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Summary of Measurement Results of Ozone, Methane, and Nonmethane Hydrocarbons for C-54 Aircraft: 1979 Southeastern Virginia Urban Plume Study

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Scientific and Technical Information Branch

SUMMARY

Methane, nonmethane hydrocarbon, and ozone data collected in a C-54 aircraft during the 1979 Southeastern Virginia Urban Plume Study are presented in this report. Three major aircraft experiments were flown on 5 separate days in August that involved the acquisition of about 20 hr of actual flight data. The purpose of each experiment, along with a discussion of the attending meteorology, is presented. Data collected on constant-altitude flight legs, along with data collected during aircraft spirals, are reported and discussed. Direct correlation between ozone and hydrocarbon plumes was observed on several occasions.

INTRODUCTION

Methane (CH₄) nonmethane hydrocarbon (NMHC), carbon monoxide (CO), and ozone (O₃) concentrations were measured from a C-54 aircraft platform in August as part of the 1979 Southeastern Virginia Urban Plume Study (SEV-UPS) (ref. 1). Since tropospheric concentrations of ozone, carbon monoxide, and hydrocarbons are frequently used as indicators of the photochemical activity of polluted air masses, measurements of these trace gases are of environmental significance. Thus, concentrations of these gases were measured as part of the SEV-UPS program. The carbon monoxide data, which were collected with a short-path infrared tunable-diode-laser system during these flights by other researchers, were not resolved at the time of this report.

The 1979 SEV-UPS program was conducted to further develop the understanding of tropospheric photochemistry, particularly those aspects that might lend themselves to study through the use of remotely sensed data. Previous phases of the SEV-UPS program had been conducted during the summers of 1977 (ref. 2) and 1978 (refs. 3 and 4). Although the SEV-UPS experiments were generally designed to evaluate remote sensors, many supportive in situ measurements were required for sensor evaluation.

Three major SEV-UPS experiments involving about 20 hr of data acquisition were flown with the C-54 aircraft. Data sets from other aircraft (as well as from ground stations) that participated in the 1979 SEV-UPS experiment are available in other reports (refs. 5 to 7). A brief description of the southeastern region of Virginia, its climatology, and a discussion of each of the flight experiments follows. A more detailed coverage can be found in reference 5.

The southeastern Virginia area, approximately 36.8° N and 76.4° W, is located on the east coast. (See fig. 1). It is centered around Hampton Roads, which is one of North America's largest natural harbors. The cities of Norfolk, Virginia Beach, Portsmouth, Chesapeake, Newport News, and Hampton surround Hampton Roads and represent a major urban center.¹ The topography of the region is flat and low, typically less than 8 m above mean sea level. To the southwest of Hampton Roads lies the Dismal Swamp, which extends into North Carolina.

In the summer, a Bermuda high pressure cell frequently controls the circulation pattern in southeastern Virginia and produces southwesterly winds. A sea breeze generally prevails; however, it does not extend deeply inland (usually less than 16 km). Other wind directions during the summer are less frequent. The summers are usually warm, often with afternoon showers. The southeastern Virginia area appeared very suitable for remote-sensor studies (ref. 1).

AIRCRAFT INSTRUMENTS

The hydrocarbon analyzer used in these experiments is described in reference 9. It is an automated chromatographic system employing flame ionization detection (FID) that produces alternate methane/total hydrocarbon (THC) peaks every 7 s. The difference between the two is reported as NMHC. The primary difference between this sytem and other commercially available hydrocarbon analyzers is that the system was designed around frontal (wave) chromatographic techniques which allow very rapid sample processing, highly desirable for aircraft measurements. Since atmospheric oxygen was eluted in both the methane and the THC frontals, FID response to oxygen was common to both peaks, minimizing the errors in the methane/THC differencing techniques. Air samples for both the ozone and hydrocarbon analyzers were collected well forward of the aircraft engines.

A pressurized cylinder of methane/butane calibration mixture (2.00/0.995 ppmv \pm 1 percent) in air was attached at the calibration inlet for in-flight calibration. Calibration was accomplished by manually changing a three-way valve position to feed in the mixture without disturbing preset flows. Calibration could usually be accomplished within 1 min. Typical methane/butane calibration peaks were within 1 percent of their means over 10-min intervals of continuous aircraft operation at constant altitude. The precision of the measurements at the 2.00-ppm level was determined to be ± 0.035 ppm under aircraft conditions.

Calibrations of the hydrocarbon analyzer were conducted before, during, and after data acquisition on each constant-altitude flight leg. The unique problems associated with calibration during altitude changes, particularly during spirals, were handled in the following manner: Calibration gas was continuously fed into the system during the ascent phase of each spiral and data were collected during the descent phase, or vice versa. The response of the instrument versus altitude was thus determined with calibration gas for each spiral.

An emissions inventory for this area can be found in reference 8.

A commercial chemiluminescence analyzer was used for continuous real-time ozone measurements. The ozone data in this report, however, are displayed as averaged data points corresponding in time to the methane/NMHC measurements for convenience. The ozone analyzer was calibrated just prior to the flight program using Environmental Protection Agency recommended procedures. In addition, the ozone analyzer was audited as part of the SEV-UPS quality-assurance program (ref. 7).

MAJOR EXPERIMENTS

Photochemical Box Experiment

This experiment was designed to provide a data set for comparison with a single-box photochemical model of an urban source area. A box about 30 by 30 km was centered on the major source area of the region. Upwind and downwind sampling legs were defined. The box experiment was flown only once, on August 31 under westerly winds, during the 1979 field program. The flight plan is shown in figure 2. Each flight leg was sampled hourly below the mixing layer with vertical spirals at preselected locations.

Three complete cycles of the photochemical box experiment were flown, beginning at 0455, 0555, and 0707 EDT. It should be noted at the outset that the aircraft did not always fly the legs exactly as shown in the plans; however, departures from the plans were small and did not substantially alter the scope or objectives of the SEV-UPS program.

Methane, NMHC, and ozone concentrations for the constant-altitude flight legs of August 31 are shown in figures 3, 4, and 5. Methane and NMHC data points represent the average of three data values and are plotted at 30-s intervals throughout this report. The starting times for each flight leg and spiral are shown on the figures. Since the aircraft flew at a constant speed (230 km/hr), the flight paths can be divided into equal time segments for spatial resolutions.

Methane levels appear fairly constant for upwind leg AB during each of the three sampling cycles. Methane levels, however, do appear higher on the downwind legs CD and EF. Although legs CD and EF were flown at 305 m at 0501 and 0509 EDT and at 455 m on subsequent legs, it still appears that NMHC increased from about 0.2 to 0.4 ppm as the morning progressed. Ozone concentrations appear to be very erratic during the morning. Data for spirals (figs. 6 and 7) suggest a layer at about 800 m and show the buildup of NMHC and O₃ below 800 m at later times in the morning.

Urban Plume Experiment

This experiment was designed to measure urban concentrations of ozone precursors and subsequent ozone formation in an aging plume downwind of the urban complex of Hampton Roads. The appropriate meteorological conditions were clear and bright days with southwest airflow. Under these conditions, the presumedly clean air arriving at Hampton Roads was mixed with the urban emis-

sions and then traveled northeast over the rural Eastern Shore of Virginia. (See fig. 8.) Flight legs and spirals were planned to emphasize the urban source input and the downwind plume photochemistry.

The flight plan shown in figure 8 was flown on August 24, 25, and on the morning of August 30. The urban plume experiment was flown once under the influence of northwesterly rather than southwesterly winds, on the afternoon of August 30. This flight plan is shown in figure 9.

The urban plume experiment of August 24 was flown under the influence of south to southwest winds of about 5 m/s up to 3000 m in altitude. Morning measurements of methane, NMHC, and ozone are shown in figures 10 to 13 and reveal average methane concentrations of about 1.65 ppm. Average NMHC and O_3 concentrations of about 0.4 ppm and 40 ppb, respectively, appeared to increase slightly over Norfolk during the morning. Ozone concentrations were relatively low overall, but hydrocarbon concentrations were high and increased toward the east (i.e., the Atlantic Ocean). Correlatable plume structure can be seen in the ozone and NMHC data in figure 13. Data for morning spirals are shown in figure 14.

Afternoon data at constant altitude for August 24 appear in figures 15 to 18. Data for methane concentrations average about 1.65 ppm, but occasionally indicate plume structure. (See fig. 15.) Plume structure can also bee seen in the O_3 and NMHC data. Large O_3 plumes are seen both on leg DC (over Norfolk) and on leg EF (downwind). Data from afternoon spirals on leg EF, shown in figure 19, reveal significant vertical structure.

The urban plume experiment of August 25 was flown under the influence of southwest winds of about 8 to 10 m/s and up to about 3000 m of altitude. The flight plan is shown in figure 8. Morning data taken at constant altitude are shown in figures 20 to 26. In general, methane concentrations average about 1.65 ppm and appear to increase slightly toward the east. This trend is absent in the companion NMHC and ozone data. Ozone measurements reveal many plumes that are not strongly reflected in the methane or NMHC data. Although O_3 concentrations were highly variable, overall concentrations were still usually below 50 ppb. Nonmethane hydrocarbon concentrations were typically between 0.3 and 0.4 ppm.

Data for morning spirals for August 25 (fig. 27) reveal progressive increases in ozone at altitudes greater than 800 m, whereas both methane and NMHC systematically decrease.

Afternoon data at constant altitude for August 25 are shown in figures 28 to 31. Ozone data are again highly variable, but concentrations are usually below 50 ppb. Methane and NMHC data reveal some plume structure, but neither correlate very well with ozone. Afternoon NMHC concentrations appear higher over downwind leg EF than over leg DC, probably reflecting the urban input. Nonmethane hydrocarbon concentrations appear to be slightly higher in the afternoon than in the morning.

The two afternoon spirals (fig. 32) conducted on leg EF revealed somewhat different methane profiles. This may have resulted because the spirals were

slightly displaced geographically. However, ozone and NMHC concentrations are very similar with respect to vertical structure.

