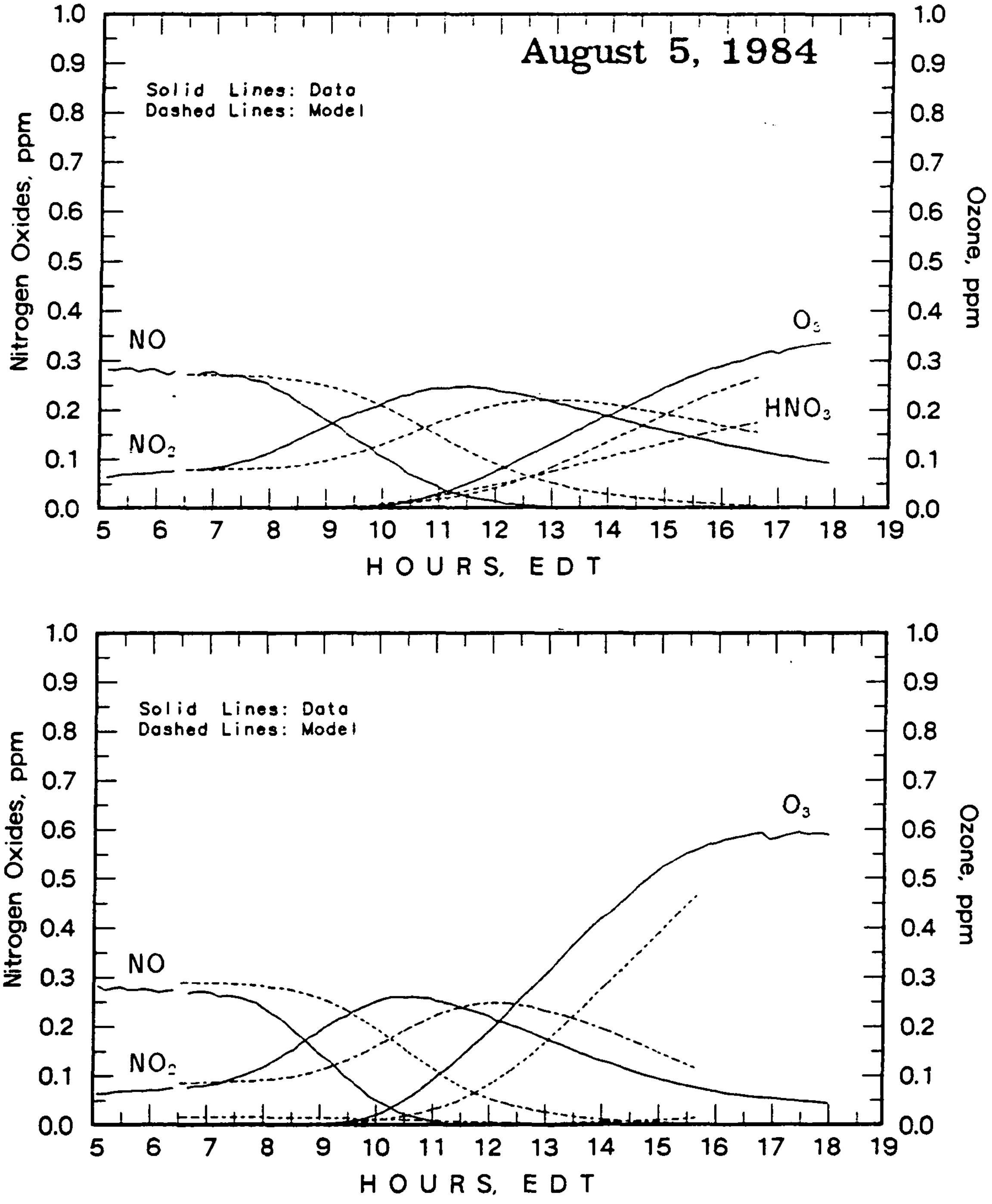


Figure 43. High Wall Conditions.
ALW model; 50 ppb Wall HCHO, 25 ppb Wall NOx, 0 ppb initial HONO; no formation of HONO on walls.
Top: 0.91 ppmC SYNAUTO, no MeOH, 0.01 ppm HCHO
Bottom: 1.31 ppmC SYNAUTO, no MeOH, 0.02 ppm HCHO

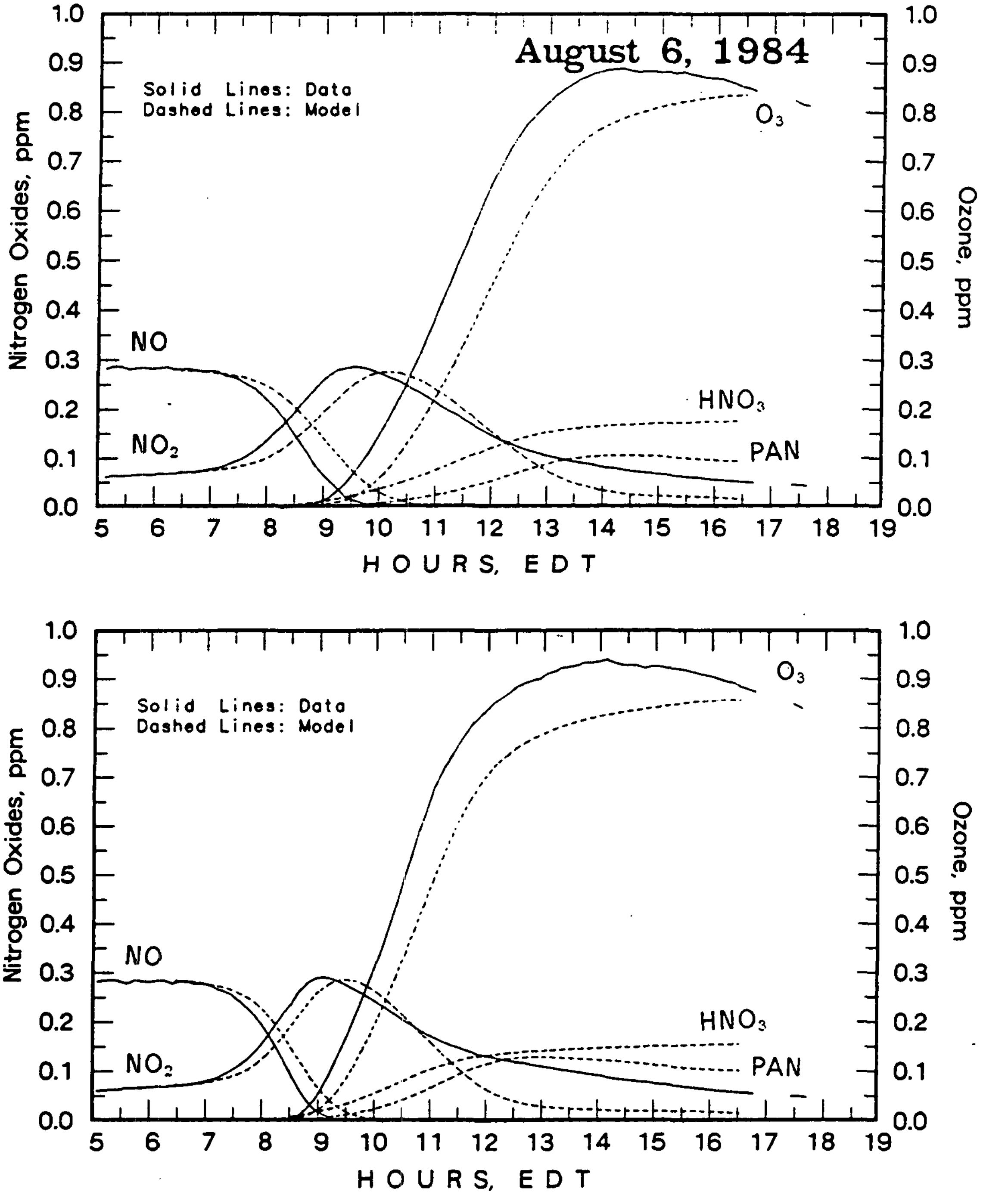


Figure 44. Only High NOx Wall Conditions.
CB3 model; 0 ppb Wall HCHO, 25 ppb Wall NOx, 0 ppb initial HONO; no formation of HONO on walls.
Top: 2.25 ppmC SYNAUTO, no MeOH, 0.04 ppm HCHO;
Bottom: 3.23 ppmC SYNAUTO, no MeOH, 0.06 ppm HCHO;

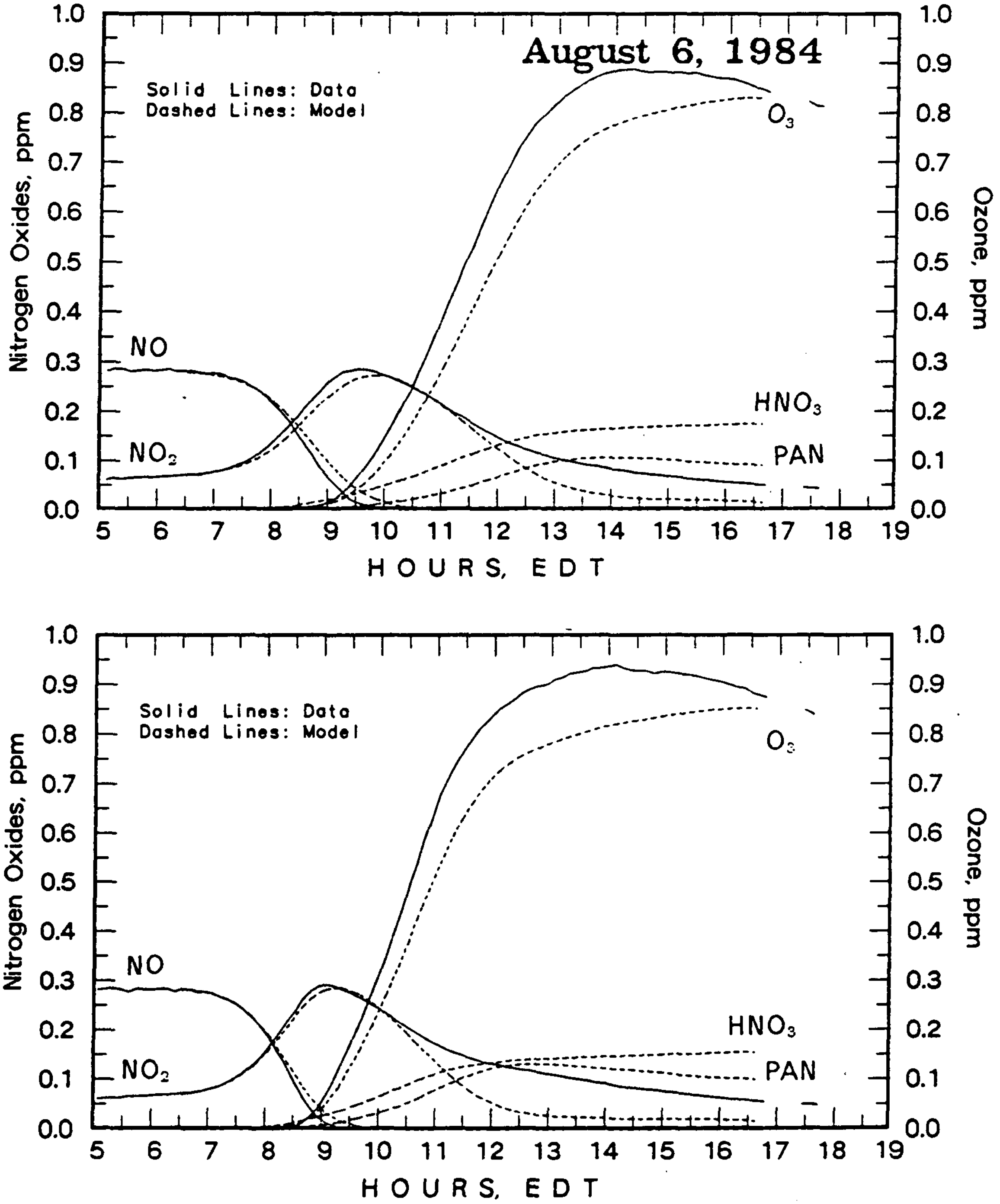


Figure 45. NO Wall HCHO Wall Conditions.
CB3 model; 0 ppb Wall HCHO, 25 ppb Wall NOx, 5 ppb initial HONO; normal formation of HONO on walls.

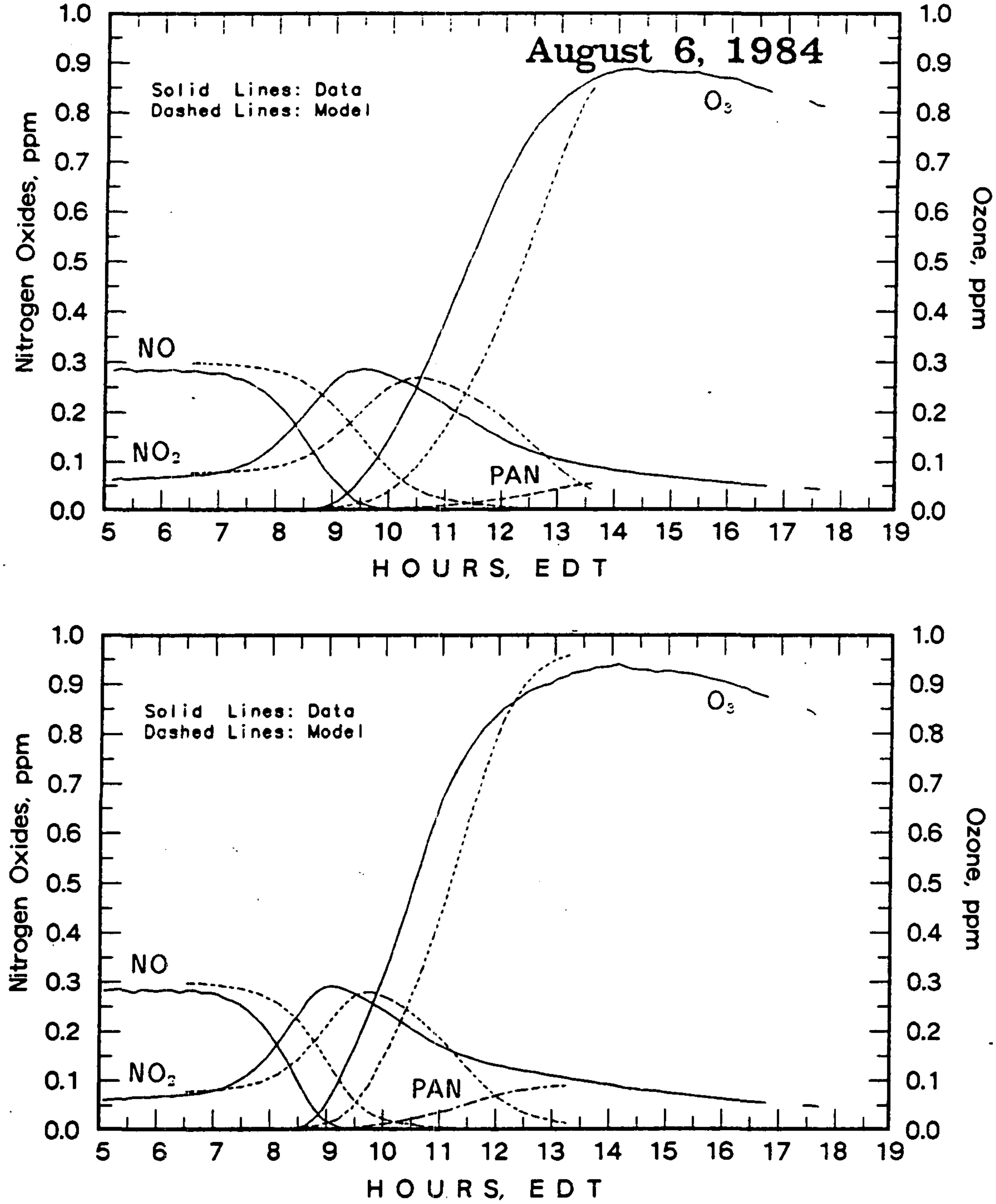


Figure 46. High Wall Conditions.
ALW model; 50 ppb Wall HCHO, 25 ppb Wall NOx, 0 ppb initial HONO; no formation of HONO on walls.
Top: 2.25 ppmC SYNAUTO, no MeOH, 0.04 ppm HCHO
Bottom: 3.23 ppmC SYNAUTO, no MeOH, 0.06 ppm HCHO

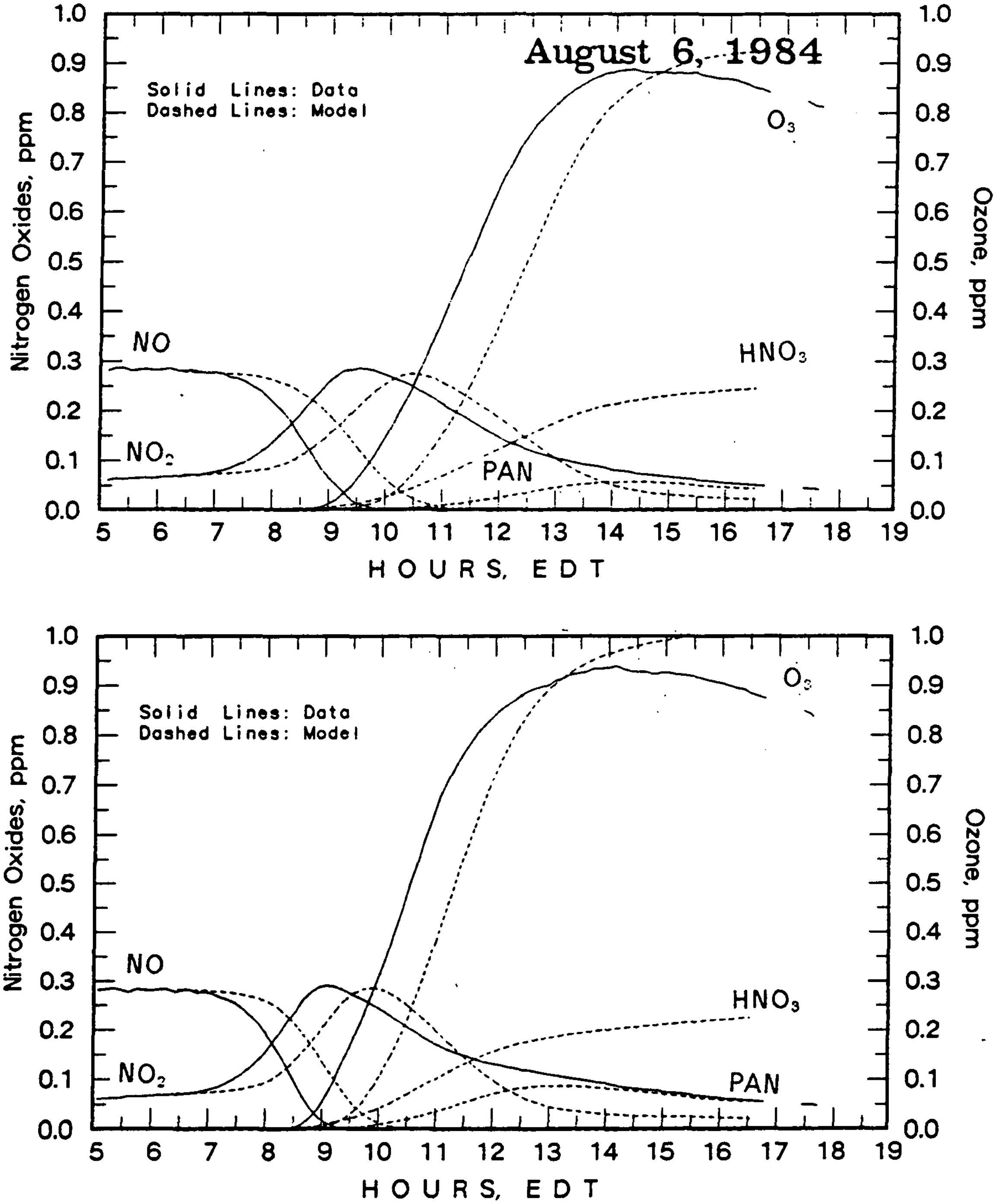


Figure 47. High Wall Conditions.
CBX model; 50 ppb Wall HCHO, 25 ppb Wall NOx, 0 ppb initial HONO; no formation of HONO on walls.
Top: 2.25 ppmC SYNAUTO, no MeOH, 0.04 ppm HCHO
Bottom: 3.23 ppmC SYNAUTO, no MeOH, 0.06 ppm HCHO

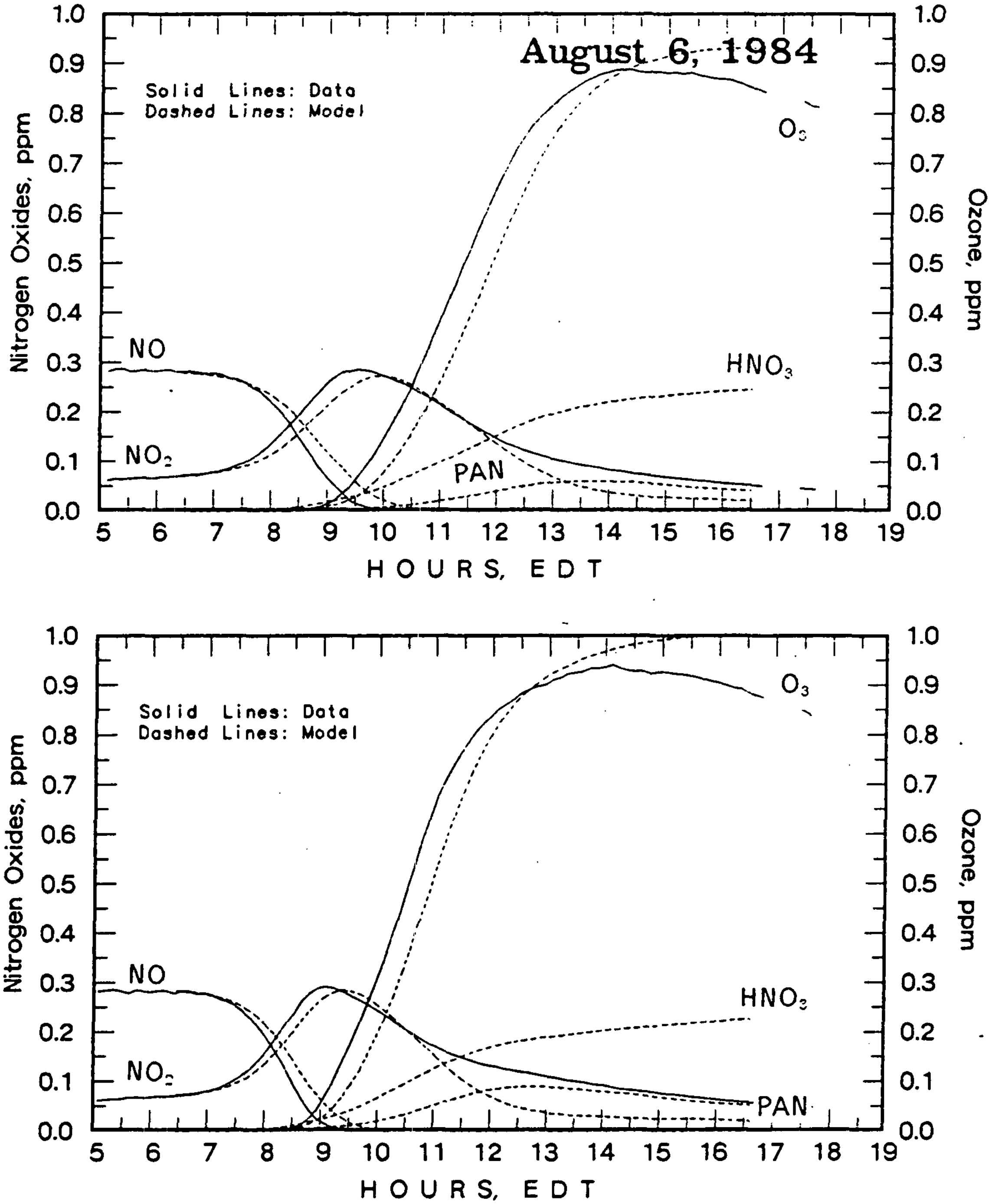


Figure 48. Extra Wall Conditions.
CBX model; 100 ppb Wall HCHO, 25 ppb Wall NOx, 5 ppb initial HONO; normal formation of HONO on walls.
Top: 2.25 ppmC SYNAUTO, no MeOH, 0.04 ppm HCHO
Bottom: 3.23 ppmC SYNAUTO, no MeOH, 0.06 ppm HCHO

