Vertical sampling and analysis of nonmethane hydrocarbons for ozone control in urban North Carolina

Jay H. Lawrimore, Mita Das, and Viney P. Aneja

Department of Marine, Earth and Atmospheric Sciences, College of Physical and Mathematical Sciences, North Carolina State University, Raleigh

Abstract. As part of an effort by the state of North Carolina to develop a State Implementation Plan for ozone control in the Raleigh Metropolitan Statistical Area (MSA), vertical measurements of C2-C10 hydrocarbons were made, in and above the surface inversion layer (SIL), as inputs to the urban airshed model (UAM). Three-hour integrated ambient air samples were collected during August 1993 from 0500-0800 eastern daylight time (EDT). Additional samples were collected from 1200-1500 and 1700-2000 EDT on selected days. Vertical sampling was achieved from a 610-m television tower located approximately 15 km southeast of the downtown area. Boundary layer wind and temperature profiles were determined by balloon soundings. For some compounds, e.g., propane, the average concentration was lower above the inversion layer (9.59 ppbC in the SIL and 2.08 ppbC above the SIL); however, other species such as 2-methylpentane had higher concentrations above the inversion layer (1.28 ppbC in and 1.40 ppbC above the SIL). In addition, the vertical distributions of hydrocarbons within the convective boundary layer were compared to the vertical distribution estimated from calculations based on surface concentration, species reactivity, and eddy diffusivity. Compounds such as isoprene and N-butane decreased as predicted by the equation, while others such as propane and benzene showed unexpected profiles. Calculations of propylene-equivalent concentrations were used to estimate the effect of reactivity on the relative importance of individual hydrocarbons. The contribution of isoprene to the local hydrocarbon budget was analyzed and surface measurements were compared with data collected in Atlanta, Georgia, during the 1992 Southern Oxidants Study. Isoprene comprised more than 70% of the total propylene-equivalent concentration in the afternoon in Raleigh but only 40% of the total in Atlanta.

Introduction

Production of ozone in the troposphere is limited in part by the supply of hydrocarbons [Logan et al., 1981]. The importance of nonmethane hydrocarbons (NMHCs) as ozone precursors depends largely on their reactivities and ambient concentrations. Because of this, a thorough knowledge of the distribution of all hydrocarbon compounds is essential for realistic modeling and prediction of the local and regional capacity for ozone production. Furthermore, the vertical distribution of NMHCs are a necessary database for accurate modeling of the photochemical system [Kanakidou, 1989].

Many studies have involved measurement of the vertical distribution of hydrocarbons in the troposphere [Bonsang et al., 1991; Greenberg et al., 1990; Kanakidou et al., 1989; Singh et al., 1988; Tille et al., 1985; Sexton and Westberg, 1984; Greenberg and Zimmerman, 1984; Rasmussen and Khalil, 1983]. In each study, mobile platforms, mostly light aircraft, were used for sample collection throughout the troposphere. Rasmussen et al. [1983] measured vertical profiles of selected hydrocarbons to determine their relationship to Arctic haze. Greenberg and Zimmerman [1984], Greenberg et al. [1990], and Singh et al. [1988] measured hydrocarbons over Colorado, the U.S. West Coast and Alaska, and Colorado and the East Pacific, respectively. Vertical variations of hydrocarbons in the remote marine boundary layer have also been studied [Bonsang et al., 1991]. But the most creative collection technique was the use of a manned hot air balloon by Kanakidou et al. [1989] to collect hydrocarbons over rural France. However, prior to this project no extensive measurements of the vertical distribution of NMHCs from a 610-m stationary platform had been attempted. The use of a stationary platform allows integrated sampling which, because of extended sampling time, reduces the impact of transient atmospheric influences that cause extreme concentrations not representative of the local air mass.

The following is a discussion of the results of a 1-month study involving the collection and analysis of the vertical distribution of C3-C7 NMHCs in an urban area of North Carolina. Samples were simultaneously collected from a 610-m television tower from three levels (surface, level 1; 250 m, level 2; and 450 m, level 3) weekdays from August 2 to 27, 1993. Three-hour integrated samples were collected from 0500-0800 EDT (period 1) to gain insight into the relationship between hydrocarbon concentrations in the surface inversion and boundary layers. Vertical profiles in the daytime boundary layer were studied by collecting samples from 1200-1500 (period 2) and 1700-2000 EDT (period 3) on selected days.

In this study we (1) compare C3-C7 hydrocarbons in and above the surface inversion layer based on ambient concentrations measured during the 0500-0800, 1200-1500 and 1700-2000 EDT periods, (2) determine the vertical distribution of selected compounds in the convective boundary layer, and (3) analyze the hydrocarbon budget using propylene-equivalent concentration, especially in relation to isoprene.

Collection and Analysis

Sample Collection

The collection site is approximately 15 km southeast of downtown Raleigh, North Carolina, population of approximately 250,000. Raleigh is located in the central part of the state about 150 km west of the Atlantic Ocean. A 610-m television tower instrumented for chemical measurements was used for sample collection.

The tower is located approximately 0.5 km from a well-traveled state highway. The tower property is accessed by way of a private entrance, and access is only permitted for professional purposes and is only possible between the hours of 0800 and 1700 EDT Tuesday through Friday. Because the tower is used by some commercial organizations, there was occasional automotive traffic to and from the tower during those hours. None of the period 1 samples were influenced by on-site traffic as sample collection was accomplished before 0800. Period 3 samples were collected after 1700, thus they were also unaffected by on-site automotive emissions. So that there would be no impact from on-site traffic during the 1200-1500 sampling period, samples were only collected during this period when no other organizations had scheduled work on the tower.

