Int. J. Global Environmental Issues, Vol. 6, Nos. 2/3, 2006

Vertical distribution of VOCs and ozone observed in suburban North Carolina

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Abstract: As a continuing effort by the State of North Carolina to develop a State Implementation Plan for ozone control in the Raleigh Metropolitan Statistical Area, vertical measurements of C_2–C_{10} hydrocarbons and ozone are made on a 610 meter multi-communications tower. Results signify that both long-range transport from fossil fuel combustion, petroleum exploration, petroleum refineries, and geogenic natural gas and local emissions from surface coating and paper production are the major sources of anthropogenic organic compounds at this location. Vertical distributions of various compounds are examined with respect to the relative abundance as well as reactivity to study the role of NMHCs in ozone production. When the concentrations of NMHCs are lower than some threshold value (60 ppbC), ozone concentrations increase with the increase of NMHC concentrations; but when NMHC concentrations are higher than 60 ppbC, ozone concentrations decrease with increase of NMHC concentrations.

Keywords: air quality; hydrocarbons; isoprene; ozone production.

Reference to this paper should be made as follows: Das, M., Aneja, V.P. and Kang, D. (2006) 'Vertical distribution of VOCs and ozone observed in suburban North Carolina', *Int. J. Global Environmental Issues*, Vol. 6, Nos. 2/3, pp.149–172.

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1 Introduction

Nonmethane hydrocarbons (NMHC) play an important role in the complex atmospheric chemistry in the troposphere as key precursors to oxidant formation (Finlayson-Pitts and Pitts, 1986; Lawrimore et al., 1995; Logan et al., 1981). Over continental areas, the degradation of NMHC occurs via reactions with hydroxyl radical (OH) and, to a lesser extent, some of them with ozone (O_3) and nitrate radicals (NO_3) (Atkinson, 1990). These reactions of NMHC act as a sink for the above oxidants although the complete oxidation scheme of NMHC could finally lead to a net destruction or a net production of OH and O_3, depending on the NO_X levels. The importance of NMHC as ozone precursors and the specific nature of the relationship between the two is the subject of ongoing research, utilising ongoing monitoring programmes as well as modelling efforts. Thus a thorough knowledge of the horizontal as well as the vertical distribution of hydrocarbon compounds is essential for the realistic modelling and prediction of the local and regional capacity for ozone production. While a fair amount of data exist on the speciation and concentration of NMHC at the surface, on the vertical variability of the NMHCs within the atmospheric boundary layer data are still very sparse.

Knowledge of vertical distribution of hydrocarbons is important for air quality studies for several reasons. Photochemical air quality models require information on top and inflow boundary conditions for the specific hydrocarbons being modelled (Killus and Moore, 1991). Since there are a lack of observational data on the vertical distribution of hydrocarbons, usually values at higher levels are estimated by models from surface level concentrations for use in these photochemical models, which could be quite erroneous. Information about the source of hydrocarbons in air masses can be obtained by examining the vertical concentration profiles of hydrocarbons to infer where the major sources and sinks are located. Hydrocarbon measurements made above and below the boundary layer, together with knowledge of their chemical reactivity and life times can give important information on the transport of these compounds from urban centres to less polluted downwind areas. The vertical profiles of hydrocarbons (and any chemical species) are controlled by the cycle of boundary layer variation, vertical transport, nocturnal inversion, sources and chemical processes (Aneja et al., 2000).

Biogenic NMHC (BNMHC) consisting of most reactive hydrocarbons has raised an increasing amount of interest in literature as one reason for the failure of cities in the eastern US to meet air quality standards for ozone (Chameides et al, 1988, 1997). Emission inventories have been compiled (Guenther et al., 1994, 1995, 2000; Lamb et al., 1987) which indicate that, on a continental scale, BNMHC emissions can comprise a large fraction of the total hydrocarbon source strength. BNMHC emissions consist of very different compounds, though isoprene and α-pinene make up the major fraction (Lamb et al., 1987, 1993; Zimmerman, 1979). The emission rates of isoprene from trees in particular can be very high, which can be as much as a few percent of net primary productivity (Guenther et al., 1995; Zimmerman et al., 1988). Because of these high emission rates and isoprene's considerable rate of reaction with OH, this species can play a major role in controlling the production of ozone within the boundary layer of both urban as well as rural areas during photochemically active periods of the year (Andronache et al., 1994; Chameides et al., 1988; Montzka et al., 1993; Trainer et al., 1987a,b).

This field experiment attempts to

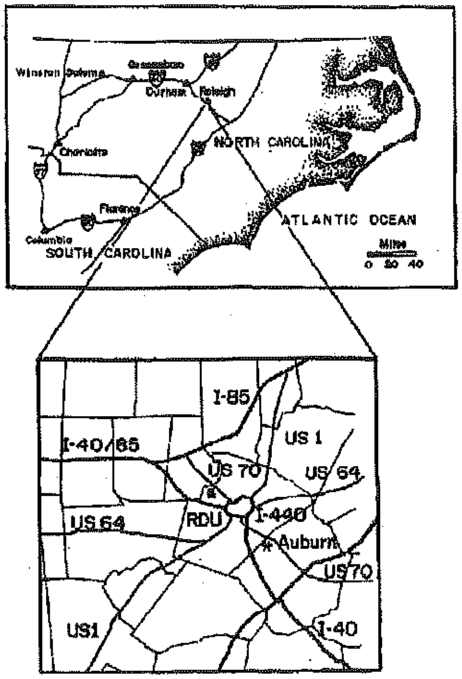
- study the vertical distribution of about 60 C_2–C_{10} nonmethane hydrocarbon compounds that have been identified as key precursors to ozone formation
- study the relative contribution of biogenic compounds to the total reactivity in the suburban area
- examine the relationship between NMHC concentrations and ozone production.

2 Methodology

2.1 Experimental site

Samples are collected at 10, 250, and 433 m on the Auburn Transmitter Tower, a 610-m multi-communications tower located near the town of Auburn, North Carolina (N Latitude 35° 40" 35'; W Longitude 78° 32" 09'). The sampling site is approximately 19 km (12 miles) east-southeast of downtown Raleigh, N.C. with a population of approximately 250,000. Major population centres within a 200 km radius of the tower as well as the close proximity of major highways, most notably US Highway 70, Interstate 40, and Interstate 95, are identified in Figure 1.

Figure 1 Sampling location



From a base elevation of 96 m above mean sea level, the tower rises over 600 m. The adjacent fetch can be described as a mixture of cleared farmlands and small forest plots composed of a mixture of deciduous and coniferous trees. Situated between the low, rolling hills of the Uwharrie mountains (elevation 180 to 275 m), approximately 100 km to the west, and the flat topography of the coastal plain to the east, the geography near the tower is fairly uniform, with small changes in elevation of 30 m or less.

Since the tower is located approximately 1 km southwest of US-70 and approximately 3 km east of I-40, automobile exhaust is expected to be the primary local source for NO_X and certain NMHCs. Besides the automotive exhaust there are also several large NO_X point sources (such as power plants) within a 200 km radius. The largest NMHC point source is determined to be a gasoline storage facility located approximately 25 km east of the collection site. Other types of point sources such as vegetable oil processing, paper production and surface coating located within a 200 km radius could also affect the NMHC concentration at the site under certain meteorological conditions.

2.2 Sample collection and analysis

Three hour integrated samples are collected on week days in 6 l electropolished SUMMA canisters using Parker Metal Bellows model MB151 pumps connected to 1/8 inch stainless steel tubing that extended outwards six feet from the tower. Pumps and canisters are housed at the surface (10 m above the ground on the tower), and in stainless steel waterproof enclosures at approximately 250 and 450 m. Samples are analysed at North Carolina State University using a Hewlett Packard 5890 Series II gas chromatograph equipped with a flame ionisation detector (FID). C_2–C_{10} hydrocarbons are separated with a fused silica 100 m × 0.25 mm capillary column coated with a 0.5 μm methylpolysiloxane (DB-1) stationary phase (J&W Scientific, Folsom, California). An Entech 2000 Automated Concentrator (Entech Laboratory Automation, Simi Valley, California) is used for preconcentration of the sample prior to injection into the GC. For a more detailed discussion of the sample collection and analysis procedures refer to Apel et al. (1994), Farmer et al. (1994), or Lawrimore et al. (1995).

Species identification is achieved by retention time comparison with a known standard acquired from the National Center for Atmospheric Research (NCAR) in Boulder, Colorado. The chromatographic peaks are also identified by a GC/MS system. Quantification of hydrocarbons is obtained using an NIST traceable standard mixture containing n-butane and benzene. It is assumed that the FID has the same ppbC response to all hydrocarbons as to n-butane (Dietz, 1967). The coefficient of variance for n-butane is calculated to be $\leq 3\%$ during the entire study period. The retention time and mass standards are analysed daily to ensure system precision. A blank consisting of zero air is also analysed daily to check for system contamination. The blank signals are small ($\leq$ 3ppbC) and observed for only a few compounds ($\leq$ 9C) (no significant blank signals are observed for $\geq$ 9C compounds). The system is also checked for reproducibility by analysing at least one canister twice every day.

