

Regional Analysis of Nonmethane Volatile Organic Compounds in the Lower Troposphere of the Southeast United States

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Abstract: Nonmethane organic compounds (NMOCs) along with ozone as well as other trace gas and meteorological parameters were measured at eight rural sites located in the Southeast United States, as part of the Southern Oxidants Study. Fifty-four C₂–C₁₀ NMOCs were collected from 1,200–1,300 local time, once every six days from September 1992 through October 1993 and intermittently during 1994. This study was undertaken to characterize the nonmethane hydrocarbons in the rural areas of Southeast United States with respect to their concentrations, reactivities, and relative importance of natural and anthropogenic abundances of NMOCs. Though the sites are well removed from large urban source regions, the observations show a clear anthropogenic influence on the hydrocarbon levels at these rural sites. The data for the sites show similar seasonal patterns for total NMOC with summer maxima (average concentrations of 198 ppbC at the Long Creek, South Carolina, site to 47 ppbC at the Candor, North Carolina site) and fall minima (average concentrations of 73 ppbC at the Long Creek site to 31 ppbC at the Centreville, Alabama site). A secondary maximum is observed during the winter. A seasonal trend was observed in the concentrations of light molecular weight C₂–C₄ NMOCs (ethane, ethene, acetylene, propane, *i*-butane, and *n*-butane) with a winter maximum and a summer minimum. An analysis of changes in C₂–C₄ hydrocarbon ratios over a period of one year indicates that the variation is most likely due to seasonal changes in OH concentrations. A seasonal trend was also observed for the biogenically emitted NMOC, isoprene, with summer maxima (average concentrations of 37 ppbC at the Long Creek, South Carolina, site to 8.6 ppbC at the Giles County, Tennessee and Metter, Georgia, sites) and winter minima with winter seasonal values below the level of detection. Isoprene was observed to be the most dominant NMOC at most sites during the summer. The ambient concentrations of isoprene measured during the summer were found to be dependent on the ambient temperature. The monoterpenes *a*-pinene, *b*-pinene, and *d*-limonene also peaked during the summer with averages ranging between 3.19 ppbC (Centreville, Alabama) and 6.38 ppbC (Oak Grove, Missouri), and a background concentration of 1.25 to 1.9 ppbC for all the sites during the winter.

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Introduction

Ozone (O₃) near the ground is one of the most geographically pervasive air quality problems in the United States today. High concentrations of ozone and other photochemical oxidants increase respiratory disease in humans, decrease yields of crop plants and forests, and cause surface damage to buildings and other engineered structures. The regulatory efforts presently being used to decrease ground-level ozone concentrations cost the United States several billions of dollars every year. However, efforts have not been sufficient to maintain ozone concentrations below the U.S. Environmental Protection Agency's one hour standard of 0.120 ppmv (NRC 1991). The new eight-hour O₃ Na-

tional Ambient Air Quality standard (0.08 ppmv) is likely to bring more locations into noncompliance (Chameides et al. 1997).

In the Southeastern United States, summertime midday concentrations of 50–70 ppbv of O₃ are common and this is not limited to urban centers (Meagher et al. 1987; Aneja et al. 1990; Aneja et al. 1994; Kleinman et al. 1994; Chameides et al. 1997). Despite the fact that the roles of volatile organic compounds (VOCs) and nitrogen oxides (NO_x=NO₂+NO) as tropospheric O₃ precursors have been firmly established, the development of an effective strategy for abating O₃ pollution in U.S. cities by decreasing anthropogenic nonmethane organic compounds (NMOC) emissions has proven to be problematic (Lindsay et al. 1989). Much of the difficulty in addressing the problem of VOC versus NO_x limitation can be traced to the ozone's complex photochemistry. The rate of O₃ production is a nonlinear function of the mixture of VOC and NO_x in the atmosphere. Unlike some other air pollutants of concern such as CO or SO₂, which are directly emitted into the atmosphere, ozone is a secondary pollutant formed in ambient air. It is formed through a complex set of sunlight-initiated reactions of its precursors, primary emissions of NO_x and VOCs from both anthropogenic and natural sources, referred to as the photochemical smog mechanism.

In many ways the South, and the Southeastern United States in particular, represent a natural laboratory for the study of oxidant formation. The same mix of sunlight, moisture, and high tempera-

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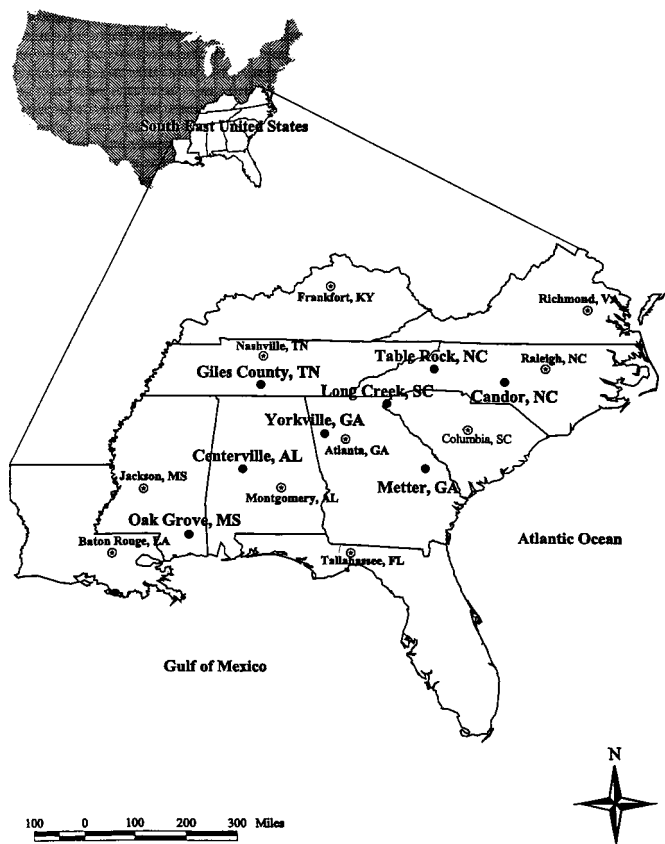


Fig. 1. Map of Southeast United States indicating SOS-SCION sites

tures that makes the South's forests and agriculture highly productive also contributes to high oxidant formation rates. Further, the relatively low population density and low level of industrialization in the region may make natural sources of ozone precursors potentially important. Vegetation, including crops, forests, and ornamental plants, is known to produce VOCs as part of natural respiratory, photosynthetic, and stress defense mechanisms. Emission rates of these VOCs typically increase with temperature and/or photosynthetic rates that are, on average, higher in the South than in more northerly locations. These emission rates in combination with a generally dense vegetation cover make natural VOC emissions particularly high in the Southern United States (SOS 1994, 1995).

Biogenic VOCs (BVOCs) as an additional source of oxidizable hydrocarbons has raised an increasing amount of interest in the recent literature as one reason for the failure of cities in the Eastern United States to meet air quality standards for ozone (Chameides et al. 1988; Fuentes et al. 2000; Guenther et al. 2000). Emission inventories have been compiled (Lamb et al. 1993; Guenther et al. 1994; 1995) which indicate that, on a continental scale, BVOCs emissions can comprise a large fraction (~60% in the United States) of the total hydrocarbon source strength. BVOCs emissions consist of many different compounds, though isoprene and α -pinene make up the major fraction (Zimmerman 1979; Lamb et al. 1993). The emission rates of isoprene from trees in particular can be very large (Zimmerman 1988; Guenther et al. 1995). Because of these large emission rates and isoprene's high rate of reaction with OH, this specie can play a major role in controlling the production of ozone within the boundary layer of both the urban as well as rural areas during photochemically active periods of the year (Trainer et al. 1987a,b;

Chameides et al. 1992; Montzka et al. 1993; Das and Aneja, unpublished, 1996; Hagerman et al. 1997; Riemer et al. 1998).

Some data concerning the abundance of VOCs in the urban and rural environments of the Southeast United States has been recently reported (Chameides et al. 1992; Lawrimore et al. 1995; Hagerman et al. 1997; Kang et al. 2001). This study complements those data by providing background information on rural non-methane hydrocarbon (NMOC) levels (which is a subset of VOCs) and seasonal trends in those rural areas of the Southeast United States known to experience occasionally high ozone levels in the summer. However, it should be borne in mind that though all the sites are rural in nature, they can be influenced by episodic pollution events. The hydrocarbon data used in this paper were sampled from September 1992 through October 1993 once every six days from 1200–1300 hrs. local time. Fifty-four NMOC species were identified based on retention times. C_2 – C_{10} hydrocarbons were analyzed using a Hewlett Packard HP 5890 Series II gas chromatograph equipped with a cryogenic cooling option and flame ionization detection (GC-FID). A large number of peaks were observed but were unidentified. Hence total NMOC is considered to be the sum of these 54 compounds.

The focus of this work is to (a) characterize the NMOC concentrations in the rural areas of the Southeast United States, (b) investigate the relative importance of natural and anthropogenic sources of NMOCs with respect to the magnitudes and abundances of the measured compounds, (c) investigate the temperature dependence of isoprene emissions, and (d) examine the factors affecting the seasonal trends of NMOCs.

Experiment

Site Description

The eight field sites chosen for this study are located in those rural regions of the Southeast United States that have been identified as experiencing high ozone episodes. The hydrocarbon, trace gas, and meteorological data was collected from eight rural SOS-SCION sites (Southern Oxidants Study-Southeastern Consortium: Intermediate Oxidant Network) located within the Southeast United States. The SOS-SCION network provides long-term spatial scale input for NMHC's for photochemical model calculations. The location of the sites used for this paper include: Candor, North Carolina; Centerville, Alabama; Giles County, Tennessee; Long Creek, South Carolina; Metter, Georgia; Oak Grove, Mississippi; Table Rock, North Carolina; and Yorkville, Georgia. 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). Fig. 1 illustrates the location of the sites.

The Centerville, Ala. site is located in Bibb County, Alabama ($32^\circ 54'N$, $87^\circ 23'W$), 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 above 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 National Oceanic and Atmospheric Administration weather radar station.

The Oak Grove, Miss. site ($30^\circ 59'N$, $88^\circ 56'W$) is located in the DeSoto National Forest in Perry County, Mississippi at an