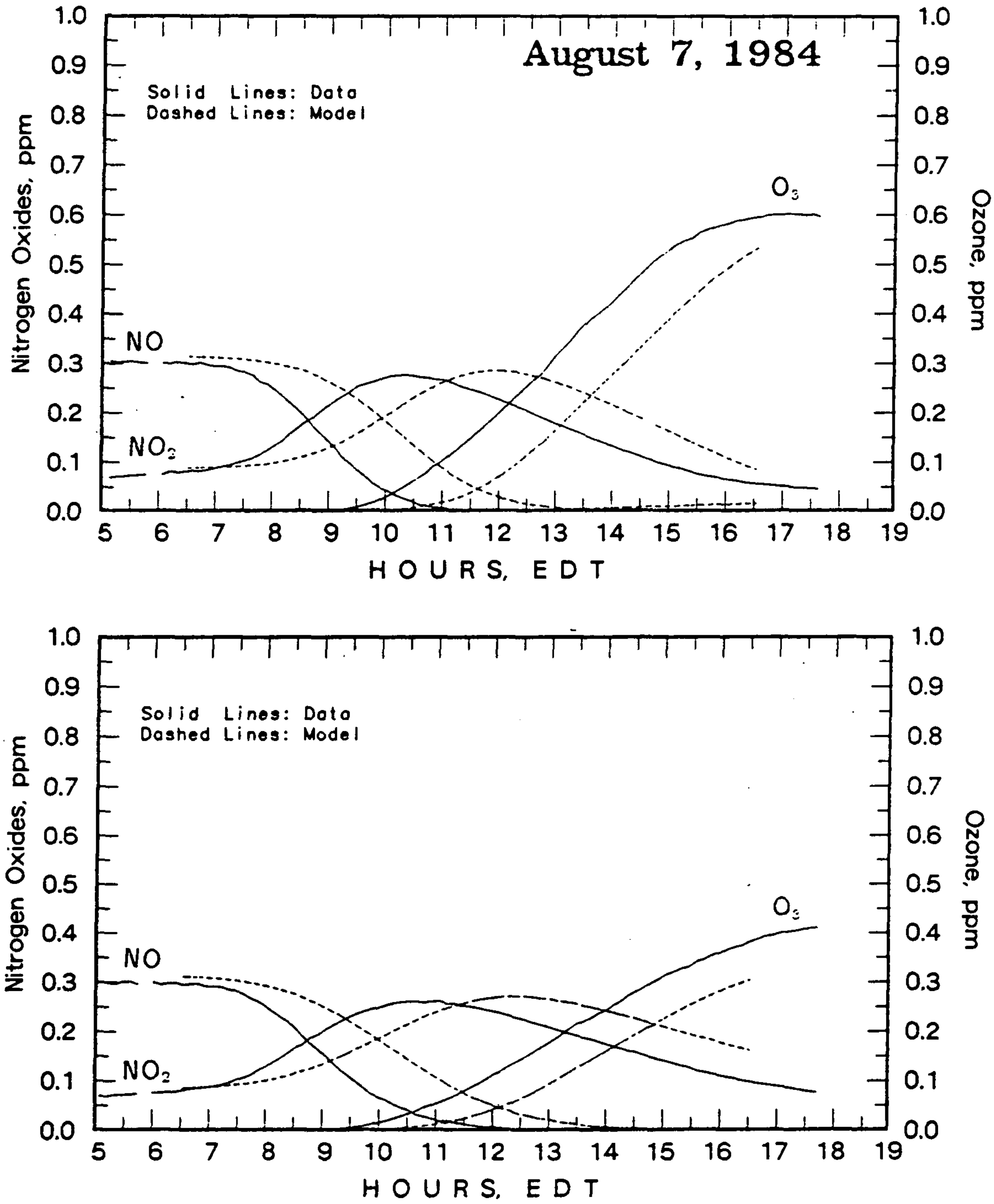
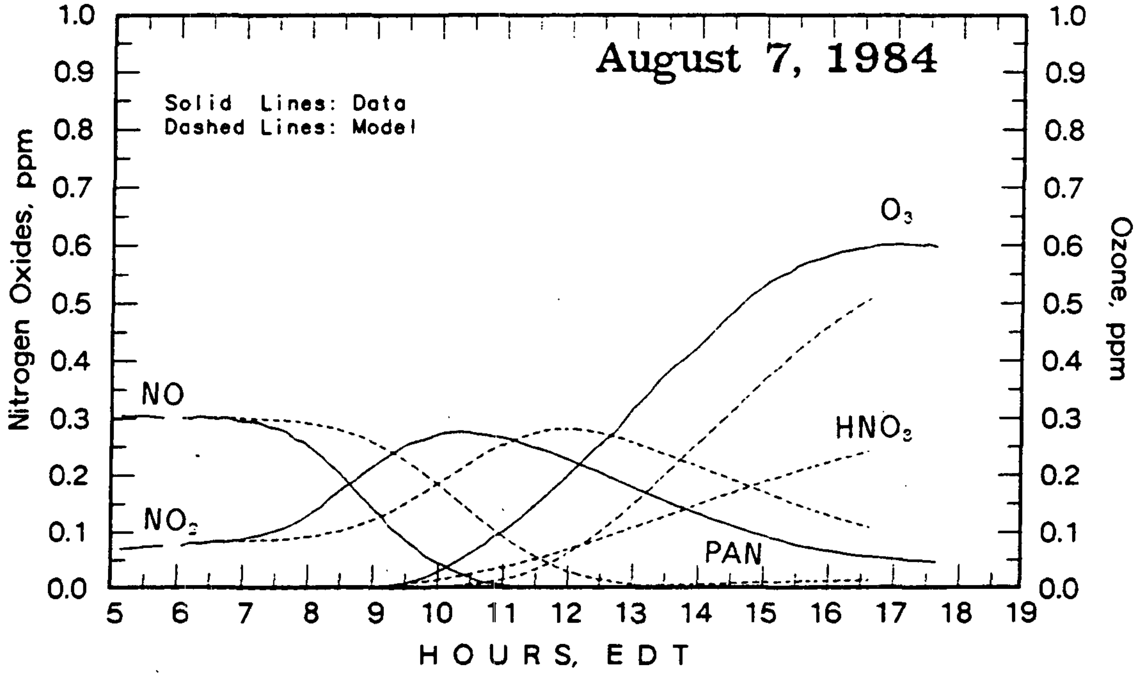


Figure 49. High . Wall Conditions.
ALW model; 50 ppb Wall HCHO, 25 ppb Wall NOx, 0 ppb initial HONO; no formation of HONO on walls.
Top: 1.32 ppmC SYNAUTO, no MeOH, 0.04 HCHO, no MeNO2
Bottom: 0.86 ppmC SYNAUTO, 0.3 MeOH, 0.06 HCHO, 3 ppb MeNO2



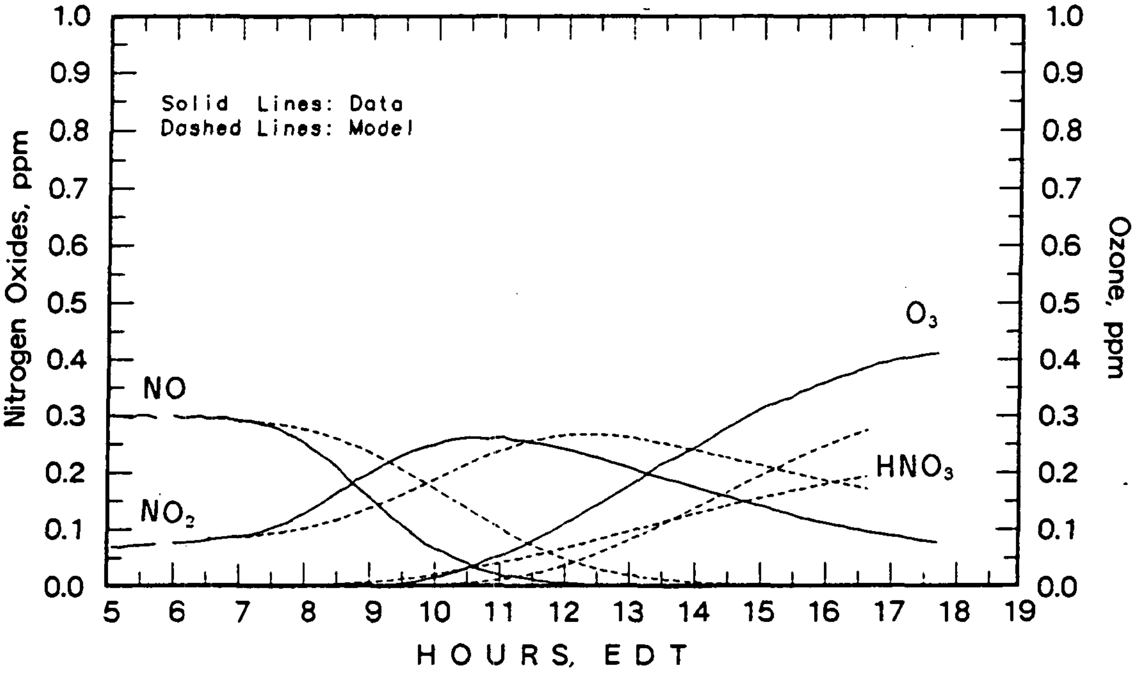


Figure 50. High Wall Conditions.
CBX model; 50 ppb Wall HCHO, 25 ppb Wall NOx, 0 ppb initial HONO; no formation of HONO on walls.
Top: 1.32 ppmC SYNAUTO, no MeOH, 0.04 HCHO, no MeNO2
Bottom: 0.86 ppmC SYNAUTO, 0.3 MeOH, 0.06 HCHO, 3 ppb MeNO2

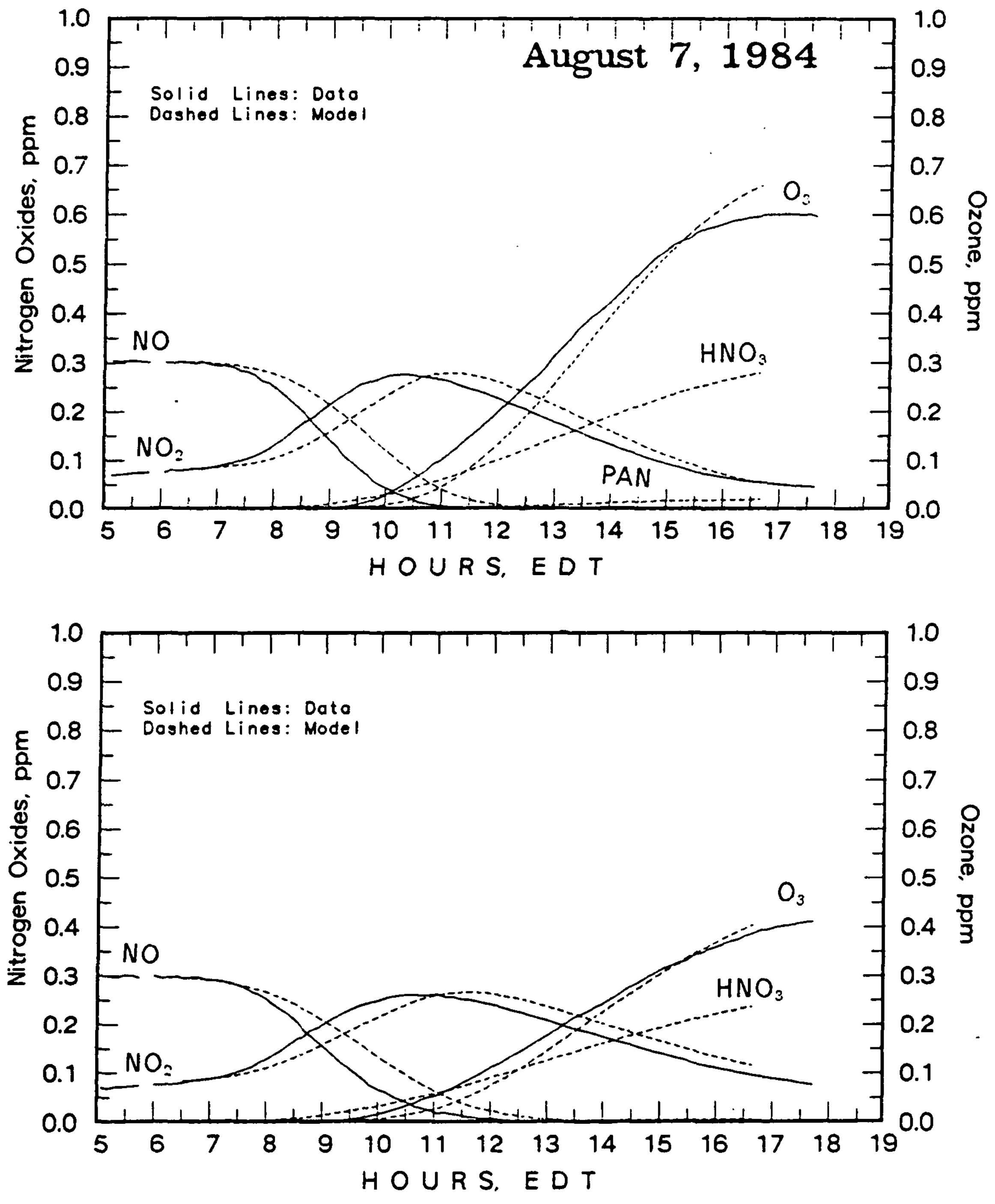
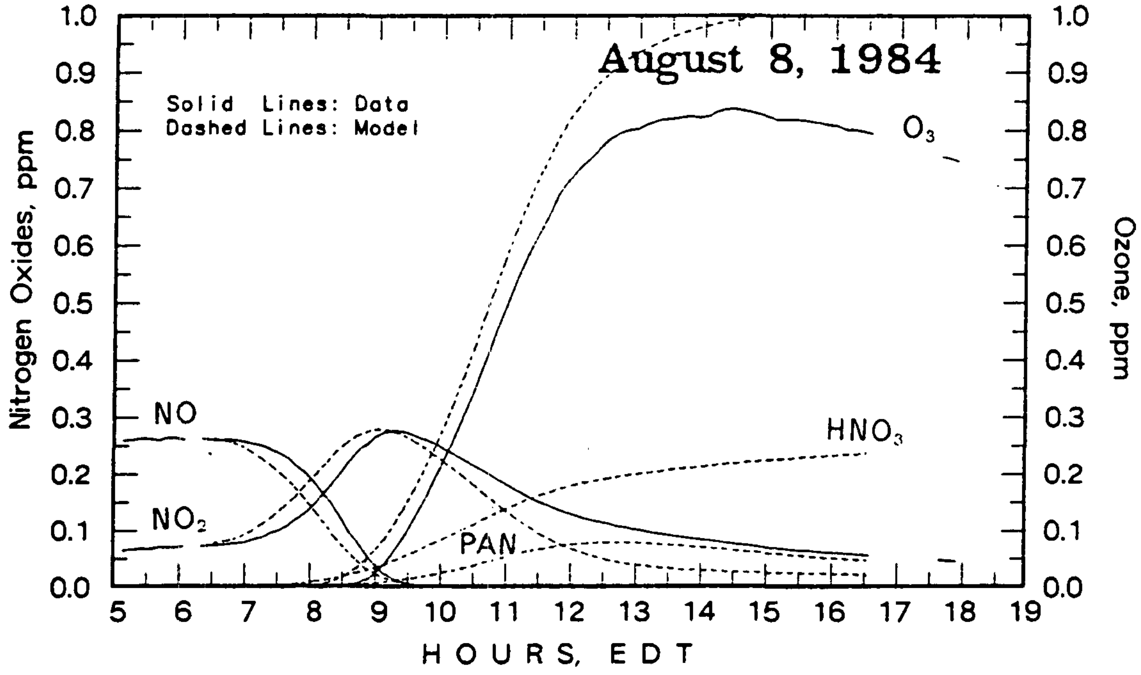


Figure 51. Extra Wall Conditions.
CBX model; 100 ppb Wall HCHO, 25 ppb Wall NOx, 5 ppb initial HONO; normal formation of HONO on walls.
Top: 1.32 ppmC SYNAUTO, no MeOH, 0.04 HCHO, no MeNO2
Bottom: 0.86 ppmC SYNAUTO, 0.3 MeOH, 0.06 HCHO, 3 ppb MeNO2



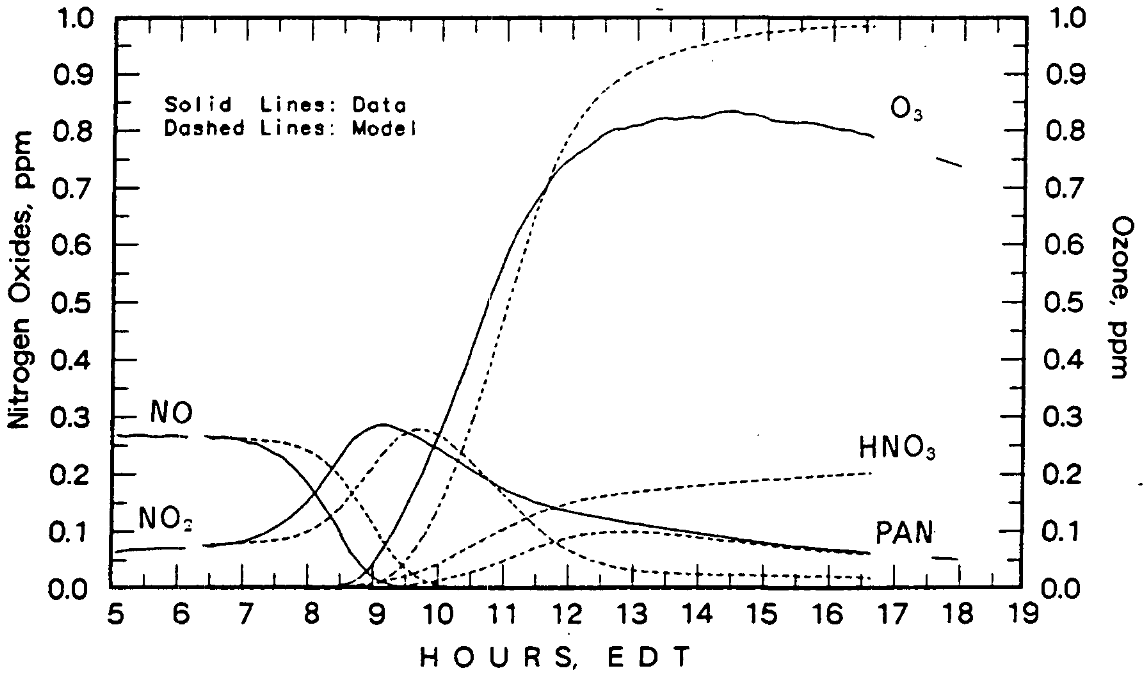
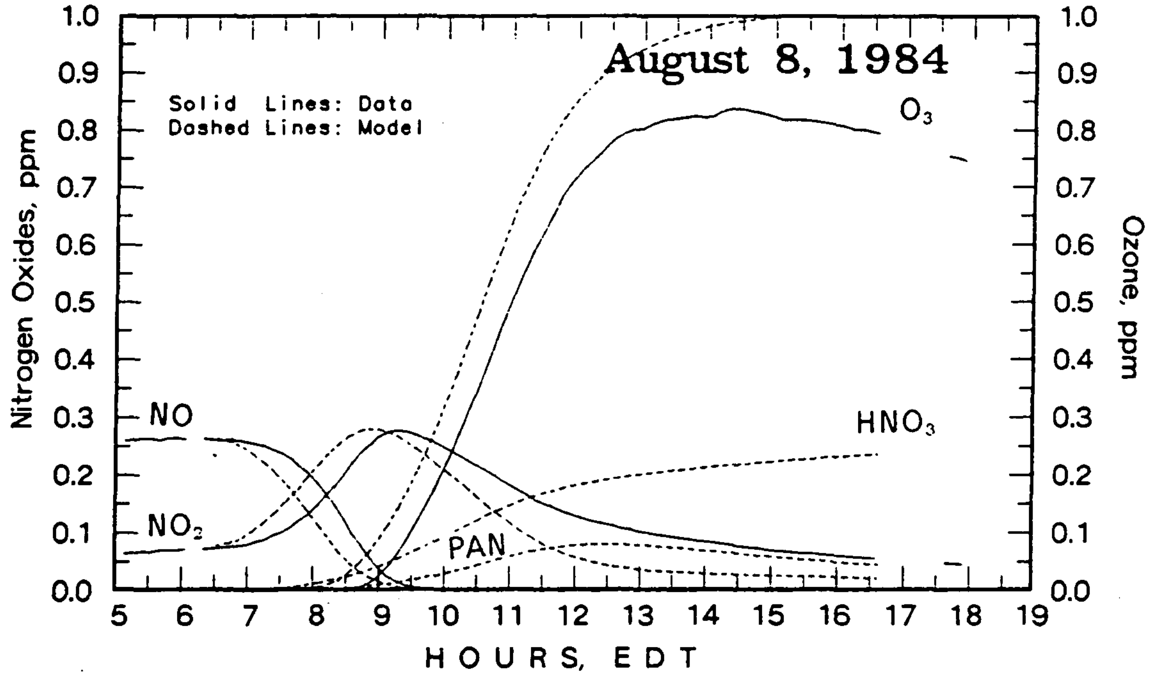


Figure 52. High Wall Conditions.
CBX model; 50 ppb Wall HCHO, 25 ppb Wall NOx, 0 ppb initial HONO; no formation of HONO on walls.
Top: 2.47 ppmC SYNAUTO, 0.79 MeOH, 0.23 HCHO, 10 ppb MeNO2
Bottom: 3.67 ppmC SYNAUTO, no MeOH, 0.06 HCHO, no MeNO2



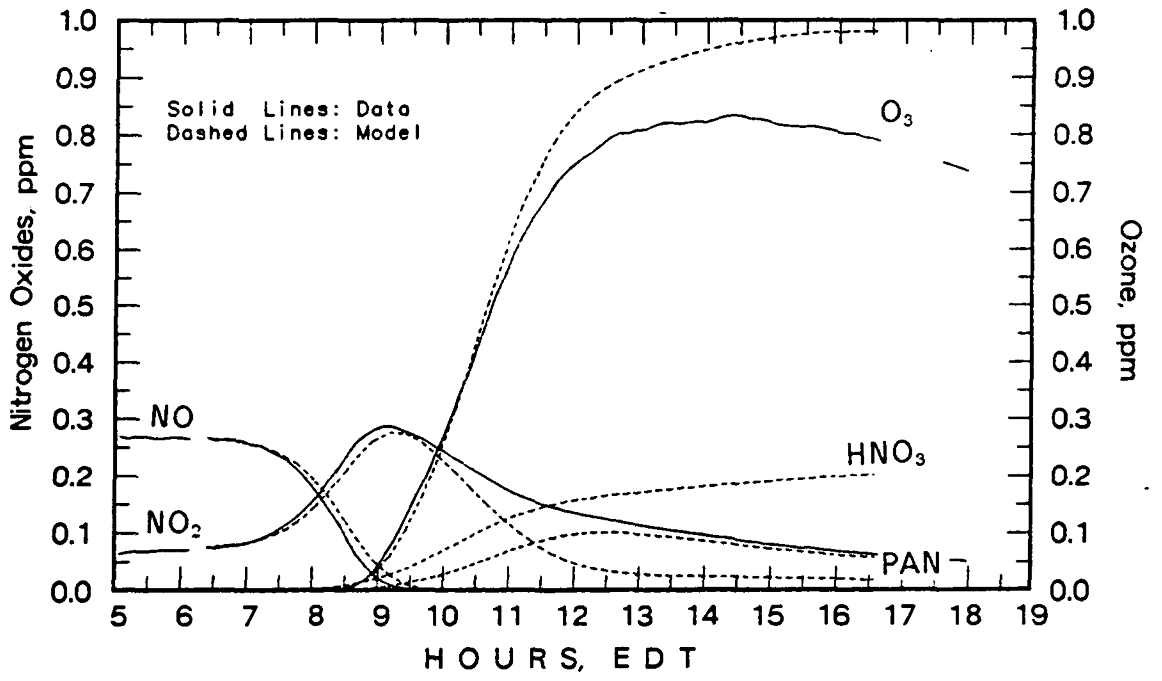


Figure 53. Extra Wall Conditions.
CBX model; 100 ppb Wall HCHO, 25 ppb Wall NOx, 5 ppb initial HONO; normal formation of HONO on walls.
Top: 2.47 ppmC SYNAUTO, 0.79 MeOH, 0.23 HCHO, 10 ppb MeNO2
Bottom: 3.67 ppmC SYNAUTO, no MeOH, 0.06 HCHO, no MeNO2

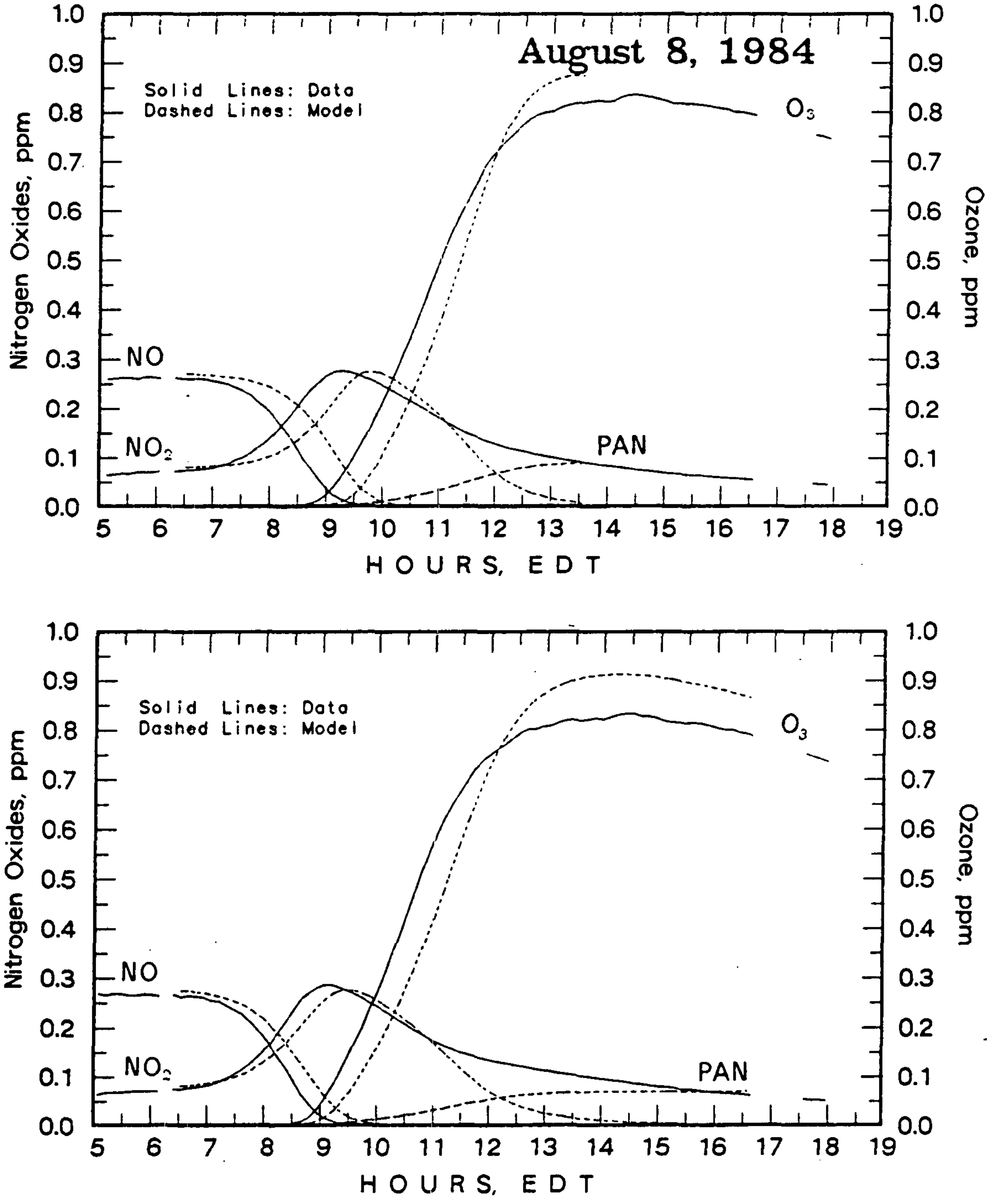


Figure 54. High Wall Conditions.
ALW model; 50 ppb Wall HCHO, 25 ppb Wall NOx, 0 ppb initial HONO; no formation of HONO on walls.
Top: 2.47 ppmC SYNAUTO, 0.79 MeOH, 0.23 HCHO, 10 ppb MeNO2
Bottom: 3.67 ppmC SYNAUTO, no MeOH, 0.06 HCHO, no MeNO2

