

INVESTIGATION OF THE ROLE OF NATURAL HYDROCARBONS IN
PHOTOCHEMICAL SMOG FORMATION IN CALIFORNIA

Final Report

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ABSTRACT

Progress is described for the first year of a two-year program designed to obtain data necessary for assessing the potential contribution of natural organics to the formation of photochemical air pollution in the California South Coast Air Basin (CSCAB). Needed data include knowledge of emission rates, ambient concentrations and oxidant- and aerosol-forming potential of biogenic hydrocarbons as well as estimates of vegetative biomass in the CSCAB.

Progress made during the initial year of this investigation included:

- Development of oxidant-precursor relationships for α -pinene based on data obtained using a 40,000-liter dual-mode outdoor irradiation chamber.
- Initial measurements of the ambient concentrations of natural hydrocarbons emitted by relevant vegetative communities in areas free of anthropogenic emissions.
- Development of plant enclosure chambers and analytical methods for measuring the emission factors of isoprene and monoterpenes from natural, ornamental and agricultural vegetation in the "source region" of the CSCAB.
- Studies of the feasibility of applying remote imagery techniques (including LANDSAT, U-2 and low altitude photography) to the task of quantifying the extent and mass of vegetation in the "source region" of the CSCAB.

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The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

I. PROJECT SUMMARY

A. Introduction and Background

This CARB-SAPRC research program was conceived at a time (ca. 1978) of growing controversy concerning the possible contribution of hydrocarbons emitted from vegetative biomass to photochemical oxidant formation in urban and rural areas. The discourse between Coffey and Westberg (1977), undertaken in the context of the U. S. Environmental Protection Agency's International Conference on Oxidants, summarized most of the published literature to that time but left unresolved many of the major questions involved in this issue. Moreover, the controversy was heightened in 1978 with the appearance in SCIENCE of a widely read report by Sandberg, Basso and Okin of the San Francisco Bay Area Air Quality Management District. They argued that higher rainfall caused greater growth of vegetative biomass which, in the following summer, released larger quantities of organic material to the atmosphere, thus causing higher photochemical ozone formation.

We (Miller, Pitts and Winer 1978) and others (Bufalini 1978) argued that the proposal by Sandberg did not give proper attention to important factors that determine the temporal and spatial concentrations of ozone in urban airsheds, including summer meteorological patterns, photochemistry, transport and hydrocarbon/NO_x ratios. Further, other workers had, at that time, obtained recent ambient air data (Zimmerman et al. 1978, Lonneman et al. 1978, Arnts et al. 1977) which suggested that vegetative hydrocarbons do not accumulate to high enough concentrations to add additional ozone to that produced from anthropogenic sources. However, such conclusions were challenged in the published literature (Sculley 1979, Ludlum and Bailey 1979).

Compounding the questions raised in the refereed literature was the absence of detailed, reliable emission inventories and ambient measurements of natural organics for any of California's urban airsheds; nor were useful determinations of oxidant-precursor relationships available for such compounds. It was recognized that the lack of this information might leave certain of the CARB's emission control programs open to challenge and might hinder development of a defensible state implementation plan for 1982.

To attempt to address these needs, the CARB initiated, in October 1979, a two-year study at SAPRC designed to assess the potential contribution of

natural organics to the formation of photochemical air pollution in the California South Coast Air Basin. Although, since this program began, new data have become available from other laboratories (e.g., Zimmerman 1979, 1980, Holdren et al. 1979, Graedel 1979, Peterson and Tingey 1980, Arnts and Meeks 1980), as discussed in two recent, excellent reviews by Tingey and Burns (1980) and Dimitriades (1981), these have failed to entirely resolve the general issues, and have certainly not provided the data required for specific assessments of the situations in California's urban airsheds.

Assessments of the "air pollution" impact of biogenic hydrocarbons requires knowledge of their emission rates (during the smog season and in the source region of the airshed), ambient concentrations and oxidant- and aerosol-forming potential. Although we have made significant progress in laying the foundation for obtaining the required data for the South Coast Air Basin, we emphasize that the most productive phases of the present study will necessarily occur during the second year of the program. Thus, much of the effort during the first year has been developmental or exploratory in nature, and some of the techniques and results reported here have been superseded by subsequent progress on this program.

During the initial study period, we have (a) developed oxidant-precursor relationships for α -pinene using our dual-mode outdoor irradiation chamber; (b) made initial measurements of the ambient concentrations of natural hydrocarbons emitted by relevant vegetative communities in areas free of anthropogenic emissions; (c) developed plant enclosure and analytical methodologies for measuring the emission rates of isoprene and the monoterpenes from such vegetation; and (d) explored the feasibility of applying remote imagery capabilities and expertise which are present on the UCR campus (including LANDSAT, U-2 and low altitude photography) to the task of quantifying the extent and estimated mass of vegetation types characteristic of the western portion of the South Coast Air Basin.

In the sections which immediately follow, we briefly summarize progress made in these areas. Detailed descriptions of the work conducted under this contract (No. A8-135-31) are given in Sections II-V. This report includes a thorough review of the literature particularly in two areas of major concern: emission rates of natural hydrocarbons and their atmospheric chemistry and oxidant forming potential.

B. Development of Plant Enclosures and Preliminary Measurements of Emission Rates

1. Introduction

We have carefully reviewed the available literature concerning previous estimates or measurements of emission rates of isoprene, monoterpenes and other organic compounds (e.g., aldehydes, alcohols and ketones) from vegetation and the experimental factors which can affect such measurements. Much of this literature is summarized in Section II.

The sampling environments represented in previous studies ranged from temperature and light controlled chambers (Rasmussen 1972) to calculations of the flux from a canopy of loblolly pine (Pinus taeda) in uncontrolled ambient conditions (Arnts et al. 1977). The units of measurement are unique to each investigation making it very difficult to compare the studies. Both concentrations and rates are reported but rarely in the same study; the former may be based on the weight of foliage and surface area of foliage, but in some cases only volume/volume units are presented.

Tingey and Burns (1980) have placed the more recent emission rate data of Zimmerman (1979a), Tingey et al. (1980), Arnts et al. (1978), Kamiyama et al. (1978) and Flyckt et al. (1980) on a common basis as shown in Table 1. For the one common species studied by two investigators (live oak), the isoprene emission rates reported differ by more than a factor of four.

An important conclusion from our survey is that few measurements have been made under southern California's Mediterranean climate regime or with a sufficient sample of plant species which are dominant or abundant in this region. Moreover, it is important to recognize that due to perturbation of the plant (by prolonged enclosure at elevated temperatures in a static atmosphere with indeterminate water vapor deficits and carbon dioxide concentrations), the emission rates obtained for individual species in enclosed atmospheres may be higher than the actual emission rates occurring in ambient air. If this is the case, then the total emissions calculated on global and regional bases may be significantly overestimated. Evidence that this may be the case is the incompatibility between the high emission rates and very low ambient concentrations of natural hydrocarbons such as isoprene and the monoterpenes reported to date, as discussed by Dimitriades (1981).

Table 1. Biogenic Hydrocarbon Emission Rates Estimated at 30°C
(Tingey and Burns 1980)

Species	g (g dry weight) ⁻¹ hr ⁻¹			References
	TNMHC ¹	Iso- prene	Mono- terpenes	
Slash Pine	4.1		2.6	Zimmerman 1979a
Longleaf Pine	7.3		5.6	Zimmerman 1979a
Sand Pine	13.6		11.0	Zimmerman 1979a
Cypress	14.2		8.1	Zimmerman 1979a
Slash Pine			6.4	Tingey and others 1980
Loblolly Pine			3.7	Arnts and others 1978
Cryptomeria			3.0	Kamiyama and others 1978
Laurel Oak	12.6	10.0		Zimmerman 1979a
Turkey Oak	26.5	23.4		Zimmerman 1979a
Bluejack Oak	56.4	43.9		Zimmerman 1979a
Live Oak	10.8	9.1		Zimmerman 1979a
Live Oak		41.2		Tingey and others 1980
Willow	22.1	12.4		Zimmerman 1979a
Saw Palmetto	11.5	8.6		Zimmerman 1979a
Mean 7 Hardwood Trees - Isoprene	20.0	15.7		Flyckt and others 1980
Wax Myrtle	7.5			Zimmerman 1979a
Persimmon	2.9			Zimmerman 1979a
Orange	9.4			Zimmerman 1979a
Grapefruit	4.3			Zimmerman 1979a
Red Maple	6.5			Zimmerman 1979a
Hickory	3.2			Zimmerman 1979a
Mean 10 Hardwood Trees - Non-Isoprene	7.3			Flyckt and others 1980

¹Total non-methane hydrocarbons.

2. Initial Enclosures and Measurements

Review of the literature reveals that the rates of emission of organic compounds from vegetation can be strongly affected by such "environmental" factors as light intensity, temperature, relative humidity, time of year, injury or foliar disturbance. Thus, all of these factors must be considered in designing a plant enclosure apparatus and in developing a protocol for emission rate measurements.

Teflon Bags. Our exploratory efforts to determine emission rates of natural hydrocarbons from selected individual plant species involved the use of simple Teflon bag enclosures. These were placed around branches of wild growing shrubs for short time intervals.

Preliminary sampling of several native shrub species permitted testing of the analytical techniques which had been developed as well as the determination of the kinds of compounds emitted by each species. Members of the native soft chaparral community present on the UCR campus or on the nearby Box Springs Mountains were selected because of their relative abundance in typical shrub stands. These species included California encelia (Encelia californica), California sage, (Artemesia californica) and chamise (Adenostoma fasciculatum).

Sampling was done between mid-morning to mid-afternoon on relatively warm, sunny days of good air quality. Portions of branches of the subject shrub were enclosed in a Teflon bag equipped with a side port to allow for insertion of a thermister probe and a Teflon tube connected to a 1-liter glass and Teflon syringe. The bag remained over the branch for times ranging from 3-10 minutes. A seal was maintained by holding the gathered film of the open end around the branch by hand.

The changes of temperature in the sunlit bag and the first evidence of water condensation on the interior of the bag were observed. The results shown in Figure 1 suggest that the minimum modification of the leaf environment may be obtained by sampling either early or late in the day and with enclosure times not exceeding five minutes.

Gas chromatographic samples were obtained for Encelia californica, Artemesia californica and Adenostoma fasciculatum in Teflon bag enclosures. A total of about 140 peaks were distinguished, the great majority of which were from the ambient air in the Teflon bag. Isoprene and α - and β -pinene were identified by their retention times and substantial concentrations of these compounds were observed (particularly for the pinenes). However, there were considerable fluctuations in concentrations observed for replicate or sequential samples.

On the basis of the data obtained, we conclude that the procedure for sampling natural hydrocarbons by enclosing branches of wild growing shrubs in flexible Teflon bags for short time intervals has serious drawbacks with

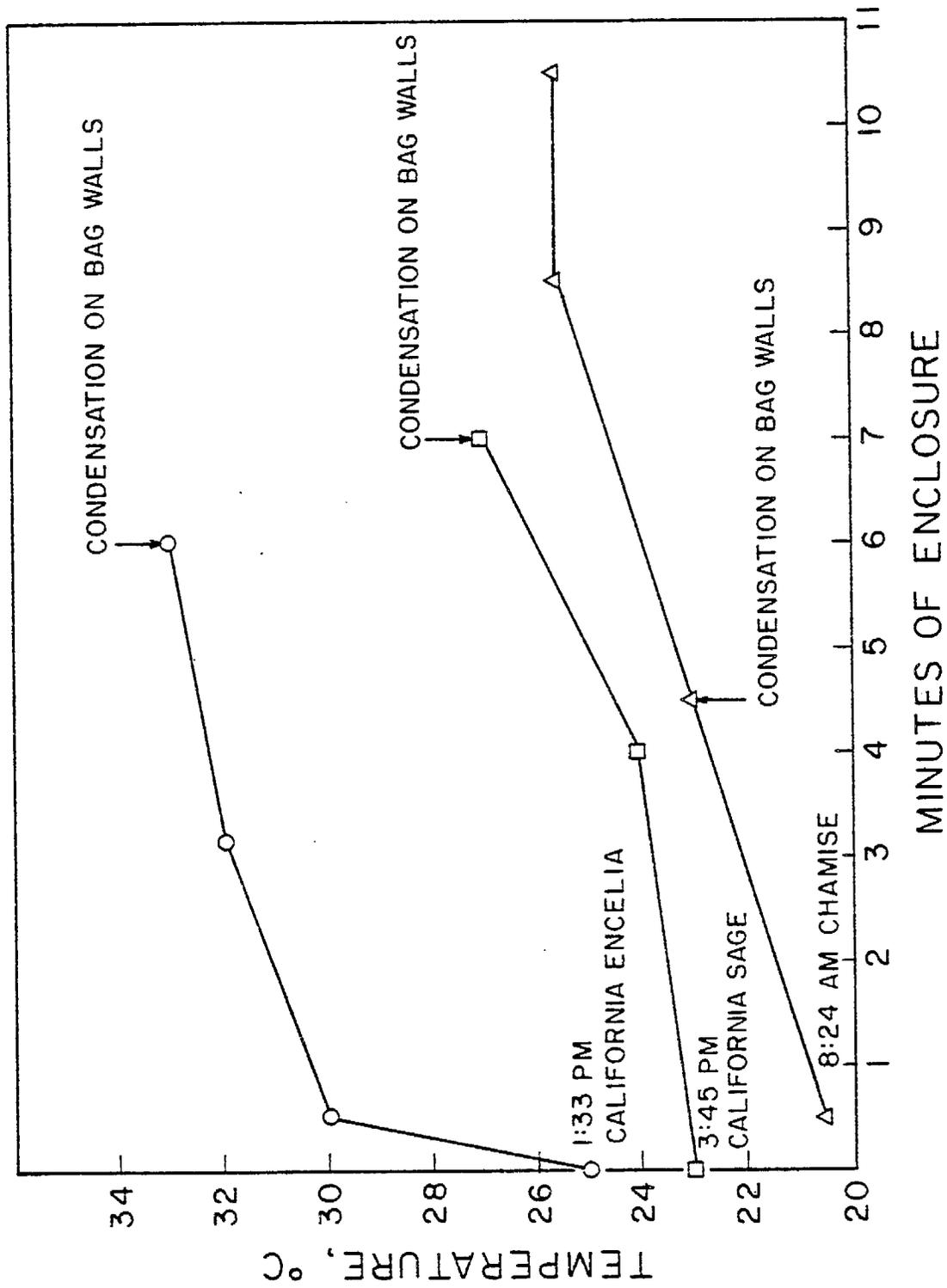


Figure 1. Behavior of temperature and humidity within Teflon bag as a function of enclosure time for three samples.

respect to obtaining reliable emission rates. Factors which can affect emissions in using this technique are mechanical injury, heat stress (including high relative humidity and depletion of CO₂) and contact with the Teflon film by the enclosed branch. Additionally, physical factors such as the volume of the bag, time period or land area to be charged with the emissions were not well defined. For these reasons the "static air" Teflon bag procedure was abandoned.

Rigid-Frame, Flow-Through Chambers. In order to address some of the problems encountered with use of the Teflon bags, two rigid-frame, flow-through chambers were designed and constructed. The sampling enclosures were built using Teflon film stretched over rectangular parallelepipeds made of plastic pipe. The smaller enclosure has a volume of about 500 liters and is designed to be used with small shrubs, either ornamental or natural. To test this enclosure, it was placed over a shrub (Pittosporum) with the lower end of the bag tied around the main stem. With a small blower forcing air through the enclosure, the temperature and humidity increase, respectively, inside the chamber was ~1°C and 19% in 30 minutes, and an additional 4°C and 19% in 130 minutes. Given a residence time of only a few minutes, and the modest changes in temperature and humidity over 30 minutes, it was felt that stress on enclosed plants could be held to acceptable levels with this chamber if enclosure times were held to periods of 10 to 20 minutes.

Use of the flow-through enclosures should yield an emission factor in units of micrograms of hydrocarbon per square meter of land surface per hour. It is only necessary to know the flow rate and the concentration of organics in order to estimate the emission factor for an enclosed plant. The flow rate was estimated by following the rate of decrease of the initial concentration of a test compound placed in the empty chamber. The dilution follows an exponential decay indicating good mixing.

When ambient air is used as the flow medium in the emission measurements, it is necessary to correct for the organic content of the incoming air. Alternatively, tank gases can be employed or matrix air from the SAPRC pure air system. With fractional ppb sensitivity, contamination from all sources must be considered, including the film from which the chamber is made and the plastic pipe which forms the frame of the enclosure. Additional samples were taken for a potted shrub of Encelia californica in the enclosure using the

SAPRC pure air system. A typical chromatogram is shown in Figure 2. A few peaks are identified and correspond to concentrations much smaller than those measured from individual Encelia branches enclosed in the plastic bags.

Field sampling using the flow-through enclosure appears to be practical using either ambient air or tank gases. It will be necessary to choose plants small enough to fit the enclosure; a larger enclosure has been constructed and others of various sizes are planned. Plants to be studied must be growing on level ground with a main stem which can be isolated from other plants. A ground sheet is designed to fit around the plant trunk and thus isolate it from surface emissions.

Illustration of Emission Inventory Calculations Based on Measured Emission Factors Using the Flow-Through Plant Enclosure Chamber. At a flow rate of air of 125 liters min^{-1} through the plant enclosure chamber a concentration of 1 ppb (of compound) corresponds to venting 5 nanomoles per minute or $0.68 \mu\text{g min}^{-1}$ of terpene ($\text{C}_{10}\text{H}_{16}$, MW = 136) from the chamber. The base area of the enclosure is about 0.38 m^2 , so this emission rate is equivalent to an emission factor of $108 \mu\text{g m}^{-2} \text{ hr}^{-1}$. For comparison, the emission factor corresponding to the emission of 100 metric tons of organics per day (~6% of the Los Angeles inventory) in an area 50 kilometers on a side with a 10% vegetative cover would be $16,700 \mu\text{g m}^{-2} \text{ hr}^{-1}$, more than 100 times greater than the value calculated above.

Thus, it appears that our present sampling enclosure and flow system will provide adequate sensitivity to establish meaningful upper limits (or actual values) for emission factors for individual plants even if our GC detection limit for the terpenes were no better than 1 ppb (our present detection limit is actually < 0.03 ppb compound).

C. Measurements of Ambient Concentrations of Natural Hydrocarbons Near Selected Plant Communities

1. Introduction

During the initial development (Year 1) of the sensitive gas chromatographic techniques required for fractional part-per-billion analysis of natural organics, it was decided to confine preliminary ambient air measurements of isoprene and the monoterpenes to locations in which hydrocarbons from anthropogenic sources would be present in low concentrations, facilitating

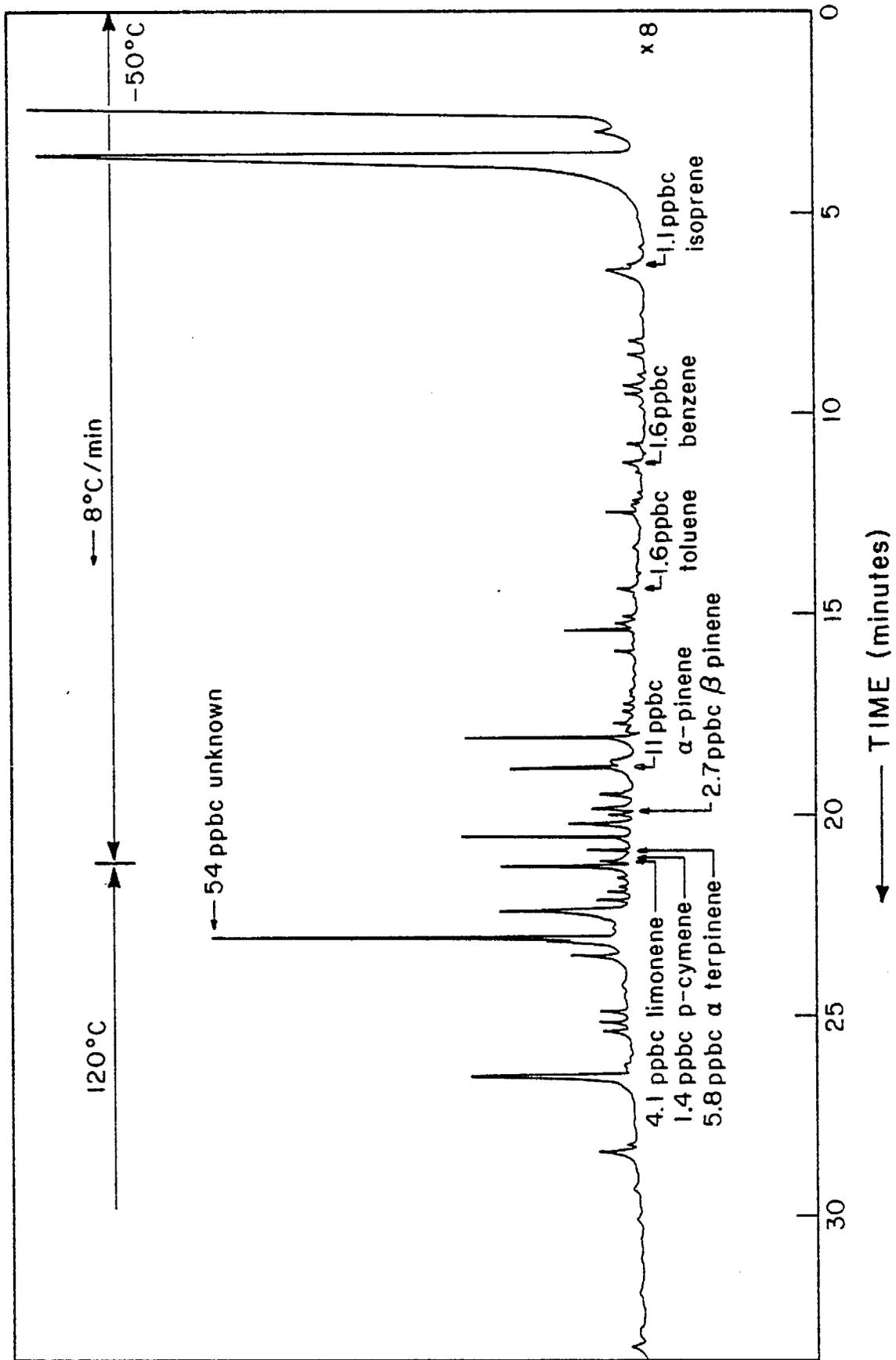


Figure 2. Capillary column gas chromatogram obtained for *Encelia californica* using rigid-frame, flow-through enclosure and SAPRC pure air system.

detection and measurement of the natural organics. In the second year of this study, emphasis will be placed on determining the ambient concentrations of isoprene and selected monoterpenes in the source area of the South Coast Air Basin.

2. Sites and Measurements

A number of possible remote sites were evaluated for studies of naturally emitted organics in areas free of anthropogenic emissions. The key criteria used in this evaluation were: (a) clean background air--no local sources of pollutants, (b) large upwind stands of the vegetative class of interest, (c) availability of electrical power and (d) accessibility. The four sites evaluated were Cibbit Flats, Mt. Laguna, Tenaja Ranger Station and De Luz. Hydrocarbon grab samples obtained at Cibbit Flats, Mt. Laguna and De Luz showed elevated levels of acetylene, ethane, propane, propene and other hydrocarbons of anthropogenic origin (most of which may be ascribed to auto exhaust).

Samples were taken at Tenaja Ranger Station in the Cleveland National Forest (see Table 2) in the early morning hours of June 11 and 17, 1980. The two sets of freeze-trap samples were analyzed by capillary GC. They did not show a high order of consistency as to peak heights, but the emergence times were reasonably consistent. The times varied by a few seconds which was the limit for the system at the time of these measurements.

The two-carbon hydrocarbons measured on June 11 indicated that little auto exhaust contamination was present. The largest peaks were the unidentified ones beyond α -pinene except for the sample obtained at site one which had a very large α -pinene peak. These data were not definitive. The diolefin terpenes (limonene and α -terpinene) seemed to emerge from this capillary column after the monoolefins. Perhaps the peaks later than 20 minutes were other single ring isomers or some of the straight chain triolefins. Limited evidence (citronellol emerges at 42 minutes) suggested that oxygenated compounds would have emergence times longer than the peaks shown in Table 2. Mass spectrometry and/or chemical tests may be helpful in identifying these compounds and this will be attempted in the second year of this program.

Table 2. Tenaja Ranger Station GC Samples, June 17, 1980

	<u>Concentration, selected peaks (ppbC)</u>			
	Trap	Bulb	Trap	Bulb
Isoprene	8.6	16.3	6.6	27.9
Toluene	8.5	12.3	8.0	10.5
α -pinene	1.7	0.6	0.2	0.
β -pinene	7.1	1.0	2.7	3.6
<u>Unknowns</u>				
20.67 min	49.3	23.4	32.5	91.5
21.30	18.2	5.5	13.2	6.6
22.35	20.1	4.8	4.8	7.1
23.14	146.9	37.1	77.2	159
25.20	13.2	0.8	7.2	2.2
26.60	58	5.6	42.6	63.6

D. Determination of Oxidant-Precursor Relationships for α -Pinene Under Simulated Atmospheric Conditions

1. Introduction

Assessments of the atmospheric impact of biogenic hydrocarbons requires knowledge of the oxidant and aerosol-forming potential of such compounds (as well as of their ambient concentrations, emission rates and the abundance of vegetation from which they are emitted). Although a substantial number of investigations of gas phase isoprene chemistry have been made comparatively few laboratory or smog chamber studies of the rates and products of the atmospheric reactions of the monoterpenes have been carried out (Stephens and Scott 1962, Ripperton et al. 1967, 1972; Lillian 1972, Japar et al. 1974, Grimsrud et al. 1975, O'Brien et al. 1975, Winer et al. 1976, Arnts and Gay 1979, Hull 1980). Moreover, the majority of the smog chamber experiments conducted to date have involved irradiations of vegetative hydrocarbons at concentrations ranging from one to three orders of magnitude higher than observed ambient levels or the use of small reactors with high surface-to-volume ratios.

Stephens and Scott (1962) were the first to study the photooxidation of pinenes (isomer unstated) and found that at high concentrations (4 ppm) their reactivity is comparable to olefins found in auto exhaust. Grimsrud and

co-workers (1975) irradiated several terpenes, including α -pinene, at concentrations of 10 ppb hydrocarbon with small amounts of added nitric oxide using a 50-liter borosilicate glass flask as a chamber and fluorescent black light as an irradiation source. Winer et al. (1976) interpreted the photooxidation data of Grimsrud et al. (1975) in terms of loss of the terpenes solely by reaction with hydroxyl radicals and derived (Winer et al. 1976, Atkinson et al. 1979) OH radical rate constants for the compounds studied (as well as measuring relative OH rate constants for α - and β -pinene and d-limonene in their own laboratory).

Lillian (1972) carried out NO_x/α -pinene photooxidations in small Teflon bags, typically with 0.5 ppm of hydrocarbon, and observed large amounts of aerosol formation as well as significant ozone concentrations. In a recent and comprehensive study, Arnts and Gay (1979) investigated the photochemistry of isoprene, propene and a series of monoterpenes, primarily in the ~0.1-1 ppm concentration range, using small Teflon bags and fluorescent black lamp irradiation. They studied in some detail the dependence of ozone formation and other reactivity parameters on hydrocarbon/ NO_x ratio. In addition, they irradiated lower concentrations of α -pinene (10-20 ppb) in the presence of NO_x and observed ~10-20 ppb of ozone after 60 minutes of irradiation.

The present study was focussed on establishing oxidant-precursor relationships for α -pinene/ NO_x mixtures (with and without other added hydrocarbons) at ambient, or near-ambient, concentrations of α -pinene under favorable environmental chamber conditions with respect to surface-to-volume ratio, total chamber volume, spectral distribution and light intensity, and normalization for variables via dual-mode chamber operation. Since α -pinene is the dominant, naturally emitted monoterpene (Graedel 1979) and has been shown to be highly reactive towards O_3 and OH radicals, it was chosen as a surrogate for other terpenes observed to be emitted in significant quantities.

2. Experimental

All experiments were conducted using a dual-mode 40 m³ outdoor chamber constructed of 50 m thick FEP Teflon film. Division into two compartments was accomplished using three metal rods to fold the film in such a manner that the chamber was "pinched" in half. Purified matrix air was provided by an activated charcoal, Hopcalite, Purafil-based air purification system described previously (Doyle et al. 1977). Sampling was done from

both sides by use of glass tubing and manifolding. Because of the chamber flexibility, no make-up air was necessary. The on-line monitoring instruments and calibration methods employed are summarized in Section IV.

Complete hydrocarbon analyses of the purified air and of the surrogate hydrocarbon mixture was by flame ionization gas chromatography (FID-GC) done as described previously (Pitts et al. 1979). α -Pinene was monitored using a Varian 1400 FID-GC, equipped with a cryogenically cooled sample trap and a Carbowax 600 (on C-22 firebrick) packed column, 3.2 m x 3.05 m, run at 75°C. α -Pinene was supplied by Aldrich and was vapor transferred prior to use. Matheson C.P. grade nitric oxide was used as received, or oxidized to nitrogen dioxide in pure oxygen prior to injection.

A typical experimental protocol for these experiments was as follows. Prior to a run, the chamber was covered with black plastic sheeting to exclude sunlight and then filled with purified air. After recording background readings, measured amounts of reactants were injected by glass syringes into a 1-liter mixing flask and then flushed into the chamber with N₂. Complete mixing was accomplished in several minutes by manually pushing on the chamber sides. The dual-mode division was made and any other reactants were added to one side as described above. Following mixing and another set of background measurements on each side, the black cover was removed and the irradiation allowed to continue for six to seven hours.

3. Results

The initial conditions and ozone maxima for 15 dual-chamber irradiations performed in this study from November 1979 to February 1980 are shown in Table 3. Time-concentration profiles from these 15 experiments are given in Section IV. The experimental sequence began with a freshly made Teflon chamber.

Following a pure air irradiation control experiment, three irradiations (Runs 2-4), were carried out in which varying amounts of α -pinene were added to one side after chamber division. Although the nitrogen oxides were at or below the detection limit of the chemiluminescence analyzer (~2 ppb), sub-ppb quantities of NO_x were undoubtedly present. These runs therefore involved high HC/NO_x ratios, characteristic of atmospheres in rural and remote regions.

The ozone and α -pinene concentration profiles observed in Run 2 are shown in Figure 3. In this, and in similar runs (Nos. 3 and 4), the addition of α -pinene lowers the amount of ozone produced, relative to the control side, by an amount dependent on the concentration of α -pinene consumed ($\Delta O_3/\Delta \text{pinene} \sim -0.6$). Consumption of α -pinene was consistently $7\text{--}9\% \text{ hr}^{-1}$ in each of these runs; thus $\sim 40\text{--}50\%$ of the α -pinene was consumed by the end of a six-hour irradiation. In Run 2 with 32 ppb of added α -pinene, the electrical mobility analyzer showed about $4 \mu^3 \text{ cm}^{-3}$ of aerosols. In Run 3, with 8 ppb added α -pinene, little aerosol formation (i.e., near the $1 \mu^3 \text{ cm}^{-3}$ detection limit) was observed.

To investigate lower HC/NO_x ratios, still involving only α -pinene, several runs (Nos. 5-7) were conducted with NO_x added to one or both sides. In Run 5, 43 ppb of NO_x (primarily NO) was added to one side with 9 ppb α -pinene in both sides. As shown in Figure 4, typical profiles were observed for oxidation of NO to NO₂ and (after an induction period relative to the side without NO_x) the side with added nitrogen oxides produced a higher ozone maximum (26 ppb vs. 19 ppb) with slightly greater consumption of α -pinene. In Runs 6 and 7, when each side contained equal concentrations of nitrogen oxides, adding α -pinene to one side produced higher ozone concentrations with little NO-to-NO₂ conversion observed in the control side. Under these conditions, no detectable response was seen from any of the particulate analyzers, with an upper limit of aerosol concentration being estimated at about $1 \mu^3 \text{ cm}^{-3}$.

To approximate the case of lightly polluted air impacting on a rural environment, or transport of rural air to urban airsheds, several irradiations were performed with addition of small amounts (9-13 ppb) of α -pinene to either lightly polluted ambient air or a three-component hydrocarbon mixture. Runs 8-10 involved mixtures of propene, isopentane, acetaldehyde and nitrogen oxides, chosen in a ratio which would provide an OH reactivity similar to that of the previously well-characterized SAPRC "smog surrogate" hydrocarbon mixture (Pitts et al. 1976). The side containing ~ 10 ppb of α -pinene exhibited an ozone peak $\sim 10\text{--}20$ ppb higher than the control side.

The ozone and α -pinene profiles for Run 8 are shown in Figure 5. α -Pinene was depleted in several hours after which time the two sides produced ozone at a similar rate. The hydrocarbon-NO_x mixture alone (Side 2) did not, as

Table 3. Initial Conditions and Ozone Maxima for α -Pinene Irradiations and Control Experiments in Outdoor Chamber^a

Run No.	Experiment Type	Control Side ^b				Hydrocarbons Added Before Chamber Division ^c				Variable Side				ΔO_3 Δ Pinene Consumed	
		Side No.	NO	NO ₂	Pinene	O ₃ Max	Side No.	None	Isopentane	Acetaldehyde	NO	NO ₂	α -Pinene		O ₃ Max
1	Pure Air vs. Pure Air	1	0	0	0	35	None			2	0	0	33	-	
2	α -Pinene vs. Pure Air	2	1	1	0	20	None			1	1	1	12	-0.6	
3	α -Pinene vs. Pure Air	2	1	1	0	12	None			1	2	2	10	-0.5	
4	α -Pinene vs. Pure Air	1	1	0	0	16	None			2	1	0	6	-0.7	
5	α -Pinene + NO _x vs. α -Pinene	2	3	3	9	19	α -Pinene			1	34	9	26	-	
6	α -Pinene + NO _x vs. NO _x	2	22	12	0	7	None			1	23	12	17	1.9	
7	α -Pinene + NO _x vs. NO _x	2	14	4	0	13	None			1	14	3	27	1.6	
8	α -Pinene + NO _x + Hydrocarbons vs. NO _x + Hydrocarbons	2	20	12	0	122	52 propene 310 isopentane 18 acetaldehyde			1	19	11	9	143	2.5
9	α -Pinene + NO _x + Hydrocarbons vs. NO _x + Hydrocarbons	1	22	7	0	111	48 propene 138 isopentane 17 acetaldehyde			2	22	10	13	128	1.3
10	α -Pinene + NO _x + Hydrocarbons vs. NO _x + Hydrocarbons	1	26	10	0	97	44 propene 180 isopentane 20 acetaldehyde			2	25	10	Added in 4 injections	108	1.0
11	NO _x + Hydrocarbons vs. NO _x + Hydrocarbons	1	26	12	0	130	52 propene 169 isopentane 18 acetaldehyde			2	24	12	0	123	-
12	α -Pinene + NO _x + Surrogate vs. NO _x + Surrogate	1	96	55	0	165	SAPRC Surrogated			2	93	57	9	180	1.7
13	α -Pinene + NO _x + Ambient vs. NO _x + Ambient	1	149	40	0	205	Ambient			2	149	40	11	201	-0.4
14	α -Pinene + NO _x vs. NO _x (high concentration)	2	69	43	0	10	None			1	71	42	139	216	1.5
15	Pure Air vs. Pure Air	2	0	0	0	25	None			1	0	0	1f	24	-

^aAll concentrations in ppb.

^bNo injection after division of chamber.

^cCommon to both Side 1 and Side 2.

^dSee Pitts et al. 1976.

^eEstimated total α -pinene added: 11 ± 3 ppb.

^fAttributed to contamination from previous high concentration runs.

