



Project Summary

Outdoor Chamber Study to Test Multi-Day Effects: Volumes I, II, and III

William P. L. Carter, Margaret C. Dodd, William D. Long, Roger Atkinson, and Marcia C. Dodge

A series of single- and multi-day indoor and outdoor environmental chamber experiments have been carried out at the Statewide Air Pollution Research Center (SAPRC) at the University of California in Riverside to derive data suitable for testing chemical models for multi-day photochemical air pollution episodes. Two environmental chambers were used during this program, ~6400-/ indoor Teflon chamber with blacklight irradiation and a ~50,000-/ dual-mode outdoor Teflon chamber that employed natural sunlight as the light source. A total of 32 indoor and 55 outdoor chamber experiments were completed during this program. These chamber experiments consisted primarily of multi-day NO_x-air irradiations of an eight-component hydrocarbon surrogate designed to represent emissions of reactive organics into urban atmospheres from all sources, and associated control and characterization runs. Most of the multi-day surrogate-NO_x-air experiments in the outdoor chamber were run with the chamber in the dual mode, where each experiment consisted of simultaneous irradiation of two different mixtures under the same temperature and lighting conditions. In addition, an isobutene-NO_x-air irradiation was carried out in the indoor chamber to test chemical computer models for the NO_x-air reactions of this surrogate component.

Problems with side inequivalency in the dual-mode outdoor chamber experiments were encountered in preliminary experiments carried out in 1982. These were subsequently resolved, and good side-to-side equivalency was obtained

in the experiments carried out in 1983. During that time, irradiations of a "standard" surrogate-NO_x-air mixture were carried out under a variety of temperature and light intensity conditions, allowing the combined effects of these to be determined. Good reproducibility of experiments carried out under similar weather conditions was observed.

The multi-day surrogate-NO_x-air irradiations were carried out in both chambers at a variety of initial hydrocarbon and NO_x concentrations. In general, it was found that runs that were less reactive on the first day with respect to O₃ formation tended to be more reactive on subsequent days, and vice versa. As a result the maximum O₃ levels in multi-day runs were much less dependent on initial reactant concentrations than expected on the basis of results of single-day irradiations.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Multi-day air pollution episodes are characteristic of most urban airsheds, especially those in the eastern and northeastern United States and the California South Coast Air Basin. Airshed computer models must thus incorporate chemical packages designed specifically for such multi-day conditions. During the

last decade there have been significant advances in our understanding of the chemistry of photochemical air pollution, resulting in the development of chemical mechanisms that have been tested against environmental chamber data and that are currently in use in airshed computer models. However, these chemical models have been validated only for, and thus are applicable only to, single-day conditions. Since the development of chemical models requires the availability of environmental chamber data against which these models can be tested, the Atmospheric Sciences Research Laboratory of the U.S. Environmental Protection Agency contracted the Statewide Air Pollution Research Center (SAPRC) at the University of California, Riverside, to conduct a series of indoor and outdoor chamber experiments simulating multi-day conditions using a hydrocarbon mixture designed to simulate that present in urban airsheds.

Procedure

Two different environmental chambers were employed in this program: a ~50,000-/ outdoor all-Teflon chamber and a ~6400-/ indoor all-Teflon chamber. These two chambers were employed because each has its own unique set of advantages. The outdoor chamber has a lower surface/volume ratio and has more realistic lighting conditions, while indoor chamber experiments can be carried out under more controlled conditions. Thus the indoor and outdoor chamber experiments are complementary, allowing a more thorough and comprehensive testing of the chemical models.

Both environmental chambers employed in this program were constructed from replaceable FEP Teflon film that could collapse as samples were withdrawn for analyses, thus avoiding dilution of their contents during the experiments. The ~50,000-/ outdoor chamber could be operated in either single or dual mode. The majority of the experiments conducted in the outdoor chamber in this program were carried out in the dual mode, and hence two separate experiments were simultaneously run with the same lighting and temperature conditions. The indoor chamber was operated solely in the single mode.

In all experiments, the reactants were injected prior to the beginning of the irradiation. In the outdoor runs, the irradiations generally were initiated by uncovering the chamber around 1000 PST, and the chamber was covered at around 1500 PST in the evening (to

avoid differential irradiation of the chamber sides caused by shadows). On subsequent days of multi-day irradiations, this chamber was uncovered at 0900 PST. For the indoor chamber runs, the lights were turned on for 12 h at a constant intensity (corresponding to an NO₂ photolysis rate of 0.30 min⁻¹, as determined by separate actinometry experiments), alternating with 12 h of darkness to simulate nighttime. Ozone, NO-NO₂-NO_x temperature and (for the outdoor runs) UV intensity and the NO₂ photolysis rate were monitored continuously; and organic reactants and selected products were monitored periodically by gas chromatography during the daytime.

