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MEASUREMENTS OF BACKGROUND HYDROCARBONS IN REMOTE AREAS,(U)
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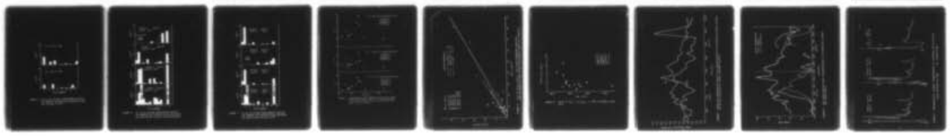

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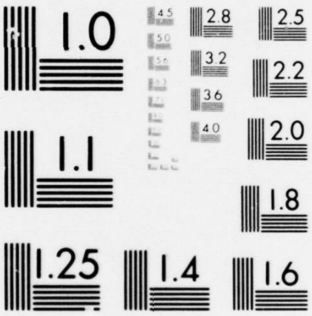

MICROCOPY RESOLUTION TEST CHART
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MEASUREMENTS OF BACKGROUND HYDROCARBONS IN REMOTE AREAS

(10)

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Volatile terpene, ozone, and condensation nuclei concentrations have been measured at a remote site in the Adirondack Mountains of New York State. Measurements were taken in a conifer forest, downwind of a conifer forest, and on a mountain summit above the tree line.

A wide variety of organic species were found. Some observations and speculations about the relationships among the organic species, condensation nuclei, and ozone are made.

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Introduction

Due to plant physiology, natural emissions of reactive hydrocarbons occur in evergreen forests. A variety of $C_{10}H_{16}$ isomers and closely related hydrocarbons, commonly called terpenes, are produced in significant amounts by conifers. In spite of the fact that such emissions are known to occur and studies have shown that terpenes are highly reactive species in laboratory smog studies, little study has been made on ambient levels and transport of these hydrocarbons.

Two important relations between terpenes and rural ozone levels should be considered: (1) these hydrocarbons are significant sources of free radicals which can initiate and propogate the chain mechanism reactions oxidizing NO to NO_2 subsequently producing ozone through photolysis reactions, and (2) the terpenes may react directly with ozone, producing organic oxidants which may undergo further reaction with ozone. Thus terpenes may have significant roles in the natural production and destruction of ozone.

Recent investigators[1,2,3,4] have shown that ozone levels in remote rural locations can significantly exceed federal air quality standards for extended periods and that such episodes occur with relative frequency. The source of the ozone, whether stratospheric or otherwise, is a matter of current debate; however, many authors believe that non-anthropogenic emissions are important precursors in ozone production[5,6,7].

Rasmussen[8] studied the rates of emission of terpenes from foliage in one-leaf assimilation chambers under varying intensities of light and temperature. Based upon the emission rates for various species and a global inventory of forested areas, he concluded that the natural sources emit more than six times the reactive hydrocarbons emitted by anthropogenic sources. Direct evidence concerning the chemical fate of these compounds in the atmosphere is lacking; however, there are strong indications that they are sources for ozone and natural aerosol[5]. Another possibility is that biological removal by plant fungi and soil is an important sink for terpenes[8]. Evidence does exist that the terpenes are highly reactive chemically; all of the olefinic terpenes are more reactive than isobutene[9].

It has been suggested that the blue heat or summer haze, so common over vegetive land masses, has its origin in a similar photochemical transformation of volatile organic matter emanating from plants; that is, similar to the photochemical transformation of olefins and other organic volatiles[10]. During the summer and autumn, considerable amounts of terpenes are released by the vegetation; in autumn, leaf litter becomes a major source of aromatic substance. Upon the death of cells, large amounts of terpenes are released. High concentrations of organic volatiles occur during periods of increased number of dying cells. In the presence of ozone, the blue haze is formed[10].

The olefinic hydrocarbons released to the atmosphere by plants can be expected to have short residence times. This hypothesis gains support from preliminary studies which have shown extremely low terpene hydrocarbon (C_{10}) levels in rural air. Further studies suggest the importance of examining products (addition and fragmentation) from these terpenic hydrocarbons since they should be plentiful constituents of natural forest air[9].

Because of the importance of these hydrocarbons to the air quality of rural areas and lack of data on the levels at which they are found, this study was undertaken to investigate terpene and ozone levels.

Study Location

The site selected for this investigation was Whiteface Mt. (4,867 ft.) in the Adirondack Mountains of northeastern New York State (see Figure 1). The mountain has a conifer forest region beginning at approximately 3,000 ft. altitude as balsam fir, mixing with an increasing percentage of red spruce as altitude increases. Above 4,500 ft., the trees are essentially all red spruce. The trees are of normal heights as the forest begins, but are stunted with increasing altitude. The tree line is approximately 300 ft. below the summit. A sampling site was established at the Whiteface Mt. Field Station, Marble

Lodge (1,980 ft.), of the Atmospheric Sciences Research Center of the University at Albany. This site was below the conifer forest, but the prevailing winds placed the site downwind from the forest. Samples were taken directly at this site and also collected in the forest along Whiteface Mt. Road, which runs to the summit (see Figure 1). Samples along Whiteface Mt. Road were collected in evacuated glass containers and returned to the Marble Lodge site for analysis.

Data collected by the New York State Department of Environmental Conservation at Glens Falls and Albany are also included. Glens Falls is located in the Hudson River Valley, approximately 80 miles south of Whiteface Mt. at an elevation of 330 ft. above sea level. Albany is located in the Mohawk and Hudson River lowlands, Figure 1 (insert).

Equipment

A Carle Analytical Gas Chromatograph, Model 211, was modified to house two Carle micro-volume sampling valves (Model 2014) and two Carle mini-volume switching valves (Model 5518). The micro-volume valves allowed for sample injection via dual sample loops (110 ml and 114 ml) and for column switching. The mini valves were used to switch a sample cold trap in and out of line and to inject 1.1 cc calibration samples. The valves were operated by Carle Model 4200 valve actuators in conjunction with a Carle Model 4100 Valve-Minder system which could sequentially operate the valves at selected time intervals and an electronic switching device which was fabricated to allow for individual valve actuation as desired.

The analytical columns employed were prepared by Carle Instruments (stock number 0341). Two columns of identical specifications were used with valving designed so that one column was on line to the detector and the other in a vented backflush mode. The columns were 6 ft. x 1/8 in. O.D. stainless steel, 8% OV-101 on Carle AWDMCS diatomite support, 80/100 mesh. The detector was a flame ionization detector located within the column oven, thus operating at column oven temperature (70°C). Detector output was monitored by a Hewlett-Packard Model 3380-A electronic reporting integrator. All gases were supplied by Linde Specialty Gases (Union Carbide) and were ultra high purity grade. Carrier helium at 65 cc/min, hydrogen at 17.5 cc/min, and oxygen at 300 cc/min were supplied to the detector. The carrier helium was passed through a 6 ft. x 1/8 in. O.D. S.S. trap immersed in liquid nitrogen to remove hydrocarbons prior to entering the chromatograph flow system.

Two sample loops were constructed of 15 ft. x 1/4 in. O.D. S.S. tubing supplied by Applied Science Laboratories (acetone and chloroform washed and oven heated overnight at 120°C). The loop volumes were measured by their liquid capacity as 110 and 114 ml. Ambient samples were introduced to the loops by one of two modes: (1) ambient samples at Marble Lodge were drawn through the loops from a Teflon sample line (10 ft. x 1/8 in. O.D.), terminating 12 ft. above ground level, by a pump at a rate of 250 cc/minute; (2) ambient samples from Whiteface Mountain Road were collected under positive pressures in glass containers; and 150 to 200 cc of sample was injected into the evacuated (1 mm mercury) loop, the excess amount flushing the loop and venting to the atmosphere.

Letter on file

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Since laboratory studies had shown some wall losses at ambient temperature, the sample loops were wrapped with heating tape, insulated, and maintained at an elevated temperature which was monitored prior to each analysis. An acceptable temperature range was determined to be 75-90°C.

