



Research Report No. UVACTS-5-14-17

August, 2003

CARBON MONOXIDE PRODUCTION IN RESPONSE TO INCREASED REFORESTATION AND TRAFFIC IN EASTERN UNITED STATES

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**A Research Project Report
For the Mid-Atlantic Universities Transportation Center (MAUTC)
A U.S. DOT University Transportation Center**

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1. Report No. UVACTS-5-14-17	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle Carbon monoxide production in response to increased reforestation and traffic in eastern United States		5. Report Date August 31, 2003	
		6. Performing Organization Code	
7. Author(s) Dr. Jose D. Fuentes Dr. Michael J. Demetsky		8. Performing Organization Report No.	
9. Performing Organization and Address Center for Transportation Studies University of Virginia PO Box 400742 Charlottesville, VA 22904-7472		10. Work Unit No. (TRAIS)	
		11. Contract or Grant No.	
12. Sponsoring Agencies' Name and Address Office of University Programs, Research and Special Programs Administration US Department of Transportation 400 Seventh Street, SW Washington DC 20590-0001		13. Type of Report and Period Covered Final Report	
		14. Sponsoring Agency Code	
15. Supplementary Notes			
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17 Key Words Oxidants, aerosols, traffic patterns, emissions, hydrocarbons		18. Distribution Statement No restrictions. This document is available to the public.	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 20	22. Price N/A

Project Abstract

This report presents results from field and theoretical studies designed to evaluate the central research hypothesis that increases in forests and vehicle inventories will augment carbon monoxide levels in eastern United States. In support of this hypothesis, results from a field investigation are reported to discern the degree of photochemical activity inside and outside a mixed deciduous forest ecosystem impacted by local vehicular traffic. The studied forest emitted large amounts ($> 40 \mu\text{g m}^{-2} \text{min}^{-1}$) of isoprene, which was the dominant biogenic hydrocarbon found in the ambient air. These fluxes gave rise to ambient isoprene levels reaching daytime maximum values of 20 parts per billion (ppb). Approximately 50% of isoprene was locally consumed through chemical reactions involving free radicals, and ensuing reactions formed oxidants such as ozone and carbon monoxide. It is concluded that the combined effect of elevated concentrations of gases such as nitrogen oxides, introduced to the rural atmosphere by vehicular traffic, can give rise to enhanced formation of oxidants.

1. Introduction

Carbon monoxide (CO) is a colorless and odorless gas pollutant found in high level (100-500 parts per billion, ppb) in the lower atmosphere (EPA, 2001). Its natural sources include emissions from oceans, plants, soils and the oxidation of methane and non-methane hydrocarbons. Anthropogenic sources include fossil fuel combustion (i.e., vehicular traffic), biomass burning and industrial processes. In its own right, CO is considered one of the most important pollutants as in high concentrations it can detrimentally impact human health. Additionally, CO rapidly reacts with hydroxyl radicals (OH) thereby leading to the indirect influence of increasing levels of methane as OH is the most effective sink for methane. Therefore, any increase in CO will deplete tropospheric concentrations of OH and may cause increases in greenhouse gases such as methane.

Over the past 20 years, the CO levels from all sources in the United States have decreased by 21% (EPA, 2001). This trend is a direct result of legislation designed to improve air quality and improved technology that permitted the automobile industry to design more efficient engines to meet established air quality standards. As the population of the United States increases, so will the demand for vehicles. There are approximately 230 million road vehicles in the United States today but national vehicle registration is increasing by an average of 2% annually (Sawyer, 2000). This rate of increase satisfies the vehicle demand for the approximately 280 million people currently living in the United States. However, the national population is expected to double by the year 2100 (Census, 2000). It is feasible that, as the demand for vehicles increases, total vehicle emissions may eventually overwhelm our emission control programs. When this occurs, continuing increases in vehicle inventories would contribute to increasing CO levels in the atmosphere. However, to obtain a more accurate portrayal of national CO emission trends, it is important to categorize CO emissions by their biogenic and anthropogenic sources. By

dissecting the total national CO emissions into individual elements, it becomes quite evident that we must delve deeper into the issue of controlling CO production.

During the last 50 years, the shifts from agricultural land-use to forested landscapes in eastern United States may have influenced the observed CO trends. Oxidation of hydrocarbon compounds released by forest can directly lead to CO formation. While it is uncommon for crop plants to emit hydrocarbons such as isoprene (C_5H_8), it is very common for deciduous tree species to emit copious amounts of isoprene (Fuentes et al., 2000). Similarly, the succession of low hydrocarbon emitting tree species to more efficient hydrocarbon emitting tree species will increase isoprene emissions (Guenther et al., 1994; Lerdau et al., 1997) and enhance CO production. It cannot be assumed that the current observed trends for CO emissions will continue to decline without investigating the combined effects of increasing reforestation and vehicle inventories. Therefore, this study is designed to investigate the contribution of oxidation of hydrocarbon compounds released by forests to CO formation. We evaluate the central hypothesis that further increases in forests and vehicle inventories and a shift to more efficient hydrocarbon emitting tree species will increase CO production in the northeastern regions of the United States. To evaluate the research hypothesis, we follow two research approaches. First, we investigate isoprene chemical processing inside and outside the canopy of an oak forest impacted by local vehicular traffic. Second, through the use of a one-dimensional photochemical model (Makar et al., 1999) we define and quantify the contribution of biogenic hydrocarbons and local traffic patterns on carbon monoxide production. This manuscript only includes the results for the first research approach.