The detection limit for a 300 ml sample is established to be ≤ 0.1 ppbC for all the species studied. The overall accuracy of the analytical system is estimated to be ~ 5%. The system has also performed well in two inter-comparison studies, one of which involves the analysis of an air sample provided by NCAR as part of the Nonmethane Hydrocarbon Inter-comparison Experiment (Apel et al., 1994).

The carbonyl sampling system consists of a pump (Parker Metal Bellows MB151) connected to the sampling cartridge which is in turn connected to a 1 m long, 1/4 inch OD copper tubing coated with KI, ozone denuder tube. An electric solenoid valve is located between the denuder tube and the cartridge. The pump and the solenoid valve are connected to a timer for unattended operation. Flow meters are used to calibrate the pump before and after sample collection.

Carbonyl sampling is achieved with silica cartridges coated with purified 2-4-dinitrophenylhydrazine. The cartridges are prepared at the University of North Alabama, shipped to the field site for exposure and returned for elution and analysis. Most of the samples are collected during the 5–8 am period at all the three levels except for a few exceptions. In addition to field blank and precision tests, sequential tests are also performed to check for cartridge breakthrough.

Carbonyl samples are analysed at the University of Alabama. High performance liquid chromatography (HPLC) is employed for the elution and analysis of carbonyls. The HPLC is an LDC Milton Roy Constametric 3000 system equipped with a variable wavelength UV detector (360 nm) and a 10μL Rheodyne fixed loop injector. Isocratic elution with 60:40 acetonitrile-water is used for samples and standards. The HPLC is calibrated using 2-4-dinitrophenylhydrazone standards that are carefully weighed and serially diluted.

Samples are collected on weekdays from June 1 to Sept 2, 1994 at the three levels. Samples collected from 5–8 am EDT (Period 1) are used to gain an insight into the relationship between hydrocarbon concentrations in the surface inversion and boundary layers. Samples collected from 12–3 pm (Period 2) and 5–8 pm EDT (Period 3) on selected days provide vertical profiles in the daytime boundary layer. Although samples are collected each week day during these periods from at least one level, only samples collected simultaneously at all three levels are included in this analysis. This ensures that meteorological conditions affecting average concentrations are uniform for all levels. Additional samples are collected for determining the carbonyl levels during Period 1 at the three levels.

A typical VOC chromatogram consists of more than 100 peaks representing the complexity of the mixture of the volatile organic compounds present in the atmosphere. A subset of these volatile organic compounds consisting of about 60 nonmethane hydrocarbons that have been identified is used in this analysis.

The analysis focuses on data collected during Period 2, i.e. 12–3 pm EDT because this is the photochemically active period and also, typically, the time of most intense vertical mixing. Data collected from this period are thought to best reflect the balance between emissions and photochemical oxidation and least homogeneity caused by local sources.

Ozone was monitored at ground level, 250 and 433 m using the ultraviolet photometric detection principle. A Dasibi model 1003 AH analyser was used for each level. The instrument is designated by the US EPA as an 'equivalent method'. The analysers were multipoint calibrated daily.

2.3 *Meteorological analysis*

Meteorological parameters such as temperature, relative humidity, wind speed, wind direction and boundary layer height were determined from balloon soundings. Balloons were launched at 7:00 am, 1:00 pm, and 7:00 pm (EDT) on certain days during this measurement. For meteorological parameters at 10 m (surface) observations from the Raleigh-Durham (RDU) airport National Weather Service (NWS) hourly and special weather observations were used. The mean meteorological parameters measured at the tower are presented in Table 1 (note that quite a number of measurements failed, due to the malfunction of equipment and other reasons; only successful measurements (N) are included in the calculation).

Table 1 Mean meteorological parameters measured at the tower

	7:00 am			*1:00 pm*			*7:00 pm*		
	10 m	*250 m*	*433 m*	*10 m*	*250 m*	*433 m*	*10 m*	*250 m*	*433 m*
N	23	22	20	7	10	11	3	3	3
Tw (°C)	19.3	19.0	18.5	18.5	21.7	20.5	12.2	19.1	18.4
Tw (°C)	(0.8)	(0.8)	(1.0)	(0.6)	(1.3)	(1.1)	(3.0)	(1.9)	(2.0)
T (°C)	21.1	21.6	21.1	19.8	25.5	23.9	12.2	24.5	22.8
T (°C)	(0.8)	(0.8)	(0.9)	(0.6)	(1.6)	(1.5)	(1.7)	(1.8)	(1.8)
θ (K)	296.3	297.3	298.6	302.7	300.6	301.1	301.1	300.0	300.2
θ (K)	(0.9)	(0.7)	(0.9)	(1.6)	(2.30)	(2.2)	(2.9)	(1.8)	(2.0)
PBL (m)	194 (34) (N = 23)			993 (169) (N = 7)			1610 (96) (N = 2)		

Notes: N is the number of measurement used in the average, Tw is wet-bulb temperature, T is dry bulb temperature, and θ is potential temperature. Values in parentheses stand for ± standard deviation

The height of the PBL, also commonly known as the mixing height, is an important parameter in studying air pollutant dispersion in the atmosphere. Mixing height is also an important parameter in modelling transport and the dispersion of chemical and photochemical pollutants on local/urban and regional scales. The height of the PBL was determined from profiles of temperature and concentrations obtained from radiosonde measurements during the measurement period. As Table 1 indicates, following sunrise in early morning, the mixing height began to increase with the increase in surface temperature, reaching about 200 m at 7:00 am, which was still lower than the middle level of hydrocarbon measurement (250 m). At 1:00 pm, the average of PBL height was about 1020 m, well above the upper level of hydrocarbon measurement (433 m). At 7:00 pm, the average of PBL height further increased to 1270 m, near its maximum value for the day.

3 Results and discussion

3.1 *Distribution of NMHC in the Lower Boundary Layer*

The statistics of the most abundant NMHCs detected during the three time periods are given in Tables 2(a–c) and Table 3 lists the average concentrations of carbonyl compounds from 5–8 am for all three levels. In general concentrations decrease from Level 1 to Level 3 for most of the alkanes and biogenic compounds, indicating surface sources for these compounds. Considerable amounts of formaldehyde, acetaldehyde and acetone are observed at higher levels. The average NMHC concentrations observed in this study are compared with those observed in other non-urban locations in Table 4. The concentrations of most compounds are comparable with other studies.

Table 2(a) Statistics of major NMHC compounds (ppbC) during three time periods at the surface

	5–8 am EDT					*12–3 pm EDT*					*5–8 pm EDT*				
Compound	*Mean*	*Median*	*STD*	*Max*	*Min*	*Mean*	*Median*	*STD*	*Max*	*Min*	*Mean*	*Median*	*STD*	*Max*	*Min*
Ethylene	1.31	1.09	1.10	3.29	0.00	0.59	0.00	0.75	2.40	0.00	1.01	1.15	0.56	1.51	0.00
Acetylene	0.90	0.75	0.95	2.45	0.00	0.60	0.69	0.53	1.34	0.00	0.79	1.07	0.62	1.30	0.00
Ethane	1.70	1.60	1.23	3.90	0.00	2.03	1.62	1.20	4.27	0.83	2.90	2.90	1.33	4.36	0.72
Propene	0.43	0.52	0.36	1.01	0.00	0.20	0.12	0.28	1.03	0.00	0.09	0.00	0.15	0.36	0.00
Propane	5.76	6.40	2.18	8.88	1.55	2.46	2.12	1.31	5.27	0.59	2.16	2.11	0.87	3.41	0.86
I-butane	0.59	0.60	0.34	1.38	0.00	0.37	0.41	0.30	0.81	0.00	0.26	0.18	0.30	0.63	0.00
n-butane	1.58	1.33	0.90	3.98	0.34	1.41	1.22	0.65	3.30	0.81	0.91	0.98	0.20	1.15	0.60
I-pentane	2.85	2.44	1.69	7.71	0.00	2.99	2.64	1.82	7.08	0.54	1.40	1.46	0.28	1.69	0.99
n-pentane	1.26	1.16	0.61	2.89	0.26	1.47	0.94	1.96	8.36	0.49	0.61	0.66	0.13	0.73	0.40
Isoprene	3.53	2.56	2.16	7.94	0.96	12.01	11.77	4.14	18.20	2.66	18.72	18.16	6.58	30.91	11.70
3-methyl-1-pentene	0.16	0.10	0.03	1.11	0.00	0.42	0.48	0.35	1.06	0.00	0.62	0.59	0.14	0.88	5.00
2-mehtylpentane	0.83	0.77	0.45	2.02	0.36	0.53	0.49	0.26	0.99	0.00	0.37	0.37	0.07	0.46	0.30
3-methypentane	1.59	1.52	0.67	2.60	0.38	5.88	2.66	6.63	21.55	1.36	8.18	8.39	5.57	17.95	1.73
n-hexane	0.72	0.71	0.32	1.46	0.00	0.52	0.37	0.67	2.79	0.00	0.21	0.27	0.18	0.43	0.00
Methylcyclopentane	0.46	0.46	0.19	0.79	0.00	2.05	1.68	1.93	6.81	0.00	2.65	2.34	1.59	5.58	1.24
Trichloroethane	0.55	0.48	0.20	1.07	0.35	0.40	0.40	0.17	0.71	0.00	0.43	0.41	0.12	0.61	0.31
Benzene	0.96	0.86	0.43	1.79	0.30	0.72	0.73	0.28	1.18	0.30	0.72	0.70	0.22	1.10	0.41
Trichloroethylene	0.67	0.71	0.41	1.43	0.00	0.40	0.40	0.26	0.90	0.00	0.28	0.37	0.22	0.48	0.00
Methylccyclohexane	0.77	0.76	0.30	1.43	0.40	0.50	0.44	0.28	1.19	0.00	0.45	0.42	0.19	0.77	0.26
Toluene	3.88	3.57	1.56	6.92	1.94	2.82	2.18	1.85	8.02	1.53	2.14	2.13	0.38	2.76	1.72
n-octane	0.49	0.45	0.17	0.89	0.28	0.49	0.39	0.25	1.19	0.24	0.37	0.35	0.07	0.46	0.30
Perchloroethylene	1.69	1.53	0.69	3.30	0.76	1.01	0.97	0.42	1.84	0.30	0.83	0.88	0.19	1.02	0.55

