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CHARACTERIZATION OF NON-METHANE HYDROCARBONS IN THE RURAL SOUTHEAST UNITED STATES

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Abstract—Measurements of non-methane hydrocarbons, as well as ozone, meteorological and trace gas data, made at four rural sites located within the southeastern United States as a part of the Southern Oxidants Study are compared. The C_2–C_{10} hydrocarbons were obtained during the 1200–1300 local time period, once every six days from September 1992 through October 1993. The light molecular weight alkanes (ethane, propane, *n*-butane, iso-butane, ethene and acetylene) display a seasonal variation of a winter maximum and summer minimum. Isoprene was virtually non-existent during the winter at all sites, and averaged from 9.8 ppbC (Yorkville, Georgia) to 21.15 ppbC (Centreville, Alabama) during the summer. The C_{10} terpene concentration was largest during the summer period with averages ranging between 3.19 ppbC (Centreville, Alabama) and 6.38 ppbC (Oak Grove, Mississippi); winter time concentrations ranged from 1.25 to 1.9 ppbC for all sites. Propylene-equivalent concentrations were calculated to account for differences in reaction rates between the hydroxyl radical and individual hydrocarbons, and to thereby estimate their relative contribution to ozone, especially in regard to the highly reactive biogenic compounds such as isoprene. The propy-equivalent concentrations from the biogenics represent at least 65% of the total non-methane hydrocarbon sum at these four sites during the summer season. A plot of ozone versus NO_y–NO highlights the NO_x limited relationship of this region. © 1997 Elsevier Science Ltd.

Key word index: Speciated non-methane hydrocarbons, rural, biogenics, annual measurements.

1. INTRODUCTION

It has long been established that non-methane hydrocarbons play an important role as precursors to ozone and other secondary photochemical pollutants. Ozone is formed in the complex reaction mechanism that involves the volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in the presence of sunlight. Since the passage of the 1970 Clean Air Act amendments, regulatory efforts to comply with the 0.12 ppmv National Ambient Air Quality standard for ozone have been inadequate (NRC, 1991; Dimitriades, 1989). Ozone exceedences continue to be a major problem, especially in the southeast region of the United States. Studies have shown that the Southeast is a region where high concentrations of ozone accumulate in both rural and urban areas (SOS, 1995). The contribution of naturally emitted volatile organic compounds (VOCs) to ozone formation in both urban and rural areas has become of greater concern within the last decade (Lamb *et al.*, 1987). Measurements of biogenically emitted VOCs such as isoprene suggest that these compounds contribute to high ozone concentrations in urban areas affected by NO_x (Trainer *et al.*, 1987; Chameides *et al.*, 1988; NRC, 1991). Various studies have measured isoprene and other ambient hydrocarbon concentrations in rural or remote sites (Lawrimore *et al.*, 1995; Andronache *et al.*, 1994; Chameides *et al.*, 1992; Colbeck and Harrison, 1985; Greenberg and Zimmerman, 1984; Rasmussen and Khalil, 1988; Sexton and Westberg, 1984). Other studies have reported the seasonal variations of hydrocarbons in continental air (Boudries *et al.*, 1994; Jobson *et al.*, 1994; Hov *et al.*, 1991; Rudolph *et al.*, 1989; Tille *et al.*, 1985).

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In this study we (1) compare C_2–C_{10} hydrocarbons measured at four rural sites during the maximum photochemical activity period, (2) analyze the contribution of rural hydrocarbons using propylene-equivalent concentrations, especially in relation to isoprene, and (3) examine the relationship between ozone and reactive nitrogen (NO_y), and between ozone and meteorological variables such as temperature, relative humidity, solar radiation, and ozone.

2. EXPERIMENT

2.1. *Site description*

The hydrocarbon, trace gas and meteorological data were obtained from four rural SOS-SCION sites (Southern Oxidants Study-Southeastern Consortium: Intermediate Oxidant Network) located within the Southeast United States. The SOS-SCION network provide long-term spatial scale input for NMHC's for photochemical model calculations. The location of the sites used for this paper include Centreville, AL; Oak Grove, MS; Yorkville, GA and Candor, NC. All these sites are classified as rural under the National Dry Deposition Network (NDDN) site classification scheme. Requirements include no large point sources of SO_2 or NO_x within 20–40 km, no major industrial complex within 10–20 km, no city of population > 50,000 within 60 km, and a number of other requirements listed elsewhere (Porter, 1988; Clarke *et al.*, 1991). Figure 1 illustrates the location of the sites.

The Centreville site is located in Bibb County, AL (32°90′N, 87°23′W), in a rural area representative of the transitional nature of the region between the lower coastal plain and Appalachian highlands, at an elevation of 136 m mean sea level (msl). Sources of anthropogenic emissions located within a 110 km radius of the sampling site include the cities of Montgomery, Birmingham, and Tuscaloosa. This site is located in a large field approximately 180 m from a NOAA (National Oceanic and Atmospheric Administration) weather radar station.

The Oak Grove site (30°99′N, 88°93′W) is located in the Desoto National Forest in Perry County, MS at an elevation 85 m msl. This site is located in a rural area representative of the lower coastal plain. It is moderately forested with a canopy at approximately 12 m, and predominantly consists of conifers. The forested areas are interspersed with cultivated farm land. The site is located in a large field approximately 46 m from the nearest row of brush and 152 m from the intersection of two dirt roads. The area immediately surrounding the site is mowed on a regular basis and is surrounded by cultivated farm land. The nearest residence

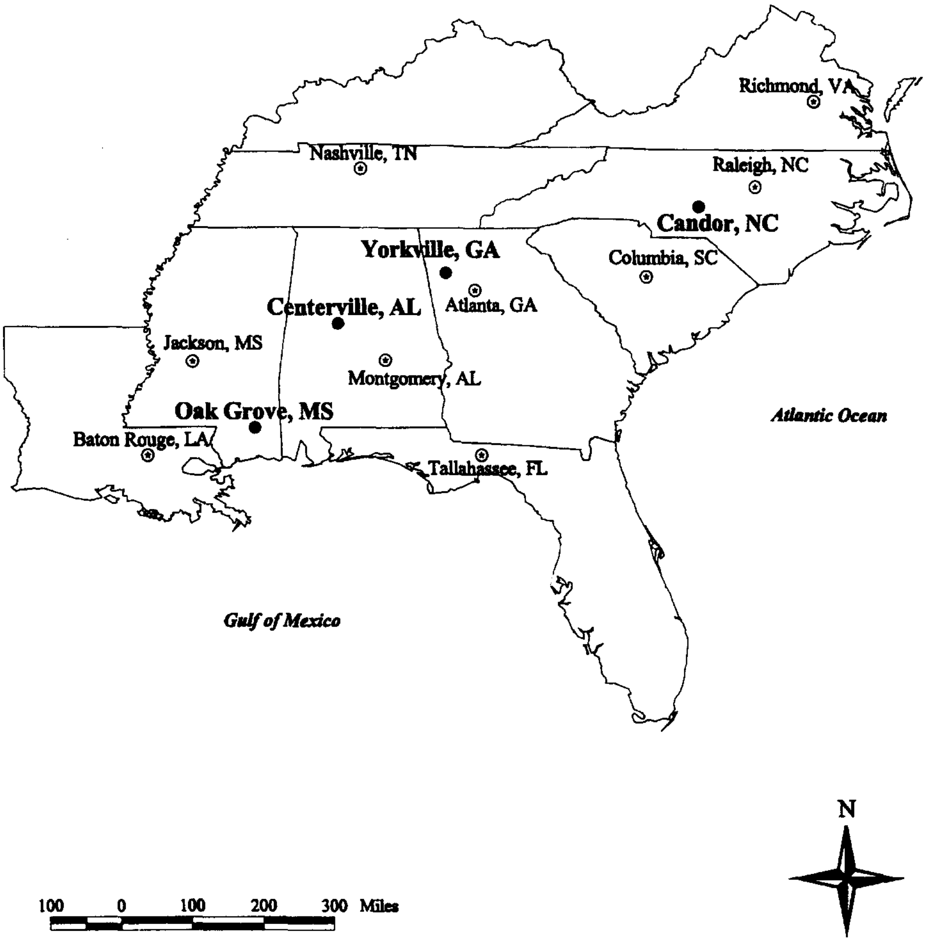

Fig. 1. Map of the sampling sites.

visible from the site is located approximately a quarter of a mile away. It is situated off state route 29 and approximately 40 km southeast of Hattiesburg, MS.

The Yorkville site (33°55′41″N, 85°02′46″W) is located in Pauldin County, GA, at an elevation approximately 400 m above sea level. The site is situated in a rural area representative of the southern highlands, consisting of hardwood forests interspersed with open pasture and tilled farmland. The site is off route 278 and is approximately 72 km west of Atlanta, and 48 km west of a power generating station.

The Candor site (35.26°N, 79.84°W, 197 m msl elevation) is located in the Central Piedmont region of North Carolina on the eastern border of the Uwharrie National Forest. The sampling site is located in an open field approximately 1200 m^2, and the field is surrounded by forests mixed with deciduous and coniferous trees. Sources of anthropogenic pollution located within a 120 km radius of the sampling site include the urban areas of Raleigh–Durham, Greensboro, Winston–Salem, and the junction between I-40 and I-85, which are all situated to the north and northeast of the site.

2.2. *Data collection and analysis*

All data used in this paper was obtained from the SOS data base (SOS, 1994; Schere, 1997). The data results have been validated and are available in electronic format. The hydrocarbon data were sampled from September 1992 through October 1993, and include data sampled during June 1992 at the Candor site. The Centreville and Candor sites each include 49 total observations; Oak Grove and Yorkville include 61 and 55 observations, respectively. The sampling days used for the seasonal averages at each site are listed at the end of Tables 1a–d. Time integrated air samples were collected in 6 ℓ SUMMA electropolished stainless steel canisters from 1200 to 1300 local time, once every six days. This sampling frequency was chosen so that each day of the week would be represented in the study. The hydrocarbon samples were collected in evacuated canisters. C_2–C_{10} hydrocarbons were analyzed at the University of Miami using a Hewlett Packard HP 5890 II gas chromatograph equipped with fused silica capillary column, a cryogenic cooling option, and flame ionization detection. Data reduction was accomplished using HP 3365 Chemstation II software on PC-DOS based personal computers. The automatic air concentrator used was a modified Entech 2000 (Entech Laboratory Automation, Simi Valley, CA). The detection limit was 0.1 ppbC (parts per billion carbon) with a reproducibility of 30%. A detailed description of the GC analysis is published elsewhere (Farmer *et al.*, 1994). Additional information concerning the sample collection procedures, quality assurance efforts, and other important components of the measurement protocols are reported in SOS Quality Assurance documents (Momberger, 1994).

Other pollutant measurements included NO, NO_y, SO_2, CO, and O_3 as well as meteorological parameters such as temperature, relative humidity, solar radiation, barometric pressure, and wind speed and direction made every day at 15 min intervals throughout the year. NO and NO_y were measured with the TECO 42 S (Thermo Environmental Instruments Inc., Whatham, MA) high sensitivity chemiluminescent analyzer. For the Centreville, Oak Grove and Yorkville sites, air samples for the continuous gas monitoring equipment, excluding the non-methane hydrocarbons, were collected through 0.625 cm o.d. Teflon tubing, each instrument equipped with a dedicated Teflon line and particulate filter located at the intake. The NO_y converter for the TECO 42 S was located within the intake dome and operated at 350°C. Cylinders containing gas standards for NO, NO_y, SO_2 and CO were present along with a TECO 146 dynamic gas calibrator to provide for calibration and zero and span checks. The site was equipped with a zero air generating system. Zero air for the O_3, NO/NO_y and SO_2 monitors was generated by passing ambient air through a series of canisters containing Purafill, activated charcoal and brominated charcoal. Zero air for the CO monitor was generated by passing ambient air through a palladium converter. The trace gas (except ozone) and meteorological data used for this work was an average of the 1200–1300 data from the corresponding hydrocarbon sampling days. The daily maximum value was used for ozone, which generally occurred mid-afternoon ($\sim$1500) at all the sites. More details about the continuous monitoring program at these sites are available elsewhere (Fehsenfeld *et al.*, 1994; SOS Report, 1994; Aneja *et al.*, 1996).

3. RESULTS AND DISCUSSION

3.1. *Measurements of* C_2–C_{10} *speciated hydrocarbons*

The gas chromatographic results were rigorously evaluated for accurate peak area integration and correct peak identification (Bernardo-Bricker *et al.*, 1995). The GC peak identifications were determined by retention time location since the FID detector was used to quantify peak areas. The University of Miami group utilized GC/MS analysis on some samples analyzed in the SOS programs to verify peak identification. Peak co-elution are always possible in such a complex matrix as ambient air. Examples of some peak co-elution in these data are reported elsewhere (Bernardo-Bricker *et al.*, 1996). Limonene was not one of those peak co-elution compounds mentioned in this paper. It is likely not all peak co-elution have been identified. Oxygenated VOCs were not reported even though measurable concentrations are expected in the ambient air at the sites sampled. In some instances these oxygenated VOCs elute near some of the 56 target VOCs reported. The presence of these compounds could have an impact on the conclusions presented in the following discussion. The speciated hydrocarbon data used in this paper were obtained from the validated SOS data base, and was scrutinized more than most speciated hydrocarbon data prior to public release.

Tables 1a–d summarize the seasonal average, median, standard deviation and range of the fifty-six target C_2–C_{10} compounds sampled at each site. The combined total sum of these fifty-six target VOC compounds is defined as total non-methane hydrocarbons (TNMHCs). Isobutene and 1-butene are reported together because of problems with coelution, as well as *m*-xylene and *p*-xylene. For the most part, the autumn through summer seasons represent the data in chronological order: autumn is associated with September through November 1992, winter includes December 1992 through February 1993, spring includes March through May 1993, and summer includes June through August 1993. However, the autumn category also includes sampling days from September and October 1993, and the summer category includes three days from June 1992 at the Candor site. The actual sampling days used for the seasonal averages are listed at the end of Tables 1a–d.