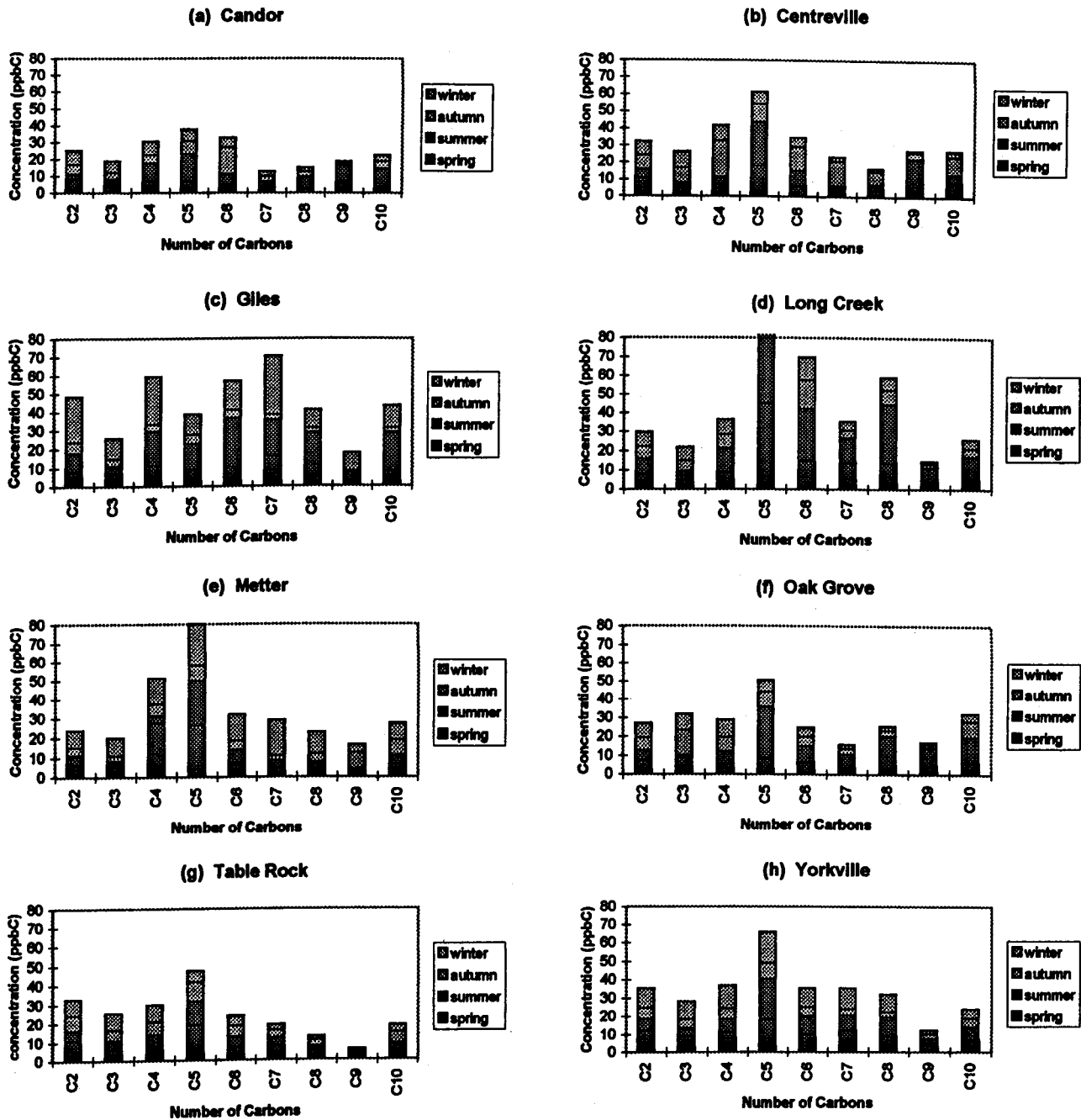


Fig. 2. Seasonal abundance of C₂–C₁₀ NMHCs at (a) Candor, (b) Centreville, (c) Giles County, (d) Long Creek, (e) Metter, (f) Oak Grove, (g) Table Rock, and (h) Yorkville.

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 farmland. 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 visible from the site is located approximately 400 m from the site. It is situated off of State Route 29 and approximately 40 km southeast of Hattiesburg, Mississippi.

The Yorkville, Ga. site (33°55'N, 85°03'W) is located in Pauldin County, Georgia, at an elevation approximately 400 m MSL. 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 Metter, Ga. site (32°55'N, 82°08'W) is located inside of the George L. Smith State Park in Candler County, approximately 110 km west-northwest of Savannah, Georgia. It is situated in a location representative of the rural southern coastal plains. The sampling site is surrounded by vegetation typical of the area, namely, mixed deciduous and conifers. The top five species of trees are found to be pine, gum, oak, sweetgum, and maple.

The Giles County, Tenn. site (35°20'N, 86°52'W) is located on Hurricane Creek Rd. off Route 64 between Lawrenceburg and Pulaski, Tenn., approximately 55 km south of Nashville, Tenn.

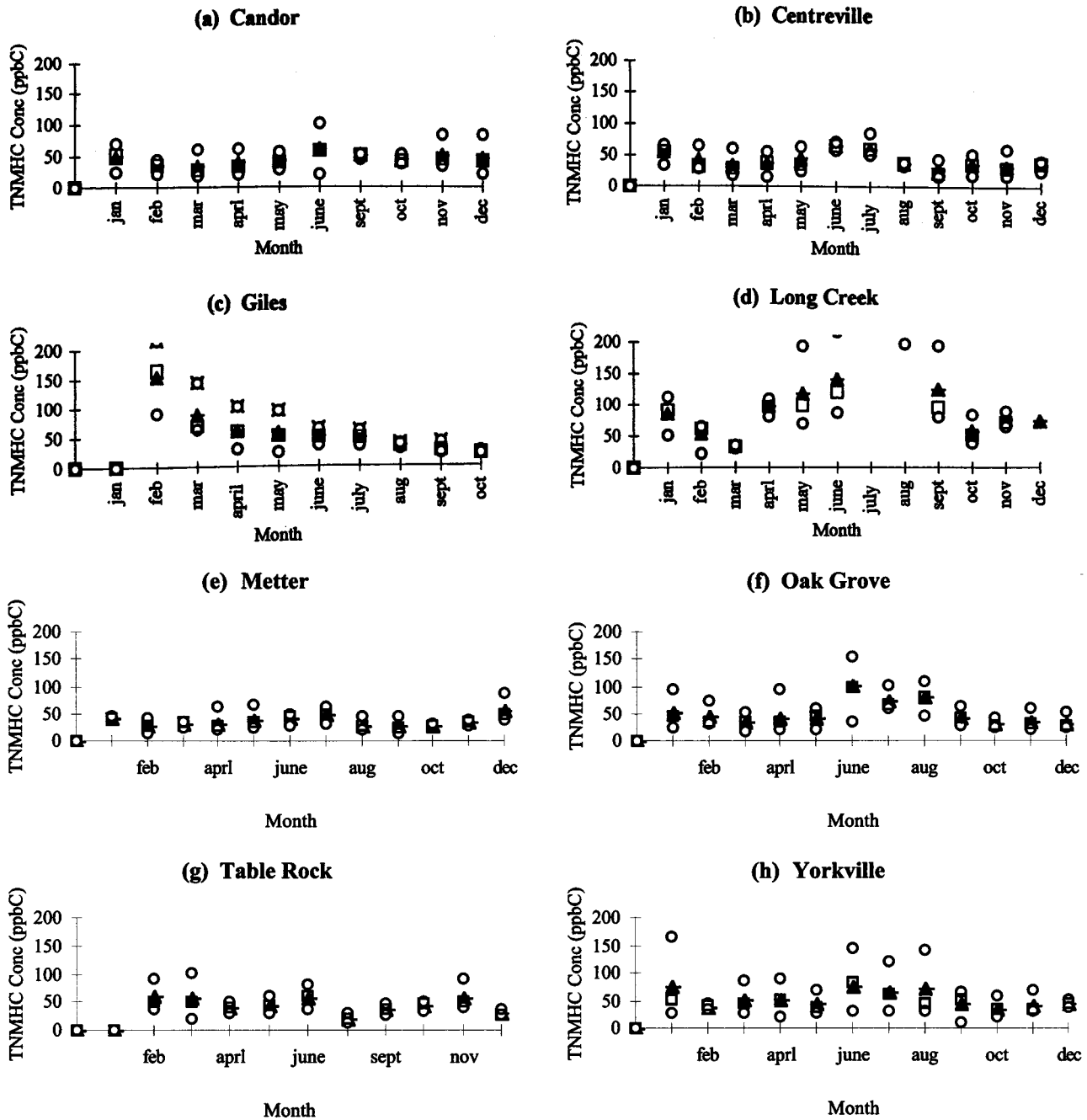


Fig. 3. Monthly variation of TNMHC at (a) Candor, (b) Centreville, (c) Giles, (d) Long Creek, (e) Metter, (f) Oak Grove, (g) Table Rock, and (h) Yorkville. Solid triangles are the monthly averages with error bars of ± 1 s.d., open circles are the maximum and minimum values, and the open squares are the monthly median values.

The site is situated in a location representative of the rural nature of the continental plateau region. The site itself is located in an open pasture approximately 100 m from the nearest wooded area consisting of mixed deciduous and coniferous trees.

The Candor, N.C., site ($35^{\circ}16'N$, $79^{\circ}50'W$, 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 1,200 m², 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.

The Table Rock, N.C., site ($35^{\circ}48'N$, $81^{\circ}51'W$) is situated in a location representative of the rural nature of foothills of the Appalachian Mountain region at an elevation of 400 m MSL, about 7.5 km northwest of Morgantown, North Carolina. The site is located in a small clearing approximately 22 m from the nearest forested area about 30–40 m from a N.C. Route 126. The highway is not heavily used. The N.C. Department of Transportation lists the highway's usage at less than 600 vehicles per day. The site is surrounded mainly by coniferous trees interspersed with deciduous trees. The canopy height around the site is approximately 13–15 m.

The Long Creek, S.C., site ($34^{\circ}48'N$, $83^{\circ}14'W$) is situated on the summit of Round Mt. at an elevation 655 m MSL. Round Mt. is located in the Sumter National Forest near Long Creek, S.C., in

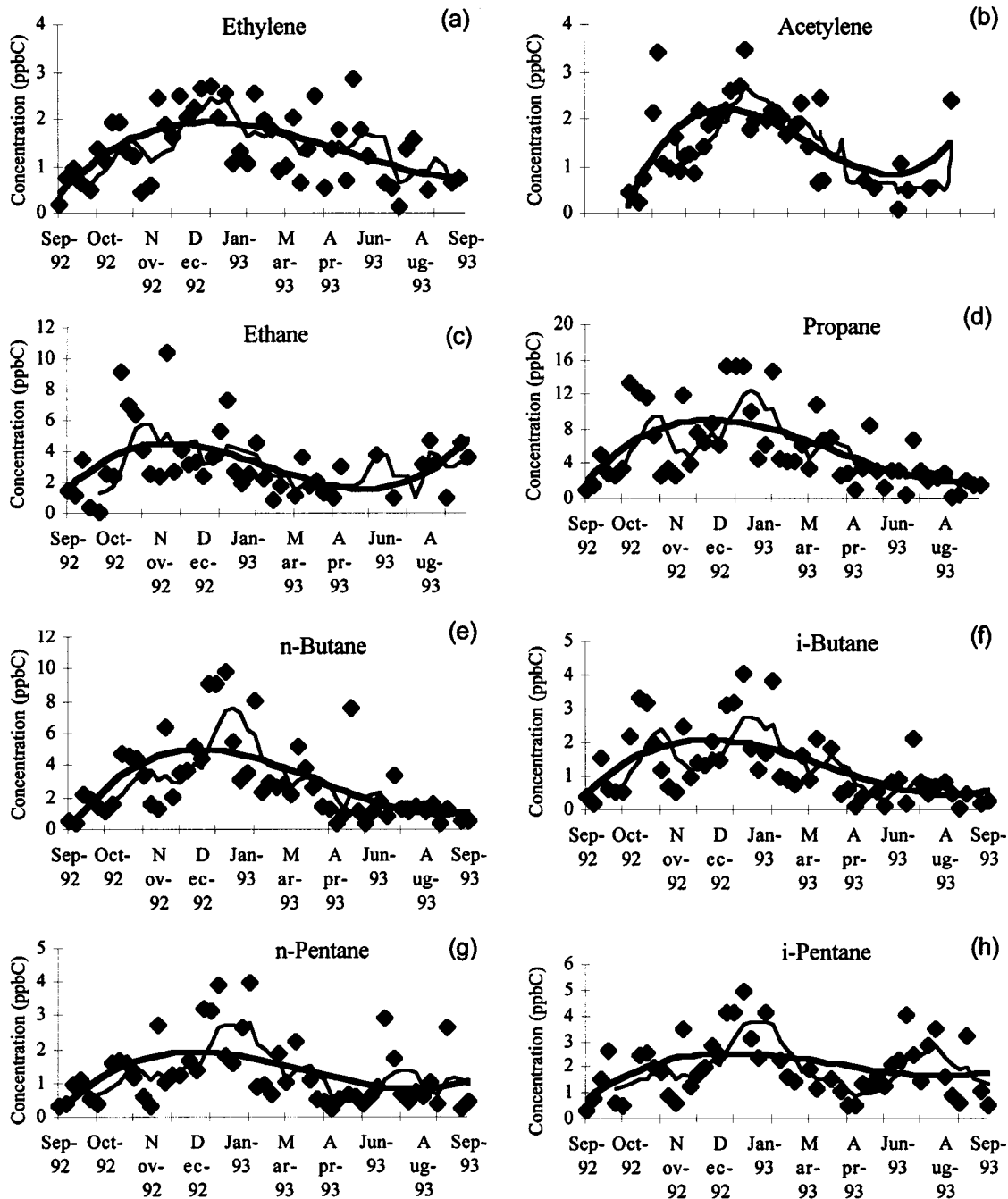


Fig. 4. Seasonal variation at Centreville, Alabama site for (a) ethylene, (b) acetylene, (c) ethane, (d) propane, (e) *n*-butane, (f) *i*-butane, (g) *n*-pentane, and (h) *i*-pentane

the northwestern part of the state; the area being representative of the Appalachian highlands. Forests surround the site clearing with some trees as near as 20 m from the shelter. The forest canopy height around the site is approximately 11 m. The Long Creek site shares the summit clearing with a fire tower.