Experiments Carried Out

The principal experimental runs in this program consisted of irradiations of "urban surrogate"-NO_x-air mixtures, which were carried out for 2 to 4 days each, with NO_x being injected on subsequent days for some of these experiments to simulate NO_x emissions into an aged air mass, and to allow renewed photochemical O₃ production to occur. The majority of these experiments were carried out to determine the effects of varying the initial reactant concentrations, with (in the case of the dual-mode outdoor experiments) a "standard" surrogate-NO_x mixture being irradiated on one side of the chamber, and a mixture with differing initial surrogate and/or NO_x concentrations on the other. The standard reactant mixture consisted of ~4 parts per million of carbon (ppmC) of this surrogate mix together with ~0.4 ppm of NO_x (at an initial [NO]/[NO₂] ratio of ~2), although many experiments were carried out with differing surrogate and NO_x concentrations to investigate the effects of varying the initial reactant concentrations. The "urban surrogate" was a mixture of eight hydrocarbons chosen to simulate emissions into urban atmospheres (Whitten and Killus, private communication), and its composition is given in Table 1. Isobutene was included in this mixture primarily to represent formaldehyde, which is an important constituent of urban emissions, but which is difficult to handle experimentally. Isobutene reacts rapidly to form formaldehyde (together with acetone) in NO_x-air photooxidations. This was confirmed in a separate isobutene-NO_x-air indoor chamber irradiation carried out under this program.

In addition, a number of conditioning, control, and characterization runs were carried out in order to make the data of

Table 1. Composition of the "Urban Surrogate" Hydrocarbon Mixture

Hydrocarbon	Percent Carbon	ppm Component ppmC Surrogate
Ethene	5.0	0.025
Propene	5.6	0.019
Isobutene	14.3	0.036
n-Butane	15.8	0.040
n-Pentane	19.6	0.039
Isooctane	14.8	0.018
Toluene	12.6	0.018
m-Xylene	12.3	0.015

maximum utility for model testing purposes. These consisted of (a) propene-NO_x control and conditioning runs, (b) ozone dark decay experiments, (c) acetaldehyde-air irradiations to measure NO_x offgassing (from the rate of formation of PAN in the absence of added NO_x), (d) radical tracer-NO_x-air and CO-tracer-NO_x-air irradiations to measure the chamber radical source, and (e) runs for the outdoor chamber side equivalency tests.

Results

Outdoor Chamber Experiments

These experiments were carried out in two separate phases, the first in the fall and the early winter of 1982, and the second during the summer and fall of 1983. During the first phase, serious problems with side equivalency were encountered, and most runs carried out during that time were side equivalency tests aimed at investigating this problem. Although the results of these tests are somewhat ambiguous, it was concluded that the problem was probably due to the method of injecting the surrogate compounds into the reaction bag (the liquid components were injected into one side before the bag was divided, and the gaseous components were injected into the other), possibly combined with inadequate conditioning of the reaction bags. This problem was corrected prior to carrying out the second phase of outdoor experiments.

A total of 12 multi-day surrogate-NO_x runs were successfully completed during the second phase of the outdoor chamber experiments. Four of these runs were side equivalency tests in which the same surrogate-NO_x mixture was irradiated on both sides of the chamber, and except for the first such run, which was apparently carried out using an insufficiently conditioned chamber, good side equivalency was observed. As an example, Figure 1 shows the results of one run where good side equivalency occurred up to the time NO was injected into side 2 on the second day of the irradiation. Except