The urban plume experiment for the morning of August 30 was flown as shown in figure 8 for southwest flow. Meteorological observations around 0900 EDT, however, indicated a wind shift had occurred, and an alternate flight plan was adopted for the afternoon flights. The afternoon flight plan is depicted in figure 9 and was devised for northwesterly flow.

Morning data for constant-altitude flight legs on August 30 are shown in figures 33 to 38. Methane measurements reveal significantly more variability than on previous urban plume days and frequently suggest strong plume structure. Methane concentrations ranged from about 1.58 to 1.75 ppm. Nonmethane hydrocarbon concentrations were highly variable also and were frequently above 0.4 ppm. Ozone concentrations averaged about 60 ppb, but revealed many ozone-depleted plumes. Correlations between ozone-depleted/hydrocarbon-enriched plumes are very visible and suggest relatively young unaged plumes in which O_3 consumption by nitric oxide (NO) has likely occurred. Data from morning spirals for leg AB are shown in figure 39.

Constant-altitude data for the afternoon of August 30 is shown in figures 40 to 43. Methane, NMHC, and ozone plume structures were more pronounced during the afternoon of August 30 than for any other urban plume experiment flown during the 1979 SEV-UPS. Frequently, ozone and NMHC concentrations almost doubled during plume traverses, and direct correlations between O_3 and NMHC were almost always observed. Ozone and NMHC concentrations over Hampton Roads were substantially higher on August 30 than on previous urban plume days. Data for afternoon spirals on leg EF (shown in fig. 44) reflect the high overall concentrations of methane and NMHC, and reveal methane and NMHC concentrations that systematically decrease with altitude above 800 m. Ozone behavior only weakly reflected this trend.

Dismal Swamp Characterization

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This experiment was devised to characterize the levels of methane and NMHC emitted by the Dismal Swamp. A flight plan was selected to sample air from the northern and southern boundaries of the swamp and to diagonally traverse the swamp. Spirals were conducted at selected sites. The flight plan is shown in figure 45. Low-level flight (150 m) was considered important. Optimum meteorological conditions were low wind speeds (1 to 2 m/s) and wind direction out of the south or east. The flights were conducted on August 15 under less than ideal meteorological conditions.

The Dismal Swamp experiment was flown under the influence of north to northeasterly winds of about 8 m/s. Constant-altitude data for these flight legs are given in figures 46 to 49. Methane concentrations at 155 m appear higher both inland and downwind and occasionally display plume structure. Overall methane concentrations appear only slightly higher downwind; however, wind speeds and direction departed drastically from what was considered ideal for this experiment, and thus the Dismal Swamp is still viewed as a potentially strong methane source for the Hampton Roads area. Nonmethane hydrocarbon con-

centrations averaged about 0.2 ppm, demonstrating occasional plume structure. Nonmethane hydrocarbon plumes were observed on several occasions to correlate Ozone concentrations became progressively higher inland. with O₂ minimums. Spiral data for August 15, given in figure 50, suggest early-morning (0600 EDT) concentrations of methane over Lake Drummond were relatively invariant from 150 to 1500 m, whereas data collected later in the morning (0835 EDT) indicate a systematic and progressive decrease in methane with altitude. Data for the only ocean spiral (B) show methane increasing to about 600 m and subsequently decreasing at higher altitudes. Nonmethane hydrocarbon concentrations progressively diminished over B with altitude. Nonmethane hydrocarbon levels measured at 0600 EDT over Lake Drummond suggest rather uniform concentrations of about 0.25 ppm up to about 600 m which then drastically dropped to about 0.15 ppm at 1500 m. The 0835 EDT spiral over Lake Drummond revealed well-mixed NMHC. Ozone data, collected only during this spiral, systematically increase with altitude.

DISCUSSION AND CONCLUSIONS

Methane, nonmethane hydrocarbon, and ozone data collected from a C-54 aircraft platform during the 1979 Southeastern Virginia Urban Plume Study have been presented. Three major aircraft experiments were flown by the C-54 aircraft. In general the nonmethane hydrocarbon (NMHC) concentrations measured during these experiments were high (usually above 0.3 ppm) in all but the Dismal Swamp experiment, in which concentrations of about 0.2 ppm were more typical. Methane concentrations usually ranged between 1.60 and 1.70 ppm; however, concentrations of methane above 1.70 and below 1.60 ppm were occasionally measured. On occasion NMHC plumes were found to strongly correlate with ozone plumes. This was particularly frequent during the urban plume experiment of August 30, when the aircraft may have intersected the plumes from a refinery and power plant located beside each other at Yorktown, Virginia. The Dismal Swamp experiment was conducted under meteorological conditions that were far from ideal and no data were collected that conclusively demonstrated the swamp to be a significant methane source.

Langley Research Center National Aeronautics and Space Administration Hampton, VA 23665 June 18, 1981

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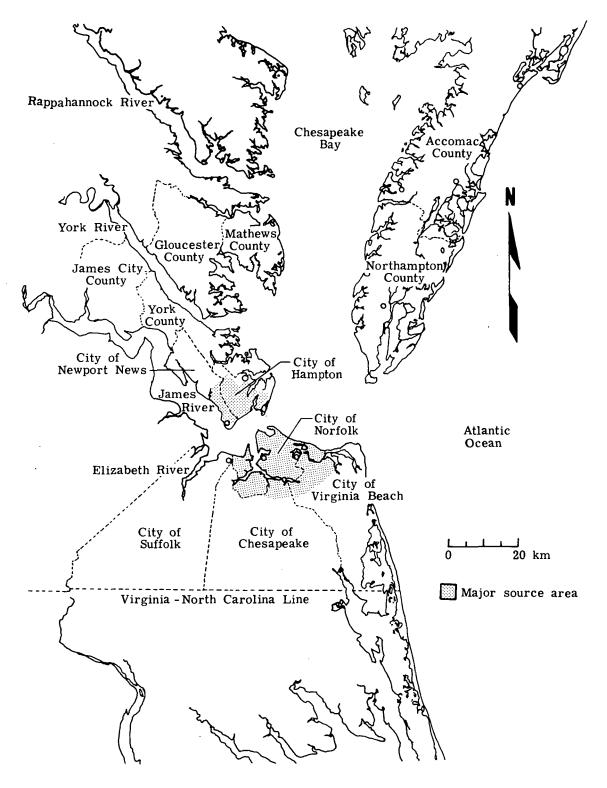


Figure 1.- Southeastern Virginia.

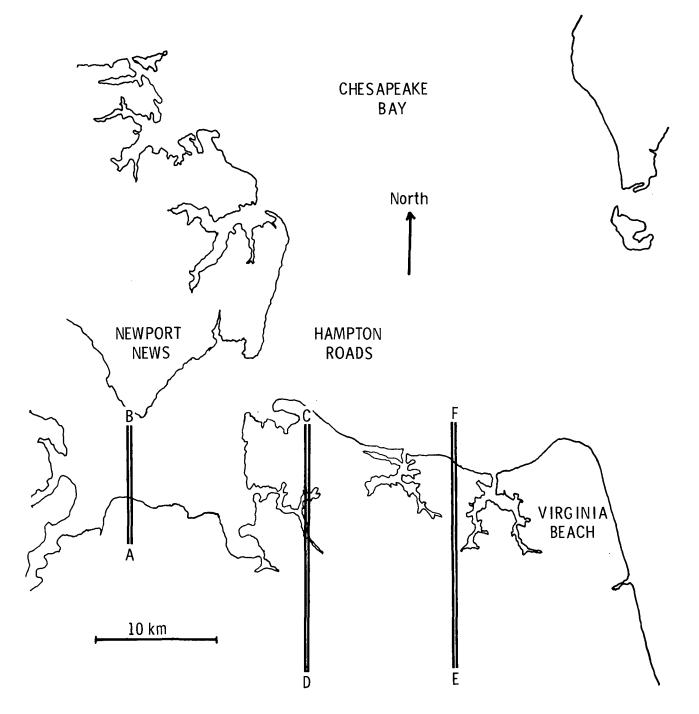


Figure 2.- Photochemical box experiment flight plan for west wind.

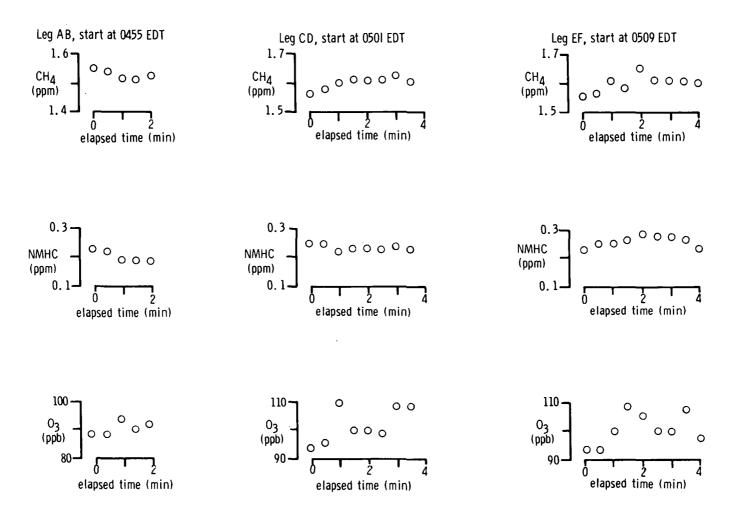


Figure 3.- Methane, NMHC, and ozone data collected on first cycle of photochemical box experiment at 455 m for leg AB and at 305 m for legs CD and EF on August 31, 1979.