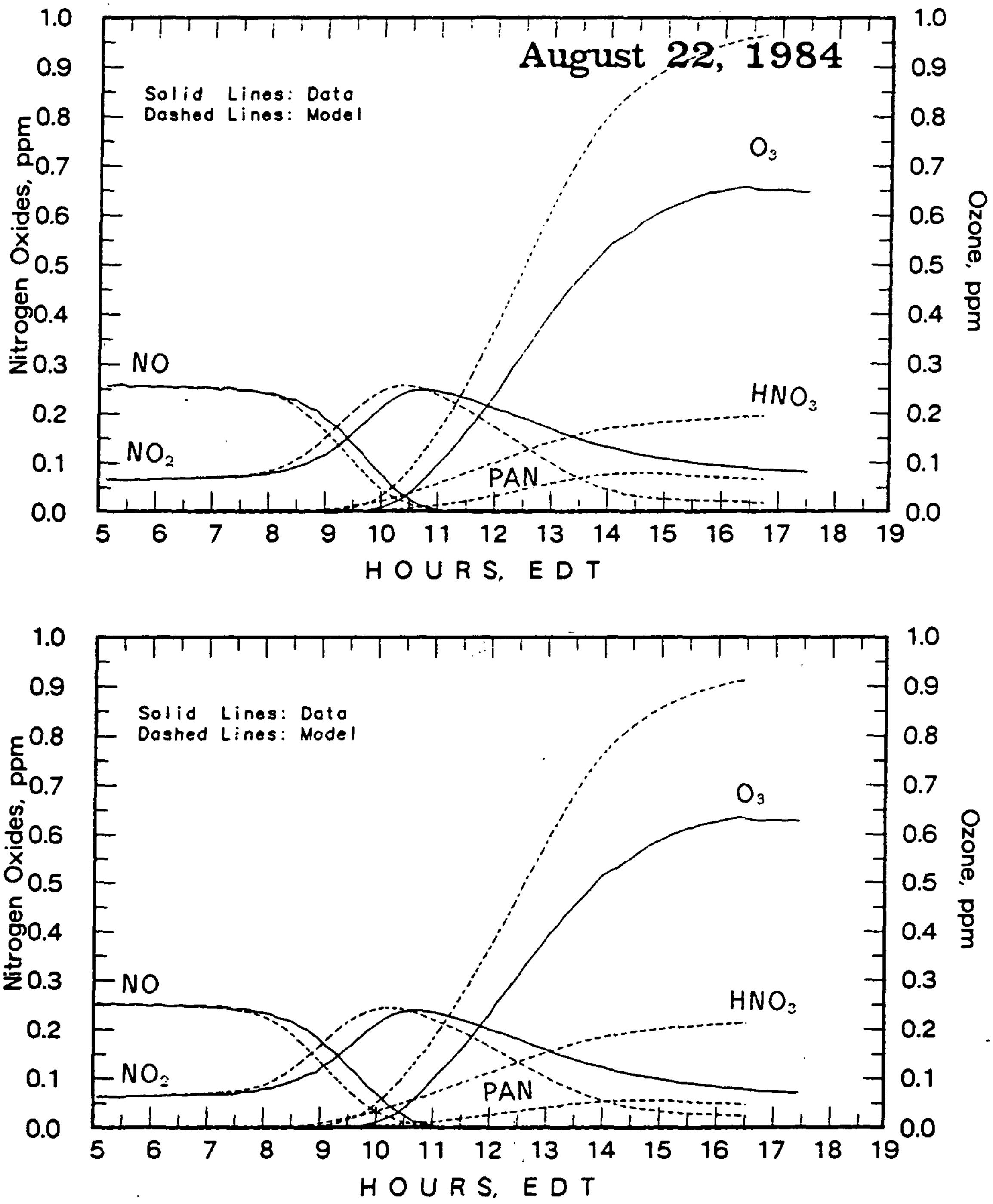


Figure 55. High Wall Conditions.
CBX model; 50 ppb Wall HCHO, 25 ppb Wall NOx, 0 ppb initial HONO; no formation of HONO on walls; no initial MeNO3 included on BLUE.
Top: 3.04 ppmC SYNURBAN, no MeOH, 0.06 ppm HCHO, no MeNO2
Bottom: 2.04 ppmC SYNURBAN, 0.87 MeOH, 0.13 HCHO, 10 ppb MeNO2

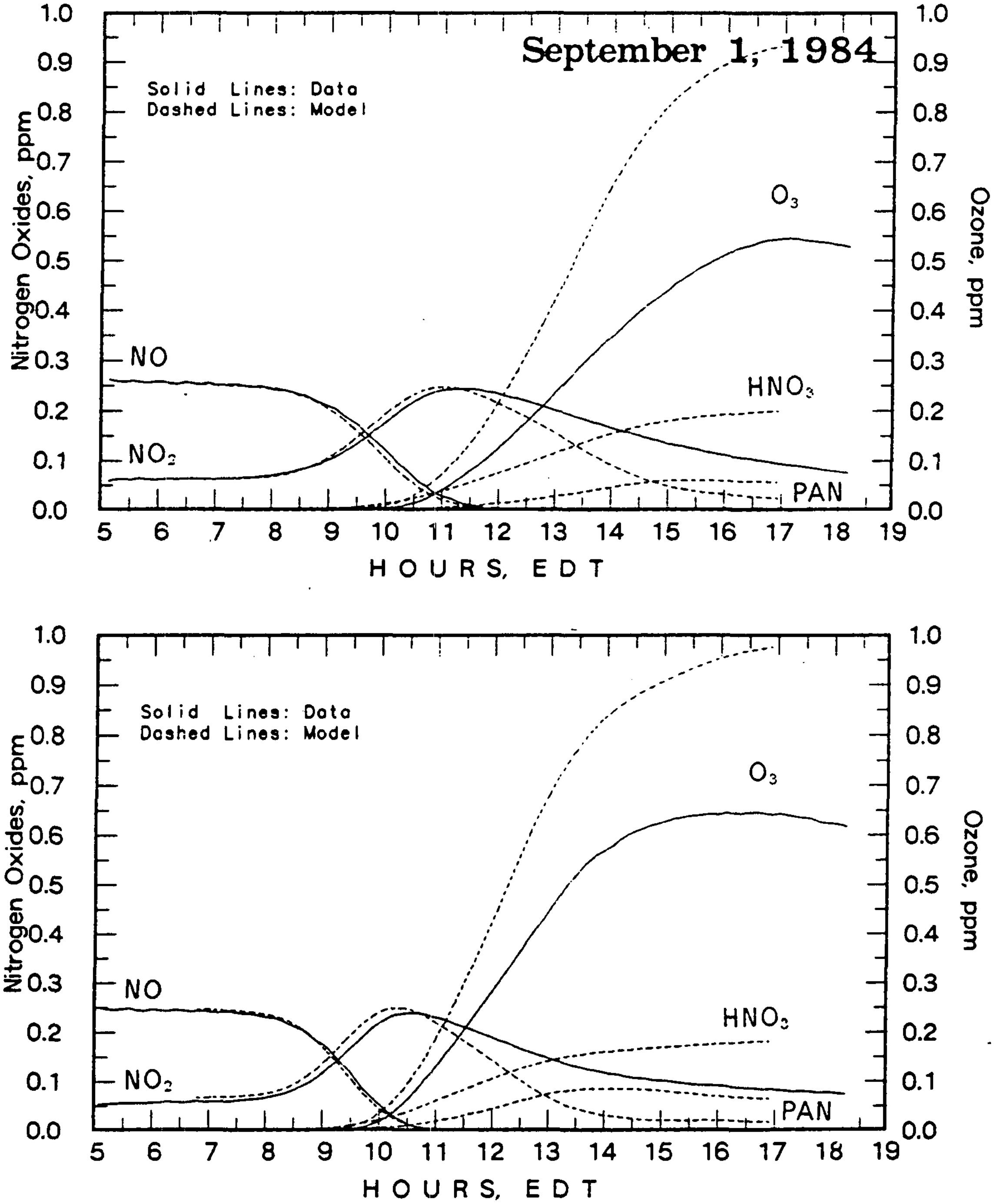


Figure 56. High Wall Conditions.
CBX model; 50 ppb Wall HCHO, 25 ppb Wall NOx, 0 ppb initial HONO; no formation of HONO on walls.
Top: 2.0 ppmC SYNURBAN, 1.0 ppm MeOH
Bottom: 3.0 ppmC SYNURBAN, no MeOH

6

Conclusions

This project clearly met its goals in terms of producing quality experiments designed to address the issue of methanol-exhaust reactivity:

1. Twenty-nine dual smog chamber runs were conducted. Eighteen of these experiments are satisfactory for model testing and fourteen are excellent, exceeding the estimates of the yield of good runs made in the planning memorandum. The other 11 experiments, while having poorer sunlight, which complicates model testing, are still quite useful to support the trends or directional effects of the substitution process.
2. Three different hydrocarbon mixtures were used:
   - SynAuto—a 13-component mixture developed by a series of direct comparisons of the reactivity of the mixture with automobile exhaust in side-by-side chamber experiments;
   - SynUrban—an 18-component mixture that conforms with the EPA recommended "default" mixture composition for use with the Carbon Bond Model in urban ozone control calculations; and
   - SynAutUrb—a 14 component mixture of intermediate reactivity between SynAuto and SynUrban.
3. Fifteen dual experiments were conducted with the SynAuto mixture; eight dual experiments were conducted with the SynUrban mixture; four dual experiments were conducted with the SynAutUrb mixture. *(In addition to these main experiments, there was one experiment with* UNCMIX *and one experiment with only the aromatic portion of the* SynAuto/SynUrban *mixture.)*

The major conclusions that can be drawn from this study are:

- Synthetic methanol exhaust substitution in these experiments never resulted in an increase in ozone maximum or a shorting of time to events over that of the reference side, even for a SynMethanol mixture with 20% formaldehyde.
- In experiments with 100% synthetic auto-exhaust with 3 ppmC on one side and 2 ppmC on the other side of the chamber (*i.e.* a 1/3 reduction), a 3–6% difference in the peak ozone was observed. In addition, the 2 ppmC side was slower in producing the ozone by about 60 minutes.
- In the 3 ppmC, 9-to-1 HC-to-NO_x ratio experiments with 100% synthetic auto-exhaust on one side and 2/3 synthetic auto-exhaust,1/3 synthetic methanol exhaust (with variable amounts of formaldehyde) on the other side of the chamber, no difference was seen between the two chamber sides for peak O_3 production. That is, the peak ozone in these experiments was essentially independent of the formaldehyde content of the synthetic methanol exhaust. This was because these system were limited by the amount of nitrogen oxides available, not by the amount or reactivity of the organic reactants. In these experiments, however, the systems were slower to produce ozone as formaldehyde in the synthetic methanol exhaust was decreased from 20% (almost no delay) to 0% (about 60 minutes delay).
- In the 1 ppmC, 3-to-1 HC-to-NO_x ratio experiments with synthetic auto-exhaust, a 32% reduction in peak ozone occurred when synthetic methanol exhaust containing 10% formaldehyde was substituted for 1/3 of the carbon in the synthetic auto-exhaust mixture.
- In the 3 ppmC, 9-to-1 HC-to-NO_x ratio experiments with 100% of the much less reactive synthetic urban mixture on one side of the chamber and with 2/3 of the synthetic urban, 1/3 synthetic methanol exhaust (with variable amounts of formaldehyde) on the other side of the chamber, no difference in peak ozone production or in time to events was seen between the two sides at the 20% formaldehyde level. At the 0% formaldehyde level, however, there was an 15% decrease in ozone maximum when methanol was substituted for synthetic urban mixture carbon. As in the synthetic auto-exhaust case, substitution of 100% MeOH for 1/3 of the carbon, resulted in essentially the same outcome as a reduction of 33% of the total carbon.
- In the 1 ppmC vs 0.66 ppmC experiments with 100% of the synthetic urban mixture, an 83% difference in peak ozone was observed.
- In the 1 ppmC, 3-to-1 HC-to-NO_x ratio experiments with 100% of the synthetic urban mixture on one side of the chamber and with 2/3 of the synthetic urban, 1/3 synthetic methanol exhaust (with variable amounts of formaldehyde) on the other side of the chamber, no difference in peak ozone production or in time to

events was seen between the two sides at the 20% formaldehyde level. At the 0% formaldehyde level there was a 50% reduction in peak ozone and at the 10% formaldehyde level there was a 30% reduction in peal ozone.

- The initial fraction of formaldehyde is the major factor in the reactivity differences seen in the experimental data.

Table 20 summarizes the relative ozone and time-to-events in the principal experiments.

The smog chamber conditions were designed to test models, not to duplicate the urban atmosphere. Large dilution and continuous injection are dominant factors in the urban atmosphere and neither of these processes were included in these experiments. Readers are cautioned about simple extrapolation of the results reported here to the urban atmosphere.

A limited amount demonstration model was conducted to show the utility of the data for model testing. General observations about the model performance are:

- Three photochemical mechanisms often used in control calculations when used to simulate both the synthetic auto-exhaust and the synthetic urban exeriments at different HC-to-NO_X-ratios, were able to reproduce the general trends in selected experiments. The absolute predictions of time to events and magnitudes of concentrations of secondary products such as ozone, nitric acid, PAN, and aldehydes, however, were poor for all models when using the usual assumptions of chamber characteristics. The newest model was used to simulate selected synthetic urban mixture experiments; its performance differed significantly between simulations of the synthetic auto-exhaust and the synthetic urban mixtures. It was generally too slow for the auto- exhaust mixture experiments and generally too reactive for the urban mixture experiments.
- The large majority of all the model simulation results were slower than the experiments, even with extreme assumptions of smog chamber wall processes. Increasing the initial reactivity *artificially* by the use of extremely high wall assumptions and radical sources, causes the models to agree with the data better in the first part of the experiment, but then when the mixture composition is changed these models greatly overpredict the ozone produced in the experiment.
- The relative responses of the models to substitution of methanol are in approximate agreement with the data. For example, if the model plots are laid over the data plots and slid to the left by 40 to 100 minutes, the model-data agreements for ozone and oxides of nitrogen are very good for the 1 ppmC synthetic auto-exhaust experiments.

- Until the mechanisms are tested with smog chamber data designed to test for the correct representation of the various components in the mechanisms, it is not possible to determine with certainty the cause of the differences between the model simulations and the chamber experiments described here. Further testing of these models is recommended.

Table 20. Summary of Relative Reactivity For Methanol Substitution.

		Change Relative to 100% Syn Mixture	
Date	Run Type	% O_3 red.	timing
	3 ppmC (9:1 HC-to-NO_x)		
AU06	2/3 SynAuto	6	slower
	2/3 SynAuto, 1/3 SynMeth		
JU26	0% HCHO	0	slower
JU25	10% HCHO	0	slow
AU08	20% HCHO	0	≈same
JN26	2/3 SynUrban	20	slower
	2/3 SynUrban, 1/3 SynMeth		
ST01	0% HCHO	15	slower
	10% HCHO	–	–
AU22	20% HCHO	0	≈same
	1 ppmC (3:1 HC-to-NO_x)		
AU05	2/3 SynAuto	42	slower
	2/3 SynAuto, 1/3 SynMeth		
	0% HCHO	–	–
AU07	10% HCHO	32	slow
AU09	20% HCHO	38*	≈same
ST02	2/3 SynUrban	83	slower
	2/3 SynUrban, 1/3 SynMeth		
AU28	0% HCHO	50	slow
AU25	10% HCHO	30	same
ST03	20% HCHO	0	slow*

* these days not clear sky conditions

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A

Facility Description

Chamber Description

Location

The site is approximately 32 kilometers from the University of North Carolina at Chapel Hill. It is in Chatham County, North Carolina and is approximately 10 kilometers from the small town of Pittsboro. Chatham County is one of the most rural, least industralized counties in North Carolina and is heavily wooded. The background concentrations of NO_x and nonmethane hydrocarbons are usually less than 5 ppb and less than 80 ppbC. More importantly, the air exhibits very low reactivity in the chamber.

Materials

The chamber surfaces are Fluorinated Ethylene Propylene (FEP) Teflon. The film's transmission in the UV and visible regions of the solar spectrum is excellent, and it has only a few absorption bands in the IR, a property necessary to reduce the "greenhouse effect". It has a very low permeability for most chemical species and can be heat-sealed to form large durable panels. For this application its worst property is its ability to hold a static charge for long periods of time. Type A film, 0.13 mm thick is used.

Physical Design

Inlet and outlet doors, stirring fans, manifolds and other fittings come in through a solid floor. The sides are free for light entry. The floor of the chamber is elevated approximately 1.2 m to allow for easy access under the chamber.

The design is an A-frame 9.14 m wide, 12.10 m long and 6.10 m high at the peak on a plywood floor 1.22 m above the ground. Wooden beams, 5.08 cm by 20.32 cm, located on edge at 99.1 cm centers form an exterior framework on top of the plywood floor. Continuous 16.46 m lengths of film are attached to the inside by aluminum u-channels, screwed firmly to the wooden beams, thus compressing the film against the external support. See Figure A1 and Figure A2.

One piece, heat sealed Teflon film panels are used in such places as the triangular end panels and floors. The floor-to-side seals are achieved by a 0.61 m overlap of side panel film over floor panel film. A rubber strip under the film and an aluminum strip over the top of the film complete the seal. All other seals are Teflon-to-Teflon under pressure of the aluminum u channel. A single unsupported heat sealed Teflon panel similar to the end panels is used to separate the chamber into two halves of equal volume. It is sealed to the floor and side panels in the same manner as described above. Aluminum foil is placed under the film on the floor to reflect the light and heat back up through the chamber. This is necessary to reduce solar heating of the air to a value that is within normal urban environments and to compensate for transmission losses through the Teflon film.

Orientation

The chamber is oriented with its long axis approximately north to south. The actual long axis orientation is along a 27–207 true heading. The orientation with respect to the sunrise and sunset at different times of the year and the altitude of the sun at noon for different times of the year are illustrated in Figure A3 and Figure A4.

Air Handling System

There are four air handling systems in each half of the chamber, one for exhausting, one for sampling, one for recirculating through dehumidifiers, and one for mixing. The exhaust system consists of two intake stacks, 0.61 m × 0.91 m intake doors, 0.61 m × 0.61 m exhaust doors, and an exhaust blower. The exhaust blower is a dual blower on a single shaft driven by a 1.5 horsepower motor. Air enters the system through the two 5.49 m high by 30.5 cm diameter stacks. This system is designed to permit rapid exhausting of chamber contents and replacement with ambient air. The filling rate is 7190 l/min. The chamber can be flushed with a 99.6% decay of initial contents in 2 hours.

The second air handling or manifold system is for sampling and injection of pollutant materials into the chamber halves. To insure representative sampling, a 3.17 cm I.D. glass manifold runs from a point 1.83 m above the floor in the center

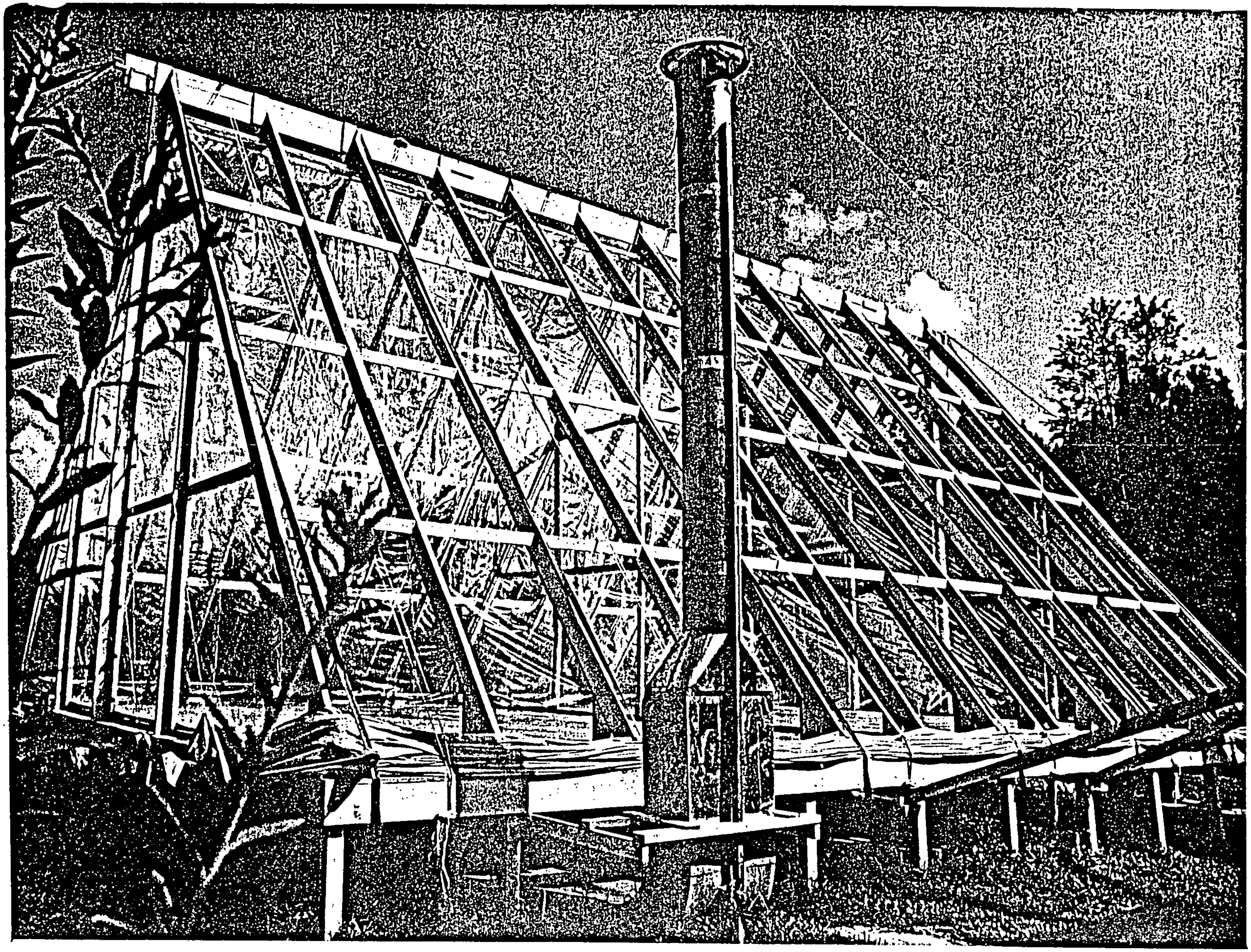

Figure A1. The University of North Carolina Smog Chamber. (Courtesy of the Greensboro Daily News)

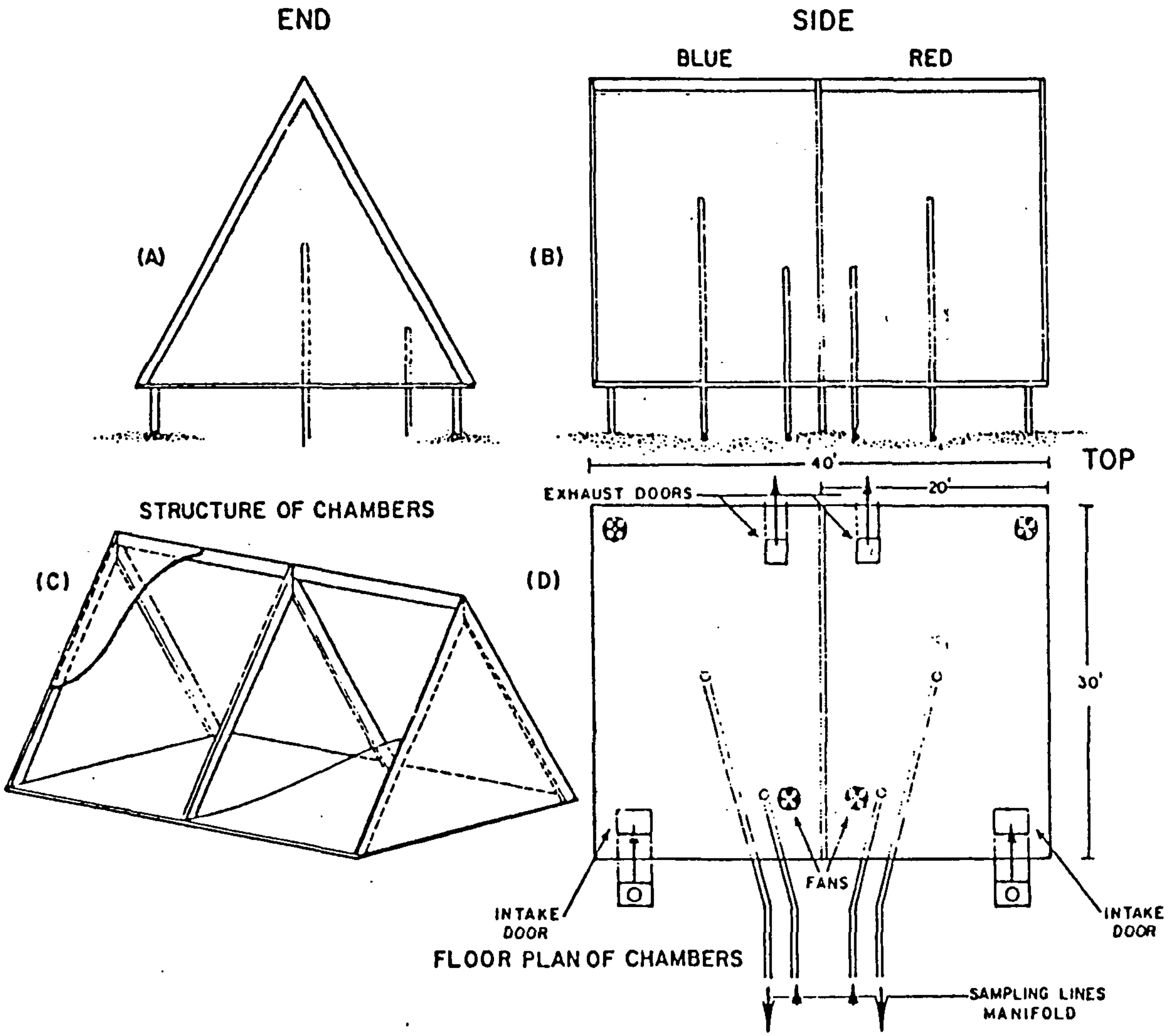

Figure A2. Schematic of UNC Outdoor Smog Chamber.