Pumps and canisters were placed at the surface and in weather-proof enclosures at approximately 250 and 450 m. The upper levels were reached by way of a two-man elevator. Three-hour integrated samples were collected weekdays in 6-L electropolished SUMMA canisters using Parker metal bellows MB151 pumps connected to 1/8-inch stainless steel tubing that extended 6 feet from the tower. Electronic timers were used for unattended sampling and 3-hour samples were confirmed with a digital meter.

Two canisters were connected to each pump system at all levels, so that collection during two sampling periods could be accomplished between tower visits if necessary. Canisters used for period 1 sampling were placed on the tower the day prior to collection (Monday's canisters were placed on Friday) and picked up within 2 hours after sample collection, except on Monday when the tower was closed. The collected samples were then returned to North Carolina State University (NCSU) for same-day analysis. Period 2 and period 3 canisters were placed in the enclosures 2 hours prior to sample collection and were analyzed the following day.

Canisters were cleaned using a process that consisted of evacuating canisters to less than 0.5 torr, continuing the evacuation for 1 hour and pressurizing to 1500 torr with humidified zero air. The process was repeated and the cans evacuated to less than 0.5 torr. On a daily basis one randomly selected canister was filled with humidified zero HC air and analyzed to verify the cleaning process.

Although samples were collected each weekday during this period from at least one level, only samples collected simultaneously at all three levels were included in this analysis. This restriction was adopted to ensure that meteorological conditions affecting average concentrations at one level would not be absent in the data collected at the other levels.

Although there were 20 weekdays during this sampling period, data were collected at all three levels on only 17 of those days. A total of 17 sets of data collected from 0500-0800 were analyzed. Additional samples were also collected from 1200-1500 and 1700-2000 on some of these same days. Ambient samples were collected at all levels from 1200-1500 on 6 days and from 1700-2000 on 2 days. Thus samples were collected at all levels during the morning, afternoon, and early evening on 2 days.

Sample Analysis

Samples were analyzed at NCSU using a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector (FID). C2-C10 hydrocarbons were separated with a fused silica 100 m X 0.25 mm capillary column coated with a 0.5-μm methylpolysiloxane (DB-1) stationary phase (J&W Scientific, Folsom, California). The gas chromatograph (GC) column was cooled to an initial temperature of -50°C and held for 3 min. Column temperature was then increased at a rate of 6°C/min to 175°C, then increased at a rate of 25°C/min to a final temperature of 250°C .

An Entech 2000 automated concentrator (Entech Laboratory Automation, Simi Valley, California) was used to preconcentrate 300 mL of sample air prior to injection into the GC system. The Entech concentrator is a computerized system that uses an internal cryotrapping module (25 cm X 0.3 cm OD) filled with 80-100 mesh glass beads (trap 1) cooled to -180°C with liquid nitrogen for preconcentration. The requested volume of sample is delivered to the trap by way of a mass flow controller. After the 300-mL sample volume has been quantitatively trapped, trap 1 is heated to 150°C and flushed with helium to transfer the trapped compounds to a small cryofocusing trap held at -185°C. The cryofocuser is rapidly heated at a rate of 6000°C/min to inject the trapped compounds onto the GC column. For a more detailed discussion of the sample analysis procedures see *Apel et al.* [1994].

Species identification was achieved by retention time comparison with a known standard acquired from the National Center for Atmospheric Research (NCAR) in Boulder, Colorado. Quantification of hydrocarbons was obtained using a National Institute for Standards and Technology (NIST) traceable standard mixture containing N-butane and benzene. It was assumed that the FID had the same ppbC response to all hydrocarbons as to N-butane [*Dietz*, 1967]. The retention time and mass standards were analyzed daily to ensure system precision. A blank consisting of zero air was also analyzed daily to check for system contamination.

Results and Discussion

Vertical Measurements of C3-C7 Speciated Hydrocarbons

Although C2-C10 hydrocarbons were separated, meaningful analysis of only C3-C7 compounds was possible due to two technical problems. There was reason to believe that the concentrations of C2 compounds (ethane, ethene, and acetylene), did not accurately reflect their actual ambient concentrations. It was also determined that contaminants, identified by GC/Mass Spectrometry (MS) as siloxanes, were present in the C8-C10 range of elution. Mass spectrometry analysis of representative samples was performed at the U.S. Environmental Protection Agency. Although the origin of the contamination is unclear, it may have resulted from silicone materials used in the construction of the sampling enclosures. The magnitude of the contaminant peaks decreased throughout the study which would be expected as the effluent from silicone materials diminishes with time.

Table 1 shows the average and median concentrations and ranges for the 14 most abundant C3-C7 hydrocarbons collected during period 1. During this sampling period the

Table 1. Vertical Distribution of Speciated Nonmethane Hydrocarbons (ppbC) for Ambient Samples Collected From 0500-0800 EDT