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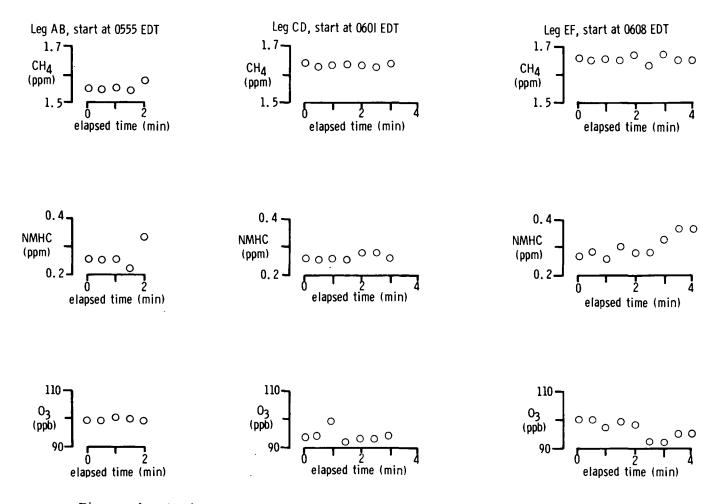
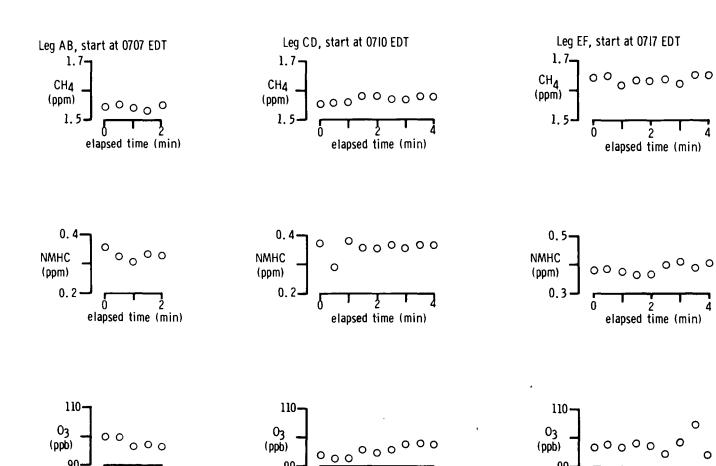
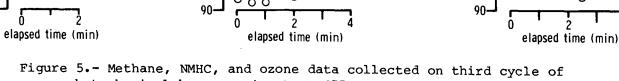


Figure 4.- Methane, NMHC, and ozone data collected on second cycle of photochemical box experiment at 455 m on August 31, 1979.





photochemical box experiment at 455 m on August 31, 1979.

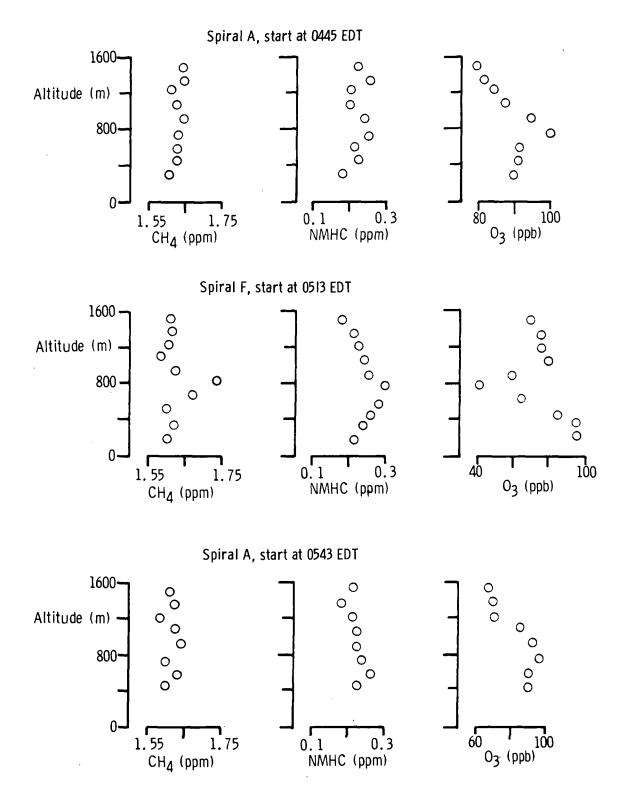


Figure 6.- Methane, NMHC, and ozone data collected during early morning spirals on August 31, 1979.

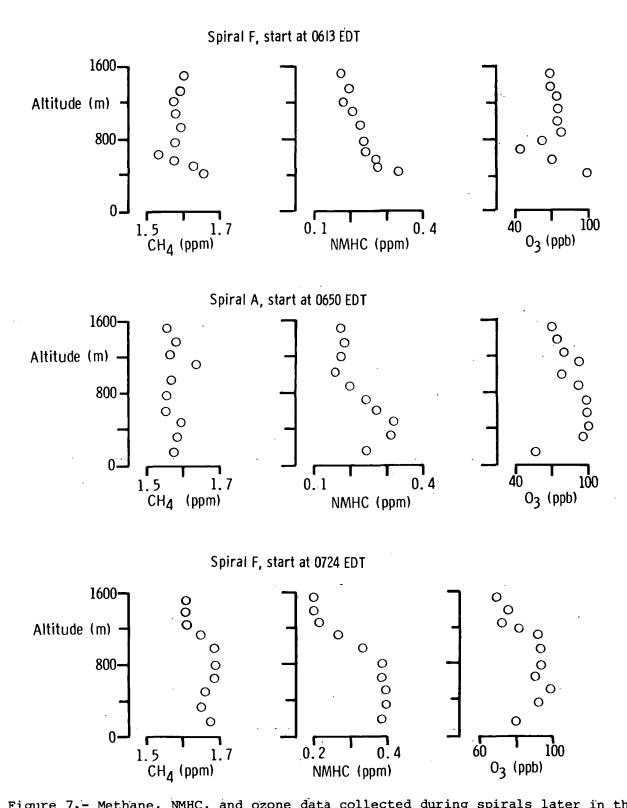


Figure 7.- Methane, NMHC, and ozone data collected during spirals later in the morning on August 31, 1979.

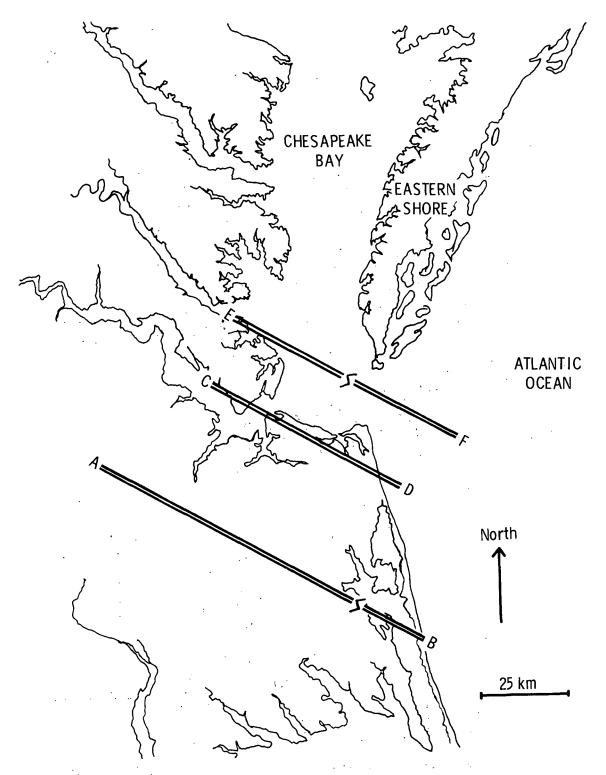


Figure 8.- Urban plume experiment flight plan for southwest wind.

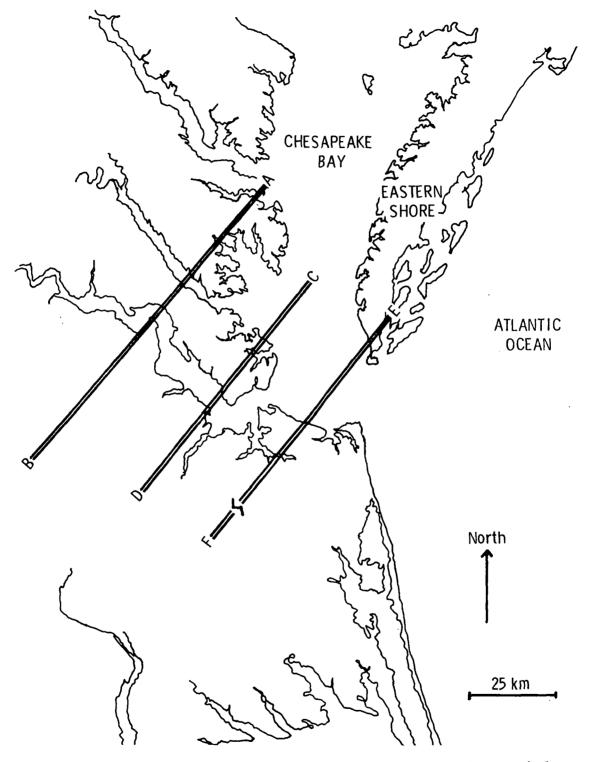


Figure 9.- Urban plume experiment flight plan for northwest wind.

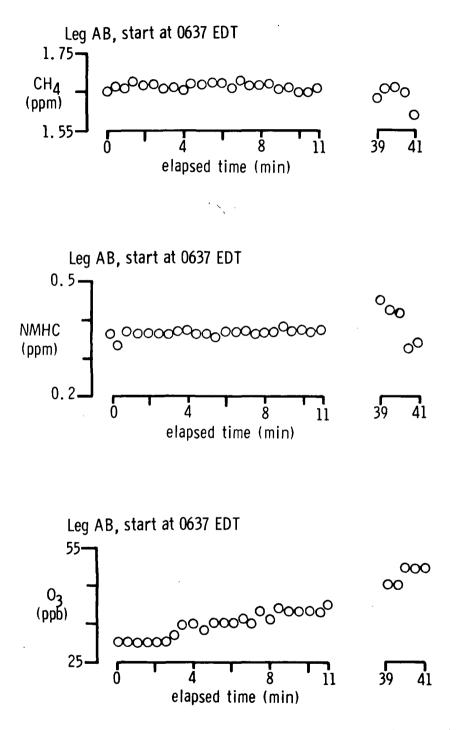


Figure 10.- Methane, NMHC, and ozone data collected at 455 m on August 24, 1979, at 0637 EDT.