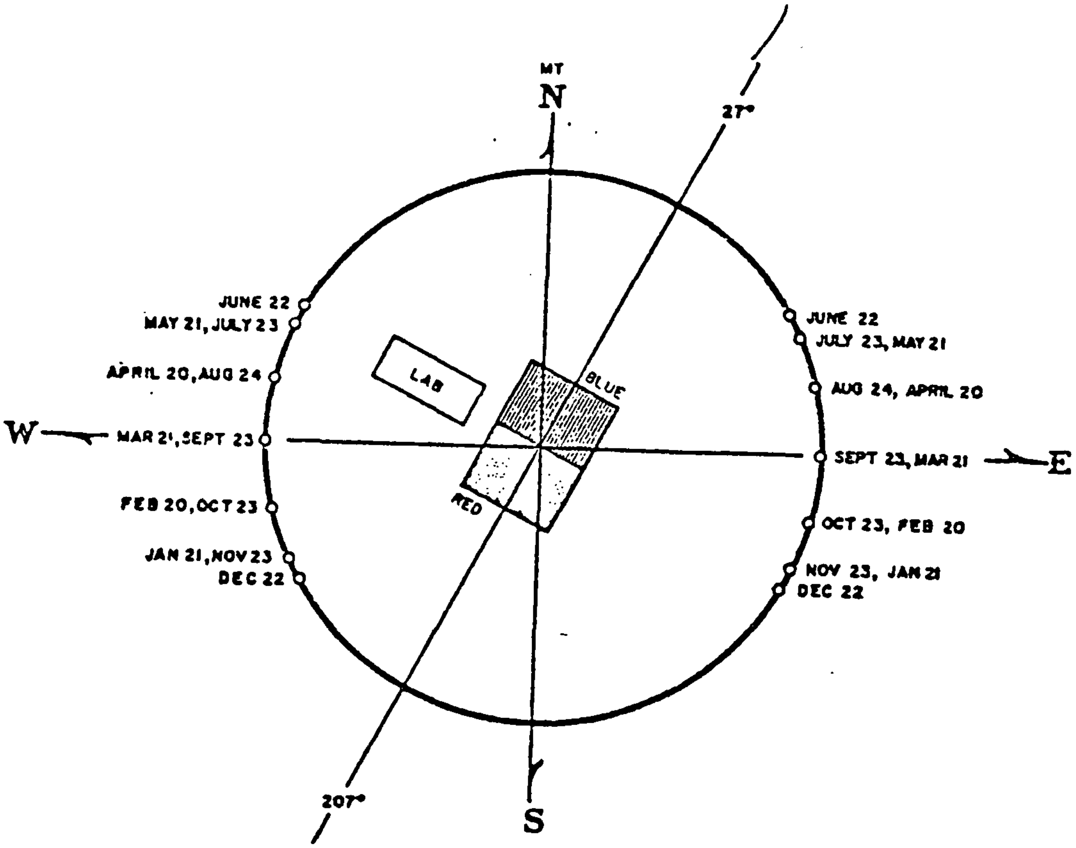

Figure A3. Orientation of UNC Outdoor Smog Chamber with respect to seasonal sunrise and sunset positions.

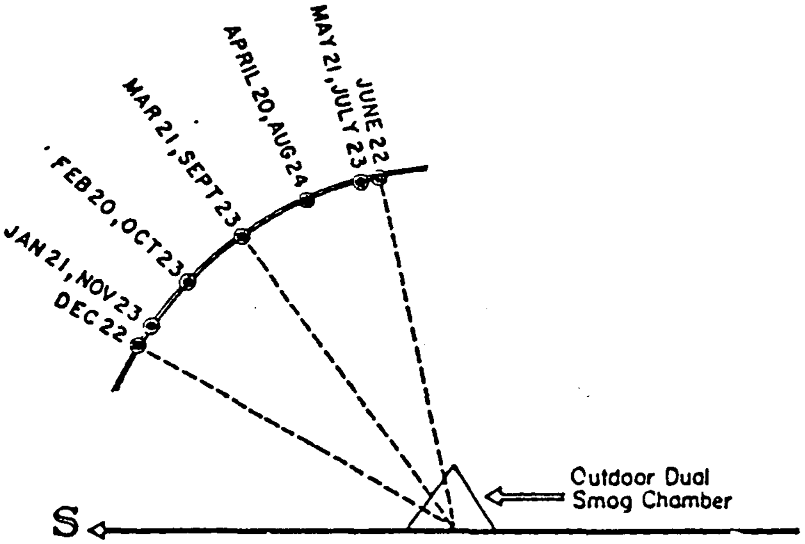

Figure A4. Solar altitude and zenith angle at noon at the UNC Outdoor Smog Chamber for each month.

of each chamber half down through the floor and over to a sampling laboratory. The sampling volume required by all the instruments does not exceed 5 lpm but to reduce losses due to long resident times it is necessary to have high flows in the manifold. The flow rate in the manifold is 60 lpm. The manifold system is wrapped with a controlled heating tape to maintain the sample slightly warmer than the chamber temperature. To avoid the necessity of makeup air, the sampling manifold is a closed loop. Squirrel cage blowers with housings and fans that are Teflon coated are used to circulate air through the manifolds. The unused sampler air is then returned through a 3.17 cm I.D. glass manifold to the chamber. These return manifolds provide a convenient method for injecting the initial reactants. There is also a special heated Teflon manifold for formaldehyde sampling.

Inside each chamber half are two mixing fans located in opposite corners. These provide circulation and mixing of the chamber contents. The fans are 50.8 cm diameter cast aluminum units that are FEP Teflon coated. They operate in a horizontal position, 0.76 m above the floor on 2.54 cm diameter Teflon coated steel shafts that extend through the chamber floor. Under the floor, 1/4 horsepower, 1750 rpm motors provide power through a belt and pulley system to each fan. Each fan operates at approximately 31.15 m^3/min.

Laboratory

The laboratory is adjacent to the chamber. It is a 3.66 m W by 15.24 m L by 3.05 m H temperature-controlled wooden structure oriented perpendicular to the chamber and 3.66 m away from it to avoid any shadowing.

The first 5.49 m nearest the chamber contain the instrumentation, manifolds, and calibration systems. At the sample inlet of each gas instrument is a three way Teflon AC solenoid valve. Since there are two intake manifolds (one for each chamber half), air from either manifold can be drawn through the three-way valve and into the instrument. In this manner timesharing of one instrument between the two chamber halves is possible.

The next 5.49 m contain the data acquisition computer system (described in the Data Acquisition System section) and the operations area. The last 4.27 m of the laboratory is a utility area with running water and storage facilities.

Gas tanks necessary to operate the instruments and perform calibration are located in a 1.22 m × 1.83 m room completely closed off from, but attached to, the laboratory. The injection system gas tanks and valves are housed in a second

1.52 m × 1.52 m well-insulated heated room adjacent to the end of the laboratory nearest the chamber.

Injection System

Pollutants are injected into the chamber sides via the return side of the sampling manifolds. The return manifolds enter the chamber sides under one of the mixing fans. The injection process uses gas cylinders containing pollutants at high concentration (1000–10,000 ppm range), two-stage stainless steel diaphragm regulators, on-off solenoid valves, and a precision needle valve. The flow rate of injected material into the manifolds is established by a mass flow meter with a 5 millisecond response time. The total injection volume is accurately controlled as a function of the time the solenoid valve is open. The open time of each solenoid valve is controlled by the computer system on command. Conditions can be varied sufficiently to have the injection time range from a few seconds for each component to 1–2 hours for a programmed injection used to simulate the buildup of pollutants in urban areas.

Data Analysis, Validation and Reporting

Data Acquisition System

A computer based data acquisition and control system (DAS) is used to acquire, process and record data for the chamber instrument system. The complete system is shown schematically in Figure A5.

Output signals from each instrument are wired to a crossbar scanner (or analog signal multiplexer). Under control of programs in the computer, the scanner connects the selected signal leads to the input of the digital voltmeter. The digital voltmeter, which has excellent noise and spurious signal suppression and can measure a 1 volt signal with a resolution of 10 microvolts, is triggered to acquire a reading and to supply the 5–1/2 digit binary coded decimal number to the computer. The computer processes the information and then commands the scanner to move to the next channel and repeat the process. Further data processing is described below in the Data Treatment Procedures Section. The timing of the computer processes is under the control of a digital date and time-of-day clock which signals event times to the computer. Another digital timer operates the Teflon solenoid valve on the inlet of each instrument to connect the instruments to one chamber half during a given cycle of data acquisition.

This system provides fully automatic acquisitions and processing of data during a run and provides the operator with immediate, full data in physical units. Given

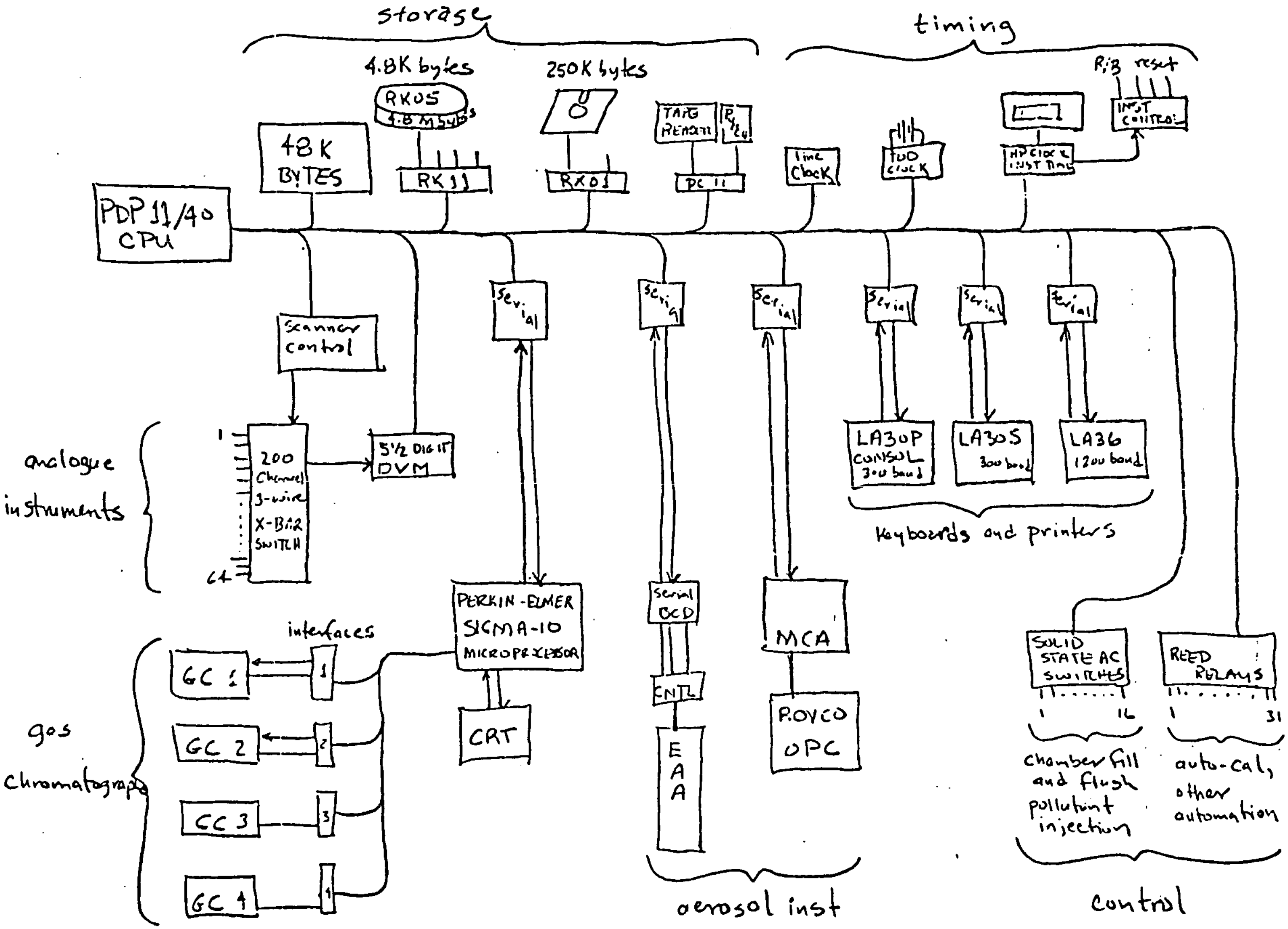

Figure A5. Data Acquisition and Control System.

this information about what is happening, the operator can then concentrate on what he wants to do. It also allows the massive amount of information generated during a run to be processed in a more effective manner after the run is over.

Standard Operating Procedure

Most experiments are initiated early in the morning by the site computer according to a detailed set of commands that have been programmed the night before. Prior to an experimental run the computer is programmed to automatically purge the chamber overnight with background ambient air. Several hours before dawn the DAS begins recording measurements of the background concentration. Single instruments are timeshared on an alternating four minute cycle between the two sides. The chamber intake and exhaust doors are then sealed by the computer and the drying fans in each side of the chamber activated to reduce humidity and minimize chamber wall effects. Finally, the initial concentrations of reactants of interest are injected before sunrise. To do this, the computer selects the proper tank and calculates the correct time to achieve the desired initial concentrations. Injections are normally short "slug" injections; most experiments have initial hydrocarbon, NO, and NO_2. Monitoring of the chemical and physical species mentioned earlier continues usually until 1900 EDT when the experiment is terminated. The computer then performs several close-down procedures, including turning off certain instruments, opening chamber vent doors, and turning on the exhaust fan to purge the chamber. If instructions for the next experiment have not been programmed during the day, the operator does so at this time.

Variations of the standard operating procedures include: 1) not changing humidity before the experiment, 2) injecting pollutants slowly during the experiment, 3) diluting the chamber(s) during the experiment to simulate mixing height profiles, 4) transferring the contents of one chamber side to the other, and 5) injecting initial conditions into the chamber containing part or all of the product of a day-old experiment. Most pollutants are injected from high concentration gas cylinders (10,000 ppm) which can be controlled by the computer. Some pollutants are liquids with vapor pressure too low to have a high vapor concentration cylinder prepared, and are injected manually. Carefully measured samples are heated in a U-tube in which warm zero air is passed through to the return manifold.

Data Treatment Procedures

General

The operations are carried out on four different computers and the Broomall plotter.

The PDP 11/40 is at the chamber site and is responsible for acquiring the data. The LSI/11, the VAX, the IBM 370/360, and the Broomall plotter are on campus grounds, and complete the data treatment procedure after a run.

During A Run

DATCOL and DATRAN are written in assembly language and PASCAL. DATCOL performs several functions, such as accepting instructions from the keyboard and interpreting a command file which prepares the chamber, makes injections, turns on the necessary instruments, and finally purges the chamber and turns off the instrumentation at the end of the experiment. Command files can be written in an easily readable English text style. An example is shown in Figure A6. DATRAN translates this file into a format which DATCOL can interpret. DATCOL also controls the data acquisition process, and records:

1) the instrument analog outputs;
2) the GC files produced by the Perkin Elmer Sigma 10 GC integrator and processor;
3) the adjustment file (computer readable instructions for data adjustment); and
4) the comments files,

all on the RK05 hard disk. It also maintains status information to restart and continue an experiment after a power failure.

The operator has several choices for printing data with DATCOL. He can have the data printed during the whole experiment, print data for only selected times during the experiment, have earlier data printed, or not print data at all.

The operator can also, at any time during the experiment, enter through the keyboard information such as calibration corrections for any instrument or that an instrument is not functional and for what time interval this information applies. This type of information is entered by DATCOL into an Adjustment file. This file can be read and interpreted by other computers and can be directly applied to correcting and processing data in later steps. The operator can at any time also enter general comments through the keyboard which DATCOL stores in a Comment file. Such information, when transferred along with the digital data, greatly aids in processing.

Strip charts are operated for almost every instrument as a back-up to the computer.

```
 RUN DX1:DATRAN
SPECIFY OPTIONS DESIRED (AS option,option,option <CR>):   GAS
INJECTION TANK VALUES AS OF: 27-SEP-79
GAS     CONC(PPMC)   FLOW(L/MIN)
NO        10700.          6.
NO2       20500.         10.
PROPYL    21396.         10.
UNCMIX    10471.         10.
ETHYL1     2028.         10.
N2      1000000.         10.
AUTOMX    10487.         10.
ACETAL     4110.         10.
BUTAN1    92400.         10.
BUTPPL    11456.         10.
CO       100000.         10.
PROPAN    22068.         10.
ETHYL2    20663.         10.
BUTAN2    20760.         10.
SOURCE FILE NAME?   FEB1
DATE OF RUN (AS dd-MMM-yy):   1-FEB-80
ERRORS ARE FLAGGED BY [NN]

 [THIS IS AN ACTUAL EXAMPLE RUN]
 IMMED VENT; CLR CHARTS;
 AT 3:30 SET CHARTS; OSC 35 ON 45 SEC EVERY 15 MIN; [CO]
 AT 3:50 CLOSE;
 AT 3:59 SET 6; [CARLE 1 AND 2]
 AT 4:00 UNTIL 19:20 START DVM;
 AT 5:00 INJECT NO 13 TO 400 PPBC IN BOTH PURGE;
 AT 5:10 INJECT UNCMIX 10 TO 4 PPMC IN BOTH PURGE;

    [ 1]          WARNING- INJECTION TOO LONG, BEING SPLIT
    [ 2]          WARNING- INJECTION TOO LONG, BEING SPLIT

 AT 5:30 INJECT NO2 12 TO 100 PPBC IN BOTH PURGE;
 AT 19:20 VENT; HALT;
 RSTART 0:00 VENT; CLR CHARTS;
 RSTART 3:30 SET CHARTS; CLOSE;
 RSTART 3:30 MOD 1 OSC 35 ON 45 SEC EVERY 15 MIN;
 RSTART 4:00 START DVM;
 !
```

Figure A6. Sample DATCOL Command File.

Data Processing Steps

Data processing involves three types of staff

- **Project Coordinator (PC)**—senior staff, makes judgements about data quality, decides on calibration factors, gives directions to other data processing staff; uses computer run tracking system to direct attention of PPs and to CTs to work that is needed by indicating the status of processing in the run tracking data base;
- **Peak Peaker (PP)**—seasoned staff, skilled at converting strip chart peaks into computer files using a high-resolution electronic digitizer pad connected to a computer; throughly familiar with the data output of each chromatograph; makes plots of digitized data for QA by PC; corrects picking mistakes by examining the raw data plots; basically works independently using computer reports from run tracking system to indicate needed work; updates run tracking system to move work to next stage;
- **Computer Technician (CT)**—staff, highly skilled at use of various computer systems (LSI-11/23, IBM PC, VAX-11/780, IBM 4341), with a through knowledge of file transfer and storage among these systems; responsible for running programs that read and convert site floppies into input for other processing programs; responsible for creating, naming, and backing up to magnetic tape all data files on all systems; in addition, the CT is usually an apprentice processing program developer and maintainer.

Data processing is organized by the type of data. The major processing effort occurs for the chromatographic type instruments. Data processing for the continuous instruments (DVM data) is less difficult than the chromatographic instruments, because the data come from the site in digital form. Both of these processing streams, however, depend upon having calibration factors to convert the voltages and raw displacements into physical units of concentration.

The "auto-cals" can be automatically stripped from the DVM data by the CT who moves the data from the site floppies. These stripped cals can be processed rather quickly by computer programs once the calibration source concentrations are known. The chromatographic calibration data, however, must be examined by a PC, picked by a PP, and stored by a CT to await the development of calibration source concentrations. Furthermore, each instrument may have 10 specie calibration factors.

Table A1 illustrates, in a flowchart, the stages in processing the GC instrument data. The flow of processing in these charts is from left to right. The three letter codes describe events in processing the data and the lines indicate which events depend on other events having occurred. As the processing events occur, the three-letter codes are entered into the on-line run processing tracking system by whoever did the step. Simple commands allow the PC, PP, and CT to create appropriate printed reports showing which runs and which instruments are at which stages of processing.

Table A2 similarly shows the flowchart for processing DVM data. Some of the processing steps for the DVM "auto-cal" data occurs on this chart also. The same program that makes the "Raw Plot" also strips the "auto-cals" into a separate file (the ACS–Auto Cals Stripped—event on the chart). These data are then processed by a program that results in a data file of instrument span responses and instrument zero values for the O_3 and NO_x monitors. An example list of these will be shown in the next section.

Once the actual run concentrations are known for both the HC and the NO_x, the run documentation, to be included in the combined data file, can be written. Here all aspects of the run are drawn together to provide a description of the run, its quality, problems, and outcome.

Table A3 illustrates the events in the documentation and in the creation of a single *segmented* file containing all the data for the run in a uniform format.

Table A1.

Processing System for Instrument Data

```
    !NTB!
   /
tot inst  __ cal processing_
   \     /                   \
    !PID!                   !CFD!        <HRU>__
        \                        \     /        \
         \                        <CRU> -------- !CQA!---- (F2V)---- (V2U)
          \                      /
          <PRU>---- <FPT> --!PQA!
```

```
!sss! == stages determined by Project coordinator (PC)
<sss> == stages determined by Peak Pickers (PP)
(sss) == stages determined by Computer Techs (CT)
```

Pers	RUNENTRY stages	Meaning
PC	PID : Pick inst det	Charts marked, Inst status sheet in folder
PC	NTB : Not to be proc	No futher processing marked on Inst Status sheet
PC	CFD : Cal fac det	Cal factors for each comp entered on Inst status sheet in folder
PP	PRU : Pick run	Data has been digitized and P-file exists
PP	FPT : FPlot done	P-file has been plotted and plot is in folder
PC	PQA : FPlot QA	Fast plot has been marked OK (no bad data points in P-file)
PP	CRU : CALCON run	C and K files exist on floppies
PP	HRU : HCANAL run	HC analysis printout in run folder
PC	CQA : Comp CS QA	Instrument QA completed on C and K files Initial Conditions updated
CT	F2V : File 2 VAX	C and K files moved to VAX
CT	V2U : Ready 2 merge	C files merged together, K files merged together
PC	BAD : Stop processing	Something is wrong with this data

Table A2.

Processing System for DVM Data

```
  cal processing
  /            \
 tot runs       (CFS)-------
  \             /           \
   \        (ACS)            \
    \       /                 \
   (URU)------(RPC)----!PQA!-<DRU>--!CQA!--!R2M!
        \                     /
        (UTV)                /
            \               /
            (V2T)-------
```

```
!sss! == stages determined by Project coordinator (PC)
<sss> == stages determined by Peak Pickers (PP)
(sss) == stages determined by Computer Techs (CT)
```

DVM data processing steps

Pers	Step	Meaning
CT	URU : Unpack run	Site floppy data expanded to ASCII Ufiles
CT	U2V : Data to VAX	Ufiles moved from LSI disk to VAX
CT	V2T : to archive tape	Data moved from VAX to tape
CT	RPC : Raw Plot done	Plot of voltages to examine data
PC	PQA : Plot QA	Initial quality check
CT	ACS : AutoCals strip	Cals separated for processing
PC	CFS : Cals done	Calibration factors determined
CT	DRU : DVMFIX run	Voltages changed to concentrations
PC	CQA : Conc QA	Concentration Quality Assurance
CT	R2M : Ready 2 merge	Merge process on VAX can be run
PC	NTB : Not to be proc	Not to be processed
PC	BAD : Stop processing	Something is wrong with this data
CT	NDV : No DVM data	

Table A3.