Meteorology of the Region

Meteorology plays an important role in the Southeast's ozone problem. Stagnant high pressure systems often develop over the Southeast United States in the summer and fall. This situation allows a steady buildup of ozone precursors. These stagnating high pressure systems often arise from the stalling of a continen-

tal high-pressure system over the Appalachian Mountains (SOS Report 1993), or from westward extensions of the semi-permanent Bermuda High, which is normally located over the Atlantic Ocean (Aneja and Yoder 1992).

The summer of 1993 was particularly conducive to ozone formation in the Southeast United States. June and July were dominated by a persistent circulation pattern which brought moisture from the Gulf of Mexico region to the Midwest, resulting in excessive precipitation which caused severe flooding, while preventing the eastward progression of weather systems which would have brought rain and cooler weather to relieve the Southeast United States of drought conditions and record breaking high temperatures. The Southeast experienced the second warmest

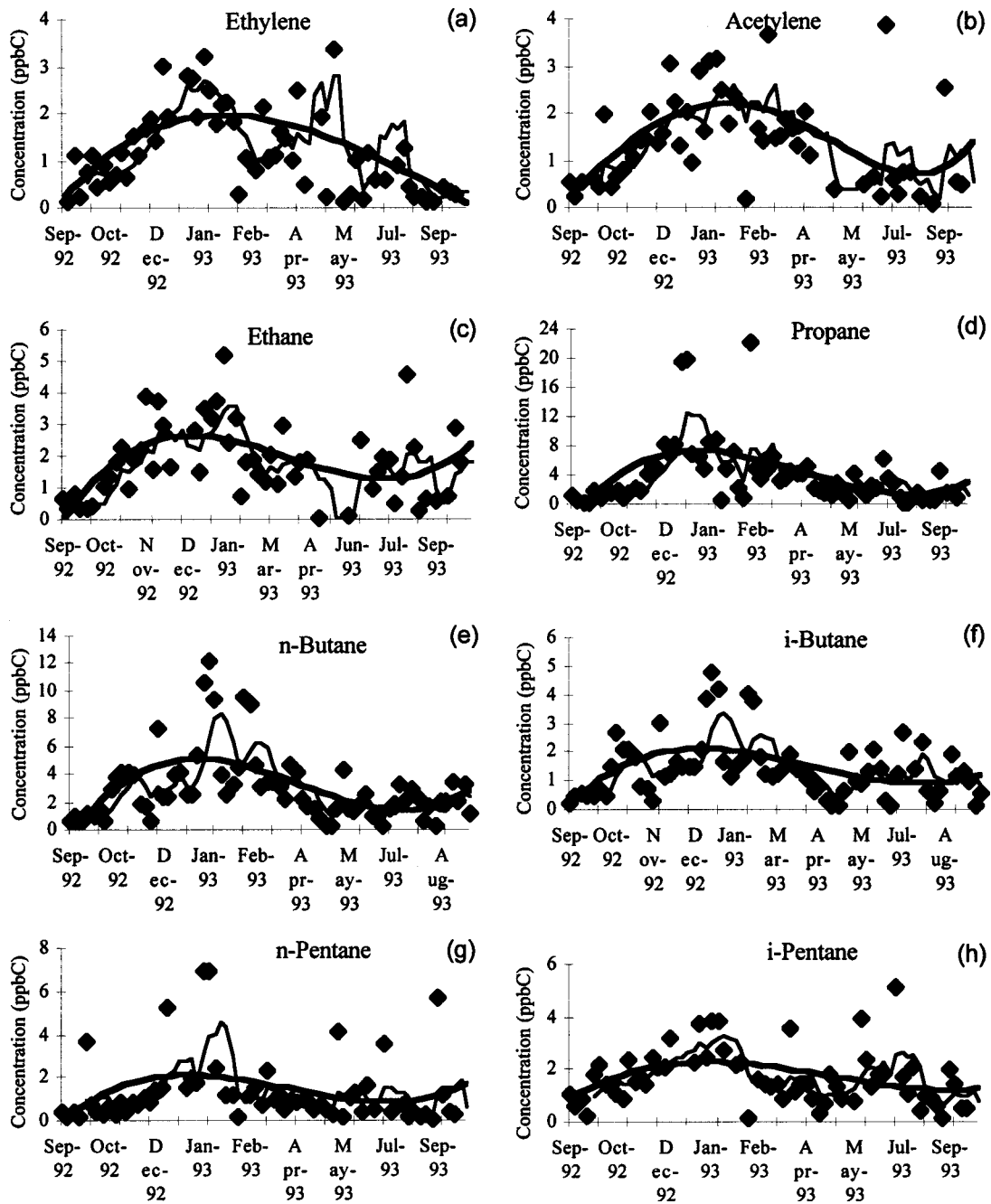


Fig. 5. Seasonal variation at Metter, Georgia site for (a) ethylene, (b) acetylene, (c) ethane, (d) propane, (e) *n*-butane, (f) *i*-butane, (g) *n*-pentane, and (h) *i*-pentane

summer in 99 years of record keeping (National Weather Service 1993). For the month of July, above normal temperatures affected the area from the southeastern Plains to the middle and southern Atlantic Coast, with temperatures averaging 30 to 80F higher than normal (National Weather Service 1993). An examination of surface and 500 mb height contours for July 19th through the 25th, when high ozone episodes were observed, reveal an upper level high pressure characterized by light 500 mb winds centered over the Southeast. During this period, a stationary blocking pattern characterized by a high amplitude ridge or an omega block was centered over the central states, then over the Mississippi valley region (Hagerman 1996).

Sample Collection

Time integrated 1-h air samples were collected in 6 L (SUMMA) electropolished stainless steel canisters from 1200 to 1300 hrs. 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 by opening the canister and allowing the internal pressure to reach ambient pressure. The samples were then analyzed using gas-chromatograph Hewlett-Packard 5890 Series II with flame ionization detection as described by Farmer et al. (1994).

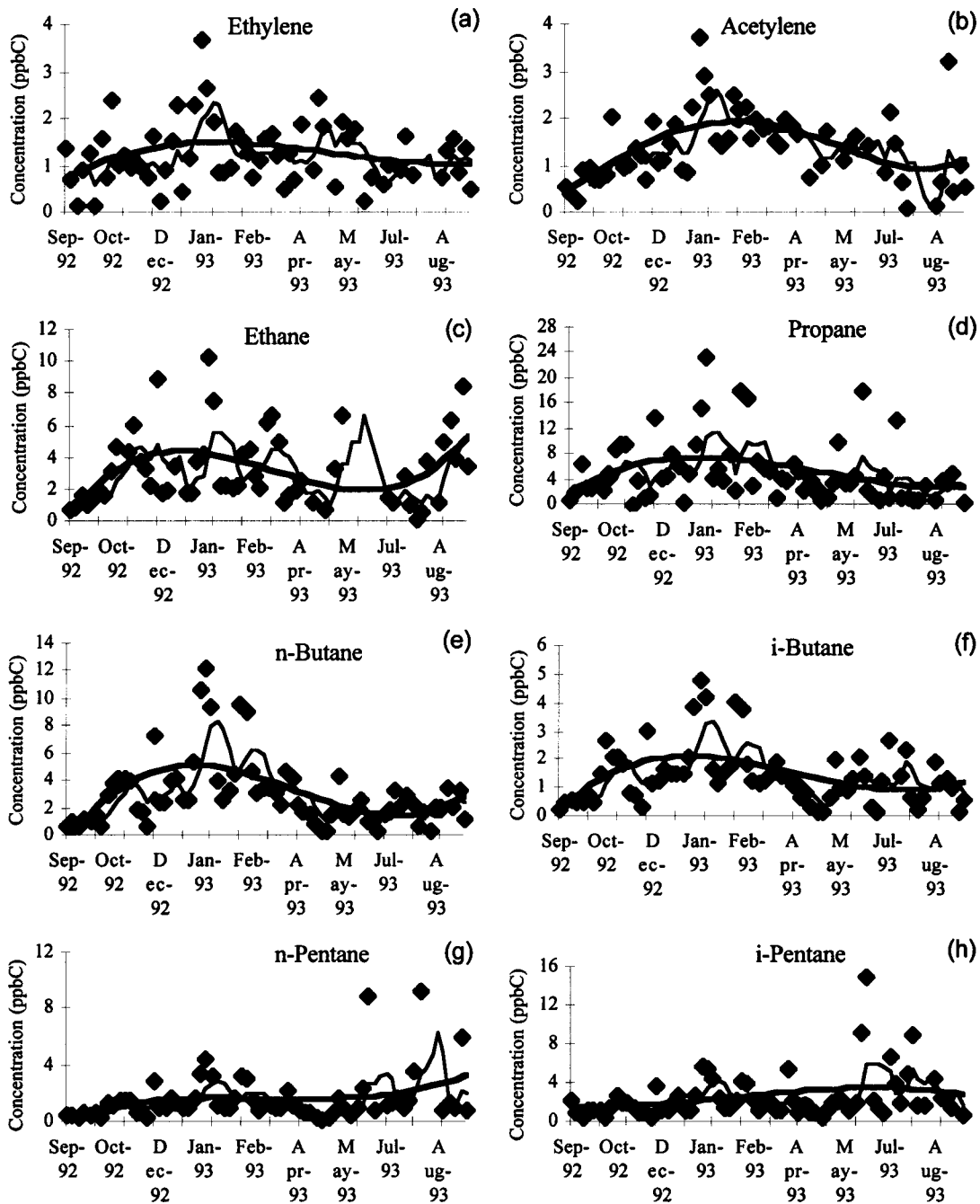


Fig. 6. Seasonal variation at Oak Grove, Mississippi site for (a) ethylene, (b) acetylene, (c) ethane, (d) propane, (e) *n*-butane, (f) *i*-butane, (g) *n*-pentane, and (h) *i*-pentane

Results and Discussion

Summary Statistics

Seasonal descriptive statistics corresponding to each site for every compound analyzed may be obtained from the corresponding writer of the paper, and Das (1996). Each datum consists of anywhere between 4–12 samples depending on the sampling schedule for the site. Isobutene and 1-butene, as well as *m*-xylene and *p*-xylene were lumped together because of problems with coelution. 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.