The cold trap tubing (3 ft. x 1/16" O.D. S.S.) was shaped to form a horizontal 1.5 inch diameter coil from the middle of 1.5 ft. of tubing, with the vertical 9 inch lengths connected to the trap switching valve. The entire 3 feet of tubing was located exterior to the chromatograph to allow for immersion into a dewar of liquid nitrogen. The trap was wrapped with glass fiber tape for electrical insulation and then wound with nichrome wire. A variable voltage supply provided an adjustable current, 0 to 2.0 amps., to the nichrome wire to effect rapid heating of the trap prior to injection. Trap temperature was monitored by an iron-constantan thermocouple and a Simpson 3324 pyrometer which was calibrated against a millivolt potentiometer for normal and reverse connections over a temperature range of -190°C to +150°C. The 1.1 cc calibration loop, used to inject high concentration calibration samples, was internal to the chromatograph but was not located in the oven. Calibration loop temperature was maintained in the same fashion as the sample loops and monitored on the Simpson pyrometer.

An in-line filter to remove ozone from the sample was considered; however, our experiences with calibration samples and the wall losses led us to believe that a filter would cause significant surface losses in ambient samples. In a test for reactive losses due to ozone, calibration samples prepared at the low parts per billion level in ambient air containing 50-60 ppb ozone and in nitrogen (0 ppb ozone) showed no significant difference.

To minimize wall losses in the sample loops, the trap temperature was maintained at 75-90°C; and to minimize any reactions at this elevated temperature, the sample was flushed from the loop to the cold trap was rapidly as possible. The estimated length of time in the trap was about 30 seconds for the front portion of the sample and two minutes for the rear portion (assuming a slug injection).

Since levels were anticipated on the order of 1 ppb, a 10 ml sample loop was initially used and direct injections without the use of a cold trap were attempted. With this procedure, the terpene concentrations at Marble Lodge were only trace or unobservable. If several 10 cc injections were trapped; however, then terpenes were observed. Therefore, the 10 ml sample loops were replaced by the previously described 110 and 114 ml loops.

Procedure

To analyze ambient samples, the sample loop was filled by either drawing air through the loop with a pump for Marble Lodge samples, or by flushing an evacuated loop with a pressurized sample collected on Whiteface Mt. Road. The sample valve was then actuated to inject the sample into the carrier stream and on to the cold trap at -170 to -180°C, the temperature being maintained by a liquid nitrogen dewar and monitored by the thermocouple-pyrometer system. A period of about five minutes was allowed to insure complete flushing of the sample from the loop to the trap. The time was also necessary to allow the air (and untrapped light organics) which passed through the trap, to pass completely from the analytical column and for the baseline signal to recover. The trap was then isolated and quickly heated to 150°C (approximately one minute). The trap valve was then actuated to inject the contents of the trap to the analytical column. Following the analysis period of about 15 minutes, the column switching valve was actuated to backflush the column and place the freshly purged column in line.

Calibration samples were prepared by the injection of liquid terpene samples into evacuated glass cylinders and then pressurizing the cylinder with nitrogen. The liquid terpenes (α-pinene, β-pinene, and p-cymene) were obtained from Theta Corp. at 98%+ purity and from Eastman Organic, practical grade (α-phellandrene, d-limonene). A 10μl syringe was used to inject from 0.2 to 1.0 μl of liquid terpene into an evacuated (< 1 mm Hg) 278 ml galss cylinder via a silicone septa injection port in the cylinder. The terpene sample immediately vaporized in the cylinder which was then pressurized with nitrogen to two atmospheres absolute pressure. The concentraiton of terpene in the cylinder was typically in the 50 to 200 ppm range. Individual cylinders containing one or two terpenes were prepared and a further dilution was made by injecting 2 to 10 cc of gas from each cylinder into an evacuated 1105 ml glass flask via a glass syringe through a silicon septa. Pressurization of this cylinder to two atmospheres with nitrogen resulted in concentrations of several hundred parts per billion or about 1 to 5 ng/cc of individual terpenes. This gas could be directly injected via the 1.1 ml calibration loop or further diluted in a 20 cc syringe and injected to give various calibration levels. Instrument sensitivity was in the order of 20 pg. The sample and calibration loop temperatures were monitored for each analysis and all volumes reduced to a standard 25°C volume using ideal gas laws. All data is reported in $\mu g/m^3$ at 25°C.

Results

Analysis of ambient air samples produced from two to twelve chromatographic peaks in the time period two to thirteen minutes following the cold trap injection. During the first two minutes, several unresolved peaks were observed which were assumed to be residual light hydrocarbons or air which was partially retained by the cold trap. The large detector response to these compounds resulted in a "solvent type" tailing baseline during the elution of peaks of interest. This presented no problem to the determination of peak areas, however, as the integrator made a "tangent skim" calculation where necessary.

Due to the use of two columns and the field location of experimental equipment without control of ambient laboratory conditions, absolute retention times (ART) were quite variable. Statistical tests (t-test for significance of difference between means of sample groups) were made to compare calibration and ambient peak absolute retention times, and one ambient peak was accepted to have the same absolute retention time as β-pinene. Since this was the most frequently observed ambient peak, it was used as the base to determine relative retention times (RRT). The RRT values had low standard deviations which allowed the identification of seventeen distinct ambient peaks by number. Three peaks were found to have retention times which were not statistically different from calibration times: β-pinene (mean ART = 8.37 min) and ambient peak number 12 (mean ART = 8.54); p-cymene (mean RRT = 1.260) and ambient peak 15 (mean RRT = 1.245); α-phallendrene and d-limonene, unresolved (mean RRT = 1.390) and ambient peak 16 (mean RRT = 1.373). Caution must be emphasized in identifying the peaks as these compounds, however, due to our very limited number of calibration species and the variety of terpene isomers. An unexpected result was the lack of an ambient peak with a relative retention time statistically comparable to α-pinene (mean RRT = .770). Peak number 10 (mean RRT = .804) is close, but the t-test rejects the null hypothesis. It is possible that α-pinene and another closely eluting specie are not completely resolved, and thus peak 10 is in part α-pinene. Due to the variable conditions of temperature and other ambient factors, calibration and ambient samples were not able to be run under uniform parameters. The use of relative retention times alleviates much of the variation, but analysis conditions may be somewhat biased so that the simple t-test is too strict. Even if we were to assign an α-pinene identification to peak 10, the observed values (0.15-6.46 $\mu g/m^3$) are relatively low considering other investigators have found this to be a major peak.

Quantitative analysis was based on average response factors of the five calibration terpenes and was applied to all seventeen ambient peaks. Table 1 presents the relative retention times, observed concentrations, and RRT statistical data for ambient samples at the Marble Lodge and Whiteface Mt. Road sites.

Figures 2 through 7 show the chromatographic "spectra" of ambient samples on the OV-101 column at the Marble Lodge and Whiteface Mt. Road sites. At Marble Lodge, the most frequent observed peaks were 2, 8, 10 and 12 with individual observations of high concentrations of 9, 11 and 16. Along Whiteface Mt. Road (WFMR), the most frequently observed peaks were 1, 2, 6, 12 and 15 with some high observations of peaks 3 and 15. Thus, it appears that the composition of hydrocarbons outside the pine forest region is significantly different than within its boundaries. Differences could be due to additional non-conifer forest emissions at the Marble Lodge site or chemical reactions during advection.

Total observed levels of organics along WFMR and at ML were similar on 8/9/75 except at WFMR-C. Levels on 8/10/75 were higher along WFMR. Of interest is the fact that significant levels of organics were observed at WFMR-E which is above the tree line and about 200 ft. below the summit.

Figure 8 presents the total observed concentrations at ML plotted against time of day. The peaks are divided into early and late eluting species somewhat arbitrarily at peak 7 under the assumption that the later peaks were terpenes and the earlier peaks were terpene fragmentation and reaction products (since the earlier peaks eluted well before the calibration terpenes). The total of peaks 1 through 7 (ΣP_{1-7}) and peaks 8 through 17 (ΣP_{8-17}) are also plotted against time. The data sets all show an afternoon maximum during the 1300-1500 hour time period. The distributions may be considered approximately Gaussian with a sharp central tendency. The linear correlation of concentration to a Gaussian function of time of the form $A\ e^{-(t-t_o)/2} + B$ was high (R = .87 to .89).