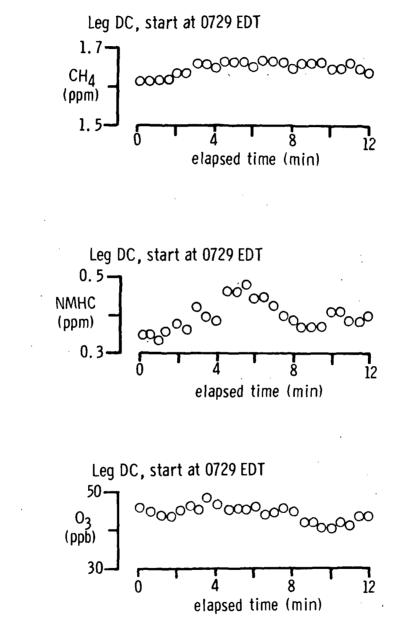


Figure 11.- Methane, NMHC, and ozone data collected at 455 m on August 24, 1979, at 0729 EDT.

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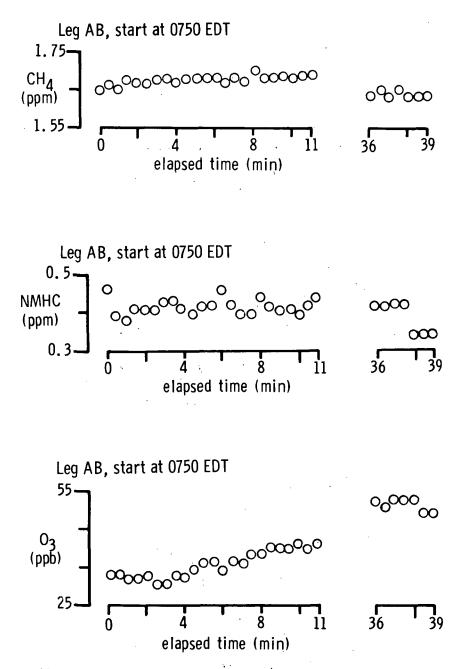


Figure 12.- Methane, NMHC, and ozone data collected at 455 m on August 24, 1979, at 0750 EDT.

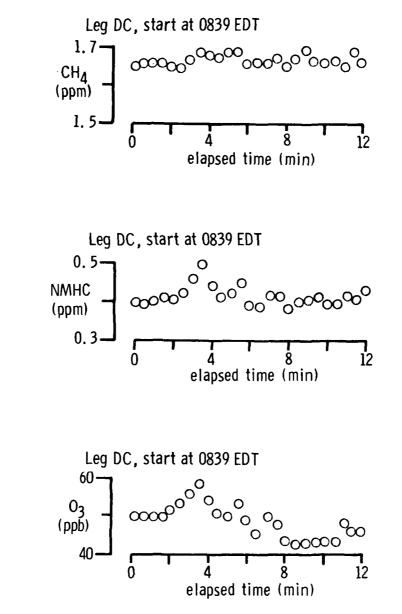


Figure 13.- Methane, NMHC, and ozone data collected at 455 m on August 24, 1979, at 0839 EDT.

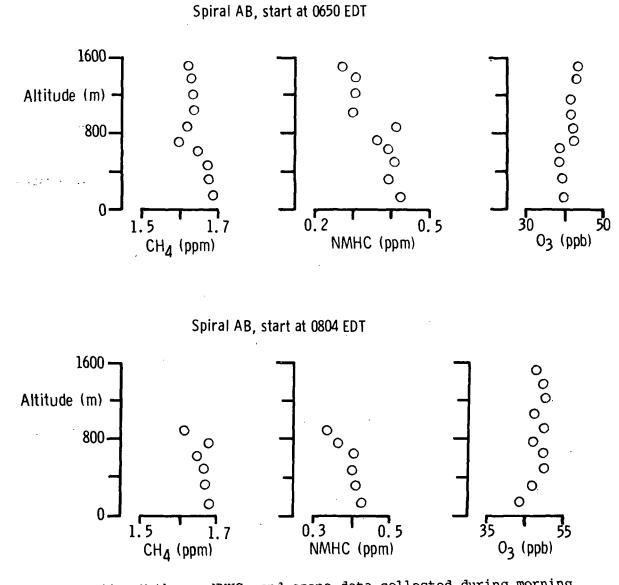


Figure 14.- Methane, NMHC, and ozone data collected during morning spirals on August 24, 1979.

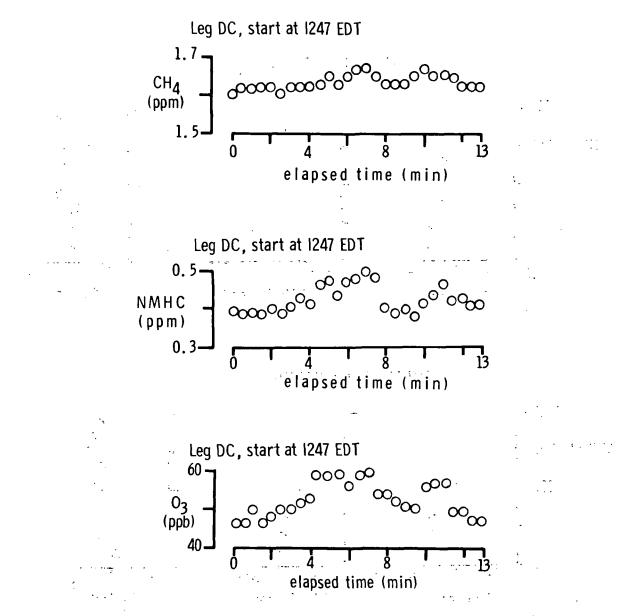


Figure 15.- Methane, NMHC, and ozone data collected at 455 m on August 24, 1979, at 1247 EDT.

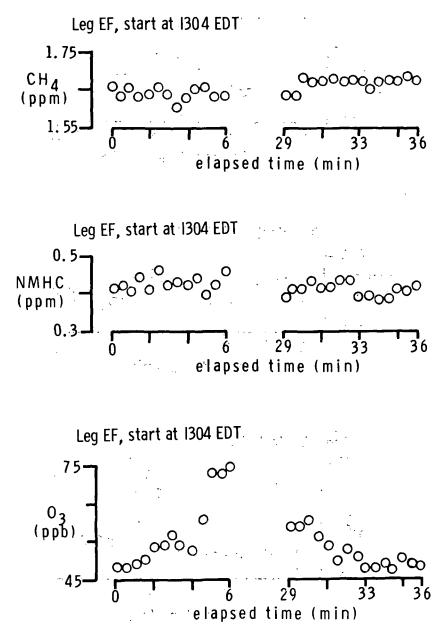


Figure 16.- Methane, NMHC, and ozone data collected at 455 m on August 24, 1979, at 1304 EDT.

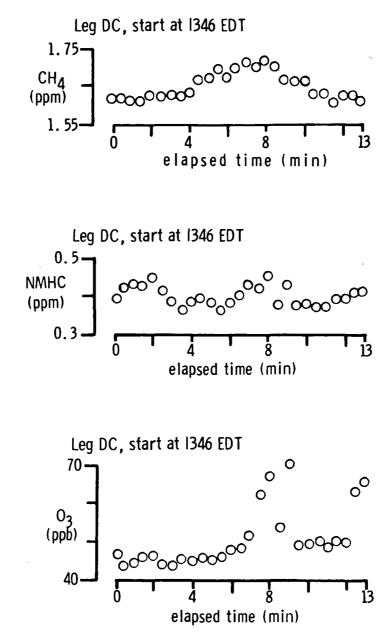
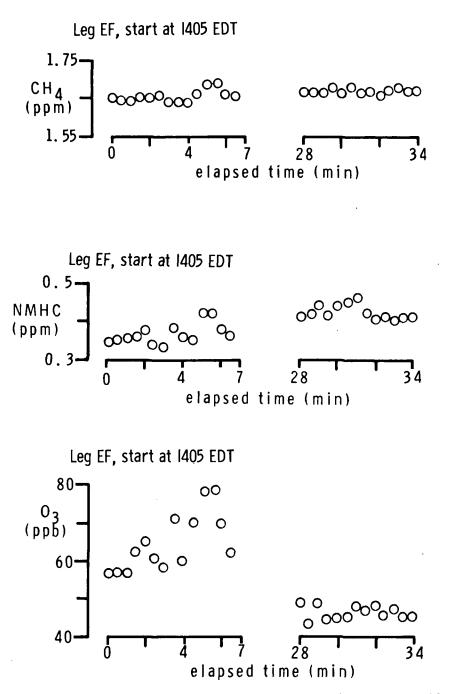


Figure 17.- Methane, NMHC, and ozone data collected at 455 m on August 24, 1979, at 1346 EDT.

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Figure 18.- Methane, NMHC, and ozone data collected at 455 m on August 24, 1979, at 1405 EDT.

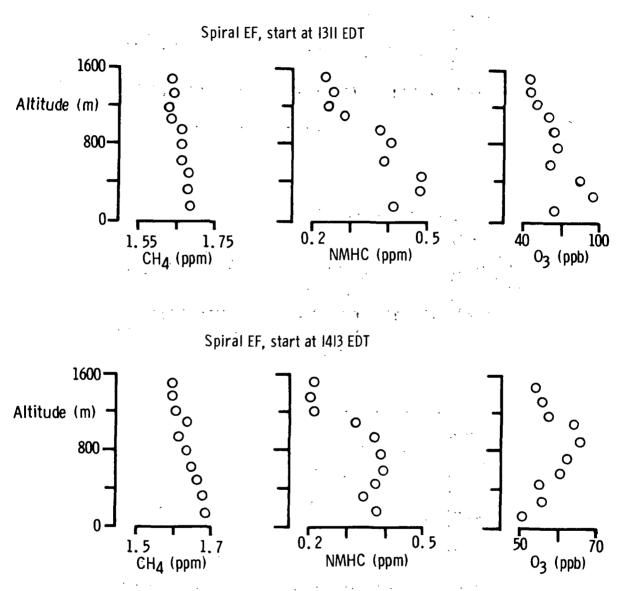


Figure 19.- Methane, NMHC, and ozone data collected during afternoon spirals on August 24, 1979.