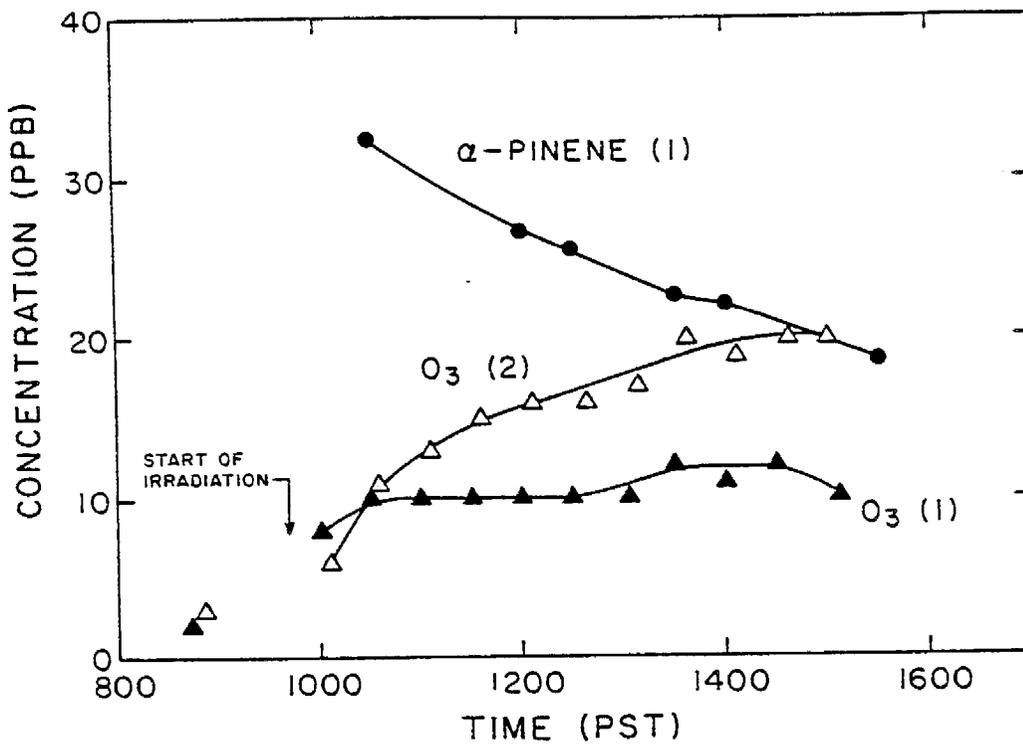


FIGURE 3. CONCENTRATION PROFILES FOR RUN 2: IRRADIATION OF α -PINENE (SIDE 1) vs. PURE AIR (SIDE 2).

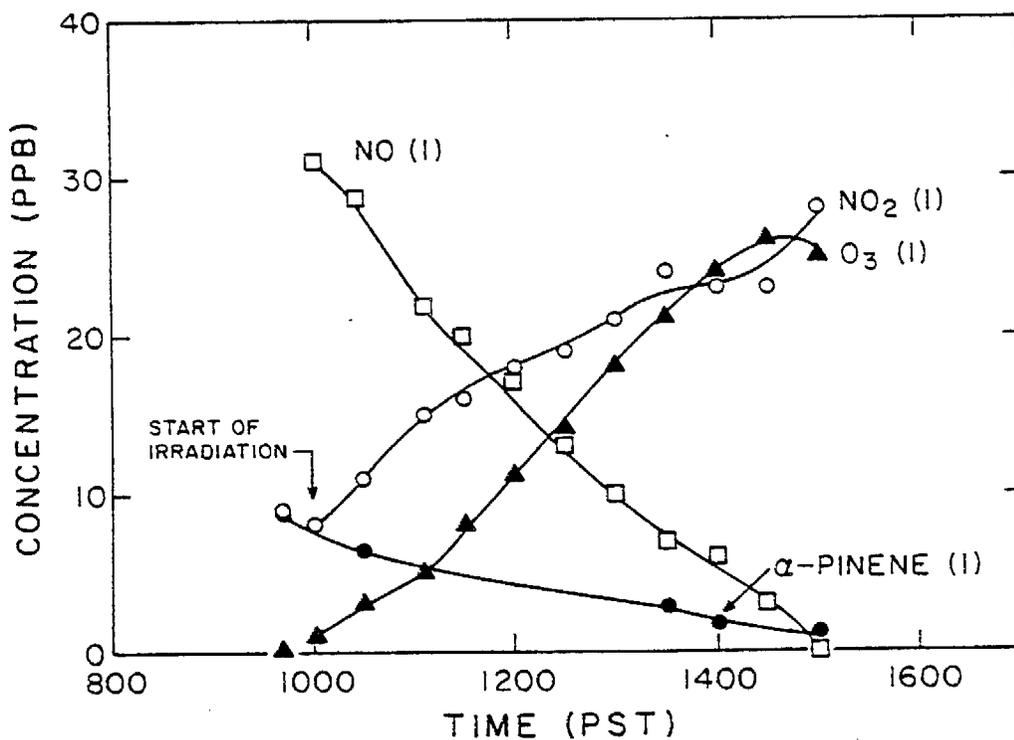


FIGURE 4. CONCENTRATION PROFILES FOR RUN 5 (SIDE 1): IRRADIATION OF α -PINENE + NO_x.

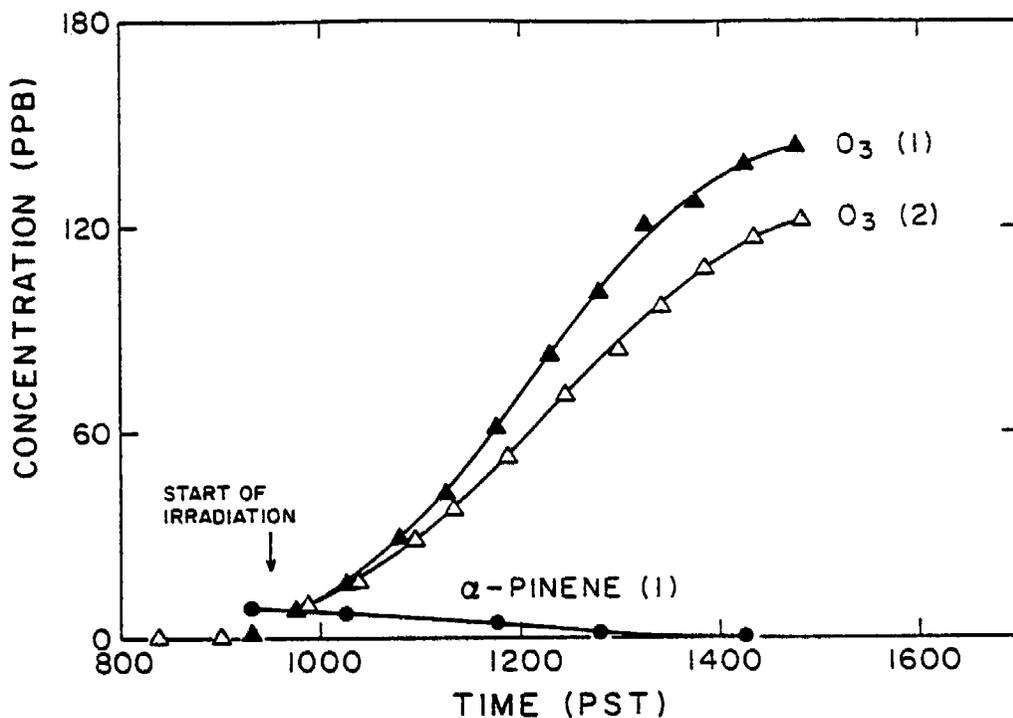


FIGURE 5. CONCENTRATION PROFILES FOR RUN 8: IRRADIATION OF α -PINENE + NO_x + HYDROCARBONS (SIDE 1) vs. NO_x + HYDROCARBONS (SIDE 2).

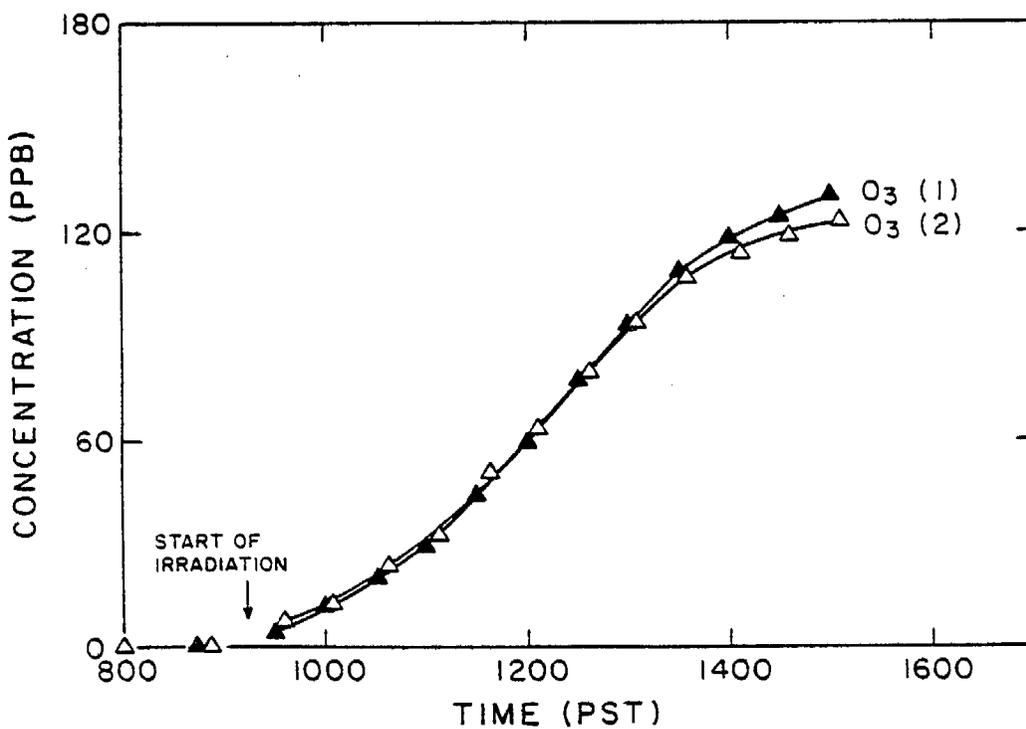


FIGURE 6. OZONE PROFILES FOR RUN 11: IRRADIATION OF HYDROCARBONS + NO_x (SIDES 1 AND 2).

expected, produce any aerosol. Only on the α -pinene side was a detectable amount of small particles observed by the electrical mobility analyzer (several $\mu^3 \text{ cm}^{-3}$) and optical particle counter. This result may be due to the more rapid and complete oxidation of the α -pinene in the presence of the propene/isopentane/acetaldehyde mixture. Similar results were obtained (Run 10) when α -pinene was added during an experiment in four equivalent injections (to simulate continuous emissions of α -pinene) or when the hydrocarbon mixture was changed (Run 12) to the more extensive (15 organics) SAPRC surrogate mixture (Pitts et al. 1976).

Control and replicate experiments were performed throughout this series of runs. Side 1 of the dual-mode chamber generally gave slightly higher (~5%) ozone peaks, especially late in the afternoon, for identical initial concentrations of α -pinene, NO_x and hydrocarbons. This effect is believed to be due to the east-west alignment of the chamber division which allowed Side 1, on the west, to potentially receive slightly more irradiation late in the day. However, during the first four hours of irradiation, the NO oxidation and ozone formation rates in the two sides were generally indistinguishable (see Figure 6).

A single Teflon chamber was used throughout this series of experiments. To test for chamber contamination, a pure air photolysis (Run 15) identical to Run 1 was carried out at the conclusion of the study. The maximum ozone concentrations (24 and 25 ppb) observed in the two sides were lower than the maximum concentrations observed in Run 1 (35 and 33 ppb). This suggests that wall contamination in these runs was less important than the variable composition of the matrix air produced by the air purification system.

3. Discussion

The consistency of the data (both relative and absolute) obtained in this study indicates that the dual-mode outdoor chamber successfully permits resolution of comparatively small incremental effects due to irradiation of α -pinene in the absence or presence of NO_x and hydrocarbons. The large volume, low surface-to-volume ratio, increased aerosol lifetime, and substantial equivalency of the control chamber affords quantitative data in a concentration regime approaching "worst case" ambient air concentrations observed for the monoterpenes.

Our data are in good agreement with the NO_x/α -pinene irradiation results of Arnts and Gay (1979) for their lowest concentration experiments. In the range of optimum carbon/ NO_x ratio (~10-15) they observed, in their "high" concentration runs, ~0.75-1.5 ppb of ozone produced per ppb of α -pinene consumed at the time of the O_3 maximum. Coffey and Westberg (1978) report somewhat lower values of 0.3-1.0 ppb O_3 per ppb of terpene consumed. In their "low" concentration experiments, Arnts and Gay observed ~1 ppb O_3 per ppb of α -pinene consumed after one hour. As shown in Table 3, we find ~1-2 ppb of O_3 produced per ppb of α -pinene consumed in experiments with added NO_x , with or without added hydrocarbons. In experiments with no added NO_x , α -pinene behaves as a sink for O_3 , removing ~0.6 ppb O_3 per ppb of α -pinene.

Other studies (Gay and Arnts 1977, Arnts and Gay 1979) have found poor carbon balances from irradiations of α -pinene/ NO_x mixtures. In the past, this has been attributed to aerosol formation coupled with subsequent wall loss. However, the half life of submicron particles in our chambers has been shown to be on the order of several hours, and in the ~10 ppb concentration range employed in this study, it appears that carbon loss cannot be attributed primarily to aerosol formation. The argument may be made that given our particle-free matrix air, nucleation was not possible for the photooxidation products. However, the net increase in aerosol formation for the α -pinene side in the run employing ambient air (Run 13) was comparable to the results obtained in runs using hydrocarbon mixtures in particle-free matrix air. Thus from our observations, it appears unlikely that α -pinene is a major aerosol precursor at ambient concentration. Verification of this tentative conclusion requires additional research concerning the gas and aerosol phase products from the photooxidation of α -pinene, and the lifetime of such products in Teflon chambers (including those of large volume).

In conclusion, our data show that when irradiated in clean air (i.e., air containing only low concentrations of oxides of nitrogen and reactive hydrocarbons) near-ambient concentrations of α -pinene appear to behave as an ozone sink rather than as an ozone precursor. Irradiation of low concentrations of α -pinene in the presence of NO_x or NO_x -hydrocarbon mixtures results in enhancement of ozone maxima (relative to α -pinene-free systems) by amounts one to two times the initial terpene concentrations on a molar basis.

The present data, when combined with the low ambient concentrations of monoterpenes expected in urban airsheds (but not yet determined for the South Coast Air Basin) lead to the preliminary suggestion that these compounds will contribute no more than ~10 ppb of O₃ in such airsheds. Moreover, it does not appear that the monoterpenes will significantly impact visibility in urban airsheds relative to visibility degradation from primary and secondary particulates originating from emissions from anthropogenic sources.

However, a quantitative assessment of the atmospheric impact of α -pinene and other vegetative hydrocarbons in airsheds such as the South Coast Air Basin must await more extensive data concerning their emission rates and ambient concentrations in the source areas of such airsheds, as well as reliable models of the transport and reactions of these compounds. Thus the principal emphasis in the second year of this program will be placed on measurements of ambient concentrations and emission rates of natural hydrocarbons in the "source" area of the South Coast Air Basin, as well as on establishing a "biomass inventory" for this portion of the basin.

E. Development and Applications of Analytical and Signaturing Techniques for Natural and Anthropogenic Hydrocarbons

1. Introduction

Studies of the organic component of polluted urban air have invariably shown components traceable to fossil fuels, especially gasoline. Indeed, anthropogenically derived hydrocarbons dominate the organic fraction so completely that contributions from vegetation have been difficult to identify in past studies.

There are two complementary approaches to the evaluation of the impact of vegetative emissions of organics on air quality.

- Measurement of total organics and determination of the fraction of these which can be ascribed to auto emissions and other man-made sources. This could place an upper limit on the natural emissions but will not yield an estimate of their actual importance, especially if it is small. This leads naturally to the complementary approach:

- Measurement of those atmospheric species which can clearly be ascribed (because of their structure) to natural sources. This will set a lower limit

to the contribution of vegetative organics but may underestimate their importance by failure to properly ascribe some organics to natural sources or to measure some naturally emitted organics. For example, n-heptane is present in gasoline and also in some pine tree emissions. The amount attributable to gasoline may be estimated by comparing the n-heptane concentration with that of other gasoline components, for example, toluene, benzene, cyclohexane, etc.

The latter approach requires development of a reliable, sensitive measurement method which will unambiguously identify and quantitatively measure naturally-emitted compounds at ambient concentrations in air contaminated with anthropogenic organic emissions. The analytical method of choice is gas chromatography, followed by detection by mass spectroscopy for positive identification and/or flame ionization for maximum sensitivity. Some forest measurements of terpenes have been made using larger sample loops, freeze-out traps followed by packed column separation and FID detection (Whitby and Coffey, 1977). However, capillary columns may be used for high resolution, particularly when the sample contains anthropogenic emissions. In addition, capillary columns are more suitable for GC-MS coupling, a necessary step for positive identification.

The purpose of this research element was to adapt and combine several gas chromatographic procedures which have been successfully used at SAPRC/UCR in recent years with advanced column techniques (Holzer et al., 1977; Rasmussen et al., 1974; Ullrich and Seifert, 1978) developed elsewhere to obtain useful signatures of atmospheric organic compounds and to provide analytical capability for the emission rate measurements and outdoor chamber study of α -pinene photooxidation.

2. Capillary Column Gas Chromatography

The usual freeze-out procedure, in use at SAPRC since the early 1960's, has been adapted successfully to a high resolution capillary column chromatograph (see Figure 7). Excellent resolution has been achieved along with high sensitivity and good carbon number coverage without sample splitting. The key step which makes this possible is chilling of the column to -50°C . All but the most volatile hydrocarbons (four carbons or less) are thereby concentrated at the front of the capillary. In striking contrast to a normal chromatogram the compounds with short retention time (i.e., $\text{C}_4\text{-C}_5$

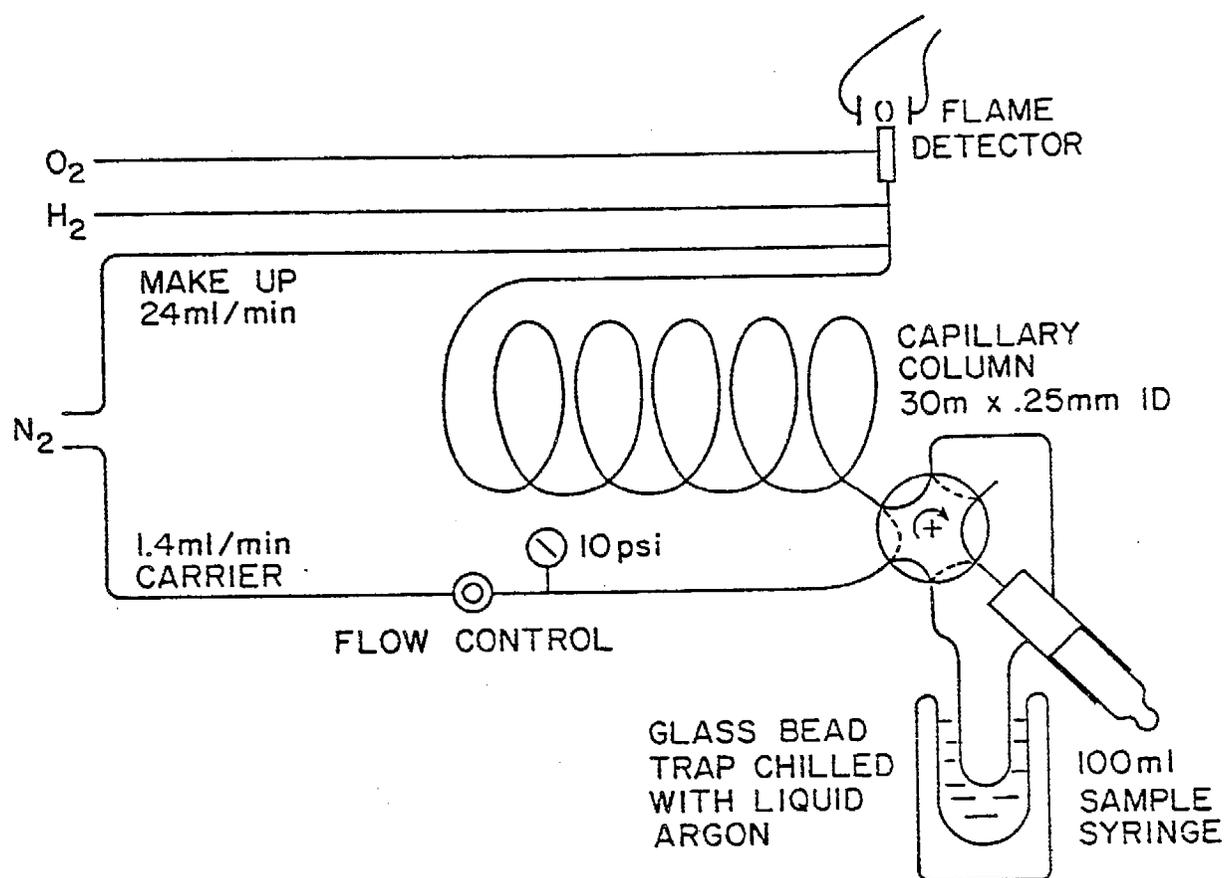


Figure 7. Schematic of capillary column gas chromatograph system.

hydrocarbons) show much poorer resolution than slower moving components because the volatile ones are not concentrated effectively at -50°C , the lowest possible temperature with the commercial sub-ambient accessory.

Temperature programming at $8^{\circ}\text{C min}^{-1}$ is started simultaneously with thaw/injection of the frozen sample. The limiting factor in the reproducibility of emergence time is probably the operator. Emergence time for α -pinene is 18.9 minutes and for β -pinene is 20.0 minutes. The full width at half height for these peaks is 2 to 3 seconds; at the baseline they are about seven seconds wide corresponding to 124 μl of carrier gas. Thus, resolution seems to be comparable to that obtained for good splitter injections into long capillaries. Theoretical plates were estimated at several hundred thousand or more.

The capillary column performance was tested by injection of several ambient air samples and a vaporized gasoline sample. All showed a great many peaks, most of which are not yet identified. The sensitivity is illustrated by the gasoline analysis. This dilution was 16.9 μg of gasoline per cubic meter or about 29.7 ppbC. About 130 peaks could be seen on the chromatogram in the first 30 minutes. The smallest peaks must therefore be less than 0.1 ppbC.

The capillary system has several extra advantages. The very small column flow of 1.1 ml min^{-1} means that column bleed causes little background signal in the flame detector and little drift during temperature programming. Since most of the flame-support nitrogen does not pass through the column, the injector valve can be closed to stop column flow as well as isolate the sample trap without snuffing the flame. This may be useful in improving the precision of the injection procedure, to protect the column or to minimize interference from carrier gas contaminants. Sensitivity may be sufficient to permit measurement by direct injection of 2-5 ml loop samples.

By programming the capillary column from -50°C to $+120^{\circ}\text{C}$ in 21.25 minutes, a broad spectrum of hydrocarbons and other organics can be covered. Emergence times and calibration factors so far ascertained are shown in Table 4. When operating properly, a peak 0.02 mv high (unattenuated) can be detected. For α - and β -pinene, this corresponds to $0.02/0.795 = 0.025$ ppb and $0.02/0.732 = 0.027$ ppb, respectively, by moles, which should be quite adequate. In real samples the limiting factor may well be the interference

Table 4. Identified Peaks on Capillary Column SE52 Chromatogram

Minutes			x1 mv/ppbv	x1 ppbC/mv
03.70	n-butane	nP ₄		
05.37	isopentane	iP ₅		
06.38	isoprene	T ₅	0.363	13.78
09.28	n-hexane	nP ₆		
11.28	benzene	A ₆	0.612	9.80
12.35	n-heptane	nP ₇	0.716	9.78
14.38	toluene	A ₇	0.701	9.98
17.02	ethylbenzene	A ₈		
17.20	para-xylene	A ₈		
17.20	meta-xylene	A ₈		
17.90	ortho-xylene	A ₈		
18.00	n-nonane	nP ₉		
18.64	isopropylbenzene	A ₉		
18.88	alpha pinene	T ₁₀	0.795	12.58
19.40	n-propylbenzene	A ₉		
19.65	para-ethyltoluene	A ₉		
19.68	meta-ethyltoluene	A ₉		
19.74	1,3,5 trimethyl-benzene	A ₉		
19.95	beta-pinene	T ₁₀	0.732	13.66
20.12	ortho-ethyltoluene	A ₉		
20.18	sec-butylbenzene	A ₁₀		
20.30	1,2,4 trimethyl-benzene	A ₉		
20.35	tert-butylbenzene	A ₁₀		
20.70	isobutylbenzene	A ₁₀		
20.90	α-terpinene	T ₁₀		
21.12	para-cymene	T;A ₁₀	0.591	16.92
21.20	limonene	T ₁₀		
21.81	1,2,3 trimethyl-benzene	A ₉		
21.90	n-butyl benzene	A ₁₀		

[All aromatics through C₉ (14 compounds) + 5 of 22 C₁₀s]

from other peaks. Ambient measurements of the terpenes therefore require careful comparison with suitable blanks and reference samples, and mass spectral studies will be necessary.

In the original sampling procedure, 100 ml syringes were used to measure the sample and force it through the freeze trap. An alternate procedure which eliminates contact between the sample and the syringe was later found to be practical. The trap is removed from the analyzer, taken to the sampling site, chilled with liquid argon and the sample pulled through the trap with a 100-ml syringe. The trap is then capped, returned to the laboratory and attached to the sample valve on the chromatograph while still frozen. Thus, the sample comes in contact only with surfaces which are finally purged into the instrument. A further refinement will be to use a four-port valve to close the sample in the field, thus permitting purging of all connecting lines prior to sample thaw.

A peak integrator was recently put in service to automate data collection. A selection of 36 terpenes, including many of the species mentioned in the literature, was recently received as a gift from Givaudan and some of these may serve as suitable authentic samples.

Development problems which remain include the following. Some chromatograms contain extraneous peaks which are suspected of being artifacts. One of these is broad, poorly shaped and on top of the α -pinene peak. Since the capillary column provides no identification of its peaks, the Finnigan GC-MS is being employed for that purpose. Each 100-ml sample of air contains about 1 μ l of water measured as liquid. This will of course freeze in the trap at liquid argon temperature. After transfer, it also freezes at -50°C in the column. It apparently is swept through the column harmlessly unless it is somehow involved in the release of the extraneous peaks mentioned above. Its effects on the mass spectrometer appear to be more serious. In both cases the role of water requires further clarification.

3. Signaturing of Organics by Backflush Gas Chromatography

An experimental apparatus to measure one- and two-carbon hydrocarbons directly by gas chromatography and to analyze for higher organics by backflushing the same sample from the column was set up. The system has been described in detail elsewhere (Stephens and Hellrich 1979). The backflush GC method of signaturing ambient hydrocarbons will supplement the use of high

resolution gas chromatography and, because it is more portable and simpler to operate in the field, it will be used to provide rapid data concerning ambient hydrocarbon concentrations during emission rate measurements. The apparatus is currently running continuously at 15-minute cycling intervals and is located in the ARB Mobile Laboratory for Air Pollution Research. A comparison with hydrocarbon data collected from the Beckman 6800 Hydrocarbon Analyzer at the same location will be made. The Beckman instrument monitors CO levels as well, a necessary parameter for signaturing efforts.

The sensitivity for the two-carbon hydrocarbons observed in the original work (Stephens and Hellrich 1979) of 1 or 2 $\mu\text{g m}^{-3}$ was obtained, but the backflush minimum detection is still several hundred $\mu\text{g m}^{-3}$. Further refinements are expected to improve the backflush detection limit to about 100 $\mu\text{g m}^{-3}$.

Throughout the contract period, many minor improvements and adjustments continued to be made to the backflush chromatograph in order to stabilize its performance. At this writing its operation has stabilized to the point where failure of ink flow is the most frequent cause of data loss.

Backflush peaks of moderate size were seen for the cleanest air but not for pure nitrogen or ultra-zero air. Humidifying ultra-zero air resulted in a significant spurious backflush peak which was nearly eliminated by lowering the temperature to 44°C. This made it necessary to increase the nitrogen flow to 78 ml min^{-1} and the hydrogen flow to 35 ml min^{-1} . This compromise has resulted in good resolution of the C₂ hydrocarbons, a well-shaped sizeable backflush peak, with little drift and acceptable noise level.

4. Hydrocarbon Correlation Analysis

We have previously pointed out that vegetative organic emissions would not be expected to correlate with automotive components. The ARB Mobile Laboratory for Air Pollution Research operated by SAPRC at UCR records total hydrocarbon (THC), methane and carbon monoxide (CO) using a Beckman 6800 air quality chromatograph. Almost all of the carbon monoxide comes from auto exhaust, thus providing a reference against which hydrocarbon concentrations can be correlated. Several years of trailer data are on tape. Therefore it was possible to compute nonmethane hydrocarbon (NMHC = THC - methane) concentrations and to construct joint distribution tables.

The data were treated in six-month batches of winter and summer data. The batches of data appear quite different, with the earlier batches showing very low correlation between NMHC and CO. The last set of edited data (winter 77/78) showed the best correlation with a slope of 3.178 ppm CO per ppmC HC and a correlation coefficient of 0.829. Conversions to weight ratio with molecular weights of 28 for CO and 16 for HC gives a weight ratio of 5.56 tons CO per ton HC. This is close to the value given in emission inventories and confirms that the bulk of the hydrocarbon does indeed come from automobile emissions. Outliers at high hydrocarbon/CO ratio may be due to a local spill of gasoline or other volatile organics. This instrument suffers the defect that methane and total hydrocarbons are measured on different air samples. If methane is not identical in the two samples, an error will be introduced by the subtraction used to calculate NMHC. Since methane is always large, this potential for error is great.

F. Investigation of Remote Sensing Applications to Biomass Estimates

During this period we have begun exploring the feasibility of applying remote imagery capabilities and expertise which are present on the UCR campus to the task of quantifying the extent and estimated mass of vegetation types characteristic of the western portion of the South Coast Air Basin. Thus we have initiated discussions with Mr. Claude W. Johnson and other staff members from the UCR Department of Earth Sciences concerning their experience and resources in applying LANDSAT, U-2 and low altitude photography to assessments of the types and abundances of vegetation in California. It appears that a "multi-stage" analysis involving (a) detailed assessments of selected frames of recent, low-altitude, high-resolution photography of the western portion of the South Coast Air Basin, (b) statistical extrapolation to larger areas of the Basin using U-2 and perhaps LANDSAT imagery and (c) a limited amount of "ground-truth" data generated by trained botanists for the areas of high-resolution photography, may be the most cost-effective and reliable means of obtaining a quantitative biomass estimate for the "source" area of the Basin. The cost, time and resources required to carry out such a multi-stage analysis are being investigated.

II. DEVELOPMENT OF PLANT ENCLOSURES AND PRELIMINARY MEASUREMENTS OF EMISSION RATES OF NATURAL HYDROCARBONS FROM SOUTHERN CALIFORNIA PLANT COMMUNITIES

A. Introduction and Background

Reactive terpenoid compounds are found in the essential oils which are produced by more than 2,000 species of higher plants. Over 500 different chemical compounds have been identified in essential oils, principally including isoprene, monoterpenes, sesquiterpenes, di- and higher terpenes (Bonner and Varner 1965) but also aldehydes, alcohols and ketones (Meigh 1955, Rasmussen 1972, Zimmerman 1979a). Robinson (1963) described the biosynthesis of these compounds. One of the most unique results of the release of these volatile compounds into the atmosphere is the phenomenon called allelopathy, that is, the deleterious effect that one higher plant has on another through the production of chemical retardants that escape into the environment (Rice 1974).

Another apparent manifestation of the volatile terpenoid compounds is the formation of aerosol particles which appear as blue haze over vegetative canopies, especially on calm, windless days (Went 1960), although recent studies (Stevens et al. 1980) indicate that this haze may be primarily associated with particles formed from anthropogenic hydrocarbons. The composition of aerosol particles produced in the photochemical reaction of terpenes with NO_x and with ozone (at high concentrations) consists of more than 30 compounds (Schuetzle and Rasmussen 1978) including aldehydes, alcohols, acids and peroxides.

1. Previous Estimates or Measurements of Emission Rates

Microscale Estimates. A survey of the results of eight studies of hydrocarbon emissions from various plant species carried out prior to 1979 is summarized in Table 5. These studies are representative of the various methods of sampling, and the units chosen for reporting the results. The sampling environments represented in these studies ranged from temperature and light controlled chambers (Rasmussen 1972) to calculations of the flux from a canopy of loblolly pine (*Pinus taeda*) in uncontrolled ambient conditions (Arnts et al. 1977). The units of measurement are unique to each

Table 5. Survey of Terpenoid Emission Estimates for Various Plants Species

Plant Community	Species	Position	Temperature	Compounds Measured	Sampling Method	Concentration or Rate	Reference
Coniferous Forest	Loblolly pine (<u>Pinus taeda</u>)	Above canopy	29.7°C	α -Pinene	Ambient (calculated flux)	52.8 $\mu\text{g m}^{-2} \text{min}^{-1}$	Arnts, et al., 1977
Coastal Chaparral	Calif. Black Sage (<u>Salvia mellifera</u>)	---	9-16°C	Camphor	Branch	13.3 $\mu\text{g m}^{-2} \text{d}^{-1}$ 3.1 $\text{kg km}^{-2} \text{d}^{-1}$	Tyson, et al., 1975
Interior Sage	Sagebrush (<u>Artemisia tridentata</u>)	Above canopy	unspecified	unspecified	Ambient	50 $\text{kg km}^{-2} \text{d}^{-1}$	Went, 1960
Coniferous Forest	Balsam fir (<u>Abies balsamea</u>) and red spruce (<u>Picea rubens</u>) birch (<u>Betula papyrifera</u>)	Below canopy down wind from forest	27°C	"Lighter species"	Ambient	23.7 to 81.8 $\mu\text{g m}^{-3}$	Whitby and Coffey, 1977
Maple	(<u>Acer saccharum</u>)			"Terpene species"	Ambient	3.5 to 47.8 $\mu\text{g m}^{-3}$	

(continued)

Table 5 (continued) - 2

Plant Community	Species	Position	Temperature	Compounds Measured	Sampling Method	Concentration or Rate	Reference
Citrus	Orange	Within canopy	unspecified	Isoprene	Ambient	<0.1 to 4.5 ppbC	Lonneman, et al., 1978
	Mango (<u>Mangifera indica</u>)	Above canopy	unspecified	Isoprene	Ambient	0.5 to 24 ppb in 5 ml of air	Rasmussen, 1970
Ornamental Planting	<u>Juniperus</u> sp. (shrubs)	Inside canopy	unspecified	"Volatile aromatics"	Branch chamber	5 to 18 ppb/?	Rasmussen and Went, 1965
	"	Above canopy		"	Ambient	5 to 8 ppb/?	
	"	Several meters from shrubs		"	"	3 to 6 ppb/?	
-----	White pine (<u>P. monticola</u>)	Laboratory	17-32°C	α -Pinene	Leaf chamber	0.4 to 2.0 ppb min ⁻¹ g ⁻¹	Rasmussen, 1972
	Ponderosa pine (<u>P. ponderosa</u>)		"	"	"	0.3 to 1.2 ppb min ⁻¹ g ⁻¹	"

(continued)

Table 5 (continued) - 3

Plant Community	Species	Position	Temperature	Compounds Measured	Sampling Method	Concentration or Rate	Reference
---	Loblolly pine (<u>P. taeda</u>)	Laboratory	17-32°C	α -Pinene	Leaf chamber	0.5 to 3.5 ppb $\text{min}^{-1} \text{g}^{-1}$	Rasmussen, 1972
	White fire (<u>Abies concolor</u>)	"	"	"	"	0.2 to 1.5 ppb $\text{min}^{-1} \text{g}^{-1}$	"
----	Oak (<u>Quercus</u>) sp.	Laboratory	28°C ^{1/}	Isoprene	Leaf chamber	1.7 ppb $\text{min}^{-1} \text{in}^{-2}$	"
	Sweet Gum (<u>Liquidambar styraciflua</u>)	"	"	"	"	0.7 ppb $\text{min}^{-1} \text{in}^{-2}$	"
	(<u>Eucalyptus</u>) sp.	"	"	"	"	0.83 ppb $\text{min}^{-1} \text{in}^{-2}$	"
	Cottonwood (<u>Populus</u>) sp.	"	"	"	"	1.2 ppb $\text{min}^{-1} \text{in}^{-2}$	"

^{1/} Light intensity = 700 foot candles

? Basis for reported value not stated

investigation making it very difficult to compare the studies. Both concentrations and rates are reported but rarely in the same study; the former may be based on the weight of foliage and surface area of foliage, but in some cases only volume/volume units are presented.