Table 2(a) Statistics of major NMHC compounds (ppbC) during three time periods at the surface (continued)

	5–8 am EDT					*12–3 pm EDT*					*5–8 pm EDT*				
Compound	*Mean*	*Median*	*STD*	*Max*	*Min*	*Mean*	*Median*	*STD*	*Max*	*Min*	*Mean*	*Median*	*STD*	*Max*	*Min*
Ethylbenzene	0.58	0.55	0.23	1.04	0.26	0.47	0.36	0.33	1.15	0.00	0.23	0.25	0.12	0.33	0.00
p-xylene	1.29	1.39	0.52	2.05	0.25	0.97	0.73	0.88	3.07	0.06	0.24	0.19	0.22	0.68	0.06
m-xylene	1.02	0.08	0.15	0.38	0.00	0.29	0.27	0.33	1.04	0.00	0.04	0.00	0.10	0.25	0.00
Styrene	0.30	0.18	0.36	1.18	0.00	0.40	0.23	0.44	1.28	0.00	0.00	0.00	0.00	0.00	0.00
o-xylene	0.61	0.54	0.23	1.08	0.30	0.48	0.39	0.33	1.15	0.00	0.23	0.27	0.11	0.31	0.00
a-pinene	3.43	3.58	1.68	6.27	1.16	1.43	1.34	0.77	3.89	0.54	2.34	1.91	1.21	4.33	1.18
m-ethyltoluene	0.62	0.70	0.60	2.21	0.00	0.23	0.00	0.37	1.06	0.00	0.22	0.00	0.36	0.82	0.00
1,2,4-trimethylbenzene	1.20	0.48	1.57	4.77	0.00	1.75	0.56	2.04	6.29	0.00	2.95	3.90	2.05	4.86	0.25
b-pinene	1.15	0.62	1.66	5.68	0.00	1.05	0.40	1.52	5.12	0.00	0.47	0.41	0.16	0.72	0.32

Table 2(b) Statistics of major NMHC compounds (ppbC) during three time periods at the mid level (250 m)

	5–8 am EDT					*12–3 pm EDT*					*5–8 pm EDT*				
Compound	*Mean*	*Median*	*STD*	*Max*	*Min*	*Mean*	*Median*	*STD*	*Max*	*Min*	*Mean*	*Median*	*STD*	*Max*	*Min*
Ethylene	0.06	0.00	0.23	0.83	0.00	0.10	0.00	0.35	1.26	0.00	0.14	0.00	0.35	0.85	0.00
Acetylene	0.40	0.00	0.55	1.61	0.00	0.72	0.00	1.02	2.78	0.00	0.81	0.40	1.07	2.65	0.00
Ethane	1.56	1.41	0.62	2.69	0.55	2.85	2.15	3.30	12.90	0.00	2.24	2.06	2.02	4.82	0.00
Propane	1.66	1.31	0.99	3.99	0.54	1.80	1.97	0.89	3.68	0.66	1.58	1.62	1.18	3.21	0.00
I-butane	0.11	0.00	0.22	0.63	0.00	0.18	0.00	0.25	0.64	0.00	0.19	0.00	0.30	0.60	0.00
n-butane	0.59	0.60	0.36	1.20	0.00	0.67	0.64	0.35	1.26	0.00	0.69	0.75	0.45	1.16	0.00
I-pentane	0.94	0.89	0.46	1.56	0.00	1.06	1.02	0.40	1.95	0.51	0.97	1.21	0.54	1.41	0.00
n-pentane	0.43	0.47	0.24	0.87	0.00	0.41	0.41	0.21	0.65	0.00	0.45	0.52	0.29	0.81	0.00
Isoprene	0.52	0.34	0.54	1.56	0.00	4.31	4.54	1.18	5.69	1.66	3.63	3.55	2.49	7.03	0.00
2-methyl-2-butene	0.42	0.00	1.16	4.07	0.00	0.02	0.00	0.08	0.29	0.00	0.00	0.00	0.00	0.00	0.00
3-methyl-1-pentene	0.32	0.37	0.38	1.26	0.00	0.34	0.33	0.36	1.08	0.00	0.55	0.54	0.34	0.93	0.00
2-mehtylpentane	0.27	0.27	0.37	1.34	0.00	0.19	0.00	0.24	0.71	0.00	0.33	0.33	0.24	0.74	0.00
3-methypentane	0.66	0.72	0.58	1.65	0.00	0.57	0.44	0.59	1.74	0.00	0.33	0.21	0.38	0.81	0.00
n-hexane	0.41	0.39	0.36	1.15	0.00	0.19	0.24	0.19	0.51	0.00	0.25	0.34	0.20	0.42	0.00
c-3-hexene	0.17	0.00	0.34	1.12	0.00	0.07	0.00	0.17	0.53	0.00	0.10	0.00	0.15	0.31	0.00
Methylcyclopentane	0.09	0.00	0.25	0.89	0.00	0.13	0.00	0.47	1.69	0.00	0.00	0.00	0.00	0.00	0.00
Trichloroethane	0.38	0.37	0.18	0.77	0.00	0.37	0.38	0.07	0.46	0.27	0.27	0.31	0.15	0.43	0.00
Benzene	0.47	0.42	0.25	0.95	0.00	0.52	0.54	0.24	0.99	0.00	0.51	0.55	0.29	0.81	0.00
Methylcyclohexane	0.55	0.54	0.28	1.37	0.29	0.44	0.38	0.27	1.18	0.00	0.35	0.36	0.21	0.57	0.00
Toluene	1.34	1.14	0.49	2.57	0.87	1.34	1.12	0.86	3.97	0.61	1.29	1.27	0.24	1.57	0.96
n-octane	0.38	0.39	0.18	0.73	0.00	0.31	0.32	0.09	0.46	0.16	0.32	0.36	0.17	0.46	0.00
Perchloroethylene	2.83	2.86	1.68	7.10	1.03	1.93	1.55	1.73	7.48	0.51	1.41	1.65	0.72	1.97	0.00

Table 2(b) Statistics of major NMHC compounds (ppbC) during three time periods at the mid level (250 m) (continued)

	5–8 am EDT					*12–3 pm EDT*					*5–8 pm EDT*				
Compound	*Mean*	*Median*	*STD*	*Max*	*Min*	*Mean*	*Median*	*STD*	*Max*	*Min*	*Mean*	*Median*	*STD*	*Max*	*Min*
Ethylbenzene	0.23	0.00	0.62	2.24	0.00	0.06	0.00	0.12	0.33	0.00	0.19	0.00	0.30	0.62	0.00
a-pinene	0.88	0.57	1.24	4.96	0.33	0.55	0.58	0.26	1.01	0.00	2.22	0.75	3.42	9.20	0.67
1,2,4-trimethylbenzene	9.81	10.59	7.79	24.18	0.00	7.65	8.06	5.04	15.01	0.00	10.37	10.79	5.68	17.51	0.26
b-pinene	2.79	0.41	4.93	15.59	0.00	1.10	0.40	1.82	5.78	0.00	0.28	0.32	0.15	0.40	0.00

Table 2(c) Statistics of major NMHC compounds (ppbC) during three time periods at the higher level (433 m)

