

80386

77-5.3

PHOTOCHEMICAL POTENTIAL OF FOREST FIRE SMOKE

W. HENRY BENNER
PAUL URONE

UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA

CHARLES K. McMAHON
PAUL RYAN

SOUTHEASTERN FOREST EXPERIMENT STATION
MACON, GEORGIA



For Presentation at the 70th Annual Meeting of the
Air Pollution Control Association
Toronto, Ontario, Canada June 20-June 24, 1977

Printed in U.S.A.

11-3-3

Photochemical Potential of
Forest Fire Smoke

Abstract

A stainless steel laboratory chamber to hold the entire combustion products from a small scale pine needle fire was useful for measuring the photochemical activity of pine needle fire smoke. Particle size distributions indicated that the nucleation of small numbers of submicron particles was sufficient to increase the amount of light a plume would scatter. Artificial daylight irradiation led to ozone and oxidant formation and typical diurnal Los Angeles type photochemical cycles were observed. Other things being equal, planning controlled forest and agricultural burns during periods of low photochemical potential (at night under clear skies) could reduce the intensity of secondary nucleation and consequent light reflectivity. Gaseous emission factors were calculated by extrapolating the concentration vs. time curves to zero time to obtain an initial concentration of each pollutant.

Introduction

Prescription burning has been commonly used in the management of commercial forests. If logging slash and undesirable undergrowth are not removed from forested areas, they become potential hazardous fuels for wild fires.¹ It is also economically attractive to remove from a forest, flora which compete for nutrients with the commercially desirable species. Prescription burning easily solves these problems, however the combustion products from these fires may degrade the quality of the air.²⁻⁴

A number of articles dealing with the characterization of emissions from open burning have been published,⁵⁻⁹ but only a few reports mention the possible photochemical involvement of the products. A few authors identified hydrocarbons in forest fire smoke which have been known to be photochemically reactive. Nitrogen oxides (NO_x) were measured in several studies in which grab samples were analyzed by a wet chemical technique.^{5,7} A report¹⁰ that ozone as high as 0.1 ppm was detected in a forest fire plume in Australia showed that secondary photochemical products are likely to be present in irradiated smoke plumes. The instrument employed in the study was not specific for ozone and in fact responded to nitrogen dioxide and other oxidants that might be present in a smoke plume.

Although the literature indicates the magnitude of pollutants released by forest fires in the United States, several questions need to be answered so that the effect of controlled burning practices on ambient air quality can be determined more accurately. For example, burning techniques and their timing can be designed so that photochemical particle precursors are produced either less abundantly or at times when photochemical activity is rendered minimal.

The emission factor for nitrogen oxides frequently cited in the literature was determined from grab samples that were obtained during a burn. Nitrogen oxide production is related to flame temperature, and since flame temperatures are not constant during a burn, the emission factor may not represent the time-averaged production of nitrogen oxides.

This study investigated the release of pollutants when a small quantity of pine needles was burned in a test chamber, and monitored the production of secondary pollutants when the smoke was irradiated with artificial sunlight. The results of these chamber studies were used to assess the potential of a prescription forest fire plume to alter the downwind air quality.

Experimental Methods and Techniques

An 11 m³ cylindrical stainless steel chamber was equipped with two 15 cm diameter ports and a 60 cm diameter manhole. One of the ports was used as a sampling port and the other was connected to a laboratory exhaust hood for drawing air through the chamber. Normally, the chamber was purged with about 100 m³ of room air between runs. The ambient air in Gainesville, Florida is relatively clean, and for this reason unscrubbed room air was considered adequate for purging the chamber. A squirrel cage blower was used to stir the chamber air and was operated for a short time at the beginning of a run until the initial smoke was mixed with the chamber air. Twenty fluorescent (F40D, Westinghouse) and twenty black light (F40BL, Westinghouse) lamps were supported above a teflon film ceiling in the top of the chamber and illuminated the chamber at about one-third the intensity of noon day summer sun. (The light intensity was measured by NO₂ in N₂ photolysis¹¹.) The room in which the chamber was located was cooled to 60-63°F by the building air conditioning system, which maintained the chamber air at about 75°F when the lights were on.