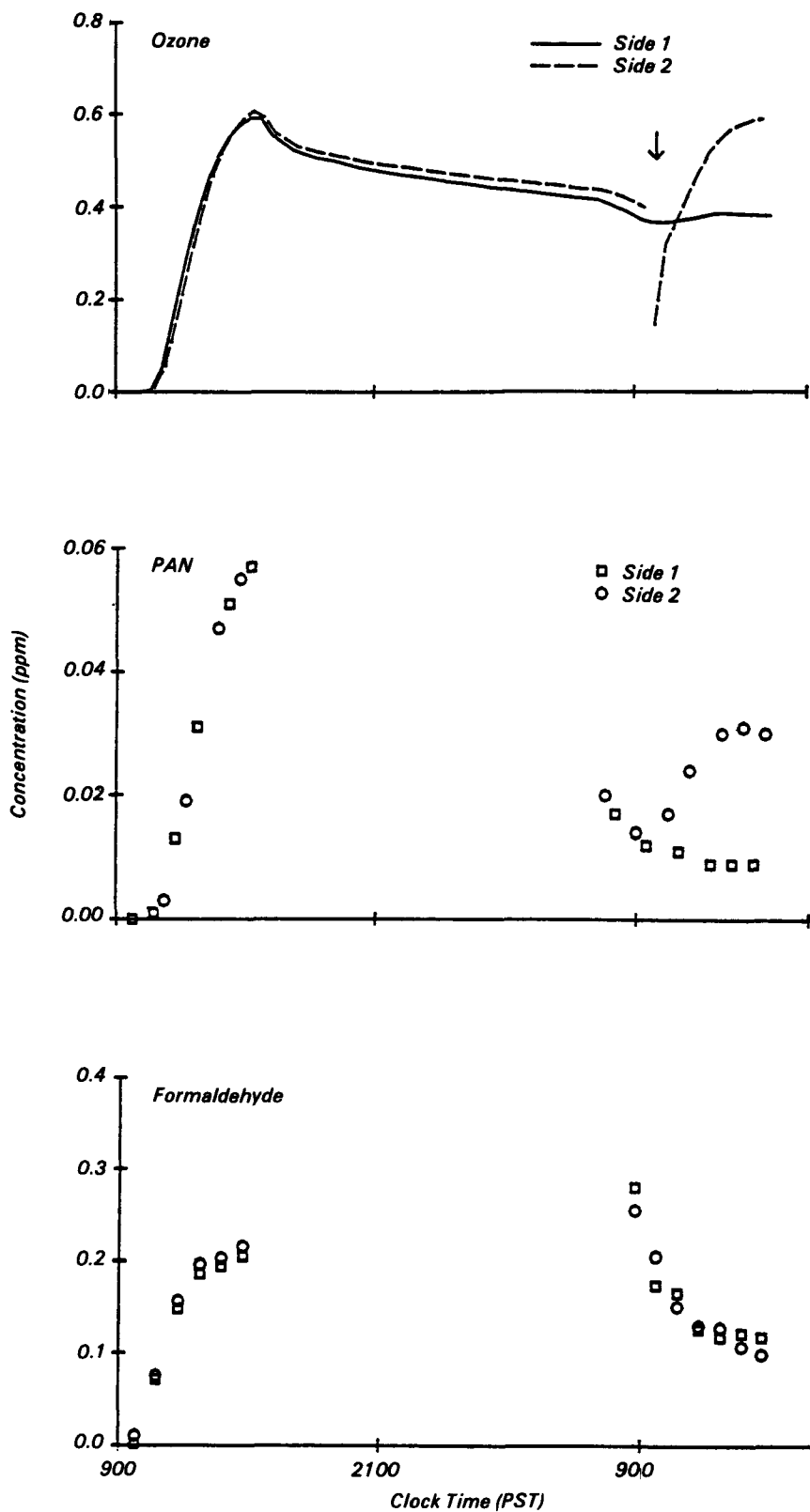


Figure 1. Concentration-time plots for O₃, PAN and formaldehyde for run OTC-199. Arrow indicates the time that ~ 0.5 ppm NO was added to side 2.

for one run, which was carried out in such a manner that the NO_x offgassing rate on day 2 was measured while the irradiation was being carried out, the multi-day runs consisted of a series of divided chamber runs where initial levels of surrogate and/or NO_x were varied. For several of these runs, NO was injected on subsequent days of the run to regenerate photochemical reactivity.

Many of these runs involved irradiation, either on one side of the divided chamber or in the undivided chamber, of a "standard" ~3.5- to 4- ppmC surrogate plus ~0.4-ppm NO_x mixture, with the average temperature (for the first day) ranging from 10°C to 42°C, and the average NO₂ photolysis rate (k_1) ranging from 0.12 min⁻¹ to 0.32 min⁻¹. A comparison of the concentration-time profiles for O₃ and NO₂ (the latter uncorrected for interferences due to organic nitrates and HNO₃) for these irradiations is shown in Figure 2. It can be seen that although some irradiations give remarkably similar results, other runs, particularly those carried out during the winter months, exhibited significantly lower reactivities.

An obvious explanation for these different reactivities shown in Figure 2 is the differences in light intensity for these irradiations. Indeed, the first-day maximum O₃ yield in the standard runs was highly correlated with the average temperature and the average light intensity data, with a 0.93 correlation coefficient in both cases. Reasonably good reproducibility was observed in separate runs carried out under similar lighting and temperature conditions.

In addition to these irradiations of the "standard" ~3.5- 4-ppmC surrogate plus 0.4-ppm NO_x mixture, irradiations were carried out in which the initial hydrocarbon or the initial NO_x concentration was varied, usually with the standard mixture on one side of the divided chamber and a modified mixture on the other. For example, Figure 3 shows selected concentration-time profiles for two variable hydrocarbon surrogate runs, and Figure 4 shows selected profiles for two variable NO_x runs that were carried out under similar conditions of temperature and light intensity. As for other such irradiations carried out in this program, and as expected from existing environmental chamber and computer modeling data, the reactivity on the first day tended to increase with increasing initial surrogate concentration and, at least at the reactant levels and conditions employed here, to decrease with increasing initial NO_x

concentration. However, as seen from these figures, this was not necessarily the case for the second day of the irradiation, where in many cases the amount of O_3 formed on the second or subsequent days tended to be negatively correlated with the reactivity on the first day.