In Figure 9, ΣP_{1-7} and ΣP_{8-17} show strong linear correlation for the six samples obtained along WFMR; however, the correlation is weak for ML samples. The ratio of ΣP_{1-7} to ΣP_{8-17} vs time for ML samples is plotted in Figure 10. Although somewhat scattered, the available data seems to indicate a decaying ratio. This data is compatible with the premise that ΣP_{1-7} represents the products of terpene-ozone reactions. The correlation is strongest near the terpene source and weaker away from it where additional sources and survival characteristics of individual species will influence the data to a greater extent. Furthermore, the early morning ratio of ΣP_{1-7} to ΣP_{8-17} would be expected to be high due to dark phase reactions. With increasing sunlight and temperature during the day, oxidation products would be subject to photolysis and foliage would emit increasing amounts of terpenes, decreasing the ratio.

Considering the data for the four study dates as representative, we may estimate total terpene concentrations (ΣP_{8-17}) to be in the 10-45 $\mu g/m^3$ range within the conifer region of the forest. Furthermore, assuming ΣP_{1-7} represents terpene reaction products, 20-80 $\mu g/m^3$ of these species may also be present. Outside the conifer region of the forest these organics are found in reduced concentrations on the order of 2-20 $\mu g/m^3$ and 5-25 $\mu g/m^3$ respectively. These levels may be significant in the formation of ozone through reactions with NO_2 and sunlight. Additionally, terpene-ozone reactions may result in the production of condensation nuclei. Possible evidence for these processes is given in Figure 11, which presents the hourly average ozone and CN concentrations at Whiteface Mt., and Figure 12 which compares ozone at other regional stations. The afternoon maximum ozone concentration on August 9 at Whiteface Mt. reached 80 ppb, exceeding the Albany maximum by 17 ppb and the Glens Falls maximum by 30 ppb. The excess ozone at Whiteface Mt. compared to Albany and Glens Falls may be partially due to terpene reactions. This does not mean that such rural forest regions will always have higher ozone maxima, however, as indicated by data for August 10. Ambient conditions and NO_2 concentrations, for instance, will also influence ozone formation. The production of aerosol through terpene-ozone reactions may be indicated by the late maximum CN concentrations of August 9 and 11 (Figure 11). Alternative explorations are possible; however, our results suggest that ozone and CN data may be examined with respect to conditions conducive to terpene emissions to further study possible terpene-ozone reactions leading to production of aerosol.

Acknowledgment

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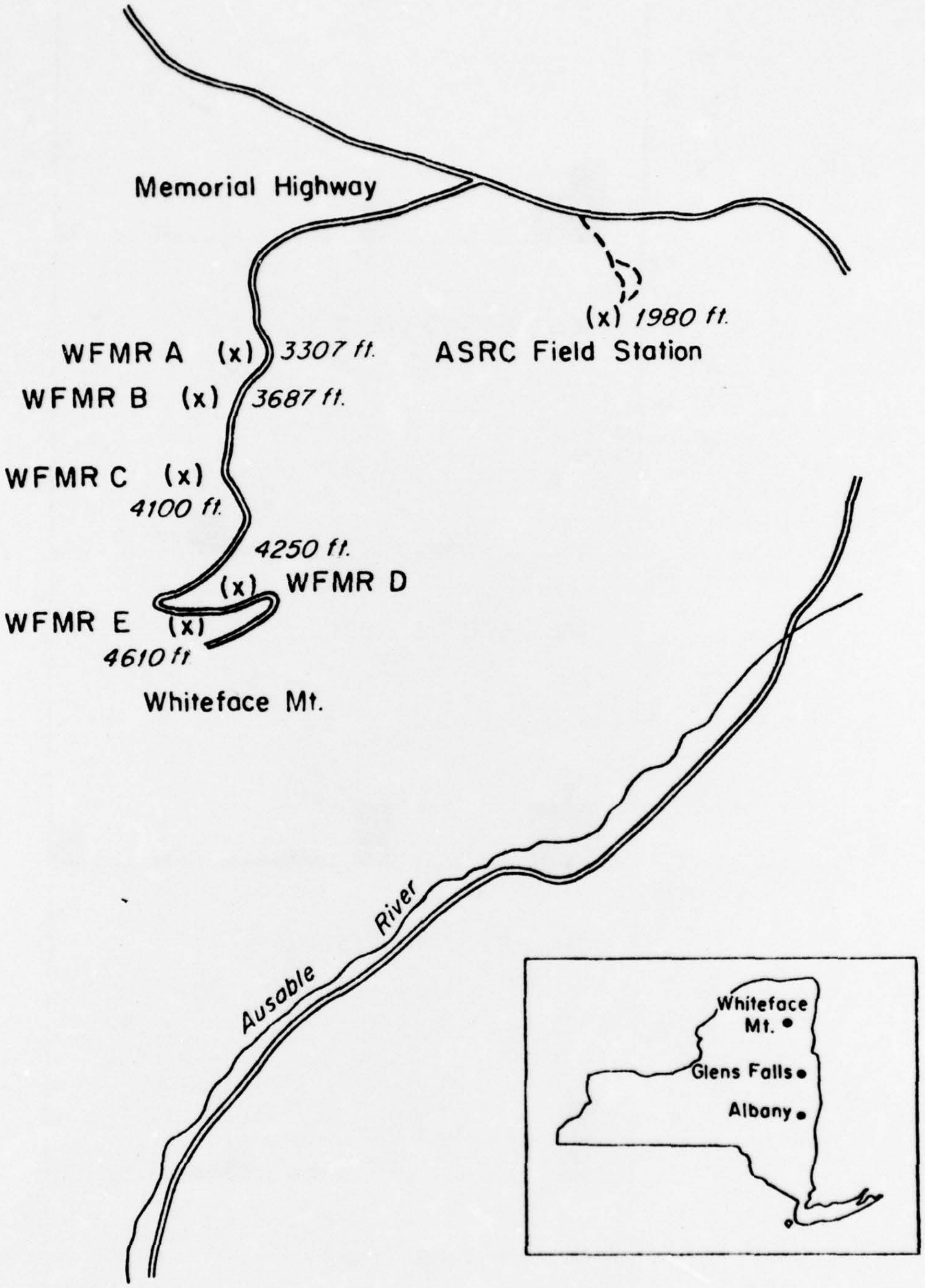

FIGURE 1 WHITEFACE MOUNTAIN ROAD (MEMORIAL HIGHWAY) SHOWING LOCATION WHERE DATA WERE TAKEN, AND (INSERT) NEW YORK STATE MAP LOCATING WHITEFACE MT., GLENS FALLS AND ALBANY.