Total oxidants were measured with a Mast oxidant meter and ozone was measured with a Bendix chemiluminescent ozone monitor. The oxidant and ozone meters were calibrated during each experimental run using a Teco ozone/NO_x calibrator. The ozone generator in the Teco instrument was calibrated using the neutral potassium iodide reference method.¹² NO_x was reported to produce a ten percent response relative to ozone in the Mast instrument.¹³ The electrical signal from the Mast meter was amplified so that 0.05, 0.5, and 1.0 ppm "oxidant" were full scale values on a strip chart recorder. The "oxidant" readings indicated the contributions of all oxidant species, including ozone and nitrogen oxides, which reacted with the electrolyte.

Carbon monoxide was measured with an Ecolyzer (Energetics Science) which was capable of measuring up to 50 ppm of CO. Carbon monoxide is a relatively stable compound, and the decrease in carbon monoxide concentration with increasing time was a measure of the total amount of sample removed from the chamber. It was estimated that during an experimental run approximately ten percent of the chamber volume would be removed for sample analysis. Since the nominal accuracy of the Ecolyzer was of the order of ten percent, it was necessary to calibrate the Ecolyzer frequently to obtain an accuracy of $\pm 3\%$.

Nitrogen oxides were measured with a McMillan NO/NO_x chemiluminescent monitor. The instrument was calibrated during each experimental run with a Teco calibrator which served to dilute a certified concentration of NO in air.

The hydrocarbon analysis system consisted of a gas chromatograph (Varian) equipped with a flame ionization detector (FID), a short unpacked column, a gas sampling valve and a system for calibrating the response of the FID. Recently, a Beckman Model 6800 carbon monoxide, methane and non-methane hydrocarbon analyzer was purchased, installed, calibrated and used for some of the later and on-going experiments.

A nephelometer (Meteorology Research Inc.) was used to determine the b_{scatter} coefficient for the chamber air. The b_{scat} coefficient is a measure of the amount of light scattered by the suspended particles and is mathematically related to the visual range.

The size distribution of the submicron smoke particles was determined with an Electric Aerosol Analyzer (Thermosystems, Inc.). The instrument was sensitive enough to detect small quantities of particles in seven particle size intervals between 0.01 and 1.0 microns in diameter.

Filtered samples of the smoke particles were collected on 47 mm diameter glass fiber filters and the total suspended particulates (TSP) was reported as micrograms per cubic meter.

Experiment. 1

Before an experimental run started, the chamber was purged with room air for at least thirty minutes. A small quantity (usually 2g) of pine needles was placed on a burning platform located on the chamber floor. The needles were supported on a piece of resistance wire that had been bent into the shape of a rectangular grill. The fuel was ignited by passing an electric current through the resistance wire which rapidly heated the wire to redness and set the needles aflame. As soon as the needles flamed, the power to the resistance wire was shut off and the manhole cover on the chamber was closed. In order to minimize the removal of chamber air, two series of runs were conducted: the first was designed to measure primarily particle parameters, and the second to measure gaseous parameters. Gaseous air samples were collected intermittently to minimize the removal of chamber air. Several gas samples were analyzed during the first few hours of the experimental run so that reliable starting concentrations of the combustion products could be determined.

The experimental runs were conducted with pine needles that had been humidified. Forest fuel equilibrium moisture contents between 8 and 15 percent (dry basis) have been reported as acceptable for prescribed fires.¹⁴ In order to approximate similar forest fire studies conducted at the Southeastern Forest Fire Experiment Station, the pine needles were humidified over a saturated sodium chloride solution. The humidified needles had a moisture content of 14 percent on a dry weight basis.

Results and Discussion

Particulate Matter

Seven experimental runs were conducted to characterize the suspended particulate matter in pine needle smoke. Three of the runs were conducted for 24

hours under continuous irradiation by the chamber lights. This set of runs was entitled "L" for light; it simulated forest fires which occurred in the daytime. The remaining four runs were conducted during a 48 hour time period in which the chamber lights were off for the first 24 hours and then turned on for the final 24 hours. This second set of runs was entitled "DL" for dark-then-light and simulated nighttime burning with the subsequent irradiation of a plume on the following day. The 24-hour time periods were used because longer periods of irradiation were needed to observe a Los Angeles type photochemical cycle.

The size distribution of the submicron particles at various times during run L-6 is shown in Figure 1. The total number of submicron particles decreased with time such that after an elapsed time of 24 hours the number was only about 5 percent of the number present at an elapsed time of 1/2 hour. During this time period the small particles grew in diameter and after several hours of irradiation the appearance of small diameter particles indicated the photochemical production of new particles.