In many experiments, NO was added on the second and/or subsequent days of the irradiation to obtain data concerning its effect on O_3 formation. A typical result of NO addition is shown in Figure 1, which shows the effect of adding ~ 0.15 ppm of NO to side 2 of the chamber at the beginning of the second day of a matched surrogate- NO_x (side equivalency test) run. It can be seen that while the addition of NO caused an initial large drop in the O_3 level, because of the rapid reaction between O_3 and NO, subsequently rapid O_3 formation occurred resulting in much higher O_3 levels at the end of the day than for the side without added NO, where no photochemical O_3 formation occurred on that day.

Indoor Chamber Experiments

The results of the six indoor chamber multi-day surrogate runs were qualitatively similar to those for the outdoor chamber runs discussed above. For example, Figure 5 compares the results of experiments with differing initial NO_x levels. It can be seen that increasing the initial NO_x resulted in relatively little O_3 formation on the first day, but resulted in greater O_3 formation on the second day, unless, as was the case for run ITC-635, the initial NO was so high that it suppressed O_3 formation on the second day as well. The effects of varying the initial hydrocarbon concentrations were also similar to those observed in the outdoor chamber experiments.

As for the outdoor chamber irradiations, the addition of NO on subsequent days of the experiments resulted in additional O_3 formation, provided that the amount of NO added was not so high that O_3 formation was suppressed by the presence of large levels of excess NO. For example, Figure 6 compares the results of two surrogate- NO_x runs (ITC-626 and 637) when NO was added on subsequent days. These two runs had approximately the same initial reactant concentrations, and good reproducibility was observed on the first day of the irradiation. In run ITC-626, the amount of NO added was so high (~ 0.8 ppm) that it completely suppressed O_3 formation, and it is interesting to note that 2 h after the first NO addition, the oxidation of NO essentially stopped,

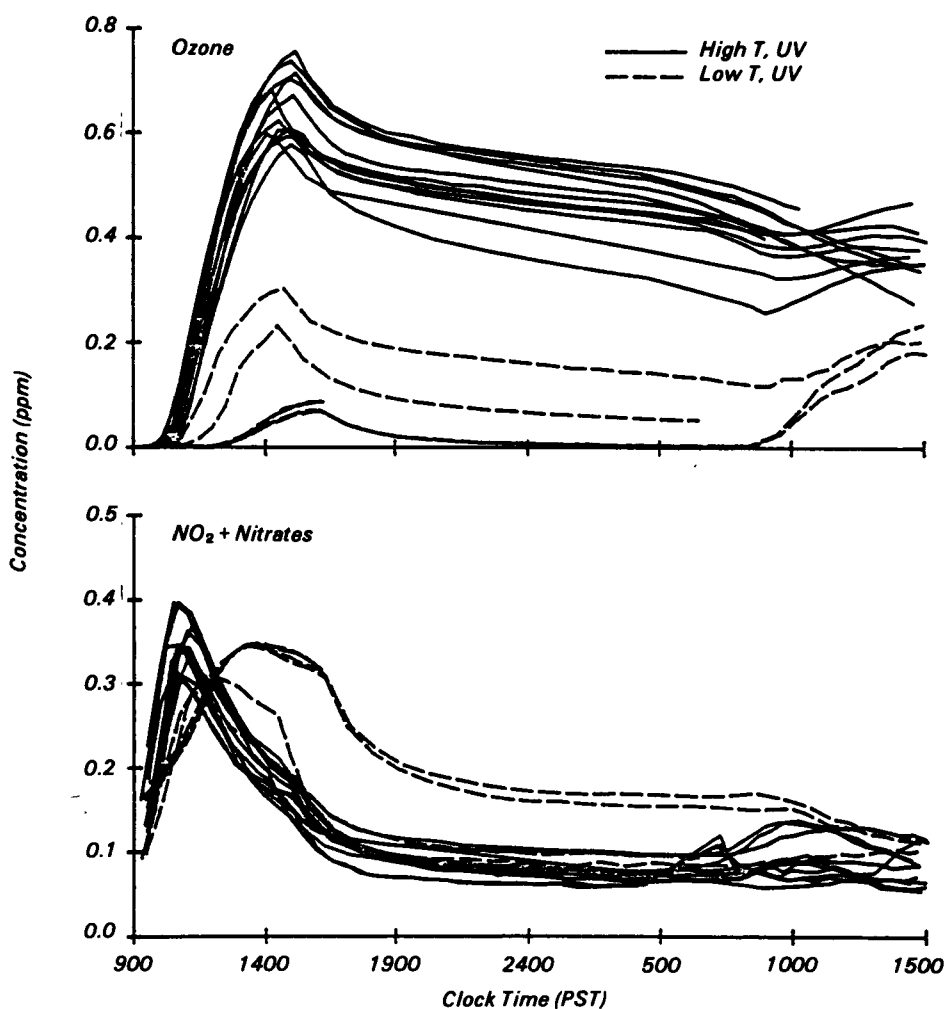


Figure 2. Concentration-time plots for ozone and uncorrected NO_2 for the standard surrogate- NO_x irradiations, where the runs are classified as either "high T, k_1 " runs (average $T > 32$ C, average $k_1 > 0.2 \text{ min}^{-1}$) or "low T, k_1 " runs (average T, k_1 both below those values).