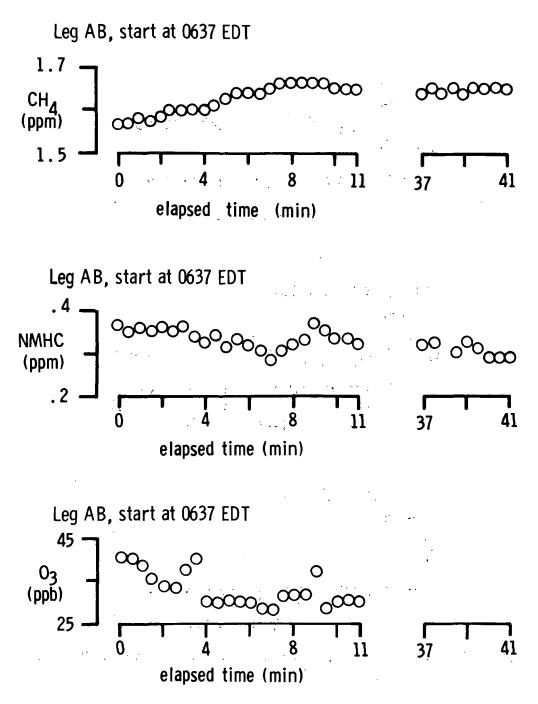


Figure 20.- Methane, NMHC, and ozone data collected at 455 m on August 25, 1979, at 0637 EDT.

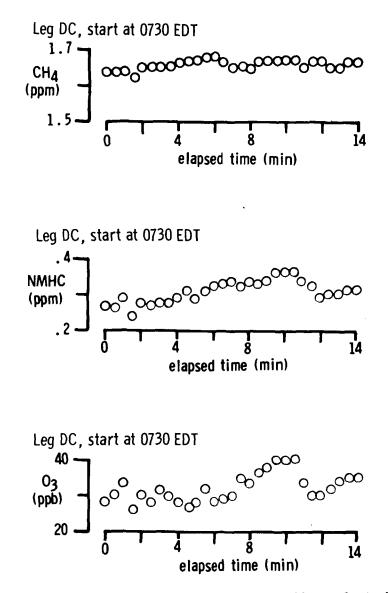
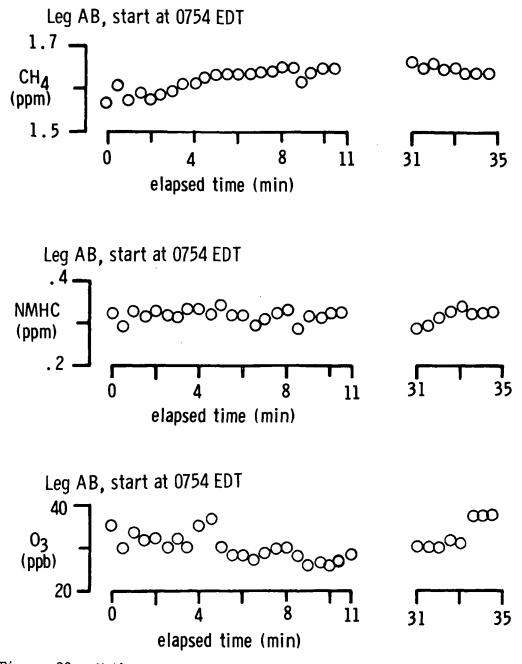
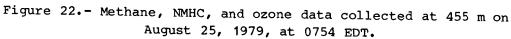
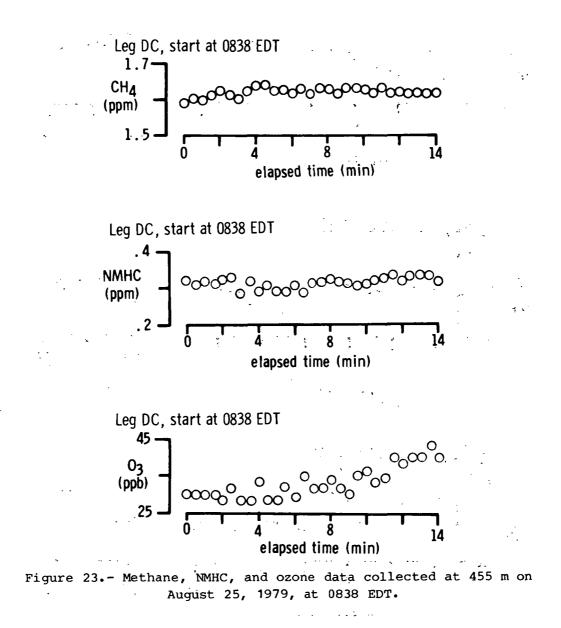


Figure 21.- Methane, NMHC, and ozone data collected at 455 m on August 25, 1979, at 0730 EDT.





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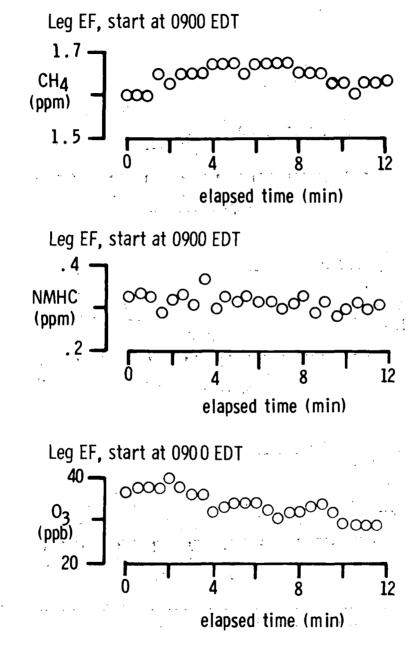


Figure 24.- Methane, NMHC, and ozone data collected at 455 m on August 25, 1979, at 0900 EDT.

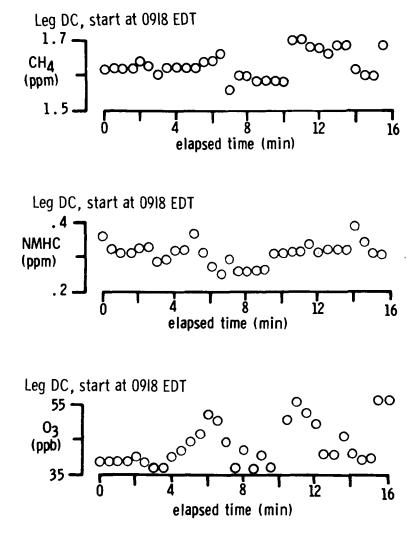
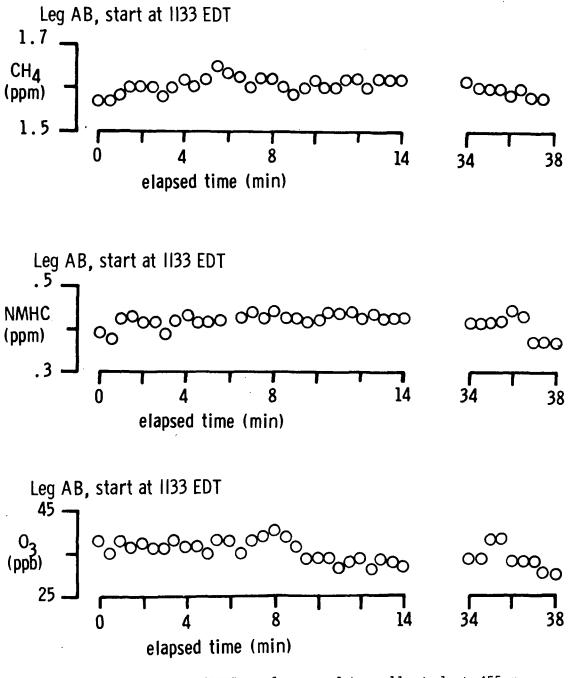
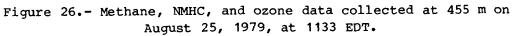


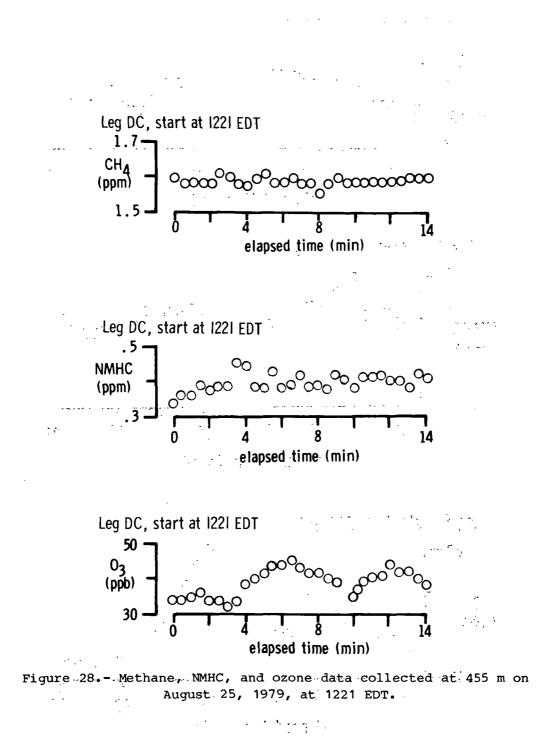
Figure 25.- Methane, NMHC, and ozone data collected at 455 m on August 25, 1979, and 0918 EDT.