No significant variations in seasonal means and medians are observed among the eight sites except for a few compounds; notably propane and isopentane during the summer time. During the wintertime, all sites had the same top four dominant compounds in the following order: propane, *n*-butane, ethane, and isopentane, with the exception of the Yorkville site, which had isopentane and ethane switched around in ranking and the Long Creek site which had isopentane and cyclopentane as the top two compounds followed by propane and *n*-butane. The compounds following the ones listed above which fall within the top ten most abundant

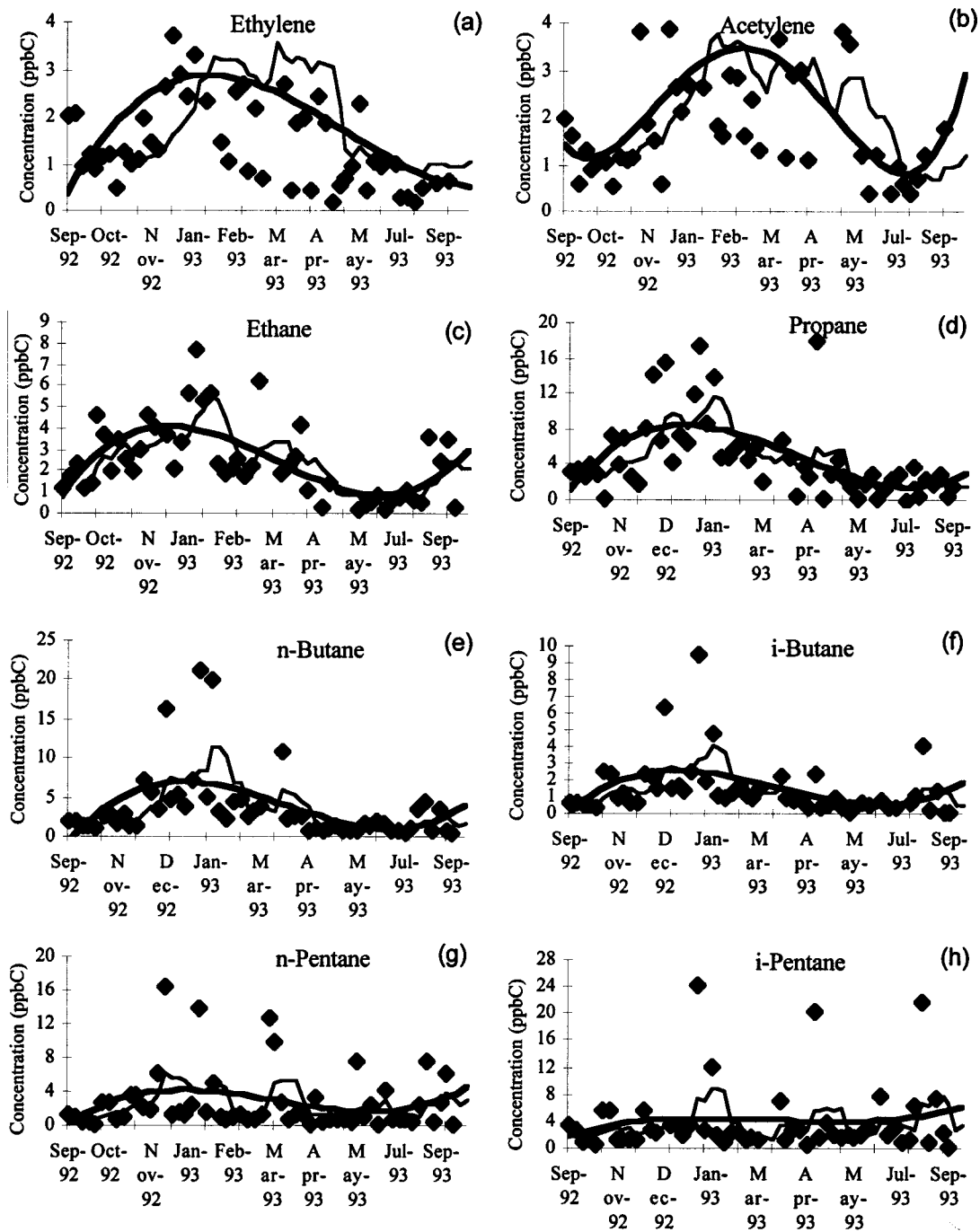


Fig. 7. Seasonal variation at Yorkville, Georgia site for (a) ethylene, (b) acetylene, (c) ethane, (d) propane, (e) *n*-butane, (f) *i*-butane, (g) *n*-pentane, and (h) *i*-pentane

species are: acetylene, *n*-pentane, ethene, isobutane, and benzene. The individual C_2 – C_5 alkanes (except cyclopentane) dominated the list of most abundant compounds for all eight sites during the winter. During the summer, the ten most abundant compounds were highly variable among the sites. Isoprene was the dominant hydrocarbon during the summer at all but the Oak Grove and Long Creek sites. *n*-Pentane was the most abundant hydrocarbon at the Oak Grove site (16.51 ± 20.97 ppbC, median = 7.68 ppbC) with isoprene immediately following with a concentration of 11 ± 4.2 ppbC whereas isopentane (43.29 ± 29.63 ppbC) followed by isoprene (37 ± 21 ppbC) was found predominantly at the Long Creek Site. The compounds isoprene, propane, isopentane,

2-methylpentane, and styrene consistently appeared in the top ten most abundant hydrocarbons among all eight sites, though not necessarily in that order.

Figs. 2(a–h) illustrate the relative abundance of seasonal C_2 – C_{10} total nonmethane hydrocarbons (TNMOCs). The seasonal average for each compound is taken and based on the number of carbons summed up to give the seasonal average for that carbon number. From Figs. 2(a–h), a seasonal trend in C_2 – C_4 compounds is observed with a winter/spring maximum and summer minimum with few exceptions from site to site and carbon number. The exceptions are more due to a few isolated high concentrations and are suspected to be related to transport of these

Table 1. Mean Winter/Summer Ratios of Selected Volatile Organic Compounds at Eight Southern Oxidants Study-Southeastern Consortium: Intermediate Oxidant Network (SOS-SCION) Rural Sites, and their Comparison with Rural Sites in Canada and Europe

	Candor NC	Centreville AL	Giles TN	Long Creek SC	Metter GA	Oak Grove MS	Table Rock NC	Yorkville GA	Fraserdale ^a Canada	Keji ^b Canada	Birkenes ^c Norway
Ethane	5.6	2.65	1.96	1.01	1.50	3.36	0.89	3.9	2.99	2.32	2.21
Acetylene	15.0	5.92	3.39	2.73	2.66	4.40	3.24	4.39	10.9	4.38	3.71
Propane	2.67	2.31	3.50	1.50	3.64	2.00	2.14	4.23	18.4	3.15	3.85
<i>n</i> -Butane	5.07	3.81	3.79	0.57	6.46	2.95	2.09	3.52	41.2	5.80	2.86
<i>i</i> -Butane	3.80	1.95	3.14	0.89	3.56	1.83	1.85	2.66	44.1	5.71	2.83
<i>n</i> -Pentane	1.55	1.92	1.42	0.44	2.72	0.92	1.83	1.42	17.7	3.20	3.58
<i>i</i> -Pentane	1.36	1.46	1.67	0.40	4.75	0.96	0.93	0.94	32.3	3.55	1.81

^aFrom Jobson et al. (1994).

^bFrom Bottenheim and Shepherd (1993).

^cFrom Hov et al. (1991).

anthropogenic compounds to the measurement site. The seasonal trend for the higher molecular compounds tends to occur with a summer maximum at most sites. The exception is the Metter site where even the higher molecular weight compounds peak during the winter. The C₅ concentrations during summer are significantly higher during the summer. The higher concentrations of C₅ compounds are attributed to increased isoprene emissions during the summer. The higher concentrations of isopentane and isoprene during the summer at the Long Creek add to the higher levels of C₅ compounds observed. Similarly, the higher C₁₀ concentrations were found to be due to increased terpene concentrations. Trimethyl benzenes were mainly responsible for higher summer concentrations of C₁₀ compounds.

Figs. 3(a–h) give a monthly summary of the total nonmethane hydrocarbons (TNMHCs) concentrations observed at the eight sites. Here data from 1994 was also used. Again a seasonal cycle is observed with little site to site variation. The TNMHC concentrations peak during June/July with a secondary maxima during December/January. The summer peak probably has a different origin from the winter maximum. The winter maximum is most likely due to long range transport of pollutants as discussed later. The Giles County site, due to poor data coverage, failed to show this trend and hence is left out of the discussion. The lowest TNMHC values were observed at the Metter site whereas the highest concentrations of TNMHC were observed at the Long Creek site. The Long Creek site has anomalous behavior from other sites due to unusually high episodes of summer *n*-pentane and isopentane levels. Most sites had similar median concentrations for most compounds leading to similar monthly median TNMHC concentrations. On a seasonal basis, the TNMHC concentration variation between sites is minimal in the winter, and greatest in the summer months. During summer, the variation is largely related to the apparent occurrence of local episodes. This is seen by the observed deviation around the mean TNMHC values. The deviations were highest during the summer and winter months coinciding with the observed summer and winter maxima.

Seasonal Variation of Selected Nonmethane Organic Compounds

Similar seasonal variations were observed in concentrations of ethane, ethene, acetylene, propane, *n*-butane, isobutane, *n*-pentane, and isopentane and methyl pentanes, i.e., maxima in winter and minima in summer. Isoprene shows an opposite seasonal cycle, i.e., the mixing ratios are below detection levels dur-

ing winter, but during the summer isoprene has large concentrations. No seasonal variations were observed for most of the other olefins and higher molecular weight alkanes.

The eight anthropogenic compounds, ethylene, acetylene, ethane, propane, *i*-butane, *n*-butane, *i*-pentane, *n*-pentane, and biogenic compound isoprene, were chosen for trend analysis because these are representative of seasonal source processes. The typical sources of anthropogenic NMOCs are the combustion of fossil fuels, and evaporative losses of those fuels and solvents. These sources are located primarily in urban areas, where transportation derived NMOCs predominate. Natural gas leakage is another anthropogenic source, but its origin is more widespread. Natural sources are biological activity such as phytoplankton in the oceans, living foliage, decaying organic matter, microbial activity, and natural gas seepage (Sexton and Westberg 1984). Acetylene and 2-methyl-butane are typical compounds that almost exclusively originate from transportation related processes, while isoprene is the most common marker for natural hydrocarbons. Ethane and propane are more complicated since they have mixed contributions from the urban sources and natural gas production (Ehhalt and Rudolph 1986). Ethane and propane comprise a few percent of natural gas, while isobutane and *n*-butane are found in smaller amounts. Isopentane comprises a significant fraction of gasoline while the contribution of *n*-pentane is smaller. The remaining hydrocarbons are associated primarily with fossil fuel consumption, and their distribution profile is necessarily an anthropogenic signature for urban areas.

Seasonal Trends in Anthropogenic Source Variations

Data from four of the eight sites for ethylene, acetylene, ethane, propane, *i*-butane, *n*-butane, *i*-pentane, and *n*-pentane are plotted in Figs. 4–7. It is seen that these compounds have an annual variation with a late December/early January maximum and a late spring minimum. Acetylene concentrations are usually low, i.e., near the level of detection during summer, while the peak is observed during January. There is a secondary peak during March with occasional high levels during the fall. Ethylene also peaks in January but the annual cycle is overlaid with few high concentrations during spring and early summer. Ethane has an annual cycle with a January maximum and an early autumn minimum at all the sites. Propane follows the same pattern as ethane except that its concentrations are elevated when compared to ethane. A propane/ethane ratio of greater than one suggests propane source is possibly from liquid propane usage. The concentrations for ethane and propane are lowest during the spring. *i*-Butane and *n*-butane peak