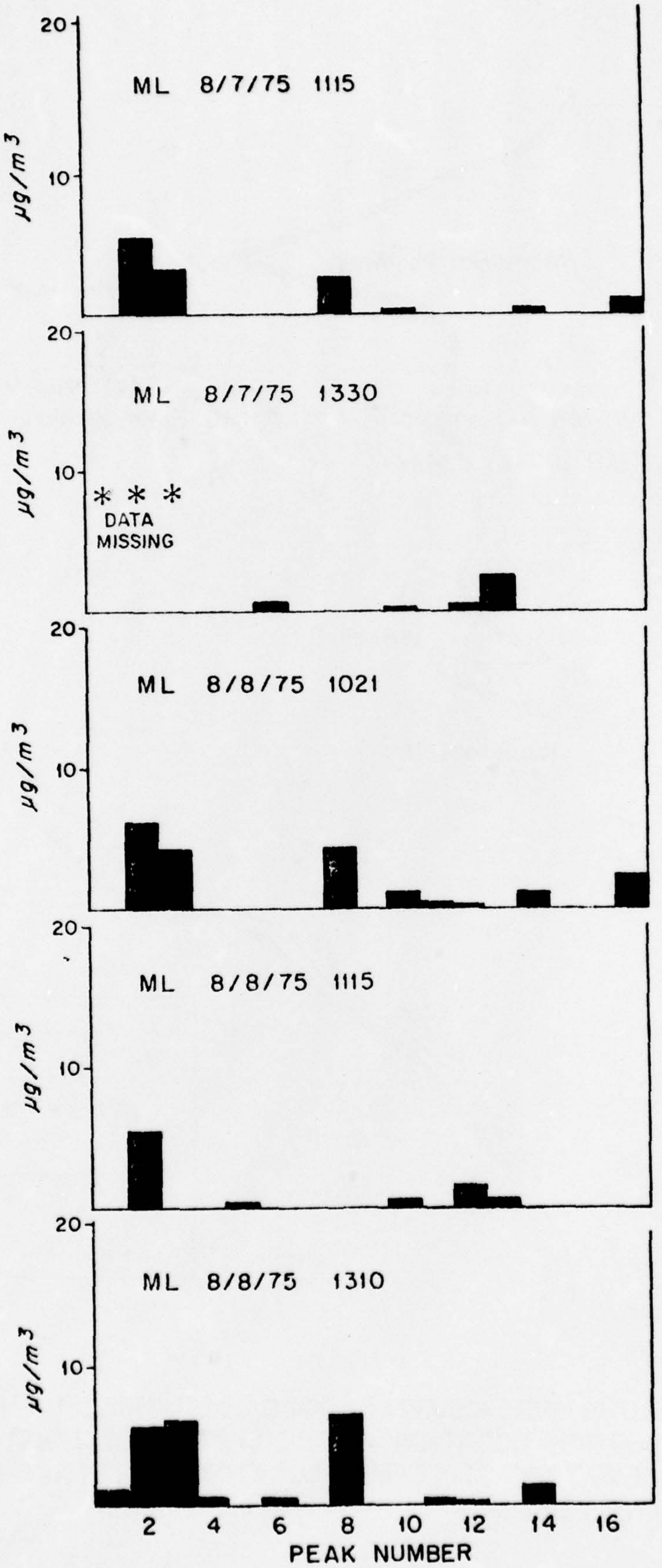

FIGURE 2 OV-101 GC COLUMN HYDROCARBON SPECTRA FOR AMBIENT AIR SAMPLES AT MARBLE LODGE SITE ON AUG. 7-8, 1975.

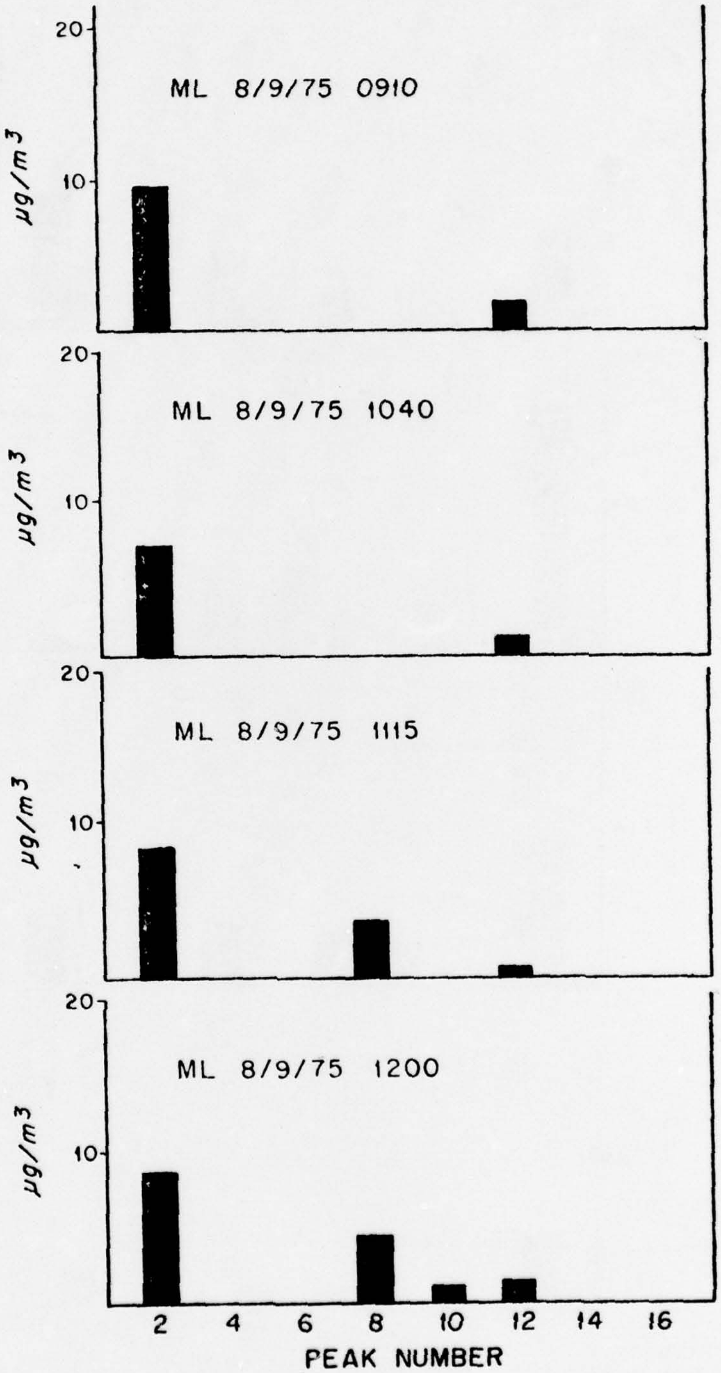

FIGURE 3 OV-101 GC COLUMN HYDROCARBON SPECTRA FOR AMBIENT AIR SAMPLES AT MARBLE LODGE SITE ON AUG. 9, 1975 (MORNING).

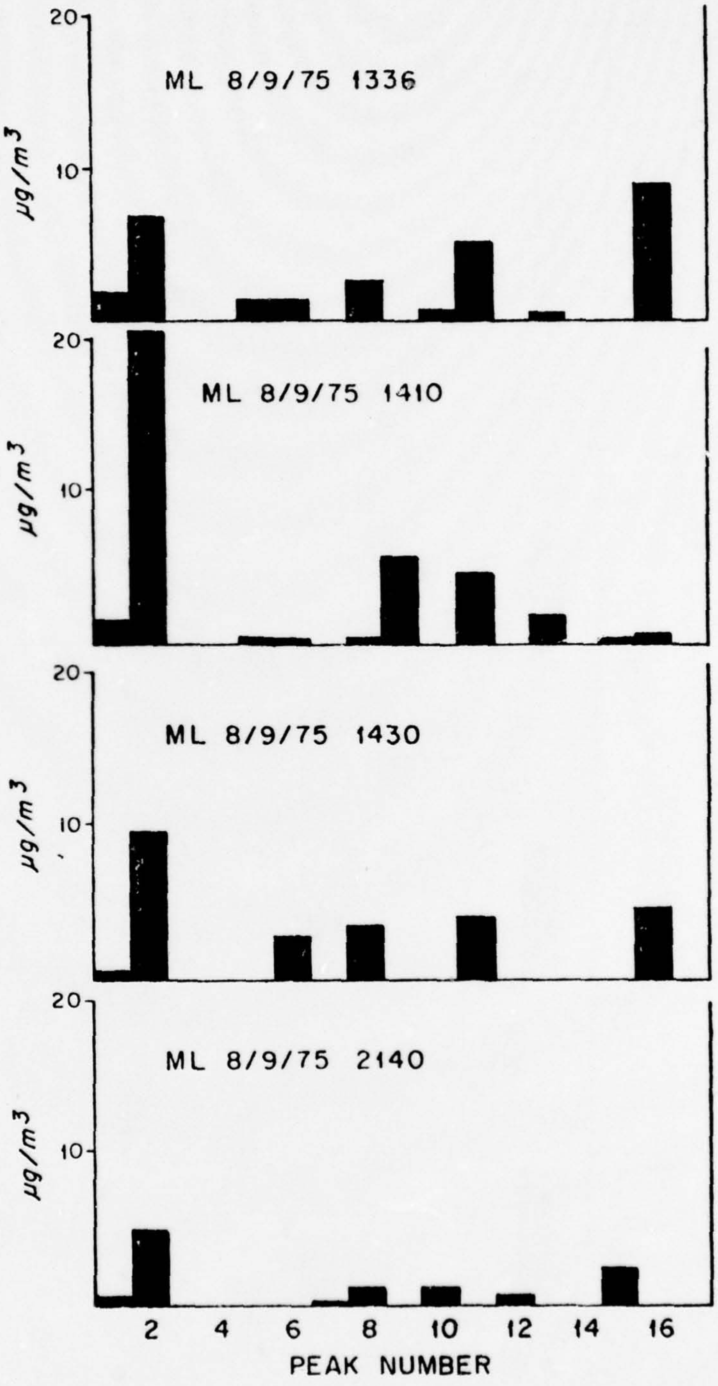

FIGURE 4 OV-101 GC COLUMN HYDROCARBON SPECTRA FOR AMBIENT AIR SAMPLES AT MARBLE LODGE SITE ON AUG. 9, 1975 (AFTERNOON).