indicating a very unreactive mixture. However, when relatively low levels of NO (~ 0.2 ppm) were added each day for the subsequent 3 days of the run, then significant O_3 formation occurred, although the increase of the O_3 concentration following each NO injection decreased monotonically each day. This indicates a gradual decrease in the reactivity of the reacting surrogate mixture with time.

Conclusions

The smog chamber data collected in this study were supplied to Systems Applications, Inc. (SAI), for analysis under EPA Contract No. 68-02-3738. The analysis of these data by SAI resulted in the development of a multi-day chemical mechanism suitable for use in regional

oxidant models. The purpose of this project report is to make the experimental data available to the scientific community at large to enable other researchers and modelers to further the development of chemical transformation models.

The project report is composed of three volumes. Volume I contains a description of the experimental facility, methods of procedure, and analytical techniques. Volume II contains printouts of the detailed data that were collected in these experiments. Volume III includes documentation on the computer-readable magnetic tape that contains the data collected in this study. All three volumes and the computer data tape are available through the National Technical Information Service, Springfield, Virginia, (see ordering information at back).

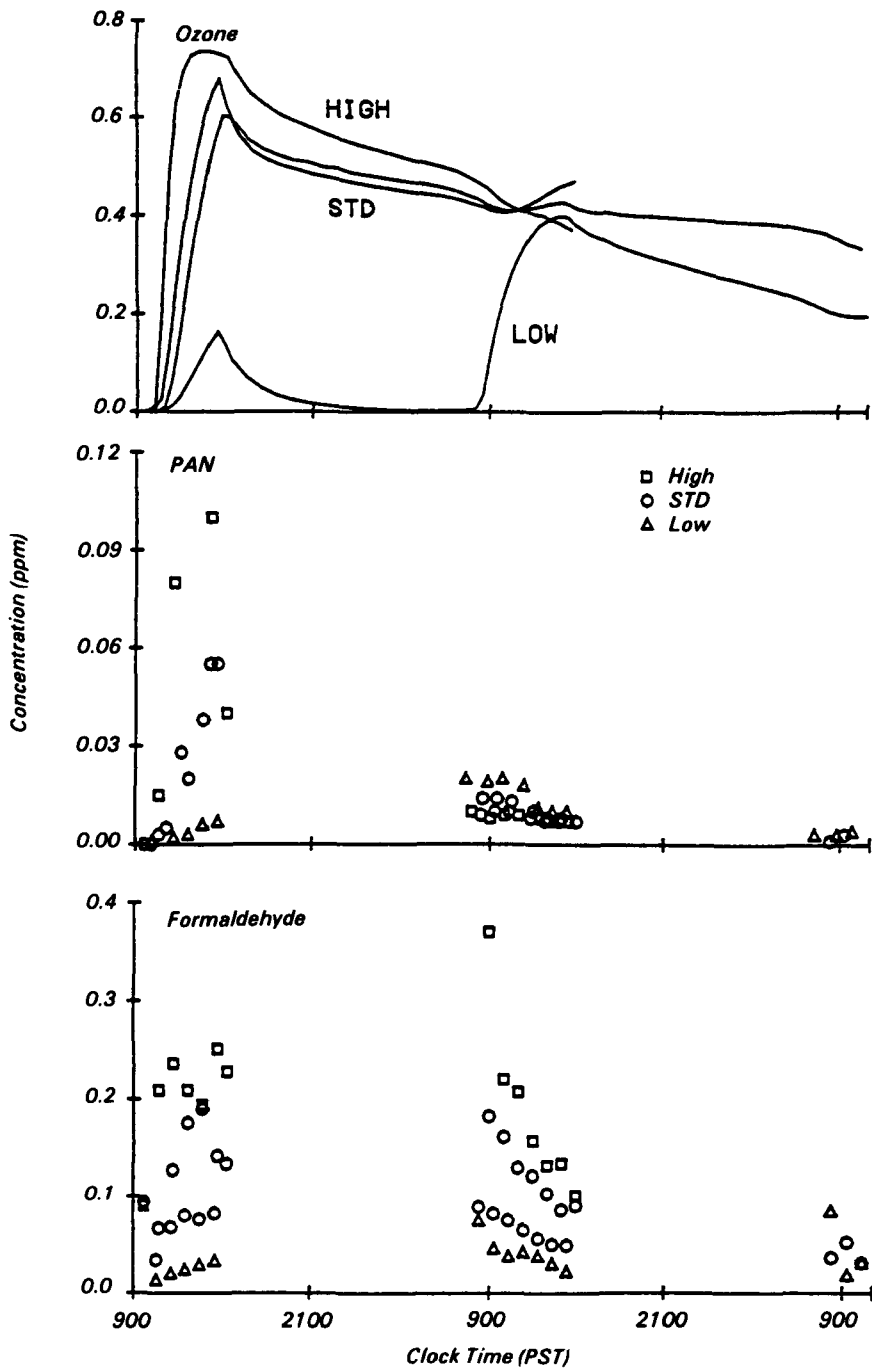


Figure 3. Concentration-time plots of O_3 , PAN and formaldehyde for the variable surrogate runs OTC-194 and 195. "High," "low" and "STD" refers to data for mixtures with initial surrogate levels of ~ 7 , ~ 2 or ~ 4 ppmC, respectively.

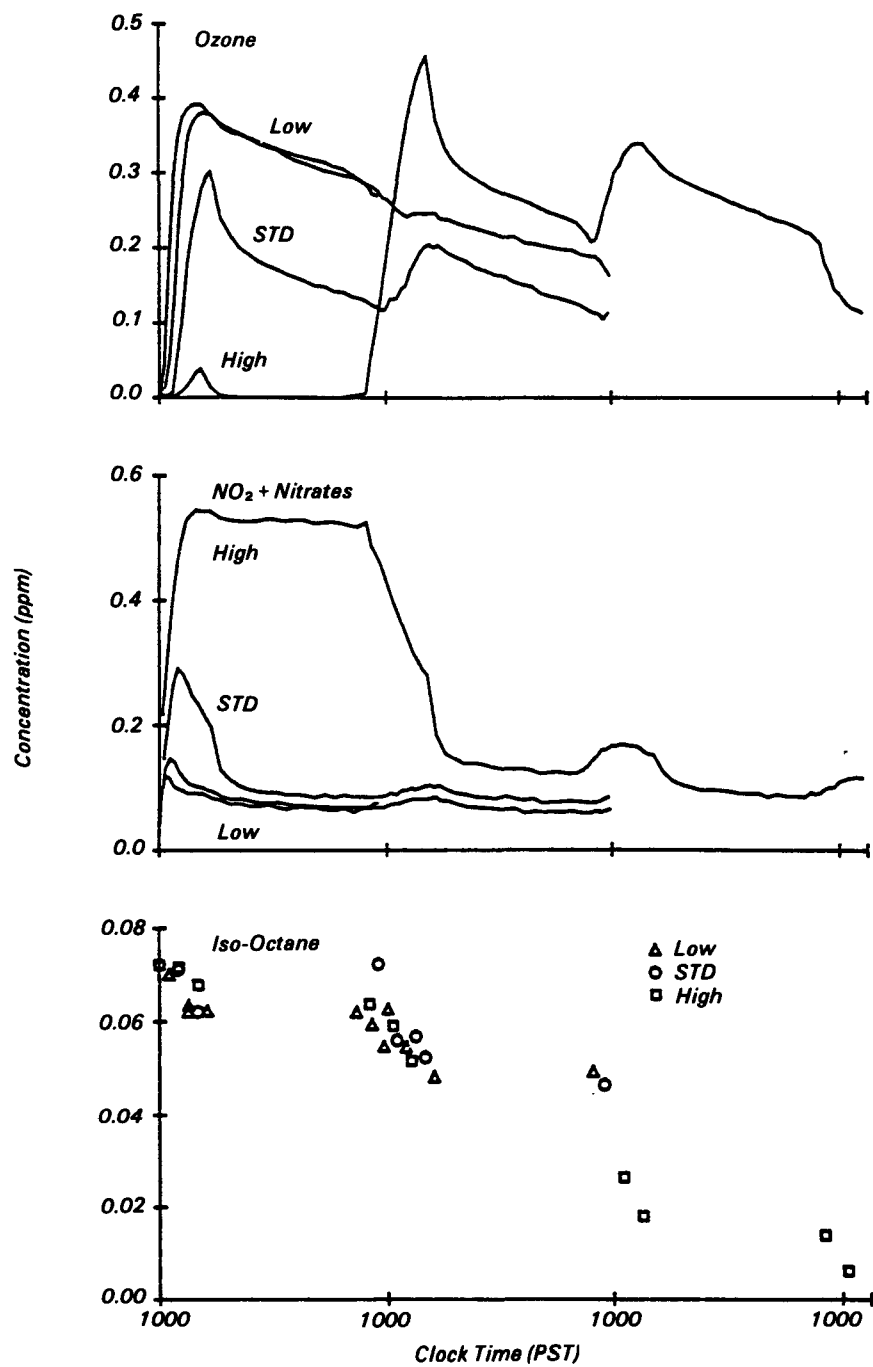


Figure 4. Concentration-time plots of O₃, uncorrected NO₂ and isooctane for the variable initial NO_x runs OTC-204 and 205. "High," "low" and "STD" refer to curves for mixtures with initial NO_x levels of ~0.8, ~0.2 and ~0.4 ppm, respectively. Data obtained after subsequent NO_x injections not shown.