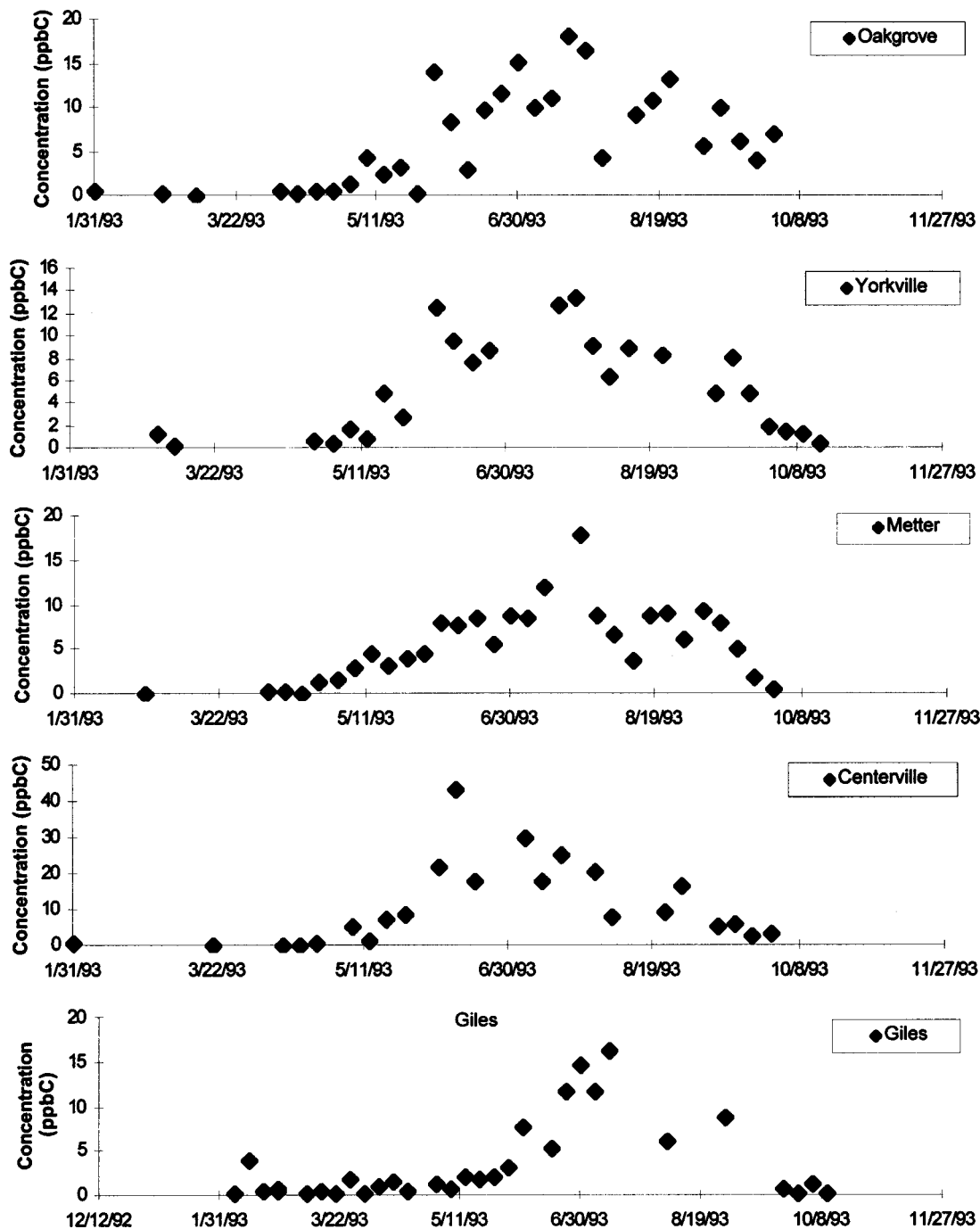


Fig. 8. Seasonal variation of isoprene at five SOS-SCION sites during 1993

in early January and have a maximum around late April/early May. There is an elevated level in July due to few isolated high values, but the summer level is typically 25% of the winter peak for *n*-butane and higher for *i*-butane. Iso- and *n*-pentane are also low during the summer, and show similar profiles with peak levels during January and minima during late spring/early summer. However, this variation for iso- and *n*-pentane is not seen at all the sites. A variety of other studies have reported on the seasonal variation of NMOCs (Rasmussen and Khalil 1982; Singh and Salas 1982; Tille et al. 1985; Blake and Rowlands 1986; Rudolph et al. 1989; Lightman et al. 1990; Ehhalt et al. 1991; Hov et al. 1991; Kessel and Bachman 1991; Jobson et al. 1994; Bottenheim and Shepherd 1995) with similar trends being observed as reported here.

To obtain a measure of the seasonal variation, the ratios of winter (December to February) to summer (June to August) averages for these compounds were calculated and are presented in Table 1. The differences represent how the sources of these compounds may vary during the two seasons, and are different from site to site in composition. The ratios in general are higher at the Candor, N.C., site and lower at the Long Creek, S.C., site. The Candor site had insufficient data coverage for the winter months and at Long Creek unusually high levels of these compounds during summer were observed leading to very low winter/summer ratios. The ratios derived at these eight SOS-SCION rural sites are compared to the ratios reported for three other rural sites, from Canada and Europe, where data covers a full year.

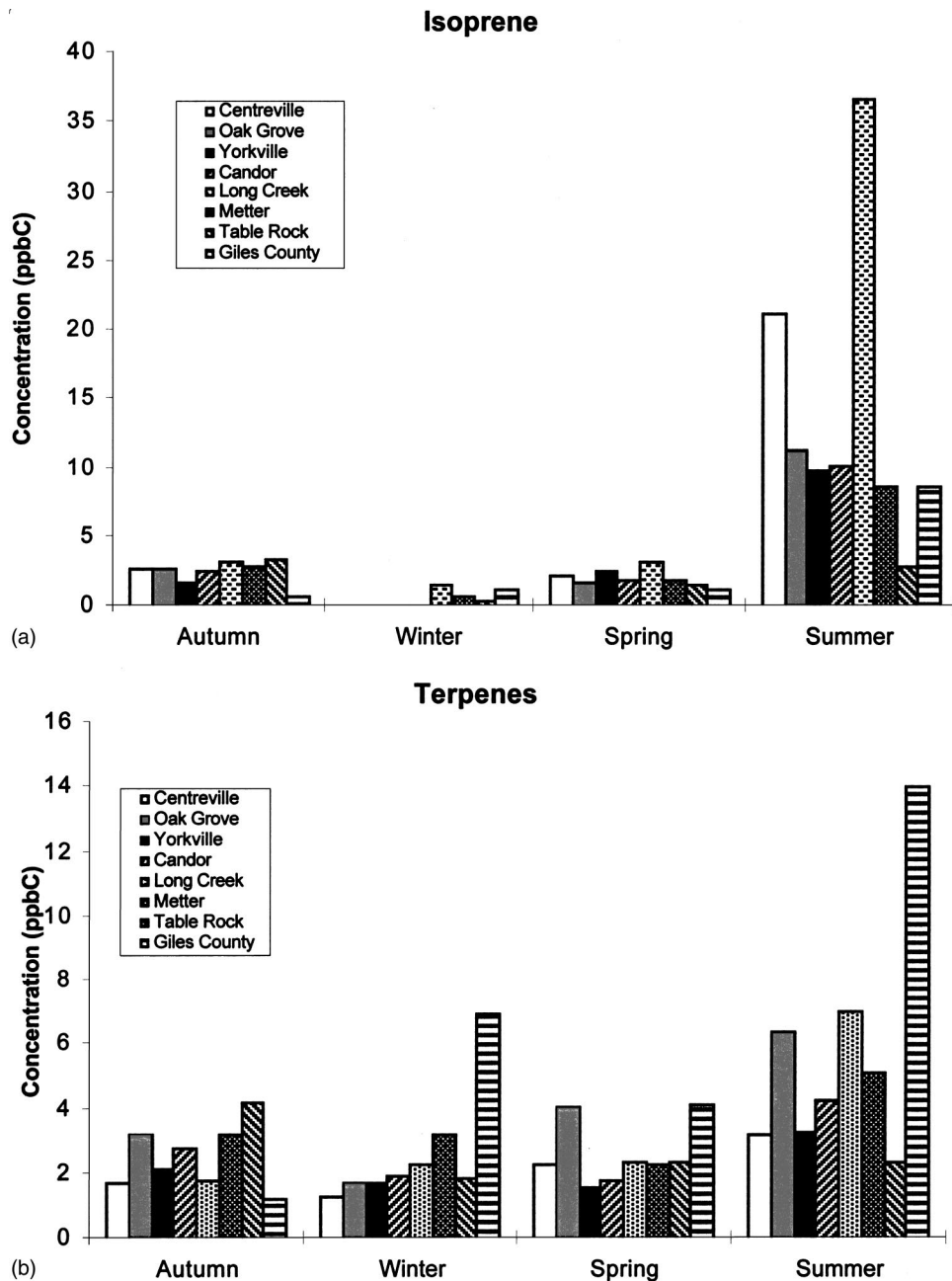


Fig. 9. Seasonal average of (a) isoprene and (b) terpenes

Fraserdale is a relatively remote location in Northern Ontario, Canada while the site at Kejimikujik National Park (Keji) is a rural forested site in Nova Scotia, Canada. Birkenes is a rural site located in rural southern Norway. The ratios observed at the SOS-SCION sites and at the Keji and Birkenes sites are within reasonable agreement and the similarity suggests the influence of air masses originating from anthropogenic source regions impacting these rural sites. Fraserdale being a remote site has very high winter/summer ratios where the high winter values are due to long range transport of longer lived hydrocarbons when the photochemical removal of these compounds from the troposphere is at its lowest.

Overall, a winter maximum and a summer minimum is observed. Since the sink of these hydrocarbons is predominantly due to reaction with OH radical, such a trend is in agreement with the results of modeling studies concerning the seasonal variation in

OH with a summer maximum in OH radical concentrations (Kastings and Singh 1986; Isaksen and Hov 1987; Bottenheim and Shepherd 1995).

Seasonal Variation of Biogenic Hydrocarbons

The seasonal variation of isoprene at five rural sites is shown in Fig. 8. Isoprene was measured in April when local daytime temperatures were generally above 15°C, and peaked during July when daytime temperatures were at their highest ($\geq 30^\circ\text{C}$). Concentrations of isoprene were observed to be as high as 29 ppbC (at the Centreville site) during the summer and then decline in fall, until reaching levels lower than the detection limit (≤ 0.1 ppbC) by late October/early November. Concentrations were generally above 1 ppbC from May to the end of October. Isoprene is a major reactant for boundary layer OH radicals in these regions. It is of interest to note peak values are observed in late June at

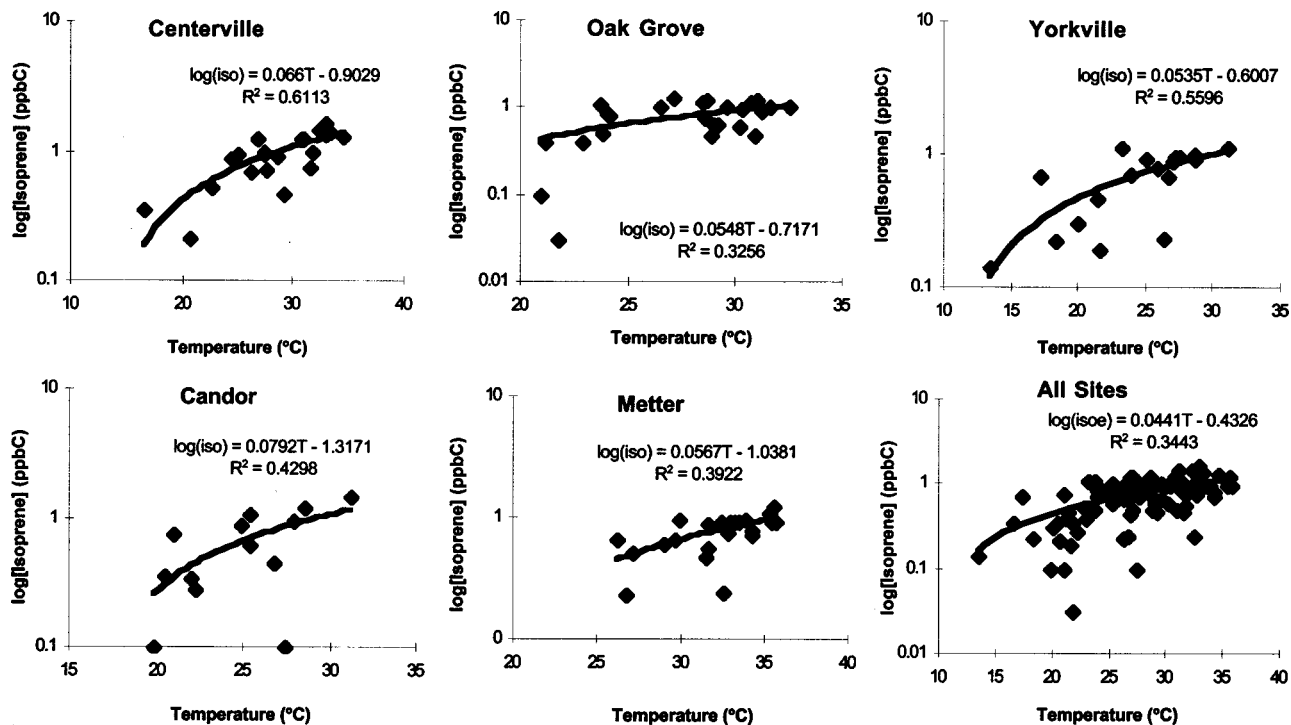


Fig. 10. Isoprene concentration as function of ambient temperature at six sites; solid line is linear fit to data

some sites and in early July at other sites. These differences are expected to be due to different meteorological conditions at the sites. Observation at these sites support recent studies (Grinspoon et al. 1991; Kuzma and Fall 1993) that revealed isoprene emissions do not begin immediately upon the emergence of leaves. Rather there is a lag between bud-break and emissions. An age-dependent developmental sequence independent of metabolic processes, such as photosynthesis rate, could thus govern the synthase activity (Silver and Fall 1991). The age-dependent development of isoprene is subject to environmental control. Sharkey and Loreto (1993) have found that the capacity for isoprene emission from kudzu leaves disappears when grown at cool temperatures. In separate experiments, it has been observed that aspen trees do not initiate isoprene emission until six weeks after leaf emergence, despite considerable potential to conduct photosynthesis (Monson et al. 1995). Thus, there appears to be an early season interaction between the onset of warm temperatures and genetic controls over leaf development that underlies the expression of maximum basal isoprene emission rates.