Compound	Surface			250 m			450 m		
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
Propane	9.59 (1)	9.50	25.50 - 3.36	2.08 (5)	2.36	5.88 -0.00	1.89 (1)	2.02	4.44 - 0.00
Toluene	8.96 (2)	5.59	26.22 - 3.32	2.30 (4)	2.16	3.77 - 1.31	1.68 (2)	1.52	8.22 - 0.00
I-Pentane	4.42 (3)	3.69	9.91 - 1.75	3.12 (1)	2.32	8.90 - 0.88	1.61 (3)	1.24	3.97 - 0.59
Isoprene	2.08 (4)	1.83	5.64 - 0.49	0.42 (9)	0.00	2.15 - 0.00	0.11 (13)	0.00	1.84 - 0.00
N-Butane	2.04 (5)	1.85	3.92 - 0.75	0.82 (8)	0.88	2.86 - 0.00	0.64 (9)	0.74	1.61 - 0.00
N-Pentane	1.97 (6)	1.68	4.65 - 0.75	2.71 (2)	2.40	6.14 - 0.00	0.98 (6)	0.74	3.75 - 0.00
Benzene	1.32 (7)	1.34	2.98 - 0.65	0.61 (9)	0.64	2.09 - 0.00	0.74 (8)	0.67	1.64 - 0.48
2-Methylpentane	1.28 (8)	1.25	2.99 - 0.64	1.40 (6)	1.28	3.04 - 0.62	1.57 (4)	1.62	2.97 - 0.57
N-Hexane	0.87 (9)	0.72	2.50 - 0.00	0.19 (13)	0.00	0.99 - 0.00	0.08 (17)	0.00	0.80 - 0.00
3-Methylpentane	0.70 (10)	0.78	1.98 - 0.00	0.95 (7)	0.89	2.08 - 0.00	0.92 (7)	1.03	1.43 - 0.00
I-Butane	0.61 (11)	0.74	1.75 - 0.00	0.14 (14)	0.00	1.76 - 0.00	0.04 (18)	0.00	0.75 - 0.00
Propene	0.54 (12)	0.75	1.59 - 0.00	0.04 (19)	0.00	0.72 - 0.00	0.00 (*)	0.00	0.00 - 0.00
Methylcyclopentane	0.30 (13)	0.00	1.08 - 0.00	0.05 (18)	0.00	0.92 - 0.00	0.17 (12)	0.00	1.15 - 0.00
2,3-Dimethylpentane	0.25 (14)	0.00	0.89 - 0.00	2.37 (3)	2.50	3.65 - 0.63	1.51 (5)	1.02	5.42 - 0.50

This table lists the averaged and median ambient concentrations and the ranges for the samples collected at each level during the 0500-0800 sampling period.
Numbers in parentheses denote relative abundance ranking.
*Species was not detected.

surface inversion layer was below the 250-m level [*Aneja et al.*, 1993]. Thus, lower platform measurements taken above 250 m during this period reflect compound concentrations in the residual layer. The residual layer is the air mass above the surface nocturnal boundary layer formed during the previous evening and reflects, for the most part, transported pollutants from surrounding cities and regions upwind of the tower site. During the breakup of the morning inversion the hydrocarbons and other pollutants in the residual layer mix with the fresh pollutants recently released in the surface layer and contribute to the production of photochemical ozone. Consequently, pollutant composition and concentration information in both the boundary and the residual layers are important photochemical ozone model inputs.

Average pollutant concentrations were determined for individual compounds at each level. Median concentrations and ranges were used to determine if the average values were influenced by any extremely high or low measurements. Propane had the highest mean concentration at the surface (9.59 ppbC) and a median concentration of 9.50 ppbC. Toluene was the next most abundant species with a mean concentration of 8.96 ppbC; however, its median concentration was only 5.59 ppbC. This large difference primarily resulted from three exceptionally high concentration observations of 19.45, 19.84, and 26.22 ppbC. The cause of these large values is unclear. These high values could not be correlated with those of any other species and the concentrations of other compounds were not abnormally high on these two days. Toluene sources either locally or upwind of the site could not be determined. Mean and median concentrations for the next four most abundant compounds at the surface were isopentane at 4.42 and 3.69 ppbC, isoprene at 2.28 and 1.83 ppbC, N-butane at 2.04 and 1.85 ppbC, and N-

pentane at 1.97 and 1.68 ppbC, respectively. All of these compounds had lower concentrations in the residual layer, except N-pentane, which had mean and median concentrations of 2.71 and 2.40 ppbC, respectively, at the 250-m level.

As expected, average pollutant concentrations for most compounds at the surface were larger than those measured at the 250- and 450-m locations during period 1. The mean sum of the C3-C7 compounds at the surface was 35.83 ppbC compared to 18.30 ppbC at 250 m and 13.36 ppbC at 450 m. Because the 250-m and 450-m levels were above the nocturnal inversion layer and thus separated from local hydrocarbon sources during the 0500-0800 sampling period, the ambient concentration of most species should be significantly higher at the surface, as compared to those measured at the upper levels during this period.

A t-test was used to compare the mean concentration of each of the 10 most abundant species at each level, during period 1, to determine if there were statistically significant differences in concentrations between the surface and 250-m and 450-m levels. Differences between the surface and 250-m level, surface and 450-m level, and 250-m and 450-m levels were tested using a two-sample t-test and evaluated at the 5% significance level. Eight of the 10 species had significantly higher concentrations at the surface when their concentrations were compared with those at the 250-m level. Nine of 10 species were also significantly higher at the surface than at the 450-m level. The vertical profiles of 2-methylpentane and N-pentane were anomalous. Not only were their surface and 250-m level concentrations not significantly different but also the concentration of each species was higher at the 250-m level. The reason for this profile is unclear. Although they both react slowly with the OH radical and have longer lifetimes than other species such as toluene and isoprene, their reactivity

cannot explain such relatively large concentrations above the inversion layer. Other compounds with similar lifetimes, such as N-butane and propane, had much higher concentrations at the surface than at the upper levels. There are also no known sources that would emit such relatively large concentrations of these species above the nocturnal inversion layer.

While most hydrocarbons had significantly higher concentrations at the surface, when the concentrations of those same species at the 250-m and 450-m levels were tested for differences, 9 out of 10 resulted in insignificant t-tests. Because both levels were above the inversion layer during the 0500-0800 sampling period, their distribution was even and extreme gradients were absent in almost all species. The only species that differed was N-pentane. The vertical profile of N-pentane was characterized by the lack of a distinct concentration gradient between the surface and the 250-m level. However, its concentration at the 450-m level dropped significantly compared to those measured at both the surface and the 250-m levels.