Spiral AB, start at 0650 EDT 1600 0000 . 0 0000 00 Altitude (m) 000000 0 0 0 800 0 О 000 0 0 0 0 20 .2 1.5 40 1.7 ſ. 0₃ (ppb) CH₄(ppm) NMHC. (ppm) Spiral AB, start at 0805 EDT 1600 000000 0 C ò 0 0... Altitude (m) 0 0 0 0.0 800 00 0 0 Ó 0 _Ō_.. 0 0 O O 0 1.5 2 20 50 1.7 CH₄(ppm) 03 (ppb) NMHC (ppm) Spiral AB, start at 1150 EDT 1600 000 О 0 000 0 Altitude (m) Ó 0 O 0 0 800 0 О з, - O Ō 0 0 00 О 0 0 f Г 2 1.5 30 5 50 1.7 NMHC (ppm) 0₃ (ppb) ' CH4(ppm)

Figure 27.- Methane, NMHC, and ozone data collected during morning spirals on August 25, 1979.



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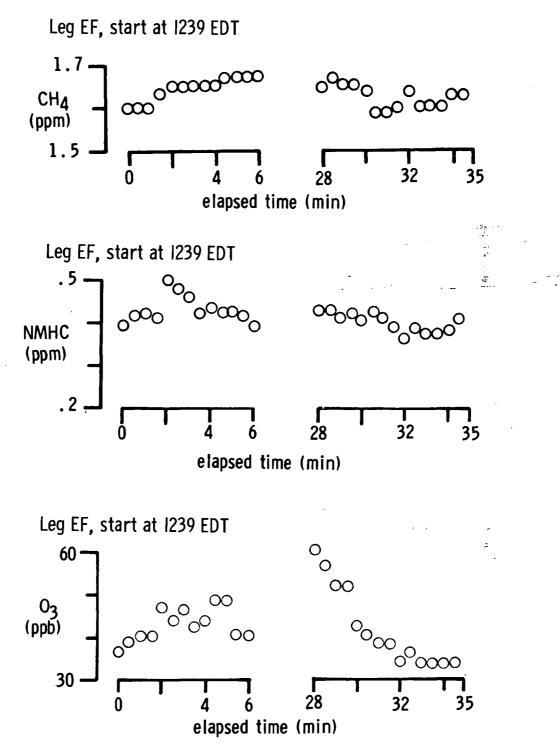


Figure 29.- Methane, NMHC, and ozone data collected at 455 m on August 25, 1979, at 1239 EDT.

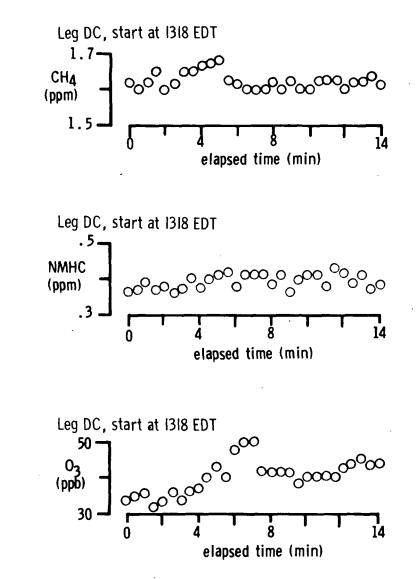


Figure 30.- Methane, NMHC, and ozone data collected at 455 m on August 25, 1979, at 1318 EDT.

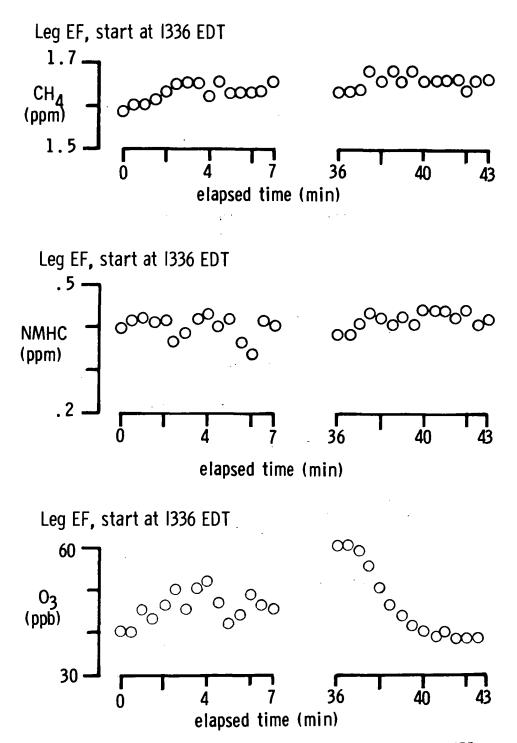


Figure 31.- Methane, NMHC, and ozone data collected at 455 m on August 25, 1979, at 1336 EDT.

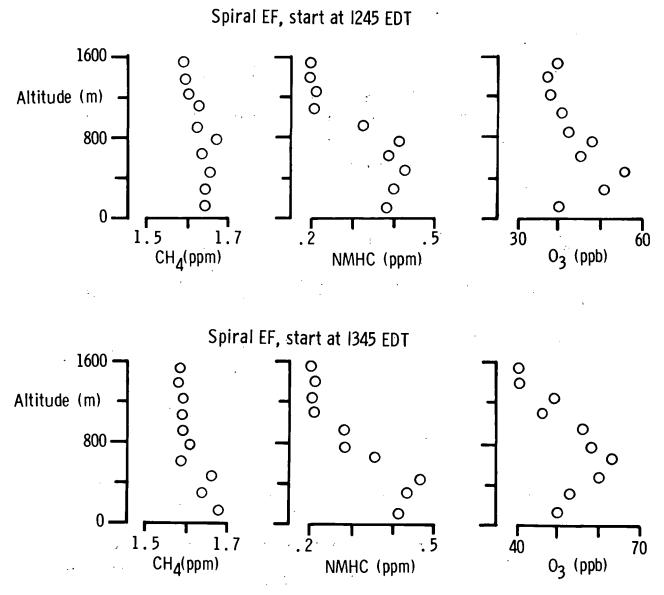


Figure 32.- Methane, NMHC, and ozone data collected during afternoon spirals on August 25, 1979.

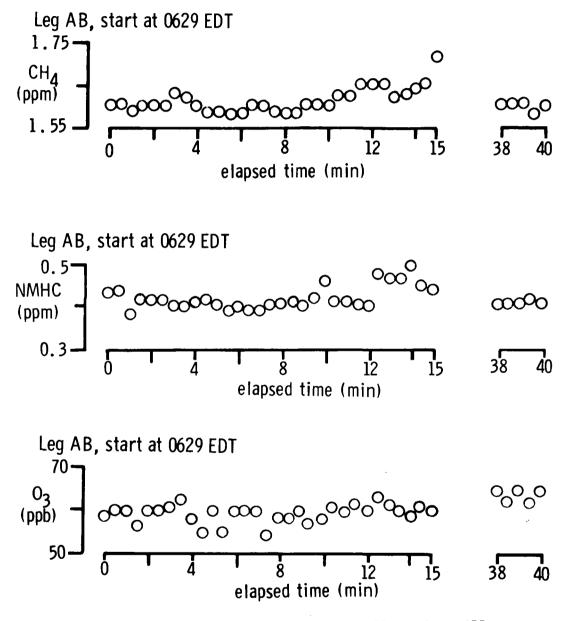


Figure 33.- Methane, NMHC, and ozone data collected at 455 m on August 30, 1979, at 0629 EDT.

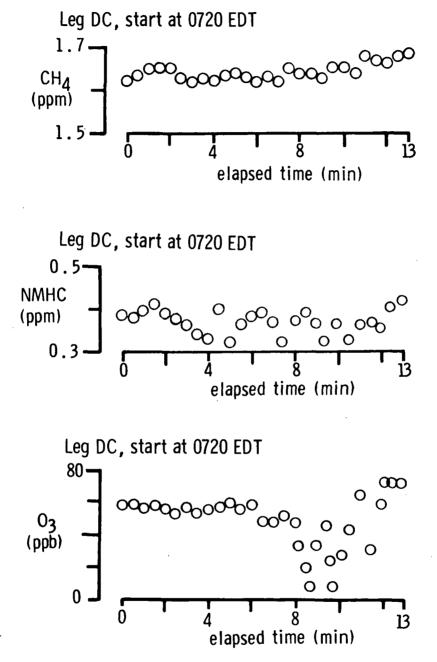


Figure 34.- Methane, NMHC, and ozone data collected at 455 m on August 30, 1979, at 0720 EDT.

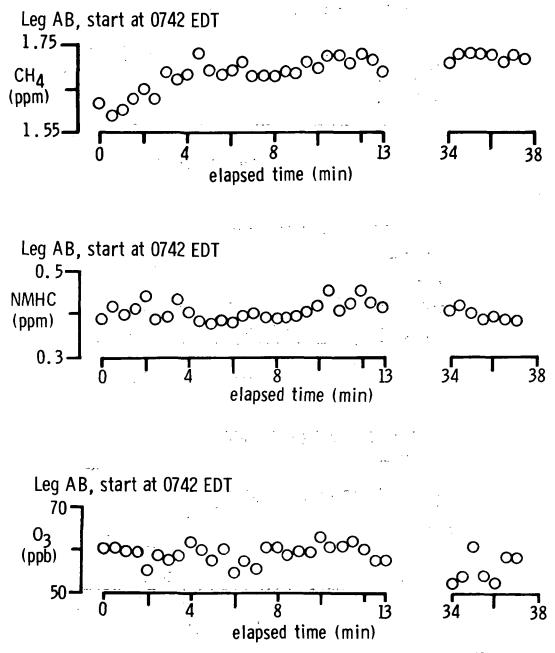


Figure 35.- Methane, NMHC, and ozone data collected at 455 m on August 30, 1979, at 0742 EDT.