Monoterpenes are also mainly of biogenic origin and show a seasonal variation similar to that of isoprene, i.e., lowest concentration during the winter and highest during the summer. However, unlike isoprene, monoterpenes are emitted throughout the winter and have a small winter abundance. Fig. 9 shows the seasonal distribution of isoprene as well as the monoterpenes *a*-, *b*-pinene, and *d*-limonene. Winter time concentrations of monoterpenes at seven sites, excluding Giles County, ranged between 1.25 and 3 ppbC; similar concentrations were observed in spring and fall.

In a study on live oak (Tingey 1979) has shown that isoprene was emitted only during daylight, and given constant light conditions, the emission rate is dependent on temperature. Using the ambient concentration of isoprene as a surrogate for emissions from plants, the temperature dependence of isoprene was investigated by plotting the logarithm of ambient concentration versus

ambient temperature. Fig. 10 shows the linear relationship between logarithm of concentration versus ambient temperature at six of the sites. Also included in this plot are all the data from all the sites. Data from days when it was overcast and lightly raining as well as clear sunny days are included in this analysis. The slope of the individual plots (0.053–0.079) are in reasonable agreement with other studies (Fehsenfeld et al. 1992; Jobson et al. 1994). However when data from all the sites is included, the slope is much lower (0.44) with lower r^2 (0.34).

Factors Affecting Atmospheric Concentrations of Biogenic Hydrocarbons

Atmospheric concentrations of biogenically produced compounds are dependent on the source strength as well as their destruction through reaction and dilution. The terpene emissions increase with temperature and solar radiation as discussed earlier. In particular isoprene emission is more strongly influenced by light intensity than monoterpenes (Tingey 1979; Monson et al. 1995). Important terpene reactions are those with ozone and OH radicals. Table 2 lists the reaction rate constants of isoprene, *a*-pinene,

Table 2. Reaction Rate Constants K ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) for Reaction of Isoprene and Terpenes with OH Radicals and Ozone at $T=298 \text{ K}$

Compound	$K_{\text{OH}} \times 10^{10}$ ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	$K_{\text{O}_3} \times 10^{16}$ ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)
Isoprene	0.76, 0.93 ^a , 1.01 ^b	0.12 ^c , 0.14 ^b
<i>a</i> -Pinene	0.56, 0.60 ^a , 0.54 ^b	0.84 ^c , 0.85 ^b
<i>b</i> -Pinene	0.66, 0.78 ^a , 0.79 ^b	0.21 ^c , 0.16 ^b
Limonene	1.70 ^b	

^aKleindienst et al. (1982).

^bAtkinson (1990).

^cAtkinson et al. (1982).

Table 3. Correlation Coefficients between Biogenically Emitted Hydrocarbons and Meteorological Variables

Centreville	Temp	RH	WS	SR	O ₃	Isoprene	<i>a</i> -Pinene	<i>b</i> -Pinene	Limonene
Temp	1.00								
RH	0.03	1.00							
WS	0.45	-0.39	1.00						
SR	0.32	-0.65	0.31	1.00					
Ozone	0.52	-0.44	0.42	0.56	1.00				
Isoprene	0.70	0.02	0.23	0.16	-0.17	1.00			
<i>a</i> -Pinene	0.55	0.32	-0.21	-0.13	-0.07	0.76	1.00		
<i>b</i> -Pinene	0.34	0.14	-0.33	0.01	0.07	0.33	0.39	1.00	
Limonene	-0.32	0.26	-0.03	-0.12	-0.19	-0.27	-0.16	-0.04	1.00
Oak Grove	Temp	RH	WS	SR	O ₃	Isoprene	<i>a</i> -Pinene	<i>b</i> -Pinene	Limonene
Temp	1.00								
RH	0.04	1.00							
WS	0.39	-0.29	1.00						
SR	0.38	-0.79	0.28	1.00					
Ozone	0.46	-0.52	0.39	0.71	1.00				
Isoprene	0.67	0.17	0.25	0.13	-0.32	1.00			
<i>a</i> -Pinene	0.45	0.31	-0.24	-0.01	-0.03	0.63	1.00		
<i>b</i> -Pinene	0.57	0.28	-0.23	0.06	0.20	0.50	0.65	1.00	
Limonene	0.02	0.22	-0.03	-0.16	-0.21	0.02	0.00	0.07	1.00
Yorkville	Temp	RH	WS	SR	O ₃	Isoprene	<i>a</i> -Pinene	<i>b</i> -Pinene	Limonene
Temp	1.00								
RH	-0.07	1.00							
WS	0.42	-0.30	1.00						
SR	0.33	-0.65	0.26	1.00					
Ozone	0.74	-0.23	0.56	0.41	1.00				
Isoprene	0.76	0.00	0.51	0.18	0.52	1.00			
<i>a</i> -Pinene	0.17	0.49	-0.23	-0.54	-0.08	0.17	1.00		
<i>b</i> -Pinene	0.60	0.31	-0.11	-0.05	0.46	0.59	0.38	1.00	
Limonene	-0.19	0.23	0.08	-0.39	-0.21	-0.09	0.40	0.12	1.00
Candor	Temp	RH	SR	O ₃	Isoprene	<i>a</i> -Pinene	<i>b</i> -Pinene	Limonene	
Temp	1.00								
RH	-0.04	1.00							
SR	0.31	-0.71	1.00						
Ozone	0.63	-0.62	0.62	1.00					
Isoprene	0.62	-0.02	0.43	0.25	1.00				
<i>a</i> -Pinene	0.43	0.53	-0.03	-0.03	0.34	1.00			
<i>b</i> -Pinene	0.31	0.55	-0.02	-0.04	0.10	0.70	1.00		
Limonene	-0.34	0.28	-0.37	-0.37	-0.03	0.36	0.30	1.00	

Note: Values in boldface indicate correlations >0.5 or <-0.5.

b-pinene, and limonene with OH and ozone. Dilution is related with wind speed. The relationship between terpenes and the meteorological variables was investigated. Table 3 lists the Pearson's correlation coefficients between the above-mentioned parameters to determine the factors most closely related to the concentrations of terpenes.

It is expected that the atmospheric concentrations of terpenes would correlate positively with solar radiation and temperature and negatively with ozone concentrations and wind speed as well as relative humidity. However, as these environmental parameters are themselves related to each other, a simple relationship cannot be expected.

From Table 3 it is seen that isoprene concentrations are positively correlated to temperature at all sites. A positive relationship with solar radiation is also seen though the correlation is not very strong. No statistically significant relationship was observed with relative humidity. Isoprene concentration is positively related to ozone and wind speed at Yorkville and Candor. A likely explanation for this correlation is that isoprene emissions mixing during the afternoon period when maximum ozone is also observed. An examination of Table 4 containing descriptive statistics of meteorological and trace gas data indicates that the Yorkville site has the highest concentrations of trace gases related to sources of anthropogenic pollution. It is most impacted by anthropogenic

Table 4. Descriptive Statistics of Meteorological and Trace Gas Data for Four Sites. Data used Represents Daily Averages from 1,000 to 1,600, for Period June 1 through August 31, 1993 ($n=92$). Daily Max O₃ Represents Maximum Ozone Concentration Occurring between 1,000 and 1,600 Each Day

Summer 1993	Centreville		Oak Grove		Yorkville		Candor	
	Mean	StDev	Mean	StDev	Mean	StDev	Mean	StDev
Temp (°C)	30.58	2.51	29.72	2.38	28.01	2.62	29.30	5.62
Relative humidity (%)	62.55	11.93	64.30	11.98	67.51	11.68	44.59	10.31
Pressure (mmHg)	746.14	2.43	754.65	1.46	728.95	1.74		
Solar Rad (W/m ²)	585.96	176.45	577.07	197.43	599.36	262.13	592.12	256.55
Daily avg O ₃ (ppb)	47.57	14.66	43.63	11.92	63.47	16.58	65.00	11.54
Daily max O ₃ (ppb)	56.19	17.88	51.22	13.54	76.13	22.67		
CO (ppb)	164.70	45.84	184.31	50.24	297.68	58.25		
SO ₂ (ppb)	2.11	2.58	1.95	1.84	5.39	5.94		
NO (ppb)	0.13	0.13	0.13	0.21	0.30	0.25		
NO _y (ppb)	4.47	2.48	2.58	0.98	5.42	2.41		

pollution from the Atlanta Metropolitan Area. Trace gas data for the Candor site is not available. Given the higher availability of NO_y at the Yorkville site, higher isoprene emissions probably lead to higher ozone at this site. However, at the other sites with lower NO_y levels, isoprene is removed from the atmosphere due to its reaction with ozone.

As expected, the monoterpenes are correlated to each other at all sites. Isoprene was also found to be positively correlated to the monoterpenes though the degree of relationship varied from site to site. Not surprisingly the monoterpene concentration correlated positively to temperature. Negative correlations with wind speed and solar radiation were observed. The difference in the relationship between isoprene and the monoterpenes to the environmental parameters can be explained by the differences in their physiological emission patterns. These differences are consistent with the biological aspects of biogenic emissions from plants reviewed by Monson et al. (1995) and are briefly discussed here.

Factors Affecting Seasonal Nonmethane Organic Compounds Trends

The seasonal NMOC trend can be influenced by a number of factors. The three main factors as outlined by Singh and Zimmerman (1992) are (1) seasonal abundance of the OH radical; (2) changing hydrocarbon source strengths; and (3) changing atmospheric mixing patterns such as enhancement of vertical mixing through increased convection during the summer months or changing air mass climatology with season. The seasonal change in anthropogenic hydrocarbon source strengths is thought to be small due to the large pool and therefore expected to have limited impact on seasonal trends (Jobson et al. 1994; Monson et al. 1995). The effect of changing air mass climatology on the seasonal trend is difficult to quantify. However, it is evident that there is a seasonal variation in atmospheric lifetime as a result of changes in OH concentration and the temperature dependence of the rate constants.

To examine the influence of photochemistry in driving the seasonal trends we follow a procedure used by Rudolph and Johnen (1990) and Parrish et al. (1992); and later by Jobson et al. (1994), and Bottenheim and Shepherd (1995). The procedure is based on determining the change in the concentration ratio of two hydrocarbons due to photochemical aging. The procedure has been extensively described by these writers, and the reader is referred to those references for detail. It is based on the notion that, if dilu-

tion effects can be eliminated, the mixing ratio of a hydrocarbon during transport from a source region will decay according to the equation

$$[\text{HC}(t)] = [\text{HC}(t_0)] \exp(-K_{\text{HC}}[\text{OH}]_{\text{av}}t) \quad (1)$$

where $[\text{HC}(t)]$ = observed concentration of the hydrocarbon at the sampling site; $[\text{HC}(t_0)]$ = initial concentration of the hydrocarbon at time of emission; $[\text{OH}]_{\text{av}}$ = temporal and spatially averaged OH concentration; K_{HC} = second-order rate constant of reaction between HC and OH; and t = time of transport from the source to the sampling location. By using ratios of hydrocarbon concentrations it is possible to eliminate the $[\text{OH}]_{\text{av}}$ term and dilution effects, and to arrive at the equation

$$\ln([\text{HC}_1]/[\text{HC}_3]) = A + B\{\ln([\text{HC}_2]/[\text{HC}_3])\} \quad (2)$$

where the intercept is given by

$$A = \ln([\text{HC}_1(t_0)]/[\text{HC}_3(t_0)]) - B\{\ln([\text{HC}_2(t_0)]/[\text{HC}_3(t_0)])\} \quad (3)$$

and the slope is determined by

$$B = (K_{\text{HC1}} - K_{\text{HC3}})/(K_{\text{HC2}} - K_{\text{HC3}}) \quad (4)$$

Using properly chosen ratios of hydrocarbon data, linear relationships are expected from Eq. (2) where the slope should be determined solely by kinetic rate constant data. Rudolph and Johnen (1990) point out that the relationship given in Eq. (2) is sensitive to effects of dilution when the diluting air is of a different photochemical age. Parrish et al. (1992) qualitatively discussed these dilution effects, arguing that dilution by both younger and older air causes the observational data to lie above and to the left of the kinetic line given by Eq. (4).