In Figure 2, run L-7 indicates that secondary nucleation occurred because the number of small particles increased later in the run. The shape of the curves for runs L-5 and L-6 do not indicate secondary nucleation but an examination of run L-6 in Figure 1 points out that the number of .0133 μm diameter particles increased at an elapsed time (et) of 33 hours. The number vs. D_p curves for run L-5 are not included in this article but showed no evidence of secondary nucleation. It was concluded that secondary nucleation occurred in runs L-6 and L-7 but not in L-5.

The curves of b_{scat} vs. time in Figure 3 show considerable variability between the "L" type runs, but the formation of secondary particles helped to maintain an elevated level of light scatter. In comparison to L-5, runs L-6 and L-7 showed a less rapid decrease in b_{scat} within a time period during which secondary particles were formed, while L-5 showed a more rapid rate of b_{scat} decrease with time and no secondary particle generation.

The size distribution of the submicron particles at various times during the DL-4 series is shown in Figure 1. The general trend showed that the number of particles produced by the burning needles decreased rapidly with time such that the number of particles remaining suspended in the chamber air after 24 hours was, as in the "L" series, about 5 percent of the number present at an elapsed time of 1/2 hour. In the dark period of the "DL" runs, delayed auto-nucleation was observed in two of the four runs (Figure). When the lights were turned on at an elapsed time of 24 hours, secondary particle nucleation was observed in three of the four runs. In the one run (DL-6) in which secondary nucleation was not observed, the number concentration of small particles ($< 0.0422 \mu\text{m}$ diameter) just prior to the time when the lights were turned on was nearly one or two orders of magnitude greater than the number concentration of the particles in the other runs. Therefore, because of the number concentration of particles present in the chamber air just prior to when the lights were turned on, a sufficient particle surface area may have been present to favor the condensation of particle precursors and, in effect, decreased the tendency of particle nucleation. During the initial 24 hour dark period of the "DL" series, the amount of scattered light was variable, and the rate of decrease of b_{scat} was exponential in DL-4 but nearly linear in DL-6. After the lights were turned on, the influence of secondary particle formation caused the b_{scat} vs.

time curve to level off for several hours (Figure 3). In run DL-6 light scatter actually increased about 2 hours after the lights were turned on, even though particle nucleation was not observed in the number of small particles vs. time curve (Figure 2). It was concluded from the "DL" series that plumes produced at night and irradiated on the following day show a tendency to remain at a constant but low level of light scattering. The magnitude of the overall effect seems to be minimal.

The mass of suspended particulate matter (grams/m³) was correlated with the amount of light scattered (b_{scat}) by pine needle smoke. Data was obtained from the "L" and "DL" runs. The regression coefficient calculated from the data pairs was 0.15 with a correlation coefficient (r^2) of 0.48.

Gaseous Emissions

Data from 16 experimental runs were used to determine gaseous emission factors for burning pine needles. The experimental conditions to which the smoke was subjected affected the shape of the concentration vs. time curves, but extrapolation to zero elapsed time was a useful technique for measuring the concentrations of the pollutants before chemical reactions or dilution of the chamber air had significantly affected the pollutant concentrations.

Table I shows the concentration extrapolated to zero elapsed time of several pollutants along with corresponding emission factors. Since all the emissions from a fuel sample were contained in the chamber, the emission factors reported here have the added quality of being averaged over the entire burn period.

The last four experimental runs (Table I) were considered to be the best controlled experiments because problems associated with chamber leaks were solved prior to these runs. The leaks affected the concentration vs. time profiles but did not affect the emission factor which was calculated from an extrapolation at zero elapsed time. The emission factor for nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) was found to be 8.6 ± 2.0 lb/ton for the last four runs in Table I. The factor is about two-fold greater than the emission factor which has been used frequently to calculate national emissions from fires.^{3,4} The NO_x emission factor calculated for all experimental runs was 9.4 ± 2.7 lb/ton.

It was thought that the larger NO_x emission factor was related to the hot wire ignition technique. In an attempt to resolve the problem, three two-gram batches of pine needles were ignited by a methanol flaming solvent ignition technique. The three runs averaged 7.4 ± 1.9 lbs/ton NO_x . It was concluded that within experimental error, the hot wire ignition technique did not affect significantly the production of NO_x and serious consideration be given to re-estimation of the established NO_x emission factor.