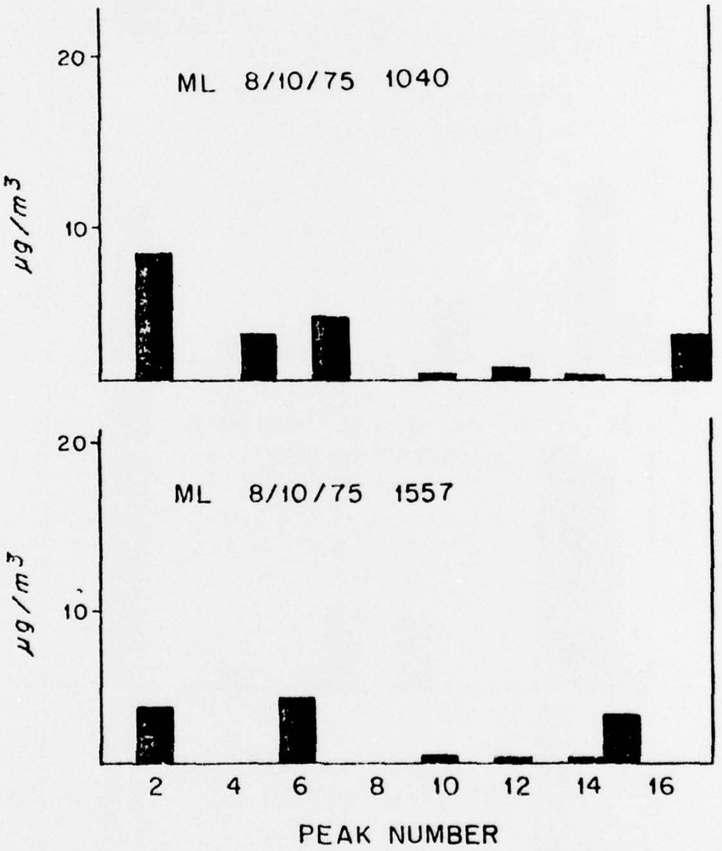

FIGURE 5 OV-101 GC COLUMN HYDROCARBON SPECTRA FOR AMBIENT AIR SAMPLES AT MARBLE LODGE SITE ON AUG. 10, 1975.

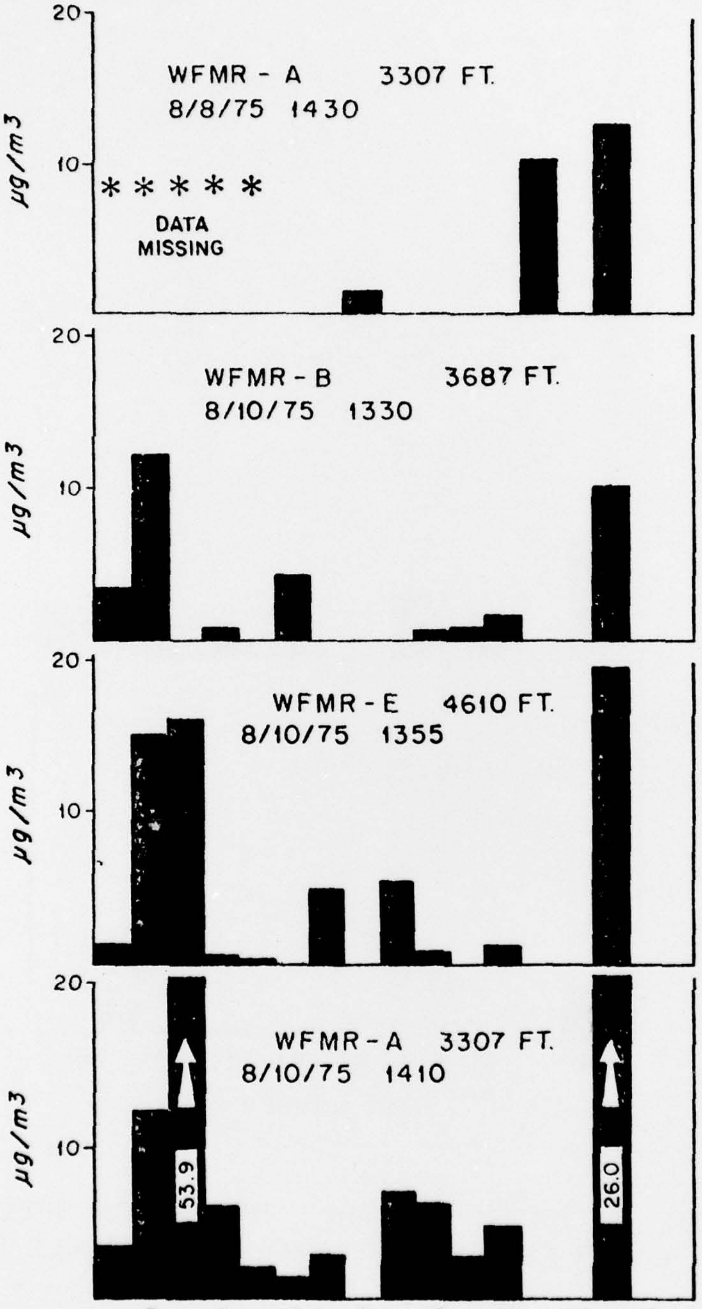

FIGURE 6 OV - 101 GC COLUMN HYDROCARBON SPECTRA FOR AMBIENT AIR SAMPLES ALONG WHITEFACE MT. ROAD (WFMR) ON AUG. 8 AND AUG. 10, 1975.

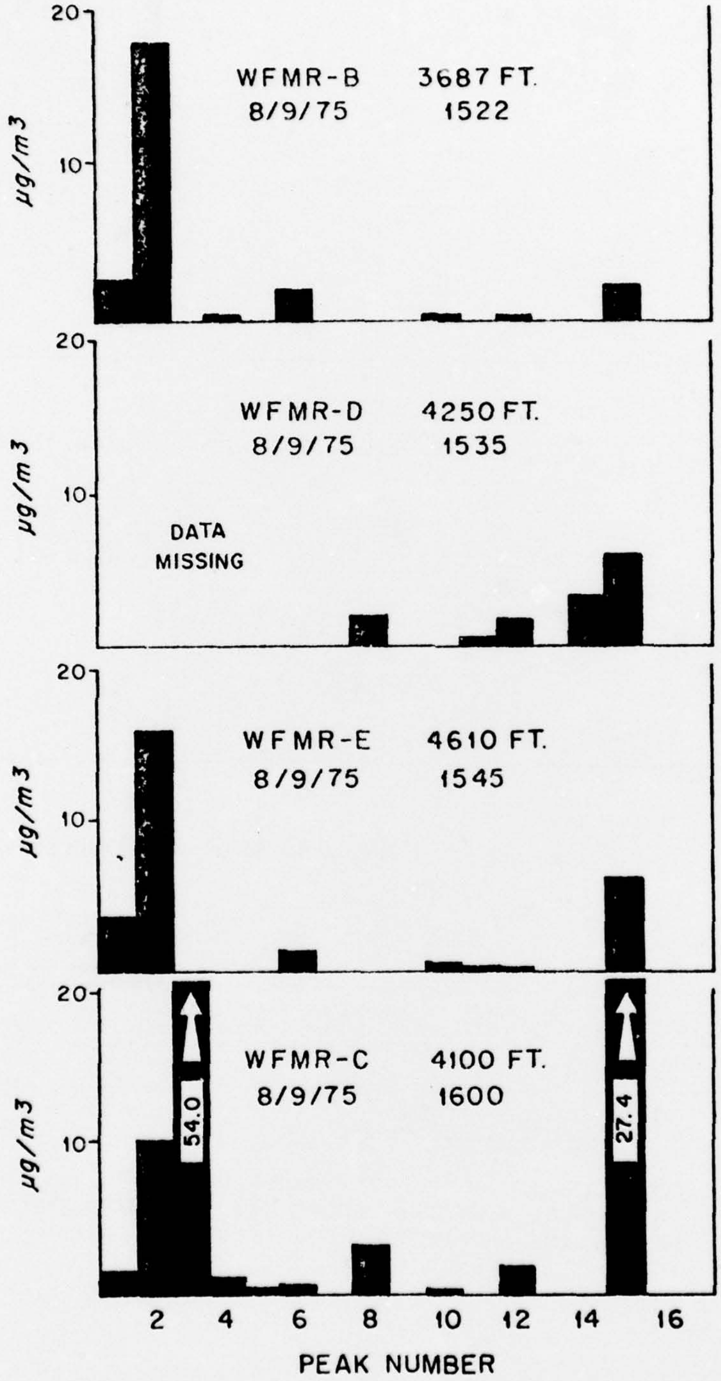

FIGURE 7 OV-101 GC COLUMN HYDROCARBON SPECTRA FOR AMBIENT AIR SAMPLES ALONG WHITEFACE MT. ROAD (WFMR) ON AUG. 9, 1975.