During the summer, the 10 most abundant compounds were highly variable among the sites. Isoprene

Table 1a. Seasonal averages of hydrocarbon compound concentrations in ppbC at Centreville, Alabama

	Autumn					Winter					Spring					Summer				
Compound	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min
Ethene	0.88	0.76	0.69	2.46	0.00	1.98	2.03	0.55	2.69	1.09	1.92	1.78	1.17	4.79	0.59	0.61	0.54	0.60	1.57	0.00
Acetylene	1.06	0.92	1.00	3.46	0.00	2.21	2.13	0.50	3.48	1.44	1.08	0.70	1.02	2.45	0.00	0.36	0.32	0.39	1.09	0.00
Ethane	3.11	2.62	2.98	10.50	0.00	3.30	2.76	1.60	7.39	0.96	1.31	1.16	1.29	3.71	0.00	1.74	1.04	1.88	4.82	0.00
Propene	0.66	0.67	0.26	1.21	0.27	0.78	0.70	0.21	1.20	0.52	0.60	0.50	0.34	1.20	0.15	0.73	0.47	0.79	2.89	0.22
Propane	4.22	2.73	3.50	12.02	1.22	8.40	6.48	4.25	15.36	4.08	4.25	3.50	2.87	10.82	1.00	2.60	2.81	1.94	6.97	0.26
Isobutane	1.03	0.61	0.92	3.25	0.22	1.95	1.50	1.07	4.05	0.96	0.89	0.66	0.69	2.15	0.12	0.77	0.77	0.56	2.16	0.10
Isobutene + 1-Butene	1.07	0.89	0.53	2.24	0.44	1.16	1.19	0.86	2.70	0.00	1.07	0.91	0.95	2.67	0.15	1.55	0.93	1.01	3.46	0.48
n-Butane	2.18	1.51	1.77	6.41	0.50	4.92	3.80	2.54	9.84	2.17	1.96	1.48	1.39	5.18	0.38	1.48	1.29	0.76	3.39	0.50
trans-2-Butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.04	0.13	0.00	0.00	0.00	0.00	0.00	0.00
3-Methyl-1-butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.10	0.00
Isopentane	1.53	1.08	1.05	3.51	0.39	3.25	2.45	2.06	9.08	1.31	2.78	1.51	3.10	10.77	0.54	2.22	2.23	1.09	4.09	0.66
1-Pentene	0.26	0.17	0.30	0.81	0.00	0.49	0.39	0.49	1.88	0.00	0.44	0.37	0.31	1.10	0.00	0.36	0.32	0.18	0.60	0.15
2-Methyl-1-butene	0.04	0.00	0.08	0.26	0.00	0.01	0.00	0.05	0.18	0.00	0.04	0.00	0.06	0.15	0.00	0.08	0.00	0.11	0.25	0.00
n-Pentane	1.04	0.66	0.82	2.78	0.29	2.00	1.61	1.09	4.00	0.95	0.90	0.61	0.64	2.27	0.25	1.04	0.74	0.78	2.98	0.42
Isoprene	2.65	1.62	3.08	9.19	0.00	0.07	0.00	0.26	0.95	0.00	2.09	0.21	3.39	8.76	0.00	21.15	19.37	10.20	43.45	8.26
trans-2-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.16	0.52	0.00	0.15	0.14	0.15	0.49	0.00
cis-2-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.10	0.00
2-Methyl-2-butene	0.03	0.00	0.05	0.14	0.00	0.05	0.00	0.07	0.18	0.00	0.05	0.00	0.07	0.18	0.00	0.06	0.00	0.11	0.29	0.00
3-Methyl-1-pentene	0.31	0.14	0.40	1.20	0.00	0.05	0.00	0.14	0.49	0.00	0.28	0.14	0.36	0.97	0.00	0.52	0.00	0.84	2.03	0.00
4-Methyl-1-pentene	0.10	0.11	0.10	0.27	0.00	0.14	0.15	0.13	0.37	0.00	0.18	0.18	0.10	0.36	0.00	0.11	0.13	0.10	0.26	0.00
Cyclopentane	0.10	0.10	0.07	0.26	0.00	0.20	0.17	0.06	0.31	0.11	0.08	0.11	0.07	0.20	0.00	0.05	0.00	0.09	0.25	0.00
2-Methylpentane	0.64	0.35	0.90	3.69	0.13	0.80	0.64	0.47	1.76	0.32	1.20	0.39	1.68	5.89	0.12	3.34	3.51	1.93	6.38	0.17
3-Methylpentane	0.50	0.41	0.41	1.41	0.00	0.89	0.95	0.29	1.37	0.41	0.67	0.53	0.38	1.26	0.24	0.82	0.80	0.36	1.36	0.30
n-Hexane	0.39	0.25	0.31	1.08	0.11	0.72	0.59	0.37	1.54	0.32	0.34	0.29	0.26	1.04	0.13	0.68	0.38	0.57	1.90	0.23
cis-3-Hexene	0.07	0.00	0.10	0.28	0.00	0.01	0.00	0.03	0.11	0.00	0.10	0.00	0.13	0.35	0.00	0.70	0.60	0.45	1.62	0.25
Methylcyclopentane	0.11	0.00	0.14	0.47	0.00	0.34	0.31	0.15	0.66	0.16	0.14	0.12	0.15	0.43	0.00	0.19	0.14	0.24	0.81	0.00
2,4-Dimethylpentane	0.07	0.00	0.08	0.24	0.00	0.14	0.15	0.06	0.21	0.00	0.10	0.00	0.13	0.34	0.00	0.29	0.16	0.41	1.40	0.00
1,1,1-Trichloroethane	0.40	0.35	0.14	0.81	0.29	0.42	0.41	0.07	0.59	0.32	0.43	0.42	0.11	0.71	0.26	0.43	0.41	0.05	0.51	0.35
Benzene	0.87	0.81	0.39	1.72	0.31	1.36	1.32	0.26	1.83	0.97	0.79	0.65	0.33	1.48	0.42	0.61	0.54	0.23	0.98	0.33
Cyclohexane	0.06	0.00	0.08	0.25	0.00	0.18	0.14	0.12	0.36	0.00	0.08	0.11	0.08	0.21	0.00	0.15	0.15	0.16	0.56	0.00
2,3-Dimethylpentane	0.57	0.49	0.39	1.72	0.12	0.35	0.32	0.10	0.62	0.18	0.67	0.55	0.54	1.71	0.00	0.86	0.71	0.41	1.50	0.36
Trichloroethylene	0.16	0.13	0.10	0.34	0.00	0.28	0.19	0.16	0.59	0.10	0.17	0.14	0.13	0.45	0.00	0.24	0.23	0.11	0.44	0.10

Table 1a. Continued

Compound	Autumn					Winter					Spring					Summer				
	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min
Methylcyclohexane	0.30	0.20	0.36	1.49	0.00	0.28	0.26	0.12	0.47	0.13	0.18	0.24	0.16	0.39	0.00	0.42	0.45	0.14	0.63	0.23
2,3,4-Trimethylpentane	0.07	0.00	0.09	0.26	0.00	0.08	0.10	0.07	0.19	0.00	0.04	0.00	0.06	0.16	0.00	0.03	0.00	0.10	0.31	0.00
Toluene	1.08	0.70	0.90	3.61	0.39	1.86	1.60	1.41	6.25	0.67	0.88	0.84	0.53	2.26	0.25	1.20	0.91	0.57	2.27	0.70
n-Octane	0.15	0.12	0.13	0.49	0.00	0.18	0.17	0.06	0.32	0.10	0.11	0.12	0.13	0.43	0.00	0.12	0.13	0.07	0.20	0.00
Perchloroethylene	0.13	0.00	0.41	1.61	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.11	0.38	0.00	0.01	0.00	0.04	0.12	0.00
Ethylbenzene	0.21	0.13	0.22	0.86	0.00	0.26	0.25	0.09	0.46	0.11	0.15	0.15	0.14	0.45	0.00	0.20	0.18	0.13	0.52	0.00
m + *p* Xylene	0.43	0.27	0.61	2.45	0.00	0.52	0.52	0.27	1.20	0.00	1.45	0.26	3.76	12.74	0.00	0.40	0.26	0.41	1.48	0.12
Styrene	0.78	0.64	0.58	2.23	0.26	0.51	0.49	0.37	1.52	0.00	1.22	1.11	0.95	3.50	0.20	1.27	1.24	0.47	2.01	0.58
o-Xylene	0.17	0.12	0.24	0.91	0.00	0.23	0.25	0.13	0.55	0.00	0.17	0.14	0.13	0.52	0.00	0.13	0.06	0.20	0.64	0.00
Isopropylbenzene	0.07	0.00	0.10	0.27	0.00	0.12	0.11	0.12	0.37	0.00	0.32	0.11	0.68	2.29	0.00	0.07	0.10	0.07	0.19	0.00
α-Pinene	0.73	0.49	0.67	2.23	0.00	0.36	0.32	0.26	0.70	0.00	0.53	0.43	0.41	1.44	0.00	1.60	1.51	0.71	2.96	0.90
n-Propylbenzene	0.09	0.10	0.10	0.25	0.00	0.06	0.00	0.08	0.23	0.00	0.18	0.16	0.16	0.54	0.00	0.15	0.14	0.08	0.25	0.00
1-Ethyl-3-methylbenzene	0.13	0.10	0.18	0.67	0.00	0.15	0.14	0.11	0.42	0.00	0.12	0.11	0.16	0.51	0.00	0.19	0.00	0.30	0.79	0.00
1-Ethyl-4-methylbenzene	0.26	0.28	0.13	0.48	0.00	0.29	0.25	0.16	0.67	0.16	0.24	0.22	0.19	0.62	0.00	0.28	0.30	0.12	0.49	0.00
1,3,5-Trimethylbenzene	0.21	0.21	0.11	0.38	0.00	0.18	0.15	0.16	0.53	0.00	0.31	0.34	0.16	0.53	0.00	0.19	0.15	0.21	0.51	0.00
1-Ethyl-2-methylbenzene	0.17	0.17	0.09	0.36	0.00	0.23	0.25	0.09	0.38	0.10	0.15	0.14	0.10	0.33	0.00	0.23	0.20	0.13	0.43	0.00
β-Pinene	0.61	0.39	0.61	2.44	0.18	0.46	0.46	0.21	0.80	0.19	1.23	0.90	1.19	4.40	0.22	1.36	1.11	0.61	2.81	0.85
1,2,4-Trimethylbenzene	0.32	0.22	0.20	0.85	0.10	0.36	0.24	0.32	1.28	0.15	0.66	0.44	0.56	2.00	0.12	0.73	0.71	0.62	1.84	0.11
Limonene	0.33	0.23	0.32	1.34	0.00	0.43	0.31	0.24	0.85	0.27	0.54	0.25	0.51	1.47	0.15	0.24	0.23	0.13	0.57	0.11
1,3-Diethylbenzene	0.44	0.33	0.59	2.50	0.00	0.93	0.86	0.53	2.18	0.15	0.69	0.39	0.70	2.47	0.20	0.70	0.33	0.73	2.50	0.12
n-Butylbenzene	0.18	0.20	0.15	0.45	0.00	0.24	0.20	0.18	0.62	0.00	0.28	0.21	0.22	0.76	0.13	0.29	0.24	0.18	0.63	0.11
Sampling days used for seasonal averages	9/3/1992 9/15/1992 9/21/1992 10/3/1992 10/9/1992 10/15/1992 10/27/1992 11/2/1992 11/8/1992 11/14/1992 11/20/1992 11/26/1992			9/10/1993 9/22/1993 9/28/1993		12/2/1992 12/8/1992 12/14/1992 12/20/1992 12/26/1992 1/1/1993 1/13/1993 1/19/1993 1/25/1993 1/31/1993 2/12/1993 2/18/1993			2/24/1993		3/2/1993 3/8/1993 3/20/1993 3/26/1993 4/13/1993 4/17/1993 4/19/1993 4/25/1993 5/7/1993 5/19/1993 5/25/1993					6/6/1993 6/12/1993 6/18/1993 7/12/1993 7/16/1993 7/18/1993 7/27/1993 8/5/1993 8/23/1993 8/29/1993				

Table 1b. Seasonal averages of hydrocarbon compound concentrations in ppbC at Oak Grove, Mississippi