While most species measured during the 0500-0800 sampling period exhibited significant negative concentration gradients between the surface and the 250-m level, this profile was not prevalent in samples collected during period 2. During the afternoon, both the surface and the 250-m levels

were within the convective boundary layer [Aneja et al., 1993]. As a result of vertical transport and greater atmospheric dispersion during period 2 as well as chemical conversion of the large pool of near-surface hydrocarbons to peroxy radicals, smaller concentration gradients between the surface and the 250 m level occurred in the afternoon.

Using the six 1200-1500 samples, t-tests were performed on the same 10 species evaluated in the 0500-0800 samples. Although 8 of 10 hydrocarbon concentrations measured from 0500-0800 were significantly higher at the surface, 7 of the 10 species collected from 1200-1500 did not have significantly different mean concentrations between any level. Toluene had lower concentrations at 250 m due to an extremely high mean concentration of 16.2 ppbC at the surface. Isoprene also had significantly lower concentrations at 250 m and 450 m. This is most likely due to the extremely high reactivity of isoprene with the OH radical. Because of its reactivity the lifetime of isoprene is only a couple of hours, and as a result, its concentration decreases rapidly with height in the convective boundary layer; 2-methylpentane once again showed an anomalous profile with increasing concentrations with height during the 1200-1500 sampling period.

Average concentrations of selected species sampled on the 2 days during the study when collection occurred at all levels
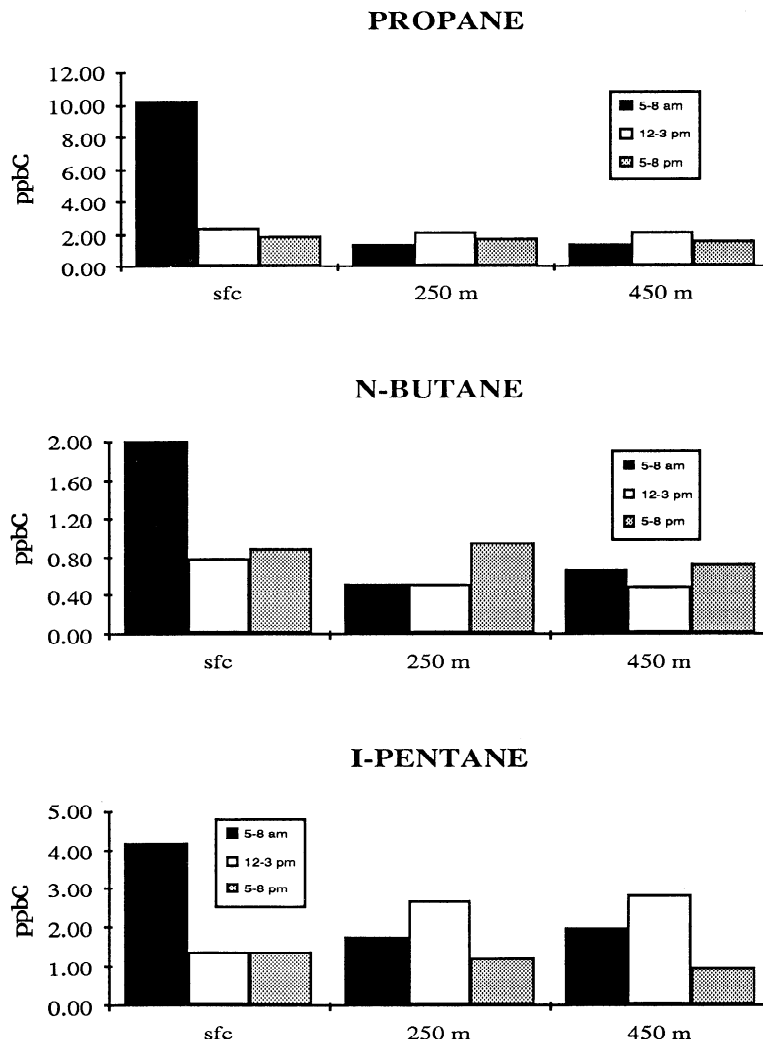

Figure 1. Diurnal profiles for selected hydrocarbons at each level based on average values from two days (August 11 and 19, 1993) when all three periods were sampled.
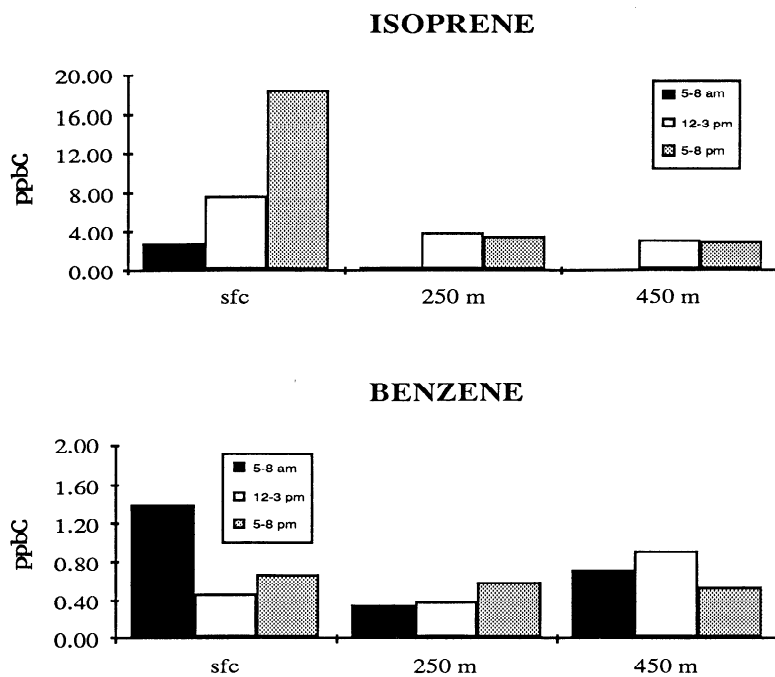
ISOPRENE