2. 1 Site characteristics

Air chemistry and micrometeorological measurements were made from 15-22 July 1999 at the United States Department of Energy reservation near Oak Ridge, TN ($35^{\circ}57'30''N$, $84^{\circ}17'15''W$; 335 m above sea level). The forested site is classified as an eastern mixed-species, broad-leaved deciduous forest. During the 1999 growing season the dominant tree species included oak (*Quercus alba* L., *Q. prinus* L.), hickory (*Carya oata*), maple (*Acer rubrum*L., *Acer saccharum*), tulip poplar (*Liriodendron tulipifera* L.), black gum (*Nyssa sylvatica* Marsh) and loblolly pine (*Pinus taeda* L.). A survey was conducted during 1999 to study the tree population within the flux footprint of the 50-m scaffolding tower used to make measured. The average composition along the established transects, on a basal area basis, was 14% pine, 16% maple, 41% oak and 13% other deciduous species (Wilson et al. 2001). The total leaf area index for this 26- m forest is 6.0. The local atmosphere is influenced by anthropogenic emissions from a road that is located approximately 1.6 km from the site. In the morning hours (8-10 local time), the traffic of approximately 4000 light vehicles impacted the measurement site as reflected by the unusually elevated concentrations of nitrogen oxides (see Section 3).

2. 1 Micrometeorological measurements

As part of the ongoing investigations at the Oak Ridge site, a suite of water vapor, sensible heat flux densities and state variables were continuously measured. Wind speed and direction were measured at 45 m above the ground, using a propeller anemometer (model 05701, RM Young Co., Rapid city, MI).

Net radiation measurements were made at 45 m above the ground using a net pyrradiometer (model S-1, Swissteco). Photosynthetically active photon flux density was measured with a quantum sensor (LICOR model LI-190S) above the canopy. Air temperature and relative humidity were measured at 36.6 m above ground (Vaisala, model HMP-35A). This sensor was shielded from the sun and aspirated to prevent condensation. Ancillary meteorological data were acquired with and stored in data loggers (model CR21X, Campbell Scientific Inc., Logan, Utah). The sensors were sampled every second and half-hour averages were computed and stored on a computer, to coincide with the flux measurements. The eddy-covariance method was used to measure flux densities of carbon dioxide, water vapor, sensible heat, and isoprene. For isoprene fluxes (i.e., the data included in this study), the eddy covariance method employed a three-dimensional sonic anemometer (model SAT-211/3K, Applied Technology, Boulder, CO) and an ozone-induced chemiluminescence instrument (FIS, Hills Scientific, Boulder, CO; Baldocchi et al., 1999). Wilson et. al., (2001) provide additional information on the measurements at the Oak Ridge tower site.

2.2 Air chemistry measurements

Mixing ratios of 89 hydrocarbon compounds, ozone and nitrogen oxides were measured at six levels (0.2, 9.4, 17.7, 25.6, 31.5 and 39.9 m) above the forest floor. Gas profile measurements were accomplished with a single gas analyzer, made possible through the use of manifold system and sequential canister air samplers from individual intake. A pumping system was used to draw atmospheric air through cleaned Teflon tubing (12.7 mm ID) from the air intakes at six levels at flow rates $> 20 \text{ L min}^{-1}$. The high flow of air is required to reduce the residence time of air in the tubing. Teflon filters (pore size 1 μm) were installed at the inlet of sampling lines to remove pollen and dust and to keep sampling lines clean. A portion of this fast-moving air was directed by automatic samplers (910A sampler and 912 sequential adapter, XonTech Inc., Van Nuys, California) into evacuated canisters. These samples were collected in 3.2 L Summa polished, stainless steel canisters (Biosphere Research Corp., Hillsboro, OR) to determine the mixing ratios of the hydrocarbons in and above the forest canopy. The air samplers were equipped with mass flow controllers that allowed constant airflow rates ($100 - 150 \text{ mL min}^{-1}$) into the canisters. The integrated air samples stored in canisters were analyzed at the study field site within 24 hours after sample collection or returned to the laboratory and analyzed within two weeks after sample gathering. Because hydrocarbons in ambient air remained in trace amounts, the analytes required water removal and pre-concentration prior to its analyses. At the study field site, a 2-m Teflon loop (3.175 mm OD) kept at -10°C was used to remove water from samples and thus reduce water-related peak retention time variations. The dried air samples were cryogenic cooled to concentrate hydrocarbon compounds. The cryogenic trap was packed with 60/80 mesh untreated glass beads, and cooled at -150°C . Air samples of known volume (regulated by a FC-260 Tylan mass flow controller) were concentrated by passing through the dryer and cryogenic trap. Concentrated samples were introduced to the chromatograph column via a six-port valve (Valco Inc.) and rapidly heating the trap to 150°C . The hydrocarbons were separated using a fused silica capillary column (HP-1, 60 m, 0.32 mm ID, 1.0 μm film thickness, Hewlett Packard). The column carrier

gas was helium, flowing at 2 ml min^{-1} . The samples were analyzed with a gas chromatograph (Model 6890 GC, Hewlett Packard, Pal Alto, CA) furnished with a mass selective detector (Model 5972 MSD, Hewlett Packard). In the laboratory, an automated pre-concentration system (EnTech 7000 with 7016 auto-sampler) employing three stages micro purge and trap technique for water removal and GC-MSD (model 6890 GC and 5973 MSD, Hewlett Packard). The GC-MSD system operated in selected ion monitoring (SIM) mode that allowed identification and quantification of target compounds based on retention times and relative abundance of selected ions. Two or two ions were measured for each of the target compounds. The SIM technique is highly specific and sensitive. Both GC-MSD systems were calibrated using standard mixtures prepared in our laboratory from multi-component liquid and gas mixtures (Scott Specialty Gases, Plumsteadville, PA). Standard mixtures were prepared by a gravimetric method, diluted with ultra-cleaned humidified air and then stored in Summa polished canisters. The prepared standards concentrations were verified with NIST 1800 (15 compounds) and NIST 1804 (19 compounds) hydrocarbon standards. Details concerning GC-MSD calibration and measurement accuracy are presented elsewhere (Fuentes et al. 1996). Ozone mixing ratio measurements were made with an ultraviolet light absorption-based instrument (model 49C, Thermo Environmental Instruments Inc., Franklin, MA). Nitrogen oxide measurements were made with a chemiluminescence instrument (model 42C, Thermo Environmental Instruments Inc.).