	5–8 am EDT					*12–3 pm EDT*					*5–8 pm EDT*				
Compound	*Mean*	*Median*	*STD*	*Max*	*Min*	*Mean*	*Median*	*STD*	*Max*	*Min*	*Mean*	*Median*	*STD*	*Max*	*Min*
Acetylene	0.23	0.00	0.69	2.52	0.00	0.69	0.36	0.82	2.23	0.00	0.45	0.00	1.00	2.23	0.00
Ethane	1.93	1.54	1.18	4.40	0.78	1.71	1.47	1.15	4.09	0.00	2.68	2.83	2.01	5.84	0.92
Propane	1.62	1.22	1.01	3.60	0.59	2.04	2.14	1.14	4.62	0.55	1.94	2.21	1.05	3.25	0.77
I-butane	0.13	0.00	0.26	0.68	0.00	0.30	0.32	0.35	1.20	0.00	0.29	0.40	0.27	0.56	0.00
n-butane	0.71	0.59	0.34	1.41	0.30	0.88	0.92	0.26	1.23	0.51	0.99	1.14	0.44	1.54	0.40
I-pentane	0.84	0.83	0.37	1.55	0.29	1.21	1.08	0.45	2.06	0.48	1.42	1.14	0.73	2.60	0.67
n-pentane	0.50	0.44	0.33	1.14	0.00	0.97	0.64	1.45	5.94	0.00	0.66	0.58	0.49	1.48	0.23
Isoprene	0.41	0.34	0.53	2.00	0.00	3.23	3.20	1.17	5.19	1.39	3.38	3.02	1.67	5.62	1.24
2-mehtylpentane	0.11	0.00	0.16	0.41	0.00	0.33	0.33	0.30	1.08	0.00	0.52	0.31	0.64	1.62	0.00
3-methypentane	0.59	0.64	0.42	1.17	0.00	0.59	0.64	0.42	1.38	0.00	0.49	0.63	0.35	0.88	0.00
n-hexane	0.29	0.28	0.28	0.96	0.00	0.37	0.32	0.35	1.12	0.00	0.39	0.33	0.52	1.28	0.00
Trichloroethane	0.41	0.40	0.11	0.67	0.28	0.37	0.37	0.08	0.50	0.25	0.50	0.41	0.26	0.96	0.32
Benzene	0.58	0.58	0.17	0.90	0.32	0.63	0.58	0.19	1.06	0.38	0.73	0.64	0.27	1.07	0.43
2,3-dimethylpentane	0.29	0.16	0.40	1.38	0.00	0.36	0.00	0.69	2.36	0.00	0.13	0.00	0.29	0.65	0.00
Methylcyclohexane	0.78	0.84	0.32	1.41	0.32	0.44	0.43	0.23	1.07	0.00	0.52	0.54	0.08	0.62	0.43
Toluene	1.77	1.02	2.18	9.18	0.63	1.53	1.29	0.88	3.99	0.61	1.25	1.21	0.29	1.66	0.89
n-octane	1.09	0.89	0.54	2.09	0.20	1.34	1.22	0.51	2.52	0.77	1.22	1.31	0.26	1.51	0.91
Perchloroethylene	0.69	0.56	0.61	2.57	0.25	0.50	0.44	0.19	0.98	0.29	0.53	0.54	0.12	0.67	0.37
Ethylbenzene	0.83	0.26	2.42	9.23	0.00	0.94	0.28	1.97	6.53	0.00	0.16	0.23	0.15	0.32	0.00
p-xylene	0.87	0.50	1.05	4.13	0.07	1.77	0.07	5.42	20.53	0.00	0.28	0.17	0.27	0.70	0.00
m-xylene	0.41	0.37	0.34	1.25	0.00	0.28	0.26	0.29	0.80	0.00	0.33	0.31	0.25	0.66	0.00
o-xylene	0.36	0.32	0.29	1.08	0.00	1.32	0.00	3.11	9.93	0.00	0.18	0.26	0.17	0.35	0.00

Table 2(c) Statistics of major NMHC compounds (ppbC) during three time periods at the higher level (433 m) (continued)

	5–8 am EDT					*12–3 pm EDT*					*5–8 pm EDT*				
Compound	*Mean*	*Median*	*STD*	*Max*	*Min*	*Mean*	*Median*	*STD*	*Max*	*Min*	*Mean*	*Median*	*STD*	*Max*	*Min*
l-propylbenzene	0.31	0.24	0.36	1.13	0.00	0.36	0.29	0.40	1.29	0.00	0.32	0.25	0.16	0.53	0.17
a-pinene	1.23	0.90	0.77	3.27	0.43	1.40	1.22	0.81	2.93	0.48	0.96	0.90	0.27	1.43	0.72
1,2,4-trimethylbenzene	3.20	2.76	2.74	7.42	0.00	2.73	2.62	2.24	7.26	0.00	2.92	1.87	1.97	6.21	1.44
b-pinene	2.23	1.91	2.04	8.59	0.44	1.33	0.86	1.71	6.75	0.00	1.20	0.65	1.20	3.04	0.25

Table 3 Mean carbonyl concentrations of ambient air (ppbC) 5–8 am

	Methanal	*Ethanal*	*Acetone*	*Propanal*	*2-Butanone*
433 Meters	2.27	2.20	5.14	0.42	0.80
250 Meters	2.45	2.08	3.08	0.42	0.92
Surface	0.85	1.64	3.06	0.39	1.24

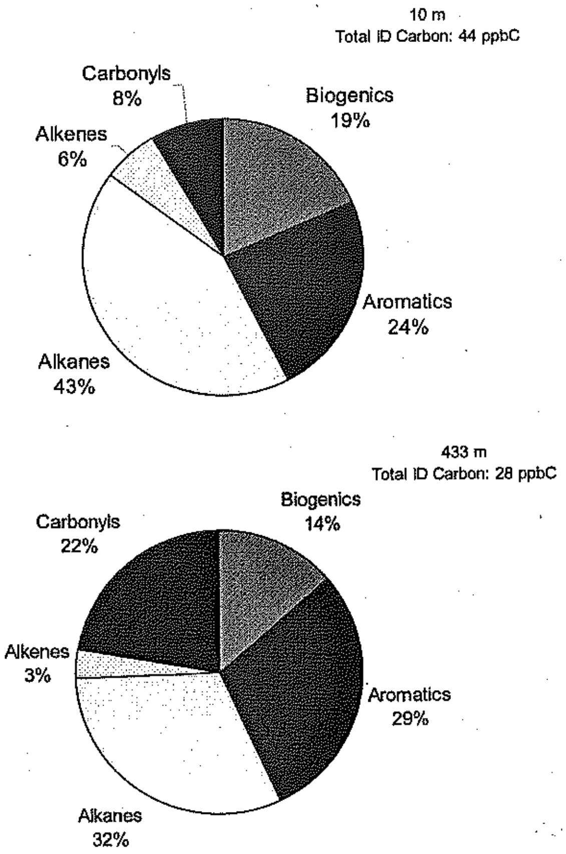
Table 4 Comparison of average NMHC concentrations* (ppbC) measured for selected hydrocarbons with other non-urban samples during period 1 (5–8 am EDT)

	Belfast, ME		*Miami, FL*		*Robinson, IL*		*Raleigh, NC*	
	Surface	*Aerial*	*Surface*	*Aerial*	*Surface*	*Aerial*	*Surface*	*433 m*
Ethane	3.5	3.5	4.0	4.0	6.0	8.0	2.0	2.0
Ethylene	2.0	1.5	0.5	≤ 0.5	2.0	1.5	1.5	1.0
Acetylene	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	1.0	1.0	1.5	1.5
Propane	2.0	2.0	2.0	1.5	12.0	8.5	4.0	1.5
Propene	0.5	1.0	≤ 0.5	≤ 0.5	1.5	1.0	1.0	0.5
i-Butane	0.5	0.5	≤ 0.5	≤ 0.5	2.5	3.0	1.0	0.5
n-Butane	2.0	1.0	1.0	0.5	8.5	0.5	1.5	0.5
i-Butene	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	0.5	0.5	0.5	0.5
i-Pentane	1.0	1.0	1.5	0.5	5.0	0.5	2.5	1.0
n-Pentane	1.0	0.5	1.0	0.5	3.5	3.0	1.0	0.5
n-Hexane					1.5	1.5	0.5	0.5
Benzene					1.5	1.5	0.5	0.5
Toluene					2.0	3.0	5.0	2.0
m-/p- xylene					1.0	1.5	2.0	1.5
o-xylene					1.0	1.5	1.0	0.5
1,2,4-Trimethyl benzene					1.0	1.0	1.0	2.5