	Autumn					Winter					Spring					Summer				
Compound	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min
Ethene	1.07	1.00	0.55	2.40	0.14	1.58	1.42	0.88	3.71	0.60	1.72	1.62	1.27	4.60	0.00	0.57	0.68	0.52	1.62	0.00
Acetylene	1.23	0.78	1.16	4.84	0.25	1.98	1.92	0.74	3.76	0.88	1.08	1.23	1.03	3.46	0.00	0.45	0.06	0.72	2.17	0.00
Ethane	3.27	2.73	2.23	8.96	0.76	3.43	2.30	2.56	10.35	0.00	1.93	1.25	2.30	6.67	0.00	1.02	0.72	1.25	3.79	0.00
Propene	0.87	0.74	0.50	2.61	0.36	0.56	0.55	0.20	0.94	0.22	0.49	0.40	0.27	1.29	0.26	0.61	0.59	0.29	1.19	0.00
Propane	4.09	3.08	3.53	13.64	0.17	8.07	6.09	6.09	23.34	2.38	3.86	3.66	2.29	9.83	0.85	4.04	1.28	5.61	17.85	0.79
Isobutane	1.13	0.79	0.84	3.07	0.25	2.29	1.72	1.25	4.85	1.18	1.04	1.04	0.55	2.01	0.19	1.25	1.34	0.92	2.74	0.00
Isobutene + 1-Butene	2.94	2.05	2.96	12.76	0.28	0.98	1.08	0.57	2.12	0.10	1.27	0.99	1.17	5.22	0.30	1.54	1.44	0.64	3.08	0.54
n-Butane	2.28	1.71	1.75	7.31	0.64	5.52	4.17	3.24	12.23	2.46	2.25	1.81	1.37	4.72	0.38	1.87	1.82	0.85	3.37	0.40
trans-2-Butene	0.01	0.00	0.02	0.10	0.00	0.02	0.00	0.04	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.09	0.00
cis-2-Butene	0.02	0.00	0.08	0.34	0.00	0.02	0.00	0.07	0.26	0.00	0.02	0.00	0.04	0.13	0.00	0.17	0.00	0.25	0.71	0.00
3-Methyl-1-butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopentane	1.55	1.38	0.89	3.76	0.46	2.76	2.36	1.52	5.74	1.25	1.81	1.56	1.15	5.61	0.58	5.90	4.82	4.42	14.89	1.50
1-Pentene	0.28	0.05	0.46	1.72	0.00	0.41	0.09	0.55	1.81	0.00	0.29	0.20	0.38	1.44	0.00	0.66	0.35	0.79	3.08	0.19
2-Methyl-1-butene	0.04	0.00	0.09	0.29	0.00	0.02	0.00	0.07	0.28	0.00	0.06	0.00	0.08	0.25	0.00	0.12	0.00	0.18	0.51	0.00
n-Pentane	0.95	0.75	0.62	2.84	0.29	1.92	1.49	1.12	4.47	0.93	0.89	0.82	0.49	2.18	0.23	16.51	7.68	20.97	58.05	0.88
Isoprene	2.65	0.97	2.95	9.97	0.00	0.06	0.00	0.17	0.65	0.00	1.69	0.38	3.53	14.02	0.00	11.19	10.93	4.02	18.09	3.07
trans-2-Pentene	0.08	0.00	0.22	0.88	0.00	0.02	0.00	0.07	0.25	0.00	0.07	0.00	0.13	0.38	0.00	0.38	0.34	0.36	1.15	0.00
cis-2-Pentene	0.01	0.00	0.04	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.04	0.14	0.00	0.07	0.00	0.09	0.24	0.00
2-Methyl-2-butene	0.08	0.00	0.12	0.42	0.00	0.07	0.00	0.11	0.30	0.00	0.04	0.00	0.09	0.29	0.00	0.10	0.11	0.09	0.25	0.00
3-Methyl-1-pentene	0.27	0.13	0.33	1.27	0.00	0.03	0.00	0.11	0.41	0.00	0.31	0.29	0.34	0.93	0.00	1.31	1.25	0.76	2.84	0.00
4-Methyl-1-pentene	0.08	0.00	0.12	0.44	0.00	0.16	0.19	0.14	0.43	0.00	0.22	0.19	0.14	0.64	0.00	0.11	0.13	0.09	0.26	0.00
Cyclopentane	0.10	0.12	0.08	0.22	0.00	0.18	0.15	0.08	0.39	0.12	0.08	0.10	0.08	0.22	0.00	0.16	0.14	0.16	0.42	0.00
2-Methylpentane	0.72	0.45	0.67	2.52	0.14	0.77	0.60	0.48	1.76	0.28	1.25	0.69	1.14	3.54	0.00	2.16	2.14	0.97	3.57	0.57
3-Methylpentane	0.58	0.49	0.34	1.22	0.00	0.97	0.91	0.45	2.00	0.39	0.87	0.71	0.50	2.04	0.41	0.93	0.84	0.42	1.91	0.42
n-Hexane	0.44	0.37	0.29	1.23	0.10	0.80	0.52	0.49	1.73	0.33	0.40	0.42	0.16	0.72	0.13	0.72	0.80	0.37	1.16	0.15
cis-3-Hexene	0.09	0.05	0.11	0.31	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.12	0.30	1.03	0.00	0.48	0.44	0.25	1.01	0.14
Methylcyclopentane	0.15	0.13	0.12	0.45	0.00	0.34	0.22	0.23	0.82	0.16	0.39	0.19	0.55	2.34	0.00	0.62	0.40	0.87	3.30	0.10
2,4-Dimethylpentane	0.15	0.15	0.14	0.41	0.00	0.16	0.13	0.15	0.54	0.00	0.12	0.13	0.09	0.27	0.00	0.25	0.22	0.19	0.81	0.00
1,1,1-Trichloroethane	0.37	0.33	0.13	0.84	0.26	0.39	0.40	0.05	0.50	0.31	0.52	0.46	0.36	1.82	0.28	0.63	0.52	0.37	1.75	0.40
Benzene	0.78	0.67	0.34	1.55	0.33	1.36	1.29	0.41	2.30	0.69	0.90	0.97	0.32	1.39	0.32	0.69	0.69	0.24	1.05	0.17
Cyclohexane	0.09	0.00	0.13	0.42	0.00	0.16	0.12	0.17	0.60	0.00	0.10	0.07	0.11	0.35	0.00	1.31	0.35	3.31	11.80	0.00
2,3-Dimethylpentane	0.62	0.44	0.58	2.08	0.00	0.41	0.31	0.24	0.84	0.10	0.68	0.58	0.47	2.13	0.09	0.80	0.73	0.27	1.28	0.40
Trichloroethylene	0.24	0.20	0.17	0.64	0.00	0.30	0.25	0.15	0.56	0.12	0.26	0.20	0.18	0.60	0.00	0.24	0.23	0.15	0.60	0.00
Methylcyclohexane	0.47	0.38	0.37	1.33	0.00	0.29	0.23	0.19	0.83	0.11	0.28	0.30	0.20	0.81	0.00	0.69	0.60	0.45	1.99	0.30

Table 1b. Continued

Compound	Autumn					Winter					Spring					Summer				
	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min
2,3,4-Trimethylpentane	0.14	0.11	0.16	0.48	0.00	0.08	0.10	0.08	0.26	0.00	0.06	0.00	0.10	0.37	0.00	0.15	0.06	0.23	0.62	0.00
Toluene	0.90	0.90	0.30	1.40	0.33	1.25	1.08	0.68	2.93	0.45	0.89	0.91	0.43	2.00	0.22	3.63	2.44	4.10	15.56	0.56
n-Octane	0.28	0.20	0.22	0.96	0.13	0.15	0.14	0.08	0.29	0.00	0.13	0.13	0.11	0.40	0.00	0.30	0.28	0.11	0.47	0.12
Perchloroethylene	0.07	0.00	0.10	0.29	0.00	0.03	0.00	0.07	0.24	0.00	0.41	0.05	1.23	5.00	0.00	0.09	0.04	0.11	0.33	0.00
Ethylbenzene	0.26	0.23	0.15	0.73	0.00	0.21	0.18	0.10	0.46	0.12	0.20	0.19	0.10	0.37	0.00	0.45	0.37	0.19	0.77	0.20
m + *p*-Xylene	0.58	0.46	0.44	1.97	0.14	0.74	0.44	1.05	4.44	0.17	0.33	0.34	0.26	0.80	0.00	0.89	0.72	0.50	1.93	0.13
Styrene	1.06	1.12	0.65	2.38	0.00	0.51	0.43	0.30	1.26	0.22	1.09	1.02	0.78	3.65	0.19	2.45	1.68	1.80	6.69	1.05
o-Xylene	0.26	0.22	0.18	0.67	0.00	0.20	0.18	0.10	0.39	0.00	0.10	0.00	0.12	0.31	0.00	0.36	0.29	0.19	0.75	0.12
Isopropylbenzene	0.18	0.11	0.22	0.69	0.00	0.12	0.11	0.10	0.31	0.00	0.29	0.11	0.59	2.43	0.00	0.21	0.14	0.28	1.09	0.00
α-Pinene	1.24	0.97	0.84	3.20	0.31	0.50	0.37	0.43	1.41	0.00	1.84	1.31	1.55	5.98	0.23	2.71	2.68	1.20	5.00	1.08
n-Propylbenzene	0.23	0.18	0.19	0.72	0.00	0.07	0.09	0.07	0.18	0.00	0.34	0.30	0.37	1.59	0.00	0.31	0.22	0.21	0.79	0.15
1-Ethyl-3-methylbenzene	0.28	0.23	0.24	0.88	0.00	0.13	0.14	0.11	0.31	0.00	0.11	0.06	0.16	0.62	0.00	0.28	0.23	0.24	0.84	0.00
1-Ethyl-4-methylbenzene	0.52	0.38	0.39	1.64	0.13	0.43	0.39	0.28	1.37	0.18	0.35	0.30	0.20	0.93	0.00	0.65	0.51	0.47	2.07	0.30
1,3,5-Trimethylbenzene	0.48	0.32	0.44	1.90	0.00	0.15	0.16	0.13	0.48	0.00	0.20	0.12	0.28	1.13	0.00	0.43	0.23	0.52	1.58	0.12
1-Ethyl-2-methylbenzene	0.32	0.21	0.27	1.12	0.00	0.21	0.23	0.09	0.36	0.10	0.19	0.18	0.15	0.57	0.00	0.45	0.50	0.19	0.81	0.16
β-Pinene	1.47	1.08	1.11	3.54	0.17	0.67	0.53	0.41	1.78	0.30	1.77	1.54	1.28	4.52	0.25	3.04	2.49	1.67	6.14	1.25
1,2,4-Trimethylbenzene	0.61	0.29	0.72	2.85	0.11	0.54	0.35	0.46	1.35	0.10	0.83	0.75	0.48	2.23	0.20	0.72	0.67	0.61	2.34	0.18
Limonene	0.48	0.35	0.39	1.49	0.00	0.53	0.47	0.22	1.00	0.21	0.41	0.27	0.26	0.89	0.18	0.63	0.45	0.42	1.46	0.25
1,3-Diethylbenzene	0.53	0.43	0.34	1.12	0.09	1.45	1.21	2.10	8.72	0.09	0.82	0.44	1.26	5.34	0.15	1.16	0.37	1.62	4.04	0.00
n-Butylbenzene	0.41	0.27	0.43	1.38	0.00	0.30	0.28	0.16	0.66	0.13	0.35	0.17	0.32	1.10	0.00	0.42	0.37	0.32	1.25	0.13
Sampling days used for seasonal averages	9/2/1992 9/9/1992 9/21/1992 9/27/1992 10/3/1992 10/9/1992 10/15/1992 10/21/1992 10/27/1992 11/2/1992 11/8/1992 11/14/1992			11/20/1992 11/26/1992 9/4/1993 9/10/1993 9/16/1993 9/28/1993		12/2/1992 12/8/1992 12/14/1992 12/20/1992 12/26/1992 1/1/1993 1/7/1993 1/13/1993 1/19/1993 1/25/1993 1/31/1993 2/6/1993			2/12/1993 2/18/1993 2/24/1993		3/2/1993 3/8/1993 3/14/1993 3/20/1993 3/26/1993 4/1/1993 4/7/1993 4/13/1993 4/19/1993 4/25/1993 5/1/1993 5/7/1993			5/13/1993 5/19/1993 5/25/1993 5/31/1993			6/6/1993 6/12/1993 6/18/1993 6/24/1993 6/30/1993 7/6/1993 7/12/1993 7/18/1993 7/24/1993 8/11/1993 8/17/1993 8/23/1993			

Table 1c. Seasonal averages of hydrocarbon compound concentrations in ppbC at Yorkville, Georgia