BENZENE

Figure 1. (continued)

during all three sample periods are shown in Figure 1. Although it is difficult to draw definitive conclusions due to the limited number of samples collected during period 3, some qualified conclusions are suggested. The surface concentration drop of some species, such as I-pentane, coincided with a large upper level increase in the afternoon. This observation is consistent with the breakup of the surface inversion layer and may be due to convective transport. Balloon soundings showed boundary layer depths of 10 to 100 m at 0700, increasing to heights of 1000 to 2000 m by midafternoon [*Aneja et al.*, 1993]. As the boundary layer depth increased, surface concentrations most likely decreased due to convective transport and mixing of the pollutants to higher levels. However, while surface concentrations for propane, N-butane and benzene significantly decreased from the morning to the afternoon, their 250-m and 450-m concentrations showed minimal change in the afternoon, suggesting that the largest portion of these surface hydrocarbons are being horizontally transported or chemically converted.

Measurements of isoprene showed large jumps in concentration at all levels from the morning to afternoon as increases in sunlight intensity and temperature resulted in higher isoprene emission rates from local deciduous trees. While isoprene concentration decreased in the late afternoon at the 250-m and 450-m levels, surprisingly, its surface concentration was highest during the 1700-2000 period.

Vertical Profiles in the Convective Boundary Layer

The vertical distribution of hydrocarbons in the convective boundary layer are influenced by both convective mixing and photooxidation processes. Samples collected from 1200-1500 were used to access the vertical distribution of individual species in a well-mixed layer. These observed profiles were compared with a simple one-dimensional model that is often used to estimate the vertical distribution of hydrocarbons when only surface measurements are available [*Chameides et al.*, 1992]. Hydrocarbon concentrations are expected to

decrease with height in the boundary layer due to diffusion and reaction with the OH radical [*Chameides and Cicerone*, 1978; *Chameides et al.*, 1992]. Compounds of high reactivity are consumed at a faster rate, resulting in larger concentration gradients, and compounds of low reactivity are carried aloft with little reduction due to photooxidant processes. To estimate the upper level hydrocarbon concentrations without measurement, *Chameides et al.* [1992] used a model, dependent on eddy diffusivity and OH rate constants, to predict an exponentially decreasing concentration (equation (1)).

$$C_J(z) = C_J(0) \exp [(-SQRT(k_{OH}(J))\, z\, (C_{OH}/K)^{1/2}] \qquad (1)$$

where

$C_J(z) =$	concentration at height z, ppbC;
$C_J(0)$	concentration at the surface, ppbC;
$k_{OH}(J)$	reactivity of species with OH radical, (cm³/molecule/s) constants from *Warneck* [1988];
z	height, cm;
C_{OH}	concentration of the OH radical, molecules/cm³;
K	eddy diffusivity coefficient cm² s⁻¹.

Eddy diffusivity was approximated to be constant throughout the sampling height with a value estimated for typical summertime conditions of 100 m² s⁻¹ (S.P. Arya, personal communication, 1993). Typical midday summertime OH concentrations have been established to be 106 molecules/cm³ [*Logan et al.*, 1981].