Note: * Geometric mean

Figure 2 gives the average contribution of each group of volatile organic compounds (VOCs) measured during Period 1 at Level 1 and Level 3 by percentage to the total ID VOCs. Alkanes contribute a major fraction (43 and 32%) to the total VOCs at both levels, whereas, carbonyls show a big increase from Level 1 to Level 3 (from 8 to 22%). The fractional contributions of alkenes and biogenics decrease with height, but that of aromatics increases with height. As discussed above, during Period 1 Level 1 is within the inversion layer and the concentration levels measured during this period reflect the composition of compounds released or emitted close to the surface. An examination of Table 2(a) shows that the concentrations of straight chain alkanes are highest during this time period. A large fraction of these compounds could be from seepage of natural gas or due to emissions from the gasoline storage facility located ~ 25 km east of the sampling location. These compounds are trapped in the shallow nocturnal boundary layer (NBL) and after the breakup of the NBL, during Period 2 the compounds are vertically mixed and the concentration at the two higher levels rises and those less reactive compounds reach steady concentrations. The sources of the carbonyl compounds are not well established. However, their presence in the rural atmosphere seems to be ubiquitous. Carbonyls are mainly secondary pollutants and are the products of photochemical degradation of primary hydrocarbons emitted into the atmosphere. The night time degradation mechanism of isoprene leading to carbonyl formation has been the focus of attention (Montzka et al., 1993). Isoprene is known to react with the NO_3 during the night leading to the formation of carbonyl compounds, mainly formaldehyde. Photolysis of formaldehyde is known to be a major source of hydroperoxyl radicals during the early morning period and play an important role in the photochemical reactions leading to ozone production under low NO_X conditions. The higher loading of carbonyls at the higher levels could have interesting implications to photochemistry at this semi-urban site.

Figure 2 Fractional contributions of various hydrocarbon classes to the total ID hydrocarbons during Period 1 at Levels 1 and 3



The relative importance of formaldehyde photolysis over its reaction with OH is investigated by estimating its photolysis rate. Assuming clear sky conditions, an approximate photolysis rate for the 5–8 am EDT time period on July 1 is estimated to be $\sim 1.0 \times 10^6$ molecules/cm^3/sec using the actinic flux data (Finlayson-Pitts and Pitts, 1986), absorption cross-section, and quantum yield data (DeMore et al., 1992) for formaldehyde. The rate constant of OH with formaldehyde is 0.9×10^{-11} molecules/cm^3/sec (Finlayson-Pitts and Pitts, 1986). In order for OH to react with formaldehyde to be equal in importance to the photolysis process, the average OH concentration during this time period would have to be 2.8×10^6 molecules/cm^3. This is slightly higher than the OH concentration during the midday period estimated from the observed decay of isoprene ($\sim 1.7 \times 10^6$ molecules/cm^3). This suggests that during this time period photolysis of formaldehyde is more important than its reaction with OH.

Figure 3 shows the vertical and temporal distribution of the average concentrations of NMHC compounds. In general, the concentrations decrease from lower to higher levels. The concentrations of alkanes and biogenics are significantly higher at the surface than at the other two higher levels (student's t-test at $p \leq 0.05$).

The biogenically emitted hydrocarbons show diurnal variations (Figures 3 and 4). The concentration steadily increases through the day and the highest concentrations of biogenics are observed at the surface during Period 3. Isoprene is the dominant biogenically emitted compound at this site. Isoprene concentrations continue to increase in the late afternoon when the mixing height has reached its maximum and all other compounds have already receded. The source strength of isoprene is larger than all anthropogenic sources combined. α-pinene, in contrast, shows a diurnal cycle different from isoprene with higher concentrations during Periods 1 and 3. It has been known that isoprene emissions are dependent on temperature and sunlight intensity (Fuentes et al., 2000; Hagerman et al., 1997; Rasmussen and Khalil, 1988) and that the emissions of terpenes are dependent on temperature alone (Tingey et al., 1979). It is, therefore, not surprising that emissions of monoterpene compounds continue during night time and that the capping effect of the nocturnal inversion tends to trap α-pinene. The morning breakdown of this inversion leads to rapid mixing and dilution. Atmospheric mixing and chemical destruction of this compound during the day outweighs the addition of the compound, due to emissions at higher temperatures. As a result, α-pinene concentration reaches a minimum during Period 2.

3.2 Hydrocarbon source attribution

Figure 3 gives the vertical concentration profiles of the major paraffins, olefins and aromatics observed during the three time periods. The composition reflects a complex mixture of aged urban air as well as fresh anthropogenic emissions at the site. The predominance of less reactive light alkanes during all three time periods at all levels is indicative of an aged air mass. On the other hand, the detection of acetylene and certain alkenes, as well as aromatics associated with automobile exhaust and industrial processes, indicates the transport of various anthropogenically emitted NMHCs from nearby sources. At all three levels, ethane, propane, n-butane, n- and i-pentane make up the major fraction of the paraffin at this site. In addition to these compounds high concentrations of 3-methylpentane are also observed at the surface. The aromatics have a fairly uniform composition at all three levels comprising benzene, toluene and xylenes.

Figure 3 Average concentrations of the various hydrocarbon classes during the three time periods at three levels. The error bars are + 1 std

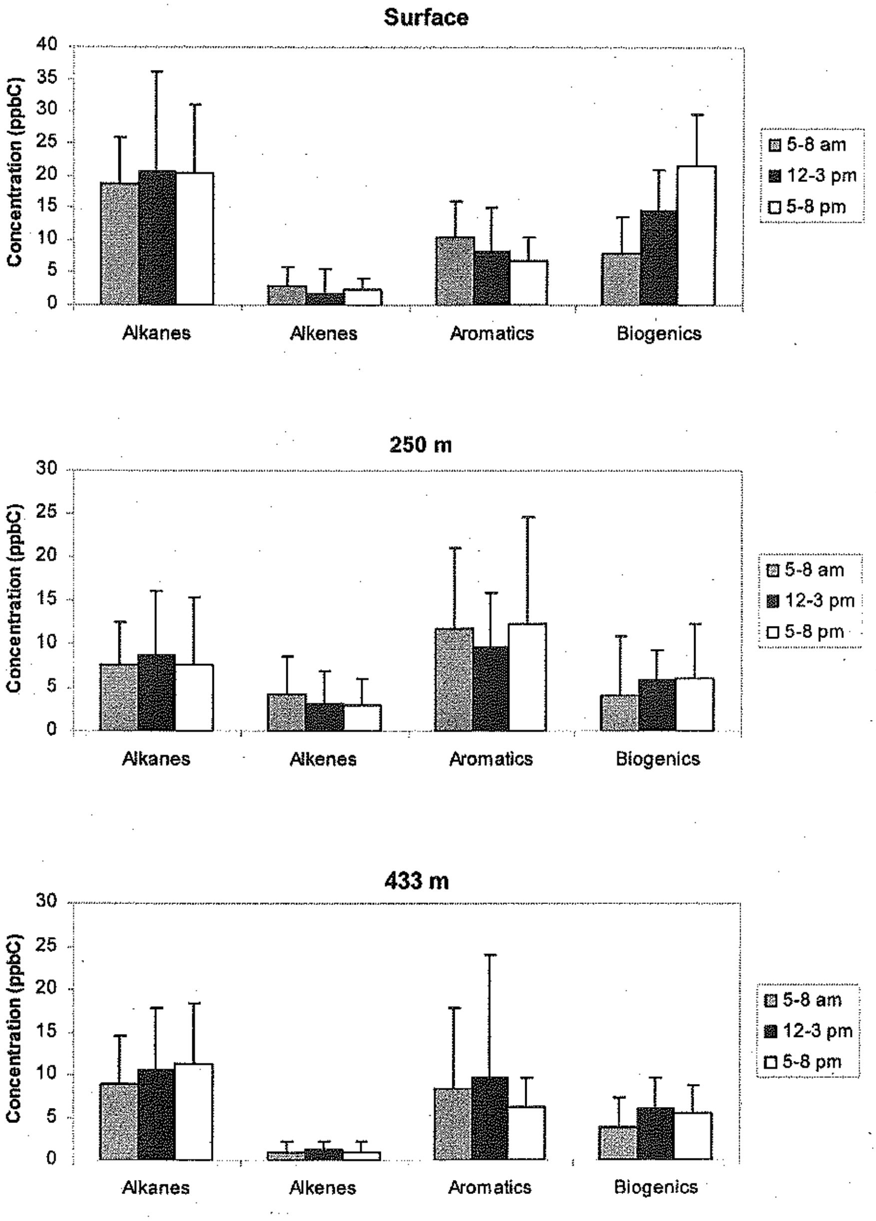
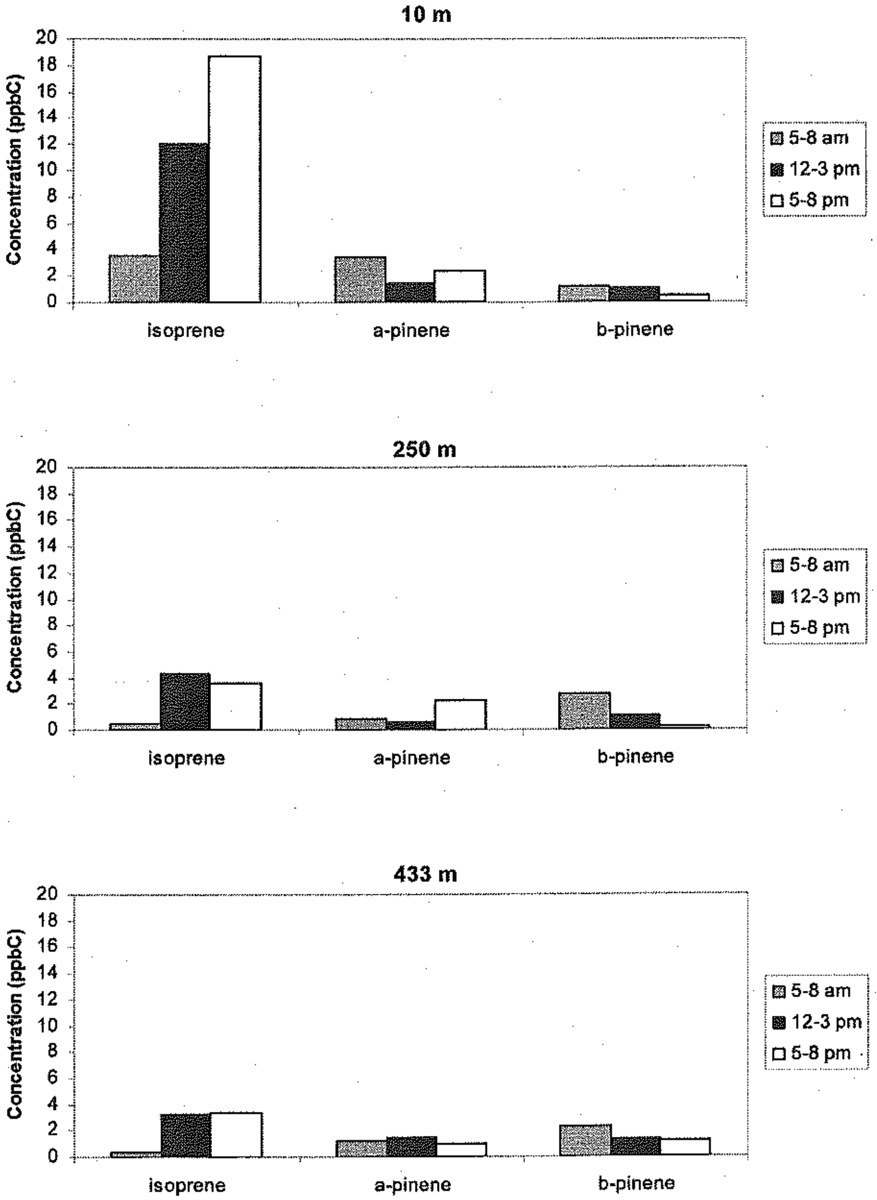