Tingey and Burns (1980) have placed the more recent emission rate data of Zimmerman (1979a), Tingey et al. (1980), Arnts et al. (1978), Kamiyama et al. (1978) and Flyckt et al. (1980) on a common basis. For the one common species investigated by two investigators (live oak), the isoprene emission rates reported differ by more than a factor of four (see below).

The heterogeneity of the present information in this sample of the literature suggests the need for standardization in reporting as well as measurement methods. For example, basing emission rates on weight of plant tissue would be desirable. Furthermore, it seems clear that measurements in static air chambers causing serious deviations in the plant environment from natural conditions should be avoided, except for special purposes. Finally, the ambient temperature, relative humidity and light intensity should be measured continuously during sampling.

An important conclusion from the information in Tables 1 and 5 is that comparatively few measurements have been made under southern California's mediterranean climate regime or with a sufficient sample of plant species which are dominant or abundant in that region.

Macroscale Estimates. Using biogenic hydrocarbon emission rates for various plant species and biomass estimates, Tingey and Burns (1980) compiled both global and regional estimates of total natural hydrocarbon emissions, as shown in Table 6. The global estimates varied over approximately a factor of five. Such variations are perhaps not surprising given the variability in emission rate data and the large extrapolations required to obtain total emission rates. The global emission rates obtained are substantially greater than those for anthropogenic hydrocarbons.

It is important to recognize, however, that due to perturbation of the plant, the emission rates obtained for individual species in enclosed atmospheres may be higher than the actual emission rates occurring in ambient air. If this is the case, then the total emissions calculated on global and regional bases may be significantly overestimated. Possible evidence that this is the case may be the incompatibility between the high emission rates and

Table 6. Estimated Emissions for Biogenic Hydrocarbons
(Tingey and Burns 1980)

Location	Emissions (Metric Tons)	Emission Factors (kg km ⁻² day ⁻¹)	References
World	1.75 x 10 ⁸ /year		Went 1960
World	4.38 x 10 ⁸ /year		Rasmussen and Went 1965
World	8.30 x 10 ⁸ /year		Zimmerman 1979b
United States	0.23-4.64 x 10 ⁷ /year		Rasmussen 1972
United States	6.5 x 10 ⁷ /year		Zimmerman 1979b
Florida (81 x 60 km)	157.0/day	32.2	Zimmerman 1979a
Texas (38 x 31 km)	32.4/day	27.5	Zimmerman 1979c
Pennsylvania	3,580.0/day	30.7	Flyckt and others 1980

very low ambient concentrations of natural hydrocarbons such as isoprene and the monoterpenes reported to date.

2. Factors Influencing Hydrocarbon Emissions from Vegetation

Time of Year. Several researchers have recorded large variations in emission rates of natural organics as a function of season of the year. Rasmussen and Went (1965) measured volatile hydrocarbons at a sample location in the summer to be 10-20 ppb compared with 2 ppb for the winter period. Holzer et al. (1977) also observed a large difference in emissions depending on seasons. Rasmussen and Went (1965) suggested that emissions are low in the spring from young foliage. They also observed two peaks of hydrocarbon emission in the vicinity of a mixed hardwood forest in autumn; these peaks were associated with leaf drop from two species of trees. It is possible that the fallen leaves are the major source of the observed peaks. Tyson et al. (1974) also suggest that the period of leaf fall from the coastal black sage (Salvia mellifera) may be a time of increased camphor emission because high summer temperatures are coincident.

Flyckt (1979) has reported sinusoidal behavior for monoterpene emissions from ponderosa pine with a maximum in May/June and a minimum in November. Isoprene emissions from red oak were observed to be maximum during July/August and decreasing during the fall to zero in the winter.

Time of Day (Influences of Light and Temperature. There is a very important difference between the diurnal concentration profiles of isoprene and the monoterpenes. Isoprene emission appears to be light dependent (Rasmussen and Jones 1973, Sanadze and Kalamadze 1966b). Chatfield (Chatfield et al. 1979, Robinson 1978) measured the highest concentrations at 1800 hr and the lowest at 0600 hr. In contrast, monoterpenes from slash pine and black sage are emitted at similar rates in the light and dark (Tingey et al. 1980, Dement et al. 1975, Rasmussen 1972). Thus, monoterpene concentrations are highest during the night and lowest during the day when the rates of dilution, photooxidation and ozonolysis are highest (Tingey et al. 1978, 1980). The influence of varying light intensity on isoprene emission rate at various leaf temperatures is shown in Figure 8 (Tingey et al. 1978).

There is general agreement among several investigators observing many plant species that isoprene and terpenoid emissions increase with increasing temperature. These reports include Rasmussen (1972) with several conifer species; Dement et al. (1975) and Tyson et al. (1974) with Salvia mellifera; Kamiyama et al. (1978) with cryptomeria; and Arnts et al. (1977) with loblolly pine. Above 43°C isoprene emission drops dramatically (Tingey et al. 1979, 1980). Generally, isoprene emissions increase sigmoidally with temperature while monoterpene emissions increase exponentially.

For average summer days in Tampa, Florida, the net influence of light and temperature resulted in more than 80% of the isoprene emissions occurring after mid-morning and ceasing at night, while approximately 55% of the total daily monoterpene emissions were expected to occur during daylight hours between 0600 and 1800 with an additional 25% emitted between sunset (1800) and midnight (Tingey et al. 1978, 1980).

Relative Humidity. Dement et al. (1975) observed increased camphor emissions as relative humidity increased. There was also the suggestion that during cool, foggy days the oil accumulated on the leaf surface and then volatilized rapidly when warm, sunny weather resumed.

Stomatal Control. Jones and Rasmussen (1975) working with leaf discs, and Dement et al. (1975) following observations of Salvia mellifera were unable to show that stomatal resistance was an important factor controlling terpenoid emission rate. Furthermore, Arnts et al. (1977) suggested that

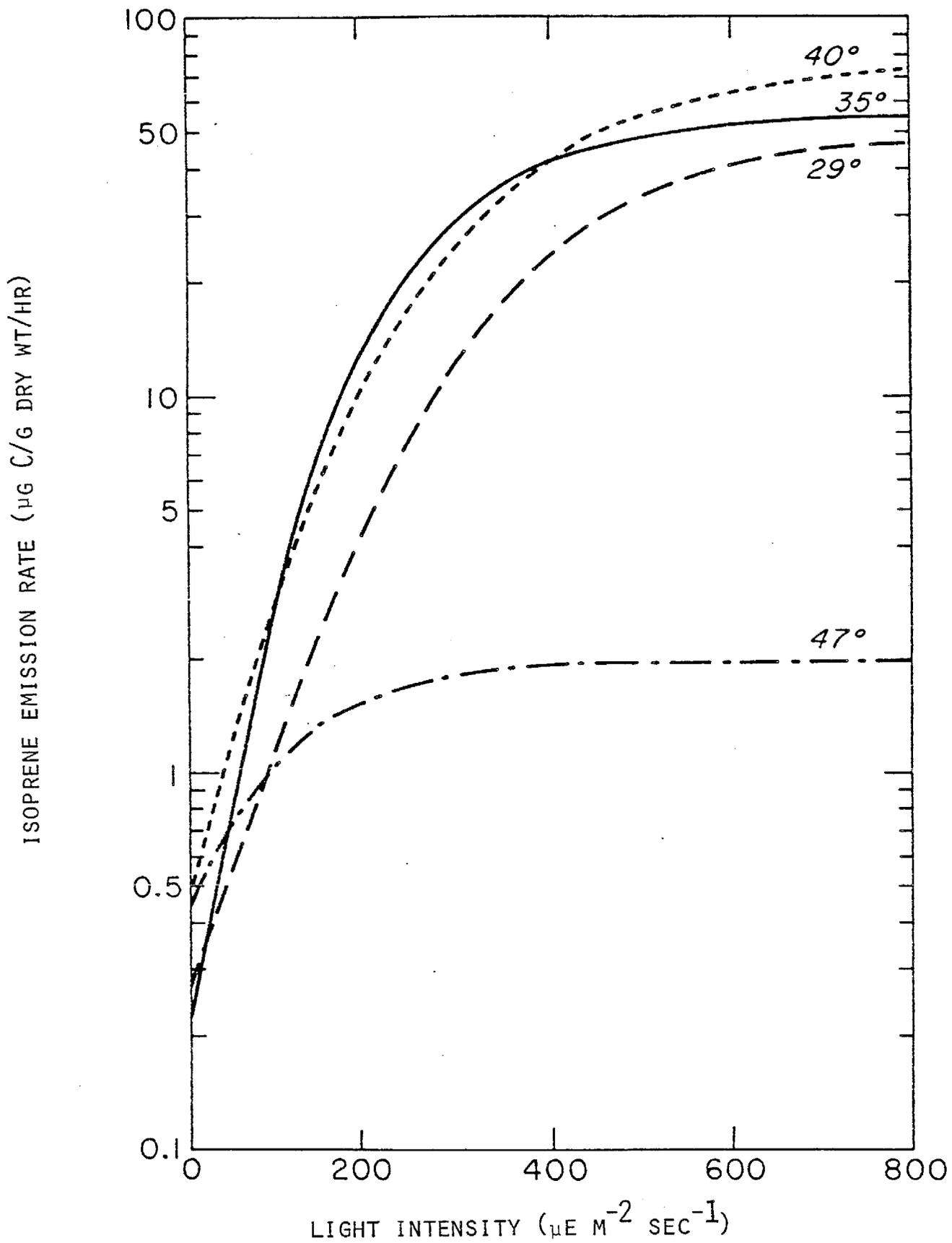


Figure 8. The influence of varying light intensity on isoprene emission rate at various leaf temperatures (Tingey and Burns 1980).

emissions from loblolly pine were greater during periods of water stress (when stomates are expected to be closed).

Injury or Disturbance of Foliage. Leaf fall has already been discussed as a time of increased terpenoid emissions. In addition, Rasmussen and Went (1965) described an incident when grass was mowed near the sampling site; ambient volatile hydrocarbon concentrations increased from 5-10 ppb to 50 ppb following the mowing and while the grass was drying out. Concentrations later declined to the former value; daily temperatures remained in the 20-30°C range during this period. Eucalyptus leaves emitted more volatiles after handling (Rasmussen, 1970), however deliberate injury to leaves of Hamamelis virginiana did not result in increased isoprene emissions.

B. Development of Plant Enclosures and Preliminary Emission Rate Measurements and Calculations

1. Teflon Bags

Our first efforts to determine emission rates of natural hydrocarbons from selected plant species involved the use of simple Teflon bag enclosures. These were placed around branches of wildgrowing shrubs for short time intervals with the results described below. Refer to Section V for a detailed description of the development of the capillary gas chromatograph used in this study.

Preliminary sampling of several native shrub species permitted testing of the analytical techniques which had been developed as well as the determination of the kinds of compounds emitted by each species. Members of the native soft chaparral community present on the UCR campus or on the nearby Box Springs Mountains were selected because of their relative abundance in typical shrub stands. These species included California encelia (Encelia californica), California sage, (Artemisia californica) and chamise (Adenostoma fasciculatum).

Sampling was done between 0930 and 1545 hours on both March 17 and 19, 1980. These were relatively warm, sunny days of good air quality (i.e., maximum hourly averages were ~40 ppb for ozone and 5-10 ppb nitrogen oxides). Portions of branches of the subject shrub were enclosed in a Teflon bag equipped with a side port to allow for insertion of a thermister probe and a Teflon tube connected to a 1-liter glass and Teflon syringe. The bag

remained over the branch for times ranging from 3-10 minutes. A seal was maintained by holding the gathered film of the open end around the branch by hand.

The changes of temperature in the sunlit bag and the first evidence of water condensation on the interior of the bag were observed. The results shown in Figure 1 suggest that in order to minimize modifications of the leaf environment due to increases in temperature and relative humidity, sampling should be conducted either early or late in the day and with enclosure times not exceeding five minutes.

The first samples were taken from Encelia californica. The Teflon enclosure bag was on the plant for six minutes. A 1-liter glass and Teflon gas-tight syringe was used to remove a 500-ml sample from the bag after three of the six minutes. The enclosure bag and syringe were immediately taken to the chromatographic laboratory for analysis while at room temperature and in the dark. 100-ml glass syringe aliquots were taken for GC injection via a glass bead filled freeze-out trap.

The major peaks are shown in Table 7. A total of about 140 peaks were distinguished. However, most of these were not traceable to the plant but are due to hydrocarbons in the matrix air (ambient air). The samples for runs

Table 7. Encelia californica Sample Collected March 17, 1980, 1333-1339 Hours

Run No.	93	94	95
Sample period, min	3	6	6
Container	1 \varnothing syringe	enclosure bag	same as #94
Analysis time, PST	1345	1430	1530
Retention time, min		<u>ppbC</u>	
6.45 (isoprene)*	----	14	38
18.8 (α -pinene)	702	5745	739
20.00 (β -pinene)	24	727	92
15.35	108	64	132
16.80	58	22	118
17.30 Unknowns	112	135	112
20.50	60	81	92
23.05	139	60	30
26.50	152	32	104

*This poorly shaped peak is probably only partly isoprene.

number 94 and 95, while taken one hour apart from the same enclosure bag, show quite different chromatograms. This indicates a possible storage problem. Isoprene, α - and β -pinene were tentatively identified by retention time.

The same sampling and analysis methods were used for Artemesia californica. The chromatographic results for the major peaks are shown in Table 8. Both pinenes, along with unknown peaks at 21.30 and 24.65 minutes appear to double during the enclosure period, indicating a biogenic source. The decrease in isoprene may have been due to losses at the walls.

Two samples were taken of Adenostoma fasciculatum (chamise); a 500-ml syringe sample after nine minutes and the entire contents of the enclosure bag after 11 minutes. In addition, at five minutes, the gas-tight syringe was used to transfer a 1-liter sample to a Teflon storage bag. All three containers were taken to the gas chromatograph within one hour. The major peaks of the analyses are shown in Table 9. There were considerable fluctuations for all three samples and no recognizable trend was observed. The storage bag was analyzed over an eight-hour period to check for losses or

Table 8. Artemesia californica Sample Collected March 17, 1980, 1543-1550 hours

Run Number	96	97
Enclosure period, min	3	6
Container	1- ϕ syringe	enclosure bag
Analysis time, PST	1600	1635
Retention time, min	ppbC	
6.35 (isoprene)*	36	13
14.30 (toluene)	23	37
17.30 (<u>p</u> & <u>m</u> xylene)	3	31
18.80 (α -pinene)	533	1434
19.95 (β -pinene)	96	141
15.35	50	73
20.62	309	350
21.10	110	189
21.30 Unknowns	1467	2649
23.05	79	71
24.65	734	1209

*This poorly shaped peak is probably only partly isoprene.

Table 9. Adenostoma fasciculatum Sample Collected March 19, 1980

Run No.	102	104	105	106	107	108
Enclosure period, min	5	9	11	5	5	5
Container	Storage bag	1-liter syringe	enclosure bag	storage bag		
Analysis time, PST	1045	1330	1415	1445	1645	1845
Retention time, min			<u>ppbC</u>			
6.35 (isoprene)*	19	16	26	32	--	37
14.65 (toluene)	14	2	11	22	3	13
18.85 (α -pinene)	6	14	152	9	20	--
20.00 (β -pinene)	31	--	11	--	--	19
15.65	94	39	31	71	47	30
20.90	50	67	--	--	--	48
23.40	83	74	32	50	79	67
26.75	42	48	14	30	40	9

*This poorly shaped peak is probably only partly isoprene.

gains of the various as yet mostly unidentified compounds. The peaks tended to vary randomly. Except for α -pinene in the enclosure bag, no large amount of organics was observed. Variation introduced in the GC analyses, storage of samples in the various containers and the use of the static Teflon bag enclosures (see next paragraph) make the data given of limited value, and work is underway in the second year of this program to provide quantitative elucidation of these effects.

As noted from the data in Tables 7 to 9, the procedures described above for sampling natural hydrocarbons by enclosing branches of wildgrowing shrubs in Teflon bags for short time intervals produced some quite high concentrations of the pinenes. However, the procedure was found to have serious drawbacks with respect to obtaining reliable emission rates. Factors which can affect emissions in using this technique are mechanical injury, heat stress and contact with the Teflon film by the enclosed branch. Additionally, physical factors such as the volume of the bag, time period or land area to be charged with the emissions were not well defined.

2. Rigid-Frame, Flow-Through Chambers

In order to address some of the problems encountered with use of Teflon film enclosures, two rigid-frame, flow-through chambers were designed

and constructed. The sampling enclosures were built using Teflon film stretched over rectangular parallelepipeds made of plastic pipe in which were mounted inlet and outlet ports as shown in Figure 9. The smaller enclosure (500 liters) was designed to be used with small shrubs, either ornamental or desert plants. To test this enclosure, it was placed over a Pittosporum shrub with the lower end of the bag tied around the main stem. With a small blower forcing air through the enclosure, the temperature and humidity increase inside the chamber was $\sim 1^{\circ}\text{C}$ and 19% in 30 minutes, and an additional 4°C and 19% in 130 minutes. Given a residence time in the enclosure of only a few minutes, and the modest changes in temperature and humidity over 30 minutes, it was felt that stress on enclosed plants should be minimal with this chamber.

The flow-through enclosure shown in Figure 9 should yield an emission factor in units of micrograms of hydrocarbon per square meter of land surface per hour. It is only necessary to know the flow rate and the concentration of organics in order to estimate the emission factor for an enclosed plant. The flow rate was estimated by following the rate of decrease of the initial concentration of a test compound placed in the empty chamber. The dilution follows an exponential decay which indicates good mixing and permits calculation of the flow rate without the need to introduce flow meters which could change the flow. By this method the flow was estimated to be 250 liters min^{-1} (i.e., 10 moles air per minute). At this flow rate a concentration of 1 ppb (by moles) corresponds to venting of 10 nanomoles of compound per minute. This is equivalent to $1.36 \mu\text{g min}^{-1}$ of terpenes ($\text{C}_{10}\text{H}_{16}$, MW = 136) from the chamber. If the base of the enclosure is taken to be the area occupied by the plant (0.38 m^2) the resulting emission factor is $216 \mu\text{g m}^{-2} \text{ hr}^{-1}$.

One feature of the enclosure method should be recognized; it is not necessary to assume that all the flow of air exits from the exit tube. Even if some air leaks through imperfect seals in the bag it will be counted since the purge method of measuring the flow rate will include all flow out of the enclosure which is effective in removing hydrocarbon vapors from the enclosure. The experimental decay of the test hydrocarbon validated this procedure.

If ambient air is used as the flow medium in the emission measurements, it will be necessary to correct for the organic content of the incoming air.

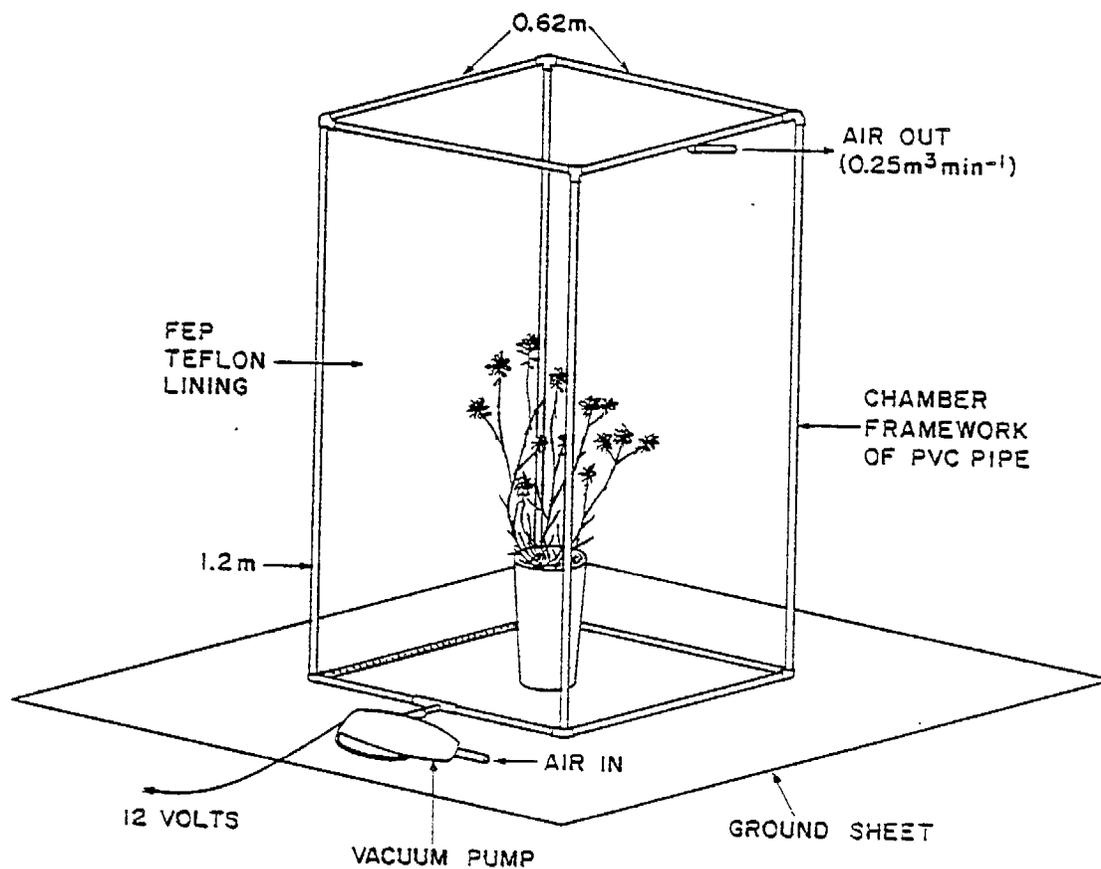


Figure 9. Rigid-frame, flow-through plant enclosure chamber for measurement of natural hydrocarbon emission factors.

With fractional ppb sensitivity, contamination from all sources must be considered, including the film from which the chamber is made and the plastic pipe which forms the frame of the enclosure. As an alternative to using ambient air, the SAPRC pure air system was tested as a matrix gas; its carbon dioxide content approaches the ambient air value of ~330 ppm. Sampling the enclosure and air system as a blank, with no plant present, yielded numerous small peaks some of which could be traced to the distilled water used to humidify the air.

Sampling was next made of a potted shrub of Encelia californica in the enclosure with the pure air system near the laboratory. A typical chromatogram is shown in Figure 2. A few peaks were tentatively identified and corresponded to concentrations much smaller than those measured from individual branches enclosed in plastic bags. Unfortunately, the matching blank sample was lost so we cannot be certain that the peaks shown came from the plant and not from the chamber or the pure air supply. The α -pinene peak corresponded to a concentration of 11 ppbC or 1.1 ppb by moles, and appeared on top of a broad tailing peak which is clearly an artifact. This artifactual peak is sometimes very much larger, usually for the first sample of the day.

Field sampling using the flow-through enclosure appears to be practical using either ambient air or tank gases. It will be necessary to choose plants small enough to fit the enclosure; a larger enclosure has been constructed but has not yet been tested. Plants to be studied must be growing on level ground with a main stem which can be isolated from other plants. The ground sheet shown in Figure 9 is designed to fit around the plant trunk and thus isolate it from surface emissions.

3. Illustration of Emission Inventory Calculations Based on Measured Emission Factors Using the Flow-Through Plant Enclosure Chamber

At a flow rate of air of 125 liters min^{-1} through the plant enclosure chamber (see above) a concentration of 1 ppb (of compound) corresponds to venting 5 nanomoles per minute or 0.68 $\mu\text{g min}^{-1}$ of terpene ($\text{C}_{10}\text{H}_{16}$, MW = 136) from the chamber. The base area of the enclosure is about 0.38 m^2 , so this emission rate is equivalent to an emission factor of 108 $\mu\text{g m}^{-2} \text{hr}^{-1}$. For comparison, the emission factor corresponding to the emission of 100 metric tons of organics per day (~6% of the Los Angeles inventory) in an

area 50 kilometers on a side with a 10% vegetative cover would be $16,700 \mu\text{g m}^{-2} \text{ hr}^{-1}$, more than 100 times greater than the value calculated above.

Thus, it appears that our present sampling enclosure and flow system will provide adequate sensitivity to establish meaningful upper limits (or actual values) for emission factors for individual plants even if our GC detection limit for the terpenes were no better than 1 ppb (our present detection limit is actually < 0.03 ppb compound).

One approach to translating this inventory into a form which can be used in conjunction with oxidant-precursor relationships is to scale the emissions to ambient concentrations using emission inventory and ambient concentration data for CO and nonmethane hydrocarbons in the South Coast Air Basin and comparing these results to the measured (or upper-limit) concentrations observed for ambient air samples.

For example, emission inventories for the South Coast Air Basin generally show around 10,000 tons day^{-1} of carbon monoxide, and about 1500 tons day^{-1} each of nonmethane hydrocarbon and nitrogen oxides. These emissions produce typical "bad day" values at downwind receptor areas of perhaps 5 ppm of CO, 1.33 ppm of NMHC and 0.33 ppm of NO_x . Conversion to weight units produces $5750 \mu\text{g CO m}^{-3}$, $763 \mu\text{g NMHC m}^{-3}$ and $620 \mu\text{g NO}_x \text{ m}^{-3}$. Division into the inventory totals yields about 2000 km^3 as the total dilution volume for this case, or a 1 km thick layer about 45 km (27.8 miles) square. This is a quite reasonable value for a "bad case" estimate.

If 100 tons day^{-1} were the terpene estimate for this basin, this would yield $50 \mu\text{g}$ of terpene m^{-3} or 9 ppb (by moles = 90 ppbC). Outdoor chamber irradiations carried out in our first year employed concentration values of this magnitude. For reference, some terpene inventory estimates have been much higher than this and yet 90 ppbC will be quite easy to measure chromatographically unless it is distributed among many different compounds.

III. MEASUREMENTS OF AMBIENT CONCENTRATIONS OF NATURAL HYDROCARBONS NEAR SELECTED PLANT COMMUNITIES

During the development phase of the sensitive gas chromatographic techniques required for fractional part-per-billion analysis of natural organics, it was decided to confine preliminary ambient air measurements of isoprene and the monoterpenes to locations in which hydrocarbons from anthropogenic sources would be present in low concentrations, facilitating detection and measurement of the natural organics. In the second year of this study, emphasis will be placed on determining the ambient concentrations of isoprene and selected monoterpenes in the source area of the South Coast Air Basin.

A number of possible remote sites were evaluated for studies of naturally emitted organics in areas free of anthropogenic emissions. The key criteria used in this evaluation were: (a) clean background air--no local sources of pollutants, (b) large upwind stands of the vegetative class of interest, (c) availability of electrical power and (d) accessibility.

Two sites in San Diego County were of sufficient interest to warrant obtaining atmospheric grab samples. They were Cibbits Flats and Mt. Laguna Observatory (operated by San Diego State University) in the Cleveland National Forest. There was no electricity at Cibbits Flats but the other criteria were met. The grab samples obtained at both locations showed ppb levels of acetylene, ethane, propane, propene and several other hydrocarbons (see Table 10). Over 100 ppb of ethene was observed; this was later traced to high ethene concentrations in the trailer where the samples were stored.

In an attempt to locate a site closer to Riverside, the areas northwest of Fallbrook were investigated. Except for lack of electrical power, the Tenaja Ranger Station in the Cleveland National Forest appeared ideal. The search for electrical power brought us to the De Luz area. This was at a lower elevation and it was thought that drainage winds from the sage and chaparral would give maximum concentrations of natural hydrocarbons. A cabin was located with electrical power and the owner permitted the use of his property.

Two grab samples were taken, one at the cabin and the other several hundred yards north. Both samples showed elevated levels (i.e., 3-5 ppb) of acetylene, propane and other hydrocarbons. Apparently De Luz is not remote

Table 10. Hydrocarbon Concentrations (ppb) Observed in Grab Samples Obtained at Gibbits Flats (#1) and Mt. Laguna Observatory (#3) on May 25, 1979

Compound	Bag #1	Bag #3
Methane	1729	1729
Ethene	116.0	113.7
Ethane	1.7	1.5
Acetylene	1.1	0.94
Propane	1.3	0.46
Propene	1.1	0.55
Isobutane	0.40	0.41
n-Butane	1.1	1.4
Acetylene	0.89	0.61
1-Butene	0.09	0.18
Isobutene	1.4	1.3
Trans-2-Butene	--	--
Isopentane	1.3	2.0
Cis-2-Butene	--	--
n-Pentane	0.71	0.98
3-Methyl Butene-1	--	--
1,3-Butadiene	--	--
Methyl Chloride	--	--
Methyl Acetylene	--	--
2,2-Dimethyl Butane	--	--
1-Pentene	--	--
2-Methyl Butene-1	--	--
Trans-2-Pentene	--	--
Cis-2-Pentene	--	--
2,3-Dimethyl Butane	--	--
2-Methyl Pentane	0.52	0.42
2-Methyl Butene-2	--	--
3-Methyl Pentane	--	--
Cyclo Pentane	--	--
n-Hexane	--	--
Cyclo Pentane	--	--
2-Methyl Butadiene-1,3 (Isoprene)	1.404 mv	.052 mv

Unknown at 18.3 min

enough from anthropogenic sources. Ozone concentrations somewhat higher than background (i.e., 0.04-0.08 ppm) were measured with a Dasibi monitor. High levels of ethene (30 and 115 ppb) were again observed.

The plant communities observed at the sites discussed above are shown in Table 11.

Samples were taken at Tenaja Ranger Station in the Cleveland National Forest (see Table 12) in the early morning hours of June 11 and 17, 1980. The two sets of freeze-trap samples were analyzed by capillary GC. They do not show a high order of consistency as to peak heights, but the emergence times are reasonably consistent. The times vary by a few seconds which seems to be the limit for the present system (summer 1980). The two-carbon hydrocarbons measured on June 11 indicate that little auto exhaust contamination was present. The largest peaks are the unidentified ones beyond α -pinene except for the sample obtained at site one which had a very large β -pinene peak. These data (shown in Tables 12 and 13) are not definitive. The diolefin terpenes (limonene and α -terpinene) seem to emerge from this capillary column after the monoolefins. Perhaps the peaks later than 20 minutes are other single ring isomers or some of the straight chain triolefins. Limited evidence (citronellol emerges at 42 minutes) suggests that

Table 11. Plant Communities Observed at Several Sites in Southern California at which Hydrocarbon Grab Samples were Obtained

CIBBITS FLATS

Mainly chamise (Adenostoma fasciculatum) with an admixture of other shrubs

MT. LAGUNA OBSERVATORY

Mixed conifer forest comprised mainly of the Jeffrey pine (Pinus jeffreyi) - black oak (Quercus kelloggii)

TENAJA RANGER STATION

Chamise and scattered oak trees (e.g., Quercus chrysolepis and Quercus wizlizenii)

DE LUZ

Extensive chamise chaparral on slopes with cottonwood, willow and oaks in the creek bottom

oxygenated compounds would have emergence times longer than the peaks shown in Tables 12 and 13. Mass spectrometry and/or chemical tests may be helpful in identifying these compounds and this will be attempted in the second year of this program.

Table 12. Tenaja Ranger Station Samples, June 11, 1980

	Concentration, selected peaks (ppbC)			
	Time PDT			
	0700 Site 1	0810 Site 2	0852 Site 3	1127 Site 1
Methane	1,795	2,161	1,924	1,792
Ethane	10	12.7	15.2	8.4
Ethene	2.4	2.8	5.4	3.4
Acetylene	5.7	4.6	7.4	5.8
Isoprene	8.6	7.3	3.2	6.6
Toluene	2.9	1.8	1.6	3.2
α -pinene	278	0.5	0.5	0.4
β -pinene	3.3	1.3	1.7	0.7
<u>Unknowns</u>				
20.60 min	37	48	32	40
21.30	18	16	22	6
22.42	26	31	19	4
23.15	84	73	48	72
25.24	11	4	3	4
26.63	71	16	18	19

Table 13. Tenaja Ranger Station Samples, June 17, 1980

	Concentration, selected peaks (ppbC)			
	Trap	Bulb	Trap	Bulb
Isoprene	8.6	16.3	6.6	27.9
Toluene	8.5	12.3	8.0	10.5
α -pinene	1.7	0.6	0.2	0.
β -pinene	7.1	1.0	2.7	3.6
<u>Unknowns</u>				
20.67 min	49.3	23.4	32.5	91.5
21.30	18.2	5.5	13.2	6.6
22.35	20.1	4.8	4.8	7.1
23.14	146.9	37.1	77.2	159
25.20	13.2	0.8	7.2	2.2
26.60	58	5.6	42.6	63.6

IV. DETERMINATION OF OXIDANT-PRECURSOR RELATIONSHIPS FOR α -PINENE UNDER SIMULATED ATMOSPHERIC CONDITIONS

Assessments of the atmospheric impact of biogenic hydrocarbons requires knowledge of the oxidant and aerosol-forming potential of such compounds, as well as of their ambient concentrations, emission rates and the abundance of vegetation from which they are emitted. Although a substantial number of investigations of gas phase isoprene chemistry have been made comparatively few laboratory or smog chamber studies of the rates and products of the atmospheric reactions of the monoterpenes have been carried out (Stephens and Scott 1962, Ripperton et al. 1967, 1972; Lillian 1972, Japar et al. 1974, Grimsrud et al. 1975, O'Brien et al. 1975, Winer et al. 1976, Arnts and Gay 1979, Hull 1980). Moreover, the majority of the smog chamber experiments conducted to date have involved irradiations of vegetative hydrocarbons at concentrations ranging from one to three orders of magnitude higher than observed ambient levels or the use of small reactors with high surface-to-volume ratios.

Stephens and Scott (1962) were the first to study the photooxidation of pinenes (isomer unstated) and found that at high concentrations (4 ppm) their reactivity is comparable to olefins found in auto exhaust. Grimsrud and co-workers (1975) irradiated several terpenes, including α -pinene, at concentrations of 10 ppb hydrocarbon with small amounts of added nitric oxide using a 50-liter borosilicate glass flask as a chamber and fluorescent black light as an irradiation source. Winer et al. (1976) interpreted the photooxidation data of Grimsrud et al. (1975) in terms of loss of the terpenes solely by reaction with hydroxyl radicals and derived (Winer et al. 1976, Atkinson et al. 1979) OH radical rate constants for the compounds studied (as well as measuring relative OH rate constants for α - and β -pinene and d-limonene in their own laboratory).

Lillian (1972) carried out NO_x/α -pinene photooxidations in small Teflon bags, typically with 0.5 ppm of hydrocarbon, and observed large amounts of aerosol formation as well as significant ozone concentrations. In a recent and comprehensive study, Arnts and Gay (1979) investigated the photochemistry of isoprene, propene and a series of monoterpenes, primarily in the ~ 0.1 -1

ppm concentration range, using small Teflon bags and fluorescent black lamp irradiation. They studied in some detail the dependence of ozone formation and other reactivity parameters on the hydrocarbon/NO_x ratio. In addition, they irradiated lower concentrations of α-pinene (10-20 ppb) in the presence of NO_x and observed ~10-20 ppb of ozone after 60 minutes of irradiation.

The present study was focussed on establishing oxidant-precursor relationships for α-pinene/NO_x mixtures (with and without added hydrocarbons) at ambient, or near-ambient, concentrations of α-pinene under favorable environmental chamber conditions with respect to surface-to-volume ratio, total chamber volume, spectral distribution and light intensity, and normalization for variables via dual-mode chamber operation. Since α-pinene is a dominant, naturally emitted monoterpene (Graedel 1979) and has been shown to be highly reactive towards O₃ and OH radicals, it was chosen as a surrogate for other terpenes observed to be emitted in significant quantities.