The *Chameides et al.* [1992] model was applied to individual species with results provided in Figure 2 for observed and estimated profiles. (Estimated concentrations were calculated using the average measured surface concentrations of all 1200-1500 samples). No consistent vertical trend could be established from the measured concentrations. Some species concentrations (e.g., isoprene and N-butane) decreased similar to those in the estimated profiles. However, the other three compounds had different vertical profiles with higher
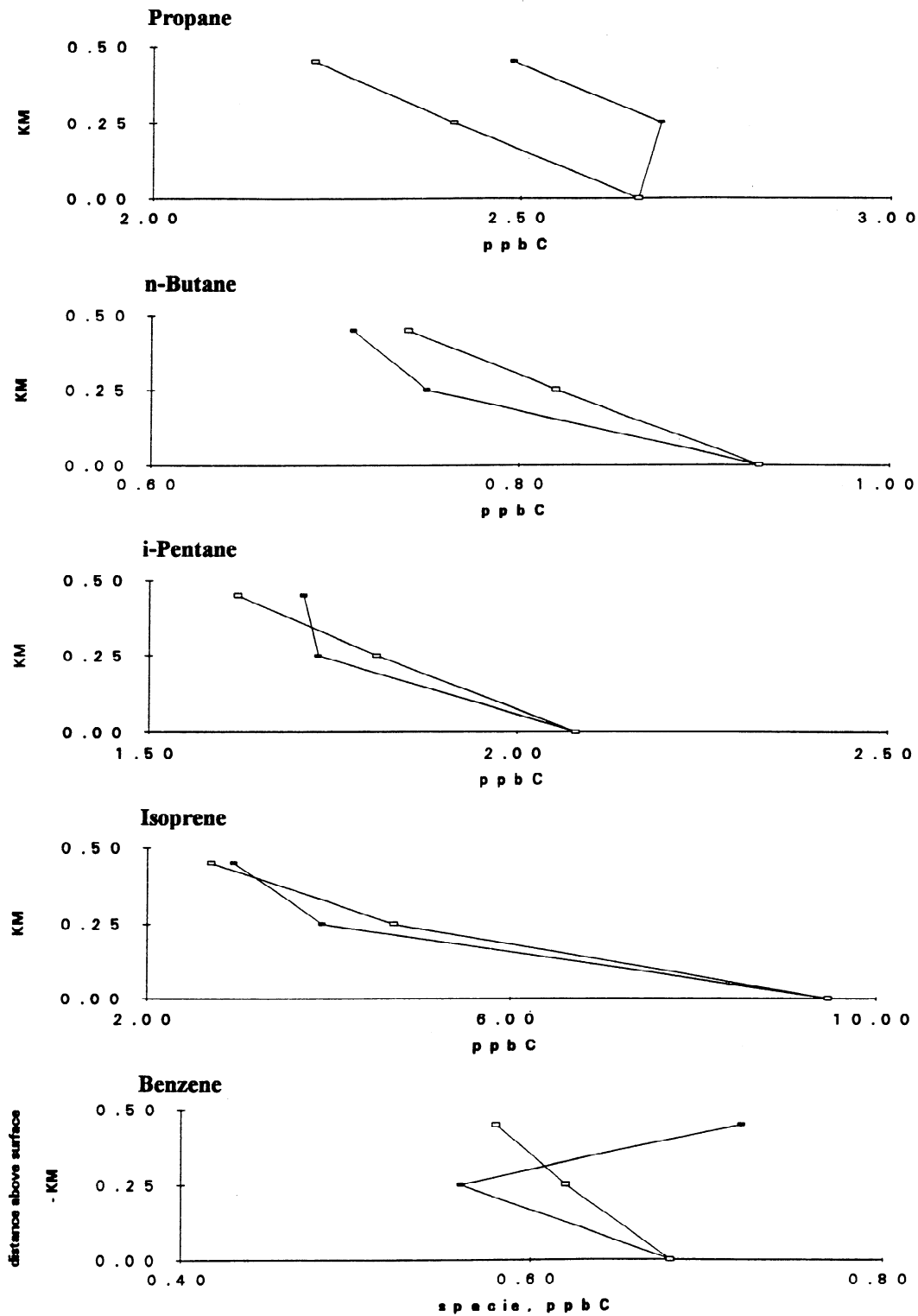
Figure 2. Comparison of measured and calculated vertical profiles for HC species for the 1200-1500 EDT sampling period. Open rectangles are the measured concentrations and solid rectangles represent the calculated concentrations.

pollutant concentrations measured at the upper levels. Inconsistent profiles for other pollutants not shown in Figure 2 were also observed and did not appear to be a function of compound reactivity.

These results are not surprising due to the limitations involved in the assumptions associated with eddy diffusion. The eddy diffusivity coefficient is based on an assumption that there is similarity between molecular and turbulent transfers such that eddy diffusivity is analogous to molecular kinematic viscosity. Just as transfer of heat occurs down the gradient from high to low temperatures, mass is expected to be transferred from areas of high to low concentration in the atmosphere. However, this analogy is only partially correct at best. Eddy diffusivities are properties of the flow, not properties of the fluid, and as such can vary by large amounts from one area of a flow to another and between flows. Also, in

a convective layer the theory of down-gradient transport is often incorrect, since heat is transported upward in large amounts even though the potential temperature gradient is near zero. In addition to inaccuracies resulting from those assumptions, the use of a constant eddy diffusivity within a boundary layer leads to additional error. Constant eddy diffusivity coefficients are most applicable in the free atmosphere, away from boundary layers. Within the near-neutral and stable planetary boundary layer (PBL), a more accurate eddy diffusivity coefficient profile consists of an increasing coefficient from the surface to the middle of the boundary layer, and then decreasing values to the top of the layer. [Arya, 1988].

Inconsistencies in vertical distribution profiles have also been noted in other studies. Greenberg et al. [1990] found that meteorological processes often distribute hydrocarbon emissions throughout the troposphere so that there often exist no vertical gradients and greater variability than predicted from considerations of eddy diffusivity and OH reactivity alone. Measurement of C2-C7 compounds over the U.S. West Coast showed large increasing concentrations from 100 to 300 m with over twice the TNMHC concentration at 300 m [Greenberg et al., 1990]. Bonsang et al. [1991] concluded that emission and transport processes of NMHCs are much too variable to lead to a reproducible typical vertical profile due to the dominance of atmospheric dynamical processes over chemical destruction. In that study, the distribution of alkanes and alkenes could not be related to their reactivities. Rasmussen and Khalil [1983] measured largest concentrations for ethane, acetylene, and propane at 1-2 km above the surface.

Effect of Hydrocarbon Reactivity With Hydroxyl Radical

Although a thorough knowledge of the vertical distribution of hydrocarbons throughout the lower troposphere is required for implementation of adequate ozone abatement policies, it is only the first step in an adequate assessment of the local hydrocarbon budget. Because of the differences in reactivity with OH, consideration of hydrocarbon concentration alone often presents an inaccurate picture of the actual ozone-producing potential of the local air mass. Just as methane, a very abundant gas in the troposphere, has little influence on ozone production because of its low reactivity, other compounds are more or less important depending on their reactivities. Even though a compound may exhibit low

ambient concentrations, it may be an important ozone precursor if its reactivity with the OH radical is high.

To account for differences in reactivity and to obtain a better assessment of the relative importance of each specie in the urban area, we used a method adopted by Chameides et al. [1992] of normalizing the concentration of each hydrocarbon to that of propylene by calculating a propylene-equivalent concentration.

$$\text{propy-equiv (J)} = C_J (k_{OH}(J)/k_{OH}(C_3H_6)) \qquad (2)$$

where C_J is equal to concentration of the species; $k_{OH}(J)$ is equal to the rate constant for the species with OH; and $k_{OH}(C_3H_6)$ is equal to the rate constant for propylene with OH.