3. Results and discussion

In this section we discuss the prevailing ambient levels of hydrocarbon compounds and oxidants measured above and inside the forest canopy. Emphasis is placed on understanding the local chemical processing of isoprene which was the most abundantly hydrocarbon species emitted by the tree species such as oaks. Approximately thirty hydrocarbon species were present in the air masses passing through the research forested ecosystem (Figure 1). Most of the observed hydrocarbons represented alkanes and alkenes whose sources came from anthropogenic activity such as local vehicular traffic. The most abundant hydrocarbon measured at the forested site was isoprene whose daytime ensemble average nearly reached 10 parts per billion (ppb). When hydrocarbon compounds were scaled to the OH reactivity then isoprene exceeded the 10 ppb level (Figure 1). It is also useful to study hydrocarbon levels based on the practical The prevailing hydrocarbons (Mixing ratios greater than 0.01 ppbv) were then sorted according to their Propylene-equivalent scale (Chameides et al., 1992) to compare the reactive nature of hydrocarbons to that of propylene. This scale is established because it accounts for the combined effect of the hydroxyl reactivity and concentration of a particular hydrocarbon species. The propylene-equivalent concentration is given by the model (Chameides et. al., 1992): $\text{Propy-Equiv (J)} = C_J [k_{\text{OH}}(\text{J}) / k_{\text{OH}}(\text{C}_3\text{H}_6)]$, where C_J is the mixing ratio of the hydrocarbon species (J) in ppbC, $k_{\text{OH}}(\text{J})$ is the rate constant for the reaction of species (J) with OH, and $k_{\text{OH}}(\text{C}_3\text{H}_6)$ is the rate constant for the reaction of propene with OH (Chameides et. al., 1992). The rate constant for isoprene ($7.8 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) was adopted from Fuentes et al. (2000), while the rate constants for the remaining hydrocarbons were retrieved from DeMore et al. (1999). Our study intended to correlate values for a rural atmosphere that is

affected by concentration levels of biogenic hydrocarbons and the photochemical reaction of these hydrocarbons with emissions from local traffic. Isoprene became the dominant reactive hydrocarbon found over the studied forest ecosystem (Figure 2). The contribution of isoprene to local daytime chemical processing is considered below.

Because isoprene is produced during the daytime, strong diurnal variations in isoprene mixing ratios are observed above forests (Figure 3). The maximum average isoprene mixing ratios observed above the forest reached 10 ppb during the early afternoon. These values reflect the strong source of isoprene from the underlying forest ecosystem. The isoprene mixing ratios exhibit strong variations with altitude (Figure 4). These variations result because of the combined effects of location of isoprene sources and degree of chemical processing. For example, Figure 4 shows that isoprene inside the forest remained substantially lower than the levels observed above the canopy. Despite having isoprene sources inside the forest canopy, isoprene levels remained lower inside the canopy due to the rapid chemical reactions taking place in the volume occupied by the forest canopy.

Emissions of isoprene depend on local forest composition and environmental variables such as light levels and foliage temperature (Fuentes et al., 1999). Therefore, isoprene emissions tend to attain maximum values in the early afternoon (Figure 5). For the Oak Ridge forest, maximum isoprene emissions reached nearly $50 \mu\text{g m}^{-2} \text{min}^{-1}$. Compared to results reported for other (more northern) ecosystems, Lerday et al., 1997; Fuentes et al., 1999), these fluxes for other forests are nearly twice as high. The greater fluxes resulted because the underlying forest was comprised of effective hydrocarbon emitting tree species.

Second to OH, ozone is an important oxidant to remove isoprene molecules from the atmosphere (Paulson et al., 1992b). The observed diurnal patterns for ozone were measured during the study but only measurements observed during the same periods as isoprene measurements will be discussed (Figure 6). Minimum ozone values were observed during the early morning hours and maximum values were observed during the late afternoon hours (Figure 6). Diurnal patterns for nitric oxide revealed that the research site was impacted by vehicular traffic as the nitric oxide levels clearly exhibited elevated concentrations that coincided with morning and late afternoon work traffic flows. Unlike isoprene and ozone, which displayed clear trends of split values above and below the canopy, there was no established trend with nitric oxide. This suggests that there was variable advection of nitric oxide to the study site. Maximum mixing ratio values for nitric oxide were observed during the late morning to midday hours.

The mixing ratio of isoprene is greatly influenced by the presence of hydroxyl radicals. Vertical profiles of isoprene show that there is an increase in the isoprene mixing ratios from the forest floor to the crown of the forest canopy and a monotonic decrease above the canopy (Figure 8). During daytime conditions, isoprene is rapidly oxidized by hydroxyl radicals (Andronache et al., 1994; Paulson et al., 1992a), which would produce a monotonic decrease of isoprene with increasing levels of actinic irradiance. Our observations of decreasing mixing ratios for isoprene with increasing height above the

canopy correspond well with results report by Andronache et. al. (1994). With an average wind speed of $1.38 \pm 0.67 \text{ m s}^{-1}$ during the isoprene measurement period, the advection of isoprene from the upwind sources would play a minimal role in the decreased values observed at the site.