Documentation and Final File Production Steps

DOCUMENTATION data processing steps

Pers	Step	Meaning
PC	SUM : Run sum done	DVM, Instrument, and Raw Quality Combined.
CT	D2V : Doc to VAX	Documentation transferred to VAX
PC	DQA : Doc QA	Documentation Quality Assurance

FINAL FILE data processing steps

Pers	Step	Meaning
CT	MR3 : Merged 3 sect	Merge pieces to final file
CT	ALT : Files to tape	Ascii labeled tape made
CT	FPC : Final plot done	Correct conc plot made
PC	FQA : Final QA	Final Quality Assurance
PC	NTB : Not to be proc	
PC	BAD : Stop processing	Something is wrong with this data

GC Calibration Processing

The GC instrument calibration processing is complex enough to require its own tracking system. Table A4 gives the flowchart for these calibration data.

A major time-consuming task on this chart is the Official Calibration Source (OCS) event. This event signals the existence of an OCS form that names a source and describes the concentration of each specie in the source. These paper forms are the results of the manual calibration comparisons described above. Filling out the form requires extensive analysis and reconciliation to arrive at a *certifiable* set of concentrations in the calibration sources. The OCS form requires the validation date and name of the individual certifying the calibration source.

These OCS values are entered into another data base and appropriate S-files (source concentration) files are created. These are used as input to the CALFAC program to match the instrument responses (stored in R-files by the PP) with the calibration sources to compute the calibration factors for each species. These calibration factors are, in turn, entered into another data base and its output is a file of calibration factors that are subjected to graphical and statistical analysis by the CALANA (calibration analysis) program. Using these plots and statistics, and other information such as the manual injections, and previous calibrations calculated for runs nearby, the PC selects a calibration factor for each instrument-species.

The actual calibration factors used in processing the runs are entered into another data base and reports of these are available for plotting and further analysis. The actual factors are also included in the automatic program documentation produced by the DVMFIX and CALCON programs (K-files) and are included as a permanent part of the documentation section of the segmented file.

Table 4

Processing System for Instrument Auto-Calibration Data

```
tot inst    cal analysis
      \   /            \
      !CPI!            !OCS!
          \                \
           \                \
            <DPR>----------<CFR>--(Q2V)--(DTR)--(C2L)--<CLR>--!CQA!
```

!sss! == stages determined by Project coordinator (PC)
<sss> == stages determined by Peak Pickers (PP)
(sss) == stages determined by Computer Techs (CT)

Step	CALENTRY stages	Meaning
PC	CPI : CAL pick Inst	Charts marked, cal status sheet in folder
PP	DPR : Digpik run	Cal data digitized and R-file exists
PC	OCS : OCS ok	Official Cal Source exists in DTR
PP	CFR : CALFAC run	Cal Factor computed, Q-file created
CT	Q2V : Qfile to vax	Q-file moved to VAX
CT	DTR : DTR file updated	Cal Data added to DTR data base
CT	C2L : Cals to LSI	DTR CAL file loaded on LSI-11
PP	CLR : CALANA run	Cal Factors analyzed
PC	CQA : Cal QA	Cal Factor Quality Assurance
PC	NTB : Not to be proc	Not to be processed
PC	BAD : Stop processing	Something is wrong with this run

B

Analytical Methods

Introduction

The analytical instrumentation in the gas laboratory adjacent to the large outdoor chamber at UNC includes: six packed column and two capillary gas chromatographs for hydrocarbon, organic nitrate, and inert tracer analysis; one liquid chromatograph for DNPH-aldehyde analysis; an automated wet chemical formaldehyde instrument; two ozone and NO_x chemiluminescent monitors; and one UV ozone photometer. The laboratory also contains all of the associated calibration systems used for these instruments. In addition, solar and UV radiation sensors are mounted on top of a 7 meter tower next to the laboratory. Chamber temperature measurements are made with an inline thermistor located in the inlet of each chamber sampling manifold. The manufacture and calibration methods for all of these systems are listed in Table B1 and Table B2. A list of the species measured on each site instrument is given in Table B3.

Hydrocarbons

Total hydrocarbons (THC), methane (CH_4) and carbon monoxide (CO) are analyzed with a Beckman 6800 gas chromatograph. Figure B1 shows a typical Beckman 6800 measurement cycle. This cycle occurs every 5 minutes and each side of the chamber is sampled for 30 minutes. Unfortunately, methane responds differently than nonmethane HC on this type instrument requiring a separate methane calibration as well as a NMHC calibration.

A manually operated six port Carle mini-valve (Carle Instruments, Inc., Anaheim, Calif. Model Mk. II, Cat. No. 5621) on a Carle 211 gas chromatograph (desig-

Table B1. Analytical Methods, Characteristics, and Operation Methods

Substance	Method	Manufact and Model	MDC	Range	Mode	Time Shared
O8	Chemiluminescence	Bendix 8002	0.001	0-2	Continuous	Yes
NO, NO_x, NO_2	Chemiluminescence	Bendix 8101-B	0.005	0-1	Cyclic, 4 min	Yes
HC's alkenes,alkanes, aromatics	Automated multiple column GC-FID	Carle 211	0.005-0.010	0-100	Cyclic, 15 min	Yes
THC, CO, CH4	Automated multiple column GC-FID	Beckman 6800	0.010	0-80	Cyclic, 15 min	Yes
HCHO	Automated Colorimetic(reverse West-Gaeke)	CEA 555	0.01	0-2	Continuous	Yes
Acetaldehyde, propionaldehyde, MEK	Automated multiple column GC-FID	Carle 211M	0.02-0.05	0-100	Cyclic, 80 min	Yes
Aromatics HC, aromatic aldehydes, phenols	GC-FID	Perkin-Elmer 900	0.010	0-100	Manual	Yes
Halocarbon tracers	GC-EC variable freq. pulsed bais detector	Analog Tech. Corp.	0.0004	0-1	Cyclic, 30 min	Yes
PAN and Alkyl nitrate	GC-EC DC based EC Model 940	Varian Aerograph	0.0003-0.0008	0-1	Cyclic, 80 min	Yes
HNO8	Chemiluminescence, molybdenum converter, nylon scrubber	Bendix 8101-B	0.008	0-1	Cyclic, 15 min	No
H2O2	sample taken manually with bubbler; analysis using automated chemilum. method		0.0001	0-1	Manual	Yes
Temperature	Thermistor	YSI	0.2°F	20-110°F	Continuous	No
TSR	Pyranometer	Eppley Black and White	0.001 Langly	0-2 Langly	Continuous	No
UV	Pyranometer	Eppley UV	0.1 mLangly	0-100 mLangly	Continuous	No
Dew Point	Cooled mirror	EGandG 880	0.1°F	-40 to 120°F	Continuous	Yes

Table B2. Calibration Sources for Gases

Species	Source	Calibration Method	References
O_3	UV-quartz O_3 generator	UV photometry Dasibi Model 1008-AH	EPA
NO	Cylinder O_3 UV photometry	Certified commercial analysis and transfer via Gas Phase titration	EPA
NO_2	Oxidaton of NO	Gas Phase Titration	EPA
CH_4, CO, THC	Cylinder	Certified commercial analysis	EPA
HC's	Cylinder	Certified commercial analysis	EPA
HCHO	paraformaldehyde and 37% HCHO	Prepared static calibration standards verified with chromotropic acid bubbler technique	
Acetaldehyde, propionaldehyde, MEK	pure compounds	Prepared static calibration standards	
Aromatics	pure compounds	Prepared static calibration standards	
PAN	PAN purified	Reference method and transfer standard	Winer, A. *et al.* EST **8** p1116, (1974)
Alkyl nitrates	pure alkyl nitrates	Prepared static calibration standards	
HNO_3	HNO_3 (gaseous)	Dynamic source (gas) calibrated by colorimetric (chromotropic acid) bubbler method	Spicer, C., Adv. Envr. Sci. and Tech. **7** p163 (1980)
H2O2	liquid H2O2	Liquid standards and iodometric analysis	

Table B3.

Species Measured by Major Site Instruments

- Bendix Ozone Monitor
    - ▷ Ozone
- Bendix Nitrogen Oxide Monitor
    - ▷ nitric oxide, NO
    - ▷ nitrogen dioxide, NO_2 and PAN
    - ▷ sum, NO_x
- CEA Formaldehyde Monitor
    - ▷ formaldehyde
- Carle I FID Gas Chromatograph
    - ▷ C_3 to C_8 alkanes
      e.g. propane, butane, isopentane, pentane, 2-methylpentane, 2,2,4-trimethylpentane, octane
    - ▷ C_6 to C_8 aromatics
      e.g. benzene, toluene, m-xylene
    - ▷ C_2 to C_8 alkenes
      e.g. ethylene, propylene, 1-butene, cis-2-butene, trans-2-butene
    - ▷ acetylene
    - ▷ Total Hydrocarbon
- Carle II FID Gas Chromatograph
    - ▷ methane
    - ▷ ethane
    - ▷ propane
    - ▷ ethylene
    - ▷ propylene
    - ▷ acetylene
    - ▷ acetaldehyde
    - ▷ propionaldehyde
    - ▷ acetone
    - ▷ methylethylketone

Table B3.

- Carle III FID Gas Chromatograph
  - ▷ C_3 to C_5 alkanes
    e.g. propane, butane, isopentane, pentane
  - ▷ C_3 to C_5 alkenes
    e.g. ethylene, propylene, isobutene, 1-butene, cis-2-butene, trans-2-butene
  - ▷ C_8 to C_{10} alkanes
    e.g. octane, 2,2,4-trimethylpentane
  - ▷ C_6 to C_9 aromatics
    e.g. benzene, toluene, m-xylene, o-xylene, 1,2,4-trimethylbenzene
  - ▷ methanol
- Varian ECD Gas Chromatograph
  - ▷ PAN
  - ▷ alkylnitrates
  - ▷ biacetyl
  - ▷ tracers
    e.g. CCl_4, C_2Cl_4, $C_2Cl_3F_3$
- Perkin Elmer 900 FID Gas Chromatograph
  - ▷ C_6 to C_{12} aromatics
  - ▷ aromatic oxygenates and nitrogen-containing products
- Perkin Elmer Sigma 2 FID Gas Chromatograph
  - ▷ C_3 to C_{12} alkanes
    e.g. propane to dodecane
  - ▷ C_3 to C_6 alkenes
    e.g. propylene to hexene
  - ▷ C_6 to C_{12} aromatics
    e.g. benzene to dimethylnapthalene
  - ▷ aromatic oxygenates and nitrogen-containing products
- Beckman 6800 NMHC, Methane and CO FID Gas Chromatograph
  - ▷ Total Hydrocarbon
  - ▷ methane
  - ▷ CO

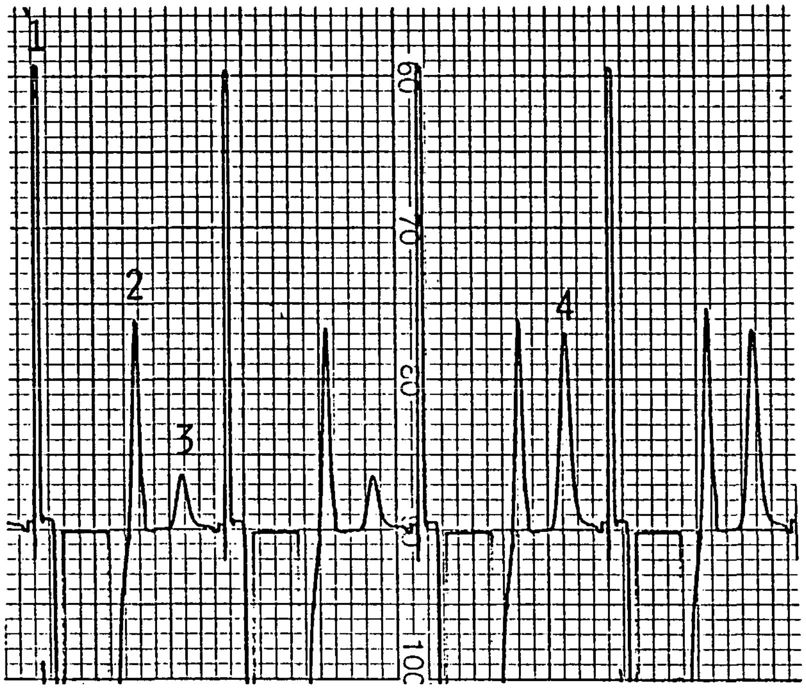

Figure B1. Example Chromatograms from Beckman 6800 Gas Chromatograph. Peaks: (1) Total Hydrocarbons — 4.0 ppmC, Attenuation × 2; (2) Methane — 2.5 ppmC, Attenuation × 1; (3) CO — 9.9 ppmC, Attenuation × 2; (4) CO — 37.2 ppmC, Attenuation × 2.

nated Carle I) is also used to obtain total hydrocarbon data. This system introduces a sample directly into a blank column and then to the FID. Figure B2 shows how this instrument is used to match the THC injected in the two chamber halves. The increase in the chamber THC is clearly shown as well as the degree of relative matching of the two chamber sides. This THC method is used primarily in the morning during injection and the regular operation of the Carle I is used for the rest of the run. By characterizing the response to zero air and methane through this system, and measuring methane separately on another column, it is possible to subtract the air and methane response from the THC response and obtain NMHC concentrations. The exact procedure that we have used is described in detail in Appendix D.

Three automated Carle Model 211 packed column FID gas chromatographs are used for C_1–C_{10} analysis. The first of these chromatographs, Carle I, is used to perform a gross analysis on C_2–C_{10} hydrocarbons. Three chromatographic columns perform the analytical separation. An additional 2' × 1/8" column of carbowax 400 was installed just before the flame detector to balance column bleed and prevent excess baseline displacement after valve switches.

The columns used in Carle I are:

Column 1	6' × 1/8" carbowax 1540 + 5% Apeizon L on Supelcoport 80/100 mesh support to separate C_6–C_8 paraffins, olefins and aromatics
Column 2	6' × 1/8" N-octane/Poracil C 100/120 mesh (baked at 240°C for 2 hrs.) + 2' × 1/8" 20% Apeizon L on Supelcoport 80/100 mesh to separate C_4 and C_5 olefins and some C_6 paraffins
Column 3	2' × 1/8" FL alumina treated with 5% NaCl to separate C_1–C_3 compounds.

Bidirectional electric motors (Carle model 4201) are used to actuate 6-port mini-valves and these shunt the sample to the appropriate columns. The valves are controlled by a 30 minute 110 volt Carle programmable timer (Carle model 4102). The column configurations for each valve position are shown in Figure B3. The indicated restrictors are adjustable S.S. 1/16" Nupro needle valves and are used to match the pressure drop across various columns as these columns are switched in and out of the flow circuit.

Automatic injection is made with all three columns in series. One and one half minutes are required for the individual compounds to become distributed into the proper columns. Since column 1 is the first to be encountered, C_6–C_8 are retained, while C_1–C_5 pass on to column 2. After this first 1.5 minutes with the columns

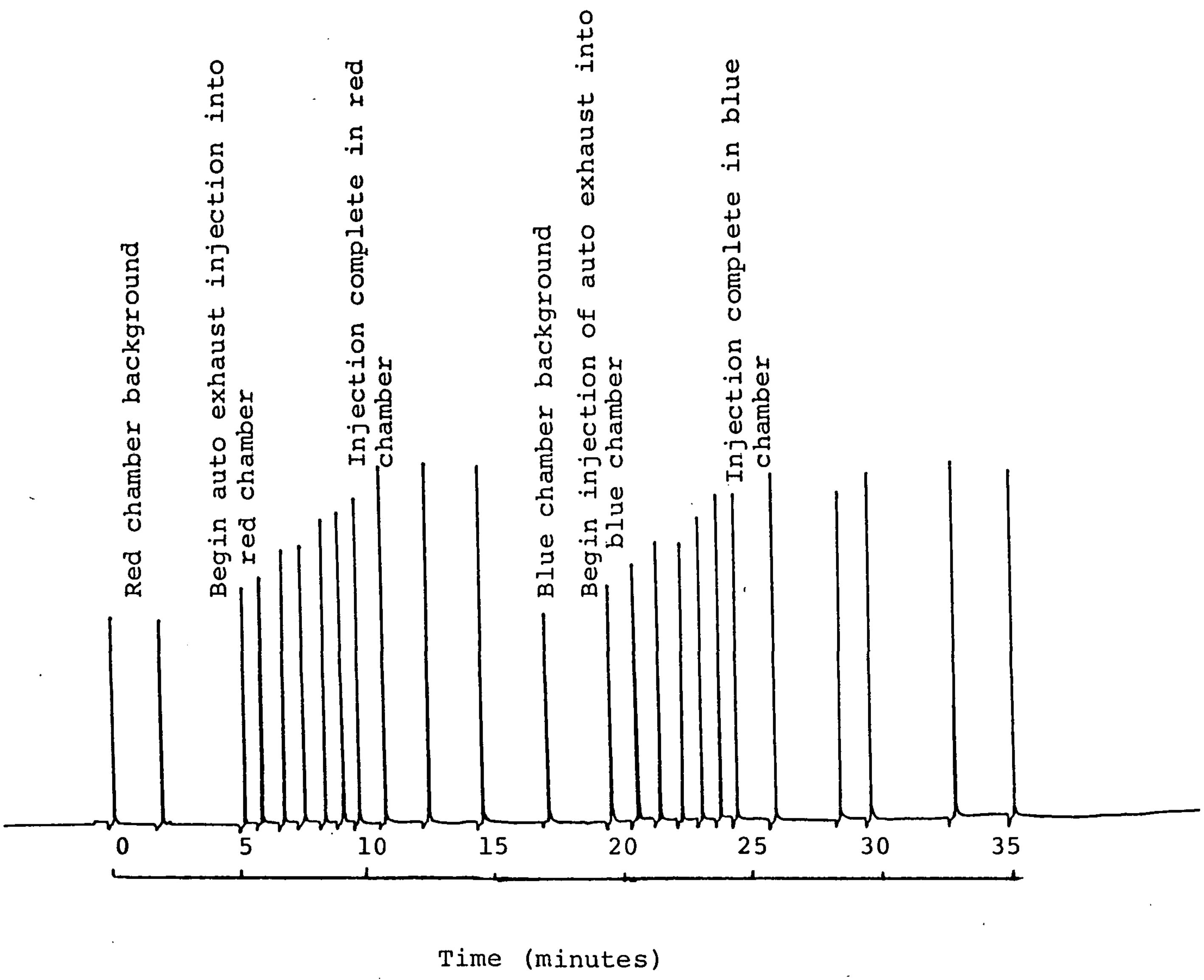

Figure B2. Monitoring of total hydrocarbon concentration as auto exhaust is injected into UNC Outdoor Chambers with a 10 cc direct injection into the flame detector of a Carle I model 211 gas chromatograph.

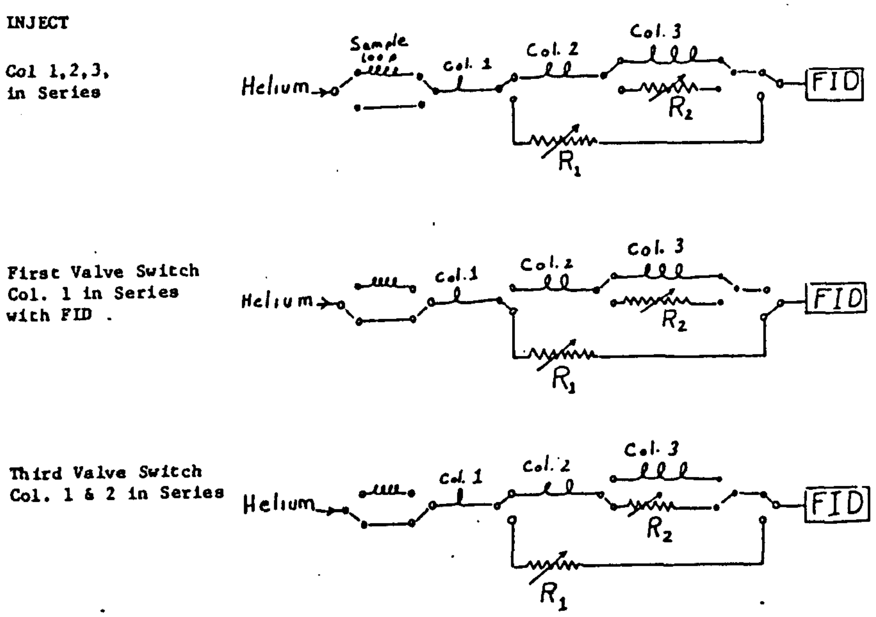

Figure B3. Column and Valve Configuration for C_1–C_{10} Automatic Carle Chromatograph.

in series, a valve switch removes column 2 and 3 from the flow path and permits the compounds in column 1 to elute into the FID. The system remains in this configuration for 5.5 minutes so that C_6–C_{10} paraffins and toluene can be eluted. We also extend this time to 14 minutes to measure xylenes or α-pinene.

A second valve switch then briefly (1 minute) places columns 1, 2, and 3 back in series so that methane and ethylene can be detected. During this period, propane and propylene move from column 2 to column 3 but do not elute before the third valve switch. This switch removes column 3 and leaves columns 1 and 2 in series with the detector. Butenes, pentanes and pentenes then elute from column 2. Finally, with only 2.5 minutes remaining in the cycle, the columns are placed back in series so that propane, propylene and acetylene can be measured.

A chromatogram of the UNC mix is shown in Figure B4. The operating sensitivity can be as low as 7 to 15 ppbC (at a signal to noise ratio of 2 on the most sensitive scale). A limitation of this system is that ethylene and ethane, acetylene and propylene, and some C_4 and C_6 compounds are not completely resolved.

A second packed column GC (Carle II) is used to measure C_1–C_3 hydrocarbons and selected carbonyl species. It employs a 2' × 1/8" ss, 60/80 mesh Porapack

CONCENTRATIONS OF INDIVIDUAL SPECIES IN
0.39 PPMC NMHC UNC MIX

	COMPOUND	CONCENTRATION (PPMC)
1	2-METHYLPENTENE	0.035
2	2,4-DIMETHYLPENTENE	0.039
3	2,2,4-TRIMETHYLPENTANE	0.040
4	ETHYLENE	0.042
5	BUTENE-1	0.010
6	BUTENE-2	0.013
7	ISOPENTANE	0.053
8	N-PENTANE	0.092
9	2-METHYLBUTENE-1	0.008
10	2-METHYLBUTENE-2	0.007
11	PROPYLENE/ACETYLENE	0.047

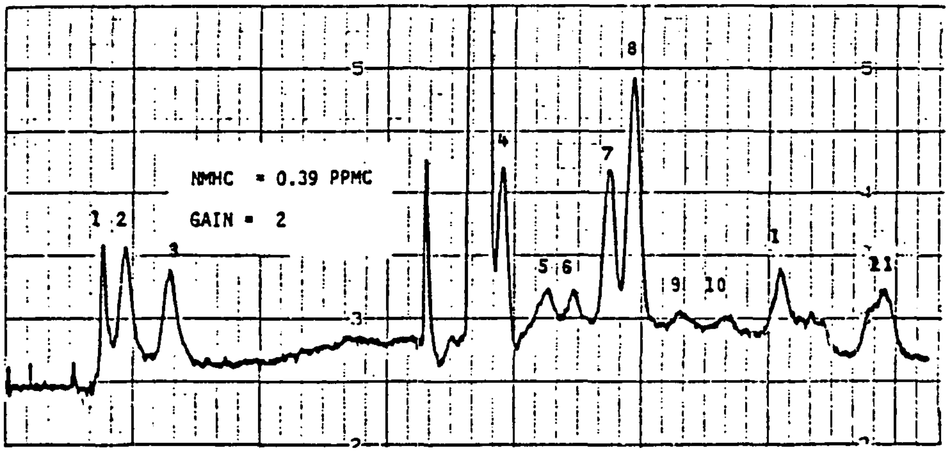

Figure B4. Maximum sensitivity of Carle chromatograph on attenuation of X1 and gain of 2.

Q column for C_1–C_3 separation and a 3 m 1/8" SS 10% carbowax 20M (80:100 supelcoport) column for the carbonyls; toluene and xylenes also elute from this column. As with Carle I, Carle II uses the same type motor-actuated valves and a programmable valve controller. A 5-cc air sample is injected onto each column every 15 minutes. While one column is in series with the flame detector, the other is being back flushed. A typical 30 minute analysis on this system is shown in Figure B5.

The third packed column chromatograph (Carle III) is used to resolve C_4 and C_5 hydrocarbons on one column and aromatics on another. It uses a GP 80/100 mesh, Carbopack 19% picric acid, 1/8" SS × 3-m column for C_4 and C_5 and 1/8" × 3-m, GP 10% TCEP, on 100-120 Chromosorb AW column for aromatics. A valve diagram of this system and a chromatographic analysis of automobile exhaust are shown in Figure B6 and Figure B7.

As can be seen, many compounds such as propylene, butenes, toluene and xylenes can be detected by two or even all three of these chromatographs. Most compounds can be quantitatively determined at concentrations of 0.05-0.1 ppmC and, in instances when peaks are sharp, at levels of 0.01 ppmC. The output from each of these instruments is monitored with a Perkin Elmer Sigma 10 integrator and also with stripchart recorders. Since 30 minutes is required for one complete analysis a sample from each chamber side is taken every hour.

Aromatic compounds are detected with greater sensitivity and resolution by two capillary FID gas chromatographs. The first system was built around a Perkin Elmer 900 gas chromatograph and the second uses a Perkin Elmer Sigma 2.

A plumbing diagram for the first system is shown in Figure B8. Programmed signals from the Sigma 10 integrator autoactuate two 6-port, pneumatically operated valves which allow multiple 11-cc samples to be trapped in a freeze-out loop. The sample is then automatically desorbed onto a 30 m DB 1 (J & W) or SP2100 (H.P.) fused silica column.