A. Experimental

All experiments were conducted using an outdoor chamber constructed of 50 μm thick FEP Teflon film. Teflon was chosen because of its chemical inertness, low permeability and excellent transmission of actinic ultraviolet (295 < λ < 406 nm) radiation. The chamber dimensions were approximately 7 m x 8 m and it was held above the ground by a wire grid attached to a metal frame, as shown in Figure 10. Division into two compartments was accomplished using three metal rods to fold the film in such a manner that the chamber was "pinched" in half. Studies using inert fluorocarbon tracers showed side-to-side contamination in the dual-mode configuration to be less than 1% hr⁻¹. Purified matrix air was provided by an activated charcoal, Hopcalite, Pura-fil-based air purification system described previously (Doyle et al. 1977). When filled in the dual-mode, each chamber compartment was inflated to a volume of about 20 m³, resulting in a surface-to-volume ratio of 2.8 m⁻¹.

Sampling was done from both sides by use of glass tubing and manifold. Because of the chamber flexibility, no make-up air was necessary. The on-line monitoring instruments and calibration methods employed are summarized in Table 14. In addition to these continuous analyses, samples were taken with a 100 ml gas-tight glass syringe for hydrocarbon and peroxyacetyl nitrate (PAN) analysis. For PAN a Varian Aerograph electron capture

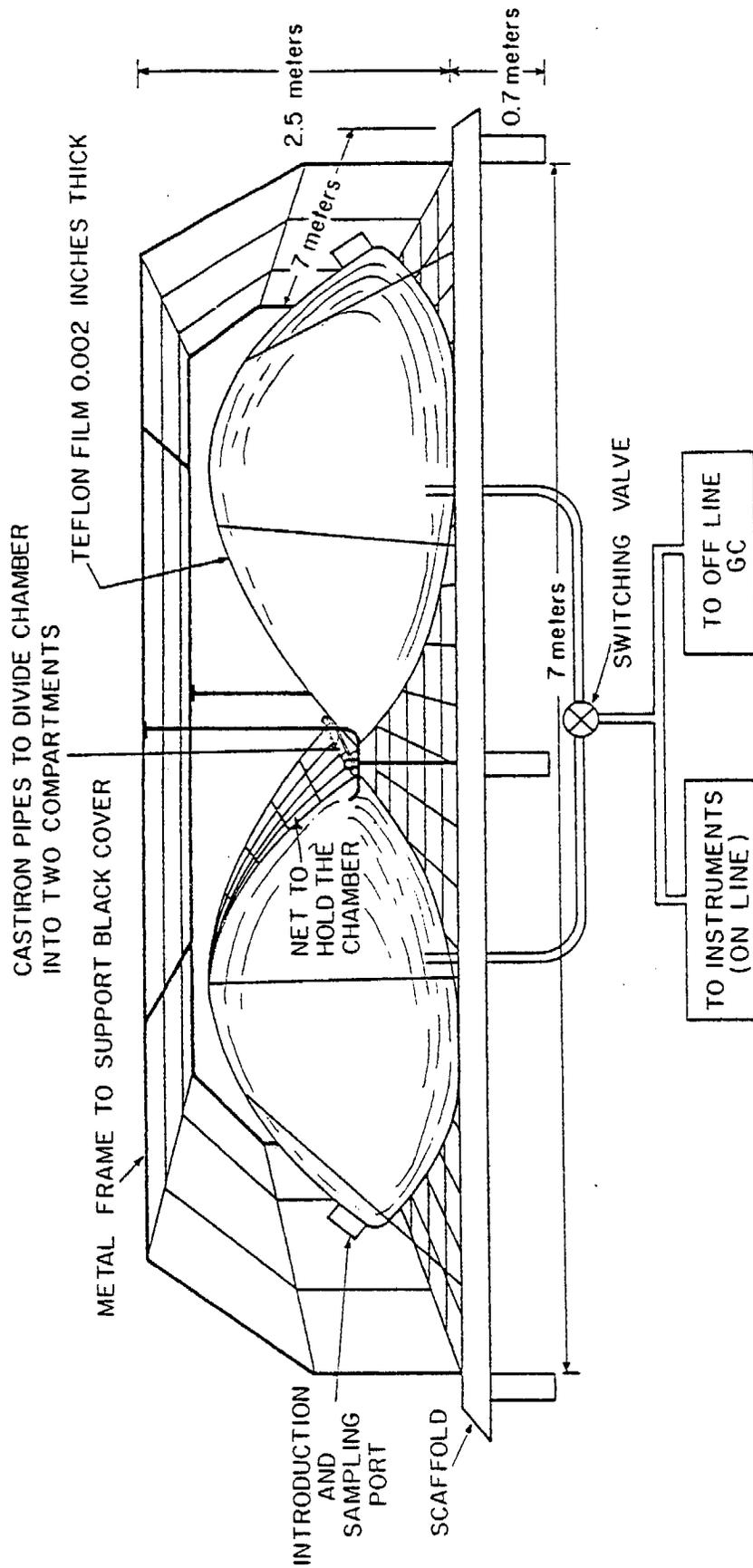


Figure 10. SAPRC 40,000 outdoor Teflon chamber shown in dual-mode configuration.

Table 14. On-Line Instrumentation for α -Pinene Photooxidation Experiments

Parameter	Instrument	Calibration Method
Ozone	Bendix Chemiluminescence Model 8002	UV Photometer
Ozone	Dasibi Ultraviolet Absorption Model 1003AH	UV Photometer
Nitrogen Oxides	Bendix Chemiluminescence Model 8101B	NSB-certified gas cylinder
Temperature	Doric Thermocouple Model DS-350-T3	NBS-certified thermometer
Condensation Nuclei	Environment One Model Rich 100	Factory
Particle Number 0.0075-0.4 μ m diameter	TSI Electrical Mobility Model 3030	Factory
Particle Number 0.3-1.0 μ m diameter	Climet Optical Counter Model 208A	Spray-dried latex beads
Light Scattering	MRI Integrating Nephelometer Model 1550	Freon 12
UV Radiation	Epply UV Radiometer	Factory

gas chromatograph (Model 600) was equipped with a six-port, 2 ml sample injector and a 3.2 mm x 15 cm Teflon column of 5% Carbowax 400 on 100-120 A/W DMCS Chromosorb W run at room temperature. PAN calibrations were performed by diluting samples of synthetically prepared (Stephens and Price 1965) PAN at concentrations determined by IR absorbance.

Complete hydrocarbon analyses of the purified air and of the surrogate hydrocarbon mixture was by flame ionization gas chromatography (FID-GC) done as described previously (Pitts et al. 1979). Total nonmethane hydrocarbons, derived by adding individual components measured by FID-GC analysis, were generally in the range of 100-200 ppbC in the purified matrix air.

For the most part, these were low molecular weight, unreactive hydrocarbons and therefore not completely removed by the purification train. Propane was the most abundant contaminant and was thought to be outgassing from the activated charcoal. α -Pinene was monitored using a Varian 1400 FID-GC, equipped with a cryogenically cooled sample trap and a Carbowax 600 (on C-22 firebrick) packed column, 3.2 m x 3.05 m, run at 75°C. α -Pinene was supplied by Aldrich and was vapor transferred prior to use. Matheson C.P. grade nitric oxide was used as received, or oxidized to nitrogen dioxide in pure oxygen prior to injection.

A typical experimental protocol for these experiments is shown in Table 15. Prior to a run, the chamber was covered with black plastic sheeting to exclude sunlight and then filled with purified air. After recording background readings, measured amounts of reactants were injected by glass syringes into a 1-liter mixing flask and then flushed into the chamber with N₂. Complete mixing was accomplished in several minutes by manually pushing on the chamber sides. The dual-mode division was made and any other reactants were added to one side as described above. Following mixing and another set of background measurements on each side, the black cover was removed and the irradiation allowed to continue for six to seven hours.

B. Results

The initial conditions and ozone maxima for 15 dual-chamber irradiations performed in this study from November 1979 to February 1980 are shown in Table 16. Time-concentration profiles from these 15 experiments are given at the end of this section in Figures 11 to 47. The experimental sequence began with a freshly made Teflon chamber. Irradiation of pure air resulted in the formation of essentially equal amounts of ozone in the two sides of the dual-mode chamber (33 and 35 ppb). This indicated the equivalence of the two sides with respect to such factors as irradiation uniformity and was regarded as an initial conditioning of the interior surfaces of the the chamber.

In three pure air irradiations (Runs 2-4), varying amounts of α -pinene were added to one side after chamber division. Although the nitrogen oxides were at or below the detection limit of the chemiluminescence analyzer (~2

Table 15. Protocol for Outdoor Irradiation Experiments for α -Pinene-NO_x Systems

Time		Task
0600-0735		Chamber filled with pure air
0800		Chamber covered
0815		NO injection, if any
0830		NO ₂ injection, if any
0845		Surrogate hydrocarbon injection, if any
0855		Bag division
Side 1	Side 2	
	0900	α -Pinene injection, if any
0930	0930	Uncovered
1530	1530	End experiment, chamber emptied

ppb), sub-ppb quantities of NO_x were undoubtedly present. These runs therefore involved high HC/NO_x ratios, characteristic of atmospheres in rural and remote regions. The "background" ozone levels found in such regions (i.e., 30-40 ppb) were not initially present in these experiments, but the small amount of O₃ formed due to impurities in the matrix air or chamber contamination (see Runs 1 and 15) during the irradiation period to some degree compensated for this.

The ozone and α -pinene concentration profiles observed in Run 2 are shown in Figure 13. In this, and in similar runs (Nos. 3 and 4), the addition of α -pinene lowers the amount of ozone produced, relative to the control side, by an amount dependent on the concentration of α -pinene consumed ($\Delta O_3/\Delta \text{pinene} \sim -0.6$). Consumption of α -pinene was consistently 7-9% hr⁻¹ in each of these runs; thus ~40-50% of the α -pinene was consumed by the end of a six-hour irradiation. In Run 2 with 32 ppb of added α -pinene, the electrical mobility analyzer showed about 4 $\mu^3 \text{ cm}^{-3}$ of aerosols. In Run 3, with 8 ppb added α -pinene, little aerosol formation (i.e., near the 1 $\mu^3 \text{ cm}^{-3}$ detection limit) was observed. No gas phase products were identified by FID-GC analysis, but several minor peaks were observed late in the runs.

To investigate lower HC/NO_x ratios, still involving only α -pinene, several runs (Nos. 5-7) were conducted with NO_x added to one or both sides.

Table 16. Initial Conditions and Ozone Maxima for α -Pinene Irradiations and Control Experiments in Outdoor Chamber^a

Run No.	Experiment Type	Control Side ^b			Hydrocarbons Added Before Chamber Division ^c	Variable Side			ΔO_3 Δ Pinene Consumed	
		Side No.	NO	Pin- ene NO ₂		Side No.	NO	α -Pinene		O ₃ Max
1	Pure Air vs. Pure Air	1	0	0	None	2	0	0	33	-
2	α -Pinene vs. Pure Air	2	1	1	None	1	1	1	32	12
3	α -Pinene vs. Pure Air	2	1	1	None	1	2	2	8	10
4	α -Pinene vs. Pure Air	1	1	0	None	2	1	0	42	6
5	α -Pinene + NO _x vs. α -Pinene	2	3	3	α -Pinene	1	34	9	9	26
6	α -Pinene + NO _x vs. NO _x	2	22	12	None	1	23	12	8	17
7	α -Pinene + NO _x vs. NO _x	2	14	4	None	1	14	3	9	27
8	α -Pinene + NO _x + Hydrocarbons vs. NO _x + Hydrocarbons	2	20	12	52 propene 310 isopentane 18 acetaldehyde	1	19	11	9	143
9	α -Pinene + NO _x + Hydrocarbons vs. NO _x + Hydrocarbons	1	22	7	48 propene 138 isopentane 17 acetaldehyde	2	22	10	13	128
10	α -Pinene + NO _x + Hydrocarbons vs. NO _x + Hydrocarbons	1	26	10	44 propene 180 isopentane 20 acetaldehyde	2	25	10	Added in 4 injections	108
11	NO _x + Hydrocarbons vs. NO _x + Hydrocarbons	1	26	12	52 propene 169 isopentane 18 acetaldehyde	2	24	12	0	123
12	α -Pinene + NO _x + Surrogate vs. NO _x + Surrogate	1	96	55	SAPRC Surrogate ^d	2	93	57	9	180
13	α -Pinene + NO _x + Ambient vs. NO _x + Ambient	1	149	40	Ambient	2	149	40	11	201
14	α -Pinene + NO _x vs. NO _x (high concentration)	2	69	43	None	1	71	42	139	216
15	Pure Air vs. Pure Air	2	0	0	None	1	0	0	1f	24

^aAll concentrations in ppb.

^bNo injection after division of chamber.

^cCommon to both Side 1 and Side 2.

^dSee Pitts et al. 1976.

^eEstimated total α -pinene added: 11 ± 3 ppb.

^fAttributed to contamination from previous high concentration runs.

In Run 5, 43 ppb of NO_x (primarily NO) was added to one side with 9 ppb α -pinene in both sides. As shown in Figure 21, typical profiles were observed for oxidation of NO to NO_2 and (after an induction period relative to the side without NO_x) the side with added nitrogen oxides produced a higher ozone maximum (26 ppb vs. 19 ppb) with slightly greater consumption of α -pinene. In Runs 6 and 7, when each side contained equal concentrations of nitrogen oxides, adding α -pinene to one side produced higher ozone concentrations with little NO -to- NO_2 conversion observed in the control side. Under these conditions, no detectable response was seen from any of the particulate analyzers, with an upper limit of aerosol concentration being estimated at about $1 \mu^3 \text{ cm}^{-3}$.

To approximate the case of lightly polluted air impacting on a rural environment, or transport of rural air to urban airsheds, several irradiations were performed with addition of small amounts (9-13 ppb) of α -pinene to either lightly polluted ambient air or a three-component hydrocarbon mixture. Runs 8-10 involved mixtures of propene, isopentane, acetaldehyde and nitrogen oxides, chosen in a ratio which would provide an OH reactivity similar to that of the previously well-characterized SAPRC "smog surrogate" hydrocarbon mixture (Pitts et al. 1976). The side containing ~10 ppb of α -pinene exhibited an ozone peak ~10-20 ppb higher than the control side. The ozone and α -pinene profiles for Run 8 are shown in Figure 26. α -Pinene was depleted in several hours after which time the two sides produced ozone at a similar rate. The hydrocarbon- NO_x mixture alone (Side 2) did not, as expected, produce any aerosol. Only on the α -pinene side was a detectable amount of small particles observed by the electrical mobility analyzer (several $\mu^3 \text{ cm}^{-3}$) and optical particle counter. This result may be due to the more rapid and complete oxidation of the α -pinene in the presence of the propene/isopentane/acetaldehyde mixture. Similar results were obtained (Run 10) when α -pinene was added during an experiment in four equivalent injections (to simulate continuous emissions of α -pinene) or when the hydrocarbon mixture was changed (Run 12) to the more extensive (15 organics) SAPRC surrogate mixture (Pitts et al. 1976).

A single run (No. 13) was conducted using lightly polluted ambient Riverside air in both sides with the addition of 11 ppb of α -pinene to one side. In this case, there appeared to be slightly faster NO oxidation and

ozone formation in the α -pinene side until the very end of the run when the ozone on the control side became slightly higher. This may be due to a slight chamber side-inequivalency discussed below. Aerosol measurement by the electrical mobility analyzer showed the α -pinene side slightly enriched in particulate concentration ($4 \mu^3 \text{ cm}^{-3}$) after several hours. No differences in condensation nuclei concentration were observed for the two sides in this run.

An experiment (Run 14) was done at concentrations of α -pinene and nitrogen oxides more typical of those employed by other investigators (Arnts and Gay 1979). With 1.39 ppmC of α -pinene and a carbon/ NO_x ratio of 12, an ozone maximum of 216 ppb was observed, with significant aerosol production measured by all of the particulate analyzers. By comparison with other runs, the electrical mobility analyzer measured a peak total volume of $40 \mu^3 \text{ cm}^{-3}$.

Control and replicate experiments were performed throughout this series of runs. Side 1 of the dual-mode chamber generally gave slightly higher (~5%) ozone peaks, especially late in the afternoon, for identical initial concentrations of α -pinene, NO_x and hydrocarbons. This effect is believed to be due to the east-west alignment of the chamber division which allowed Side 1, on the west, to potentially receive slightly more irradiation late in the day. However, during the first four hours of irradiation, the NO oxidation and ozone formation rates in the two sides were generally indistinguishable (see Figure 35).

A single Teflon chamber was used throughout this series of experiments. To test for chamber contamination, a pure air photolysis (Run 15) identical to Run 1 was carried out at the conclusion of the study. The maximum ozone concentrations (24 and 25 ppb) observed in the two sides were lower than the maximum concentrations observed in Run 1 (35 and 33 ppb). This suggests that wall contamination in these runs was less important than the variable composition of the matrix air produced by the air purification system.

C. Discussion

The consistency of the data (both relative and absolute) obtained in this study indicates that the dual-mode outdoor chamber successfully permits resolution of comparatively small incremental effects due to irradiation of α -pinene in the absence or presence of NO_x and hydrocarbons. The large

volume, low surface-to-volume ratio, increased aerosol lifetime, and substantial equivalency of the control chamber affords quantitative data in a concentration regime approaching "worst case" ambient air concentrations observed for the monoterpenes.

Our data are in good agreement with the NO_x/α -pinene irradiation results of Arnts and Gay (1979) for their lowest concentration experiments. In the range of optimum carbon/ NO_x ratio (~10-15) they observed, in their "high" concentration runs, ~0.75-1.5 ppb of ozone produced per ppb of α -pinene consumed at the time of the O_3 maximum. Coffey and Westberg (1978) report somewhat lower values of 0.3-1.0 ppb O_3 per ppb of terpene consumed. In their "low" concentration experiments, Arnts and Gay observed ~1 ppb O_3 per ppb of α -pinene consumed after one hour. As shown in Table 16, we find ~1-2 ppb of O_3 produced per ppb of α -pinene consumed in experiments with added NO_x , with or without added hydrocarbons. In experiments with no added NO_x , α -pinene behaves as a sink for O_3 , removing ~0.6 ppb O_3 per ppb of α -pinene.

Other studies (Gay and Arnts 1977, Arnts and Gay 1979) have found poor carbon balances from irradiations of α -pinene/ NO_x mixtures. In the past, this has been attributed to aerosol formation coupled with subsequent wall loss. However, the half life of submicron particles in our chambers has been shown to be on the order of several hours, and in the ~10 ppb concentration range employed in this study, it appears that carbon loss cannot be attributed primarily to aerosol formation. The argument may be made that given our particle-free matrix air, nucleation was not possible for the photooxidation products. However, the net increase in aerosol formation for the α -pinene side in the run employing ambient air (Run 13) was comparable to the results obtained in runs using hydrocarbon mixtures in particle-free matrix air. Thus from our observations, it appears unlikely that α -pinene is a major aerosol precursor at ambient concentration. Verification of this tentative conclusion requires additional research concerning the gas and aerosol phase products from the photooxidation of α -pinene, and the lifetime of such products in Teflon chambers (including those of large volume).

In conclusion, our data show that when irradiated in clean air (i.e., air containing only low concentrations of oxides of nitrogen and reactive hydrocarbons) near-ambient concentrations of α -pinene appear to behave as

an ozone sink rather than as an ozone precursor. Irradiation of low concentrations of α -pinene in the presence of NO_x or NO_x -hydrocarbon mixtures results in enhancement of ozone maxima (relative to α -pinene-free systems) by amounts one to two times the initial terpene concentrations on a molar basis. Thus, the ambient concentrations of α -pinene observed even in forest and citrus canopies would not appear to contribute significantly to ambient ozone concentrations relative to O_3 levels produced from photooxidation of anthropogenic hydrocarbons. The present data, when combined with the low ambient concentrations of monoterpenes expected in urban airsheds (based on such measurements to date), suggest that these compounds will contribute no more than 10 ppb of O_3 in such airsheds. Moreover, it does not appear that the monoterpenes will significantly impact visibility in urban airsheds relative to visibility degradation from primary and secondary particulates originating from emissions from anthropogenic sources.

A quantitative assessment of the atmospheric impact of α -pinene and other vegetative hydrocarbons in urban airsheds must await more extensive data concerning their emission rates and ambient concentrations in the source areas of such airsheds, as well as reliable models of the transport and reactions of these compounds. Thus the principal emphasis in the second year of this program will be placed on measurements of ambient concentrations and emission rates of natural hydrocarbons, from abundant plant species, in the "source" area of the South Coast Air Basin.

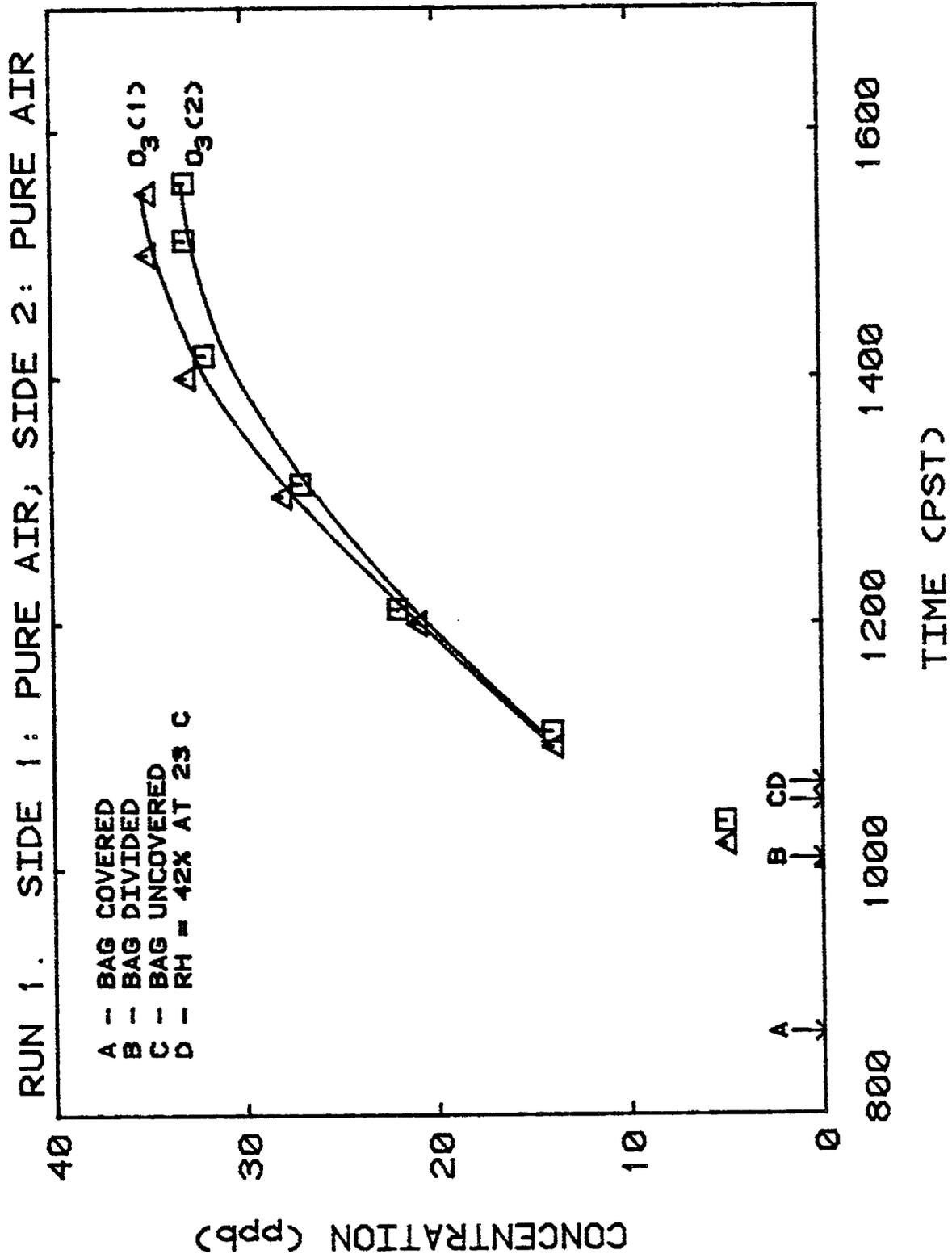


Figure 11. Concentration profiles for ozone in Run 1 of α -pinene photooxidation study.

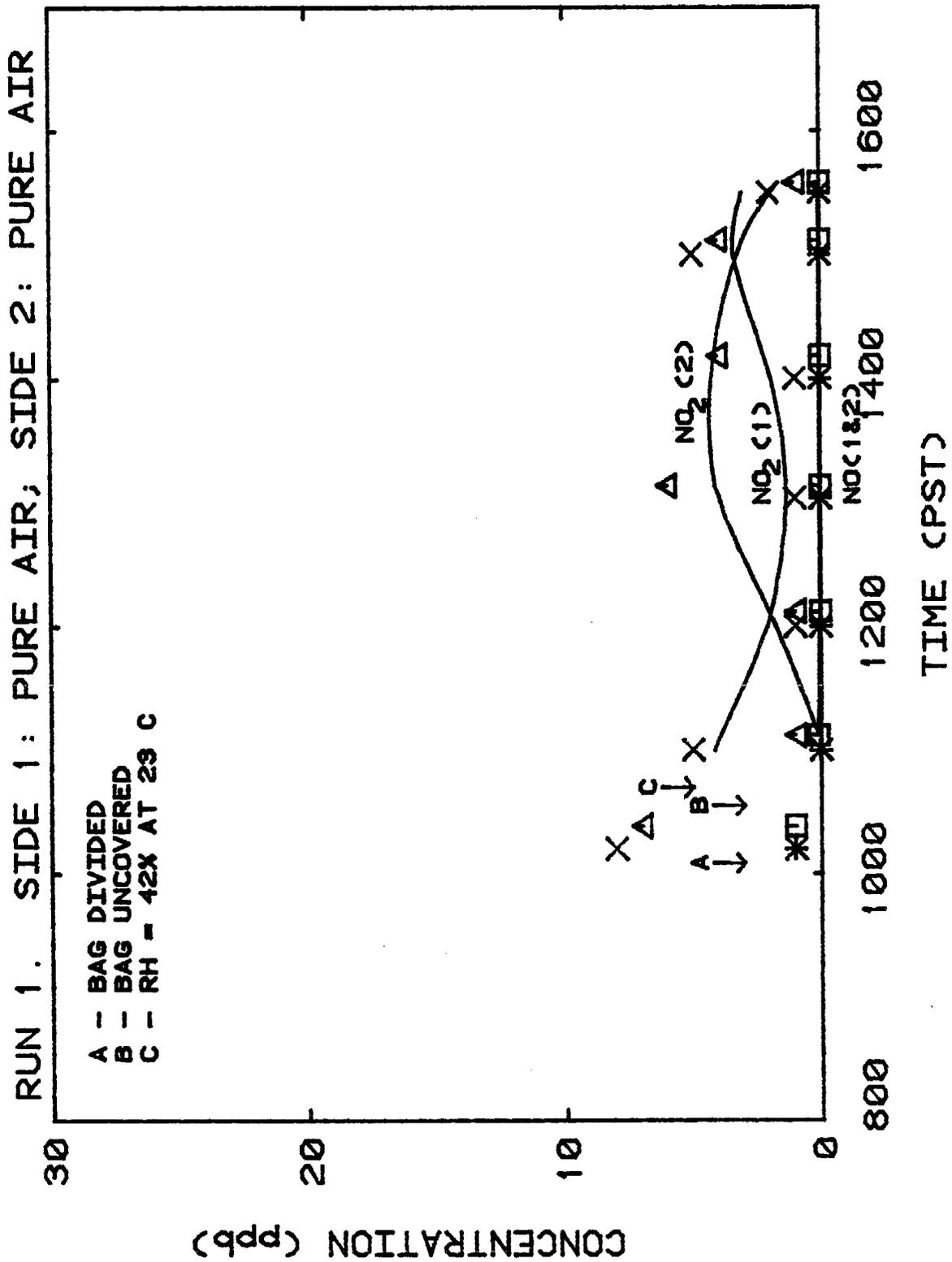


Figure 12. Concentration profiles for NO and NO₂ in Run 1 of α-pinene photooxidation study.

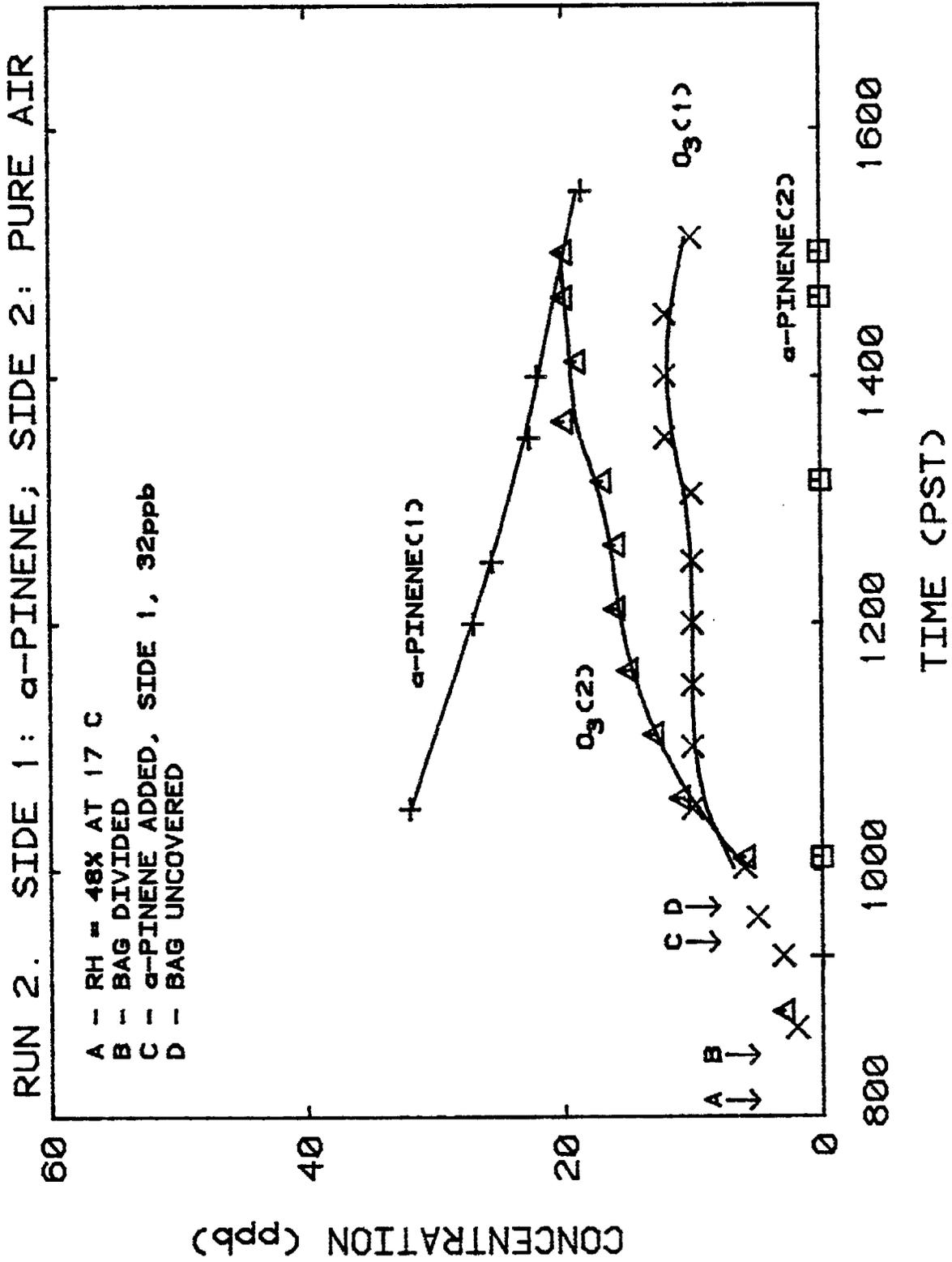


Figure 13. Concentration profiles for ozone and α -pinene in Run 2 of α -pinene photooxidation study.

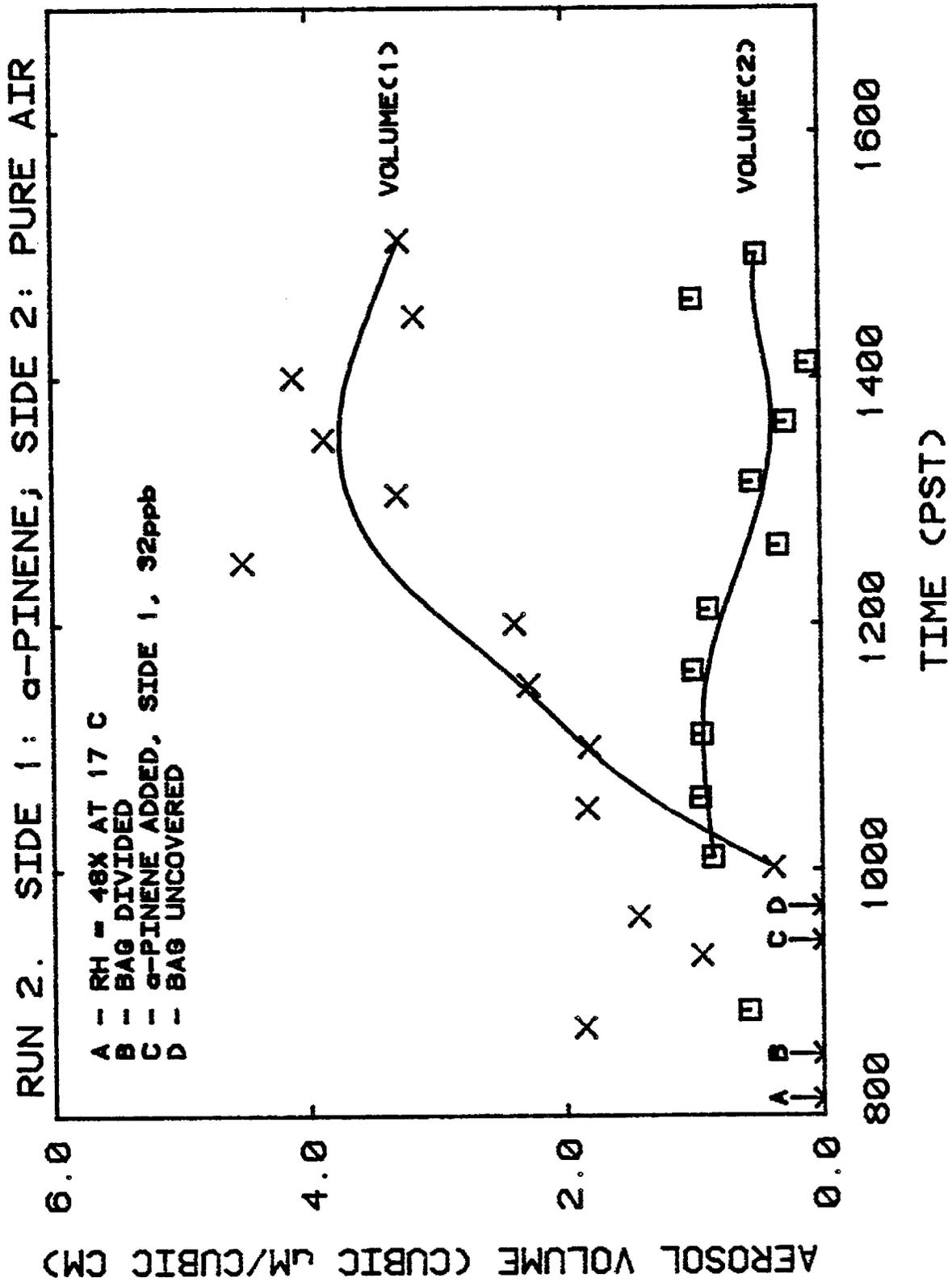


Figure 15. Aerosol volume in Run 2 of α -pinene photooxidation study.