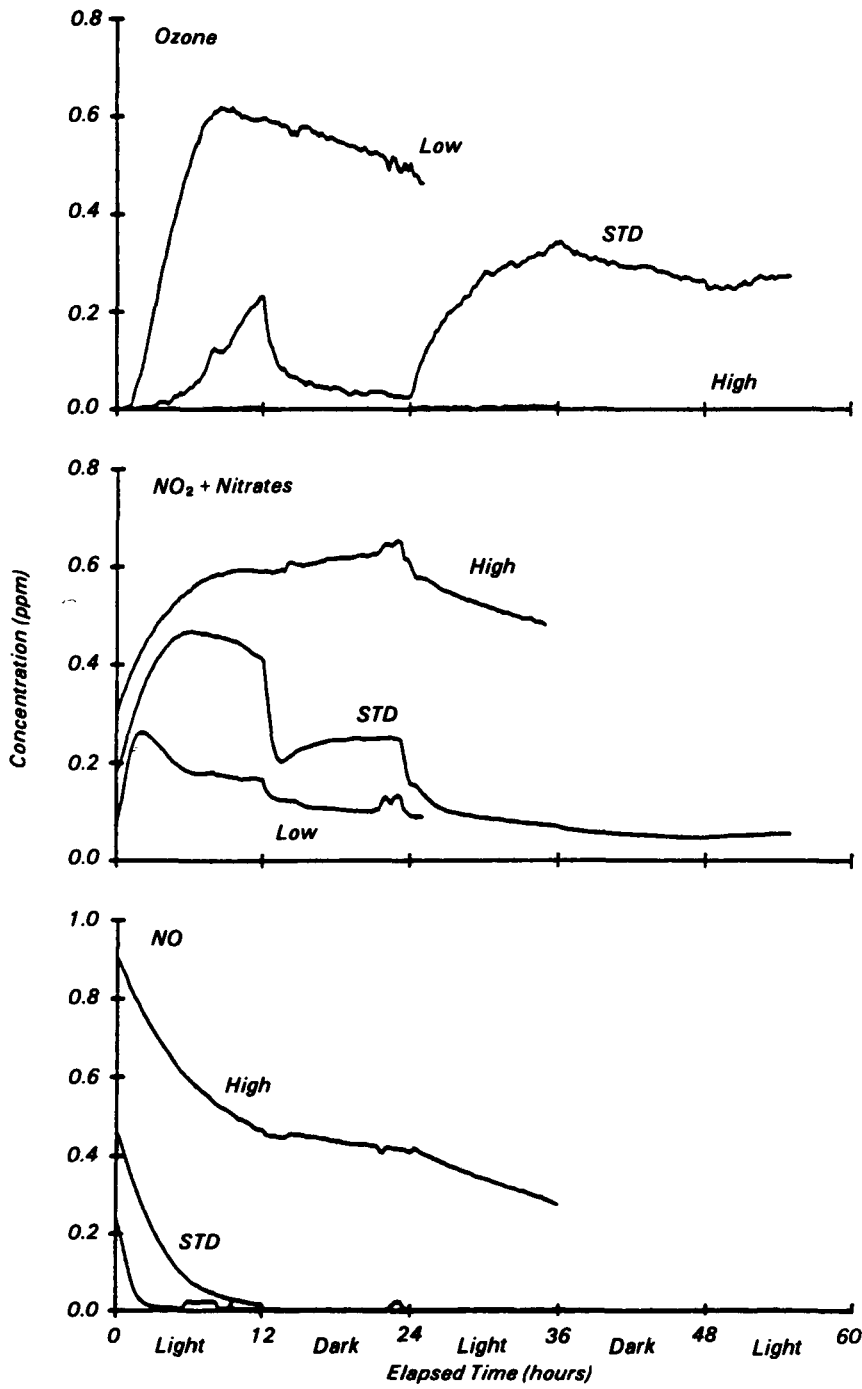


Figure 5. Concentration-time plots of O₃, uncorrected NO₂ and NO observed in indoor Teflon chamber runs 633, 635 and 637. "Low," "STD" and "high" refer to runs with ~0.3, ~0.6 and 1.2 ppm initial NO_x, respectively. Data obtained for subsequent NO_x injections not shown.