The propy-equiv concentration takes into account the combined effect of hydrocarbon concentration and reactivity with OH. A compound twice as reactive as propylene would have a propy-equiv concentration twice its ambient concentration and vice versa, if their ambient concentrations were the same.

The effect of hydrocarbon/OH radical reactivity can be seen in a comparison of period 1 measurements converted to propy-equiv concentration. (The OH rate constants used to calculate the propy-equiv concentrations were obtained from Middleton and Stockwell [1990] and Warneck [1988].) Four of the six most abundant compounds at the surface are alkanes and as a group are the least reactive compounds. Thus when reactivity with the OH radical is considered, the impact of these high-concentration species decreases significantly. As a group, C3-C7 hydrocarbons were less reactive than propylene. The average C3-C7 concentration at the surface during period 1 was about 35 ppbC, while the propy-equiv concentration was less than 15 ppbC.

The potential influence of OH radical reactivity on ozone production is most clearly evident for the species isoprene. Isoprene had the highest average propy-equiv concentration at the surface during all three periods (7.65, 36.33, and 70.63 ppbC during periods 1, 2, and 3, respectively). As evidenced by those concentrations, isoprene may have more impact on ozone production in urban areas than some of the most common anthropogenically produced compounds.

In the past, major efforts have been placed on the control of anthropogenic hydrocarbon emissions in urban areas, while the influence of natural hydrocarbons has been disregarded. Natural emissions, particularly isoprene, have only recently been viewed as having a significant impact on ozone
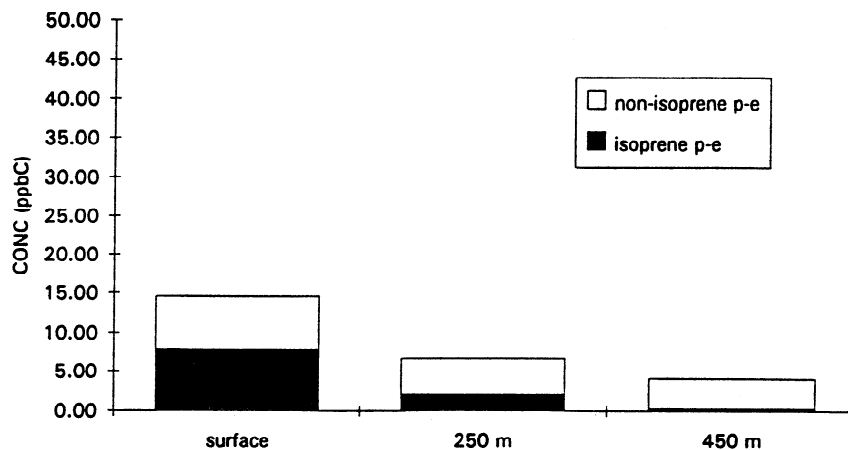

Figure 3. Propylene-equivalent concentration of isoprene and sources other than isoprene at each level from 0500-0800.
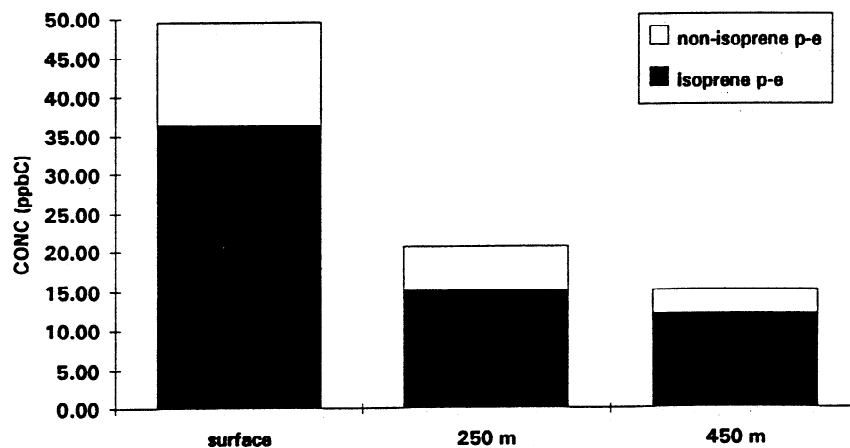
Figure 4. Propylene-equivalent concentration of isoprene and sources other than isoprene at each level from 1200-1500.

production in urban areas in the Southeast United States [*Chameides et al.*, 1988]. The failure to recognize the importance of naturally emitted compounds as a major source of ozone-producing hydrocarbons in urban areas may be one reason for the lack of success in reducing ozone in U.S. cities [*Chameides et al.*, 1988].

Isoprene comprises approximately 50% of all biogenic hydrocarbons emitted in the southeast during the summer months [*Lamb et al.*, 1987]. These large emissions coupled with its extremely high reactivity with the OH radical (k_{OH} = 78 X 10^{12} cm^3 molecule^{-1} s^{-1}) suggest that isoprene may be the most important naturally emitted compound in the southeast. *Chameides et al.* [1988] estimated that the emission rate of isoprene in Atlanta was large enough that a 70% reduction in anthropogenic hydrocarbon emissions was required to reach the National Ambient Air Quality Standard for ozone versus only a 30% reduction if isoprene emissions were not included.