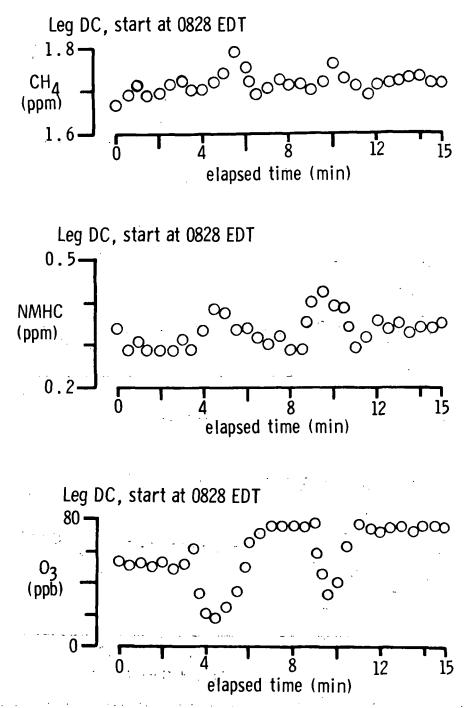


Figure 36.- Methane, NMHC, and ozone data collected at 455 m on August 30, 1979, at 0828 EDT.

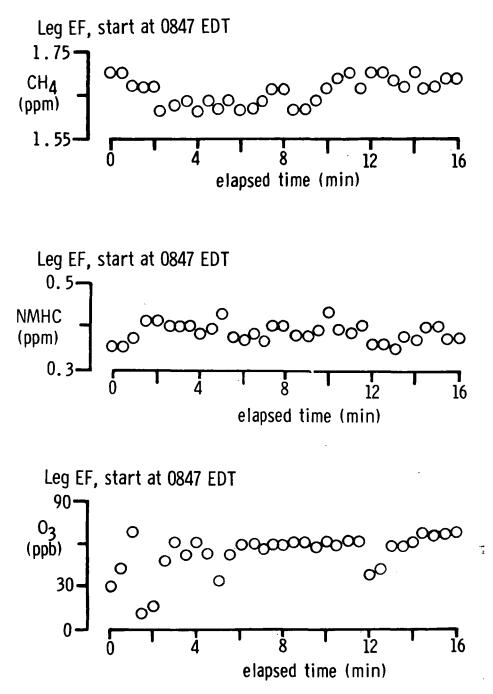


Figure 37.- Methane, NMHC, and ozone data collected at 455 m on August 30, 1979, at 0847 EDT.

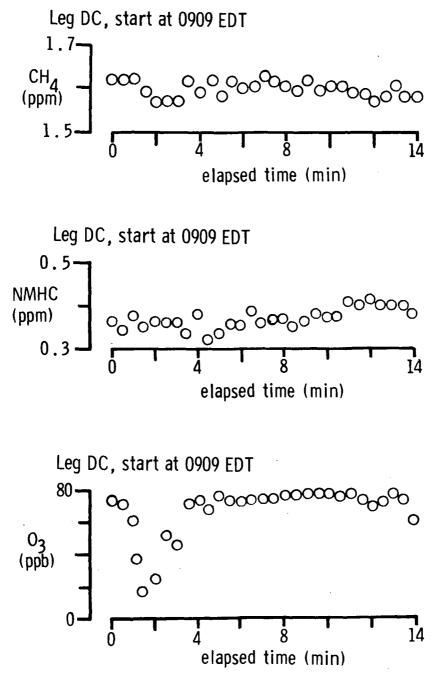
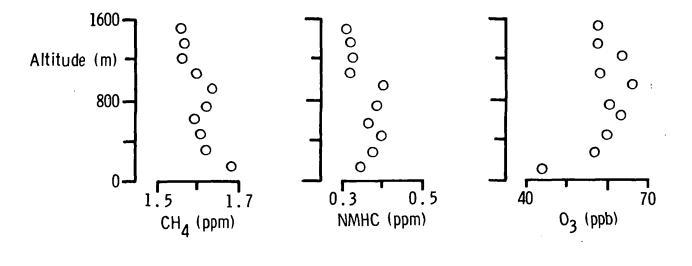


Figure 38.- Methane, NMHC, and ozone data collected at 455 m on August 30, 1979, at 0909 EDT.

Spiral AB, start at 0645 EDT



Spiral AB, start at 0756 EDT

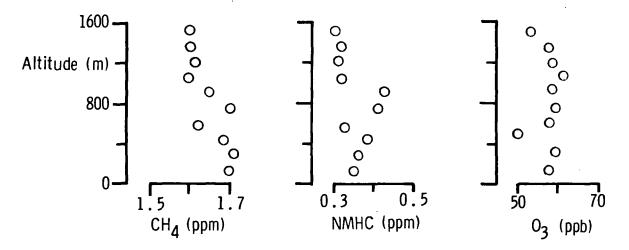


Figure 39.- Methane, NMHC, and ozone data collected during morning spirals on August 30, 1979.

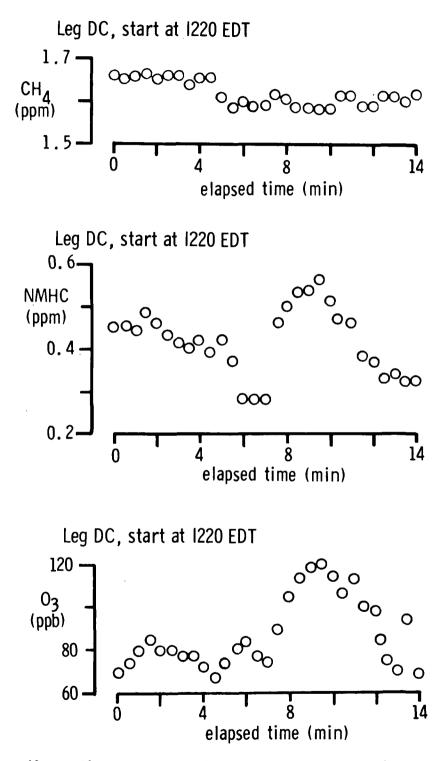


Figure 40.- Methane, NMHC, and ozone data collected at 455 m on August 30, 1979, at 1220 EDT.

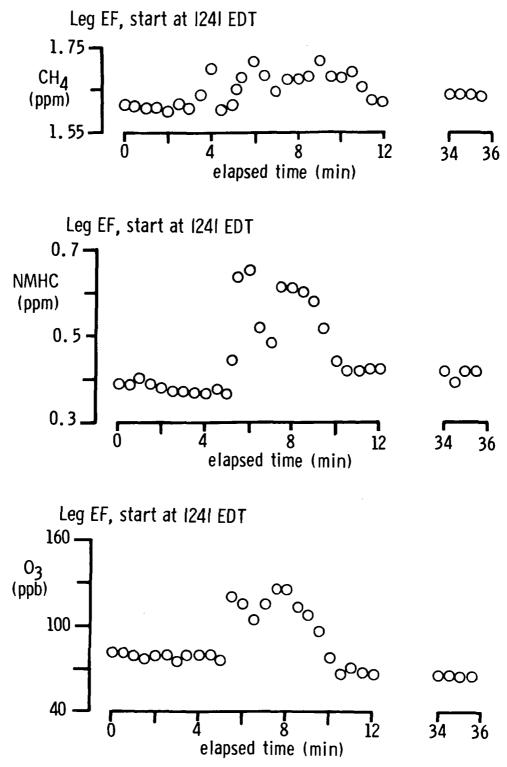


Figure 41.- Methane, NMHC, and ozone data collected at 455 m on August 30, 1979, at 1241 EDT.

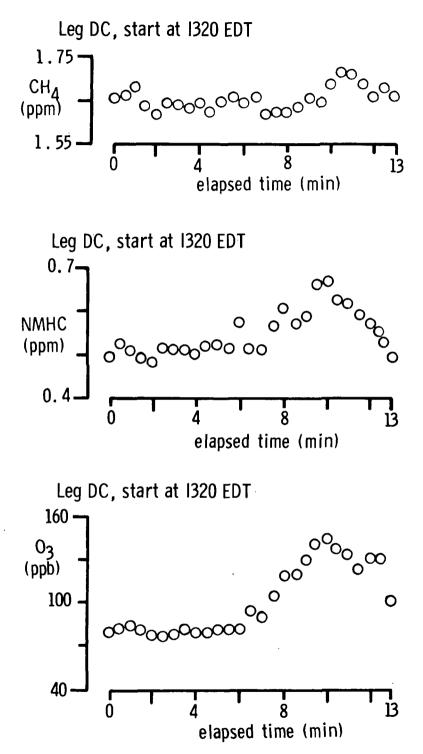


Figure 42.- Methane, NMHC, and ozone data collected at 455 m on August 30, 1979, at 1320 EDT.

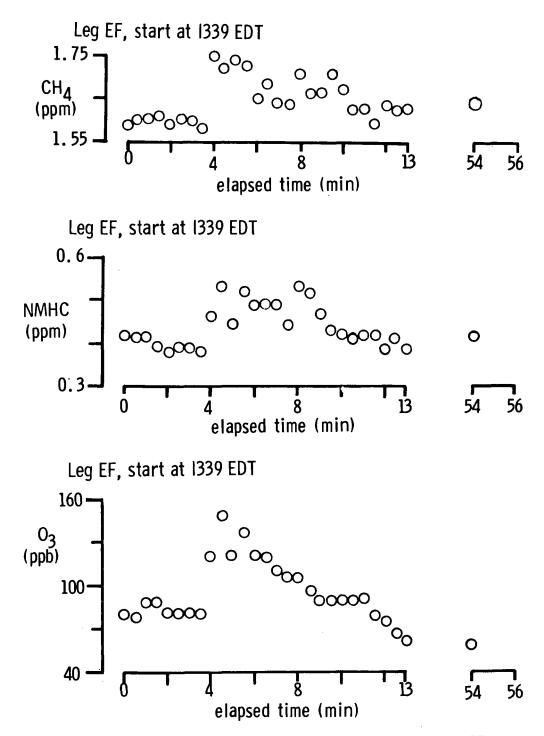


Figure 43.- Methane, NMHC, and ozone data collected at 455 m on August 30, 1979, at 1339 EDT.