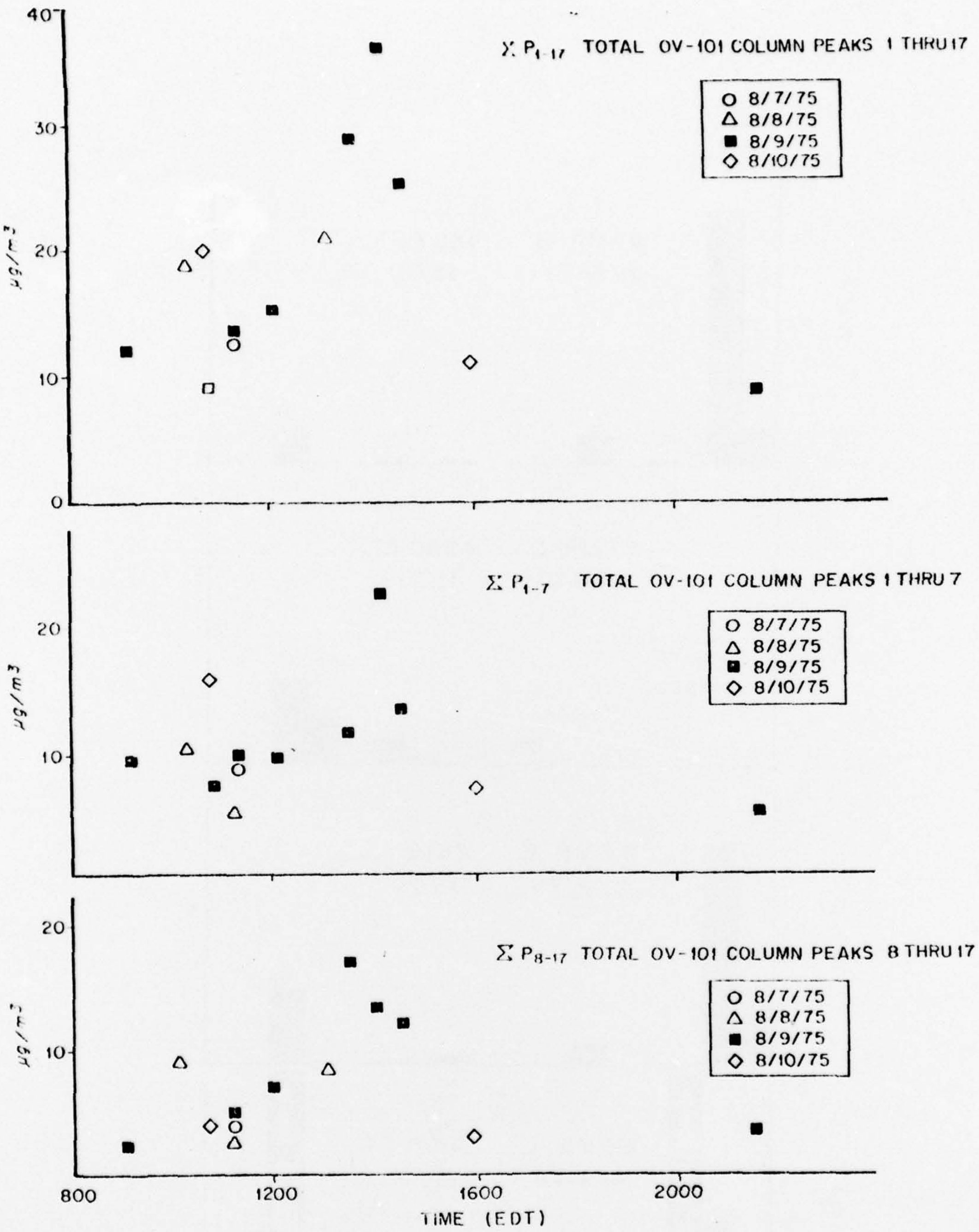

FIGURE 8 CONCENTRATION OF HYDROCARBONS ELUTED ON OV-101 COLUMN AS OBSERVED AT MARBLE LODGE SITE vs. TIME OF DAY (TOTAL OF ALL OBSERVED PEAKS, TOTAL OF EARLY FRACTION, AND TOTAL OF LATE FRACTION). [16]