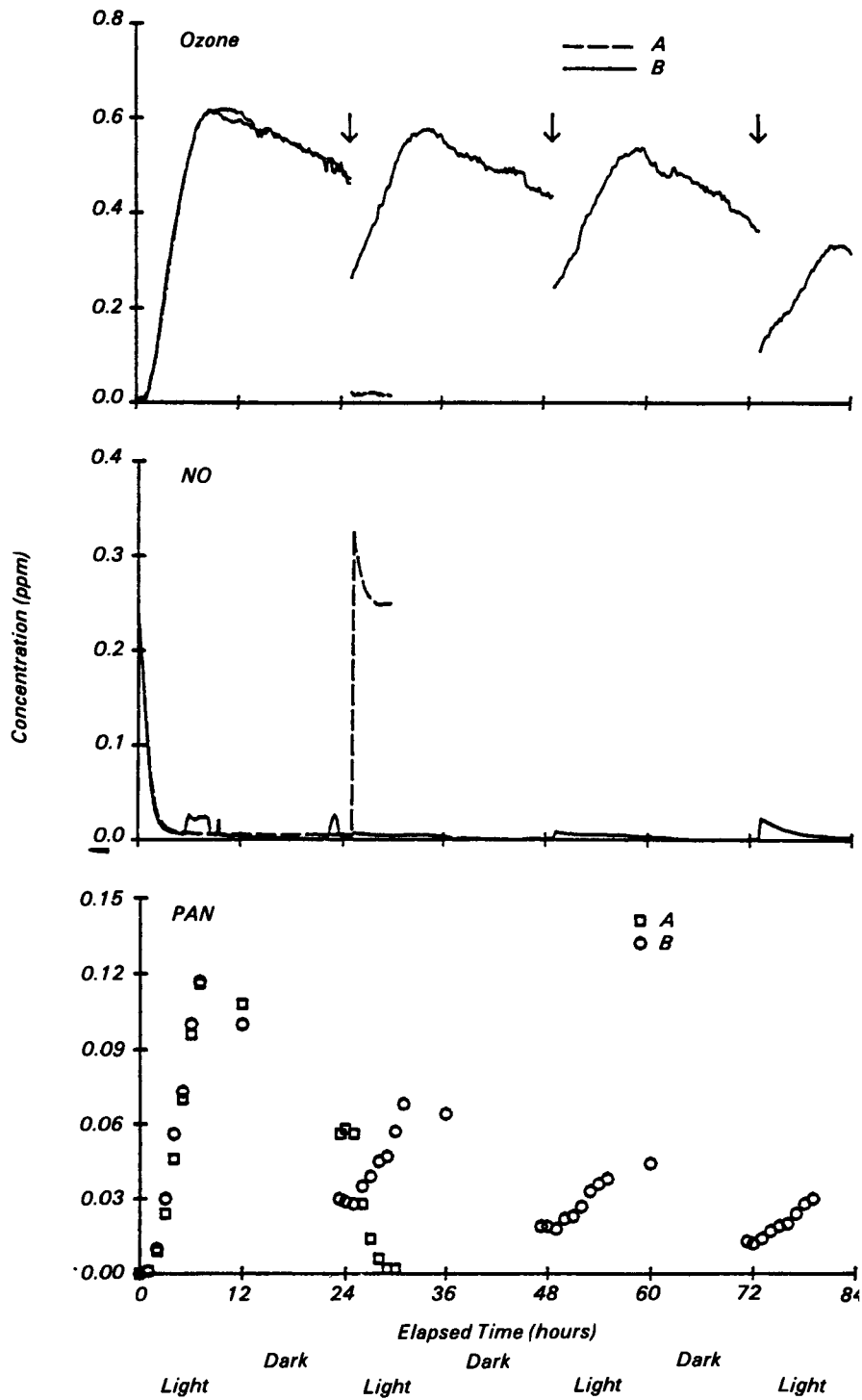


Figure 6. Concentration-time plots for O_3 , NO and PAN for indoor chamber runs 626 and 637. Arrows indicate times NO was injected. "A" = run 626, "B" = run 637.

W. P. L. Carter, M. C. Dodd, W. D. Long, and R. Atkinson are with the Statewide Air Pollution Center, University of California, Riverside, CA 92521; the EPA author Marcia C. Dodge (also the EPA Project Officer, see below) is with the Atmospheric Sciences Research Laboratory, Research Triangle Park, NC 27711.

The complete report consists of four volumes, entitled "Outdoor Chamber Study to Test Multi-Day Effects:"

"Volume I. Results and Discussion," (Order No. PB 85-161 628; Cost: \$14.50)

"Volume II. Environmental Chamber Data Tabulations," (Order No. PB 85-161 610; Cost: \$47.00)

"Volume III. Computer-Readable Environmental Chamber Data," (Order No. PB 85-161 602; Cost: \$7.00)

"Volume IV. Magnetic Tape," (Order No. PB 85-161 636; Cost: \$140.00)

The above reports and magnetic tape will be available only from: (costs subject to change)

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:
Atmospheric Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711*

Cincinnati OH 45268

ness
Private Use: \$300

0000329 PS

U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604

RECEIVED
MAY 10 1980
LIBRARY
MAY 10 1980
MAY 10 1980