The emission factor calculated from the last four experimental runs for carbon monoxide was 135 ± 56 lb/ton, which agrees reasonably well with the emission factor that has been reported in earlier studies.^{3,4} The emission factor calculated from the last four experimental runs for hydrocarbons was 17.4 ± 6 lb/ton expressed as methane. The gaseous hydrocarbon emission factor reported here is lower than the 24 lb/ton factor reported in the literature^{3,4} for a variety of agricultural and forest fuels.

Figure 4 shows typical data plots for "light" (L) and "dark-then-light" (DL) experimental runs. The DL series of runs showed several interesting phenomena. Approximately seventy percent of the NO_x released from the fire was NO and the remainder was NO_2 . The NO_x ($\text{NO} + \text{NO}_2$) concentration decreased rapidly in the first five hours, after which the rate of disappearance leveled off so that the NO_x concentration after twenty-four hours of darkness was approximately fifty percent of the initial NO_x concentration.

The gaseous hydrocarbon concentration also was observed to decrease rapidly at first and then to level off. Adsorption or reaction with the particles or reaction with the nitrogen oxides were possible explanations for the disappearance.

The fire did not generate ozone or oxidants as primary combustion products. In fact, the ozone concentration in the tank before a quantity of needles was burned was at times as high as thirty parts per billion and dropped to virtually zero as soon as the needles were burned.

Shortly after the lights were turned on, singular changes in the nitrogen oxides were observed in the DL experiments (Figure 4). The NO_x and NO concentrations dropped off rapidly while the NO_2 concentration began to increase. The NO_2 concentration proceeded through a maximum and then decreased with time, such that the NO_2 concentration at an elapsed time of forty-five hours was similar to the NO_2 concentration just prior to when the lights were turned on. The peak in the NO_2 curve is commonly observed in diurnal photochemical cycles. As the secondary NO_2 peak began to appear, the production of "oxidants" as well as ozone was observed to start. The generation of oxidants began before the generation of ozone, and the peak in the oxidant curve occurred before the ozone concentration reached a maximum (Figure 4).

The L (light) series of experiments demonstrated the concentration profile that may be expected to occur in a plume irradiated by sunlight. The initial rate of disappearance of NO_x in the L series was not as rapid as the initial rate of disappearance of NO_x in the DL series. In the L series, the NO_x concentration vs. time curve did not level off until nearly all of the NO_x had been depleted from the gas phase. In the DL series, the NO_x concentration after 24 hours of darkness was approximately fifty percent of the initial NO_x concentration, whereas in the L series, the NO_x concentration after 24 hours of irradiation was only twenty percent of the initial NO_x concentration.

The maximum concentration of either ozone or oxidants was similar in the DL and L experiments, indicating that their precursors were not significantly depleted in the dark. The length of time that the chamber air was irradiated until the maximum ozone or oxidant concentration was observed was variable and generally was shorter in the DL series than in the L series.

Summary and Conclusions

The propensity of a real plume to alter the air quality downwind from a fire was studied by artificially irradiating laboratory generated plumes. By permitting the smoke to stand in a darkened chamber, diffusional deposition of the smoke onto the chamber walls emulated atmospheric dispersion and artificial irradiation simulated natural sunlight.

The total number of submicron particles in the chamber air decreased rapidly with time, but the total number of particles $<.0422 \mu\text{m}$ diameter did not always follow this rapid rate of decrease. In two of four "DL" type runs, delayed autonucleation of very small ($D_p = .0422$) particles occurred during the dark period. When dark periods were followed by periods of artificial irradiation, the tendency for secondary particle generation was observed. Secondary nucleation was also observed in two of three "L" type runs.

Not all laboratory plumes generated secondary particles when exposed to experimental conditions in the chamber. The plumes in which secondary particles were formed showed the amount of light scatter to be directly related to the presence of the secondary particles. The significance of the presence of such particles depends on when they were produced. It appears that the irradiation of a fresh plume causes the amount of light scattered by the plume to remain at a relatively high level, while the irradiation of a plume which was permitted to disperse overnight adds only a small contribution to the low level of light scatter found in a day old plume. The mass of suspended particulate matter was related to the light scattering coefficient by the following equation:

$$\text{TSP}(\text{g}/\text{m}^3) = 0.15 \times b_{\text{scat}}$$

The effect of artificial sunlight irradiation of the combustion products of small scale pine needle fires produced obvious changes in the gas phase pollutants. Plots of pollutant concentration vs. time indicated that typical diurnal cycles found in Los Angeles type pollution systems were observed when the smoke was irradiated with artificial sunlight illumination. The concentration of NO plus NO₂ decreased more rapidly when irradiated than when permitted to stand in the dark. During experimental runs in which the pine needles were burned during irradiation, the curve of concentration of NO₂ vs. time did not always pass through a maximum. In several irradiated runs of the L series, the NO₂ concentration decreased in an exponential fashion similar to the decrease in the NO_x (NO plus NO₂) concentration. Maximum oxidant and ozone formation under artificial irradiation equivalent to one-third noonday summer sunlight varied from 0.03 to 0.04 ppm. In all probability, with greater light intensity the rate of NO₂ photolysis would increase and the ozone concentration would consequently be greater.