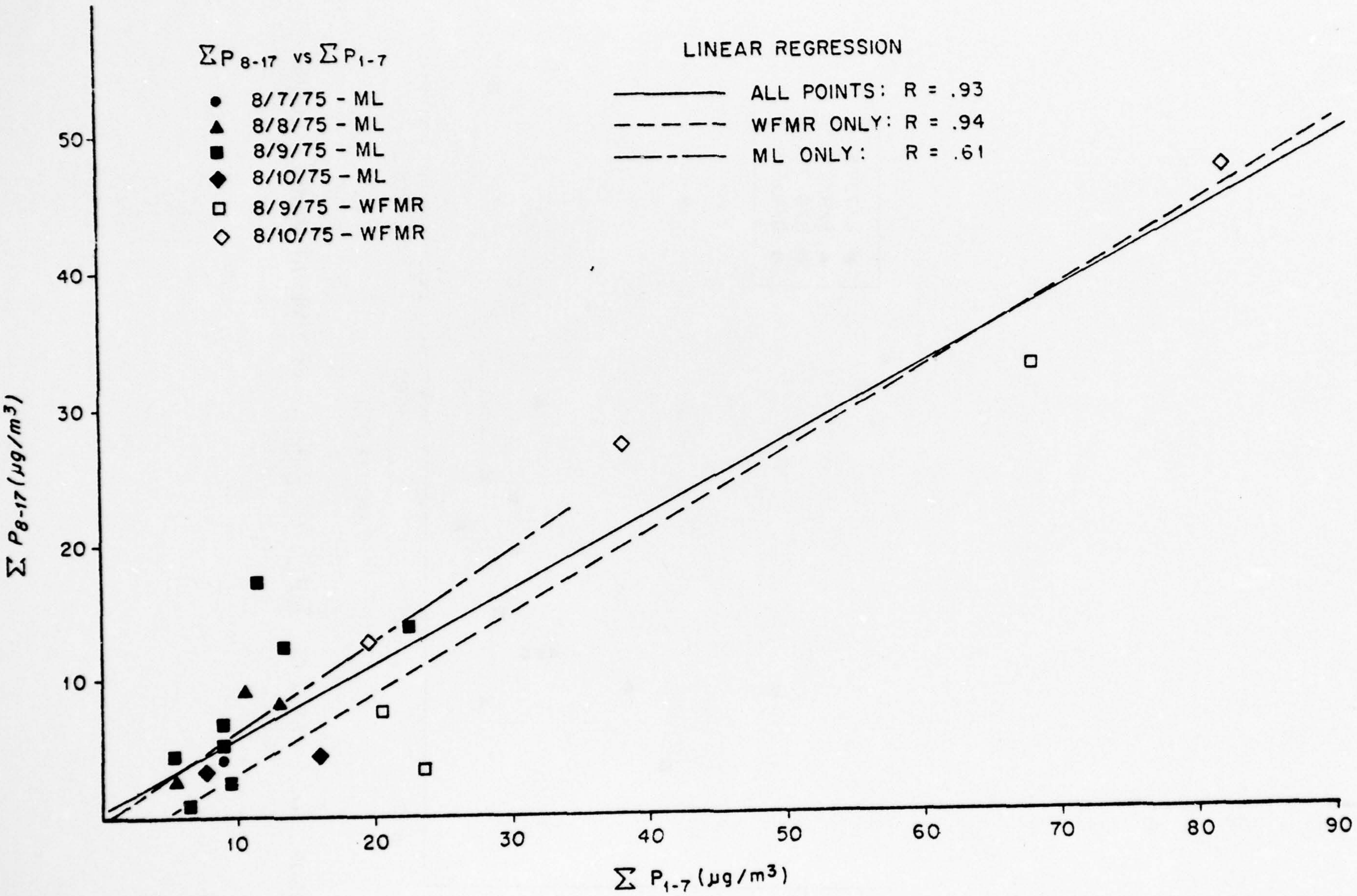

FIGURE 9 PLOT OF ΣP_{8-17} vs ΣP_{1-7} AND LINEAR REGRESSION EQUATIONS FOR WHITEFACE MT. ROAD (WFMR) AND MARBLE LODGE (ML) SAMPLES.

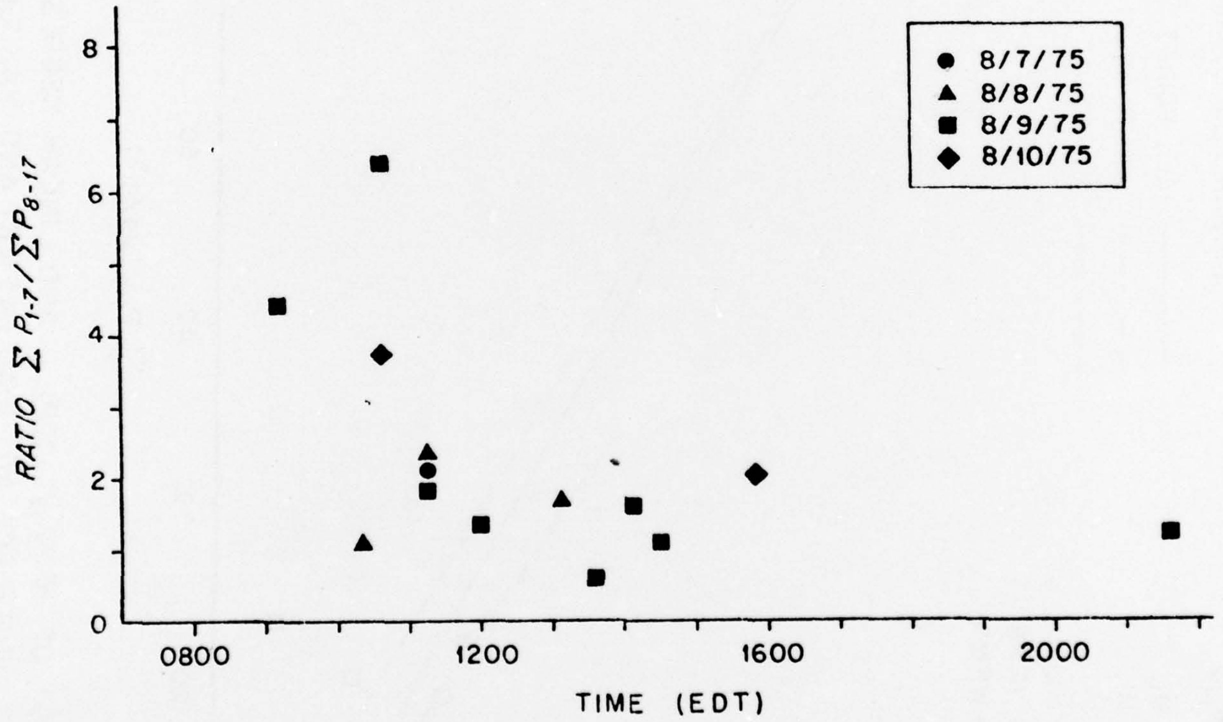

FIGURE 10 RATIO OF $\sum P_{1-7}$ TO $\sum P_{8-17}$ vs TIME AT MARBLE LODGE SITE.

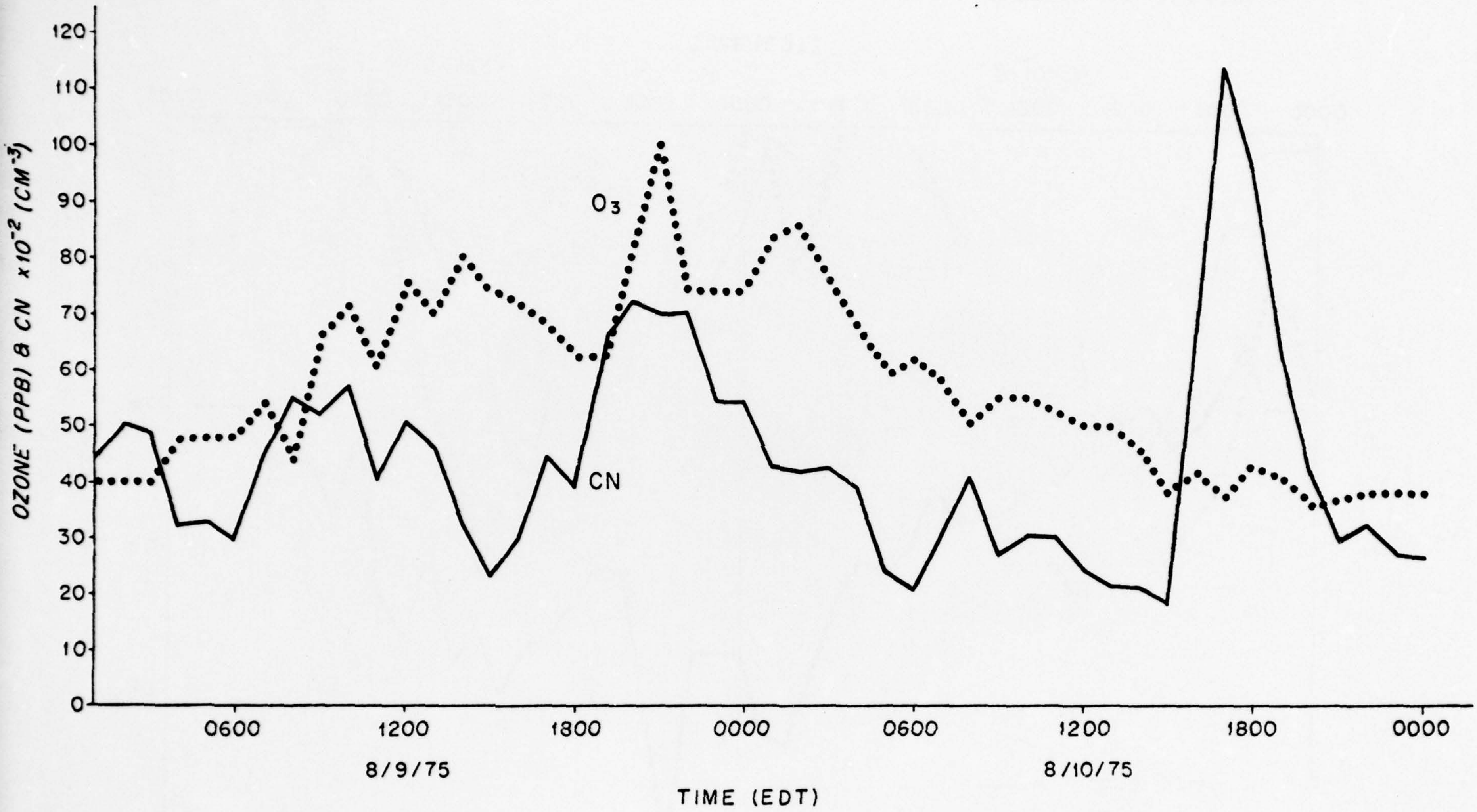

FIGURE 11 OZONE AND CONDENSATION NUCLEI (CN) CONCENTRATIONS AT WHITEFACE MT. SUMMIT STATION ON 8/9/75 AND 8/10/75 (HOURLY AVERAGE VALUES).