	Autumn					Winter					Spring					Summer				
Compound	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min
Ethene	1.05	1.01	0.61	2.06	0.00	2.85	2.58	1.70	6.56	0.87	1.37	0.99	0.91	2.70	0.22	0.90	0.49	1.17	4.05	0.00
Acetylene	1.16	1.12	0.96	3.85	0.00	3.16	2.67	1.96	8.08	1.52	1.55	1.16	1.56	3.83	0.00	0.72	0.66	0.43	1.25	0.00
Ethane	2.41	2.37	1.30	4.69	0.00	3.75	3.36	1.86	7.70	1.84	1.54	1.18	1.90	6.28	0.00	0.96	0.65	0.96	3.61	0.18
Propene	0.81	0.67	0.60	2.69	0.20	1.09	0.74	0.73	2.90	0.47	1.50	0.66	2.37	8.76	0.21	1.61	0.99	2.10	7.12	0.00
Propane	4.07	3.18	3.12	14.24	0.50	8.01	6.59	4.03	17.45	4.27	4.38	2.96	4.56	18.01	0.23	1.89	2.21	1.28	3.80	0.13
Isobutane	0.97	0.79	0.73	2.45	0.16	2.42	1.51	2.36	9.52	0.99	0.96	0.84	0.72	2.45	0.14	0.91	0.67	1.19	4.15	0.00
Isobutene + 1-Butene	3.02	1.67	2.97	7.78	0.15	1.26	0.77	1.34	5.23	0.17	0.84	0.97	0.66	2.47	0.12	1.16	1.06	0.63	2.10	0.00
n-Butane	2.41	1.90	1.72	7.33	0.70	6.91	4.89	6.24	21.34	2.45	2.48	1.16	2.80	11.12	0.81	1.96	1.64	1.23	4.67	0.75
trans-2-Butene	0.01	0.00	0.03	0.11	0.00	0.04	0.00	0.09	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
cis-2-Butene	0.01	0.00	0.04	0.16	0.00	0.04	0.00	0.10	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.21	0.68	0.00
3-Methyl-1-butene	0.01	0.00	0.03	0.11	0.00	0.03	0.00	0.07	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.08	0.19	0.00
Isopentane	2.69	1.88	1.97	7.51	0.52	4.93	2.65	6.47	24.42	1.15	3.84	1.94	5.25	20.44	0.62	5.02	2.73	6.40	21.88	0.00
1-Pentene	0.33	0.35	0.27	0.85	0.00	0.31	0.13	0.46	1.60	0.00	0.25	0.23	0.22	0.84	0.00	1.91	0.39	3.11	10.06	0.32
2-Methyl-1-butene	0.40	0.09	1.16	5.00	0.00	0.10	0.00	0.19	0.52	0.00	0.07	0.00	0.10	0.27	0.00	0.19	0.14	0.24	0.72	0.00
n-Pentane	1.75	1.16	1.52	6.36	0.26	3.05	1.53	3.66	13.88	0.82	1.68	0.83	2.01	7.62	0.30	2.15	1.06	2.28	7.61	0.19
Isoprene	1.73	0.65	2.18	8.13	0.00	0.04	0.00	0.07	0.21	0.00	2.41	0.58	5.01	18.38	0.00	9.80	9.02	2.39	13.53	6.40
trans-2-Pentene	0.10	0.00	0.18	0.60	0.00	0.10	0.00	0.22	0.65	0.00	0.45	0.14	0.85	3.06	0.00	1.44	0.17	3.82	12.28	0.00
cis-2-Pentene	0.02	0.00	0.07	0.29	0.00	0.06	0.00	0.13	0.36	0.00	0.05	0.00	0.16	0.59	0.00	0.07	0.00	0.16	0.51	0.00
2-Methyl-2-butene	0.08	0.03	0.13	0.56	0.00	0.14	0.00	0.23	0.67	0.00	0.82	0.00	2.34	8.43	0.00	0.19	0.06	0.28	0.81	0.00
3-Methyl-1-pentene	0.25	0.15	0.31	0.99	0.00	0.10	0.05	0.13	0.38	0.00	0.45	0.16	0.60	1.91	0.00	1.79	1.84	1.23	3.68	0.00
4-Methyl-1-pentene	0.07	0.00	0.10	0.35	0.00	0.09	0.00	0.12	0.32	0.00	0.17	0.16	0.16	0.58	0.00	0.26	0.13	0.46	1.52	0.00
Cyclopentane	0.15	0.14	0.09	0.36	0.00	0.25	0.19	0.19	0.81	0.14	0.12	0.11	0.10	0.27	0.00	0.19	0.08	0.26	0.65	0.00
2-Methylpentane	0.68	0.52	0.47	1.62	0.16	1.21	0.81	1.07	3.49	0.31	1.63	1.65	1.63	6.20	0.13	3.92	3.38	3.17	9.18	0.14
3-Methylpentane	0.78	0.72	0.47	1.76	0.16	1.04	0.78	0.69	2.44	0.34	0.66	0.57	0.36	1.30	0.13	1.05	0.77	0.77	2.77	0.25
n-Hexane	0.51	0.42	0.29	1.07	0.13	0.96	0.69	0.72	2.79	0.36	0.42	0.38	0.30	1.27	0.00	0.68	0.38	0.75	2.64	0.00
cis-3-Hexene	0.05	0.00	0.07	0.21	0.00	0.03	0.00	0.06	0.15	0.00	0.14	0.00	0.17	0.44	0.00	0.72	0.35	1.11	3.82	0.14
Methylcyclopentane	0.24	0.22	0.16	0.55	0.00	0.48	0.35	0.40	1.53	0.18	0.31	0.22	0.32	1.31	0.10	0.29	0.16	0.37	1.30	0.00
2,4-Dimethylpentane	0.15	0.13	0.15	0.50	0.00	0.25	0.18	0.23	0.67	0.00	0.13	0.14	0.09	0.30	0.00	0.43	0.25	0.44	1.22	0.00
1,1,1-Trichloroethane	0.43	0.39	0.12	0.71	0.30	0.45	0.36	0.23	0.99	0.28	0.77	0.48	0.90	3.66	0.27	0.64	0.49	0.36	1.55	0.31
Benzene	0.98	0.89	0.51	2.35	0.40	1.79	1.65	0.99	4.46	0.97	0.92	0.77	0.38	1.94	0.57	1.22	0.91	0.93	3.57	0.41
Cyclohexane	0.16	0.00	0.38	1.59	0.00	0.28	0.14	0.59	2.21	0.00	0.12	0.14	0.11	0.38	0.00	1.00	0.25	1.63	4.93	0.00
2,3-Dimethylpentane	0.39	0.39	0.20	0.82	0.00	0.54	0.38	0.38	1.32	0.21	0.58	0.57	0.38	1.32	0.00	1.11	1.03	0.55	2.45	0.49
Trichloroethylene	0.23	0.18	0.18	0.73	0.00	0.37	0.33	0.22	0.78	0.10	0.29	0.16	0.25	0.93	0.12	0.18	0.15	0.14	0.39	0.00

Table 1c. Continued

Compound	Autumn					Winter					Spring					Summer				
	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min
Methylcyclohexane	0.23	0.20	0.17	0.72	0.00	0.39	0.25	0.35	1.29	0.12	0.30	0.32	0.24	0.89	0.00	0.57	0.38	0.38	1.40	0.20
2,3,4-Trimethylpentane	0.14	0.09	0.16	0.51	0.00	0.25	0.15	0.31	0.99	0.00	0.11	0.13	0.12	0.34	0.00	0.22	0.17	0.25	0.90	0.00
Toluene	2.14	1.20	2.11	8.37	0.36	3.01	1.95	3.20	11.73	0.68	1.40	1.43	0.78	3.01	0.33	4.75	1.43	5.94	15.22	0.81
n-Octane	0.21	0.15	0.24	1.13	0.00	0.18	0.14	0.11	0.41	0.00	0.10	0.10	0.11	0.27	0.00	0.24	0.16	0.29	0.93	0.00
Perchloroethylene	0.11	0.00	0.23	0.97	0.00	0.08	0.00	0.11	0.33	0.00	0.04	0.00	0.10	0.32	0.00	0.14	0.14	0.15	0.38	0.00
Ethylbenzene	0.29	0.19	0.24	0.86	0.00	0.41	0.24	0.40	1.33	0.13	0.26	0.25	0.19	0.61	0.00	0.95	0.34	1.08	3.22	0.19
p + *m* Xylene	1.47	0.44	1.76	4.38	0.10	1.16	0.50	1.36	4.26	0.36	0.50	0.54	0.38	1.41	0.00	1.80	0.40	2.49	7.18	0.18
Styrene	0.69	0.49	0.48	1.82	0.16	0.56	0.50	0.31	1.48	0.29	0.76	0.65	0.72	2.09	0.00	1.83	1.83	0.70	3.07	0.86
o-Xylene	0.31	0.20	0.32	1.10	0.00	0.45	0.21	0.47	1.48	0.14	0.20	0.23	0.14	0.46	0.00	0.73	0.23	0.92	2.75	0.11
Isopropylbenzene	0.15	0.02	0.26	1.02	0.00	0.15	0.16	0.11	0.31	0.00	0.09	0.09	0.10	0.28	0.00	0.12	0.06	0.15	0.36	0.00
α-Pinene	0.88	0.58	0.86	3.78	0.19	0.45	0.27	0.47	1.74	0.14	0.51	0.50	0.34	1.42	0.11	0.71	0.60	0.37	1.70	0.41
n-Propylbenzene	0.16	0.11	0.19	0.73	0.00	0.15	0.11	0.11	0.37	0.00	0.20	0.18	0.18	0.49	0.00	0.28	0.23	0.18	0.65	0.00
1-Ethyl-3-methylbenzene	0.27	0.20	0.33	1.09	0.00	0.34	0.21	0.31	1.01	0.00	0.20	0.21	0.17	0.54	0.00	0.30	0.17	0.35	1.08	0.00
1-Ethyl-4-methylbenzene	0.37	0.29	0.40	1.69	0.00	0.42	0.34	0.23	0.94	0.21	0.23	0.24	0.15	0.49	0.00	0.42	0.33	0.30	1.04	0.12
1,3,5-Trimethylbenzene	0.50	0.33	0.57	2.04	0.00	0.26	0.16	0.20	0.66	0.11	0.26	0.15	0.35	1.33	0.00	0.74	0.52	0.60	2.06	0.25
1-Ethyl-2-methylbenzene	0.25	0.18	0.22	0.70	0.00	0.23	0.22	0.12	0.47	0.10	0.15	0.16	0.10	0.29	0.00	0.21	0.15	0.21	0.74	0.00
β-Pinene	0.82	0.75	0.62	2.38	0.00	0.59	0.51	0.48	2.02	0.13	0.75	0.60	0.65	2.08	0.00	2.06	1.70	1.00	3.74	0.94
1,2,4-Trimethylbenzene	1.11	0.49	2.10	9.21	0.12	0.54	0.36	0.48	1.57	0.14	0.85	0.81	0.48	1.75	0.17	0.77	0.59	0.53	1.50	0.12
Limonene	0.45	0.31	0.44	1.59	0.00	0.67	0.50	0.40	1.35	0.18	0.29	0.27	0.16	0.62	0.00	0.46	0.31	0.36	1.02	0.13
1,3-Diethylbenzene	0.50	0.17	0.73	2.76	0.00	0.99	0.87	0.76	2.49	0.12	0.37	0.31	0.17	0.68	0.18	0.34	0.26	0.23	0.78	0.13
n-Butylbenzene	0.30	0.20	0.37	1.57	0.00	0.31	0.25	0.17	0.62	0.00	0.18	0.19	0.14	0.41	0.00	0.27	0.26	0.12	0.49	0.14
Sampling days used for seasonal averages	9/26/1992 10/2/1992 10/9/1992 10/15/1992 10/21/1992 10/27/1992 11/2/1992 11/8/1992 11/14/1992 11/20/1992 11/26/1992 9/10/1993			9/16/1993 9/22/1993 9/28/1993 10/4/1993 10/10/1993 10/16/1993		12/2/1992 12/14/1992 12/20/1992 12/26/1992 1/1/1993 1/7/1993 1/13/1993 1/19/1993 1/25/1993 1/31/1993 2/6/1993 2/13/1993			2/18/1993		3/2/1993 3/8/1993 3/20/1993 4/1/1993 4/7/1993 4/19/1993 4/25/1993 5/1/1993 5/7/1993 5/13/1993 5/19/1993 5/25/1993			5/31/1993		6/6/1993 6/12/1993 6/18/1993 6/24/1993 7/18/1993 7/24/1993 7/30/1993 8/5/1993 8/11/1993 8/23/1993				

Table 1d. Seasonal averages of hydrocarbon compound concentrations in ppbC at Candor, North Carolina