Two of the major compounds produced by the oxidation of isoprene by hydroxyl radicals and ozone are methacrolein (MACR) and methyl vinyl ketone (MVK) (Montzka et al., 1993). These two products are important because they are very reactive and can contribute to the production of ozone and peroxy and alky free radicals (Biesenthal and Shepson, 1997). The MACR and MVK measured for this study show that there is generally an increase in the mixing ratios of MACR and MVK from the forest floor to the top of the forest canopy and then a decline in mixing ratios above the canopy height (Figures 9 and 10). This suggests that the photochemical activity within the canopy is the source of these isoprene reaction products. The mixing ratio for both MAC and MVK increased during the day above the canopy but reached peak values around 16:00 h below the canopy. This may have resulted because of decreases in actinic irradiance reaching the deep in the forest canopy during late afternoon. The MVK mixing ratios typically had higher values than those for MACR. These findings can be explained by the more rapid reaction of MACR with hydroxyl radicals, which create a strong sink for MACR (Pierotti et al., 1990). The daytime average mixing ratio for MACR was 0.95 ppbv below the canopy and 0.90 ppbv above the canopy and was 1.30 ppbv below the canopy and 1.21 ppbv above the canopy for MVK. Montzka et al. (1995) found mean mixing ratios for MACR and MVK of 0.48 and 0.74 ppbv, respectively, above a rural forested site in western Alabama.

To determine the percentage of isoprene that is converted into MACR and MVK through chemical reactions, it is necessary to sum the mixing ratios of MACR and MVK and then divide the sum by the mixing ratio of isoprene. If the ratio is equal to one (1), then all of the isoprene was converted into MACR and MVK. If the ratio is less than one (1), then part of the isoprene was converted into other products. Figure 11 shows that less than half of the isoprene was converted into MACR or MVK at any height above or below the canopy. Vertical profiles show that there is an increasing trend in the ratio with an increase in height. This suggests that the oxidation of isoprene in higher levels of PAR produces larger quantities of MACR and MVK. The ratio of MACR and MVK to isoprene also increases during the day peaking at 16:00 h thus displaying a bell-shaped curve (Figure 11). Montzka et al. (1995) reported similar findings for a forested site in Alabama for data obtained. During the two-week measurement period, approximately 50% of the locally produced isoprene was oxidized and converted to methacrolein and methyl vinyl ketone. Based on these *in situ* measurements, these yields in oxidation products contributed to about 25% of the ozone produced above the forest canopy.

4. Summary and conclusions

This study revealed intense photochemical processing of biogenic hydrocarbons inside and outside a forest canopy. Isoprene was the most abundant biogenic hydrocarbon measured inside and outside the forest canopy, reflecting the strong source from the underlying surface. Daytime isoprene mixing ratios averaged about 20 ppb. Maximum isoprene levels over the forest were measured during the early

afternoon, when photochemistry was the most intense. Isoprene oxidation produced high (> 3 ppb) yields of methacrolein and methyl vinyl ketone. Based on their vertical distribution, greatest isoprene oxidation occurred just above the canopy. The ratio (MACR+MVK)/isoprene indicated that nearly 50% of the isoprene was locally oxidized. The rest of the isoprene was transported out of the local atmospheric boundary layer. This degree of photochemical activity augmented local ozone formation. During the study, air masses remained stagnant and observed ozone levels likely resulted from local photochemistry. Local traffic of about 4000 light vehicles impacted the measurement site as manifested in increases in nitric oxide levels during 08:00-10:00 h, when nitric oxide mixing ratios reached 2-3 ppb. Greatest nitric oxide consumption took place in the forest crown in response to intense photochemistry. By noon most of the nitric oxide was converted to nitrogen dioxide, which subsequently underwent photolysis to produce ozone in the local atmospheric boundary layer. Future studies will assimilate the presented data sets in photochemical models to investigate ozone formation from traffic-related nitrogen oxide emissions and biogenic hydrocarbons emitted by forests. Additionally, these data sets will be utilized to estimate the carbon monoxide production rates resulting from the oxidation of biogenic hydrocarbons such as isoprene.

Acknowledgments

The University of Virginia Transportation Center supported the data analyses of this study through a research assistantship provided to master student Jody Marshall (in the Department of Environmental Sciences).