RUN 3. SIDE 1: α -PINENE; SIDE 2: PURE AIR

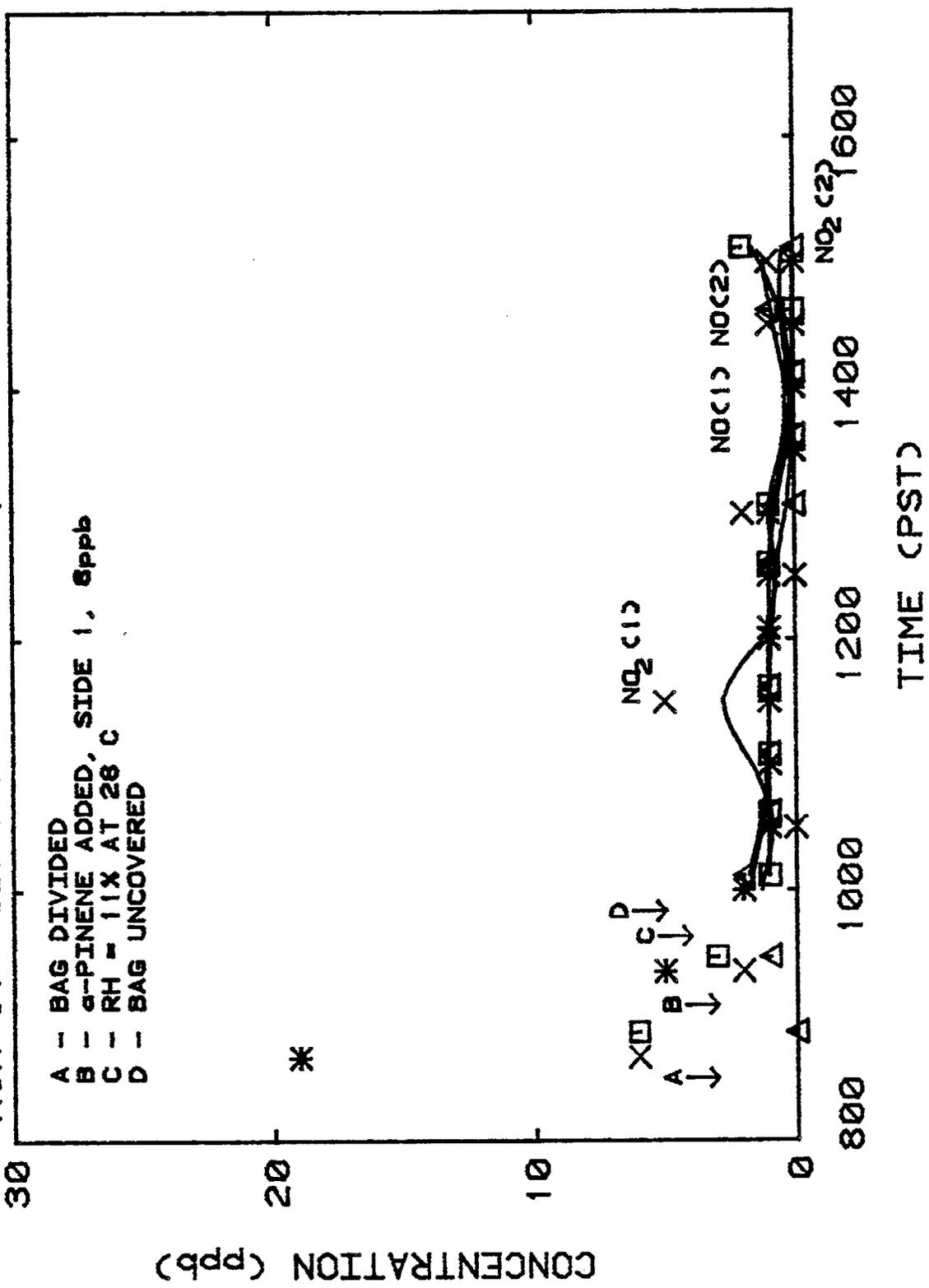


Figure 17. Concentration profiles for NO and NO₂ in Run 3 of α -pinene photooxidation study.

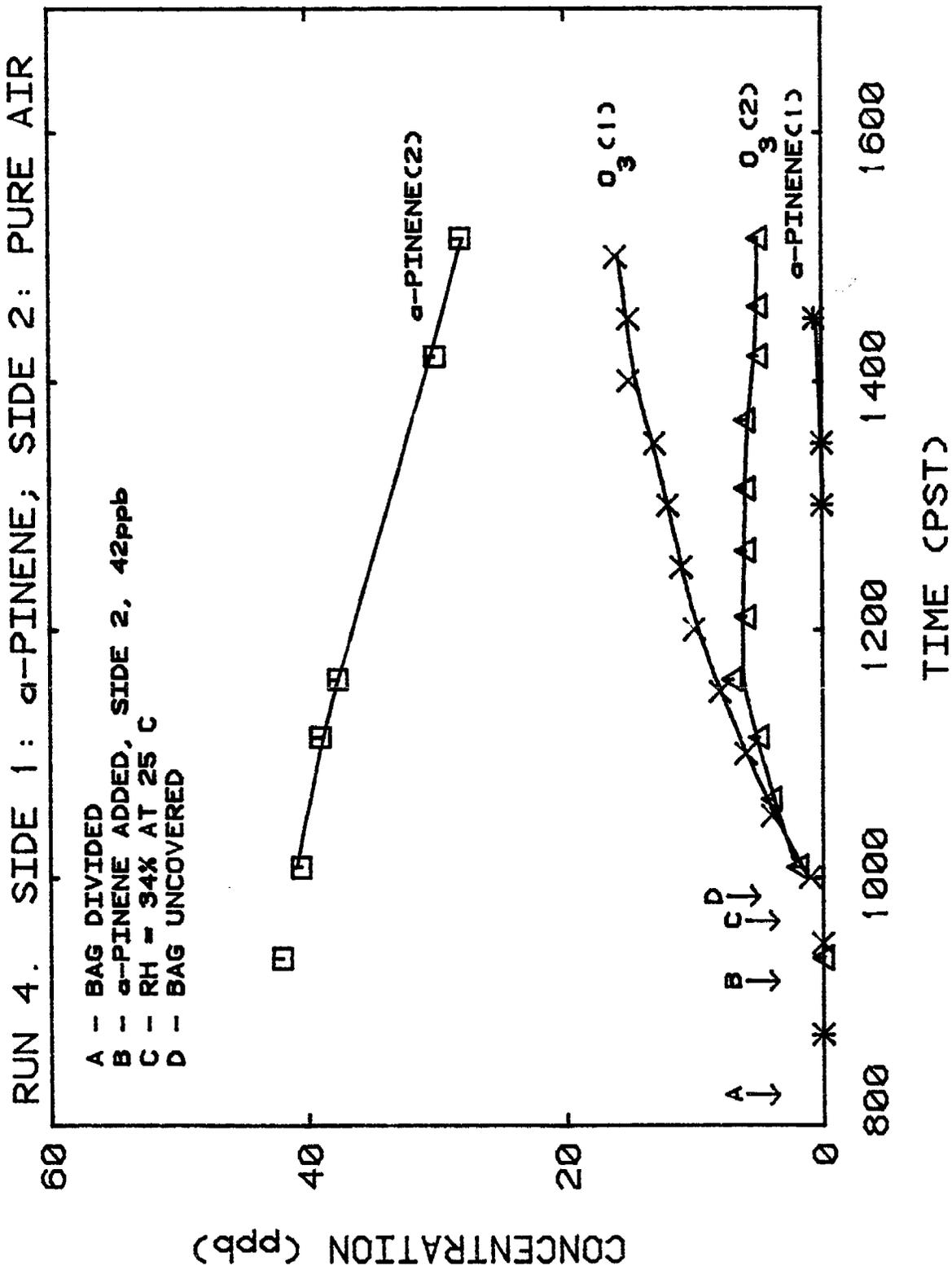


Figure 18. Concentration profiles for ozone and α -pinene in Run 4 of α -pinene photooxidation study.

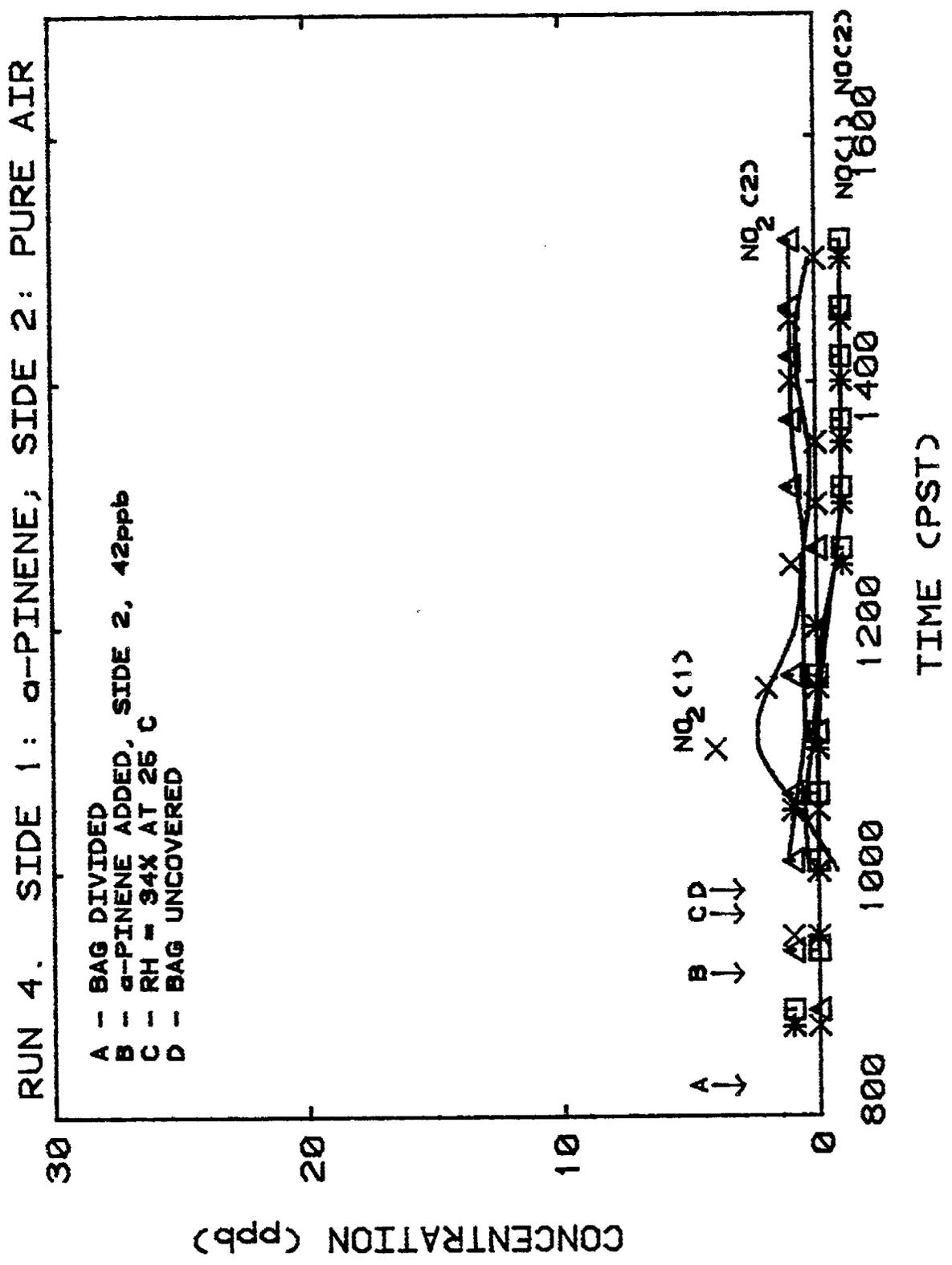


Figure 19. Concentration profiles for NO and NO₂ in Run 4 of α -pinene photooxidation study.

RUN 5. SIDE 1: α -PINENE + NO_x; SIDE 2: α -PINENE

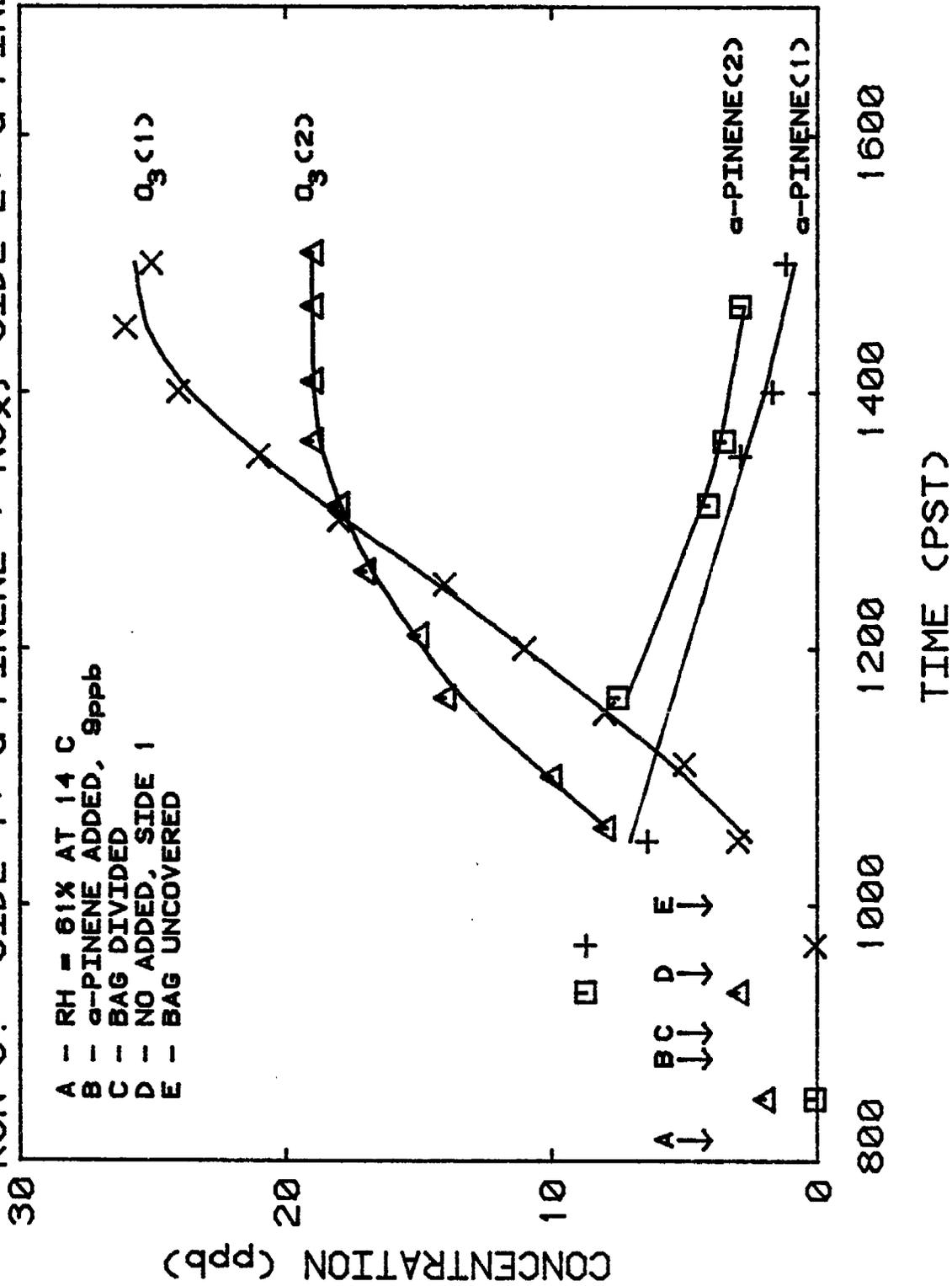


Figure 20. Concentration profiles for ozone and α -pinene in Run 5 of α -pinene photooxidation study.

RUN 5. SIDE 1: α -PINENE+NO_x; SIDE 2: α -PINENE

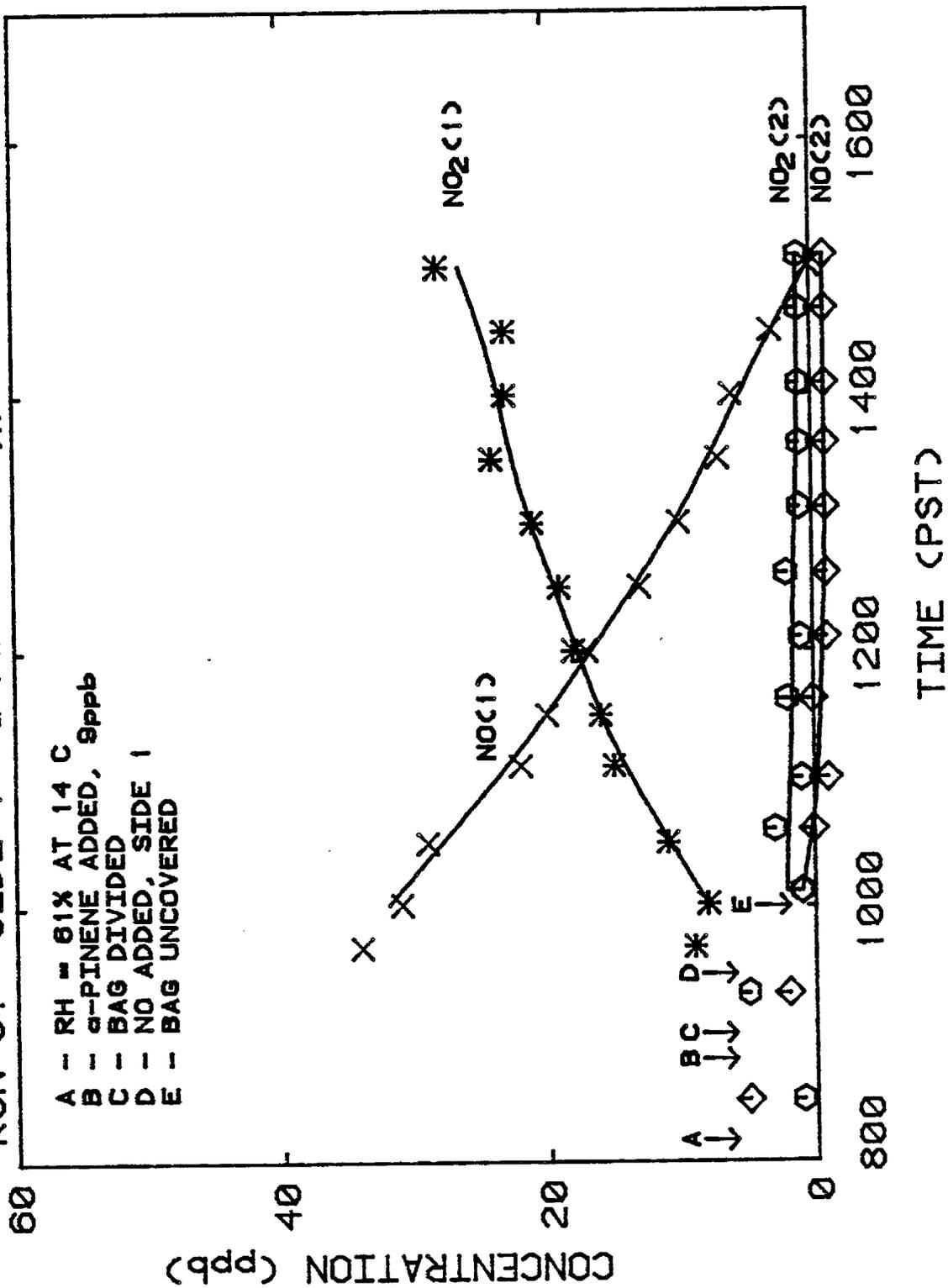


Figure 21. Concentration profiles for NO and NO₂ in Run 5 of α -pinene photooxidation study.

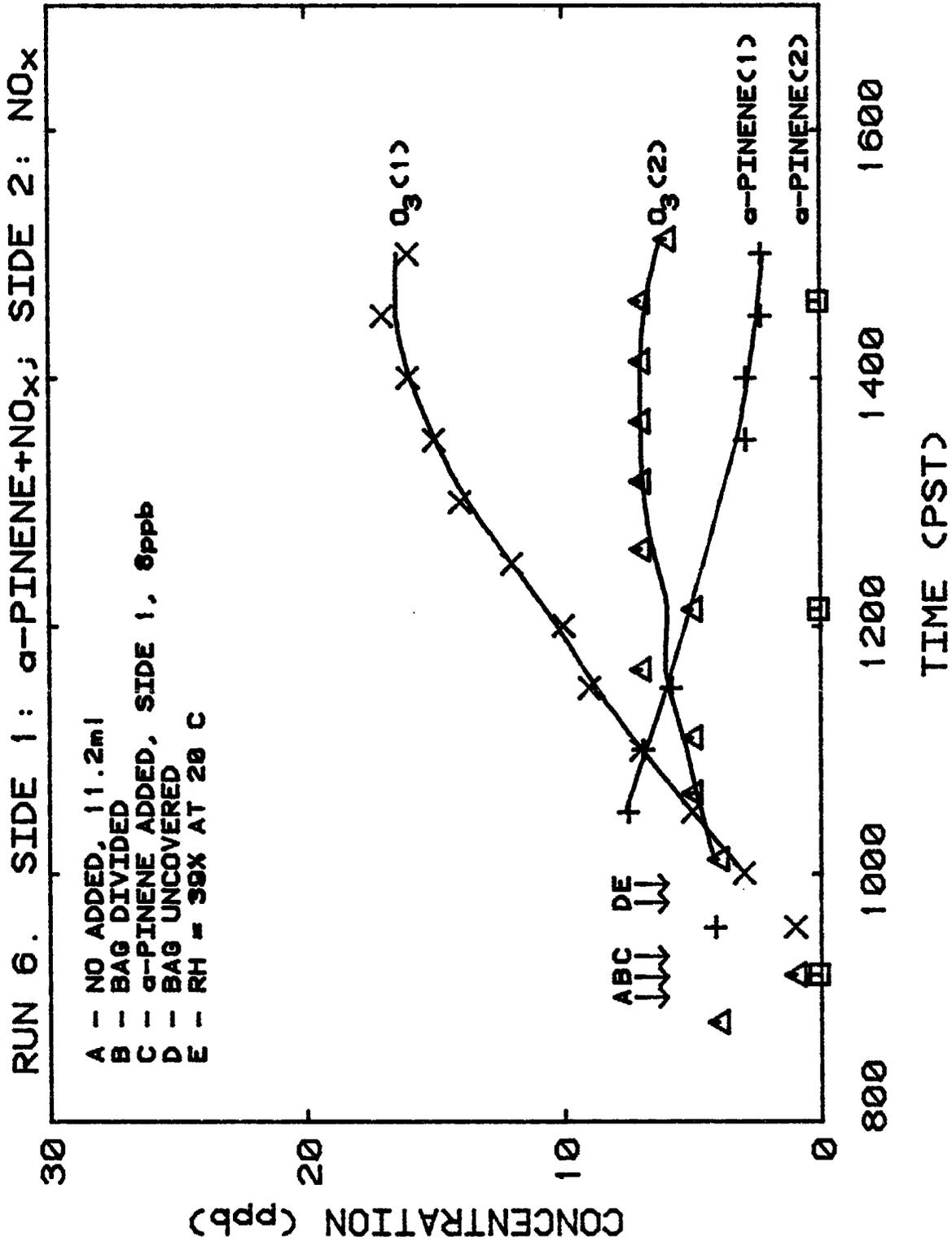


Figure 22. Concentration profiles for ozone and α -pinene in Run 6 of α -pinene photooxidation study.

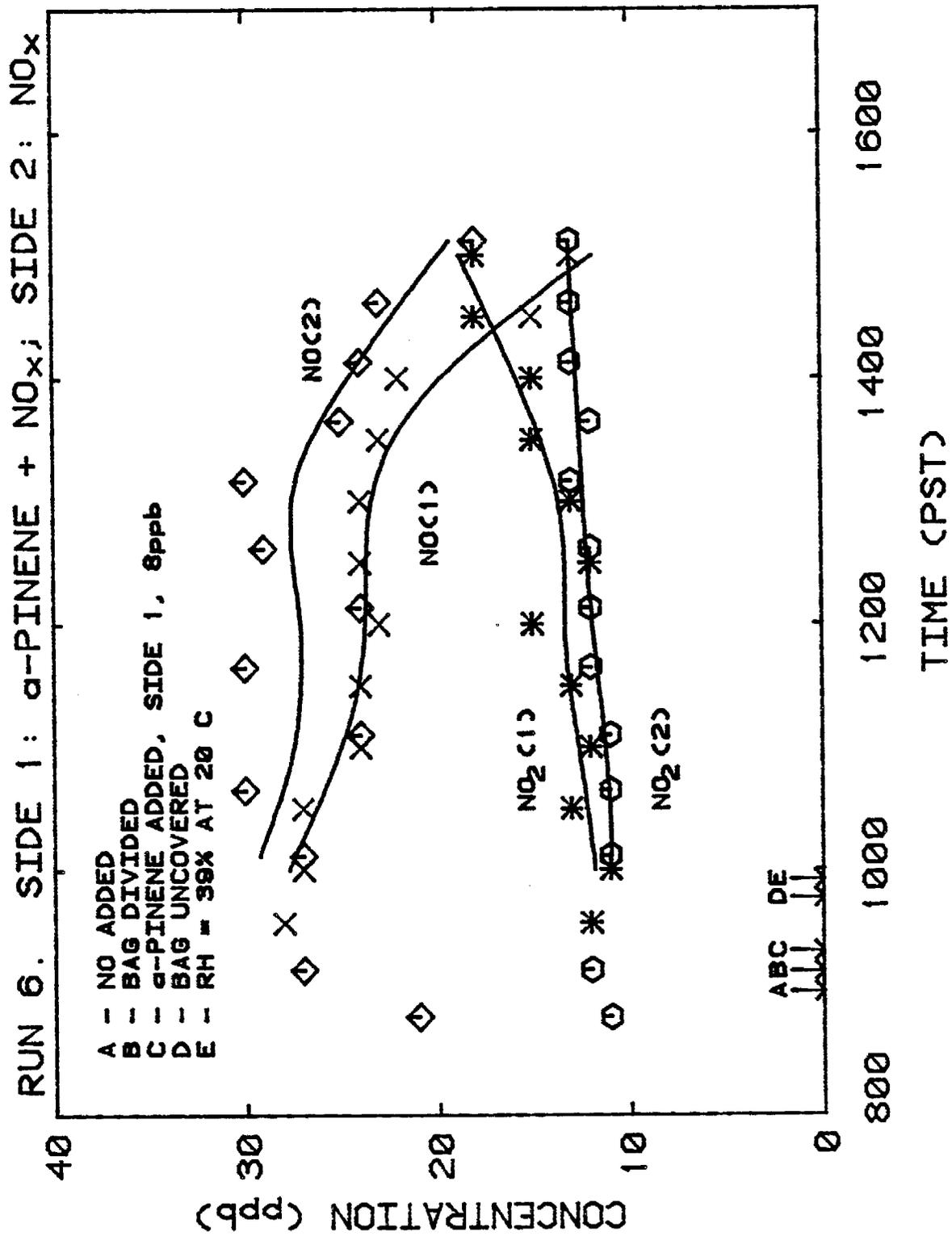


Figure 23. Concentration profiles for NO and NO₂ in Run 6 of α -pinene photooxidation study.

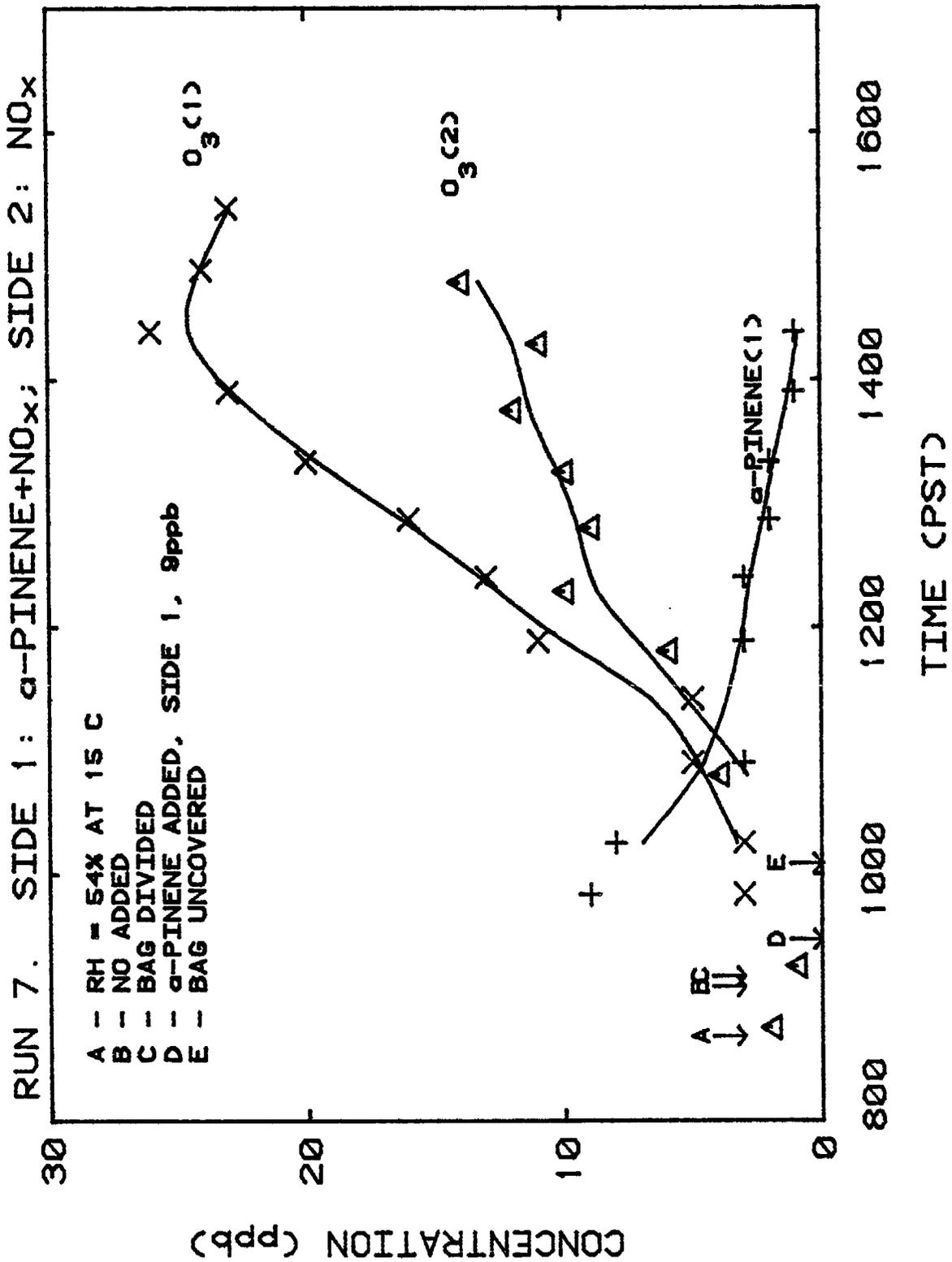


Figure 24. Concentration profiles for ozone and α -pinene in Run 7 of α -pinene photooxidation study.

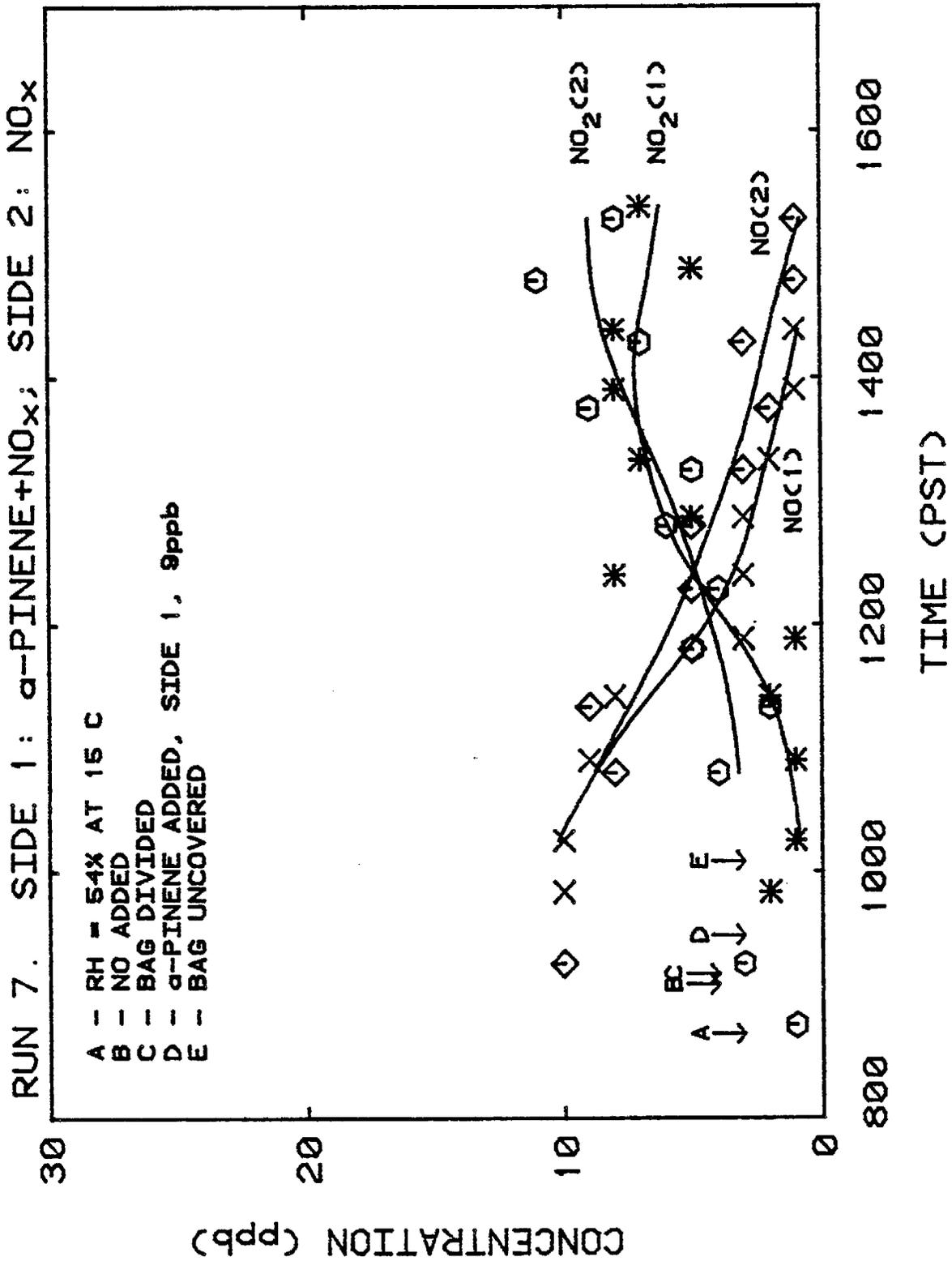


Figure 25. Concentration profiles for NO and NO₂ in Run 7 of α -pinene photooxidation study.