Figure 4 Average diurnal variation of biogenic hydrocarbons at all three levels



The major source of ethane is natural gas, either from the commercial network or from the direct geological exploitation of resources. Propane appears to derive from natural gas as well as from petrochemical industries. The principal sources of butane and pentane are automotive exhaust and gasoline, although contributions from natural gas and industrial processes are not negligible. The alkenes, especially ethylene, derive primarily from automobile exhaust. However, a major fraction is also released from industrial processes. Studies also indicate significant emissions from vegetation. The sole source of acetylene is automobile exhaust. For this reason acetylene has been suggested to serve as a useful trace for automobile emissions. For aromatic compounds, three-quarters of benzene and xylenes arise from automobile exhaust and the rest from gasoline. Toluene and ethylbenzene originate partly from automobile exhaust, gasoline and solvent emissions (Fujita et al., 1995).

Both ethene and acetylene are primarily produced by automobile exhaust and the ratio of ethene/acetylene at the source is ~ 2.9 (Fujita et al., 1995). Ratios of 1–1.4 are observed at the surface and much lower at the higher levels. Ethene is 9.5 times as reactive as acetylene with OH. The ethene/acetylene ratios observed signify the long-range transport of emissions from automobile.

The typical benzene/toluene ratio from US cities (Kang et al., 2001; Sexton and Westberg, 1984; Spicer et al., 1996; Warneck, 1988) is about 0.40. The average benzene/toluene ratios at the three levels from surface to higher levels are 0.28, 0.37 and 0.44. Because toluene reacts nearly five times faster than benzene with OH, benzene/toluene ratios in vehicle emissions would increase during long-range transport. However, the ratios at the surface and 250 m level observed at the site are even less than the ratio of fresh urban emissions; even the ratio at the 433 m level signifies fresh urban emissions. This can be explained only by contribution from another source that emits large amounts of toluene, such as solvent, and that may be the surface coating and paper production point sources located within a 200 km radius. Of course, benzene and toluene concentrations may be the combined result of local and distant sources. The increase of benzene/toluene ratios with height is due to the fact that higher levels receive more influence from long-range transported air masses than lower levels. In other words, the surface is more easily affected by local emissions.

3.3 *Hydrocarbon reactivity*

The distribution of NMHC depicted in Figure 3 gives the magnitude of the various classes of hydrocarbons present but little about their ozone formation potential. To account for the combined effect of concentration and reactivity, we use the propylene-equivalent (propyl-equiv) concentration method proposed by Chameides et al. (1992):

$$propy-equiv(j) = conc(j)\frac{K_{OH}(j)}{K_{OH}(C_3H_6)},$$

where *propy-equiv(j)* is a measure of the concentration of species *j* on an OH reactivity based scale, normalised to the reactivity of propylene (C_3H_6); *conc(j)* is the concentration of species *j* in ppbC; $K_{OH}(j)$ is the rate constant for the reaction between species *j* and OH; and $K_{OH}(C_3H_6)$ is the rate constant for the reaction between OH and propylene.

The effect of hydrocarbon/OH reactivity can be evaluated in a comparison of data presented in Figure 2 converted to Propy-Equiv concentration (The OH rate constants used to calculate the Propy-Equiv concentrations are obtained from Middleton and Stockwell, 1990 and Warneck, 1988) (Figure 5). This analysis suggests that biogenic compounds are far more important in contributing to ozone formation than any other hydrocarbons combined. The fractional contribution of biogenics to the total Propy-Equiv concentration increases from 72% during Period 1 to a staggering 90% during Period 3 at Level 1. This is similar to that observed in rural areas of the eastern United States (e.g. Chameides et al., 1988; Kang et al., 2001). However, at higher levels, the total Propy-Equiv concentrations as well as the fractional contributions of biogenics are significantly reduced. At Period 3, the total Propy-Equiv concentration at Level 2 is 35.3 ppbv that is only 40% of the concentration at Level 1 (87.2 ppbv), and it reduces further to 25.6 ppbv at Level 3. The fractional contributions of biogenics to the total Propy-Equiv concentrations range from 43 to 74% at the higher levels. This means that even though biogenic compounds dominate at the surface level, anthropogenic compounds may still play an important (up to 60%) role in atmospheric chemistry at higher levels in terms of the reaction with OH. Therefore, when evaluating the atmospheric chemistry in the troposphere, the vertical profiles of various VOC species and their relative reactivity must be taken into consideration.

3.4 *Effect of NMHC concentration on ozone production*

Maximum ozone observed during the day is regressed on total NMHC measured during Period 1 to study the effect of NMHC on ozone production at this site (Figure 6). It is interesting to observe that ozone increases with the increase of total NMHC concentrations when total NMHC concentrations are less than 60 ppbC; whereas, ozone decreases with an increase in NMHC levels at higher concentrations of NMHC. The figure also indicates that for every ppbC increase of NMHC, one ppbv of ozone is added at lower concentrations of NMHC. At higher concentrations, for every ppbC increase of NMHC over 60 ppbC, half a ppbv of ozone is reduced. This is in agreement with a model sensitivity study (Kang et al., 2003). Production of ozone is a non-linear function of NMHC and NO_X. In rural areas, where insufficient NO_X is available for ozone formation, ozone production becomes NO_X limited. The existence of significant natural sources of VOCs in these areas may further reduce NO_X levels by forming organic nitrates (Kang et al., 2003; Kasibhatla, et al., 1997) and hence reduce ozone production. This research site is found to be NOX limited. Measurements of NO_X at 10 m are made about 1 km from the tower site during the later half of the sampling period. The average NO_X concentrations at this site are found to be ≤ 2 ppbv. This is well below the transition ridgeline of 15/1 of NMHC/NO_X to become NO_X limited in ozone production (Dodge, 1977).

To investigate the relationship between ozone concentrations and natural hydrocarbons, ozone concentrations during Period 1 at Level 1 are regressed on the natural hydrocarbons at the site during the same period (Figure 7). Natural hydrocarbons show a distinct negative trend with r^2 of 0.59 which is significant at $p = 0.05$ level. During Period 1, when Level 1 is still under the effect of nocturnal boundary layer and photochemistry is at its minimum, natural VOCs tend to reduce ozone production.