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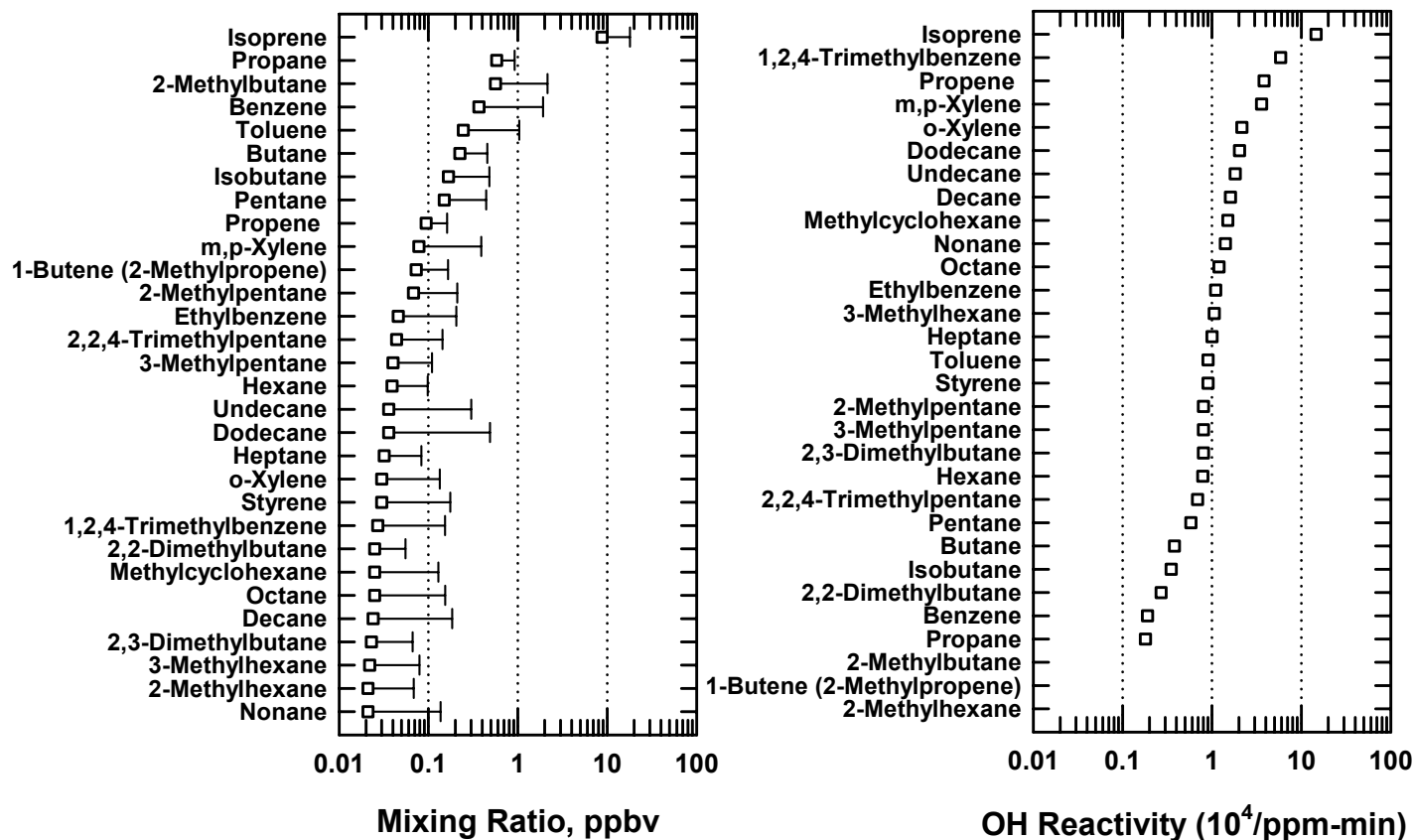


Figure 1: Prevailing hydrocarbons measured at a forested area in Oak Ridge, TN. The observed hydrocarbon compounds were sorted by mixing ratio and OH reactivity to illustrate the most photochemically important gases.

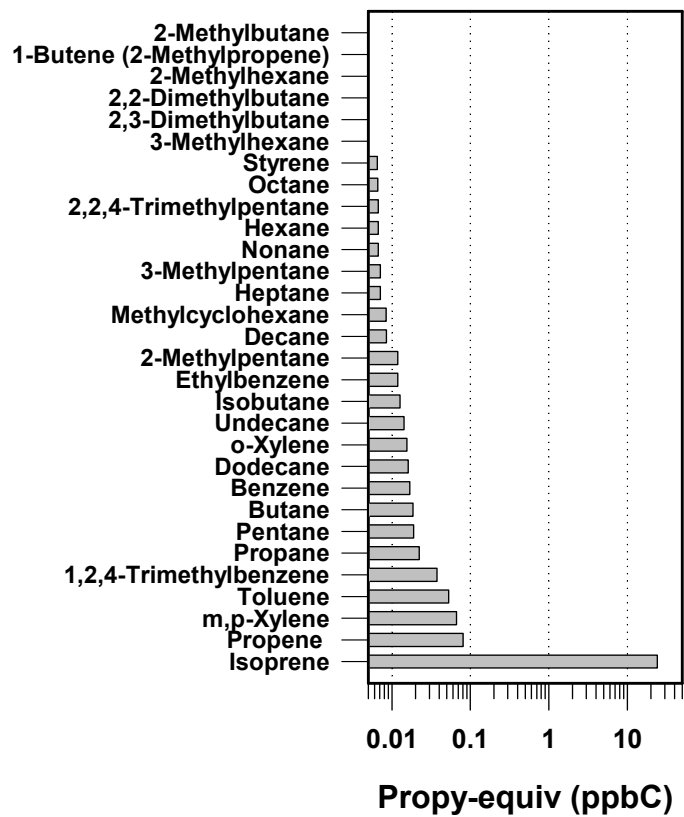


Figure 2: Hydrocarbon compounds scaled to the propylene equivalent reactivity. The ensemble hydrocarbon averages were estimated based on daytime measurements above the Oak Ridge mixed deciduous forest.

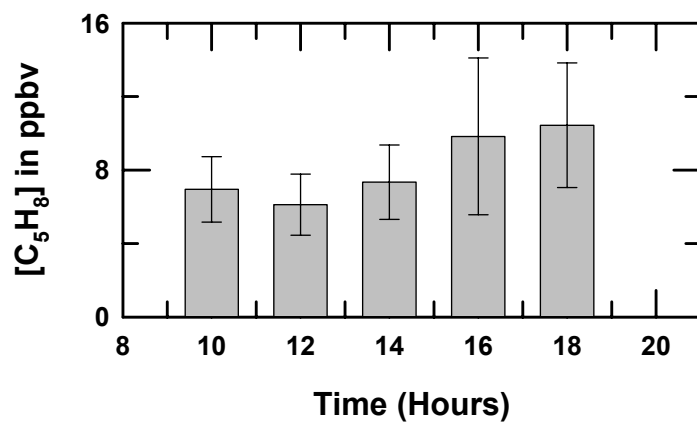


Figure 3: Diurnal variations of average isoprene mixing ratios measured above the Oak Ridge mixed deciduous forest. The vertical bars denote standard deviations around the average values.