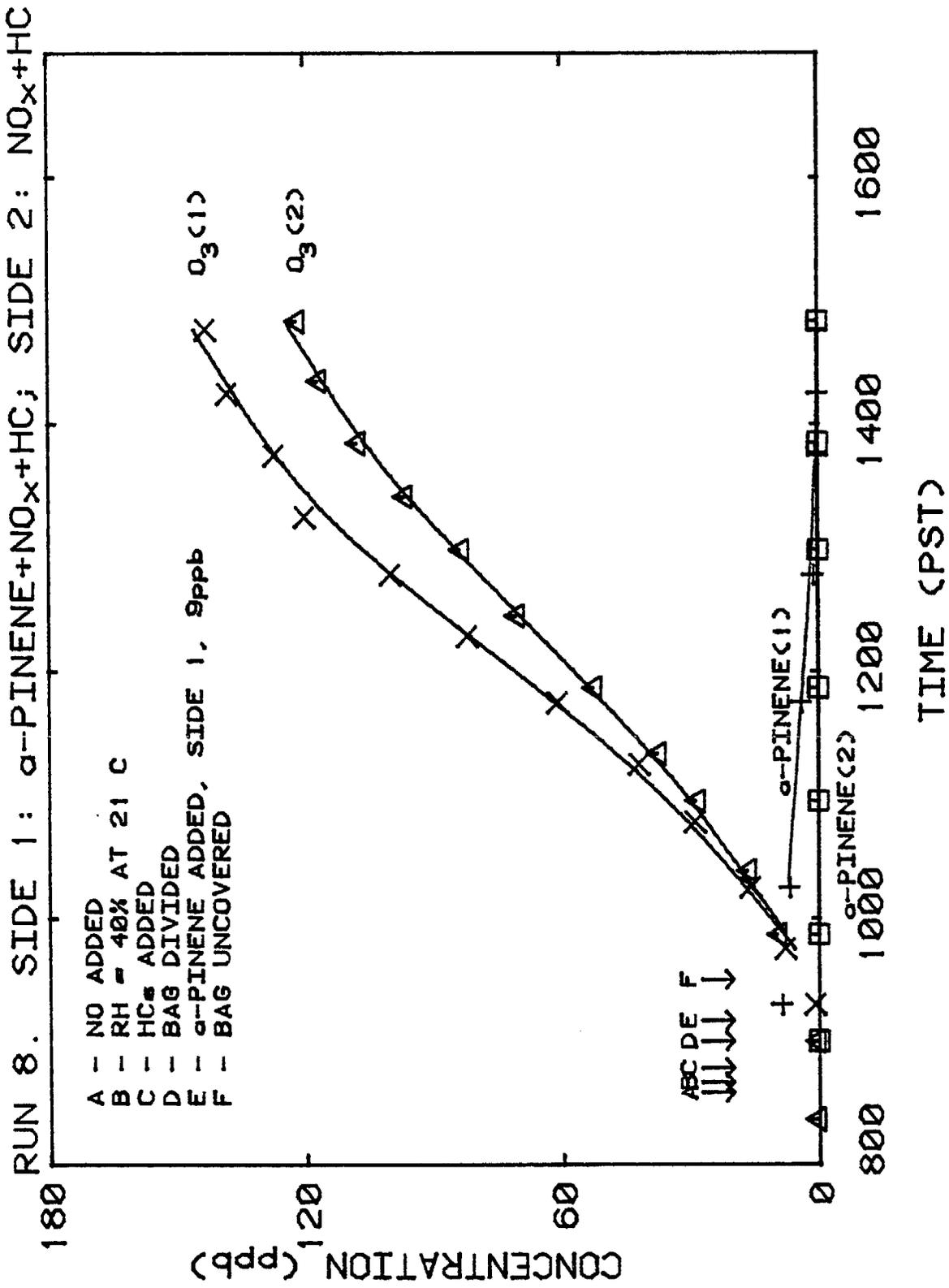


Figure 26. Concentration profiles for ozone and α -pinene in Run 8 of α -pinene photooxidation study.

RUN 8. SIDE 1: α -PINENE+NO_x+HC; SIDE 2: NO_x+HC

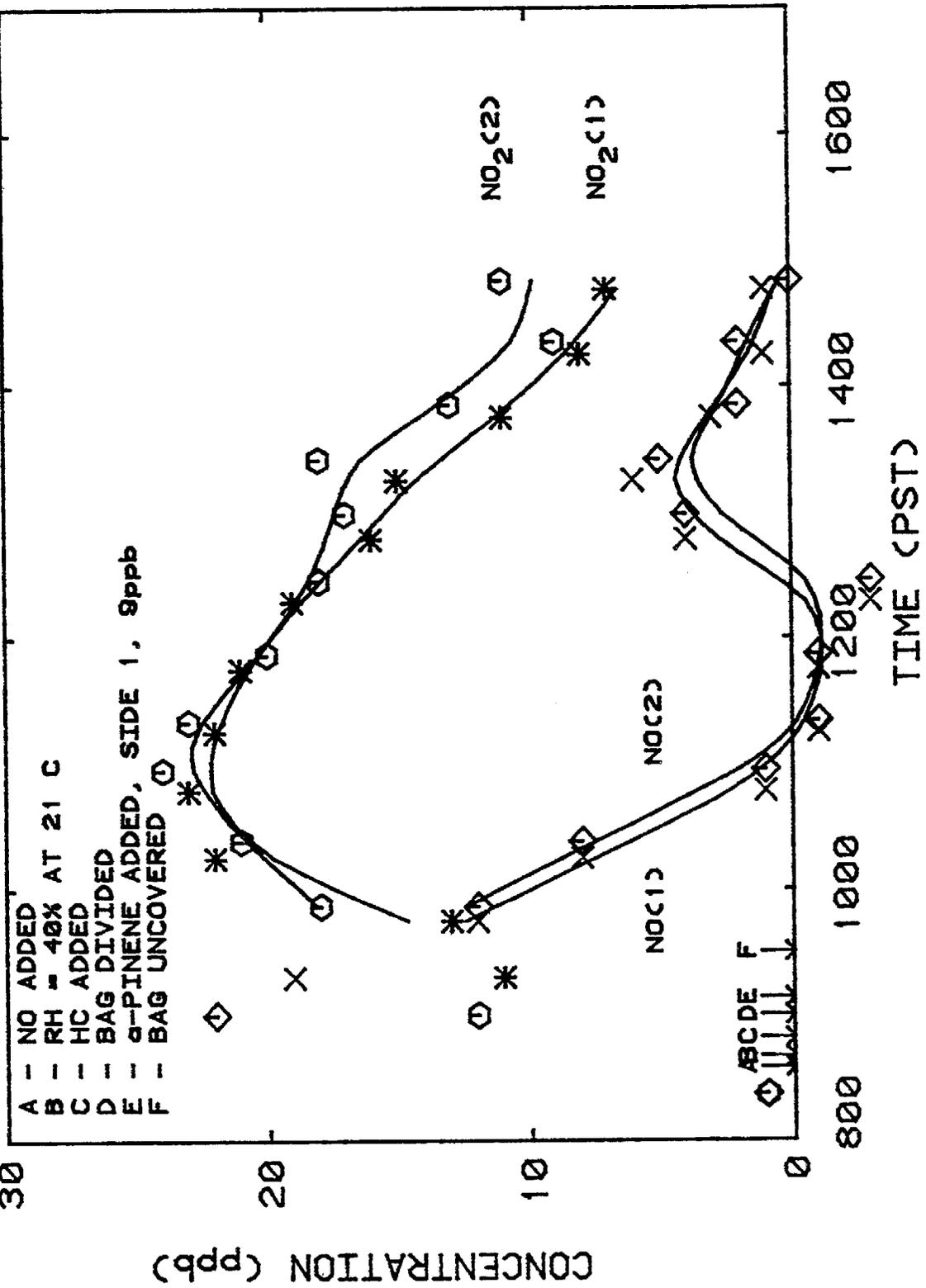


Figure 27. Concentration profiles for NO and NO₂ in Run 8 of α -pinene photooxidation study.

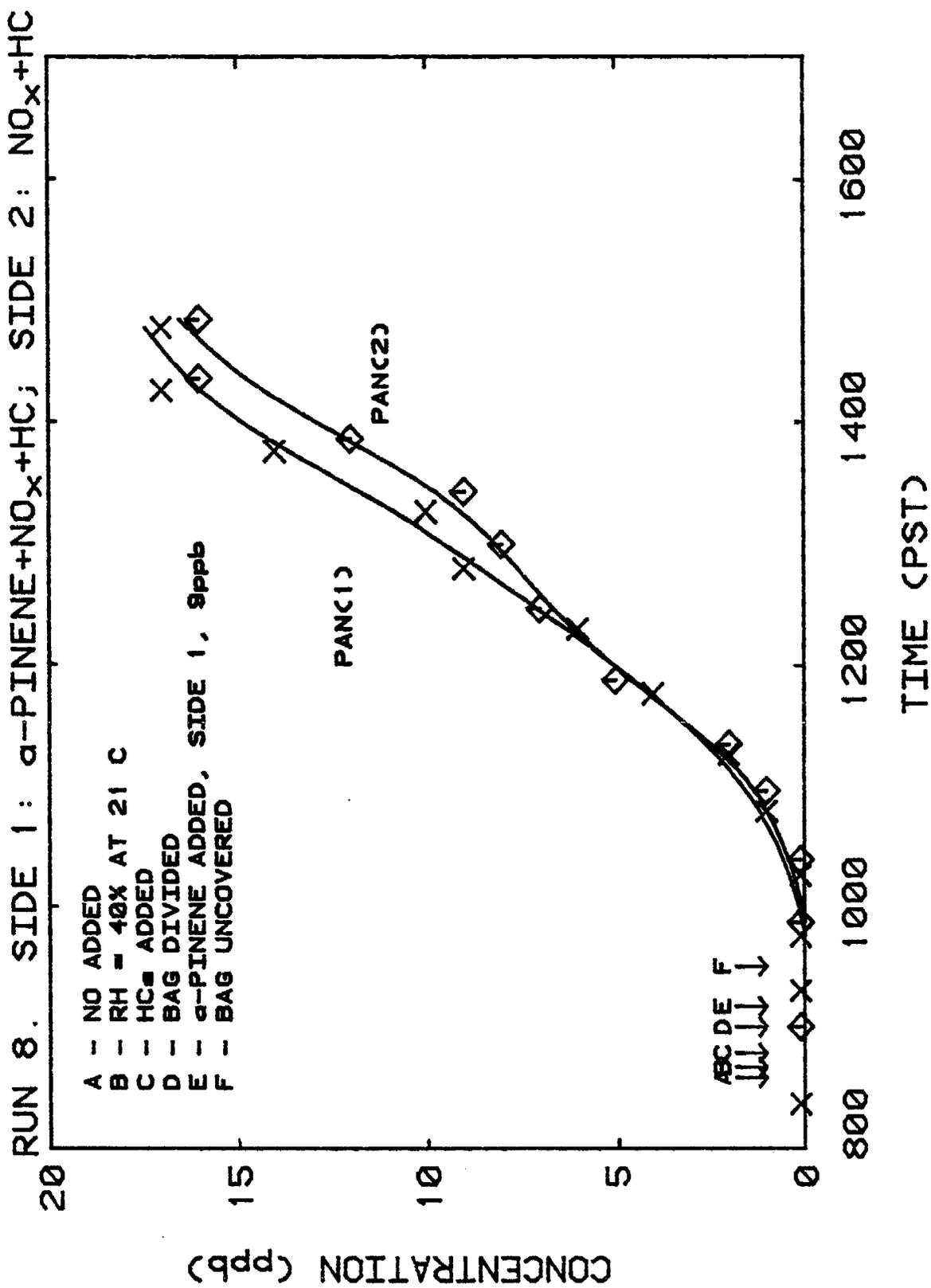


Figure 28. Concentration profiles for PAN in Run 8 of α -pinene photooxidation study.

RUN 9. SIDE 2: α -PINENE+NO_x+HC; SIDE 1: NO_x+HC

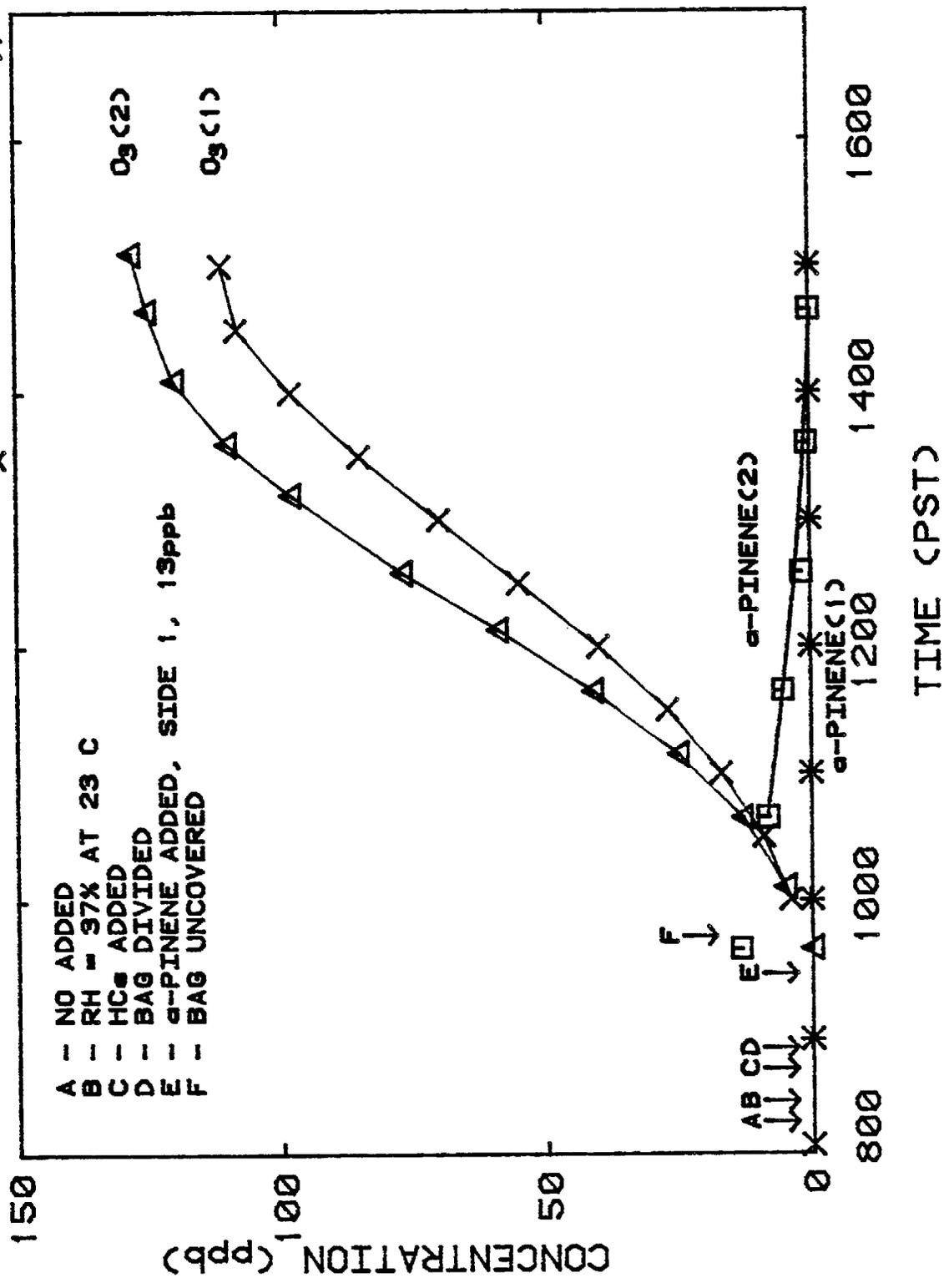


Figure 29. Concentration profiles for ozone and α -pinene in Run 9 of α -pinene photooxidation study.

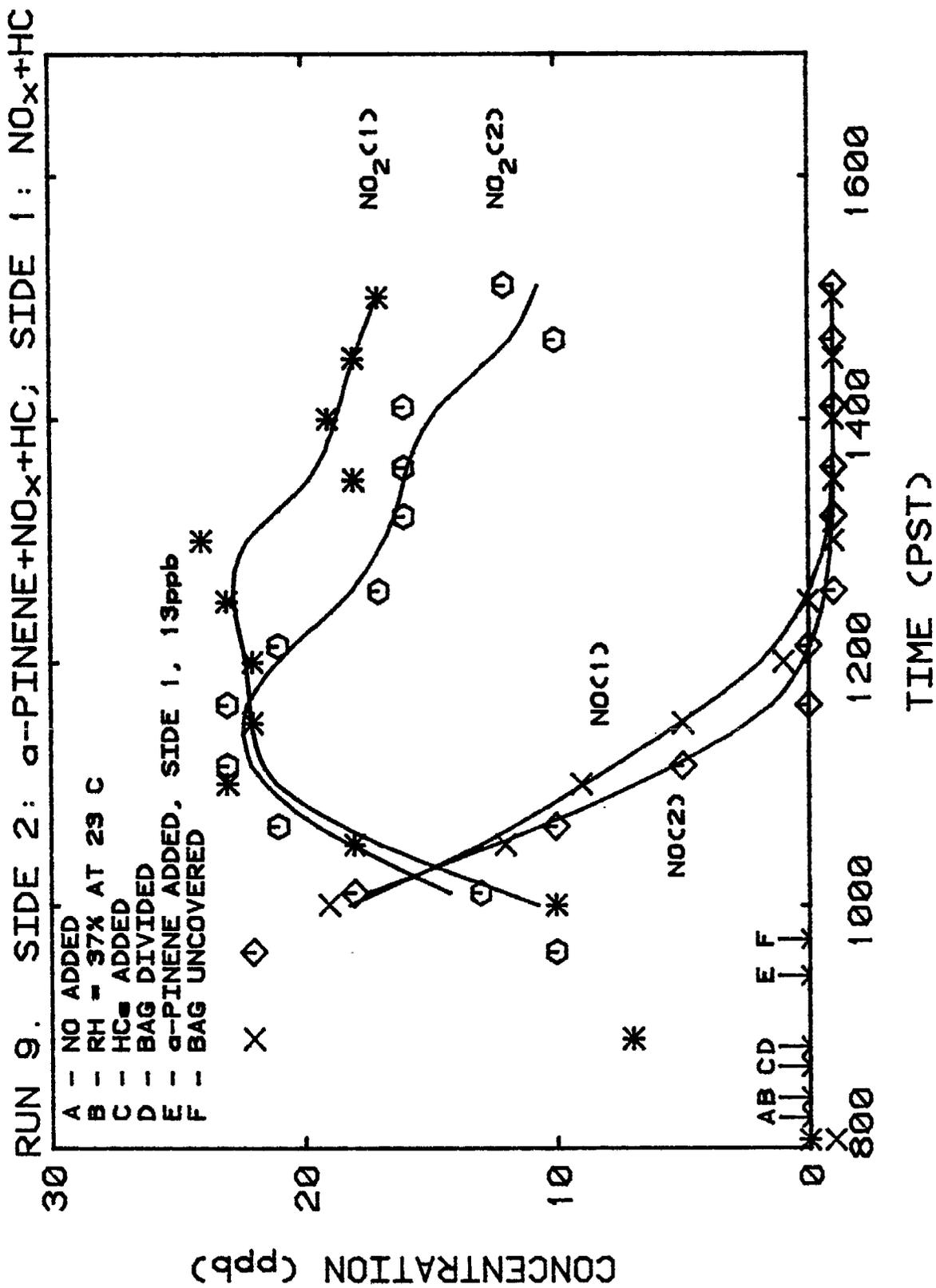


Figure 30. Concentration profiles for NO and NO₂ in Run 9 of α -pinene photooxidation study.

RUN 9. SIDE 2: α -PINENE+NO_x+HC; SIDE 1: NO_x+HC

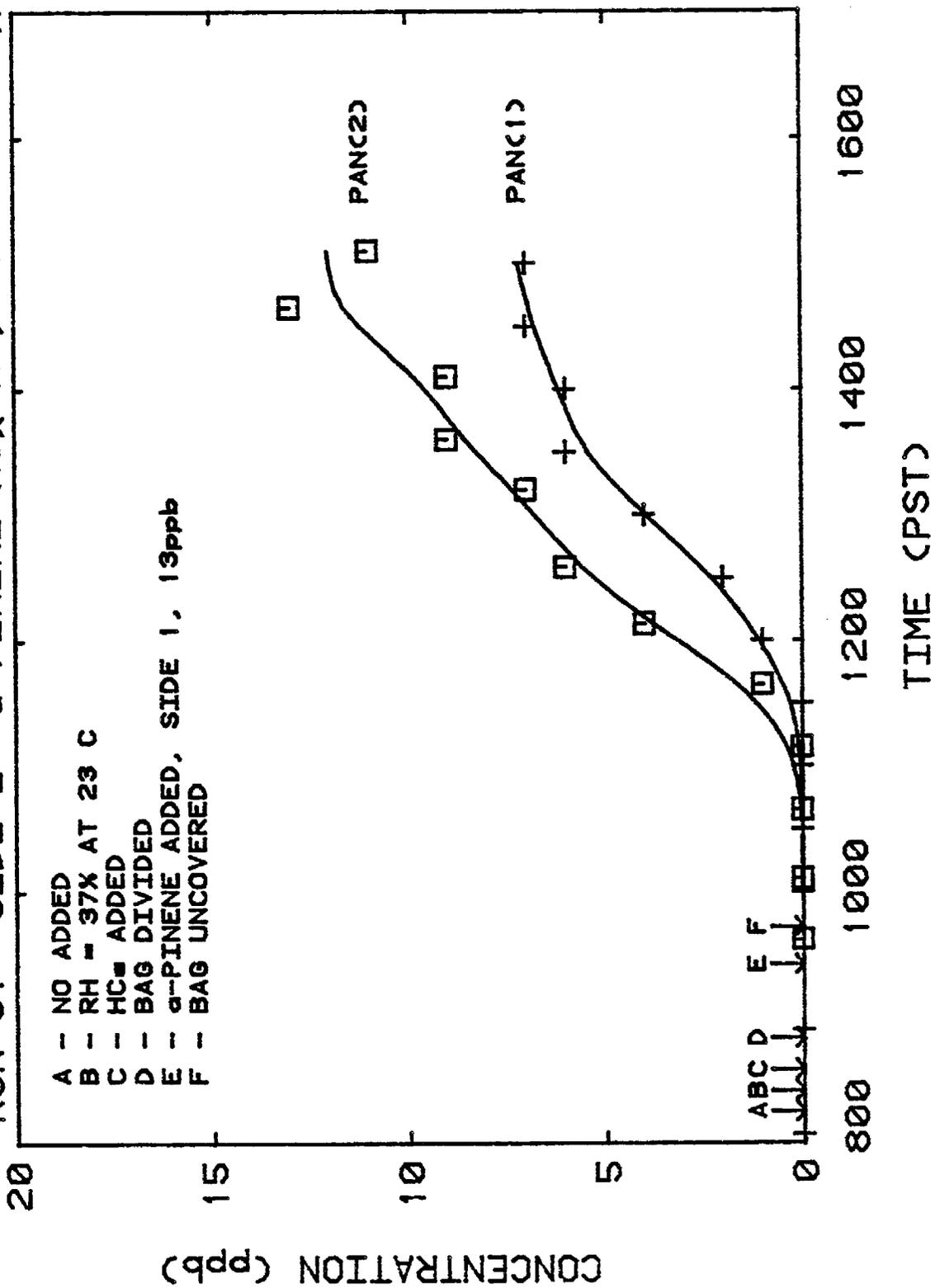


Figure 31. Concentration profiles for PAN in Run 9 of α -pinene photooxidation study.

RUN 10. SIDE 2: α -PINENE+NO_x+HC; SIDE 1: NO_x+HC

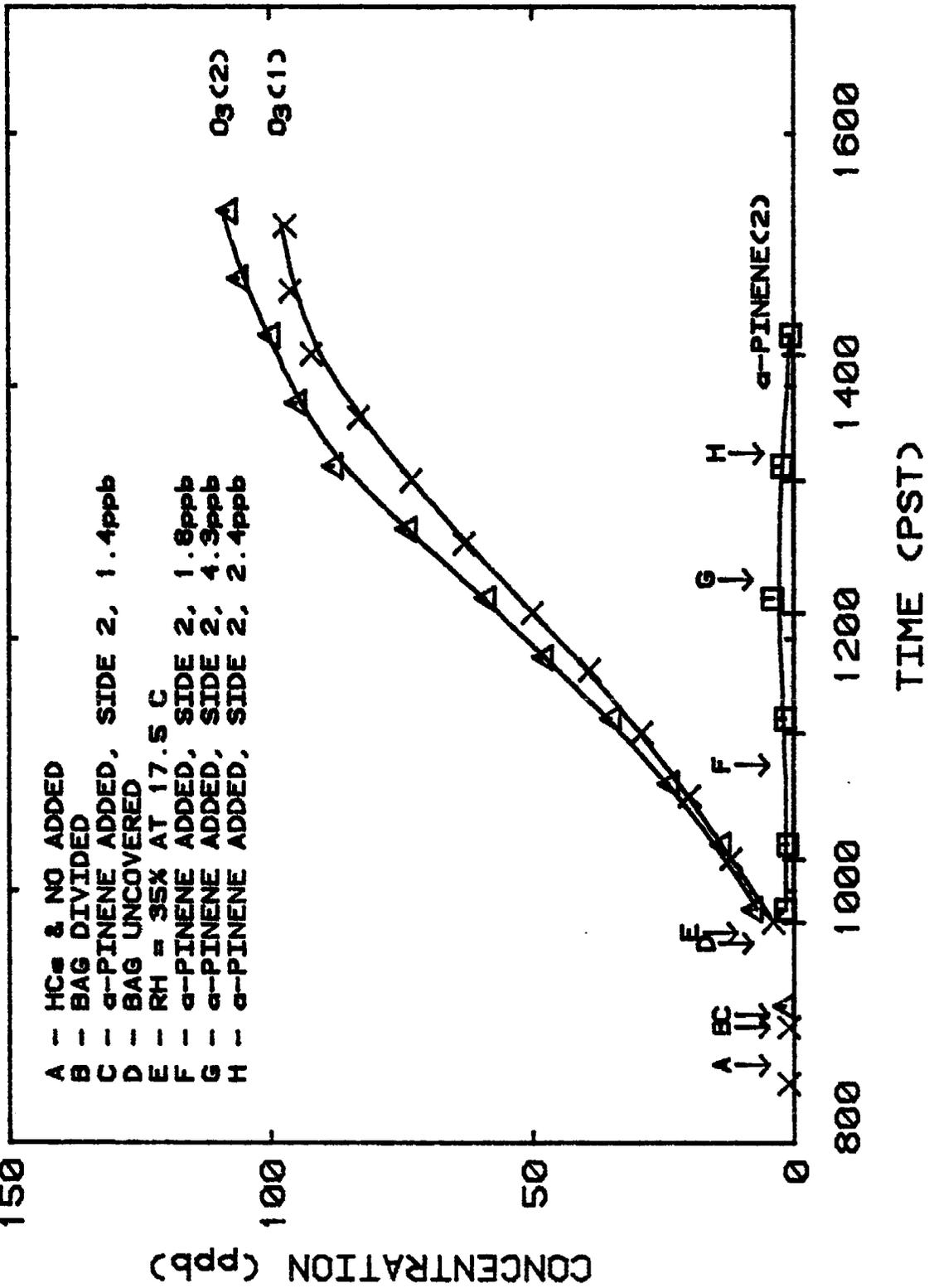


Figure 32. Concentration profiles for ozone and α -pinene in Run 10 of α -pinene photooxidation study.

RUN 10. SIDE 1: α -PINENE + NO_x + HC;
 SIDE 2: NO_x + HC

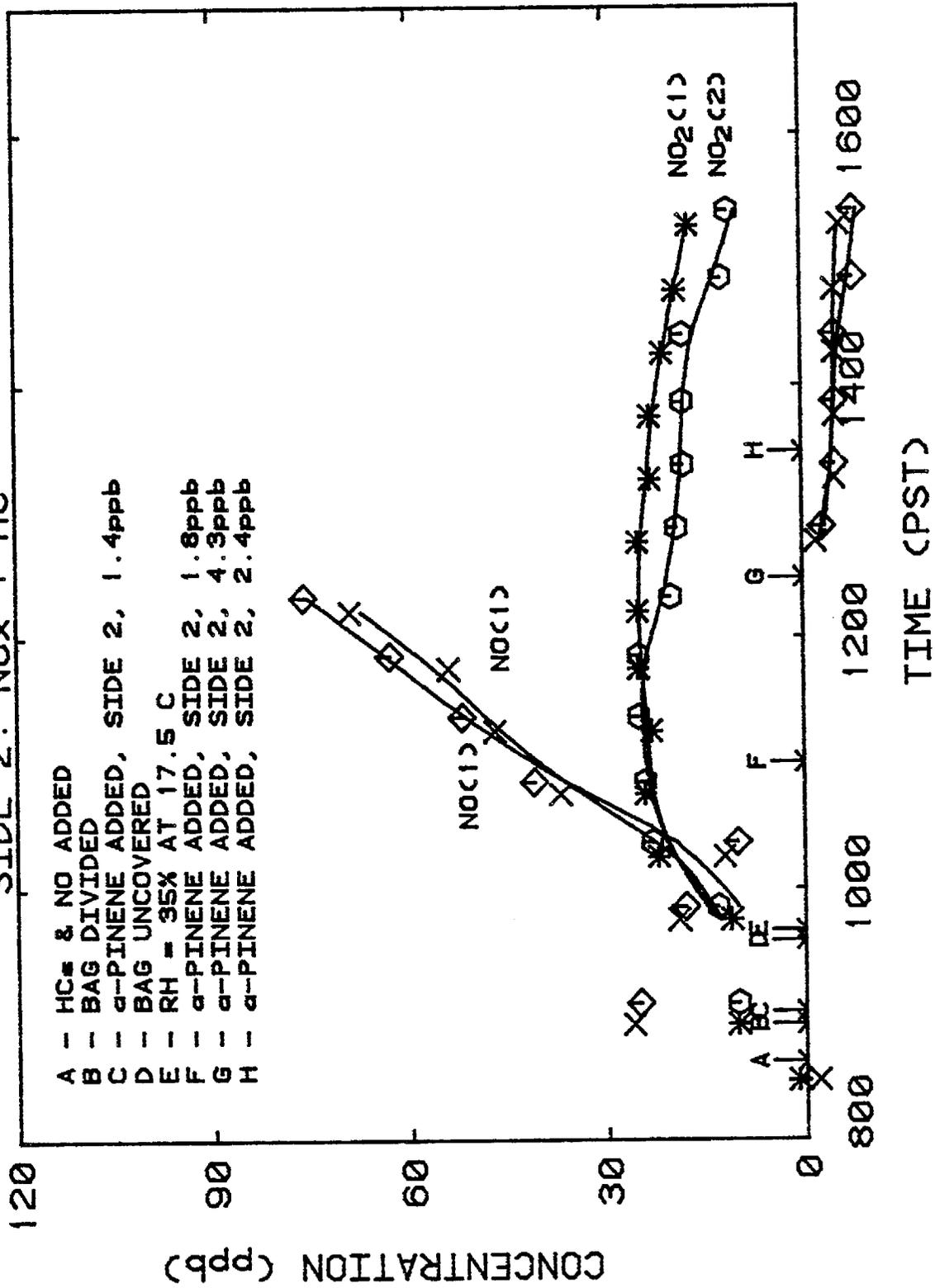


Figure 33. Concentration profiles for NO and NO₂ in Run 10 of α -pinene photooxidation study.

RUN 10. SIDE 1: α -PINENE + NO_x + HC;
 SIDE 2: α -PINENE + NO_x + HC

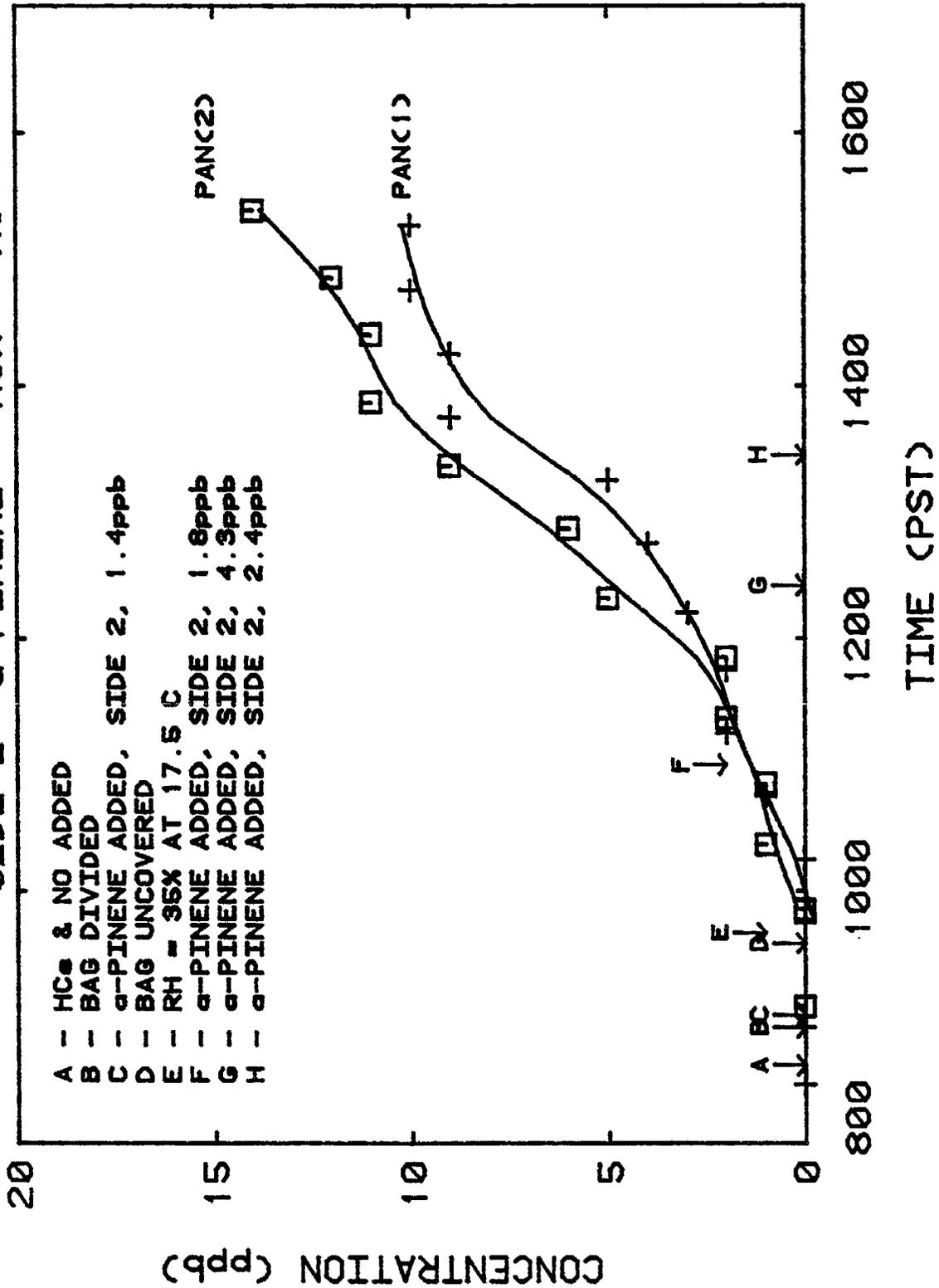


Figure 34. Concentration profiles for PAN in Run 10 of α -pinene photooxidation study.

RUN 11. SIDE 1: SURROGATE + NOx;
 SIDE 2: SURROGATE + NOx

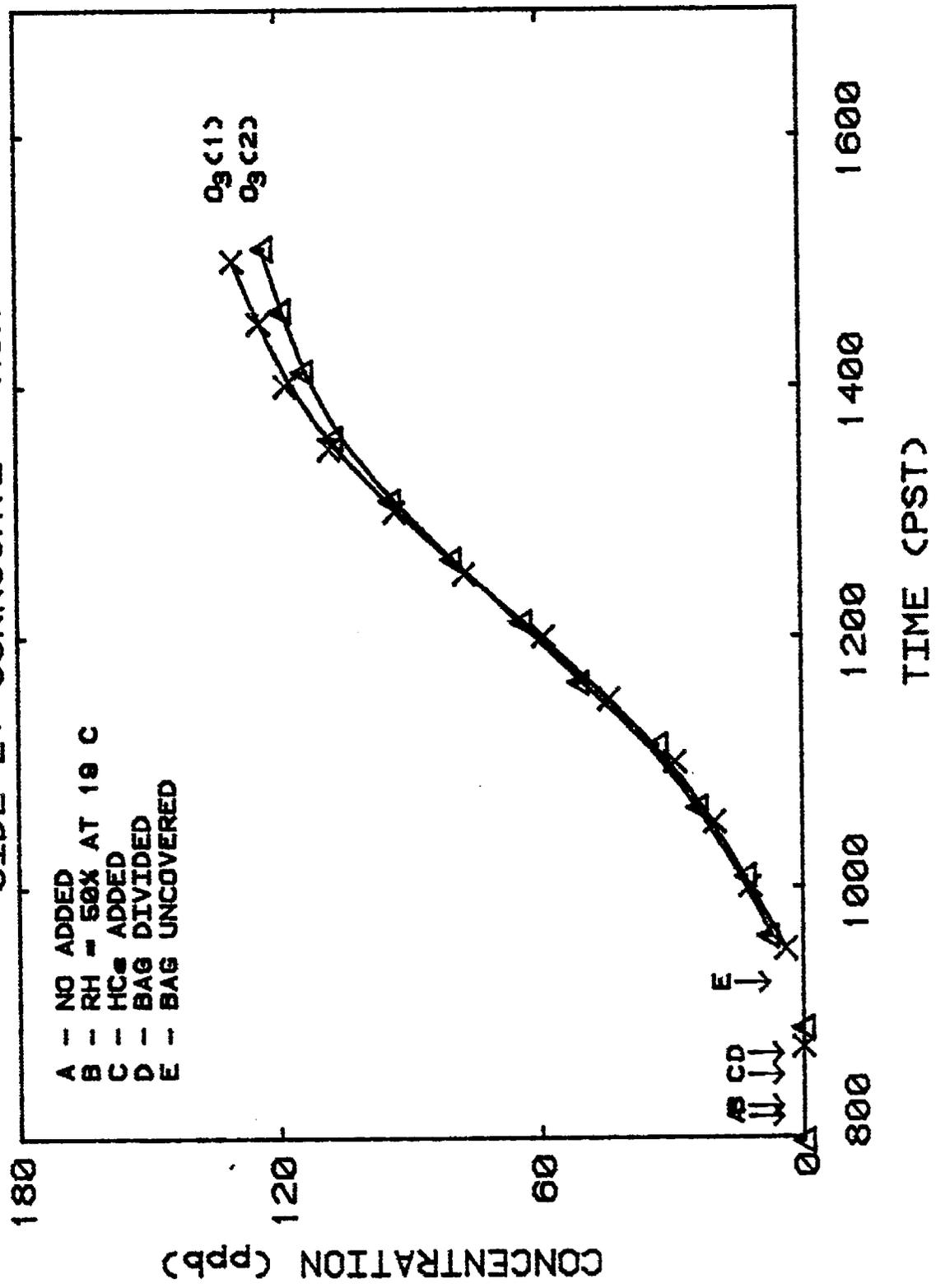


Figure 35. Concentration profiles for ozone in Run 11 of α -pinene photooxidation study.