Figure 5 Propylene-equivalent concentrations (ppbv) of various hydrocarbon classes at the three levels

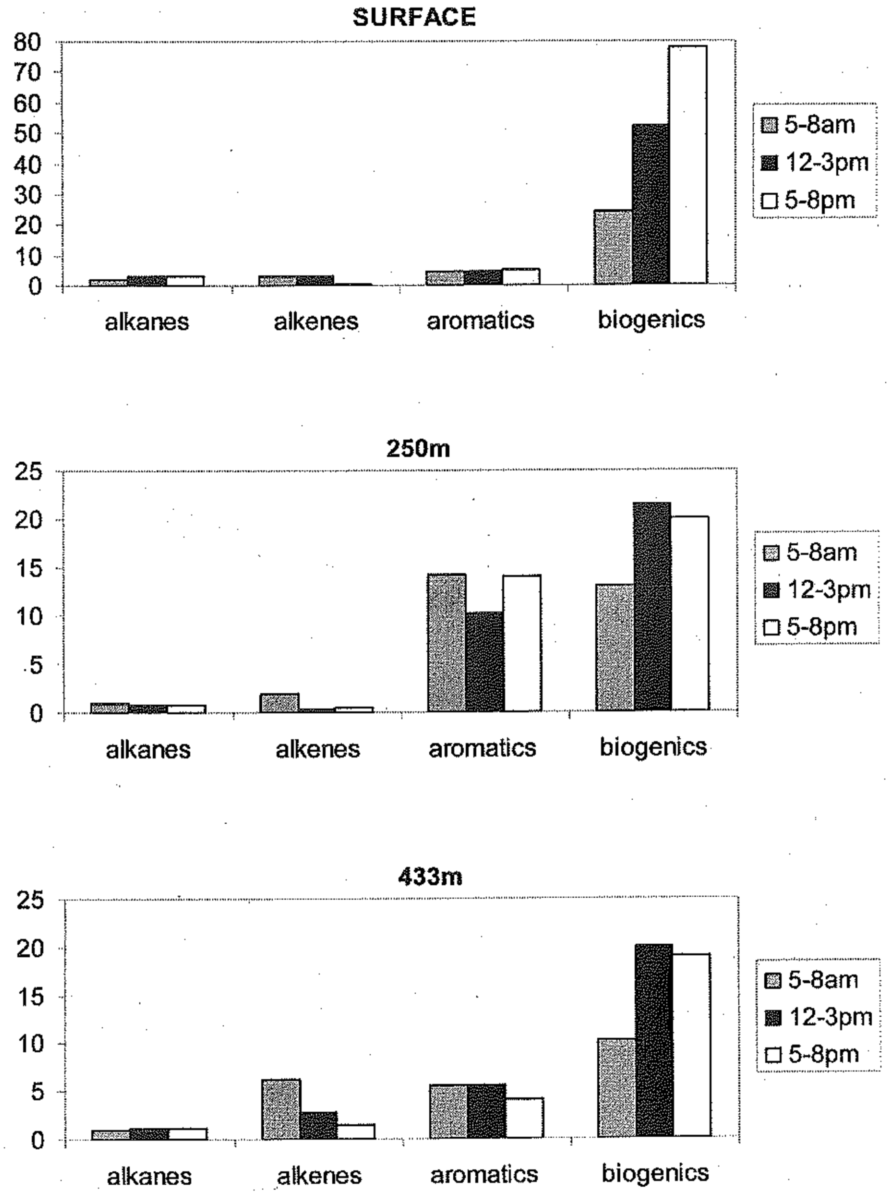


Figure 6 Relationships between daily maximum ozone concentration and NMHC from 5–8 am

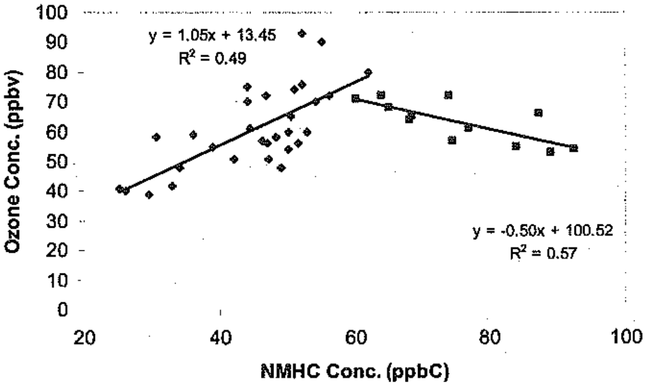
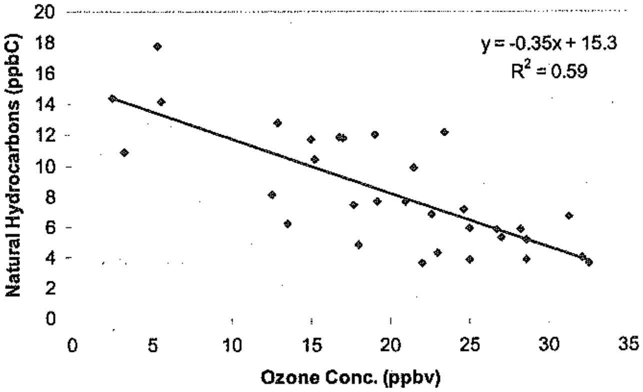


Figure 7 Relationships between ozone and natural hydrocarbons



4 Conclusions

An analysis of vertical profiles of VOCs measured during the summer of 1994 at a non-urban site located about 19 km southeast of downtown Raleigh reveals a clear anthropogenic influence as well as significant natural emissions. Both long-range transport of emissions from fossil fuel combustion, petroleum refineries, geogenic natural gas and solvent and local sources contribute to the composition of NMHCs at this site. The average concentrations of most species reflect the concentrations found at most non-urban sites. Ambient levels of VOCs measured within and above the early morning inversion layer showed a significant vertical variation with higher surface layer concentrations. Except for alkanes and biogenically emitted compounds, midday concentrations of most compounds are similar at all three levels. This is attributed to the fact that these compounds have sources close to the ground and during Period 1 are trapped in the surface layer. After the breakup of the NBL the concentration rises due to vertical mixing. However due to loss with OH radical reaction, the concentrations at the upper levels are lower for more reactive compounds.

A significant temporal variation of the biogenics is observed. Isoprene, which is the dominant biogenic compound, is found to increase through the day with peak concentrations observed during Period 3. The natural emission of isoprene dominates the chemistry at this site by virtue of its magnitude as well as reactivity. The fractional contribution of biogenics to the total Propy-Equiv concentration at the surface is found to be ~ 90% with isoprene contributing more than 60%. Thus the source strength of this natural compound outweighs the contribution from anthropogenic compounds at this site.

Ozone production at this site is NO_X limited. When NMHC concentrations are below 60 ppbC ozone is produced, while ozone is destroyed otherwise. Though the concentrations of biogenic VOCs are significant at this site, due to insufficient NO_X availability, biogenic VOCs act as sinks rather than sources of ozone.

This study provides a unique opportunity for making time integrated vertical measurements of trace species. The use of a stationary platform makes the data more reliable than measurement made using a mobile platform because it eliminates the problem of transient turbulent eddies. The present analysis is based on measurements gathered at three different heights at a fixed location. A more robust understanding of the vertical variability of the NMHCs in the boundary layer can be obtained by

- adding a few more measurement heights and measurement periods
- making simultaneous measurements of meteorological parameters at the same heights to study the effect of meteorology on the vertical variability of the NMHCs.

Acknowledgments

This research has been funded through a contract from North Carolina Department of Environment, Health and Natural Resources (Contract EA 8001). We thank George Murray and Thomas Manuszak of NCDEHNR for their assistance and providing the ozone data. Also thanks to Regi Oommen and Jay Lawrimore for assistance in sample collection and analysis. We acknowledge Dr E. Apel, National Center for Atmospheric Research, for providing the retention time standard; Dr R. Zika, University of Miami, for providing the mass standard; Dr Tom Murray for analysing the carbonyl samples; and Ms Irene Joyner, Auburn Tower Partnership, Capitol Satellite Operations for providing space for conducting the research on the 2000 feet tower.

References

Andronache, C., Chameides, W.L., Rodgers, M.O. and Martinez, J. (1994) 'Vertical distribution of isoprene in the lower boundary layer of the rural and urban southern United States', *J. Geophys Res.*, Vol. 99-D8, pp.16989–16999.

Aneja, V.P., Mathur, R., Arya, S.P., Li, Y., Murray, G.C. and Manuszak, T.L. (2000) 'Coupling the vertical distribution of ozone in the atmospheric boundary layer', *Environ. Sci. Technol.*, Vol. 34, pp.2324–2329.