When the combustion products were permitted to stand in the dark, the concentrations of gaseous hydrocarbons, NO, and NO₂ decreased initially and then leveled off. When dark periods were followed by irradiation, the NO₂ concentration passed through a maximum value due to photochemical conversion of NO to NO₂, but the total of NO plus NO₂ (NO_x) decreased exponentially. The hydrocarbon concentration decreased somewhat faster when the lights were turned on, but the rate of decrease of the hydrocarbons in the chamber was not as rapid as the rate of decrease of NO_x. It is possible that by the time the lights were turned

on in the DL series, the more reactive hydrocarbons had reacted and the slower disappearance rate of NO_x was a result,

Ozone and oxidants were also formed when dark periods were followed by periods of irradiation. In general, oxidant formation commenced shortly after the lights were turned on. Non-ozone oxidant formation always occurred before ozone formation was observed.

Emission factors for gaseous and particulate emissions were calculated by extrapolating the concentration vs. time curves to zero time to obtain an initial concentration of a specific pollutant. The gaseous emission factors for two gram pine needle burns under the conditions of this study are as follows for NO_x ($\text{NO} + \text{NO}_2$), CO, gaseous hydrocarbons (as CH_4): 8.6 ± 2.0 , 135 ± 56 , and 17.4 ± 6 pounds per ton of fuel, respectively.

Acknowledgment

This report was supported by the United States Department of Agriculture, Forest Service, grant A8fs-9, 961, supplement number 19.

References

1. Fritschen, L., et al., "Slash Fire Atmospheric Pollution", U.S.D.A. Forest Service Research Paper PNW - 97, Pacific Northwest Forest and Range Experiment Station, Portland, Oregon, 1970.
2. Ward, D.E., et al., "An Update on Particulate Emissions from Forest Fires", Presented at the 69th Air Pollution Control Association Meeting, Portland, Oregon, 1976.
3. Yamante, G., "Development of Emission Factors for Estimating Atmospheric Emissions from Forest Fires", U.S. Environmental Protection Agency publication, EPA-450/3-73-009, October, 1973.
4. Yamante, G. and Stockman, J., "An Inventory of Emissions from Forest Fires, Forest Managed Burns, and Agricultural Burns", Presented at the 68th Air Pollution Control Association Meeting, Boston, Ma., 1975.
5. Darley, E.F., et al., J. Air Pollution Control Assoc., 11, (12), 685 (1966).
6. Feldstein, H., et al., J. Air Pollution Control Assoc., 13, (11), 542 (1963).
7. Gerstle, R.W., and Kemnitz, D.A., J. Air Pollution Control Assoc., 17, (5), 324 (1967).
8. Biswell, H.H., "A Summary of Research on Smoke and Air Pollution from Forest and Wildland Burning", Arizona Water Commission Report No. 5, 17th Arizona Watershed Symposium, Phoenix, Arizona, September 19, 1973.
9. Sandberg, D.V., Pickford, S.G. and Darley, E.F., J. Air Pollution Control Assoc., 25, (3), 278 (1975).
10. Evans, L.F., et al., Environmental Science and Technology, 8, (1), 75 (1974).
11. Seinfeld, J.H., "Air Pollution - Physical and Chemical Fundamentals", Ch. 4, McGraw-Hill, N.Y., 1975.

12. Code of Federal Regulations, Title 40, Appendix D, Reference Method for the Measurement of Photochemical Oxidants Corrected for Interference Due to Nitrogen Oxides and Sulfur Dioxide, U.S. Government Printing Office, Washington, D.C., 1971.
13. Cherniack, I., and Bryan, R.J., J. Air Pollution Control Assoc. 15, (8), 351 (1965).
14. Blackmar, W.H., Equilibrium Moisture Content of Common Fire Fuels Found in Southeastern Forests", U.S.D.A. Forest Service Research Paper SE-74, January 1971.