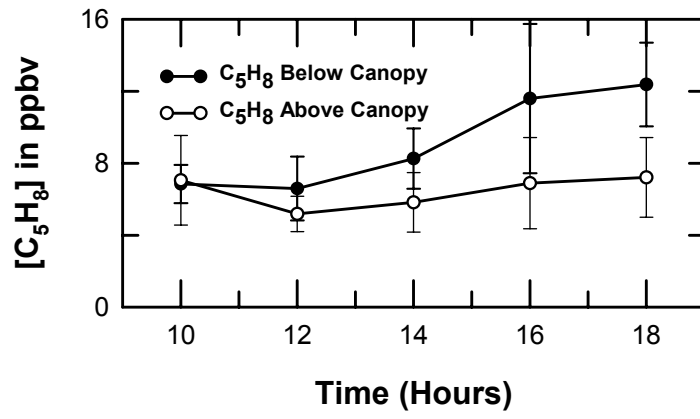


Figure 4: Diurnal variations of average isoprene mixing ratios measured outside and inside the Oak Ridge mixed deciduous forest. The vertical bars denote standard deviations around the average values.

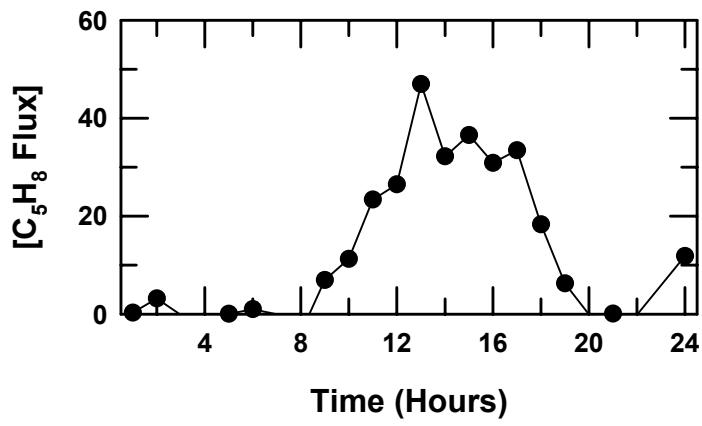


Figure 5: Diurnal variations of isoprene flux densities measured above the Oak Ridge mixed deciduous forest. The fluxes are expressed in mg (isoprene) per (m^2 minute).

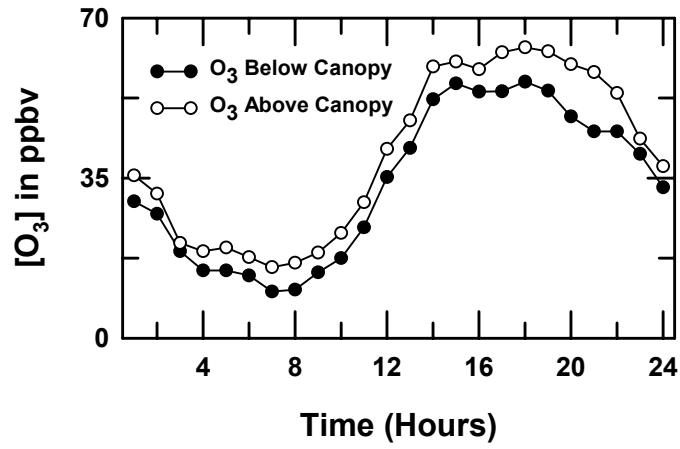


Figure 5: Diurnal variations of averaged ozone mixing ratios observed above and below the forest canopy height. The observed gradients resulted due to both chemical destruction and physical deposition to the foliage elements.

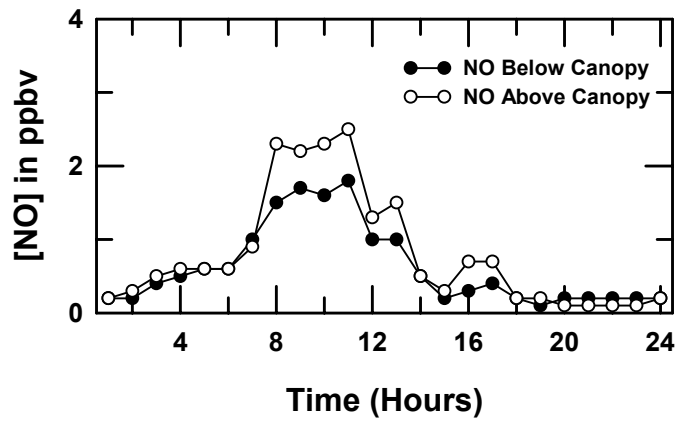


Figure 6: Diurnal variations of averaged nitric oxide mixing ratios observed above and below the forest canopy height. The elevated nitric oxide levels measured in the morning hours resulted due to local vehicular traffic from a busy road located 2 km from the measurement site.

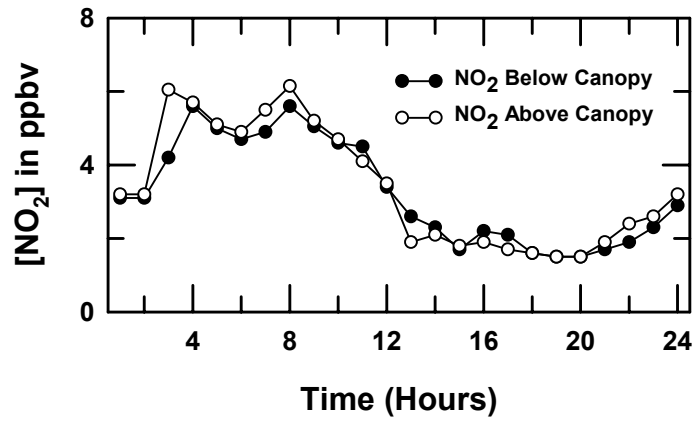


Figure 7: Diurnal variations of averaged nitrogen dioxide mixing ratios observed above and below the forest canopy height.