	Autumn					Winter					Spring					Summer				
Compound	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min
Ethene	1.67	1.25	1.06	3.87	0.77	2.28	2.30	1.17	4.64	0.72	1.93	1.18	1.83	6.37	0.00	0.47	0.31	0.55	1.43	0.00
Acetylene	1.34	0.92	1.07	3.84	0.37	2.53	2.56	0.86	4.55	1.37	1.12	0.64	1.34	3.85	0.00	0.17	0.00	0.42	1.03	0.00
Ethane	2.51	1.84	2.42	8.08	0.00	2.81	2.46	1.73	6.66	0.00	1.67	1.59	1.90	5.67	0.00	0.09	0.00	0.21	0.52	0.00
Propene	0.70	0.77	0.34	1.31	0.11	0.78	0.74	0.30	1.39	0.40	0.41	0.29	0.29	1.20	0.18	1.75	1.76	1.47	3.29	0.27
Propane	3.77	1.87	4.36	15.63	0.43	5.84	5.16	3.23	12.70	0.61	3.44	3.19	2.69	10.82	0.00	2.19	2.20	0.59	3.04	1.37
Isobutane	0.97	0.64	0.99	3.61	0.10	1.71	1.74	0.85	3.78	0.71	0.83	0.76	0.61	2.20	0.00	0.45	0.40	0.18	0.73	0.26
Isobutene + 1-Butene	1.24	0.85	1.13	4.54	0.43	0.48	0.50	0.28	0.80	0.00	0.66	0.57	0.70	2.67	0.00	0.96	0.68	0.87	2.61	0.29
n-Butane	2.83	1.81	2.63	9.74	0.52	4.97	4.86	2.97	13.11	1.74	2.15	1.76	1.58	5.41	0.00	0.98	1.04	0.34	1.38	0.43
trans-2-Butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.00	0.54	1.76	0.00	1.43	0.00	3.51	8.59	0.00
cis-2-Butene	0.01	0.00	0.05	0.16	0.00	0.01	0.00	0.03	0.11	0.00	0.18	0.00	0.38	1.31	0.00	0.00	0.00	0.00	0.00	0.00
3-Methyl-1-butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopentane	2.91	2.52	1.50	5.94	1.12	2.65	2.67	1.50	6.33	0.86	2.08	1.52	1.57	5.66	0.33	3.13	1.96	2.91	8.70	0.83
1-Pentene	0.10	0.00	0.27	0.93	0.00	0.35	0.15	0.41	1.13	0.00	0.32	0.20	0.37	1.53	0.00	0.14	0.07	0.21	0.54	0.00
2-Methyl-1-butene	0.03	0.00	0.06	0.18	0.00	0.02	0.00	0.06	0.17	0.00	0.04	0.00	0.06	0.14	0.00	0.02	0.00	0.05	0.13	0.00
n-Pentane	1.17	0.60	1.14	3.30	0.22	1.55	1.47	0.84	3.50	0.62	1.04	0.89	0.70	2.32	0.29	1.00	0.76	0.67	2.24	0.41
Isoprene	2.45	0.55	3.62	9.23	0.00	0.01	0.00	0.03	0.10	0.00	1.84	0.44	2.97	10.99	0.00	10.02	6.70	9.96	27.54	1.40
trans-2-Pentene	0.03	0.00	0.07	0.23	0.00	0.05	0.00	0.10	0.35	0.00	0.07	0.00	0.11	0.34	0.00	0.02	0.00	0.05	0.12	0.00
cis-2-pentene	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.04	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Methyl-2-butene	0.14	0.14	0.03	0.18	0.09	0.07	0.00	0.15	0.41	0.00	0.05	0.00	0.07	0.16	0.00	0.87	0.84	0.81	2.01	0.00
3-Methyl-1-pentene	0.19	0.16	0.16	0.56	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.18	0.46	1.24	0.00	0.32	0.17	0.38	0.88	0.00
4-Methyl-1-pentene	0.04	0.00	0.11	0.34	0.00	0.17	0.19	0.09	0.29	0.00	0.16	0.15	0.10	0.31	0.00	0.02	0.00	0.05	0.13	0.00
Cyclopentane	0.15	0.14	0.08	0.30	0.00	0.19	0.18	0.06	0.35	0.11	0.11	0.13	0.09	0.28	0.00	0.07	0.00	0.12	0.29	0.00
2-Methylpentane	0.81	0.75	0.54	1.77	0.16	0.88	0.80	0.48	1.85	0.24	1.22	1.11	1.01	3.98	0.22	2.81	2.43	1.62	5.44	1.17
3-Methylpentane	0.57	0.49	0.42	1.30	0.11	0.86	0.85	0.37	1.37	0.23	0.69	0.55	0.41	1.52	0.20	0.39	0.48	0.21	0.54	0.00
n-Hexane	0.73	0.38	0.69	1.97	0.13	0.73	0.63	0.43	1.57	0.24	0.56	0.39	0.43	1.53	0.15	0.28	0.27	0.19	0.57	0.00
cis-3-Hexene	0.13	0.16	0.10	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.05	0.15	0.53	0.00	0.22	0.07	0.29	0.63	0.00
Methylcyclopentane	0.22	0.18	0.23	0.73	0.00	0.33	0.34	0.17	0.74	0.13	0.19	0.16	0.16	0.48	0.00	0.19	0.16	0.20	0.52	0.00
2,4-Dimethylpentane	0.13	0.13	0.11	0.34	0.00	0.13	0.14	0.10	0.32	0.00	0.13	0.13	0.12	0.37	0.00	0.13	0.08	0.17	0.44	0.00
1,1,1-Trichloroethane	0.44	0.38	0.18	0.99	0.30	0.40	0.39	0.07	0.52	0.30	0.51	0.47	0.16	0.80	0.27	0.58	0.54	0.14	0.79	0.45
Benzene	12.77	12.86	8.35	24.67	2.14	1.59	1.47	0.53	2.73	0.97	1.00	0.87	0.40	1.83	0.45	0.90	0.85	0.36	1.52	0.58
Cyclohexane	0.05	0.00	0.09	0.26	0.00	0.26	0.12	0.39	1.35	0.00	0.11	0.12	0.11	0.32	0.00	0.02	0.00	0.05	0.12	0.00
2,3-Dimethylpentane	0.40	0.36	0.16	0.68	0.13	0.32	0.30	0.14	0.53	0.00	0.59	0.41	0.54	2.09	0.00	0.75	0.67	0.29	1.31	0.53
Trichloroethylene	0.21	0.16	0.11	0.44	0.11	0.30	0.28	0.16	0.65	0.10	0.22	0.18	0.12	0.47	0.10	0.36	0.36	0.11	0.50	0.23

Table 1d. Continued

Compound	Autumn					Winter					Spring					Summer				
	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min	Mean	Medn	StD	Max	Min
Methylcyclohexane	0.34	0.28	0.17	0.68	0.10	0.26	0.22	0.12	0.53	0.14	0.29	0.23	0.34	1.42	0.00	0.41	0.27	0.25	0.74	0.21
2,3,4-Trimethylpentane	0.18	0.14	0.11	0.37	0.00	0.12	0.13	0.11	0.31	0.00	0.10	0.11	0.10	0.30	0.00	0.13	0.00	0.21	0.43	0.00
Toluene	2.26	1.79	1.22	5.33	1.31	1.83	1.83	0.91	3.49	0.63	1.43	1.25	0.86	3.26	0.44	2.94	2.53	1.97	6.31	1.20
n-Octane	0.37	0.20	0.37	1.29	0.12	0.16	0.12	0.16	0.61	0.00	0.17	0.13	0.21	0.73	0.00	0.49	0.47	0.48	1.12	0.00
Perchloroethylene	0.08	0.00	0.25	0.88	0.00	0.02	0.00	0.05	0.18	0.00	0.05	0.00	0.07	0.18	0.00	0.56	0.00	0.98	2.39	0.00
Ethylbenzene	0.31	0.30	0.13	0.66	0.19	0.29	0.29	0.13	0.47	0.00	0.20	0.20	0.16	0.49	0.00	0.48	0.48	0.30	1.02	0.19
m + *p*-Xylene	0.77	0.62	0.42	1.81	0.42	0.67	0.62	0.30	1.13	0.12	0.47	0.37	0.37	1.35	0.00	1.63	1.75	1.31	3.38	0.12
Styrene	0.81	0.82	0.21	1.16	0.41	0.47	0.52	0.18	0.79	0.14	0.98	1.15	0.74	2.28	0.00	2.75	2.32	1.28	5.09	1.81
o-Xylene	0.30	0.25	0.15	0.75	0.19	0.27	0.27	0.12	0.48	0.00	0.17	0.13	0.17	0.56	0.00	0.81	0.67	0.86	2.36	0.00
Isopropylbenzene	0.15	0.15	0.10	0.36	0.00	0.09	0.10	0.10	0.24	0.00	0.10	0.00	0.15	0.56	0.00	0.56	0.51	0.59	1.40	0.00
α-Pinene	1.31	0.95	0.92	3.53	0.41	0.71	0.40	0.67	2.48	0.10	0.73	0.75	0.46	1.73	0.13	2.25	2.31	0.86	3.22	0.71
n-Propylbenzene	0.16	0.16	0.07	0.27	0.00	0.09	0.11	0.07	0.19	0.00	0.21	0.14	0.17	0.54	0.00	0.94	0.54	1.17	3.22	0.14
1-Ethyl-3-methylbenzene	0.26	0.24	0.13	0.60	0.13	0.20	0.21	0.10	0.36	0.00	0.11	0.00	0.17	0.51	0.00	1.21	0.82	1.50	3.99	0.00
1-Ethyl-4-methylbenzene	0.45	0.40	0.16	0.87	0.30	0.36	0.32	0.11	0.56	0.22	0.26	0.25	0.13	0.51	0.00	1.30	0.99	1.18	3.33	0.34
1,3,5-Trimethylbenzene	0.23	0.27	0.11	0.42	0.00	0.16	0.14	0.07	0.38	0.09	0.13	0.11	0.12	0.37	0.00	0.56	0.28	0.73	1.78	0.00
1-Ethyl-2-methylbenzene	0.21	0.22	0.09	0.41	0.10	0.21	0.20	0.09	0.36	0.10	0.18	0.20	0.11	0.33	0.00	1.01	0.99	1.00	2.56	0.00
β-Pinene	0.97	0.80	0.66	2.24	0.17	0.68	0.67	0.38	1.51	0.21	0.69	0.67	0.45	1.60	0.00	1.30	1.29	0.39	1.88	0.89
1,2,4-Trimethylbenzene	0.39	0.37	0.13	0.68	0.19	0.53	0.36	0.48	1.99	0.19	6.26	5.10	5.98	17.04	0.35	6.79	8.30	4.66	12.29	1.11
Limonene	0.47	0.44	0.23	0.87	0.18	0.50	0.37	0.24	1.02	0.22	0.33	0.29	0.35	1.47	0.00	0.69	0.60	0.53	1.32	0.12
1,3-Diethylbenzene	0.44	0.25	0.41	1.24	0.10	0.86	0.95	0.55	1.78	0.10	0.42	0.31	0.39	1.56	0.00	0.84	0.85	0.71	1.77	0.11
n-Butylbenzene	0.26	0.24	0.11	0.49	0.14	0.30	0.31	0.14	0.62	0.00	0.21	0.19	0.20	0.76	0.00	1.49	1.42	1.47	3.58	0.00
Sampling days used for seasonal averages	9/3/1992 9/9/1992 9/27/1992 10/3/1992 10/15/1992 10/21/1992 10/27/1992 11/2/1992 11/8/1992 11/14/1992 11/20/1992 11/26/1992					12/2/1992 12/8/1992 12/14/1992 12/20/1992 12/26/1992 1/1/1993 1/7/1993 1/13/1993 1/19/1993 1/25/1993 1/31/1993 2/6/1993			2/12/1993 2/18/1993 2/24/1993		3/2/1993 3/7/1993 3/8/1993 3/13/1993 3/14/1993 3/20/1993 3/26/1993 4/1/1993 4/19/1993 4/25/1993 5/1/1993 5/7/1993			5/13/1993 5/19/1993 5/25/1993 5/31/1993		6/6/1993 6/12/1993 6/18/1993 6/11/1992 6/14/1992 6/17/1992				

was the dominant hydrocarbon at all but the Oak Grove site, where *n*-pentane was the most abundant hydrocarbon (16.51 ± 20.97 ppbC, median = 7.68 ppbC) with isoprene immediately following with a concentration of 11 ± 4.2 ppbC. Isoprene, propane, isopentane, 2-methylpentane, and styrene consistently appeared in the top 10 most abundant hydrocarbons at all four sites, though not necessarily in that order.

During the wintertime, the same top four dominant compounds, i.e., in the following order: propane, *n*-butane, ethane, and isopentane were observed at three sites. The Yorkville site had isopentane and ethane switched around in ranking. At all sites acetylene, *n*-pentane, ethene, isobutane, and benzene were within the top 10 most abundant species. Toluene was also within the top 10 at all sites except at Oak Grove,

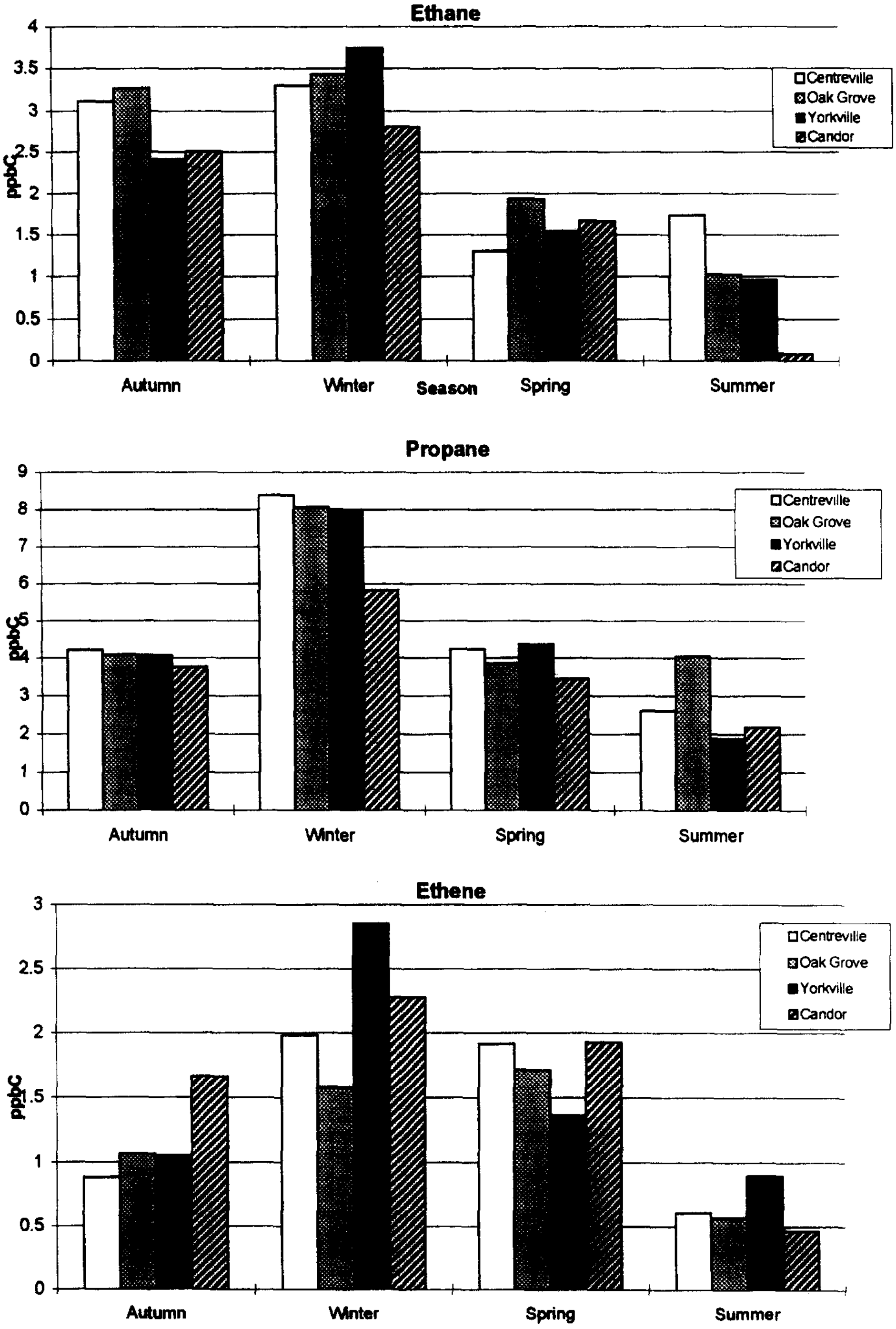

Fig. 2. Seasonal averages of select C_2–C_3 hydrocarbons.

where it ranked 11th. The individual C_2–C_5 alkanes (except cyclopentane) dominated the list of most abundant compounds for all four sites during the winter.