RUN 11. SIDE 1: SURROGATE + NOx;
SIDE 2: SURROGATE + NOx

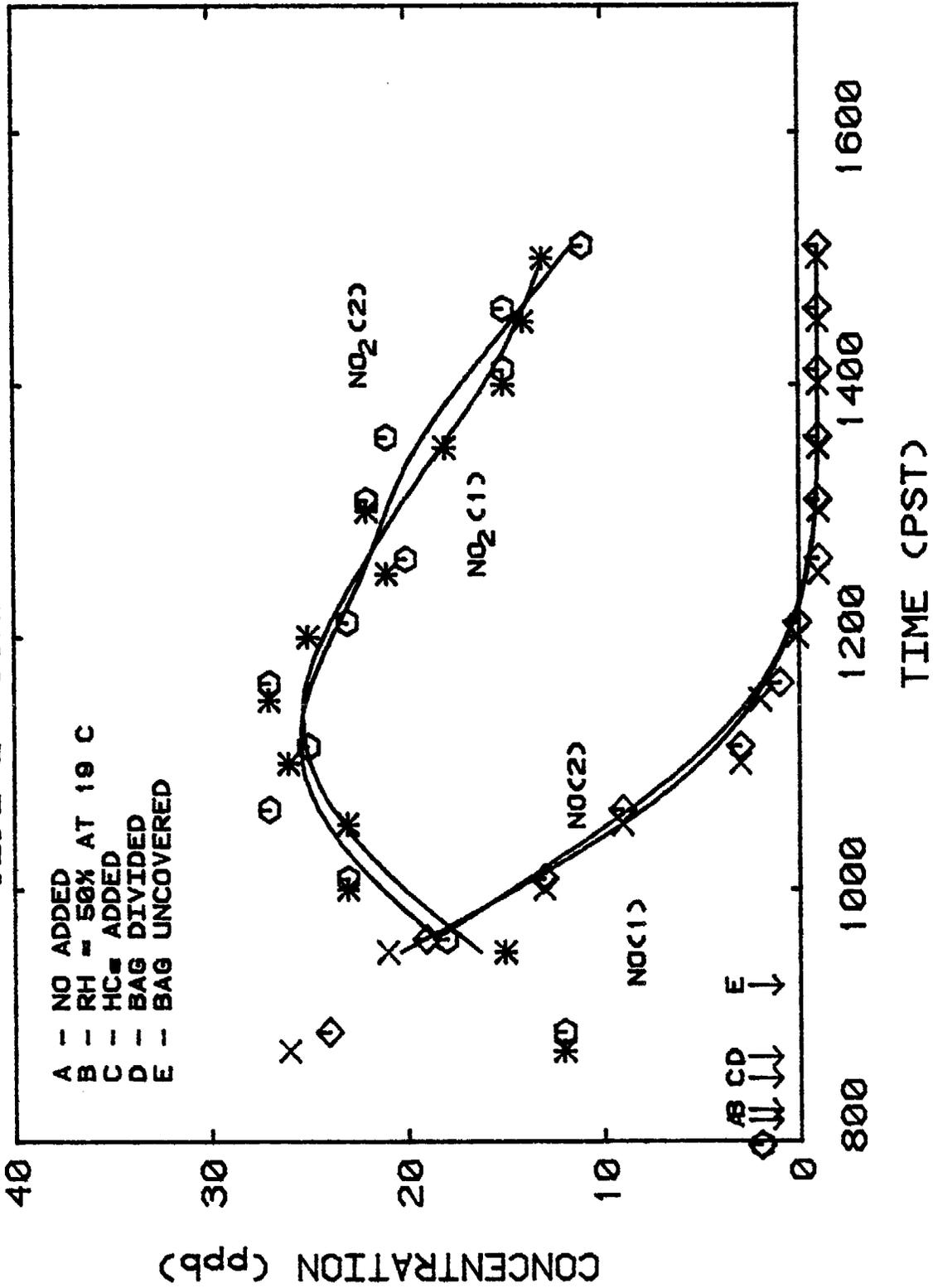


Figure 36. Concentration profiles for NO and NO₂ in Run 11 of α-pinene photooxidation study.

RUN 12. SIDE 2: α -PINENE + NO_x + SURR HC;
 SIDE 1: NO_x + SURR HC

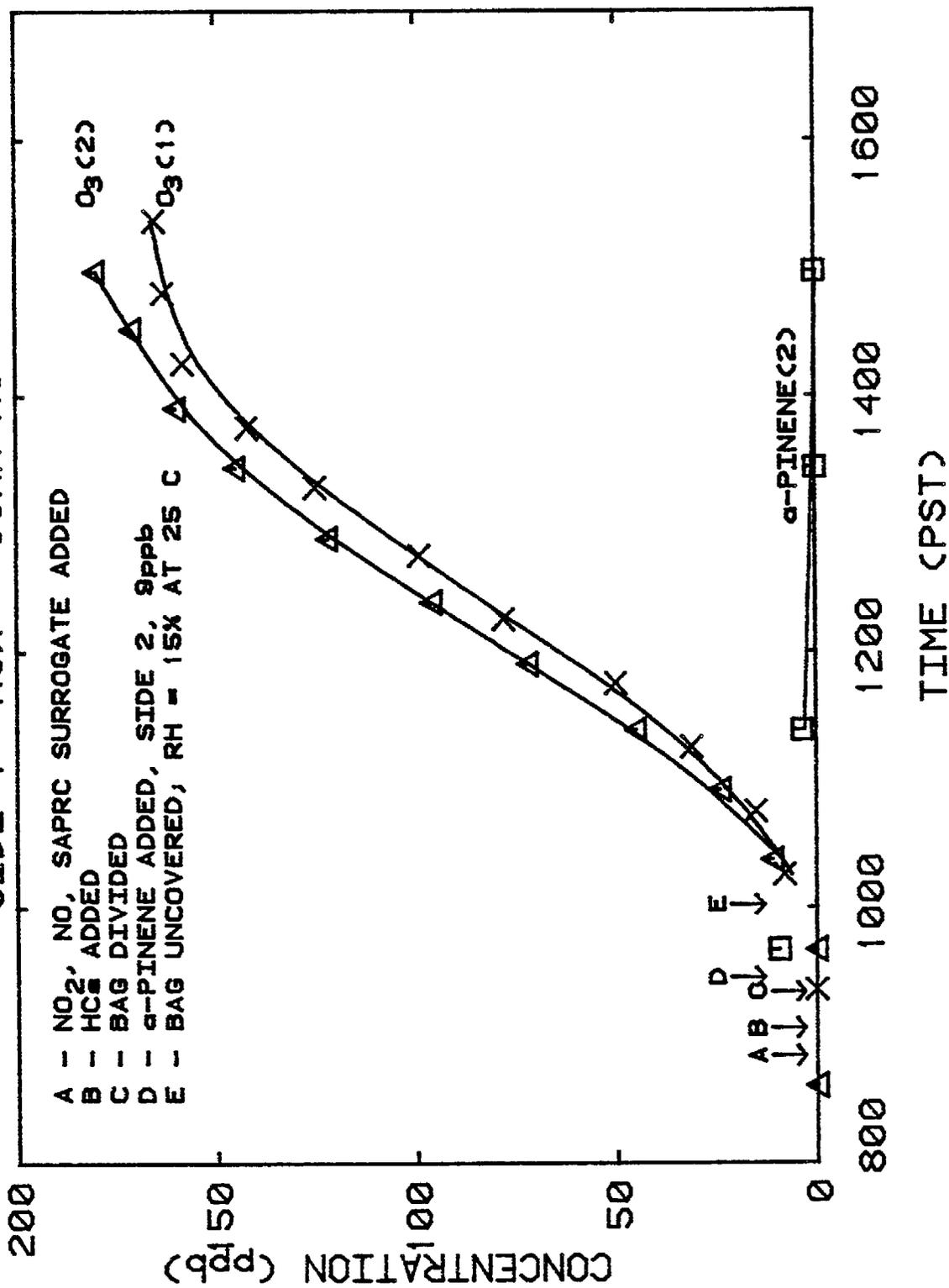


Figure 37. Concentration profiles for ozone and α -pinene in Run 12 of α -pinene photooxidation study.

RUN 12. SIDE 2: α -PINENE + NO_x + SURR HC;
 SIDE 1: NO_x + SURR HC

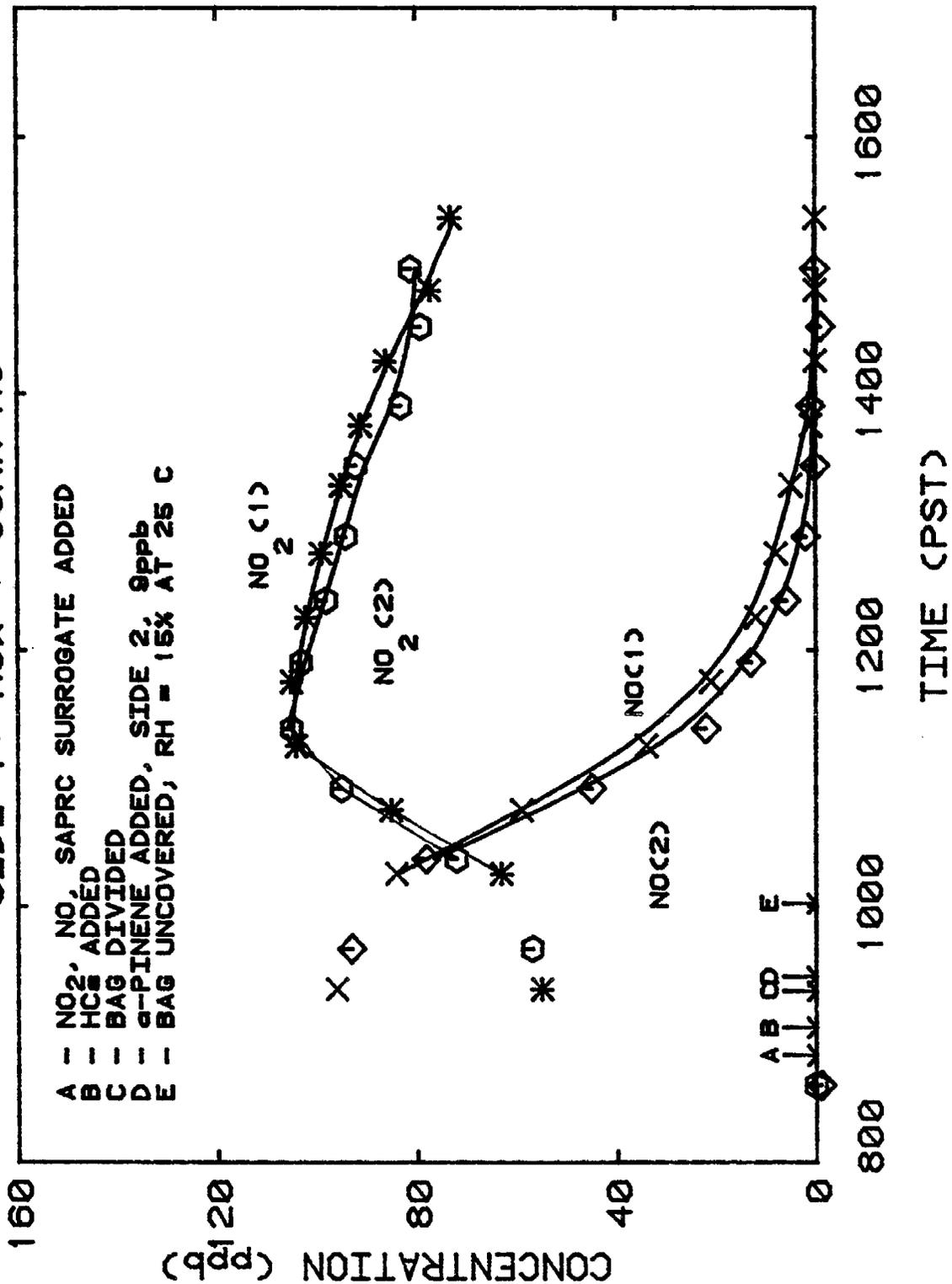


Figure 38. Concentration profiles for NO and NO₂ in Run 12 of α -pinene photooxidation study.

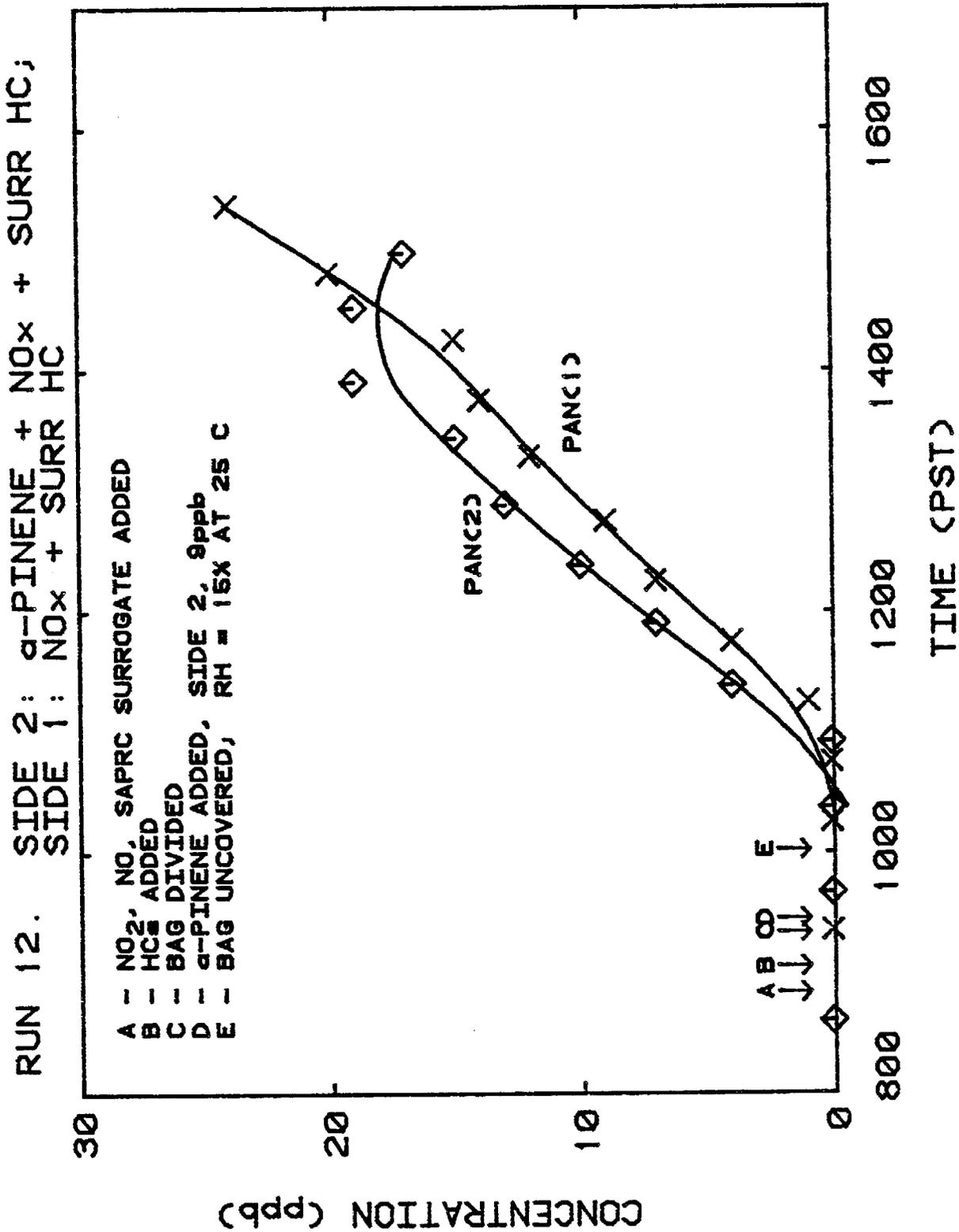


Figure 39. Concentration profiles for PAN in Run 12 of α -pinene photooxidation study.

**RUN 13. SIDE 2: α -PINENE + NO_x + AMBIENT AIR;
SIDE 1: NO_x + AMBIENT AIR**

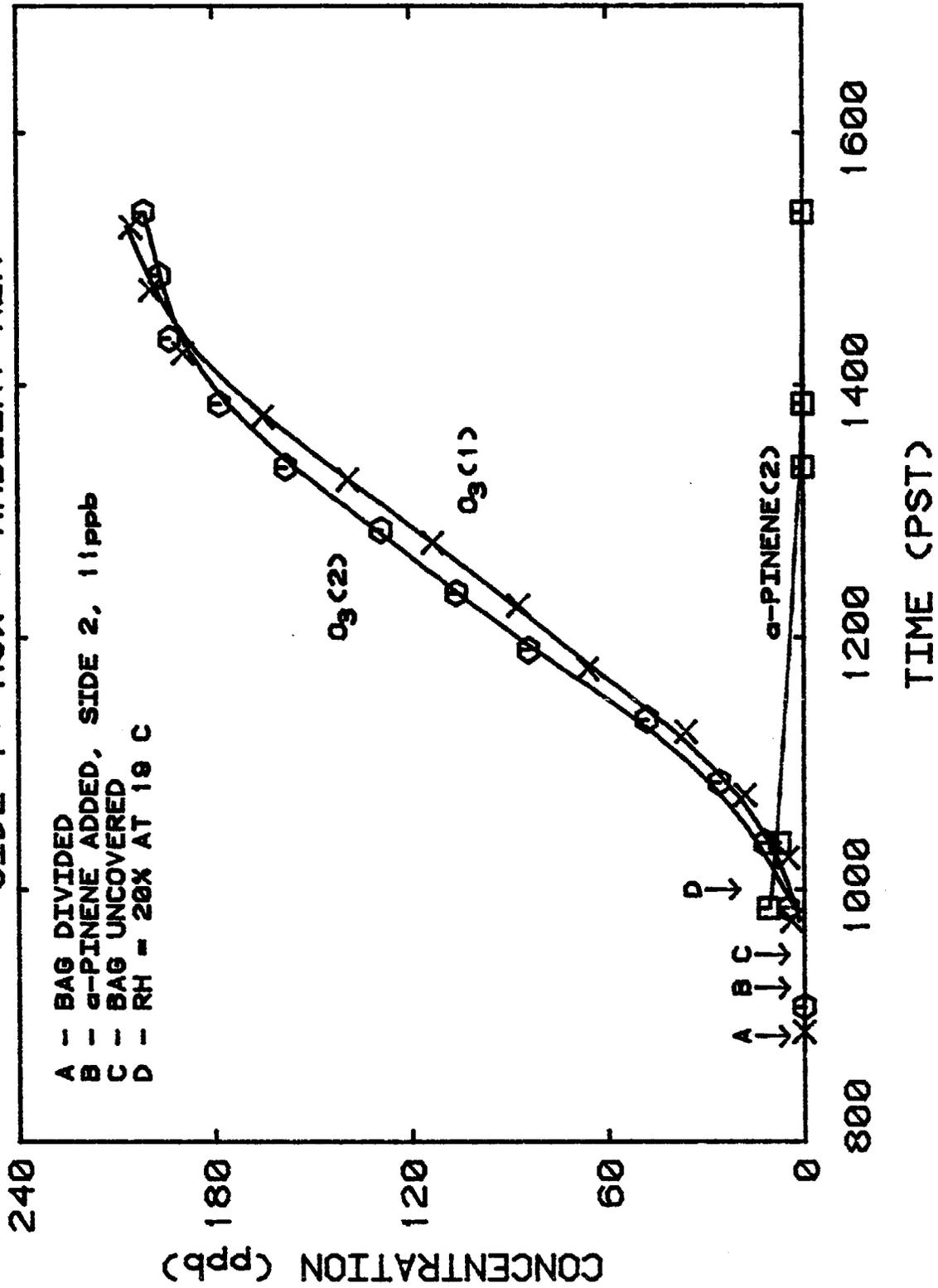


Figure 40. Concentration profiles for ozone and α -pinene in Run 13 of α -pinene photooxidation study.

RUN 13. SIDE 2: α -PINENE + NO_x + AMBIENT AIR;
 SIDE 1: NO_x + AMBIENT AIR

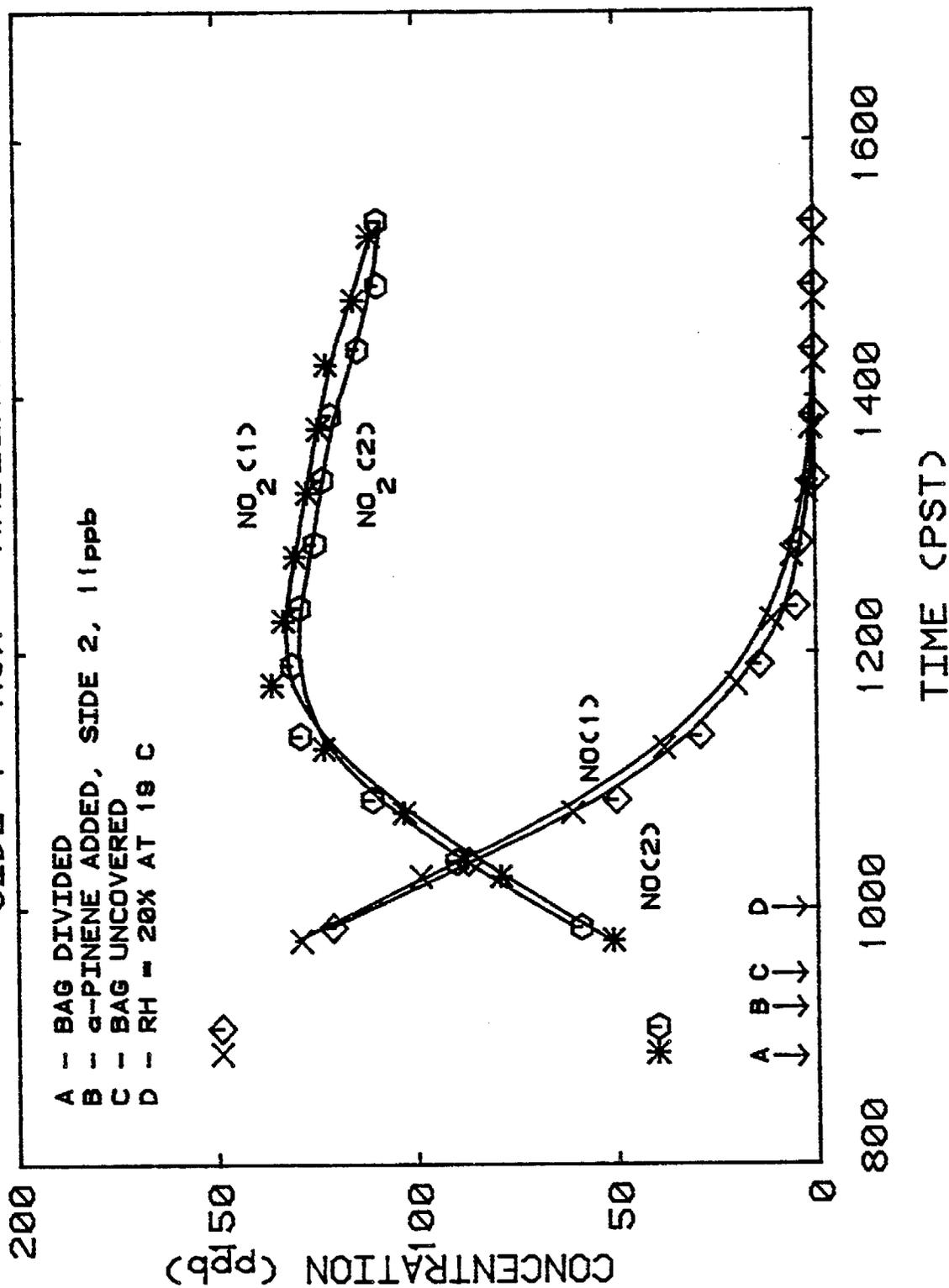


Figure 41. Concentration profiles for NO and NO₂ in Run 13 of α -pinene photooxidation study.

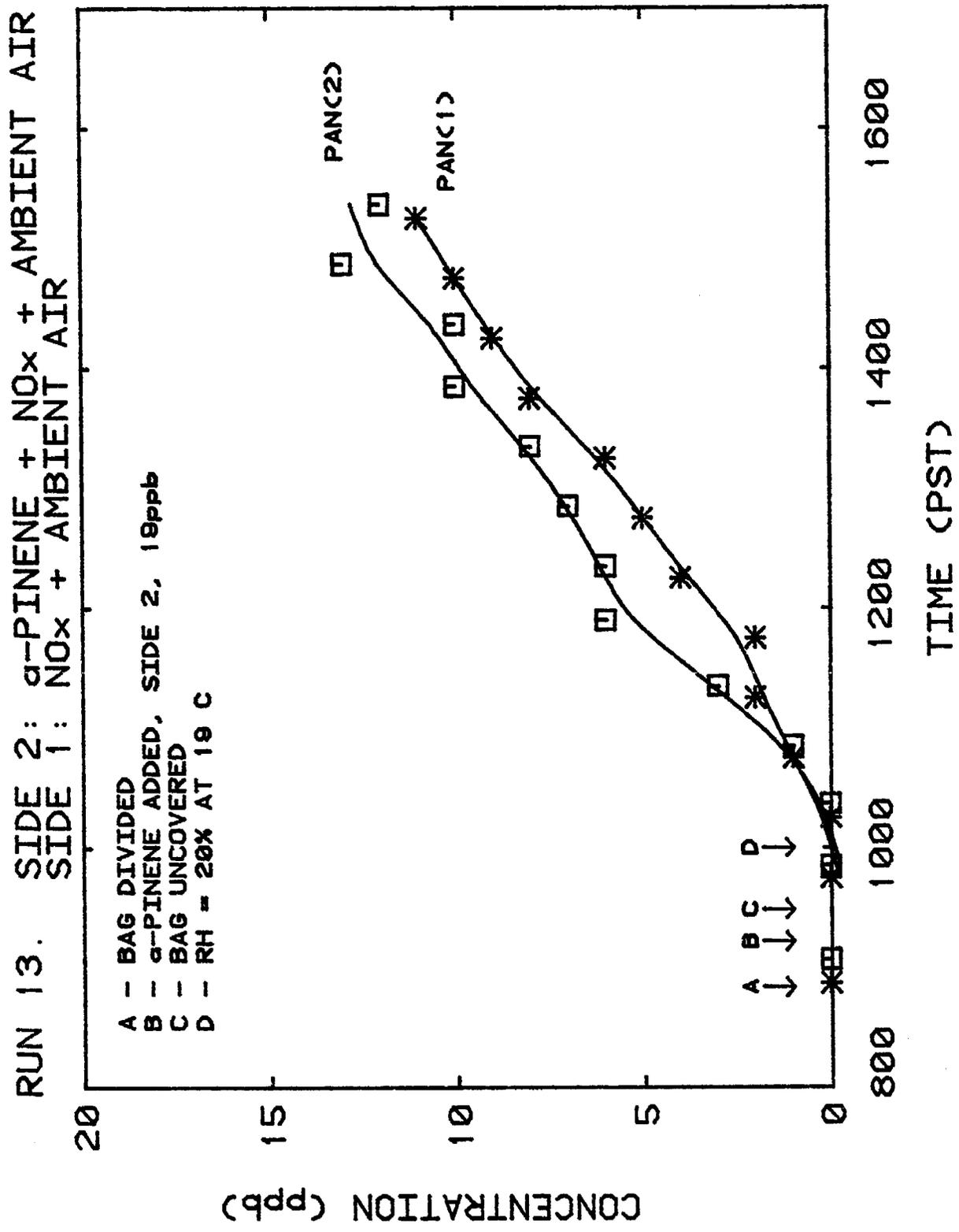


Figure 42. Concentration profiles for PAN in Run 13 of α -pinene photooxidation study.

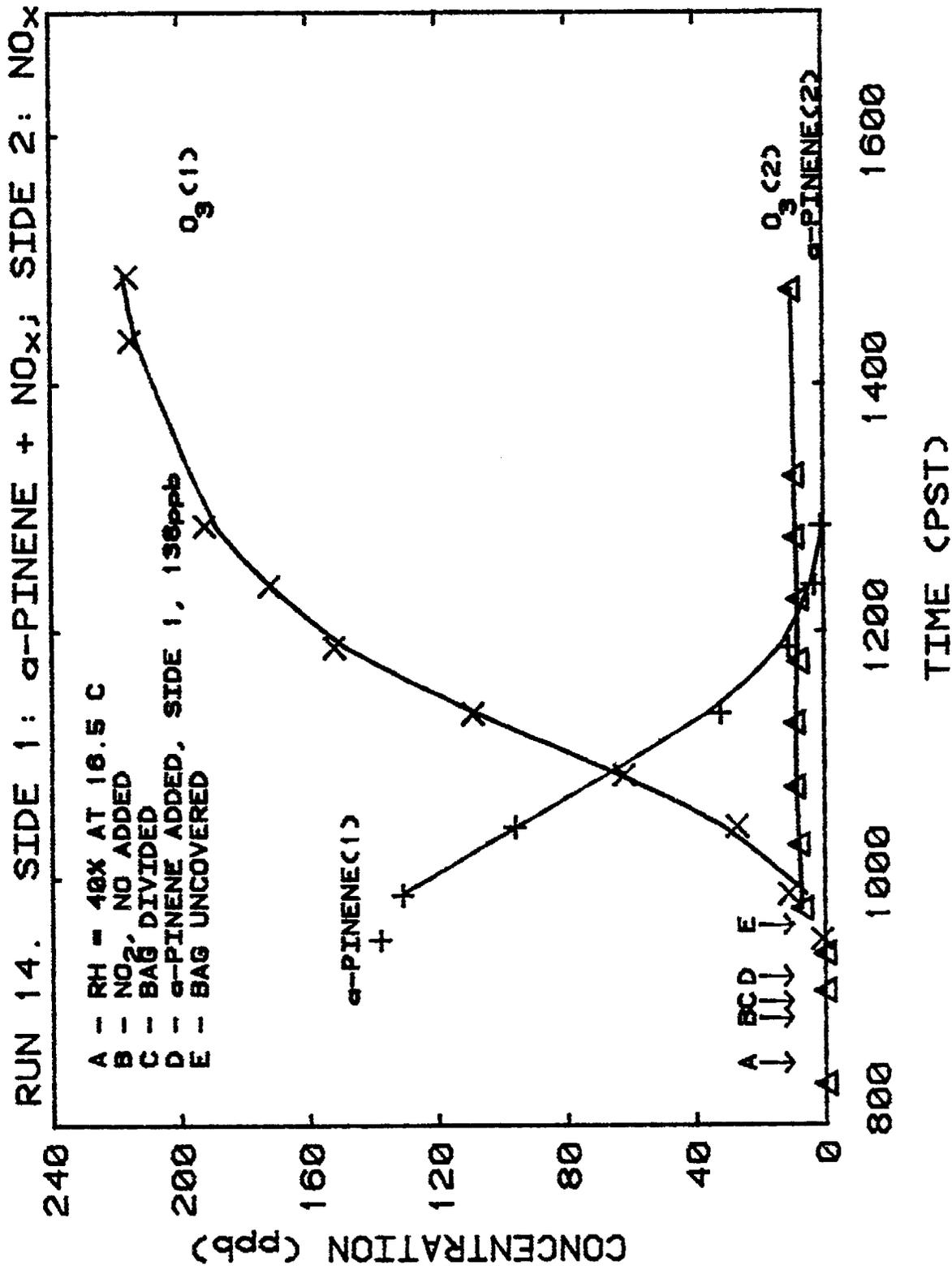


Figure 43. Concentration profiles for ozone and α -pinene in Run 14 of α -pinene photooxidation study.

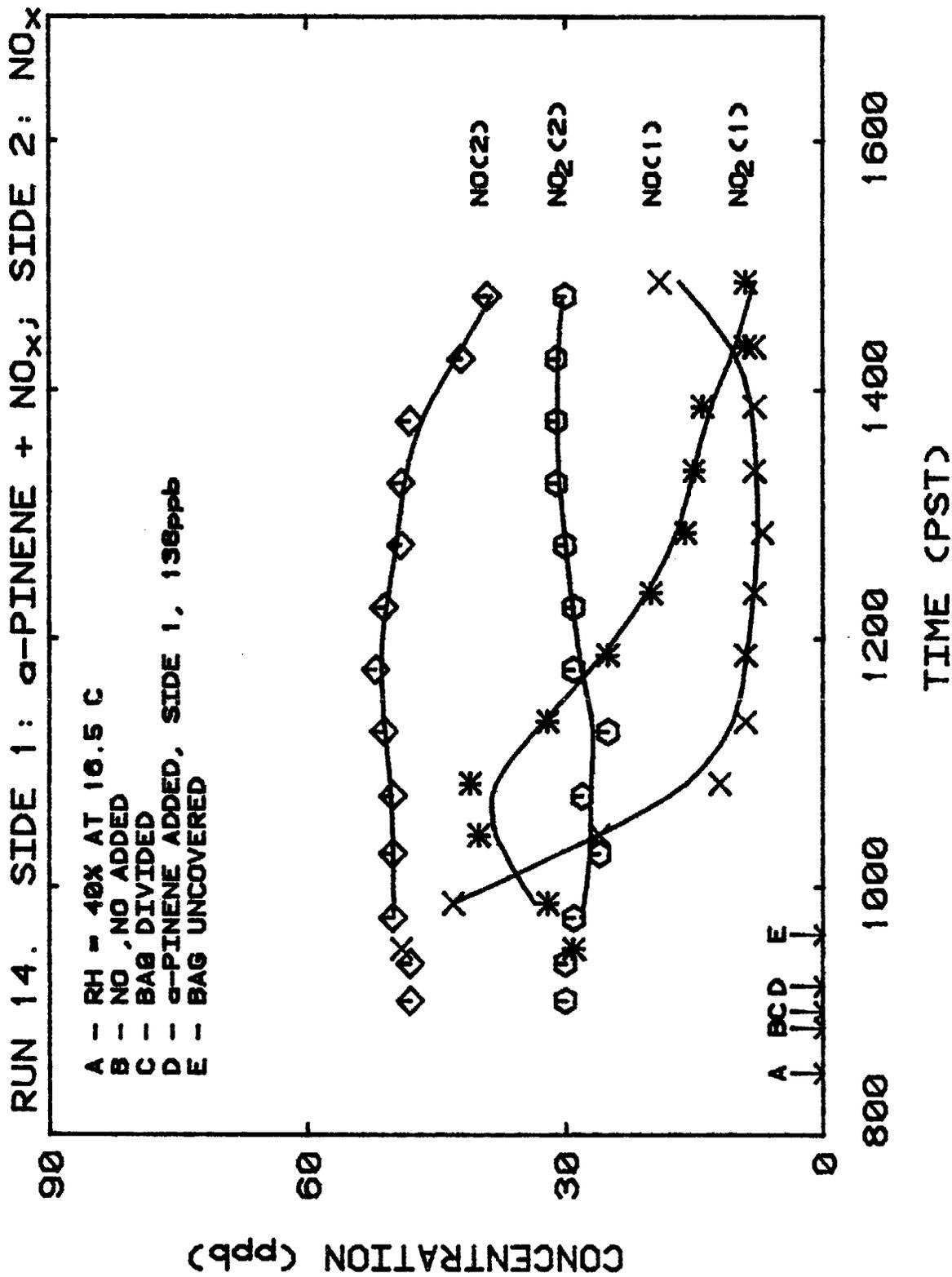


Figure 44. Concentration profiles for NO and NO₂ in Run 14 of α -pinene photooxidation study.