To determine the potential impact of isoprene in the Raleigh area, the propy-equiv concentration of isoprene was compared to the total C3-C7 propy-equiv concentration during the 0500-0800 and 1200-1500 sampling periods. By not including all NMHCs, this comparison may exaggerate the influence of isoprene; however, the comparison gives an approximation for the importance of isoprene. In the morning, when anthropogenic emissions are highest and isoprene emissions lowest, isoprene made a substantial contribution to hydrocarbon reactivity. Isoprene was found to comprise 54% of the total C3-C7 propy-equiv concentration during the 0500-0800 sampling period (Figure 3). By midday the contribution of isoprene far exceeded the combined concentration of all other C3-C7 compounds. In samples collected during the 1200-1500 sampling period, isoprene contributed over 70% of the total concentration at the surface and between 75 to 80% of the total prop-equiv concentration at the two upper levels (Figure 4).

These values were compared to surface data collected by the Air Quality Group at NCSU during the 1992 Southern Oxidants Study in Atlanta, Georgia at the South Dekalb site, located southeast of downtown Atlanta. A similar comparison was accomplished for data collected from 0700-0800 and 1200-1500 at the South Dekalb site. (Ambient air samples were not collected from 0500-0700.) Isoprene contributed about 20% to total C3-C7 propy-equiv concentration in the morning and about 40% in the afternoon. The reduced influence of isoprene

as compared to the Raleigh site is not surprising. Because Atlanta is a substantially larger metropolitan area, a larger percentage of emissions should be of anthropogenic origin.

The increasing influence of isoprene during the afternoon is partly due to increases in isoprene vapor pressure in the leaves of deciduous trees [*Tingey et al.*, 1979]. These processes that result in higher ambient air concentrations are enhanced by greater sunlight intensity and higher air temperatures [*Rasmussen and Jones*, 1973; *Tingey et al.*, 1979]. However, during midday hours the processes become sunlight saturated and temperature becomes the controlling factor [*Tingey et al.*, 1979]. Others [*Monson and Fall*, 1989; *Sharkey and Loreto*, 1993] found sharp increases in isoprene emissions from deciduous trees and plants as leaf temperatures increased from 20°C to 40°C.

We compared the six ambient surface measurements made during the 1200-1500 sampling period and found a strong positive linear correlation between air temperature and surface concentration. (Figure 5) At the measured temperature ranges, this concentration profile is very similar to isoprene emission profiles observed by *Monson and Fall* [1989] and *Sharkey and Loreto* [1993]. Although linear regression resulted in a correlation coefficient of 0.95, it must be noted that the slope is strongly influenced by one of the data points. It is difficult to draw definitive conclusions from a data set consisting of only six data points.
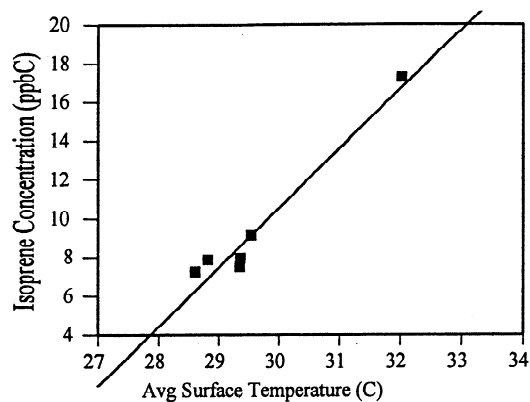

Figure 5. The concentration of isoprene at the surface during sampling period 2 (1200-1500 EDT) versus average surface air temperature. The linear regression best fit line is also shown.

Conclusion

Vertical measurements of speciated C3-C7 hydrocarbons collected as 3-hour integrated samples from 0500-0800 EDT are presented. Results from samples collected from 1200-1500 and 1700-2000 EDT on selected days are also discussed. Ambient concentrations and adjusted concentrations based on reactivity with the OH radical (propylene-equivalent concentration) were determined within and above the early morning surface inversion layer. As expected, total surface values exceeded those in the residual layer; however, some compounds, i.e., 2-methylpentane and N-pentane, showed maximums at the 250-m level. Based on concentration and reactivity with the OH radical, the largest contribution to the C3-C7 hydrocarbon budget was attributed to isoprene, a very reactive naturally emitted species. Isoprene constituted more than 50% of potential hydrocarbon reactivity in the morning and over 70% in the early afternoon at the surface. Afternoon measurements also showed that isoprene surface concentration linearly increased with air temperature.

Diurnal profiles for selected compounds showed that concentrations at the surface decreased from the morning to the early afternoon sampling period. This distribution was attributed to convective mixing of pollutants throughout the boundary layer and chemical conversion to peroxy radicals. Samples collected from 1200-1500 were also used to calculate the vertical distribution of selected hydrocarbons in the convective boundary layer. These measurements were compared with a one-dimensional model that predicts exponentially decreasing concentration dependent on reactivity with the OH radical and eddy diffusivity. Some observed profiles compared well with the profiles predicted by the model.

This unique experiment has provided the opportunity to determine the vertical structure of ozone precursor concentrations, i.e., speciated hydrocarbons, in the layer of the troposphere comprising the largest vertical concentration gradients of the most reactive hydrocarbons. The use of a 610-m tower enabled 3-hour integrated vertical ambient sample collection which is often not possible when using a mobile platform. Integrated sampling prevented measurement of extreme hydrocarbon concentrations caused by turbulent eddies that distort actual concentrations present in the local air mass. With the use of these vertical measurements as inputs to the urban airshed model (UAM), a more accurate assessment of future ozone control strategy requirements and other issues dealing with the Clean Air Act amendments will be possible.

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V.P. Aneja (corresponding author), M. Das, and J.H. Lawrimore, Department of Marine, Earth and Atmospheric Sciences, College of Physical and Mathematical Sciences, North Carolina State University, Box 8208, Raleigh, NC 27695-8208. (email: VINEY_ANEJA@ncsu.edu)