The freeze-out loop has an internal volume of 50 to 150 μliters. It is packed with 60/80 mesh glass beads to increase the internal surface area and decrease the internal dead volume. The effective internal volume is $\approx$25-75μliters. A dry ice/methanol bath is manually used to cool the trap. The loop is wrapped with fiberglass insulated nichrome wire for the thermal desorption and will heat the loop from liquid nitrogen temperatures to 200°C in less than one minute.

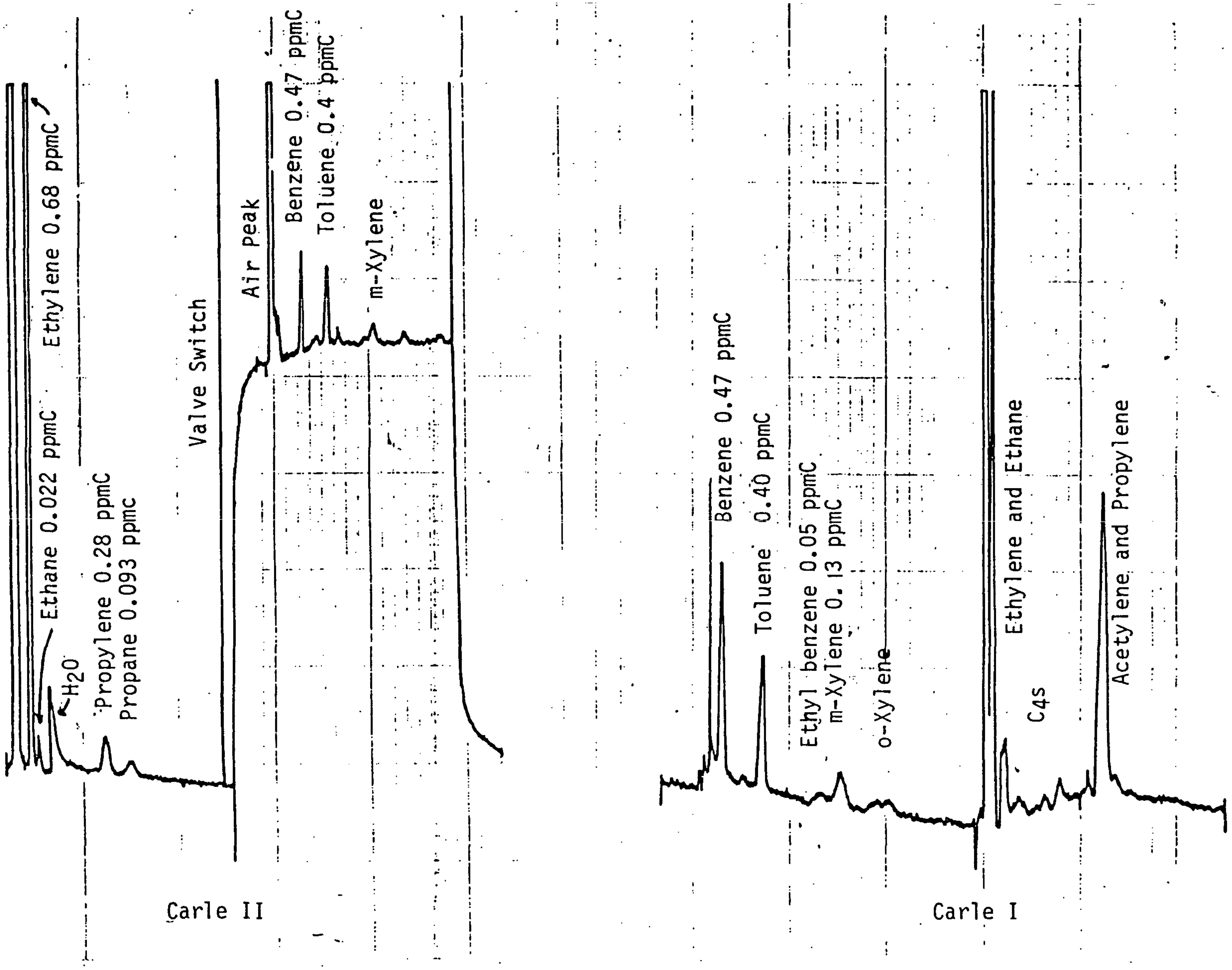

Figure B5. Analysis of C_1-C_3 hydrocarbons in 4 ppmC dilute chamber auto exhaust on Carle II (Model 211) packed column gas chromatograph (July 1, 1982).

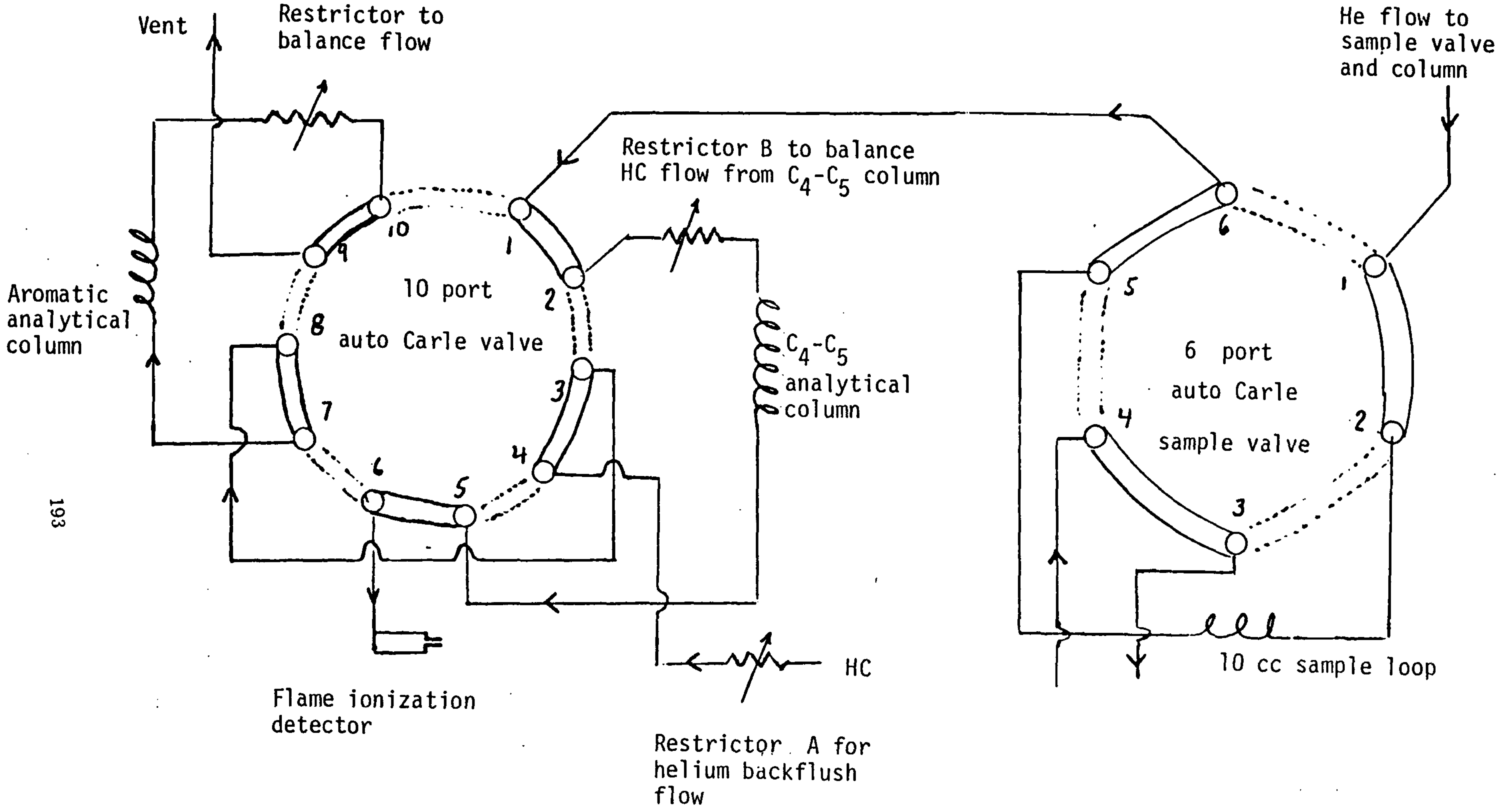

Figure B6. Plumbing diagram to Carle III pack column as chromatograph for the analysis of C_4-C_5 hydrocarbons and aromatic compounds. He flow through columns – 35 cc/min, backflush He – 45 cc/min, restrictions are 1/16" SS needle valves, oven temperature 60°C.

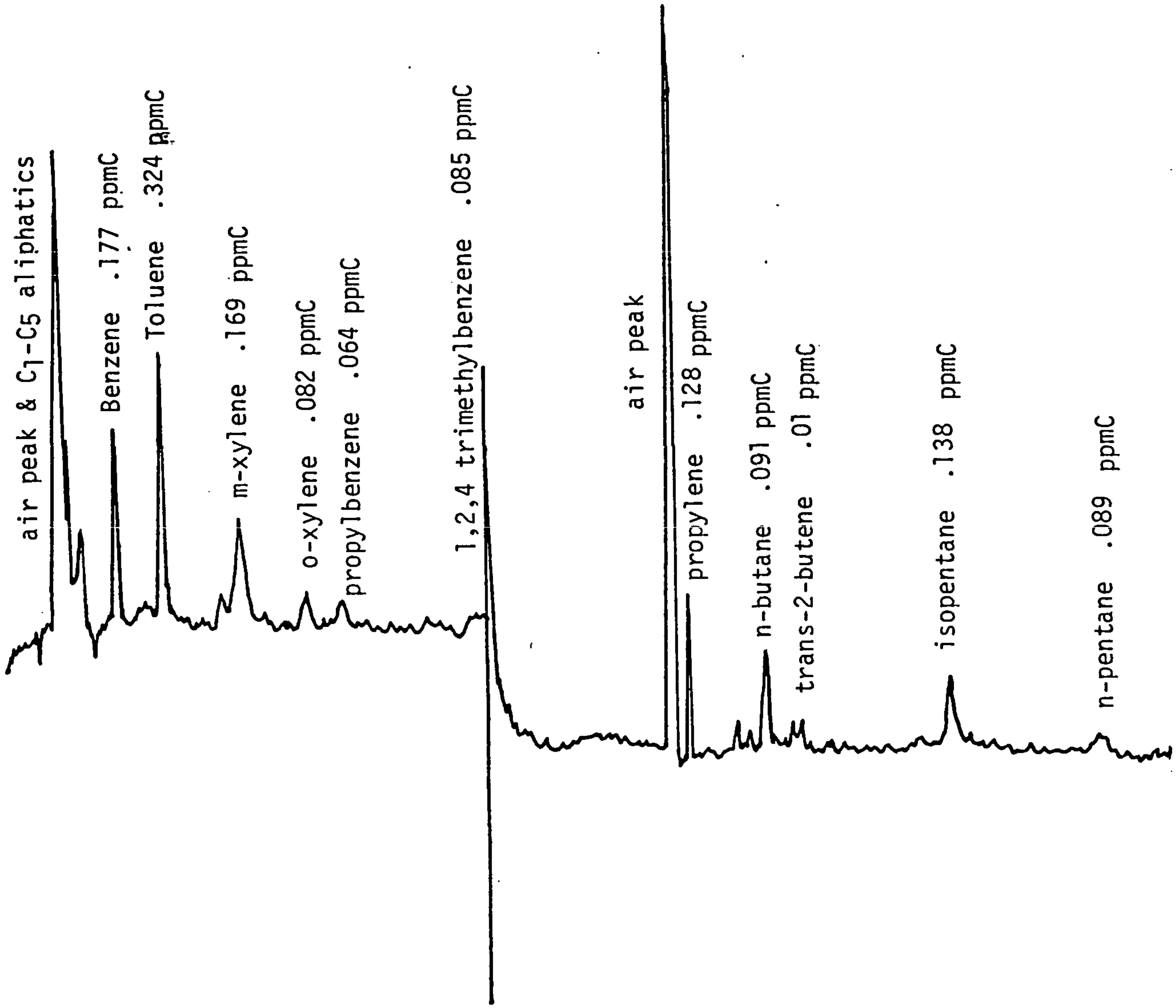

Figure B7. Analysis of aromatics and C_4-C_5 hydrocarbons from dilute auto exhaust injected into UNC outdoor chambers, October 4, 1983.

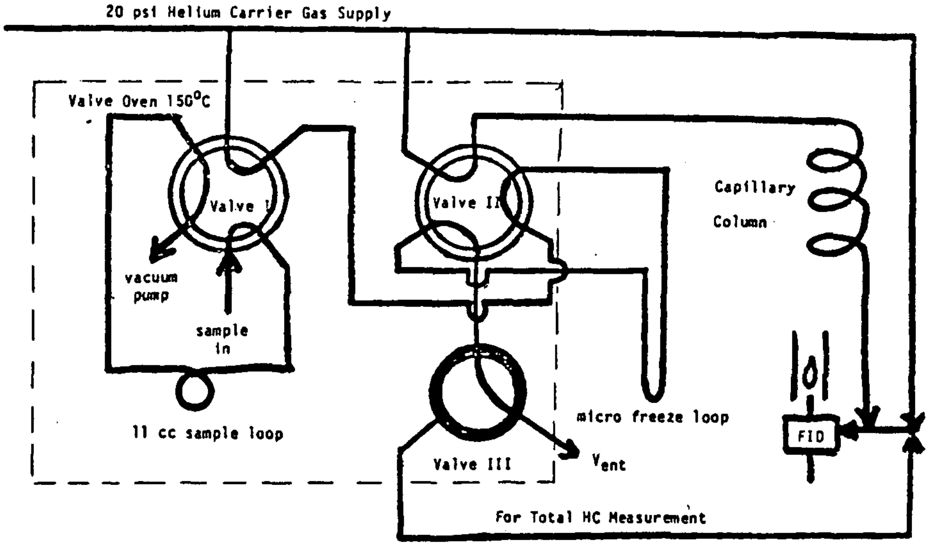

Figure B8. Plumbing Diagram for Perkin Elmer Capillary GC for Aromatic Analysis.

The operating cycle is controlled by a solid state controller. After an initial hold of 6 minutes for valve switching, the column is programmed from 40°C to 150°C at 6.5°C per minute.

This system will separate hydrocarbons from C_6 through C_{14}. A wider range is possible using sub-ambient column temperatures. A typical calibration chromatogram from a mixture of hydrocarbons injected into the chambers is shown in Figure B9 and an analysis of dilute chamber automobile exhaust in Figure B10. Benzaldehyde, tolualdehydes, cresols, nitro benzenes, nitro and toluenes, nitro cresols and dimethyl phenols can also be monitored with this system. The analytical sensitivity of this GC to most compounds is in the 5 ppbC range. A complete analysis requires 45 minutes, including oven cooldown and injection. Thus one sample is taken from each chamber every 1.5 hours.

The fully automated capillary system was designed at UNC around a Perkin Elmer Sigma 2 GC and a Spectra Physics 4100 integrator. A separate controller box was built to drive a LN_2 cryogenic sample concentrator and then thermally degas the trapped HC species onto a 30m DB-1 capillary column. Prior to the start of an analysis the oven is cryogenically cooled with LN_2 to -40°C and then, during the

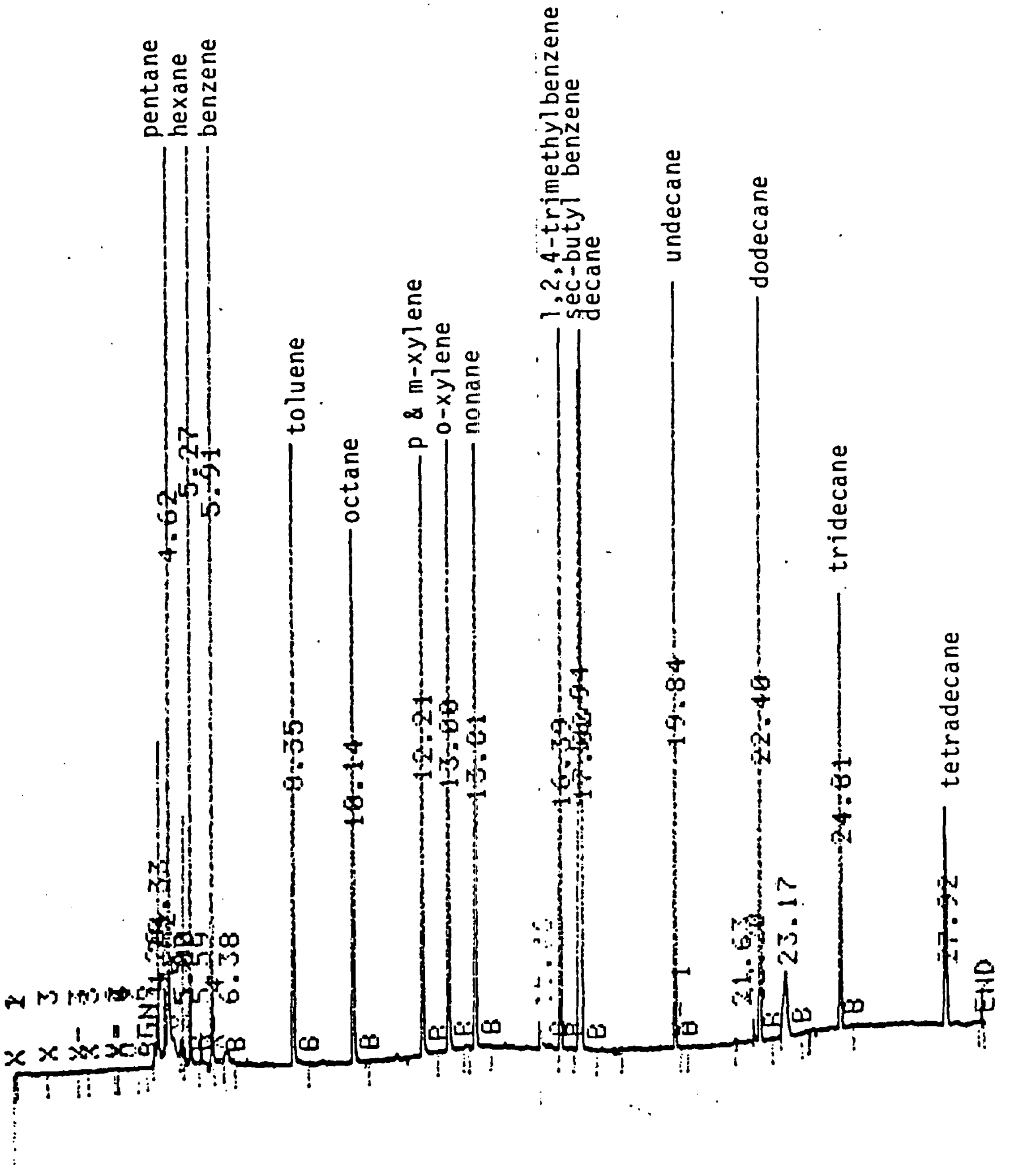

Figure B9. Calibration Chromatogram on PE 900 FID Gas Chromatograph 30 m DB-1 fused silica column (J&W), 22 cc air sample concentrated in 1/16" × 8" SS tube packed with 60/80 mesh glass beads (internal volume 25-75 ul) cooled with MeOH dry ice and thermally desorbed at 200°C with heat tape. Initial oven temperature = 40°C and programmed at 6.5°C/min to 150°C.

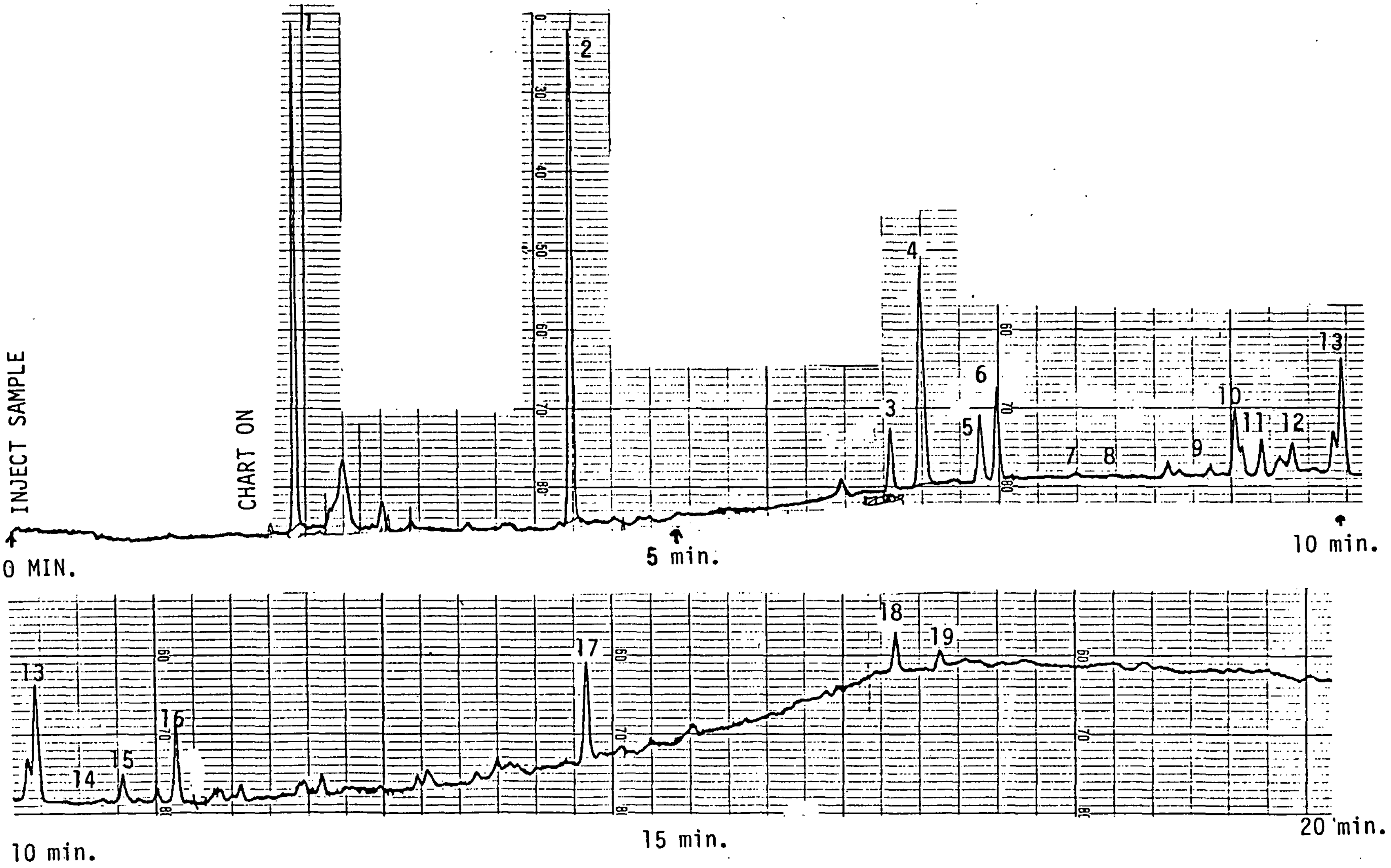

Figure B10. Analysis of C_6C_{12} aromatics on PE 900 FID capillary gas chromatograph from a 3 ppmC dilute auto exhaust chamber run on June 30, 1982. Compound identities and concentrations are: 1) benzene, 0.337 ppmC 2) toluene, 0.366 ppmC 3) ethylbenzene, 0.051 ppmC 4) m&p-xylene, 0.187 ppmC 5) styrene, 0.059 ppmC 6) o-xylene, 0.078 ppmC 7) nonane 8) isopropylbenzene 9) n-propylbenzene, 0.012 ppmC 10) m-ethyltoluene, 0.057 ppmC 11) 1, 3,5-trimethylbenzene, 0.032 ppmC 12) o-ethyltoluene, 0.017 ppmC 13) 1,2,4 trimethylbenzene + tert-butylbenzene, 0.097 ppmC 14) decane + secbutylbenzene 15) 1,2,3 trimethylbenzene, 0.019 ppmC 16) dimethylethylbenzene, 0.062 ppmC 17) napthylene, 0.083 ppmC 18) 2-methylnapthylene, 0.0313 ppmC 19) 1-methylnapthylene, 0.015 ppmC.

analysis, it is programmed to 180°C; one complete cycle requires 45 minutes and compounds in the C_3–C_{10} range can be analyzed with a sensitivity of 1-3 ppbC. The advantage of this system is its increased sensitivity and the potential to ultimately monitor C_3–C_{12} hydrocarbons in one chromatographic cycle. This permits us to analyze most hydrocarbons on one system and provide better estimates of paraffin to olefin ratios. An example chromatogram of a calibration mixture is shown in Figure B11.

A list of pure compounds and standard mixtures used to calibrate this gas chromatograph is given in Table B4.