In Fig. 11, the natural log of C₄/ethane and C₅/ethane concentration ratios are plotted against the log of the propane/ethane ratio for the Centreville site. Although a good linear fit was obtained for the C₄ ($R^2 > 0.9$), the derived slope (1.0) is lower than the derived slope of other studies i.e., 1.5 (Parrish et al.), 1.6 (Rudolph and Johnen), 1.5 (Jobson et al.), and 1.4 (Bottenheim and Shepherd 1995) and much smaller than the theoretical value of 2.6. Similarly for the C₅'s too, the slope is much lower than that expected from theory. The rate constants used for the calculations are from Atkinson (1990). A possible explanation for the deviation from the kinetic value is due to the effects of dilution and mixing of air parcels of different age (Bottenheim and Shepherd 1995). This has been substantiated by model calculations of

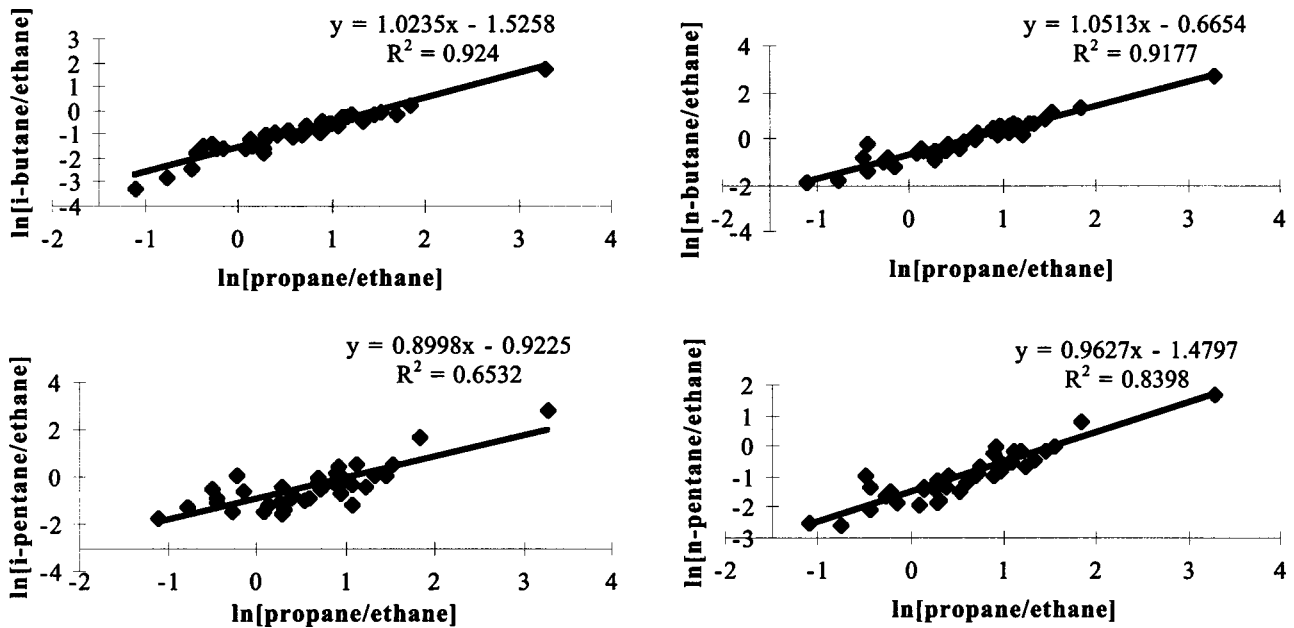


Fig. 11. Ratios of (a) $\ln([i\text{-butane}]/[\text{ethane}])$, (b) $\ln([n\text{-butane}]/[\text{ethane}])$, (c) $\ln([i\text{-pentane}]/[\text{ethane}])$, and (d) $\ln([n\text{-pentane}]/[\text{ethane}])$ versus $\ln([propane]/[\text{ethane}])$ for period September 1992 to September 1993 at Centreville, Alabama site

Mckeen and Liu (1993). It has been suggested by Jobson et al. (1994), that a better choice of hydrocarbons would be two compounds with virtually identical OH rate constants.

In Fig. 12, hydrocarbons with similar atmospheric lifetimes, as evaluated from Eq. (2) are plotted against each other for the Centreville site. Since the OH lifetimes are similar, dilution effects caused by mixing air of different photochemical ages will be minimized, and the observational data should be in accord with the kinetic slope (Jobson et al. 1994). A plot of the log of *i*-butane/ethane and *n*-butane/ethane concentration ratios gives a least-squares fit slope of 0.92 which is very close to the kinetic slope of 0.91 at 298 K. However, a similar plot of the log of acetylene/ethane and propane/ethane concentration ratios has a derived slope of 0.80, slightly higher than the kinetic slope of 0.72 at 298 K. The values obtained by Jobson et al. (1994) are 0.97 and 0.66, respectively, for the slopes of the regression lines of the log of *i*-butane/ethane and *n*-butane/ethane concentration ratios and the plot of the log of acetylene/ethane and propane/ethane concentration ratios i.e., quite similar to the values observed in this study.

Similar plots for the other sites are depicted in Figs. 13 and 14. Fig. 13 gives the log-log plot of *i*-butane/*n*-butane and *n*-butane/ethane concentration ratios at the various sites; whereas Fig. 14 gives the log-log plot of acetylene/ethane and propane/ethane concentration ratios. It is worth noting that the summer data are at the lower end of the regression lines, and the winter data at the upper end indicating more extensive reaction of the hydrocarbon in summer than in winter. The plots of the log of *i*-butane/ethane and *n*-butane/ethane concentration ratios for most of the sites are in good agreement with the calculated kinetic value though at some of the sites the scatter is larger. However, the slopes for the plot of the log of acetylene/ethane and propane/ethane concentration ratios at some of the sites are quite different from the kinetic slopes. This is probably due to high acetylene levels observed at these sites sporadically which is generally associated with the transport of pollutants from highways as acetylene is a marker for automotive emissions.

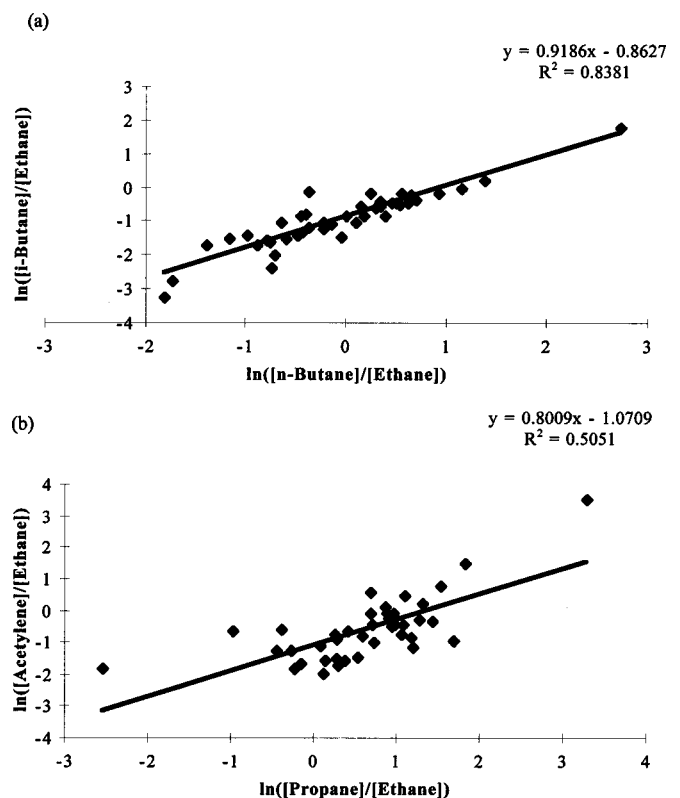


Fig. 12. Correlation of hydrocarbon ratios with similar lifetimes. Plot of (a) $\ln([i\text{-butane}]/[\text{ethane}])$ versus $\ln([n\text{-butane}]/[\text{ethane}])$ and (b) $\ln([acetylene]/[\text{ethane}])$ versus $\ln([propane]/[\text{ethane}])$ for period September 1992 to September 1993 at Centreville.

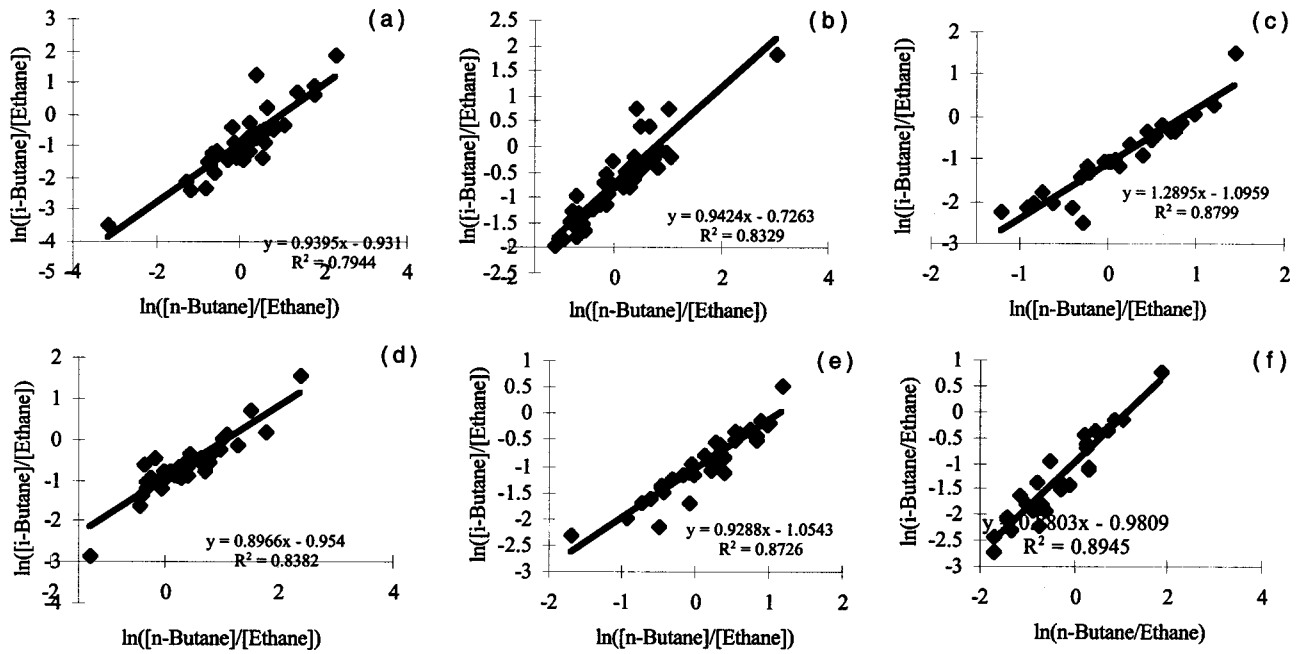


Fig. 13. Correlation of hydrocarbon ratios with similar lifetimes. Plot of $\ln([i\text{-butane}]/[\text{ethane}])$ versus $\ln([n\text{-butane}]/[\text{ethane}])$ for (a) Metter, (b) Oak Grove, (c) Table Rock, (d) Yorkville, (e) Candor, and (f) Giles County for the period September 1992 to September 1993.