Figure 2 displays the distinct seasonal variation of ethane, propane, *n*-butane, isobutane, ethene and acetylene with maxima occurring during the winter. These observed seasonal variations of the paraffins and acetylene are consistent with the literature. Jobson *et al.* (1994) reported that, alkane compounds and acetylene concentrations displayed a winter maximum and summer minimum at a remote boreal site in Canada. Penkett *et al.* (1993) observed similar seasonal trends in hydrocarbon concentrations in ambient air measured over the North Atlantic Ocean. Seasonal variations of atmospheric hydrocarbons were also measured in western France (Boudries *et al.*, 1994) and at a rural site in Norway (Hov *et al.*, 1991). The winter maximum and summer minimum of the lower alkanes and acetylene has been attributed to hydroxyl chemistry and the seasonal abundance of the OH radical (Jobson *et al.*, 1994; Penkett *et al.*, 1993; Boudries *et al.*, 1994; Lightman *et al.*, 1990; Spivakovsky *et al.*, 1990). Seasonal variation in hydrocarbon source strengths, and differences in atmospheric behavior such as increased convection and vertical mixing in the summer, and differences in air mass climatology with season, also play a role in the hydrocarbon seasonal variation (Jobson *et al.*, 1994).

TNMHCs did not vary greatly between the autumn, winter, and spring, ranging from approximately 30 to 50 ppbC for these three seasons (Fig. 3). However, the summer period shows much higher concentrations, accounted for primarily by increased concentrations of the biogenic hydrocarbons.

The paraffin sum displays a seasonal pattern with a winter maximum for all but the Oak Grove site, which displays its maximum during the summer. Peculiarity of the Oak Grove site can be attributed to *n*-pentane concentration (16.51 ± 20.97 ppbC, median = 7.68 ppbC), which is 8–10 times greater than that measured at the other three sites. Comparison of the mean and median *n*-pentane concentration indicates that the measurements are not well distributed. Out of 12 observations, two days had values of ~57 ppbC, one day measured 29 ppbC and two days measured approximately 15 ppbC. The reason for these high *n*-pentane values are uncertain; however, auto emissions is ruled out as a possible source because of the expectation of equally high values for many of the target hydrocarbons that were not observed.

The olefins sum, which excludes the biogenic hydrocarbons isoprene, α-pinene, β-pinene and limonene, shows little variation throughout the year. With the exception of the summer mean of 10.7 ppbC measured at Yorkville, the mean concentration ranges from 4 to 7 ppbC for all seasonal periods. Other studies have shown no distinct seasonal trend for olefins at continental remote sites unaffected by anthropogenic sources (Jobson *et al.*, 1994), and very little seasonal variation in the free troposphere over the Atlantic (Penkett *et al.*, 1993). Hov *et al.* (1991) found a seasonal trend for ethene and propene with a late January maxima and a secondary maxima

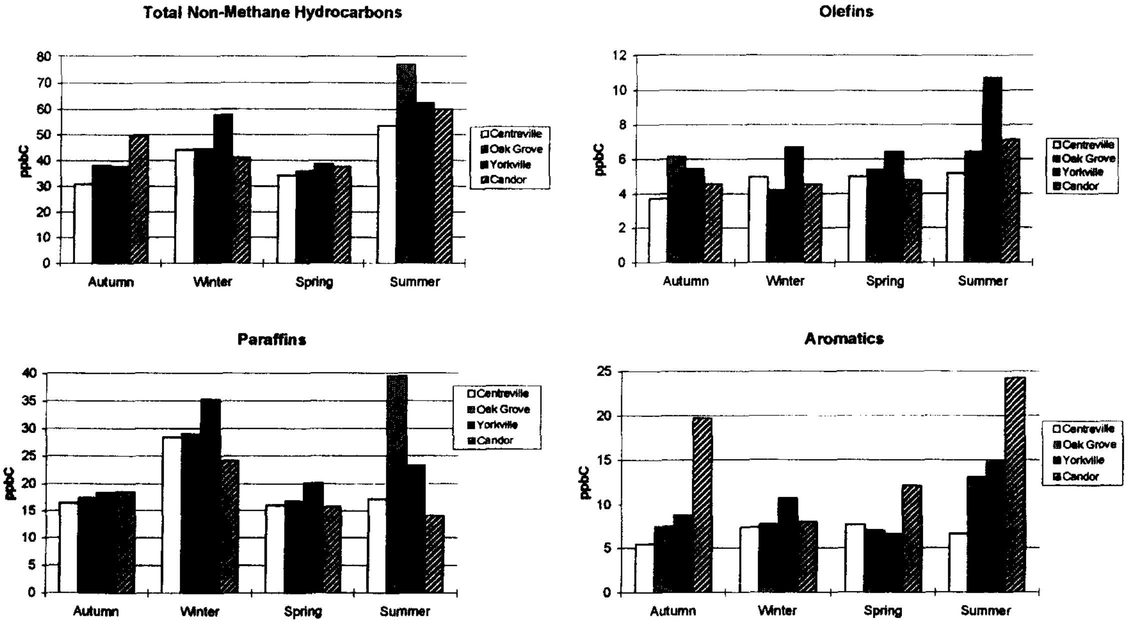

Fig. 3. Seasonal averages of hydrocarbon sums (olefins do not include isoprene, α-, β-pinene, and limonene).

during July–August, but attributed this summer maxima to point sources from areas upwind of the site. Yorkville is affected by two potential emission sources including the city of Atlanta, located approximately 45 miles (72 km) southeast of the site, and a large power generating station located approximately 30 miles (48 km) east of Yorkville (D. Kirk, pers. commun., 1996). Composition of the olefins compounds at Yorkville during this period appears to be similar to the other three seasonal periods. The summer maxima for the olefins at Yorkville may be due to transport from these anthropogenic emission sources.

With the exception of Centreville, there appears to be seasonal difference for the sum of aromatics at the rural sites. Largest aromatic concentrations occur during the summer period. Highest sum of aromatic concentrations occurs at the Candor site except during the winter period. The difference between the high aromatic concentration during autumn at Candor (19.75 ppbC) and the other three sites (~5–8 ppbC) is accounted for by benzene 12.77 ± 8.35 ppbC). The difference between the high summer aromatic sum at Candor and the Yorkville site is due primarily to 1,2,4-trimethylbenzene (6.79 ± 4.66 ppbC), along with the compounds styrene (2.75 ± 1.28 ppbC) and toluene (2.94 ± 1.97 ppbC). The reason for the high levels of these particular compounds is unclear. Surface wind direction appears to have a random relationship with excessively high concentrations of *n*-pentane, benzene, and 1,2,4-trimethylbenzene.

Table 2 summarizes selected hydrocarbons measured during the summer at various rural and remote sites. It can be seen that hydrocarbon concentrations at the Centreville site are comparable to the other sites designated as rural in Table 2. The Fraserdale site in Canada appears to be the least affected by anthropogenic sources, given its lower concentrations of acetylene and the other lower molecular weight hydrocarbons.

3.2. *Biogenic hydrocarbons*

Isoprene averaged approximately 2 ppbC during the autumn and spring, and was virtually non-existent during the winter period for all four sites (mean <0.1 ppbC) (Fig. 4a). Isoprene concentrations were highest during the summer, with Centreville having concentrations twice as high as the other three sites. These observations are consistent with other reports of seasonal dependence on isoprene levels (Rasmussen and Khalil, 1988). Isoprene emissions are directly related to plant growth period and sunlight intensity. As shown later, the magnitude of emissions is directly related to ambient temperature. The terpenes, which include the naturally emitted compounds α-pinene,

Table 2. Average hydrocarbon concentrations (ppbC) at various rural sites during the summer months

Compound	Fraserdale Canada[a]	Birkenes Norway[b]	Belfast Maine[c]	NW[d] England	Centreville Alabama[e]	Raleigh NC[f]	Brazil[g]
Ethene		1.67	2.0	1.6	0.61		3.78
Acetylene	0.15	0.51	<0.5	0.6	0.36		
Ethane	1.64	3.05	3.5[h]	14.9	1.74		4.18
Propene		0.82	0.5	4.1	0.73	0.54	0.93
Propane	0.23	2.01	2.0	10.3	2.60	9.59	1.35
Isobutane	0.028	0.70	0.5	0.8	0.77	0.61	
n-Butane	0.06	1.67	2.0	1.1	1.48	2.04	0.96
Isopentane	0.04	1.00	1.0		2.22	4.42	
n-Pentane	0.065	0.62	1.0	5.1	1.04	1.97	<DL
2-Methylpentane				<0.5	3.34	1.28	
3-Methylpentane				<0.5	0.82	0.70	
n-Hexane				5.1	0.68	0.87	<DL
cis-3-Hexene				<0.5	0.70		
Benzene					0.61	1.32	3
Toluene					1.20	8.96	0.84

Reference	Sampling Period
[a] Jobson *et al.* (1994)	July to September 1990, 1991 and 1992, collected midmorning (0900 to 1200). Samples from June to July 1990 were collected throughout the day
[b] Hov *et al.* (1991)	June–August 1987
[c] Sexton and Westberg (1984)	June–July 1975
[d] Colbeck and Harrison (1985)	May–July 1983
[e] This study	June–August 1993, 1200–1300 local time
[f] Lawrimore *et al.* (1995) (semi-urban)	Surface, August 1993, 0500–0800 EDT
[g] Greenberg and Zimmerman (1984)	Surface, August and September 1979 and 1980

[h] Geometric mean.

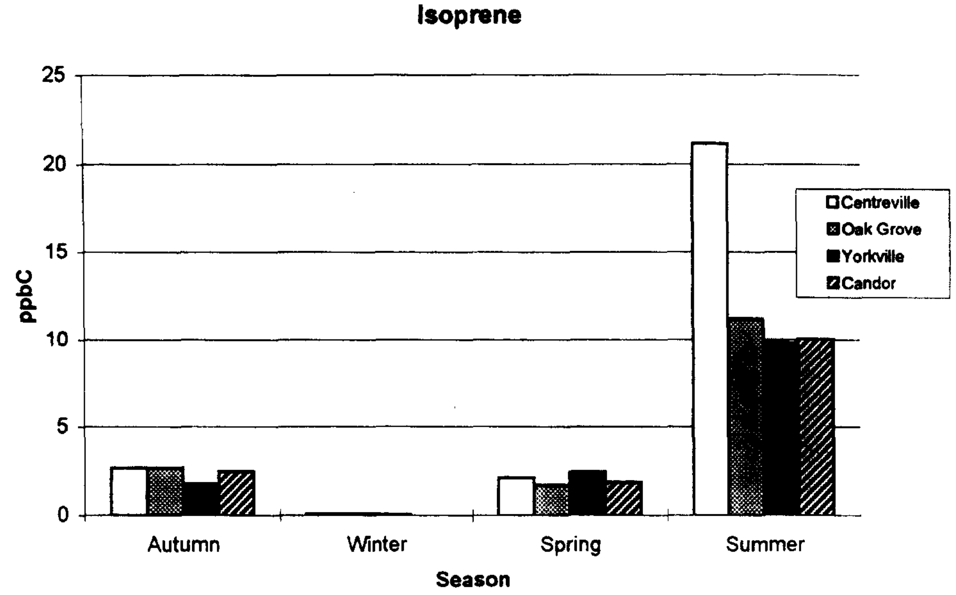

Fig. 4a. Seasonal average of isoprene.

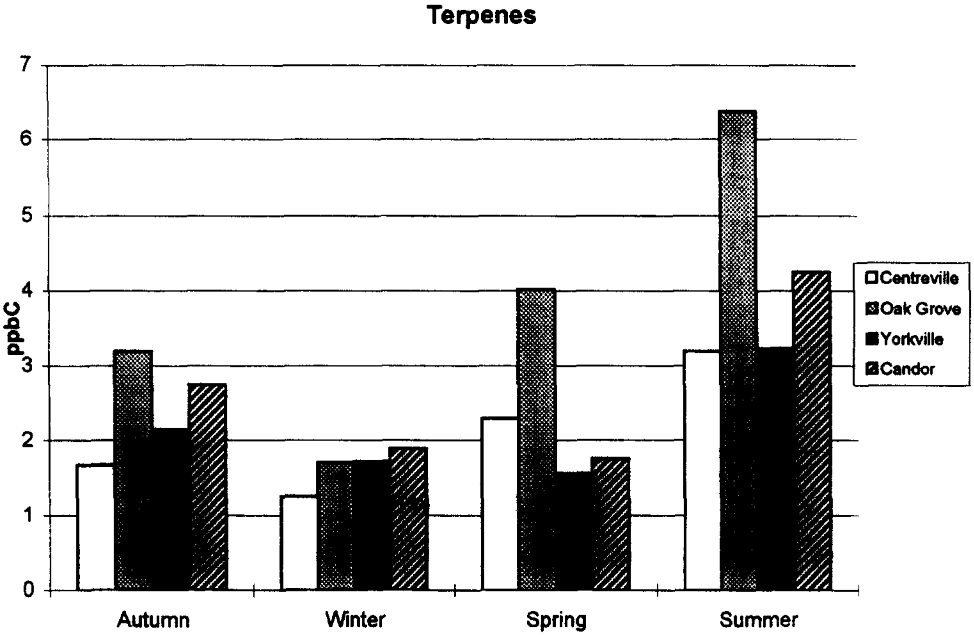

Fig. 4b. Seasonal average of terpene sum (α-, β-pinene, limonene).