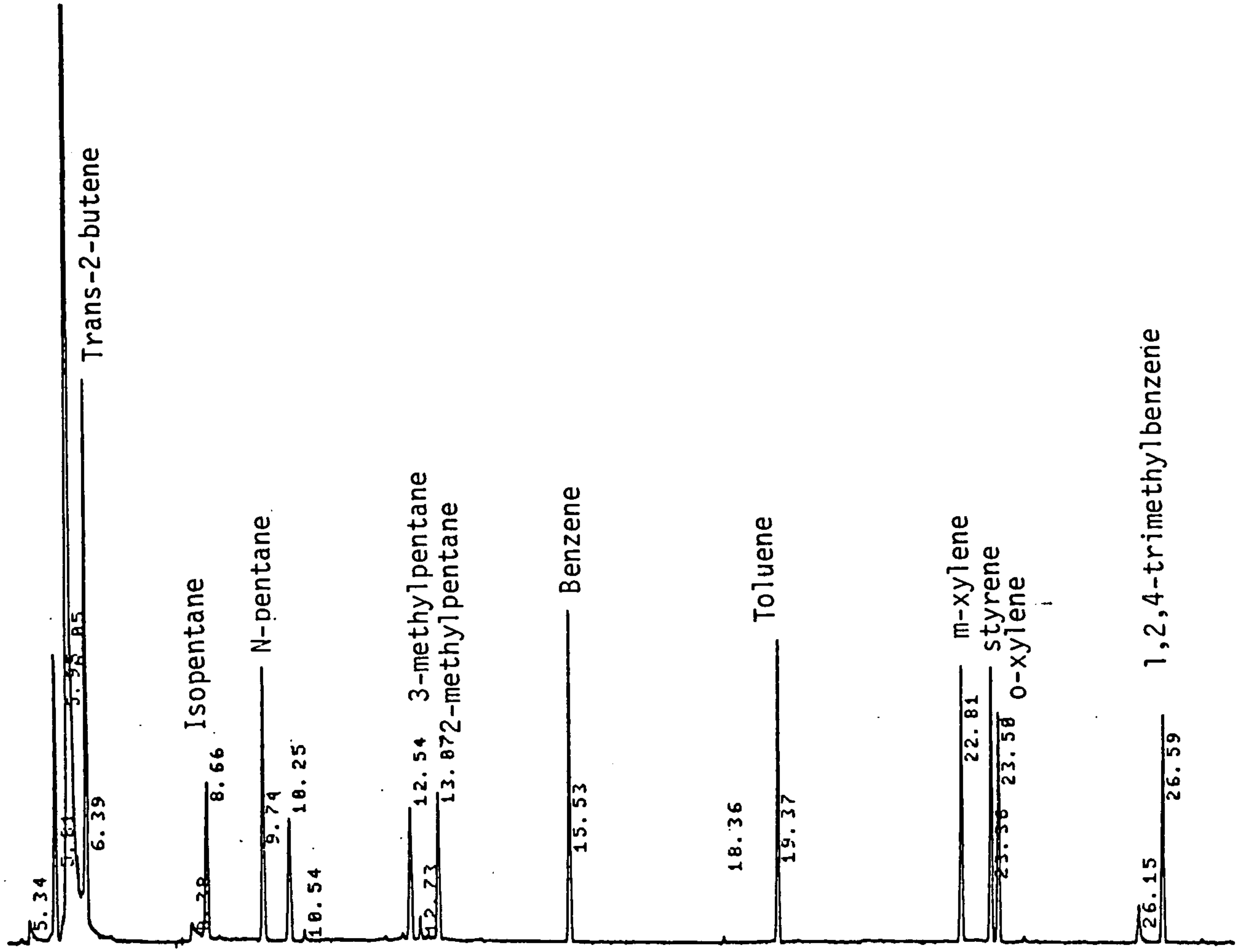

Figure B11. Chromatograph of calibration mixture on auto sampling Perkin Elmer Sigma 2 capillary gas chromatograph with 30 m DB-1 column (J&W). 30 cc air sample (with 0.5 ppmC of each alkane and 1 ppmC of each aromatic) to auto LN_2 trap, oven = -40°C hold (5 min hold) program rate 5°C/min to 150°C, final hold 5 min. Signal attenuated 10 fold.

Table B4 Species Use for Identification and Calibration on PE Sigma 2

Species	Source
propylene	1
propane	1
propadiene	1
butane	1
isobutane	2
1-butene	1
1,3-budtadiene	1,6
cis-2-butene	1
trans-2-butene	1
2-me-1,3-butadiene	1
2-methylpropene	5a,6
2-methyl-1-butene	3
2-methyl-2-butene	3
isopentane	1
n-pentane	1
1-pentene	2
cyclopentene	4
2,2-dimethylpropane	5a,6
benzene	2
2-methylpentane	2
3-methylpentane	4
2-methyl-1-pentene	5a,6
4-methyl-1-pentene	5a,6
cyclohexene	4
cyclohexane	2
n-hexane	2
n-heptane	2
2,3-dimethylpentane	2
3-methylhexane	5a

Table B4 Species Used for Identification, continued

Species	Source
toluene	2
methylcyclohexane	4
n-octane	1
m-xylene	2
o-xylene	2
styrene	4
ethylbenzene	2
o-ethyltoluene	4
m-ethyltoluene	4
1,2,3-trimethylbenzene	4
1,2,4-trimethylbenzene	4
1,3,5-trimethylbenzene	4
n-propylbenzene	4
isopropylbenzene	4
n-butylbenzene	4
s-butylbenzene	4
t-butylbenzene	4
diethylbenzene	5b
dimethylethylbenzene	4
naphthalene	5b
1-methylnaphthalene	4
2-methylnaphthalene	4

1 Certified Cal. tank, LOMW
2 Certified Cal. tank, HIMW
3 Calibrated Injection tank, UNCMIX
4 UNC General Chemical Supply
5a Mobile Sources Emissions Research Branch, EPA
5b Mobile Sources Measurements Research Section, EPA
6 William Lonneman, Gas Kinetics and Photochemistry Branch, EPA

Mass Spectrometry

Individual identification of hydrocarbon species in mixtures as complex as automobile exhaust is performed at UNC on a VG micro-mass 707F mass spectrometer interfaced to a Hewlett Packard 5710A capillary gas chromatograph. One to two cc of raw automobile exhaust are injected onto a 30 m, SE54, or DB-1 fused silica column. The first 0.3 meters of the column are coiled into a cup of liquid nitrogen so that on-column trapping of the sample can be accomplished. The oven is then programmed from 10°C to 150°C at 5°C/min. Identification is performed by comparison to the mass spectrum from authentic samples and to literature spectra available in the EPA-NIEHS mass spectra libraries. An analysis of raw automobile exhaust and gasoline is shown in the reconstructed ion chromatographs in Figure B12 and Figure B13. Figure B14 is a library mass spectrogram of napthalene and Figure B15 is the mass spectrogram of peak 43 in Figure B12, and there is little doubt that peak 43 is napthalene.

Quantification of individual hydrocarbon species is performed on an "off line" Carlo Erba 4130 FID gas chromatograph. The same fused silica column, cryotrap and temperature program which were used for the GCMS analysis are used here. Identifications are made by comparing the FID chromatogram (Figure B16) with the GCMS reconstructed ion chromatograms. Response factors are determined from a mixture of 15 authentic compounds which are analyzed on the Carlo Erba.

Formaldehyde by Automated Colorimetry

Since 1979. UNC has used an automated colorimetric formaldehyde instrument manufactured by CEA corporation (Westwood, NJ). This system employs a reverse West and Gaeke technique[1] and hence requires a constant supply of wet chemicals which include highly purified pararosanaline, mercuric chloride, sodium chloride, and sodium sulfite.

Liquid standards are prepared from 37% formalin solution and diluted in the same sodium tetra mecurate (TMC) used in the instrument. A dynamically generated HCHO airstream using a formaldehyde permeation tube (Metronics Corporation, Santa Clara, CA) is used to supply known levels of gas phase formaldehyde. In addition, calibration samples of formaldehyde are prepared in the chamber. The chamber is usually dried to a dew point of less than 60°F and known quantities of solid paraformaldehyde are then injected. During the course of a six month data season when the chambers are in operation, we have found this system's calibration not to change by more than 10%.

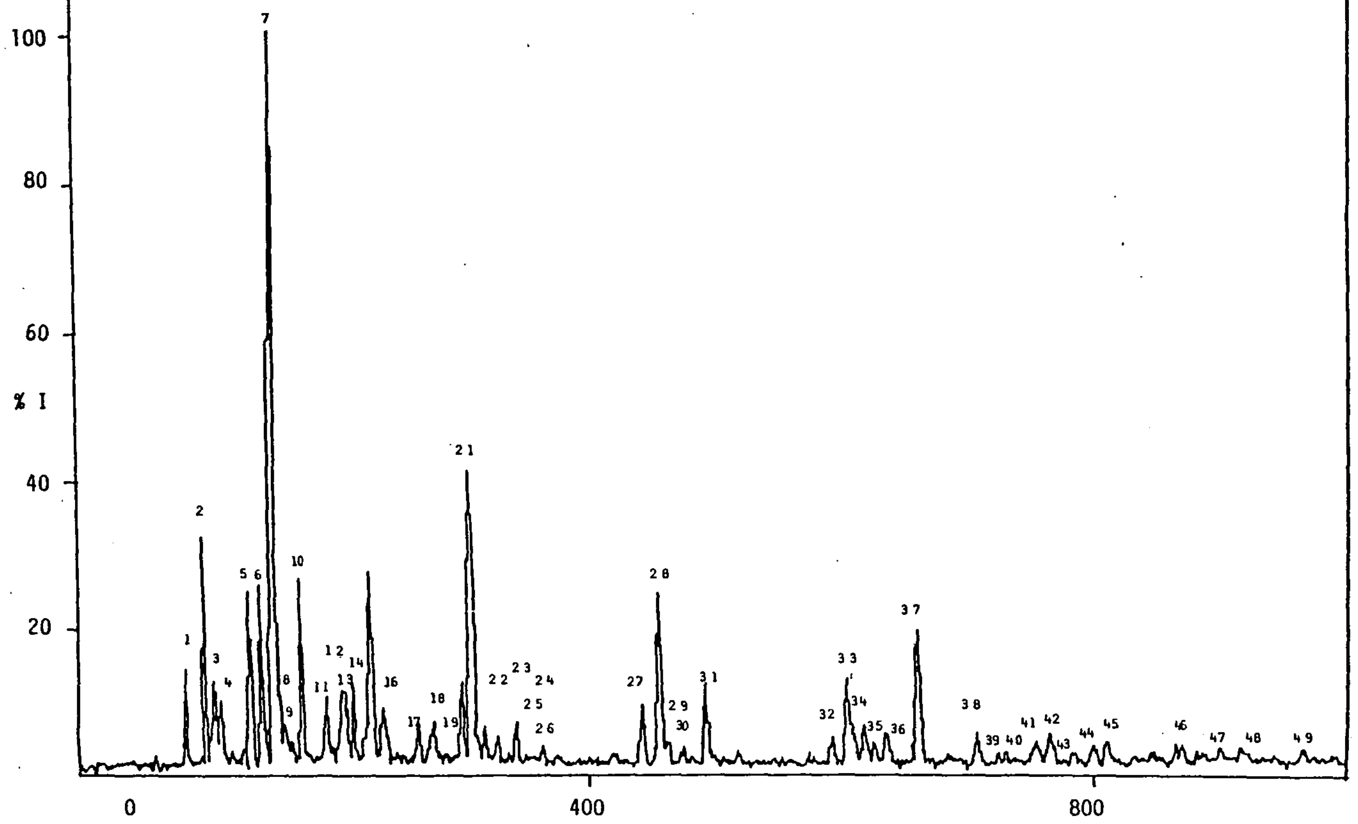

Figure B12. Reconstructed ion chromatograph of EPA summer gasoline using DB-1 column. Identities based on comparison with literature mass spectra. Compounds listed in order of elution are: 1) *n*-butane 2) 2-methylbutane 3) *n*-pentane 4) methylbutene or 2-pentane 5) 2-methylpentane 6) 3-methylpentane 7) n-hexane 8) hexadiene or a methylcyclopentene + a hexene 9) e-methyl-2-pentene 10) methylcyclopentane 11) benzene 12) 2- methylhexane 13) 2,3-dimethylpentane 14) 3-methylhexane 15) 2, 2,4-trimethylpentane 16) n-heptane 17) methylcyclohexane 18) 2 ,5-dimethylhexane 19) 2,4-dimethylhexane 20) 2,3,4- trimethylpentane or 4-methylheptane 21) toulene 22) 2,3- dimethylhexane 23) 2-methylheptane 24) 3-methylheptane 25) 2,2 ,4- or 2,2,5-trimethylhexane 26) n-octane 27) ethylbenzene 28) m- and/or p-xylenes 29) methylpentanes 30) 3-ethylheptane 31) xylene 32) n-propylbenzene 33) m- and/or p-ethyltolune 34) 1,3 ,5-trimethylbenzene 35) 2- or 4-methylnonane 36) p-ethyltoluene 37) 1,2,4-brimethylbenzene 38) 1,2,3-trimethylbenzene 39) n- decane and other $C_{1}0$ alkylbenzene 40) indan or a methylstyrene 41) sec-butylbenzene and other C_4 alkylbenzene (m-tp-n-propyltoluenes and maybe some tert–butylbenzene) 42) n- butylbenzene and other C_4 alkylbenzene (maybe some diethylbenzenes) 43) n-propyltoluene and some undecane 44) dimethylethylbenzenes 45) a dimethylethylbenzene 46) tetramethylethylbenzenes 47) C_5 alkylbenzene and C_4 alkenebenzene 48) C_4 alkenebenzene 49) naphthalene.

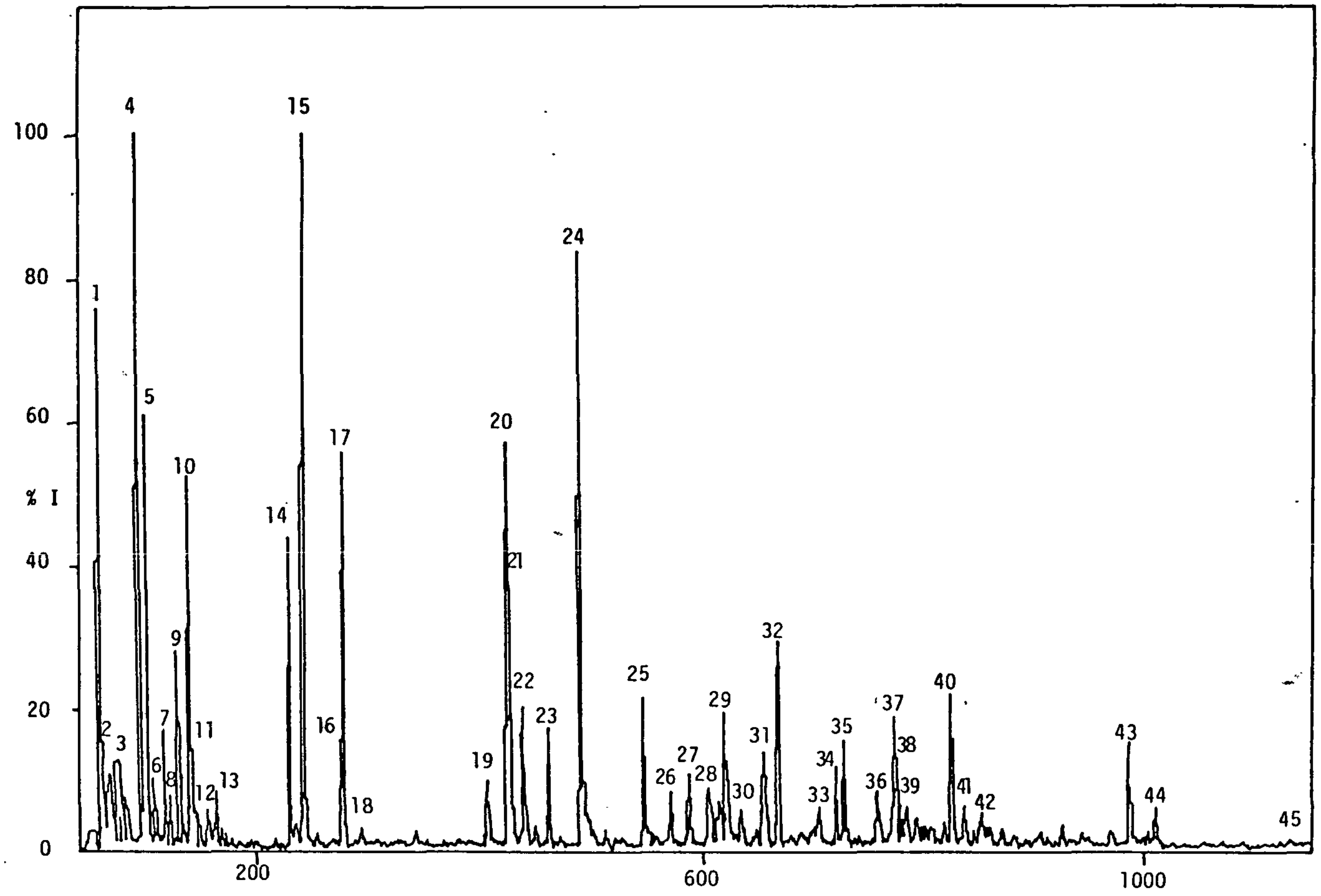

Figure B13. Reconstructed ion chromatograph of 1972 Dodge Charger exhaust, running 2200 rpm, using EPA summer gasoline, with 30 m SE54 column. Identities based on comparison with literature mass spectra, compounds listed in order of elution are: 1) butadiene and a butene or cycle-butane 2) 2-methylbutane 3) a pentadiene, or methylbutene; cyclopentadiene, 2-methylpentane, several hexenes; methylcyclopentane 4) benzene 5) 2,2,3 or 2,2,4- trimethylpentane 6) n-heptane + heptene + heptadiene 7) methylcyclohexane 8) 2,4-dimethylhexane 9) a trimethylcyclopentane then 2,3,3-trimethylpentane and 2,3- dimethylhexane 10) toluene 11) 3-methylheptane then 2,2,4- or 2, 2,5-trimethylhexane or 2,2-dimethylheptane 12) 2-ethyl-1-hexane 13) n-octane + trace of an octene 14) ethylbenzene 15) m- and p-xylenes 16) styrene 17) o-xylene 18) isopropylbenzene 19) n -propyl-benzene 20) m-ethyltoluene 21) p-ethyltoluene 22) 1,3, 5-trimethylbenzene 23) o-ethyltoluene 24) 1,2,4- trimethylbenzene and small amount of methylstyrene or indan 25) 1,2,3-trimethylbenzene 26) indan or a methylstyrene 27) indene 28) sec-butylbenzene and some m & p-n,propyl-toluene and maybe some t-butylbenzene; then n-propyltoluene; then n-butylbenzene and some diethylbenzene 29) a dimethylethylbenzene 30) po-n, propyltoluene 31) a dimethylethylbenzene 32) a dimethylethylbenzene and trace C_4 alkenebenzene 37) a C_4 ene and a C_5 alkylbenzene 38) a tetramethylbenzene 39) a C_5 alkylbenzene 40) naphthalene 41) a C_5 alkenebenzene 42) a pentylbenzene 43) 2-methylnaphthalene 44) 1- methylnaphthalene 45) a dimethyl-naphthalene

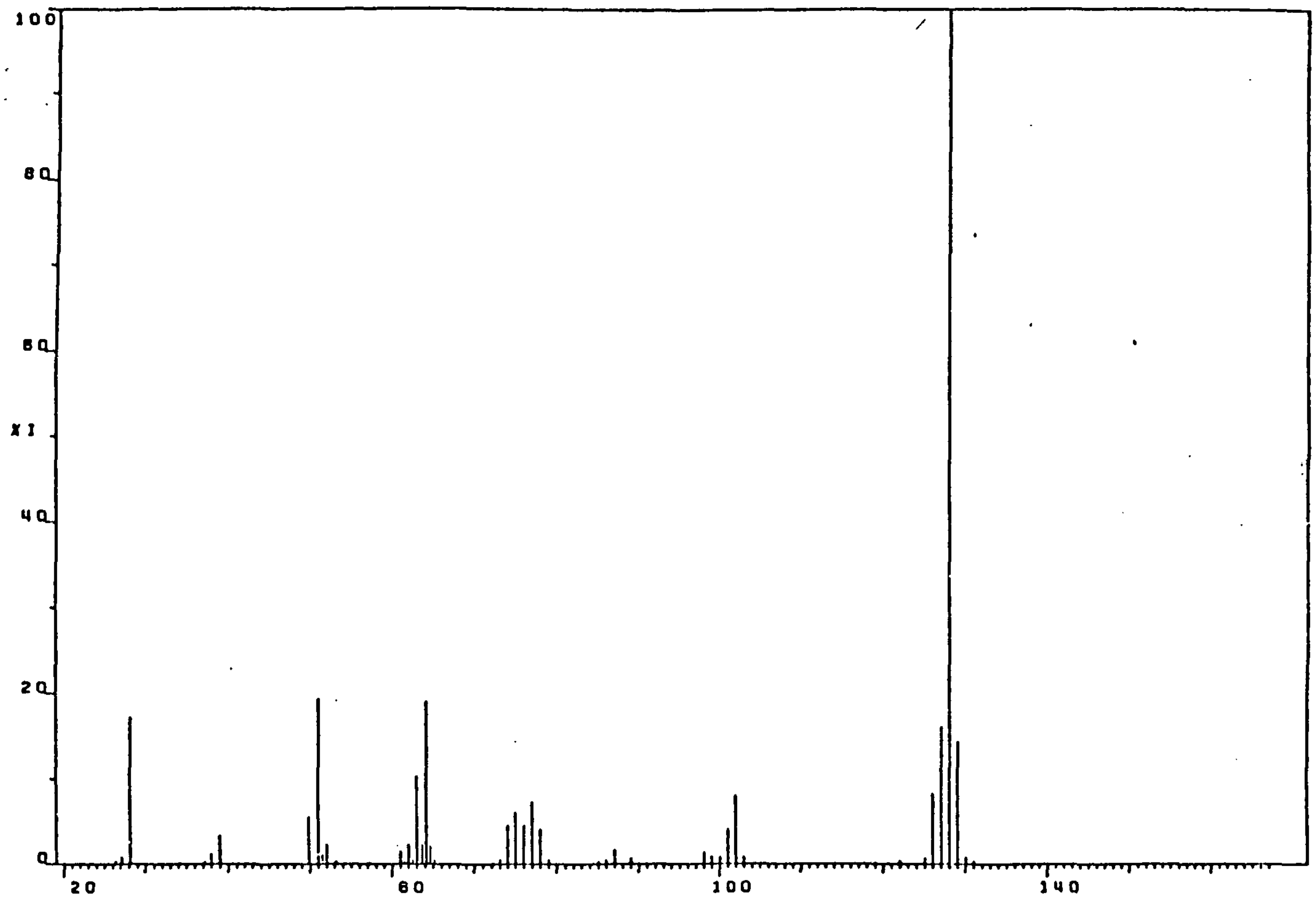

Figure B14. Library mass spectrogram of Naphthalene on the VG Micro-Mass 707F Mass Spectrometer.

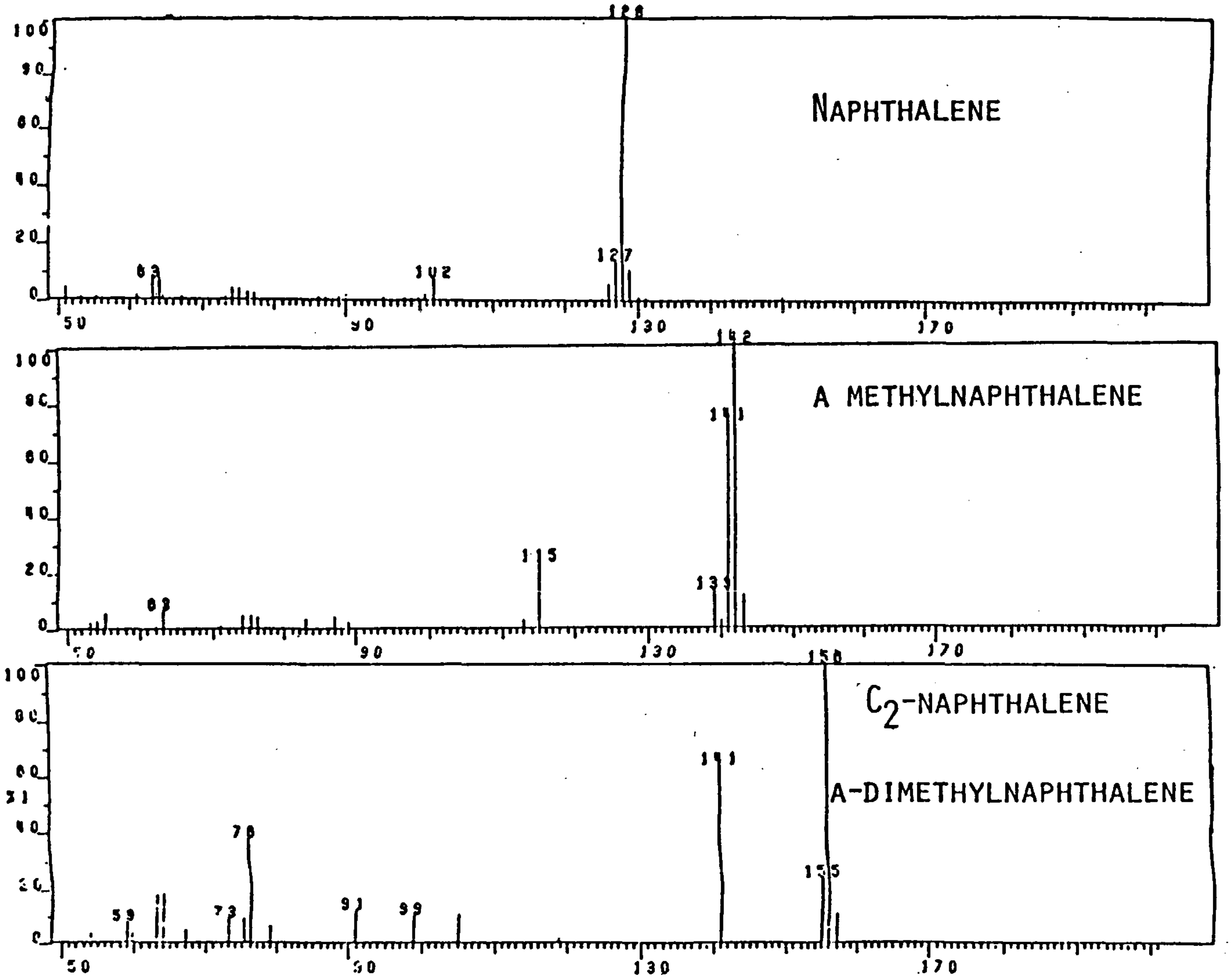

Figure B15. Mass spectrograms of Peaks 43, 44, and 45 of Figure 12, Auto Exhaust.