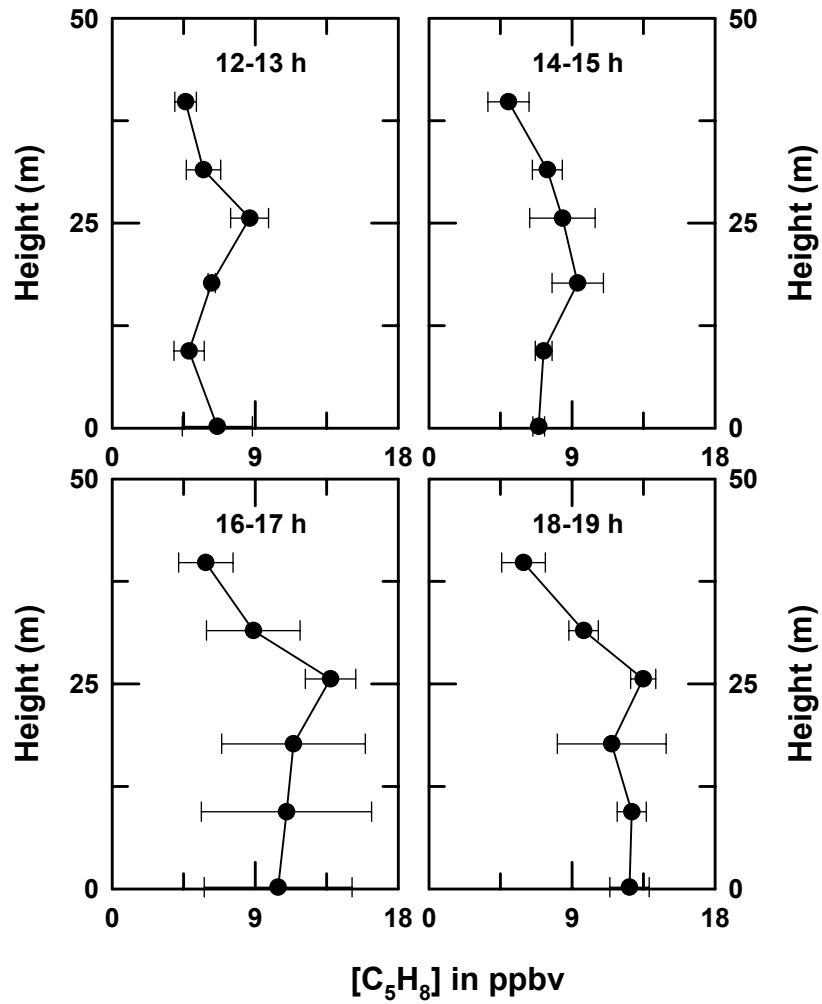


Figure 8: Vertical variation of averaged isoprene mixing ratios observed at selected times of day. The horizontal bars denote the standard deviation around the average values.

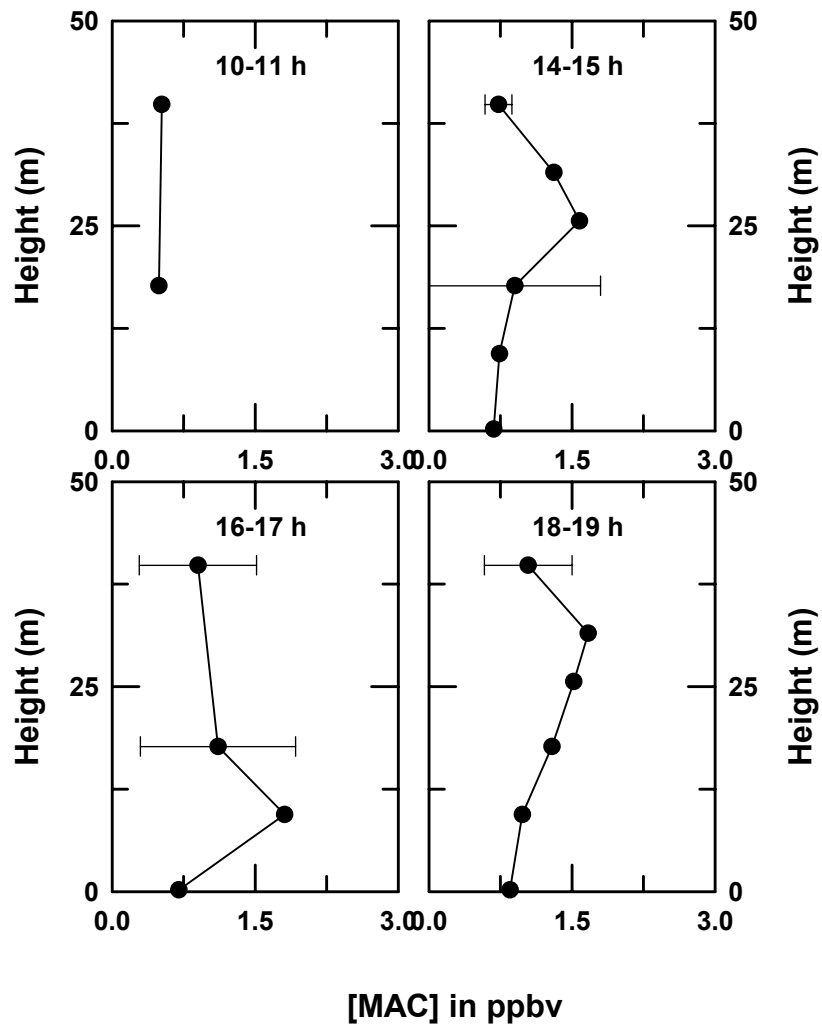


Figure 9: Vertical variation of averaged methacrolein mixing ratios observed at selected times of day. The horizontal bars denote the standard deviation around the average values.