Apel, E.C., Calvert, J.G. and Fehsenfeld, F.C. (1994) 'The Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Tasks 1 and 2', *J Geophys Res.*, Vol. 99-D8, pp.16651–16664.

Atkinson, R. (1990) 'Gas-phase tropospheric chemistry of organic compounds: a review', *Atmos. Environ.*, Vol. 24, pp.1–41.

Chameides, W.L. and Cicerone, R.J. (1978) 'Effects of nonmethane hydrocarbons in the atmosphere', *J. Geophys. Res.*, Vol. 83-C2, pp.947–952.

Chameides, W.L., Fehsenfeld, F., Rodgers, M.O., Cardelino, C., Martinez, J., Parrish, D., Lonneman, W., Lawson, D.R., Rasmussen, R.A., Zimmerman, P., Greenberg, J., Middleton, P. and Wang, T. (1992) 'Ozone precursor relationships in the ambient atmosphere', *J. Geophys. Res.*, Vol. 97-D5, pp.6037–6055.

Chameides, W.L., Lindsay, R.W., Richardson, J. and Kiang, C.S. (1988) 'The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study', *Science*, Vol. 241, pp.1473–1475.

Chameides, W.L., Saylor, R.D. and Cowling, E.B. (1997) 'Ozone pollution in the rural United States and the new NAAQS', *Science*, Vol. 276, p.916.

DeMore, W.B., Sanders, S.P., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., Ravishankara, A.R., Kolb, C.E. and Molina, M.J. (1992) 'Chemical kinetics and photochemical data for the use of stratospheric modeling: evaluation number 10', JPL publication 92–20, Jet Propulsion Labs, Pasadena, CA.

Dietz, W.A. (1967) 'Response factors for gas chromatographic analysis', *J. Gas Chromatog.*, Vol. 5, pp.68–71.

Dodge, M.C. (1977) 'Combined use of modeling techniques and smog chamber data to derive ozone precursor relationships', *Proceedings of the International Conference on Photochemical Oxidant Pollution and its Control*, Dimitriades (Ed) Vol. II, pp.881–889, EPA-600/3-77-0016, RTP, NC: US EPA.

Farmer, C.T., Milne, P.J., Riemer, D.D. and Zika, R.G. (1994) 'Continuous hourly analysis of C_2-C_{10} non-methane hydrocarbon compounds in urban air by GC-FID', *ES&T*, Vol. 28, pp.238–245.

Finlayson-Pitts, B. and Pitts, J. Jr. (1986) *Fundamentals of Atmospheric Chemistry: Fundamentals and Experimental techniques*, New York: Wiley.

Fuentes, J.D., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J.W., Ciccioli, P., Lamb, B., Geron, C., Gu, L., Guenther, A., Sharkey, T.D. and Stockwell, W. (2000) 'Biogenic hydrocarbons in the atmospheric boundary layer: a review', *Bull Am. Meteor Soc.*, Vol. 81, pp.1537–1575.

Fujita, E.M., Watson, J.G., Chow, J.C. and Magliano, K.L. (1995) 'Receptor model and emissions inventory source apportionments of nonmethane organic gases in California's San Joaquin Valley and San Francisco Bay area', *Atmos. Environ.*, Vol. 29, pp.3019–3035.

Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley, R. and Fall, R. (2000) 'Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America', *Atmos. Environ.*, Vol. 34, pp.2205–2230.

Guenther, A., Hewitt, C., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M. and Zimmerman, P. (1995) 'A global model of natural volatile organic compound emissions', *J. Geophys. Res.*, Vol. 100-D5, pp.8873–8892.

Guenther, A., Zimmerman, P. and Wildermuth, M. (1994) 'Natural volatile organic compound emission rate estimates for U.S. woodland landscapes', *Atmos. Environ.*, Vol. 28, pp.1197–1210.

Hagerman, L.M., Aneja, V.P. and Lonneman, W.A. (1997) 'Characterization of non-methane hydrocarbons in the rural southeast United States', *Atmos. Environ.*, Vol. 31, pp.4017–4038.

Kang, D., Aneja, V.P., Mathur, R. and Ray, J. (2003) 'Nonmethane hydrocarbons and ozone in three rural southeast United States national parks: a model study and measurement analysis', *J. Geophys. Res.*, Vol. 108-D19: 4606, doi: 10.1029/2002JD003054.

Kang, D., Aneja, V.P., Zika, R.G., Farmer, C. and Ray, J.D. (2001) 'Nonmethane hydrocarbons in the rural southeast United States national parks', *J. Geophys. Res.*, Vol. 106-D3, pp.3133–3155.

Kasibhatla, P., Chameides, W.L., Duncan, B., Houyoux, M., Jang, C., Mathur, R., Odman, T. and Xiu, A. (1997) 'Impact of inert organic nitrate formation on ground-level ozone in a regional air quality model using the carbon bond mechanism 4', *Geophys. Res. Lett.*, Vol. 24, pp.3205–3208.

Killus, J.P. and Moore, G.E. (1991) 'Factor analysis of hydrocarbon species in the South-Central Coast air basin', *J. Appl. Meteor*, Vol. 30, pp.733–743.

Lmab, B., Gay, D., Westberg, H. and Pierce, T. (1993) 'A biogenic hydrocarbon emission inventory for teh USA using a simple forest canopy model', *Atmos. Environ.*, Vol. 27, pp.1709–1713.

Lamb, B., Guenther, A., Gay, D. and Westberg, H. (1987) 'A national inventory of biogenic hydrocarbon emissions', *Atmos. Environ.*, Vol. 21, pp.1695–1705.

Lawrimore, J.H., Das, M. and Aneja, V.P. (1995) 'Vertical sampling and analysis of speciated non methane hydrocarbons in urban North Carolina', *J. Geophys. Res.*, Vol. 100-D11, pp.22785–22793.

Logan, J.A., Prather, M.J., Wofsey, S.C. and McElroy, M.B. (1981) 'Tropospheric chemistry: a global perspective', *J. Geophys. Res.*, Vol. 86-C8, pp.7210–7254.

Middleton, P. and Stockwell, W.R. (1990) 'Aggregation and analysis of volatile organic compound emissions for regional modeling', *Atmos. Environ.*, Vol. 24A, pp.1107–1133.

Montzka, S.A., Trainer, M., Goldan, P.D., Kuster, W.C. and Fehsenfeld, F.C. (1993) 'Isoprene and its oxidation products, methyl vinyl ketone and methacrolein, in the rural troposphere', *J. Geophys. Res.*, Vol. 98, pp.1101–1111.

Rasmussen, R.A. and Khalil, M.A.K. (1988) 'Altitudinal and temporal variation of hydrocarbons and other gaseous tracers of Arctic haze', *Geophys. Res. Lett.*, Vol. 10, pp.144–147.

Sexton, K. and Westberg, H. (1984) 'Nonmethane hydrocarbon composition of urban and rural atmospheres', *Atmos. Environ., Vol. 18, pp.1125–1132.*

Spicer, C.W., Buxton, B.E., Holdren, M.W., Smith, D.L., Kelly, T.J., Rust, S.W., Pate, A.P., Sverdrup, G.M. and Chuang, J.C. (1996) 'Variability of hazardous air pollutants in an urban area', *Atmos. Environ.*, Vol. 30, pp.3443–3456.

Tingey, D.T., Manning, M., Grothaus, L.C. and Burns, W.F. (1979) 'The influence of light and temperature on isoprene emission rates from live oak', *Physiol. Plant*, Vol. 47, pp.112–118.

Trainer, M., Hsie, E.Y., Mckeen, S.A., Tallamraju, R., Parrish, D.D., Fehsenfeld, F.C. and Liu, S.C. (1987b) 'Impact of natural hydrocarbons on hydroxyl and peroxy radicals at a remote site', *J. Geophys. Res.*, Vol. 92, pp.11,879–11,894.

Trainer, M., Williams, E.J., Parrish, D.D., Buhr, M.P., Ellwine, E.J., Westberg, H.H., Fehsenfeld, F.C. and Liu, S.C. (1987a) 'Models and observations of the impact of natural hydrocarbons on rural ozone', *Nature*, Vol. 329, pp.705–707.

Warneck, P. (1988) 'Volatile hydrocarbons and halocarbons', in R. Dmowska and J.R. Holton (Eds) *Chemistry of the Natural Atmosphere*, San Diego, CA: Harcourt, Brace, Jovanovich, pp.226–227.

Zimmerman, P.R. (1979) Determination of emission rates of hydrocarbons from indigenous species of vegetation in the Tampa/St. Petersburg, Fla., area, Final Appendix C., Report EPA-904/9–77–028, Washington, D.C.

Zimmerman, P.R., Greenberg, J.P. and Westberg, C. (1988) 'Measurements of atmospheric hydrocarbons and biogenic emission fluxes', *J. Geophys. Res.*, Vol. 93-D2, pp.1407–1416.