β-pinene and limonene, show a seasonal distribution with lowest concentrations in the winter and highest in the summer (Fig. 4b). However, unlike isoprene, variation of terpenes concentration levels are less dramatic; and these compounds are observed throughout the winter, with the sum ranging between 1.25 and 1.9 ppbC for all sites. A study done by Tingey (1981) on live oak found that isoprene was emitted only in daylight, and given constant light conditions, the emission rate is temperature dependent. Terpene emissions from slash pine do not vary with light, but emission rates are log-linearly related to temperature (Tingey, 1981). While isoprene is highly dependent on temperature and virtually negligible during the winter, the terpenes have a small winter abundance. Likewise, terpene emissions in general come from plants that have seasonal growth patterns but do not lose their foliage like deciduous plants. Table 3 lists isoprene and monoterpene data from this work and other literature.

Table 3. Summer averages of biogenic hydrocarbons (ppbC)

Location	Isoprene	α-Pinene	β-Pinene	Limonene
Raleigh, NC[a]	2.08			
Brazil[b]	12	2.7		
Niwot Ridge, CO[c]	3.15	1.4	0.7	
Candor, North Carolina[d]	10.01	2.25	1.30	0.69
Centreville, Alabama[e]	21.15	1.60	1.36	0.24
Oak Grove, Mississippi[e]	11.19	2.71	3.04	0.63
Yorkville, Georgia[e]	9.8	0.71	2.06	0.46

[a] Lawrimore *et al.* (1995) (surface, August 1993, 0500–0800 EDT).

[b] Greenberg and Zimmerman (1984) (surface, August and September 1979 and 1980).

[c] Greenberg and Zimmerman (1984) (surface, August–September and November 1982).

[d] This work (June 1992 and 1993, 1200–1300 local time).

[e] This work (June–August 1993 1200–1300 local time).

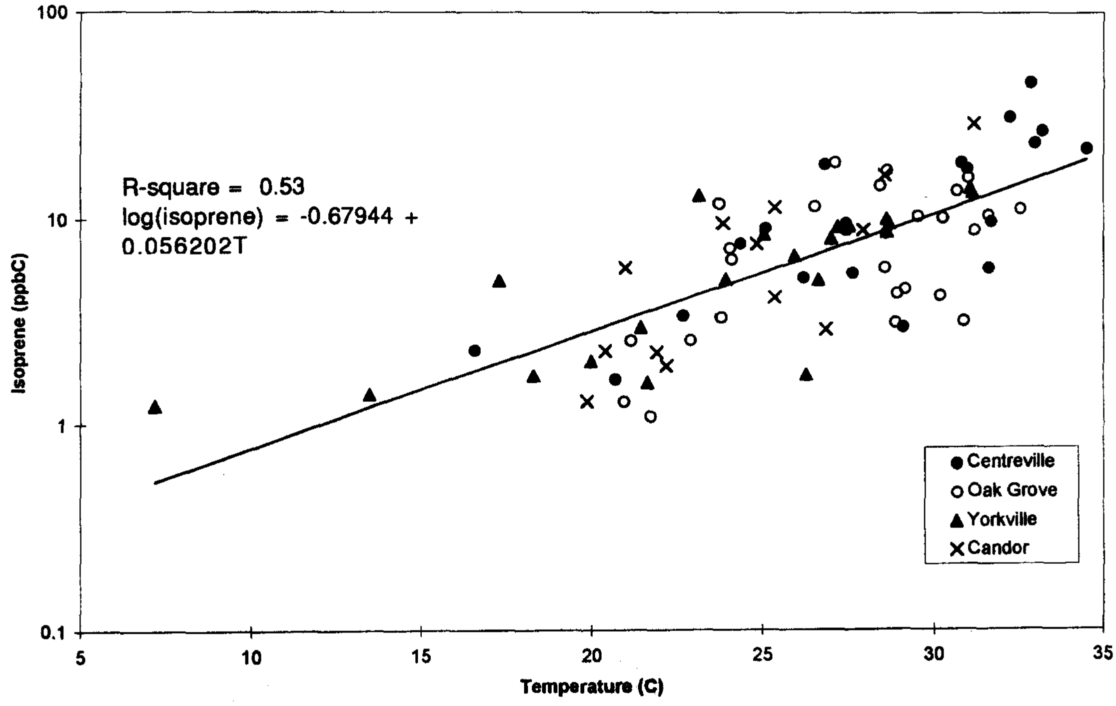

Fig. 5. Isoprene concentration vs temperature for the months April through September (1992 and 1993).

To demonstrate temperature dependence, Fig. 5 shows the linear relationship between the logarithm of isoprene concentration (ppbC) and temperature (°C) using data collected from all four sites. The temperature and isoprene concentrations were measured and integrated during the same time interval of 1200 to 1300 local time. The plot includes all values for which isoprene was greater or equal to 1 ppbC (April through September). The regression equation determined is given in equation (1)

$$\log(\text{isoprene}) = -0.67944 + 0.056202T \quad (1)$$

with an R-squared value of 0.53. The units of isoprene are in ppbC. The slope of the best fit line (0.056) is lower than the 0.071 value reported by Jobson *et al.* (1994). The regression equation reported by Jobson in units of ppbv is shown in equation (2)

$$\log(\text{isoprene}) = -1.40 + 0.071T \text{ (in units of ppbv)}, \quad (2)$$

$$\log(\text{isoprene}) = -0.70103 + 0.071T \text{ (converted to units of ppbC)}. \quad (2a)$$

Converting this equation for units of ppbC changes only the intercept to a value of −0.70103 and the slope remains the same (equation (2a)). Considering a temperature range of 18–35°C, the predicted isoprene concentrations using Jobson's regression equation was two to three times greater than the predicted concentrations using the regression equation found in this work. Part of this discrepancy may be due to the fact that in this work, four sites were used for the equation (1) regression, versus Jobson's one site, which increases the variability of isoprene concentrations. Vegetation composition and site location with respect to the vegetation is expected to have an impact on observed isoprene concentration. To account for this difference, a regression of isoprene at only one site, Centreville, resulted in a higher R-squared value (0.61) and a slope very similar to Jobson (0.066), but with a lower intercept. The regression equation for Centreville is given in equation (3).

$$\log(\text{isoprene}) = -0.9029 + 0.066T. \qquad (3)$$

Equations (2a) and (3) appear to be in better agreement.

Another reason which may explain the difference in regression equation terms is that the relationship between isoprene and temperature is affected not only by the type of surrounding vegetation, but also the atmospheric concentration of OH and ozone as well. Other factors which can influence measured isoprene concentrations include the time of day when samples were collected, and atmospheric conditions, such as the height of the boundary layer or vertical mixing and turbulence in the atmosphere. The most important observation of Fig. 5 is the observed strong dependence of isoprene concentration with ambient temperature.

3.3. *Effect of hydrocarbon reactivity with hydroxyl radical*

Characterizing composition and abundance of hydrocarbons at a site provides information concerning source contribution. However, individual compound reactivities with OH and O_3 affect the observed concentration. Consequently using source-receptor approaches to relate observed composition to emission is complicated by the oxidation reactions. Olefin compounds are particularly unusable.

The contribution of the hydrocarbon compounds to the production of photochemical ozone is related to their reaction with hydroxyl radicals and ozone in the complex photooxidation mechanism. For most hydrocarbons, the OH radical is the most important reaction pathway. Several reactivity approaches have been proposed to estimate the contribution of the individual compounds contribution to the production of photochemical ozone. To estimate for the reactivity of the hydrocarbon compounds, we have adopted the method used by Chameides *et al.* (1992), and Lawrimore *et al.* 1995, by calculating the propylene-equivalent concentration:

$$\text{Propy-Equiv}(j) = \text{Conc}(j)\frac{k_{\text{OH}}(j)}{k_{\text{OH}}(\text{C}_3\text{H}_6)}.$$

Propy-Equiv(j) is a measure of the concentration of species j on an OH-reactivity based scale, normalized to the reactivity of propylene, Conc(j) is the concentration of species j in ppbC, $k_{\text{OH}}(j)$ is the rate constant for the reaction between species j and OH, and $k_{\text{OH}}(\text{C}_3\text{H}_6)$ is the rate constant for the reaction between OH and propylene (Chameides *et al.*, 1992). The propylene-equivalent concentration is literally the concentration, in ppbC, required of propylene to yield a carbon oxidation rate equal to that of the species j. For example, if a species j had a concentration of 5 ppbC and was twice as reactive as propylene, it would have a propylene-equivalent concentration of 10 ppbC. This method is useful since it ranks the reaction rate of a species as well as its atmospheric concentration. Table 4 lists the rate constant k multiplied by 10^{12} for the gas-phase reactions of the OH radical with hydrocarbons. Units of k are in cm^3 $\text{molecule}^{-1}\,\text{s}^{-1}$. The OH rate constants for some of the reported hydrocarbon compounds could not be found in the literature and were therefore omitted from the propylene-equivalent hydrocarbon sums. These compounds include 3-methyl-1-pentene, 4-methyl-1-pentene, *cis*-3-hexene, 2,3-dimethylpentane, 1,3-diethylbenzene and *n*-butylbenzene. Because these compounds were left out, the propylene-equivalent concentrations of the sums are somewhat underestimated, though not by much since the sum of these six compounds range between ~3 and 4.5 ppbC at the four sites during the summer and between ~1.5 and 2 ppbC during the winter.

Figure 6a and b shows selected hydrocarbon sums in propylene-equivalent concentrations. The hydrocarbon sums were calculated by first individually calculating the propylene-equivalent concentration for each hydrocarbon, then summing the compounds into their appropriate categories. Figure 6a shows that, by taking reactivity into account, the summer contribution of the biogenics at Candor is at least 65% of the total sum of hydrocarbons given as propy-equivalent concentrations. The biogenics include isoprene, α-pinene, β-pinene, and limonene. The biogenic contribution was highest at the Centreville site, contributing 90% to the total sum. The biogenics at the Oak Grove and Yorkville sites represented 78% and 69% of the total, respectively. Isoprene was clearly the dominant compound during the summer, having a propylene-equivalent concentration ranging from 81.22 ppbC at the Centreville site, to 37.63 ppbC at the Yorkville site. Also from Fig. 6a, the propylene-equivalent concentrations for the paraffins, olefins and aromatics are much lower than the biogenic compounds. For example, the propylene-equivalent alkane sums range from 2 to 5.5 ppbC among the sites.

In contrast to the summer propylene-equivalent concentrations, the total propylene-equivalent non-methane hydrocarbon sum was four to seven times lower for the winter season, ranging from 15 to 21 ppbC, as shown in Fig. 6b. Despite virtually negligible isoprene emissions during the winter season, the biogenics still dominate in the winter due to the emissions of terpenes throughout the year. When taking

Table 4. Rate constants k (cm^3 $molecule^{-1}$ s^{-1}) for the reactions of OH radicals with hydrocarbons at $T = 298$ K (from Atkinson, 1990, except where noted)

Compound	$10^{12} \times k$	Compound	$10^{12} \times k$
Ethene	8.52	2,4-Dimethylpentane	5.1
Acetylene	0.9	1,1,1-Trichloroethane[c]	0.0119
Ethane	0.268	Benzene	1.23
Propene	26.3	Cyclohexane	7.49
Propane	1.15	2,3-Dimethylpentane	
Isobutane[a]	2.5	Trichloroethylene[c]	2.36
Isobutene[a]	51	Methylcyclohexane	10.4
1-Butene[a]	31.4	2,3,4-Trimethylpentane	7
n-Butane	2.54	Toluene	5.96
trans-2-Butene	64	*n*-Octane	8.68
cis-2-Butene	56.4	Perchloroethylene[c]	2.16
3-Methyl-1-butene	31.8	Ethylbenzene	7.1
Isopentane[a]	3.1	*p*-Xylene	14.3
1-Pentene	31.4	*m*-Xylene	23.6
2-Methyl-1-butene	61	Styrene[b]	5.71
n-Pentane	3.94	*o*-Xylene	13.7
Isoprene	101	Isopropylbenzene	6.5
trans-2-Pentene	67	α-Pinene	53.7
cis-2-Pentene	65	*n*-Propylbenzene	6
2-Methyl-2-butene	68.9	1-Ethyl-3-methylbenzene[c]	22.4
3-Methyl-1-pentene		1-Ethyl-4-methylbenzene[c]	13.6
4-Methyl-1-pentene		1,3,5-Trimethylbenzene	57.5
Cyclopentane	5.16	1-Ethyl-2-methylbenzene[c]	13.2
2-Methylpentane	5.6	β-Pinene	78.9
3-Methylpentane	5.7	1,2,4-Trimethylbenzene[b]	37.23
n-Hexane	5.61	Limonene	170
cis-3-Hexene		1,3-Diethylbenzene	
Methylcyclopentane[b]	6.596	*n*-Butylbenzene	

[a] Warneck (1988).

[b] Middleton and Stockwell (1990).

[c] NIST Chemical Kinetics Database, Version 5.0 (Westley *et al.*, 1993).

reactivity into account, limonene was the dominant terpene compound at all sites, ranging from ~3 to ~4 ppbC. This is in sharp contrast to the regular concentrations, in which the alkanes dominate. While the paraffins range from 28 to 35 ppbC during the winter, their calculated propylene-equivalent concentrations are approximately 3 ppbC. It must be pointed out that the propylene-equivalent approach, or any other OH reactivity concept, prioritizes the individual compounds in terms of its reaction with OH radicals. However, the production of RO_2 radicals and the availability of NO_x are essential for the production of photochemical ozone. Also, ozone present at these rural sites will compete with OH for the reaction with the olefinic compounds, complicating the reaction mechanism of ozone production. Although the rate coefficients for reactions between olefins and ozone are much smaller than those between olefins and the OH radical, the reactions become competitive with OH when the concentration of ozone builds up (Warneck, 1988).