Table I: Gas Emission Factors*

Run	Wt. Needles** Ignited	NO _x Emission		NO Emission		NO ₂ Emission		CO Emission		HC Emission ^A	
		[NO _x] _e	Factor ^B	[NO] _e	Factor	[NO ₂] _e	Factor	[CO] _e	Factor	[HC] _e	Factor ^A
TA-1	2.0 g	.46	8.0	.32	4.8	.14	3.2	7.3	103	---	---
TA-2	1.0	.36	12.7	.25	7.6	.11	5.1	6.8	192	---	---
TA-3	1.0	.41	13.7	.33	10.0	.08	3.7	4.9	118	---	---
TA-4	1.0	.43	14.8	.32	9.7	.11	5.1	8.2	232	---	---
TA-5	2.0	.29	4.9	.22	3.3	.07	1.6	12.4	175	---	---
TA-6	2.0	.83	10.2	.60	9.1	.23	1.1	12.1	171	---	---
TA-13	2.0	.70	8.8	.35	5.3	.15	3.5	9.2	130	---	---
TA-15	2.0	.57	10.3	.36	5.4	.21	4.9	13.3	188	---	---
TA-16	2.0	.53	9.5	.34	5.1	.19	4.4	11.4	161	---	---
TB-1	2.0	.44	7.4	.34	5.1	.10	2.3	---	---	---	---
TC-1	2.0	.46	7.7	.36	5.4	.10	2.3	---	---	---	---
TC-2	2.0	.48	8.0	.38	5.7	.10	2.3	---	---	---	---
TB-2	2.0	.59	10.0	.46	7.0	.13	3.0	13.6	192	---	---
TB-3	2.0	.62	10.4	.50	7.6	.12	2.8	6.9	97	2.0	16
TC-3	2.0	.36	6.2	.27	4.1	.09	2.1	12.2	172	1.5	12
TC-4	2.0	.46	7.7	.37	5.6	.09	2.1	5.5	78	3.0	24.2
Average ± Std. Dev.											
all data		9.4 ±2.7		6.3 ±2.0		3.1 ±1.3		156 ±44		19 ±6	
last four runs		8.6 ±2.0		6.1 ±1.6		2.5 ±1.50		135 ±56		17.4 ±6	

*Emission Factors in pounds pollutant per ton of fuel ignited.
^ANO_x emission factor = NO₂ emission factor + NO emission factor.
^Bas CH₄.
 **Needles were humidified.