The similarity in the derived slopes with the cited literature and the calculated kinetic slopes leads to the notion of OH chemistry being the most important factor driving the observed seasonal trends.

Hydrocarbon Reactivity

Because of the differences in reactivity with OH, consideration of hydrocarbon concentration alone often presents an inaccurate picture of the actual O_3 producing potential of local air mass. To account for differences in reactivity and to obtain a better assess-

ment of the relative importance of every species in a region, reactivity as propylene equivalents was obtained by normalizing the concentration of each hydrocarbon to that of propylene by calculating a propylene-equivalent concentration

$$\text{Propy-Equiv } (J) = \text{Conc } (J) \frac{K_{\text{OH}}(J)}{K_{\text{OH}}(\text{C}_3\text{H}_6)} \quad (5)$$

where $\text{Conc } (J)$ = concentration of the species J , ppbc; $K_{\text{OH}}(J)$ = rate constant for the species J with OH; and $K_{\text{OH}}(\text{C}_3\text{H}_6)$ = rate concentration for propylene with OH.

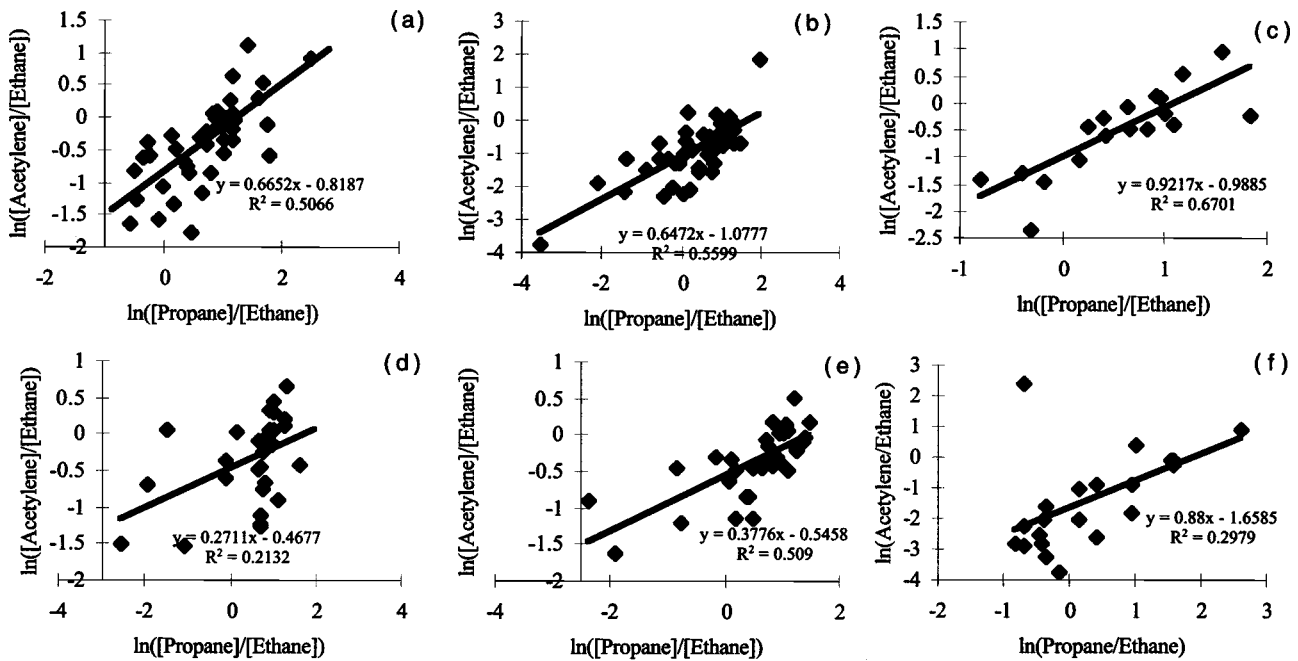


Fig. 14. Correlation of hydrocarbon ratios with similar lifetimes. Plot of $\ln([\text{acetylene}]/[\text{ethane}])$ versus $\ln([\text{propane}]/[\text{ethane}])$ for (a) Metter, (b) Oak Grove, (c) Table Rock, (d) Yorkville, (e) Candor and (f) Giles County for period September 1992 to September 1993.

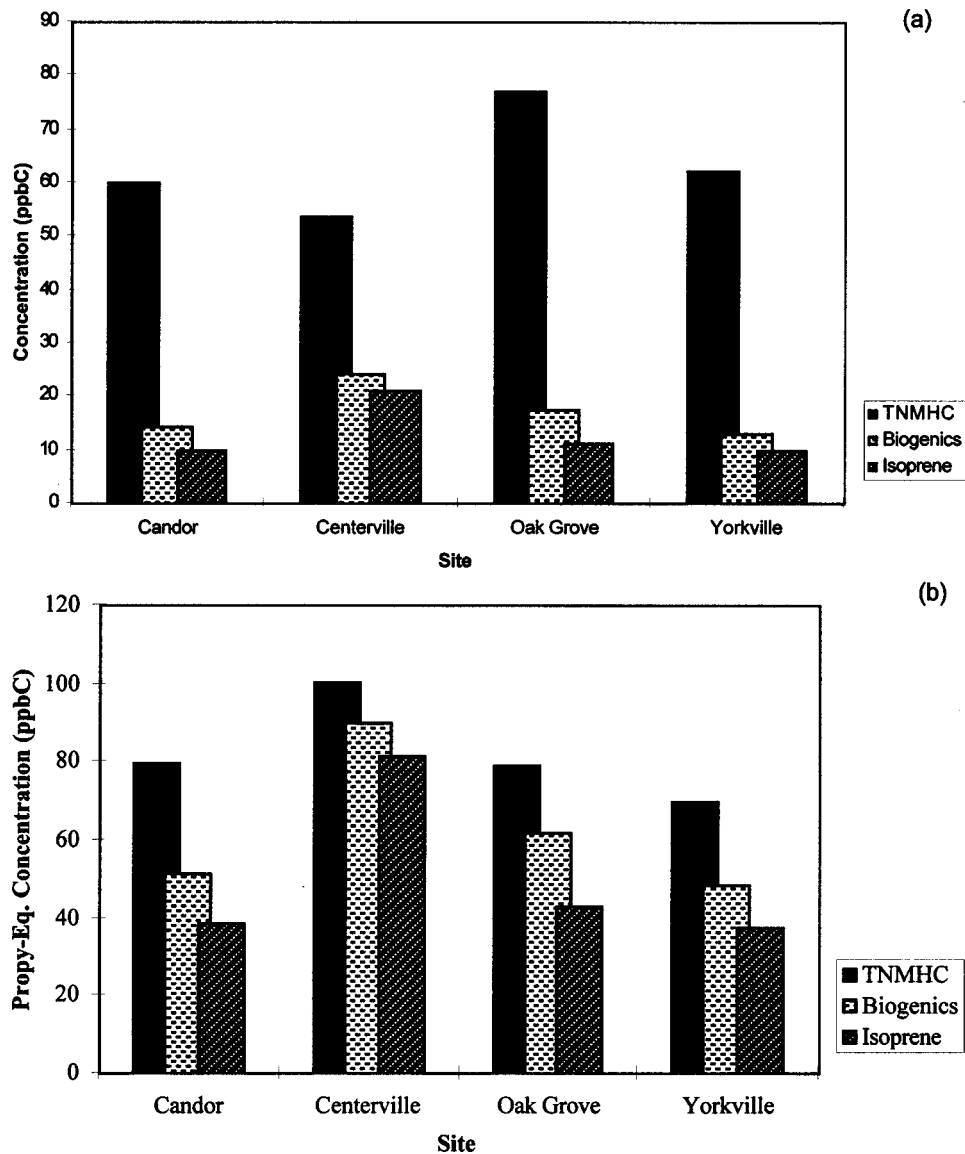


Fig. 15. Biogenic and isoprene fraction of TNMHC expressed as (a) concentration in ppbC and (b) propy-equiv concentration

The propylene-equivalent concentration takes into account the combined effect of hydrocarbon concentration and reactivity with OH. A compound twice as reactive as propylene would have a Propy-Equiv concentration twice its ambient concentration.

The effect of hydrocarbon/OH reactivity can be seen in comparison of the TNMOC concentration expressed as carbon and as propylene-equivalent for four of the eight sites depicted in Figs. 15(a and b). Fig. 15 shows the dramatic impact of the highly reactive natural or biogenic hydrocarbon fraction of which isoprene is the major contributor. Biogenic hydrocarbons which comprise about 25–40% of the total hydrocarbons by carbon contribute almost 50 to 90% to the total propylene-equivalent concentration. The potential influence of OH radical reactivity on O_3 production is most clearly evident for the species isoprene. Isoprene had the highest average propylene-equivalent concentration at all sites. Isoprene may have more impact on O_3 production in rural areas when both abundance and reactivity are taken into account. It must be pointed out that the propylene-equivalent approach, or any other OH reactivity concept, prioritizes the individual compound 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 OH radical, the reactions become competitive with OH when the concentration of ozone builds up (Warneck 1988).

Conclusions

A regional analysis of rural Southeastern United States data for hydrocarbons has shown distinct seasonal trends in the anthropogenic nonmethane organic compounds, and in the biogenic hydrocarbon isoprene. Though the sites were well removed from large anthropogenic sources, most compounds observed at these sites are of urban anthropogenic origin. The data for the sites show similar seasonal patterns with maximum concentrations of nonmethane organic compounds during the summer followed by a secondary peak in the winter and lowest concentration in the spring.

The light (C_2 – C_4) anthropogenic nonmethane hydrocarbons peaked during the winter months and exhibited the lowest concentrations during fall. The seasonal oscillation of the C_2 – C_4 hydrocarbons appears to be dominated by seasonal changes in atmospheric lifetime by OH oxidation as evidenced by the close agreement between observed and kinetic slopes in correlation plots of hydrocarbon ratios with similar lifetimes. The overall scenario for the Southeast United States is that of a rather broad, stable background of hydrocarbons of anthropogenic origin, kept relatively constant by a combination of widely spread natural sources, and a slow removal by OH radical chemistry during winter months.

Seasonal trends in the concentrations of biologically emitted hydrocarbons (isoprene, *a*-pinene, and *b*-pinene) were also observed. Isoprene was the most abundant NMOC during the summer, with mean concentrations exceeding 20 ppbC at certain sites, and greater than 8 ppbC at all sites. Isoprene concentrations were found to be a function of the ambient temperature. Isoprene levels were below the level of detection during winter and early spring and they appeared in late spring when the temperatures were generally above 15°C. A seasonal trend in monoterpene concentrations were also observed with summer highs and winter lows. However, unlike isoprene, monoterpenes maintained a low persistent winter time background concentration.

Propylene-equivalent concentrations for the various compounds were determined for four of the eight sites and the contribution of biogenic compounds to the total propylene-equivalent concentrations was investigated to account for the reactivity of the compounds. It was found that biogenics, primarily isoprene, dominate the total NMOC concentrations in the Southeast United States.

The focus of the nation's ozone abatement strategy so far has been on the reduction of anthropogenic hydrocarbon. In spite of over a decade of these efforts, with an estimated reduction of about 50% on anthropogenic hydrocarbon emission inventories, average and peak levels of ozone still continue to be high in the Southeastern United States. It appears that a uniform abatement policy for all areas of the country may not be adequate. In the Northeastern section of the United States which is a heavily industrialized area, hydrocarbon emissions are dominated by anthropogenic sources. The South, on the other hand, receives the majority of its hydrocarbon input from its forests. This study suggests that biogenically emitted hydrocarbons dominate the total nonmethane organic compound concentrations in the Southeastern United States. Thus a combination of VOC and NO_x reduction for ozone control might prove to be more effective than merely VOC or NO_x control.

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data set published in this paper may be requested from the corresponding writer, Dr. Viney P. Aneja (Viney_Aneja@NCSSU.edu).

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