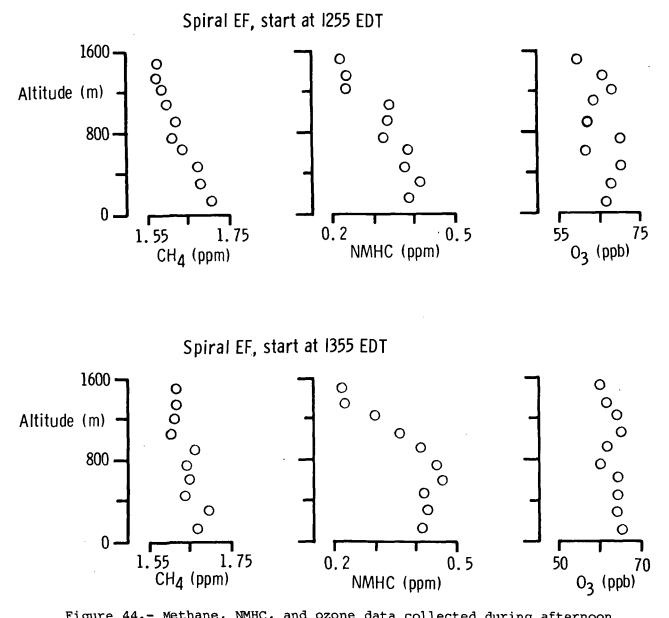
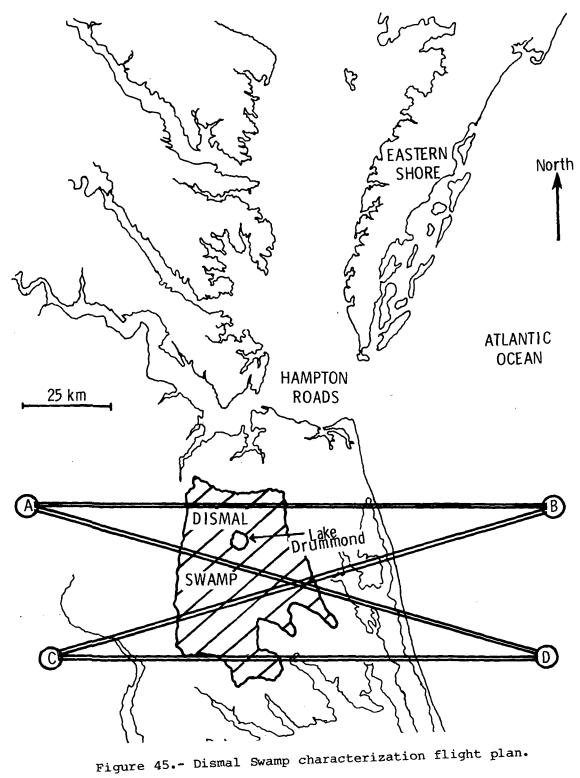
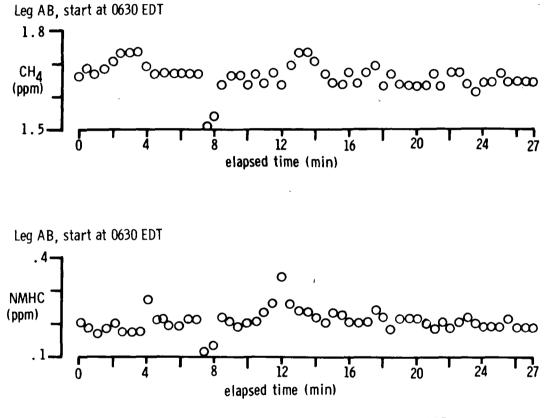
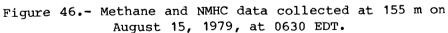


Figure 44.- Methane, NMHC, and ozone data collected during afternoon spirals on August 30, 1979.







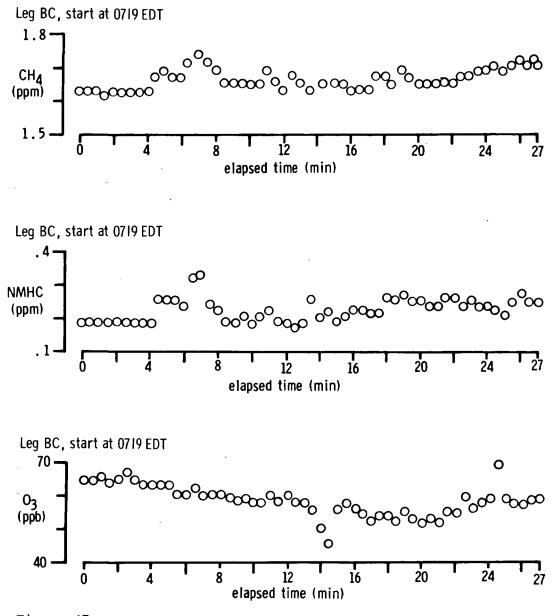


Figure 47.- Methane, NMHC, and ozone data collected at 155 m on August 15, 1979, at 0719 EDT.

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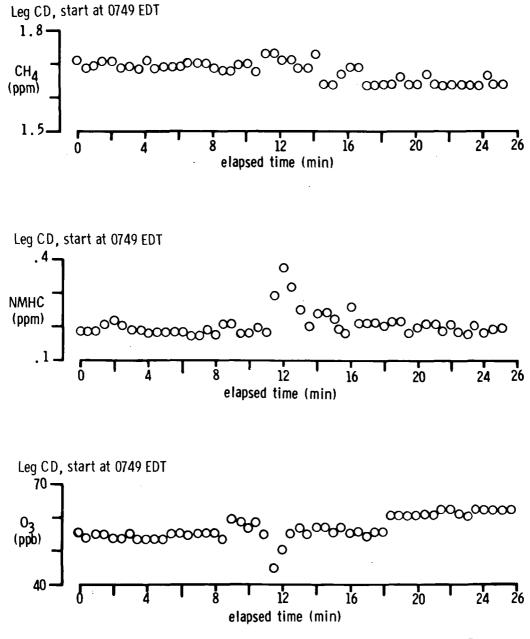


Figure 48.- Methane, NMHC, and ozone data collected at 155 m on August 15, 1979, at 0749 EDT.

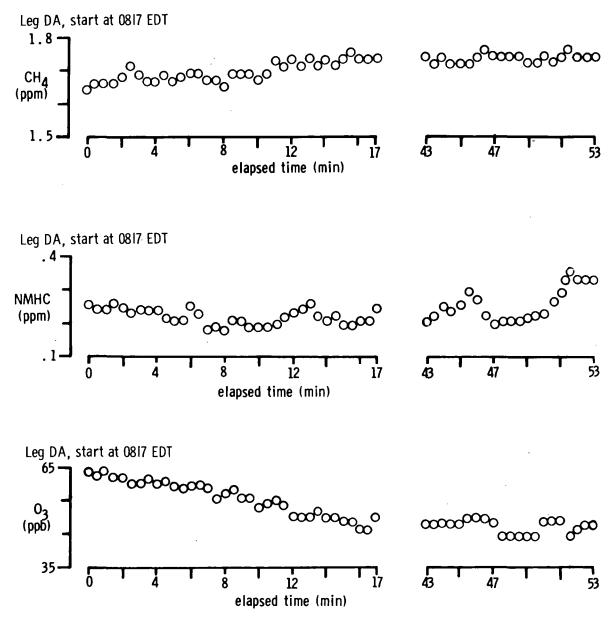


Figure 49.- Methane, NMHC, and ozone data collected at 155 m on August 15, 1979, at 0817 EDT.

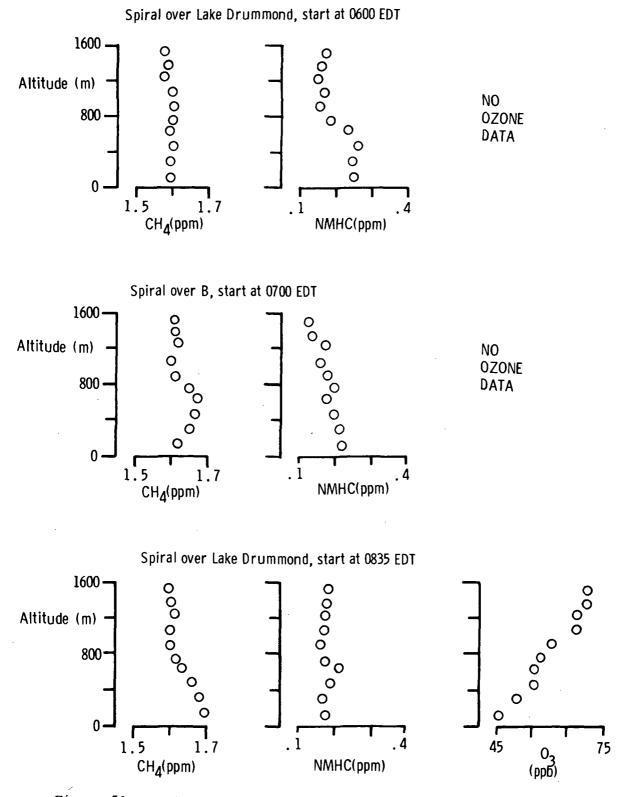


Figure 50.- Methane, NMHC, and ozone data collected during morning spirals on August 15, 1979.

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| 16. Abstract | | | | | |
| Data for methane, nonmethane hydrocarbons, and ozone collected in a C-54 aircraft during the 1979 Southeastern Virginia Urban Plume Study are presented. Three major aircraft experiments were flown on five separate days in August that involved the acquisition of about 20 hr of actual flight data. The purpose of each experiment, along with a discussion of the attending meteorology, is presented. Data collected on constant-altitude flight legs, along with data collected during aircraft spirals, are reported and discussed. Methane concentrations were usually 1.6 to 1.7 ppm and nonmethane hydrocarbon concentrations were usually above 0.3 ppm. Nonmethane hydrocarbon plumes correlated well with ozone plumes on some occasions. | | | | | |
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