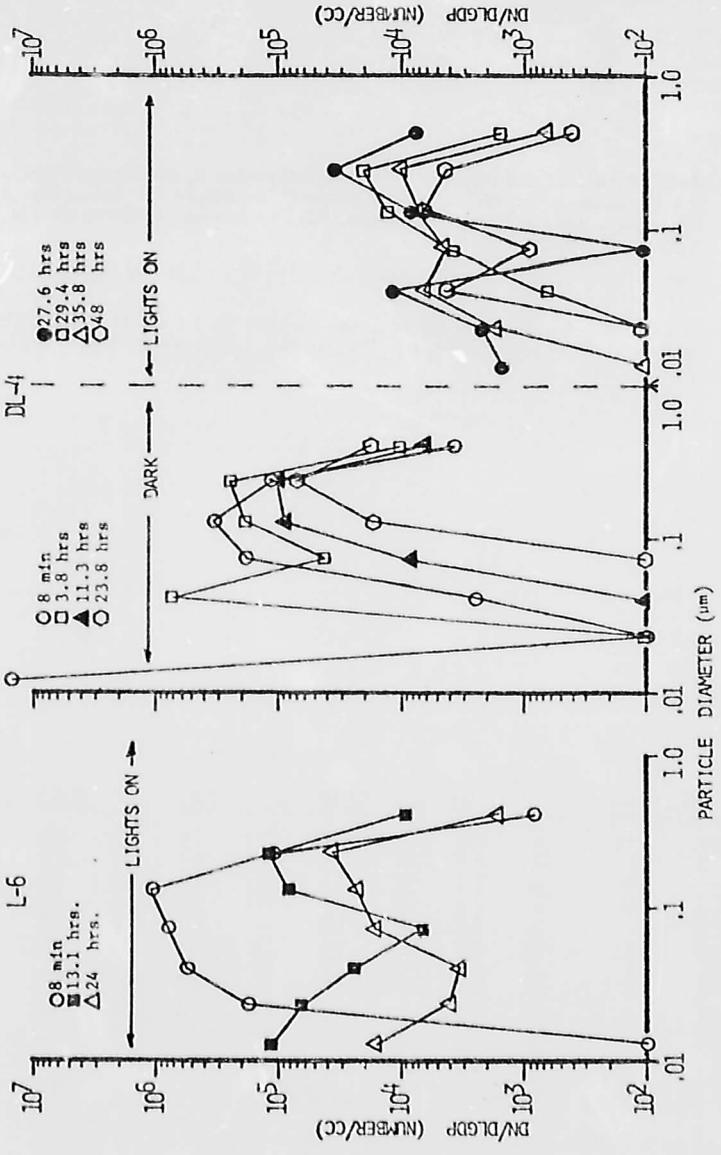
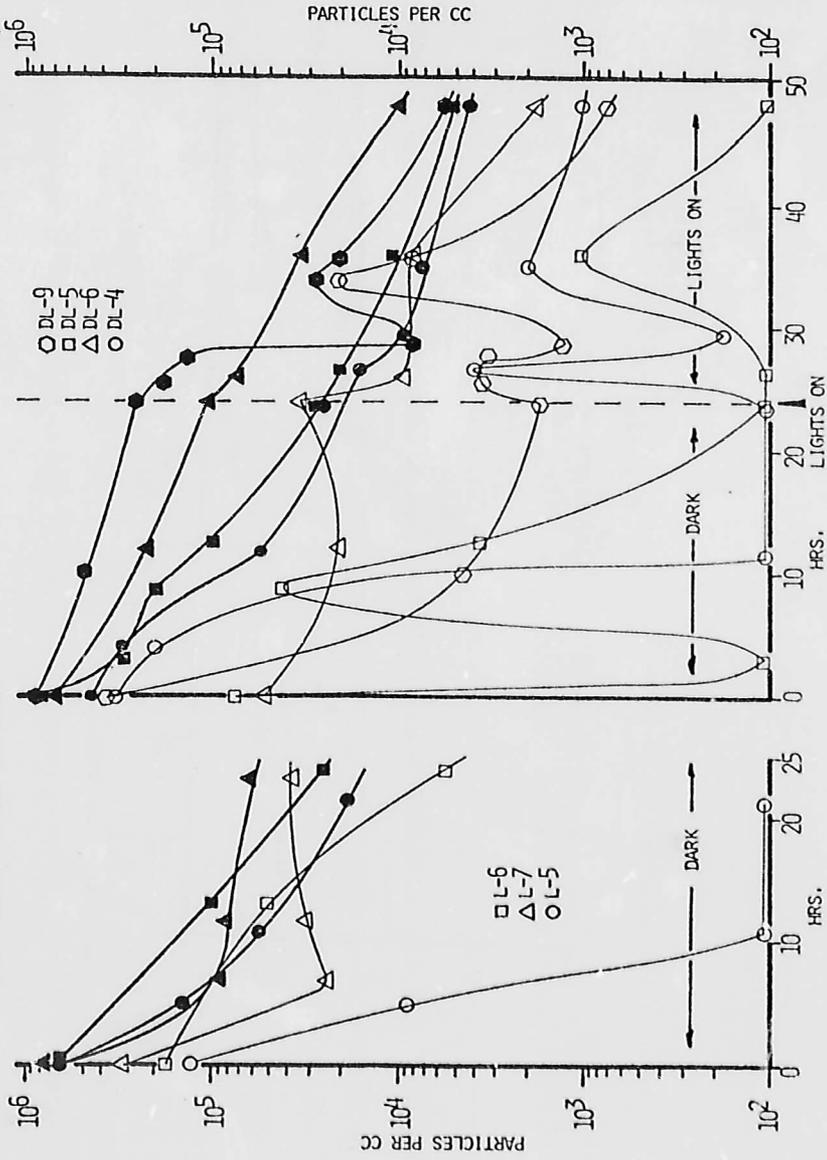
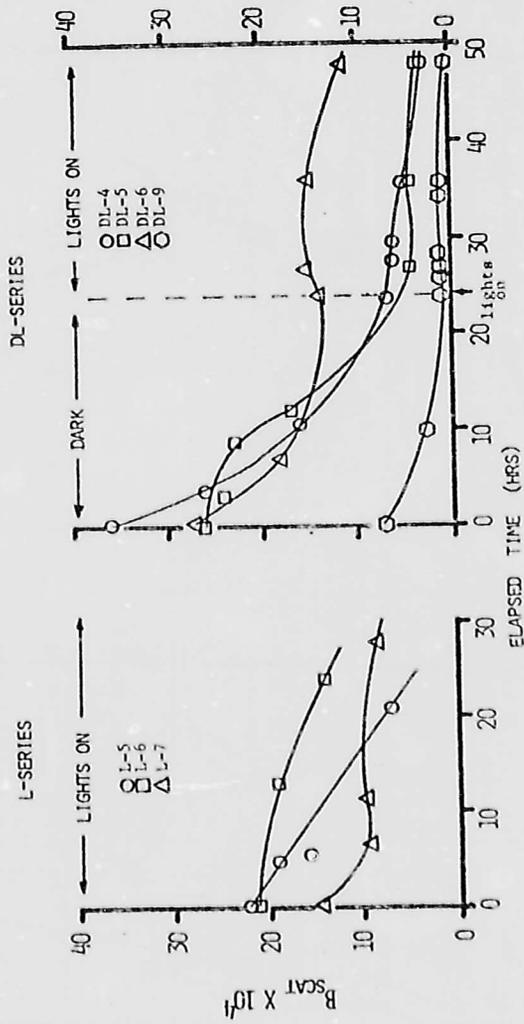