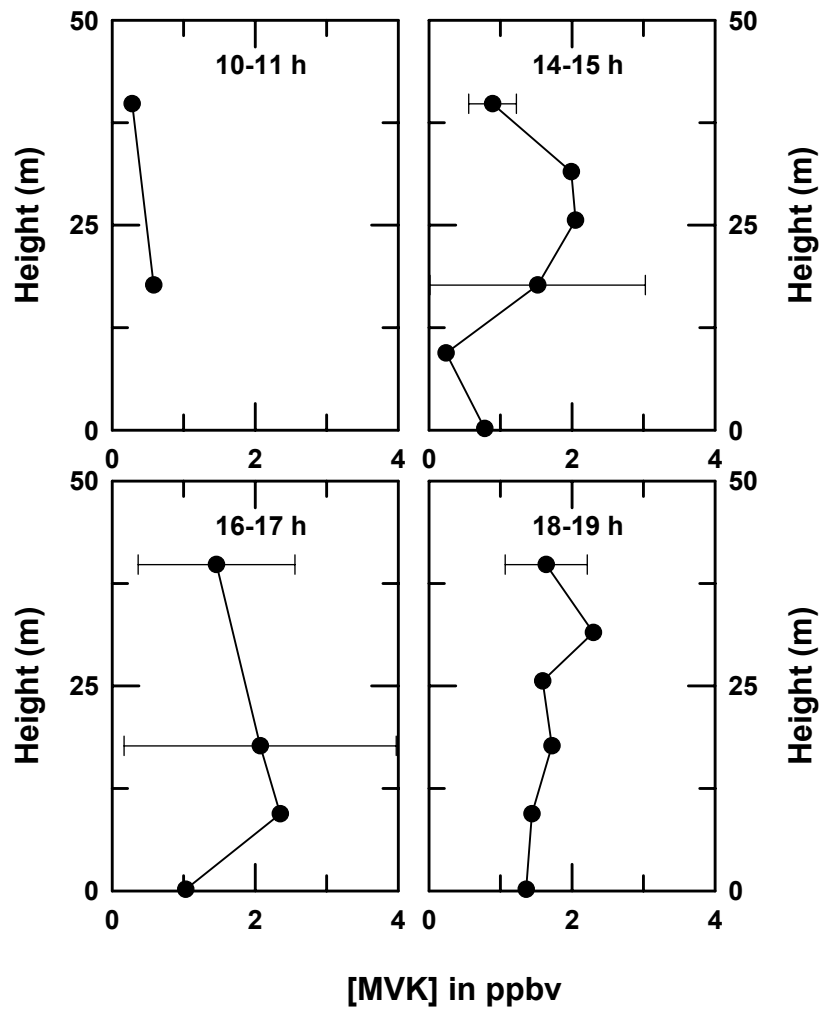


Figure 10: Vertical variation of averaged methyl vinyl ketone mixing ratios observed at selected times of day. The horizontal bars denote the standard deviation around the average values.

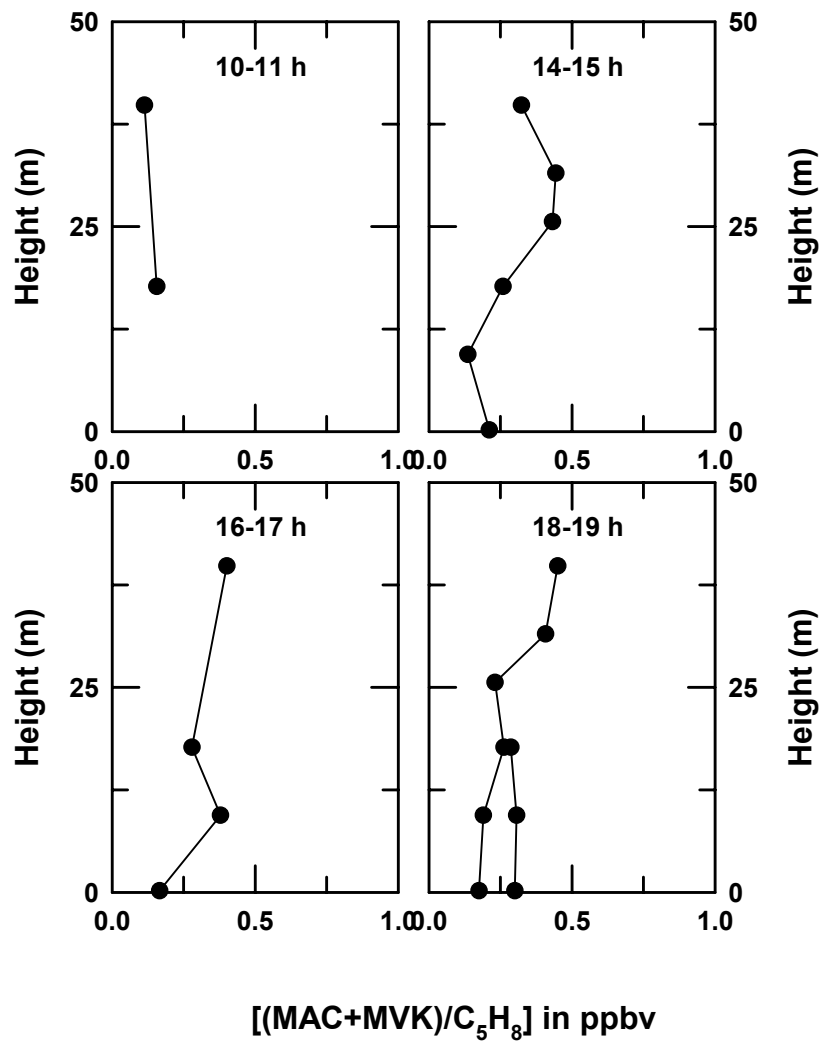


Figure 11: Vertical variation of averaged ratios for methacrolein and methyl vinyl ketone to isoprene observed at selected times of day. The horizontal bars denote the standard deviation around the average values.