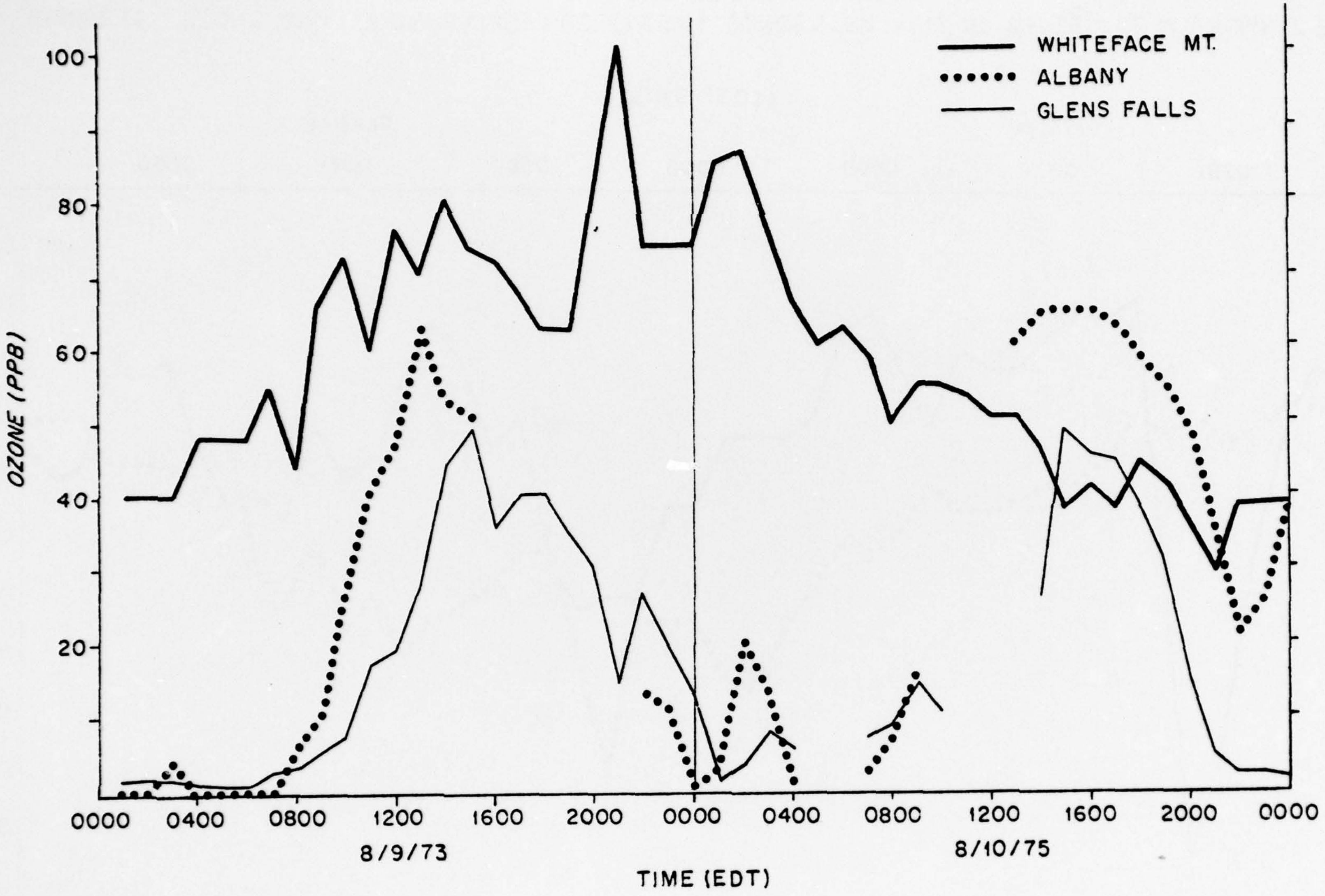

FIGURE 12 ONE-HOUR AVERAGE OZONE CONCENTRATIONS AT WHITEFACE MT., ALBANY AND GLENS FALLS.

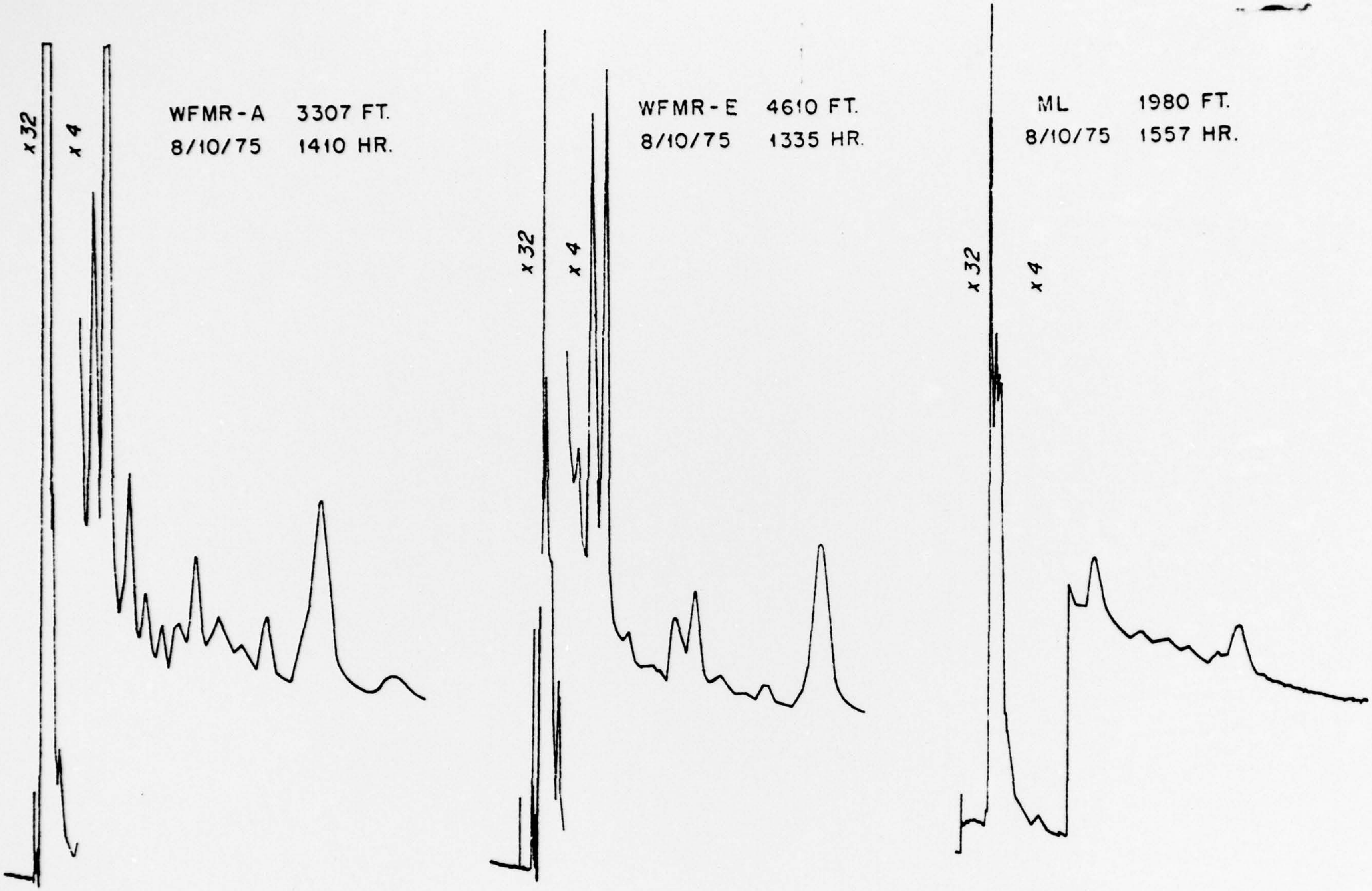

FIGURE 13 REPRESENTATIVE AMBIENT CHROMATOGRAMS AT WHITEFACE MT. ON 8/10/75.

WFMR = WHITEFACE MT. ROAD ML = MARBLE LODGE