FIGURE 1. PARTICLE SIZE DISTRIBUTIONS AT VARIOUS TIMES.

FIGURE 2. NUMBER OF SUBMICRON AND SMALL ($<0.042\mu\text{m}$) PARTICLES VS. TIME. SOLID SYMBOLS = SUBMICRON, OPEN SYMBOLS = SMALL PARTICLES.



FIGURE 3. b_{scat} VS. TIME.

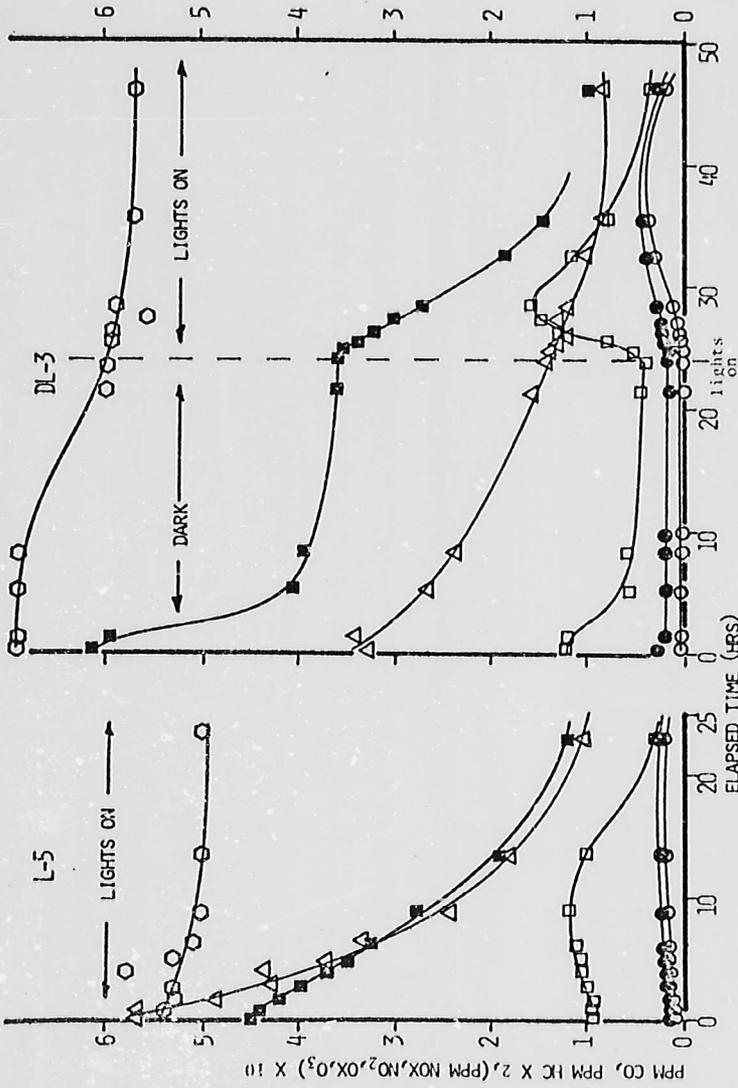


FIGURE 4. GAS PHASE COMPONENTS VS. TIME.