Figure 7 shows the trace gases (O_3, CO, SO_2, NO_y) measured at the sites during the hydrocarbon sampling period (every 6 d, 1200 to 1300). The only trace gas measured at Candor was ozone. From Fig. 7 we see that the Yorkville site has the highest summer average of ozone of all the sites (93 ± 22 ppb). It also has the highest CO, SO_2, NO, and NO_y among the three sites for which measurements were taken. This indicates that Yorkville, while perhaps located in a rural site, is subject to strong influence of anthropogenic emissions. Yorkville is located approximately 45 miles (72 km) west of Atlanta, Georgia, and wind trajectories suggest that pollutant transport is most likely the reason for these high values. The average ozone for Centreville and Oak Grove during the summer remained essentially the same as during the spring and autumn.

Daily average ozone was plotted against the difference of daily averaged NO_y–NO in Fig. 8. The data used were for the period from 1 June to 31 August 1993, averaged from 10 am to 4 pm for each day (92 observations). Ideally, one would plot the difference $NO_y - NO_x$, where $NO_x = NO + NO_2$, because this is a direct measure of the products of the NO_x oxidation and minimizes the variability due to differences in photochemical aging of the sampled air mass (Trainer *et al.*, 1993). Unfortunately, NO_2 was not measured and therefore NO_x could not be determined. Therefore, the age of the air mass was not taken into account. A correlation can be seen between ozone and NO_y–NO at each site. Observed ozone at Yorkville is

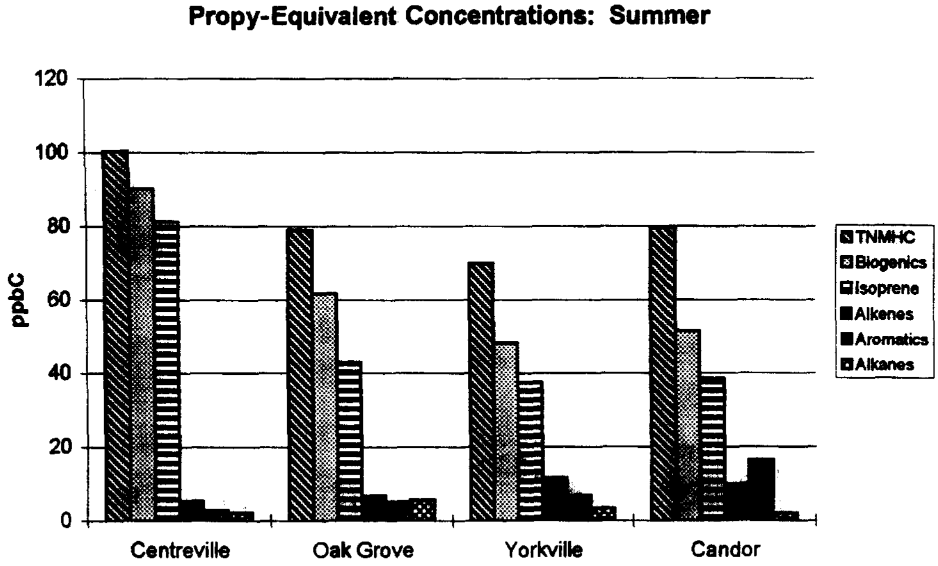

Fig. 6a. Hydrocarbon sums calculated in propylene-equivalent concentrations for the summer season. Biogenics include isoprene, α-pinene, β-pinene, and limonene.

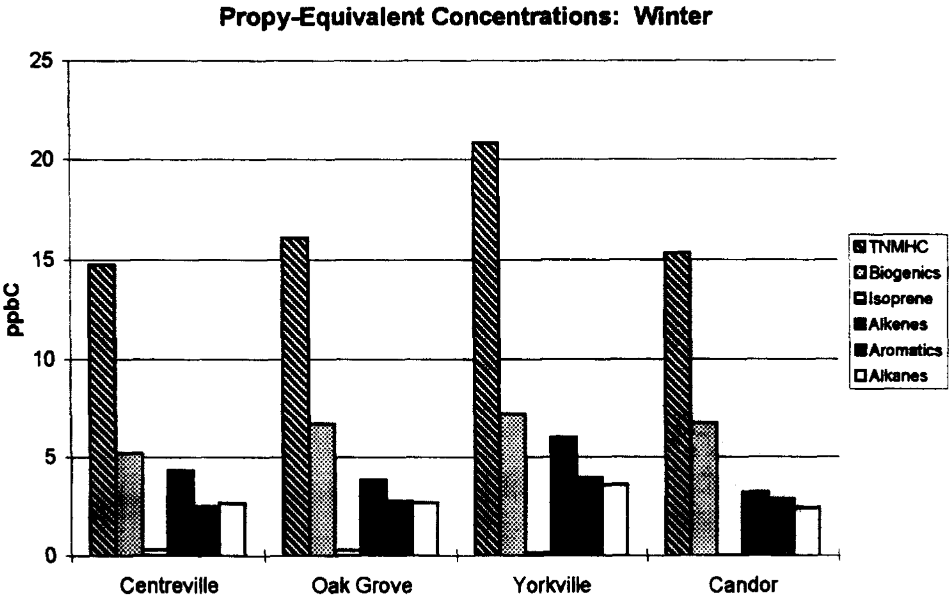

Fig. 6b. Hydrocarbon sums calculated in propylene-equivalent concentrations for the winter season. Biogenics include isoprene, α-pinene, β-pinene, and limonene.

higher than that observed at Centreville for a given NO_y–NO value. This may be explained by the fact that Yorkville is 45 miles west of a large anthropogenic area source (Atlanta, Georgia), and 30 miles west of a large power generating station, and is affected by air containing relatively unaged NO_y, which, in the presence of biogenic hydrocarbons, can result in the production of ozone. In contrast Oak Grove is a particularly clean site, with daily average ozone values not exceeding ~70 ppb and NO_y–NO not exceeding ~5 ppb, so the regression line for Oak Grove is much steeper and has a lower intercept. This relationship implies that ozone production is more efficient at lower precursor concentration. On the other hand, it is impossible to discriminate between ozone transported and ozone produced to validate such a conclusion. Earlier in this work it was shown that during the summer, the Yorkville site had lower concentrations of isoprene (Fig. 4a) and non-methane hydrocarbons calculated in propylene-equivalent

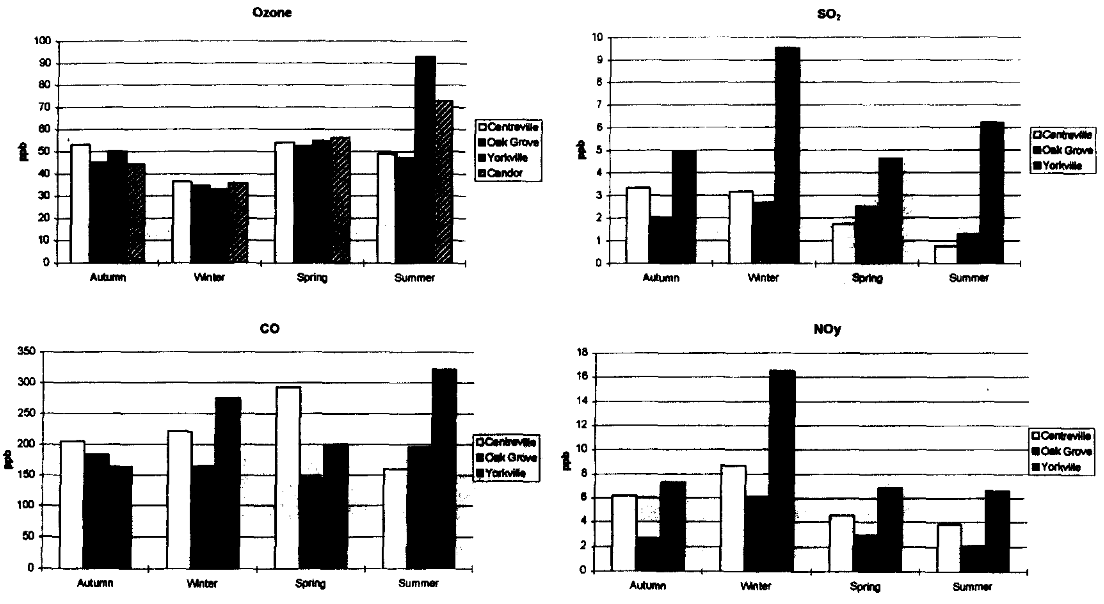

Fig. 7. Seasonal averages of trace gases measured during the hydrocarbon sampling period. Ozone represents the seasonal average of daily maximum ozone.

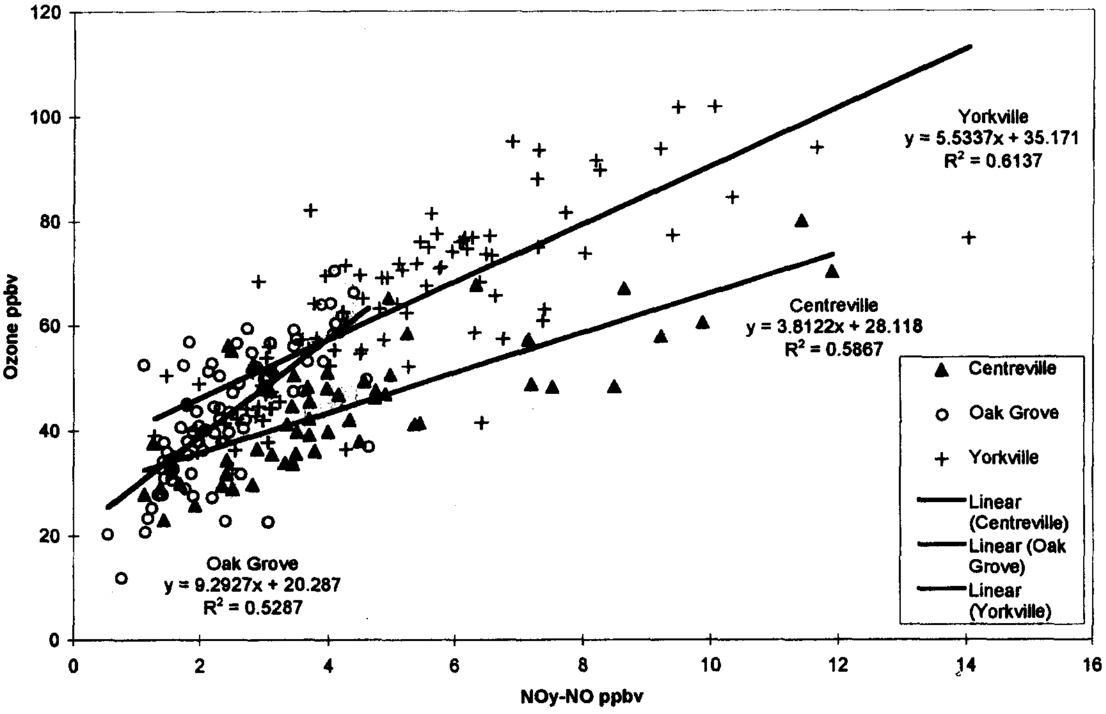

Fig. 8. Ozone vs NO_y–NO. Data used were daily averages from 1000 to 1600, 1 June through 31 August 1993.

concentrations (Fig. 6a) than at Centreville or Oak Grove, yet Yorkville had the highest concentrations of ozone. Ozone production in rural areas is typically limited by the availability of NO_x rather than hydrocarbons, since isoprene and other biogenic VOCs provide a ubiquitous source of hydrocarbon precursors for ozone production particularly during the summer ozone period. The high ozone concentrations at Yorkville reinforces this NO_x limited characteristic, showing that greater concentrations of reactive nitrogen (NO_y) at Yorkville play a more significant role in ozone formation than greater concentrations of highly reactive biogenic hydrocarbons (Centreville).

4. SUMMARY

An analysis of hydrocarbons sampled from 1992 through 1993 at four rural sites in the Southeast U.S. shows a seasonal variation of light molecular weight (C_2–C_4) alkanes, ethene and acetylene, with a maximum during the winter and minimum during the summer. The biogenic hydrocarbons (isoprene and the terpenes) also display a seasonal variation, with a summer maximum and winter minimum. Isoprene was virtually non-existent during the winter at all sites, and averaged from 9.8 ppbC (Yorkville, GA) to 21.15 ppbC (Centreville, AL) during the summer. The terpene concentration was greatest in the summer with averages ranging 3.19 ppbC (Centreville, AL) to 6.38 ppbC (Oak Grove, MS), but was also emitted during the winter months, with a range of 1.25 to 1.9 ppbC for all sites. The seasonal variability of the biogenic hydrocarbons agrees with previous literature reports. When considering the reactivity of hydrocarbons with the OH radical, the biogenics dominate the total non-methane hydrocarbon sum, representing between 65% and 90% of TNMHCs during the summer season, while the impact of the other hydrocarbons are less important. The propylene-equivalent TNMHC sums during the summer at the four sites range between 70 and 100 ppbC with isoprene being the dominant hydrocarbon; this propylene-equivalent range drops during the winter season with a range of 15–20 ppbC, when isoprene emissions are negligible.

Seasonal averages of the trace gases show that Yorkville was the most affected by anthropogenic emissions, while Oak Grove was the cleanest of the sites. Despite the fact that Yorkville had the lowest concentration of summer propylene-equivalent total NMHCs, it had the highest values of ozone, SO_2, NO_y and CO than the other two rural sites for which measurements were taken. A plot of ozone versus NO_y–NO shows that with a given concentration of NO_y–NO, the Yorkville site had higher ozone concentrations than either the Centreville or Oak Grove sites. These observations reinforce the NO_x limited characteristic of this region, namely, that because hydrocarbons are ubiquitous in this region due to natural hydrocarbon emissions, the ozone producing potential is limited to the availability of NO_x, in this region, greater levels of NO_x play a more significant role in ozone formation than greater concentrations of reactive biogenic hydrocarbons.

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