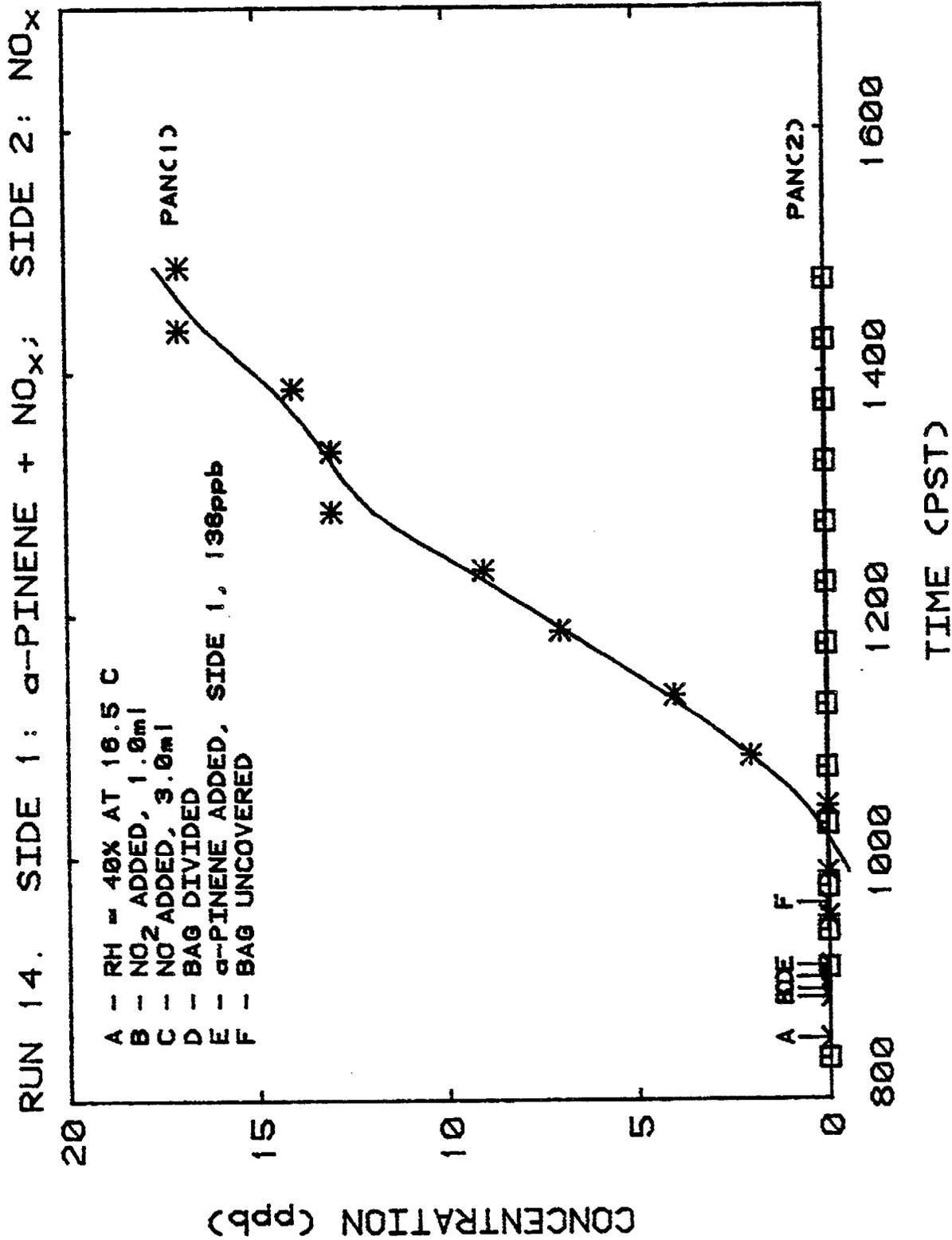


Figure 45. Concentration profiles for PAN in Run 14 of α -pinene photooxidation study.

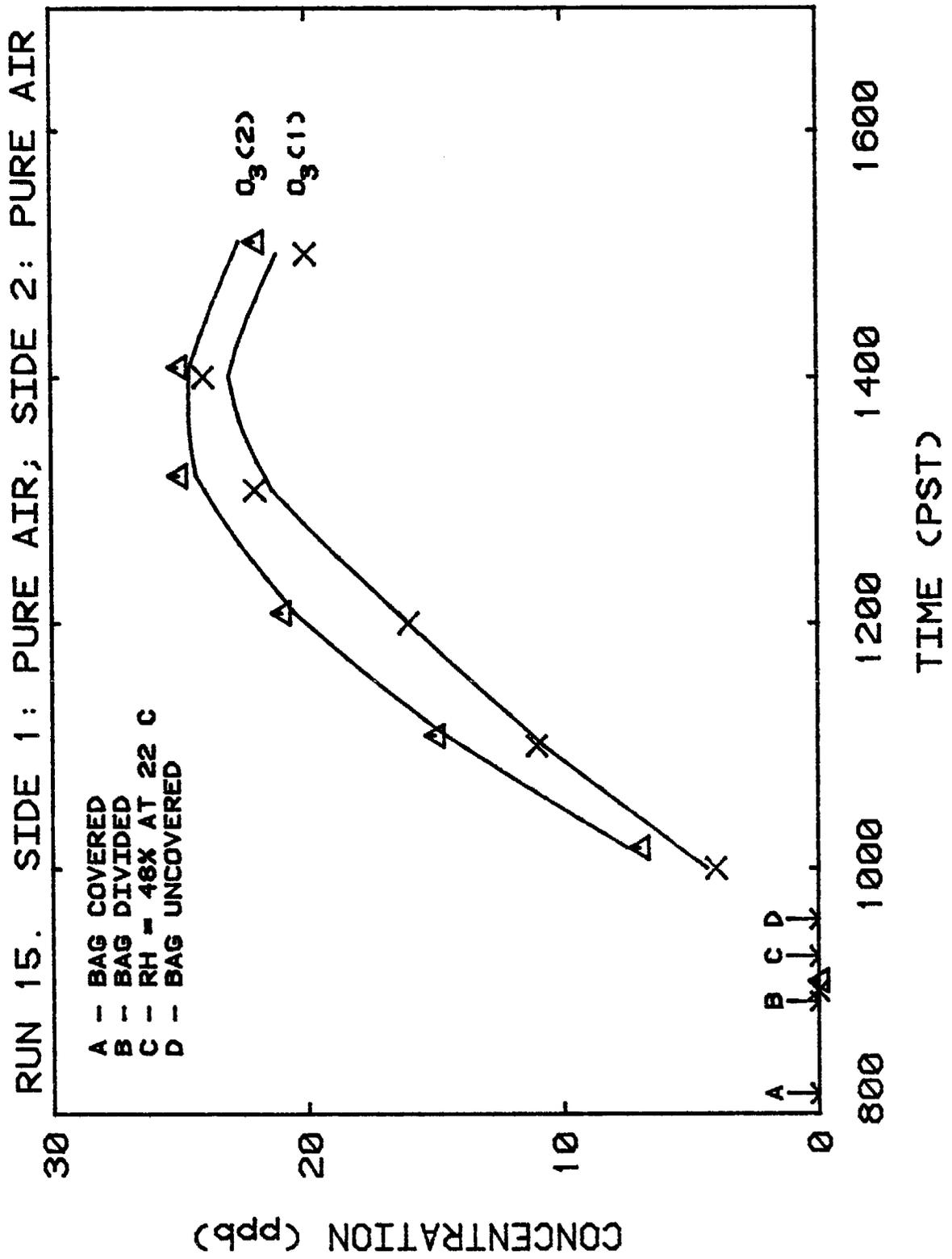


Figure 46. Concentration profiles for ozone in Run 15 of α -pinene photooxidation study.

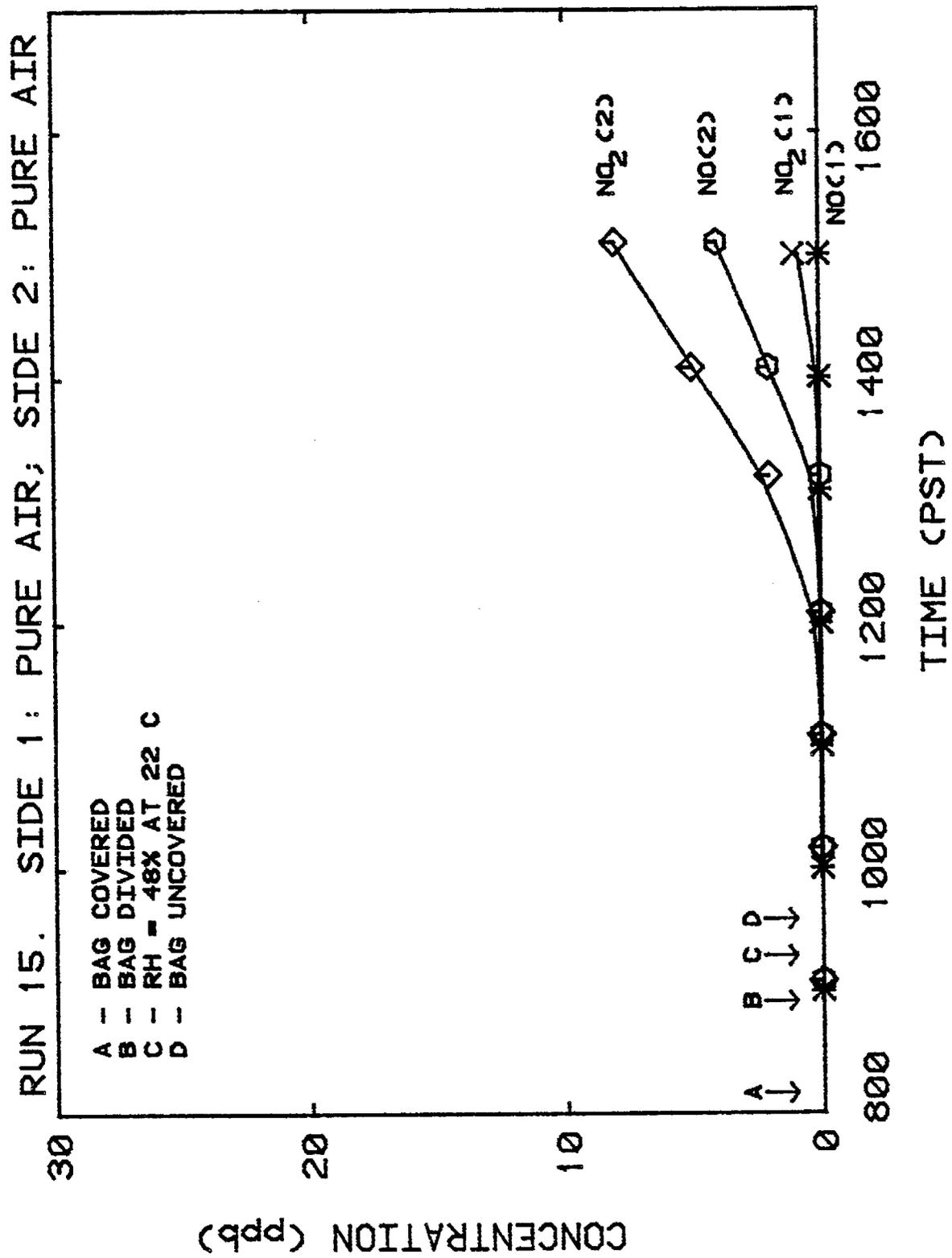


Figure 47. Concentration profiles for NO and NO₂ in Run 15 of α -pinene photooxidation study.

V. DEVELOPMENT AND APPLICATIONS OF SIGNATURING TECHNIQUES FOR NATURAL AND ANTHROPOGENIC HYDROCARBONS

A. Introduction

Studies of the organic component of polluted urban air have invariably shown components traceable to fossil fuels, especially gasoline. Indeed, anthropogenically derived hydrocarbons dominate the organic fraction so completely that contributions from vegetation have been difficult to identify in past studies.

There are two complementary approaches to the evaluation of the impact of vegetative emissions of organics on air quality.

- Measurement of total organics and determination of the fraction of these which can be ascribed to auto emissions and other man-made sources. This could place an upper limit on the natural emissions but will not yield an estimate of their actual importance, especially if it is small. This leads naturally to the complementary approach:

- Measurement of those atmospheric species which can clearly be ascribed (because of their structure) to natural sources. This will set a lower limit to the contribution of vegetative organics but may underestimate their importance by failure to properly ascribe some organics to natural sources or to measure some naturally emitted organics. For example, n-heptane is present in gasoline and also in some pine tree emissions. The amount attributable to gasoline may be estimated by comparing the n-heptane concentration with that of other gasoline components, for example, toluene, benzene, cyclohexane, etc.

The latter approach requires development of a reliable, sensitive measurement method which will unambiguously identify and quantitatively measure naturally-emitted compounds at ambient concentrations in air contaminated with anthropogenic organic emissions. The analytical method of choice is gas chromatography, followed by detection by mass spectroscopy for positive identification and/or flame ionization for maximum sensitivity. Some forest measurements of terpenes have been made using larger sample loops, freeze-out traps followed by packed column separation and FID detection" (Whitby and Coffey 1977). However, capillary columns may be used for high resolution, particularly when the sample contains anthropogenic emissions. In addition,

capillary columns are more suitable for GC-MS coupling, a necessary step for positive identification.

The purpose of this research element was to adapt and combine several gas chromatographic procedures which have been successfully used at SAPRC/UCR in recent years with advanced column techniques (Holzer et al., 1977; Rasmussen et al., 1974; Ullrich and Seifert, 1978) developed elsewhere to obtain useful signatures of atmospheric organic compounds and to provide analytical capability for the emission rate measurements and outdoor chamber study of α -pinene photooxidation.

Capillary Column Gas Chromatography. The usual freeze-out procedure, in use at SAPRC since the early 1960's, has been adapted successfully to a high resolution capillary column chromatograph (see Figure 7). Excellent resolution has been achieved along with high sensitivity and good carbon number coverage without sample splitting. The key step which makes this possible is chilling of the column to -50°C . All but the most volatile hydrocarbons (four carbons or less) are thereby concentrated at the front of the capillary. In striking contrast to a normal chromatogram the compounds with short retention time show much poorer resolution than slower moving components because the volatile ones are not concentrated effectively at -50°C , the lowest possible temperature with the commercial sub-ambient accessory.

Temperature programming at $8^{\circ}\text{C min}^{-1}$ is started simultaneously with thaw/injection of the frozen sample. The limiting factor in the reproducibility of emergence time is probably the operator. Emergence time for α -pinene is 18.9 minutes and for β -pinene is 20.0 minutes. The full width at half height for these peaks is 2 to 3 seconds; at the baseline they are about seven seconds wide corresponding to 124 μl of carrier gas. Thus, resolution seems to be comparable to that obtained for good splitter injections into long capillaries. Theoretical plates were estimated at several hundred thousand or more.

The capillary column performance was tested by injection of several ambient air samples and a vaporized gasoline sample. All showed a great many peaks, most of which are not yet identified. The dilution in the gasoline analysis was 16.9 μg of gasoline per cubic meter or about 29.7 ppbC. About 130 peaks could be seen on the chromatogram in the first 30 minutes. The smallest peaks must therefore be less than 0.1 ppbC.

The capillary system has several extra advantages. The very small column flow of 1.1 ml min^{-1} means that column bleed causes little background signal in the flame detector and little drift during temperature programming. Since most of the flame-support nitrogen does not pass through the column, the injector valve can be closed to stop column flow as well as isolate the sample trap without snuffing the flame. This may be useful in improving the precision of the injection procedure, to protect the column or to minimize interference from carrier gas contaminants. Sensitivity may be sufficient to permit measurement by direct injection of 2-5 ml loop samples.

By programming the capillary column from -50°C to $+120^{\circ}\text{C}$ in 21.25 minutes, a broad spectrum of hydrocarbons and other organics can be covered. Emergence times and calibration factors so far ascertained are shown in Table 17. When operating properly, a peak 0.02 mv high (unattenuated) can be detected. For α - and β -pinenes, this corresponds to $0.02/0.795 = 0.025$ ppb and $0.02/0.732 = 0.027$ ppb, respectively, by moles, which appears to be quite adequate. In real samples the limiting factor may well be the interference from other peaks. Ambient measurement of the terpenes will therefore require careful comparison with suitable blanks and reference samples, and mass spectral studies will be necessary.

In the original sampling procedure, 100 ml syringes were used to measure the sample and force it through the freeze trap. An alternate procedure which eliminates contact between the sample and the syringe was later found to be practical. The trap is removed from the analyzer, taken to the sampling site, chilled with liquid argon and the sample pulled through the trap with a 100-ml syringe. The trap is then capped, returned to the laboratory and attached to the sample valve on the chromatograph while still frozen. Thus, the sample comes in contact only with surfaces which are finally purged into the instrument. A further refinement will be to use a four-port valve to close the sample in the field, thus permitting purging of all connecting lines prior to sample thaw. Peaks from the gas capillary column are so narrow it was necessary to install a two-pen recorder with the second channel set at a tenfold reduced sensitivity so that loss of data because of off-scale peaks is minimized.

A peak integrator was recently put in service to automate data collection. A selection of 36 terpenes, including many of the species mentioned in

Table 17. Identified Peaks on Capillary Column SE52 Chromatogram

Retention Time (min)	Compound	Hydrocarbon Type	Sensitivity Factors (x 1)	
			ppbv/mv	ppbC/mv
3.70	n-butane	nP ₄		
5.37	isopentane	iP ₅		
6.38	isoprene	T ₅	2.75	13.78
9.28	n-hexane	nP ₆		
11.28	benzene	A ₆	1.63	9.80
12.35	n-heptane	nP ₇	1.40	9.78
14.38	toluene	A ₇	1.43	9.98
17.02	ethylbenzene	A ₈		
17.20	para-xylene	A ₈		
17.20	meta-xylene	A ₈		
17.90	ortho-xylene	A ₈		
18.00	n-nonane	nP ₉		
18.64	isopropylbenzene	A ₉		
18.88	alpha pinene	T ₁₀	1.26	12.58
19.40	n-propylbenzene	A ₉		
19.65	para-ethyltoluene	A ₉		
19.68	meta-ethyltoluene	A ₉		
19.74	1,3,5 trimethylbenzene	A ₉		
19.95	beta-pinene	T ₁₀	1.37	13.66
20.12	ortho-ethyltoluene	A ₉		
20.18	sec-butylbenzene	A ₁₀		
20.30	1,2,4 trimethylbenzene	A ₉		
20.35	tert-butylbenzene	A ₁₀		
20.70	isobutylbenzene	A ₁₀		
20.90	α-terpinene	T ₁₀		
21.12	para-cymene	T;A ₁₀	1.69	16.92
21.20	limonene	T ₁₀		
21.81	1,2,3 trimethylbenzene	A ₉		
21.90	n-butyl benzene	A ₁₀		

[All aromatics through C₉ (14 compounds) + 5 of 22 C₁₀s]

the literature, was recently received as a gift from Givaudan and some of these may serve as suitable authentic samples.

Development problems which remain include the following. Some chromatograms contain extraneous peaks which are suspected of being artifacts. One of these is broad, poorly shaped and on top of the α -pinene peak. Since the capillary column provides no identification of its peaks, the Finnigan GC-MS is being employed for that purpose. Each 100-ml sample of air contains about 1 μ l of water measured as liquid. This will of course freeze in the trap at liquid argon temperature. After transfer, it also freezes at -50°C in the column. It apparently is swept through the column harmlessly unless it is somehow involved in the release of the extraneous peaks mentioned above. Its affects on the mass spectrometer appear to be more serious. In both cases the role of water requires further clarification.

B. Signaturing of Organics by Backflush Gas Chromatography

An experimental apparatus to measure one- and two-carbon hydrocarbons directly by gas chromatography and to analyze for higher organics by backflushing the same sample from the column, was set up as shown in Figure 48. The system has been described in detail elsewhere (Stephens and Hellrich 1979, 1980). The backflush GC method of signaturing ambient hydrocarbons will supplement the use of high resolution gas chromatography and, because it is more portable and simpler to operate in the field, it will be used to provide rapid data concerning ambient hydrocarbon concentrations during emission rate measurements. The apparatus is currently running continuously at 15-minute cycling intervals and is located in the ARB Mobile Laboratory for Air Pollution Research. A comparison with hydrocarbon data collected from the Beckman 6800 Hydrocarbon Analyzer at the same location will be made. The Beckman instrument monitors CO levels as well, a necessary parameter for signaturing efforts.

Since the backflush GC originally developed at SAPRC by Stephens and Hellrich had not been used for several years, reactivation necessitated cleaning all the components, replacing the column and "trouble shooting" the electronics. A further improvement was made by enclosing the entire system in a metal covered instrument rack and installing a proportional temperature controller.

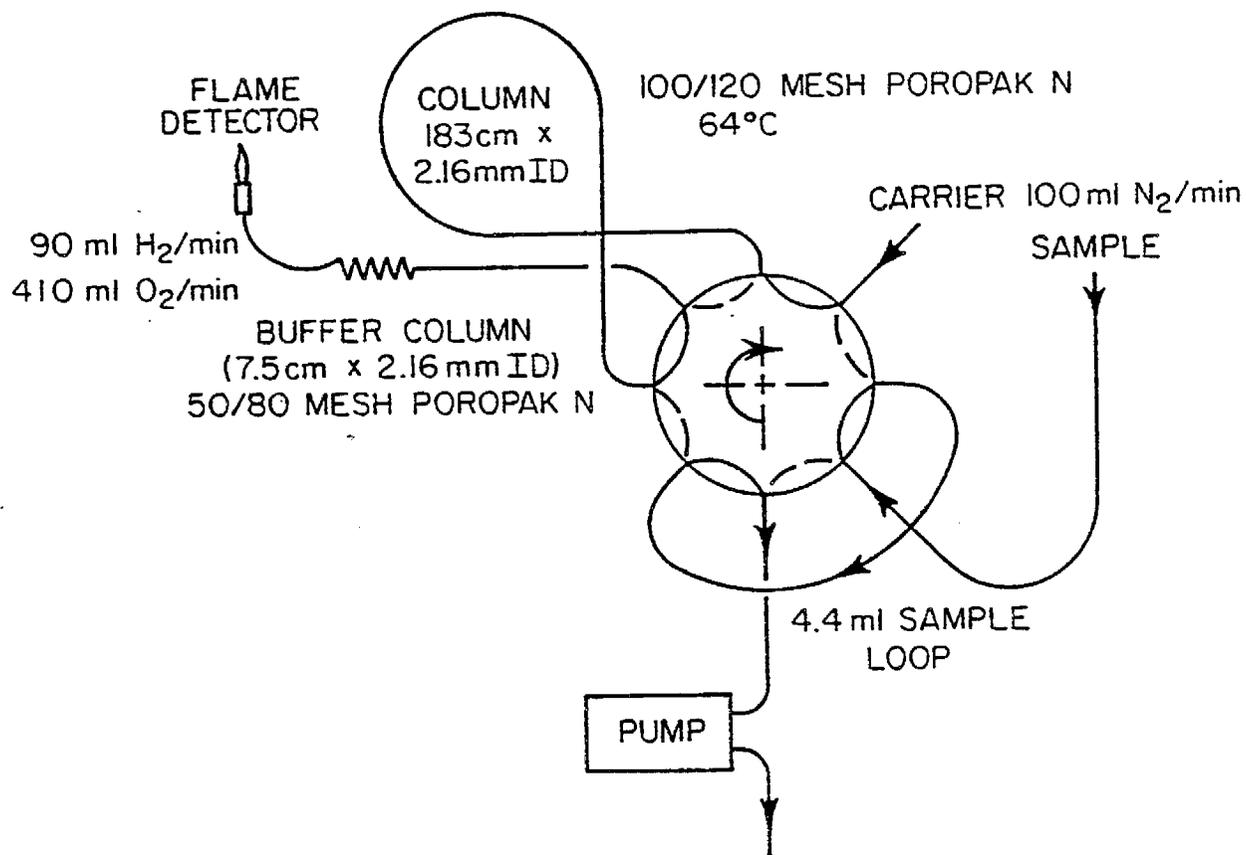


Figure 48. Schematic for SAPRC backflush gas chromatograph.

The sensitivity for the light hydrocarbons observed in the original work (Stephens and Hellrich 1979, 1980) of 1 or 2 $\mu\text{g m}^{-3}$ was obtained, but the backflush minimum detection is still several hundred $\mu\text{g m}^{-3}$. Further refinements are expected to improve the backflush detection limit to about 100 $\mu\text{g m}^{-3}$. A typical trace for ambient air is shown in Figure 49.

Throughout the contract period, many minor improvements and adjustments continued to be made to the backflush chromatograph in order to stabilize its performance. At this writing its operation has stabilized to the point where failure of ink flow is the most frequent cause of data loss.

Backflush peaks of moderate size were seen for the cleanest air but not for pure nitrogen or ultra-zero air. Humidifying ultra-zero air resulted in a significant spurious backflush peak which was nearly eliminated by lowering the temperature to 44°C. This made it necessary to increase the nitrogen flow to 78 ml min^{-1} and the hydrogen flow to 35 ml min^{-1} . This compromise has resulted in good resolution of the C_2 hydrocarbons, a well-shaped sizeable backflush peak, with little drift and acceptable noise level.

Sporadic high ethylene values were traced to leaks and/or permeation of trailer air into the sample inlet. This air contains several ppm ethylene due to leaks from the chemiluminescent ozone analyzer. The TFE 1/8" Teflon sampling line was replaced with a 1/8" FEP Teflon line, which appeared to have partially solved the problem. The recorder trace continues to show sporadic increases in ethylene levels not accompanied by increase in acetylene or backflush hydrocarbon, still believed to be derived from the ethylene used by the ozone chemiluminescence analyzer. When the backflush GC system was operated in another location in a prior program, no such ethylene outliers were observed. The cleanest air, from Santa Ana winds, showed all five peaks (CH_4 , C_2H_4 , C_2H_2 , C_2H_6 and backflush), although most were barely detectable.

An attempt was made to calibrate the backflush peak using gasoline. One microliter of gasoline was vaporized into a 13.5-liter glass jug filled with pure air. The expected concentration was 58,000 $\mu\text{g m}^{-3}$; lower concentrations were made by dilution using a 100 ml all-glass syringe. A sample containing 580 $\mu\text{g m}^{-3}$ gave 1-2% of scale readings on full sensitivity of the chromatograph. A sample containing 1160 $\mu\text{g m}^{-3}$ showed 2-4% of scale. Although the peaks are poorly defined and noise appears to be a problem, good

AMBIENT AIR
0815 PST
NOV. 6, 1979

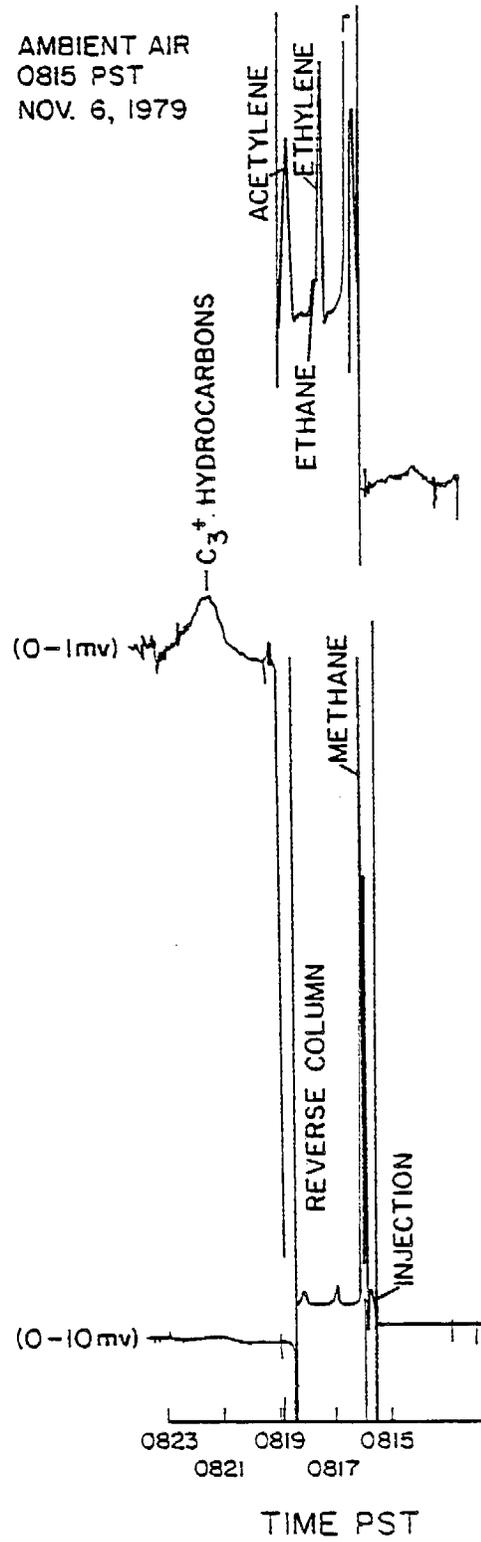


Figure 49. Typical ambient air analysis obtained with SAPRC backflush gas chromatograph.

linear calibration curves are observed. Methane, ethylene and acetylene are calibrated using a dynamic dilution of a 1 ppm gas standard. The detection limit for these compounds is about 1 ppbC. These results indicate that using gasoline as a calibration standard is a problem. Ambient air gives backflush peaks of better shape and reproducibility. A better method of calibration appears necessary and will be pursued.

C. Hydrocarbon Correlation Analysis

We have previously pointed out that vegetative organic emissions would not be expected to correlate with automotive components. The ARB Mobile Laboratory for Air Pollution Research operated by SAPRC at UCR records total hydrocarbon (THC), methane and carbon monoxide (CO) using a Beckman 6800 air quality chromatograph. Almost all of the carbon monoxide comes from auto exhaust, thus providing a reference against which hydrocarbon concentrations can be correlated. Several years of trailer data are on tape. Therefore it was possible to compute nonmethane hydrocarbon (NMHC = THC - methane) concentrations and to construct joint distribution tables.

The data were treated in six-month batches of winter and summer data. The batches of data appear quite different, with the earlier batches showing very low correlation between NMHC and CO. The last set of edited data (winter 77/78; see Table 18) showed the best correlation with a slope of 3.178 ppm CO per ppmC HC and a correlation coefficient of 0.829. Conversions to weight ratio with molecular weights of 28 for CO and 16 for HC gives a weight ratio of 5.56 tons CO per ton HC. This is close to the value given in emission inventories and confirms that the bulk of the hydrocarbon does indeed come from automobile emissions. Outliers at high hydrocarbon/CO ratio may be due to a local spill of gasoline or other volatile organics. The extreme outliers were identified and listed as shown in Table 19 in the hopes that an explanation would become apparent, but so far none has. This instrument suffers the defect that methane and total hydrocarbons are measured on different air samples. If methane is not identical in the two samples, an error will be introduced by the subtraction used to calculate NMHC. Since methane is always large, this potential for error is great.

Table 18. Nonmethane Hydrocarbon vs Carbon Monoxide Distribution for Half-Hourly Averages (number of readings),
November 1977-April 1978

NMHC ppm	CO ppm													Total		
	0.0-0.2	0.2-0.4	0.4-0.6	0.6-0.8	0.8-1.0	1.0-1.2	1.2-1.4	1.4-1.6	1.6-1.8	1.8-2.0	2.0-2.2	2.2-2.4	2.4-2.6			
0.0-0.4	3137	380	48	12	5	3	0	1	0	1	0	0	0	0	0	3587
0.4-0.8	894	482	76	19	17	1	1	0	0	0	0	0	0	0	1	1482
0.8-1.2	168	464	157	10	9	3	3	0	0	0	0	0	0	0	0	814
1.2-1.6	35	253	233	14	5	2	0	0	1	0	0	0	0	0	0	543
1.6-2.0	11	100	258	47	4	2	1	1	0	0	0	0	0	0	0	424
2.0-2.4	2	23	142	88	14	2	0	0	0	0	0	0	0	0	0	271
2.4-2.8	3	5	40	83	15	0	2	0	0	0	0	0	0	0	0	148
2.8-3.2	1	5	11	60	33	2	0	0	0	0	0	0	0	0	0	112
3.2-3.6	1	1	6	37	48	7	1	0	0	0	0	0	0	0	0	101
3.6-4.0	1	1	5	10	35	16	2	1	1	0	0	0	0	0	0	72
4.0-4.4	1	0	3	6	23	17	2	0	1	0	0	0	0	0	0	53
4.4-4.8	0	0	0	1	10	10	3	1	0	0	0	0	0	0	0	25
4.8-5.2	0	0	2	0	7	5	6	2	0	0	0	0	0	0	0	22
5.2-5.6	0	1	0	1	0	3	3	1	2	0	0	0	0	0	0	11
5.6-6.0	0	0	0	1	2	2	5	0	1	1	1	1	0	0	0	13
6.0-6.4	0	0	1	0	1	1	2	0	0	1	0	0	0	0	0	6
6.4-6.8	0	0	0	2	0	0	1	0	0	1	0	0	0	0	0	4
6.8-7.2	0	0	0	1	0	1	3	0	0	0	1	0	0	0	0	6
7.2-7.6	0	0	1	0	0	0	0	0	0	1	0	0	0	0	0	2
7.6-8.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
8.0-	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1
TOTAL	4254	1715	983	392	229	77	35	7	6	6	2	1	1	1	1	7707

(CO) = 3.178 (NMHC) + 0.0347 correlation coefficient = 0.829.

*Outliers, see Table II-13.

Table 19. Outliers in Nonmethane Hydrocarbon vs Carbon Monoxide Distribution for Half-Hourly Averages, November 1977-April 1978

Date	Half Hour	HCT	HCM	NMHC	CO
<u>NMHC > 1.4 CO < 2.0</u>					
12-12-77	48	2.980E 00	1.540E 00	1.440E 00	1.670E 00
3-6-78	37	3.590E 00	1.820E 00	1.770E 00	1.250E 00
4-10-78	21	3.630E 00	1.720E 00	1.910E 00	3.300E-01
4-11-78	34	4.120E 00	1.890E 00	2.230E 00	5.140E-01
4-11-78	35	3.800E 00	1.920E 00	1.880E 00	5.430E-01
4-14-78	35	3.200E 00	1.640E 00	1.560E 00	9.460E-02
<u>NMHC < 0.8 CO > 4.4</u>					
11-2-77	36	2.690E 00	2.000E 00	6.900E-01	6.750E 00
11-8-77	18	2.370E 00	1.860E 00	5.100E-01	6.360E 00
11-23-77	17	2.550E 00	2.070E 00	4.800E-01	4.860E 00
12-2-77	3	2.840E 00	2.080E 00	7.600E-01	7.190E 00
12-5-77	18	2.770E 00	2.060E 00	7.100E-01	4.530E 00
12-7-77	16	2.590E 00	2.140E 00	4.500E-01	7.410E 00
12-8-77	45	3.690E 00	3.000E 00	6.900E-01	5.950E 00
12-13-77	18	2.720E 00	2.030E 00	6.400E-01	6.680E 00
1-11-78	--	2.070E 00	1.840E 00	2.300E-01	5.500E 00
1-18-78	37	2.280E 00	1.750E 00	5.300E-01	5.140E 00
1-25-78	20	2.560E 00	1.860E 00	7.000E-01	5.220E 00

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