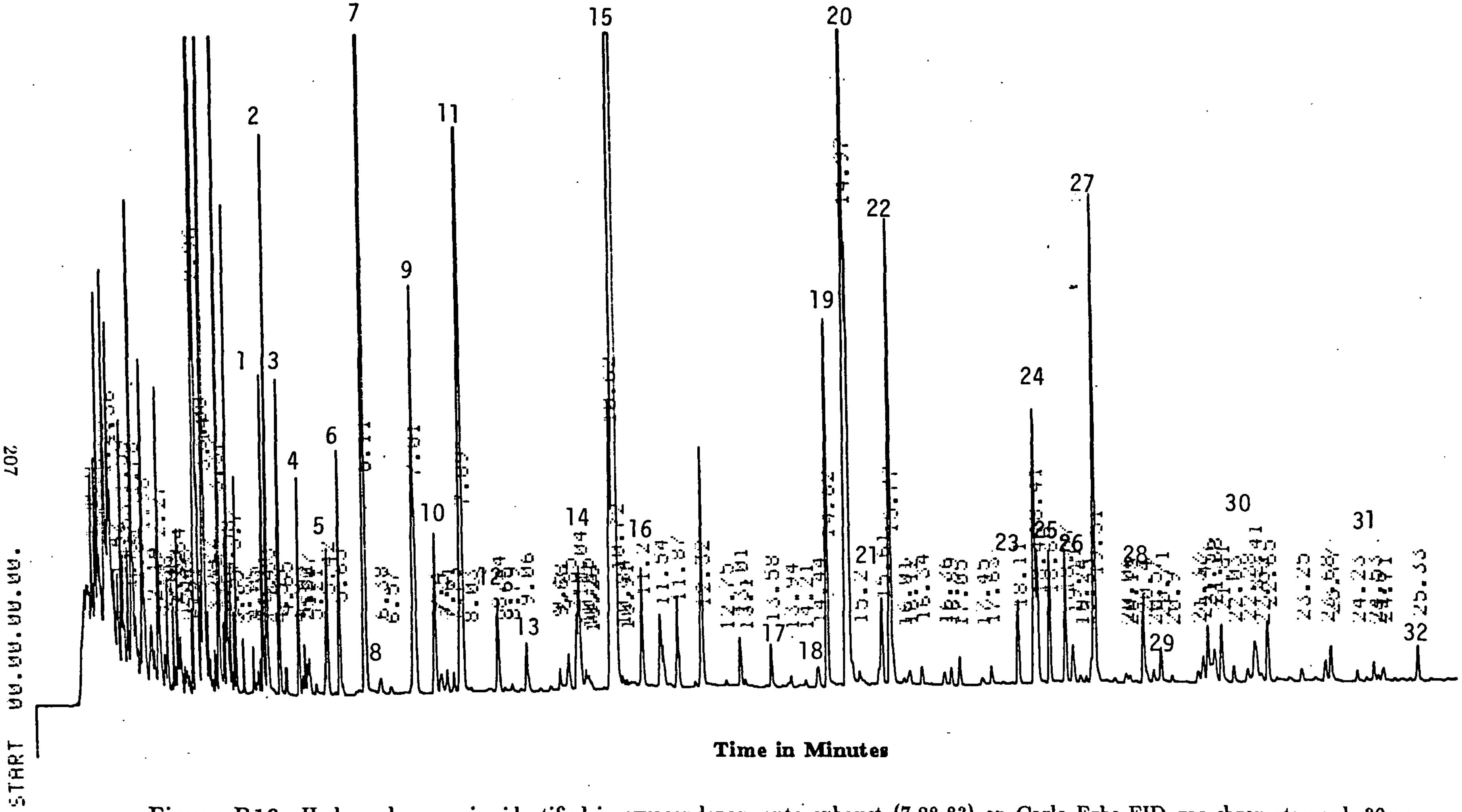

Figure B16. Hydrocarbon species identified in cryocondenser auto exhaust (7-28-83) on Carlo Erba-FID gas chromatograph 30 m DB-1 column (J&W) on column liquid oxygen freeze out. Temperature programmed 10°C hold 7 minutes program at 5°C/min to 150°C. Identities bases on comparison with reconstructed ion chromatographs generated under similar operating conditions. 1) 2,3-dimethylbutane 2) 2-methylpentane 3) 3-methylpentane 4) n- hexane 5) methylcyclopentane 6) 2,2- and/or 2,4-dimethylpentane 7) benzene and some methylcyclopentene 8) cyclohexane 9) 2- methylhexane 10) 3-methylhexane 11) 2,2,4-trimethylpentane 12) n-heptane 13) methylcyclohexane 14) 2,4-dimethylhexane 15) toluene 16) 2,3-dimethylhexane 17) n-octane 18) 2,5- dimethylheptane 19) ethylbenzene 20) m-& p-xylene 21) 3- methyloctane 22) o-xylene 23) n-propylbenzane 24) m-& p- ethyltoluene 25) 1,3,5-trimethylbenzene 26) o-ethyltoluene 27) 1,2,4-trimethylbenzene 28) 1,2,3-trimethylbenzene 29) indan 30) C_4-benzene 31) methylindans 32) naphthalene.

The minimum detectable concentration for this instrument is 20 ppb and a continuous sample on each chamber is taken every 30 minutes. Using the solutions recommended by CEA we observed a 5% positive interference from acetaldehyde in the concentration range of 0.1-1 ppmV. When appreciable acetaldehyde is generated, the HCHO data are adjusted to subtract out the positive acetaldehyde interference. Interferences from other carbonyls such as acetone, propionaldehyde, MEK or methacrolein produced are not significant. Finally, the system that we have been using exhibits a 30-50% zero drift over a 3-4 hour period. This drift does not affect the span response but requires frequent zero samples. Examples of the system's response to 1.2 and 0.5 ppmC formaldehyde air samples are shown in Figure B17.

Carbonyl Analysis

The analysis of C_1–C_8 carbonyl species in ambient air by reaction with 2,4 dinitrophenylhydrazone (DNPH) and subsequent reverse phase high pressure liquid chromatography of the hydrazone derivatives has been reported by Kuwata *et al.*[2] This procedure is fairly specific and can also be used to measure dicarbonyls. We have used this method to monitor C_2 and greater carbonyls and have generally used the previously described automated colorimetry method to obtain more continuous formaldehyde measurements.

Ambient aldehydes are sampled with an impinger arrangement into an absorbing reagent which contains acidified DNPH. Three to four recrystallizations of the DNPH (Eastman Kodak cat. no. 1866, 10% water added) with acetonitrile (ACN) are required to remove impurities from the DNPH. The absorbing reagent is prepared by dissolving 0.25 g of purified DNPH in one liter of HPLC grade ACN. This is followed by the addition of 0.2 ml of H_2SO_4. Two ml of absorbing reagent are used in a Mae West type bubbler with a sample flow rate of one l/min, as described by Kuntz *et al.*[3]. We have observed collection efficiencies of 75–85% for most of the carbonyl compounds which have been tested. These include formaldehyde, acetaldehyde, propionaldehyde, methylvinylketone, benzaldehyde, glyoxal, methylglyoxal, biacetyl and o-tolualdehyde.

Analysis is performed on a Varian 5010 HPLC with a Varian micropak MCH-10 reverse phase, 30 cm, 9 mm column and a fixed 254 nm detector. To eliminate interferences from toluene and xylenes a 365 nm cut off filter can be used. The mobile phase is run isocratically at a 60:40 ACN:H_2O mixture and a solution flow of 1.6 ml/min. High concentration liquid standards in the gas phase equivalent range of 2-6 ppmV were prepared by direct dilution of 5 μl of authentic knowns (liquids available from Aldrich or Eastman, purity 98–99%, except for 40% gloxal in water, 40% methylglyoxal, 37% formaldehyde, 85% methacrolein and 95% biacetyl. These

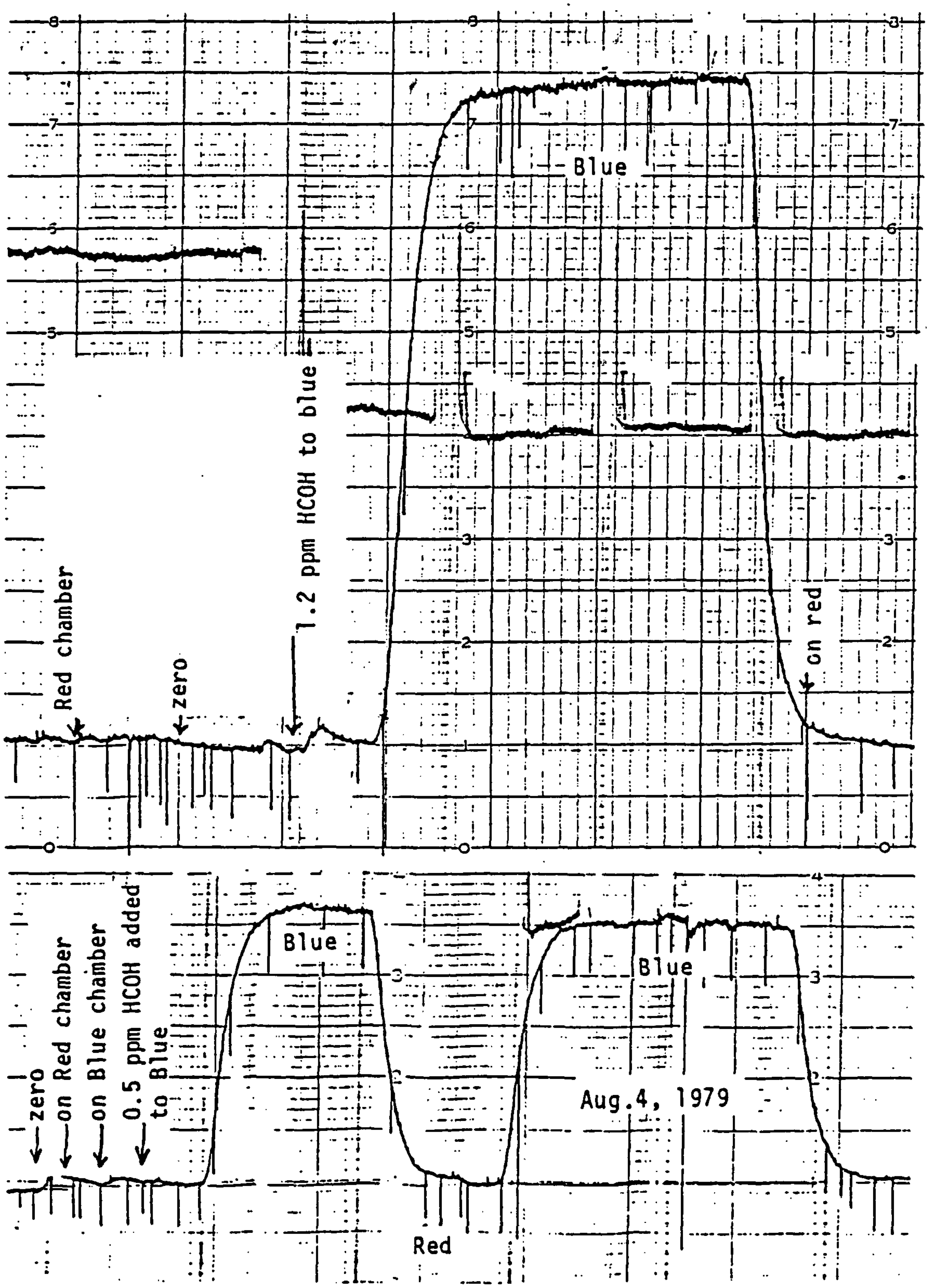

Figure 17. Response of CEA Auto Formaldehyde Instrument to 0.5 and 1.2 ppm of HCOH injected in dry UNC chambers on August 4, 1979 and August 5, 1979.

standards were used as received and not further purified.) to twenty μl of this solution were then added to 2 ml of DNPH absorbing reagent. The final DNPH samples were heated in 2 ml Supelco reaction vials at 70°C for 30 minutes. Comparisons with gas phase and liquid calibration samples are made. A sample chromatogram of a mixture of aldehydes, ketones and dicarbonyls is shown in Figure B18.

PAN Analysis

PAN measurements are made on a 1/8" × 36" glass column packed with 10% Carbowax 600 on Gaschrom G (60-80 mesh) and detected with a Varian 940 electron capture detector. Both the column and the detector are held at room temperature and 5% methane-argon is used as the carrier gas. A 6-port automatic sample valve was installed so that unattended sample injection and analysis could be performed. With a standing current of 20×10^{-9} amps we found that the response was linearly between 0.01 ppmV and 0.5 ppmV of PAN. The response of this system to 0.12 ppmV of PAN is shown in Figure B19.

PAN calibration samples are prepared from an irradiated 5ppmC biacetyl/NO_x bag system. The bag is irradiated for 1 hour in midday sun so that essentially all of the NO_2 is converted to PAN. The PAN is purified with a 10% Carbowax 600 prep-column (25 cm × 7 mm) and a liquid nitrogen freeze-out concentrator. PAN from the cryotrap is then diluted into a clean Teflon bag and measured with a calibrated chemiluminescence NO_x analyzer. The response of the chemiluminescent monitor to PAN is 100% and thus a pure PAN sample can be standardized.

When the above procedure is not possible, then 4 ppmC of propylene and 0.5 ppm NO_x (40% NO_2) are irradiated outdoors for 3-4 hours during the mid-morning and the early afternoon. With a chemiluminescent NO_x meter, the NO_2 concentration is followed beyond the NO_2 peak until NO_2 stabilizes. The PAN GC responses are then related to chemiluminescent PAN readings assuming that all NO_2 that is reported by the meter is actually PAN.

Alkynitrates

The C_1–C_5 alkylnitrates can be detected on the same system that is used to measure PAN. Calibration for ethyl, isopropyl, propyl, and butylnitrates were performed by injecting microliter volumes of the authentic samples into the outdoor chambers and applying the appropriate dilution and temperature factors (Figure B20). Calibration factors for compounds for which we did not have authentic samples (*e.g.*, sec-butylnitrate and isopentylnitrate) were estimated from the ECD response of n-butylnitrate. An uncertainty of ±40% is assigned to these compounds with no authentic standards.

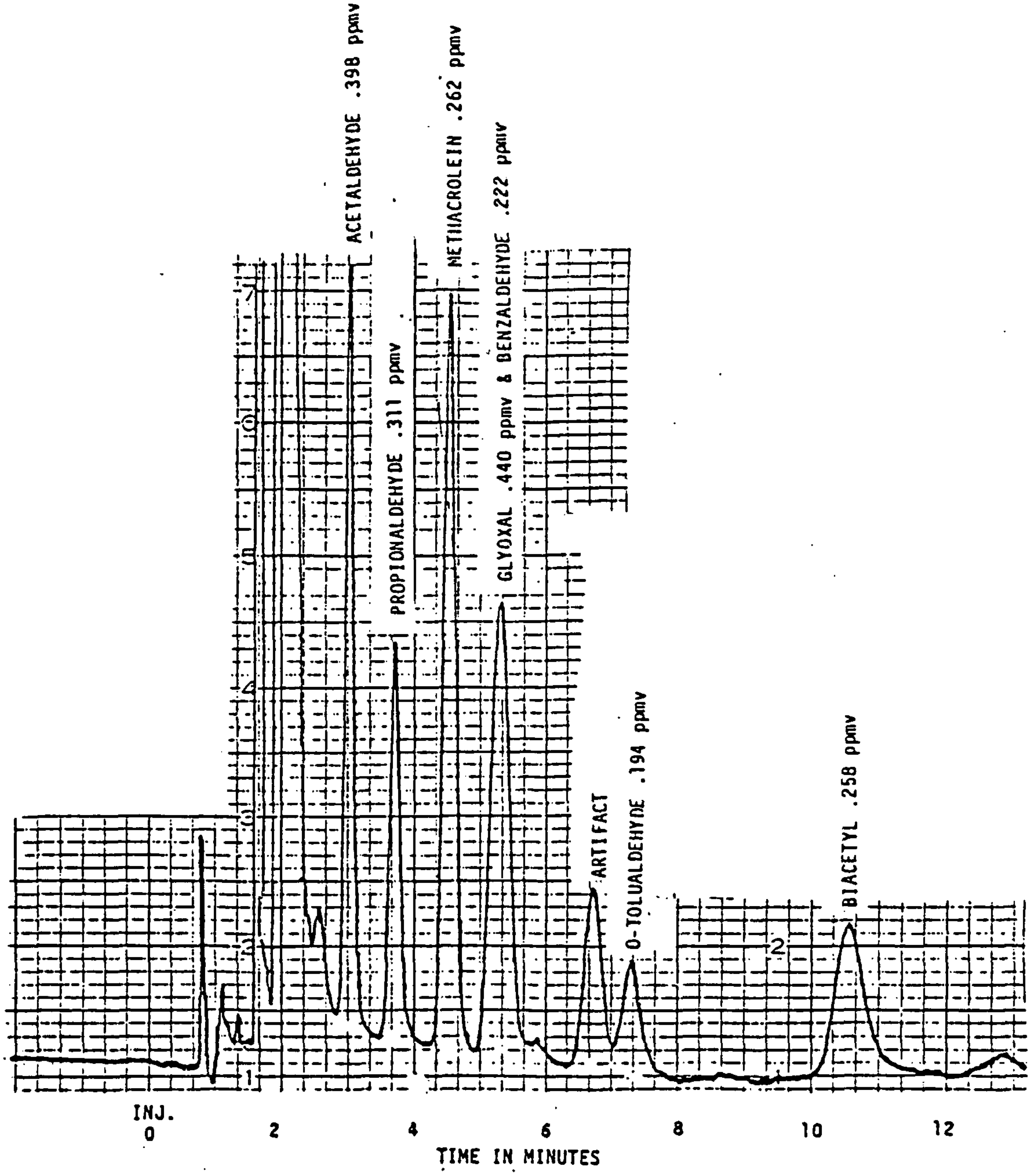

Figure B18. An example of the response of the HPLC with DNPH Method.

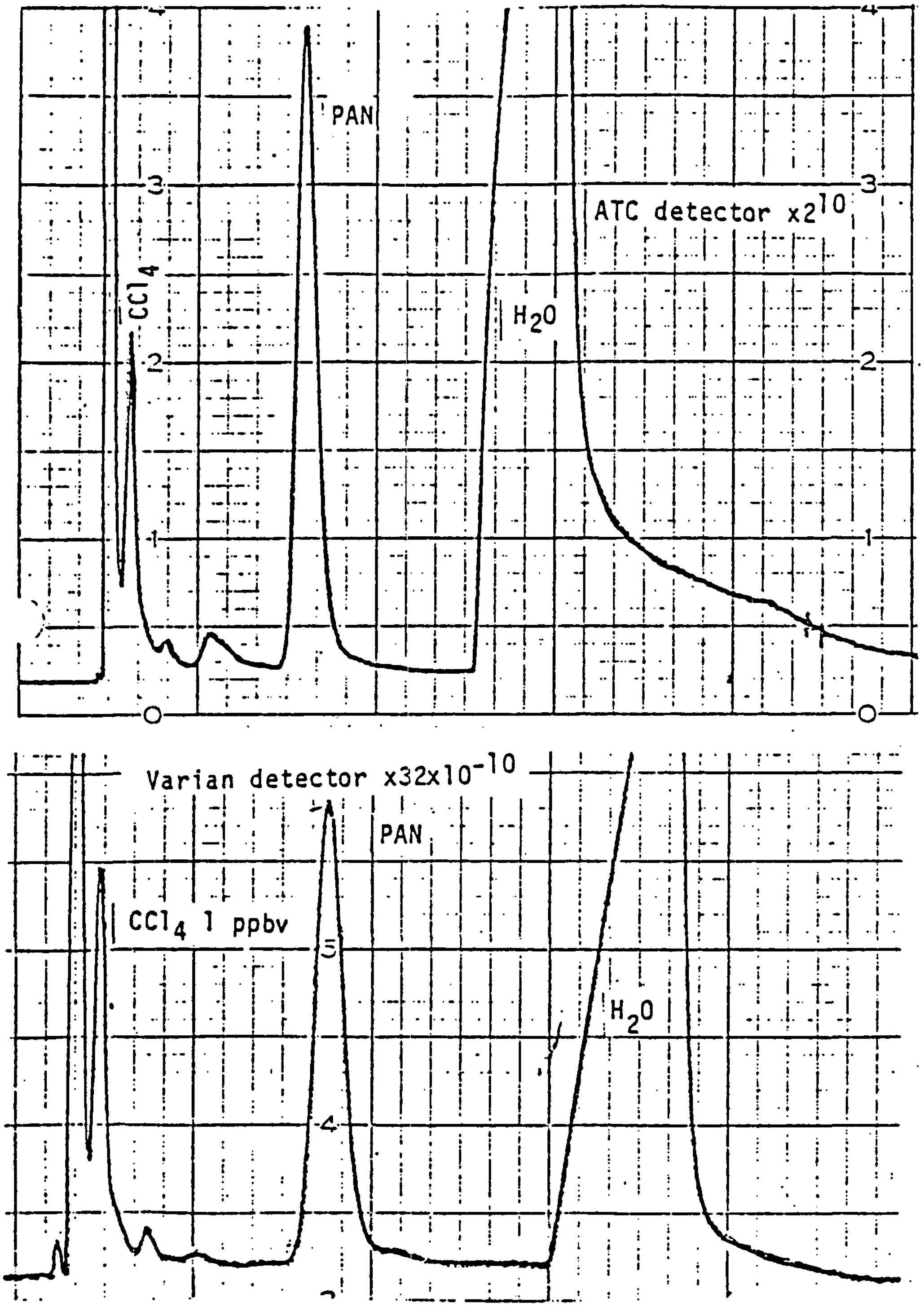

Figure B19. Response of two UNC electron capture detectors to 0.12 ppmV PAN May 1978.

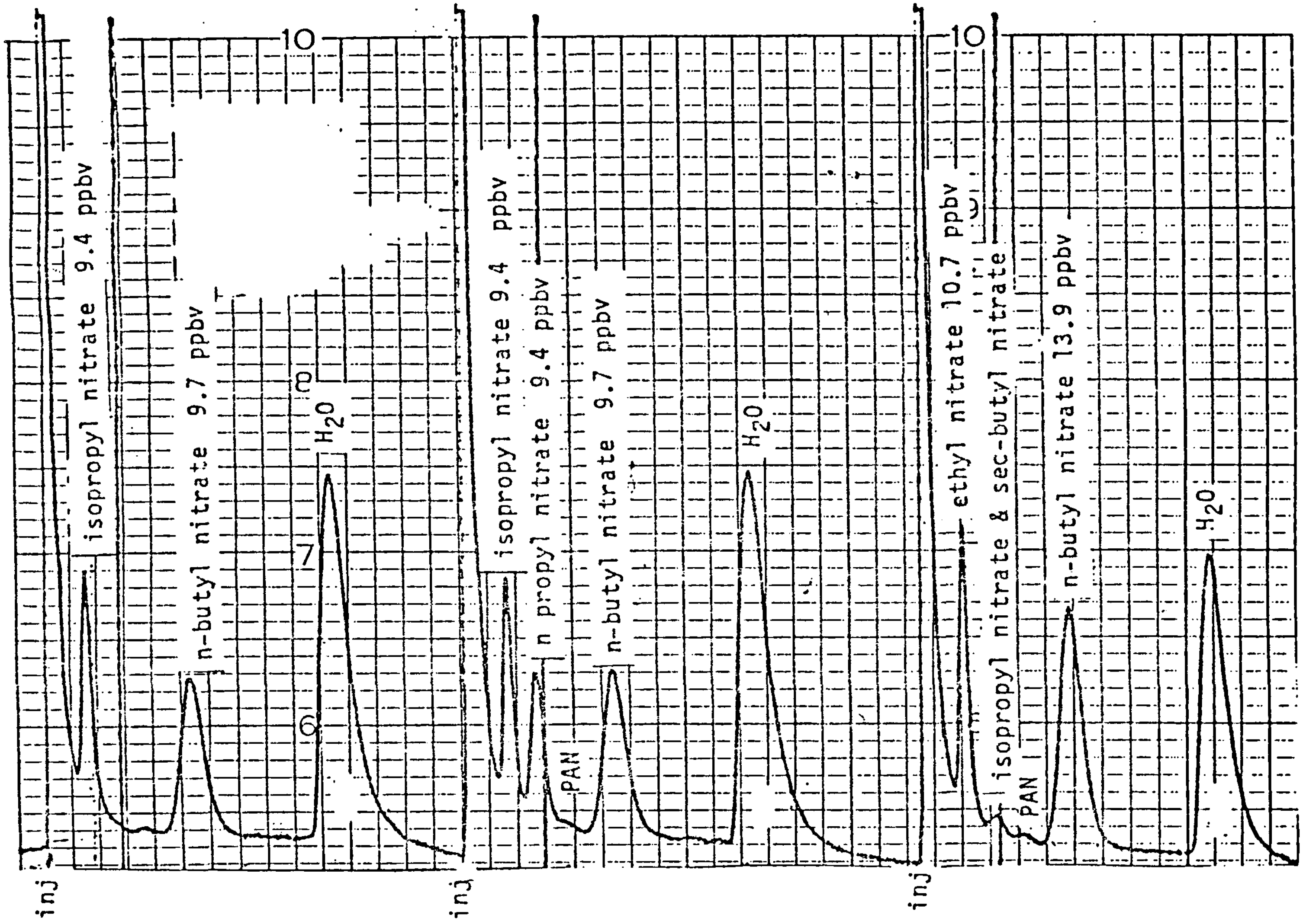

Figure B20. Detection of alkylnitrates with automated PAN GC, Varian 940 ECD. N_2 flow = 5 cc/min, oven and detector at 24.5°C, standing current on 32×10^{-9} amps = 91% of full scale, chart = .1"/min, atten. = $\times 32 \times 10^{-10}$ amps.

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