

Nonmethane hydrocarbons in the rural southeast United States national parks

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Abstract. Measurements of volatile organic compounds (VOCs) were made at three rural sites in the southeast U.S. national parks: Mammoth Cave National Park, Kentucky; Cove Mountain, Great Smoky Mountains National Park, Tennessee; and Big Meadows, Shenandoah National Park, Virginia. In 1995 the three locations were sampling sites for the Southern Oxidants Study (SOS) Nashville Intensive, and the measurements of VOCs for Shenandoah were also made under contract with the National Park Service. Starting in 1996, the National Park Service added the other two parks to the monitoring contract. Hydrocarbon measurements made during June through September for the years 1995, 1996, and 1997 were analyzed in this study. Source classification techniques based on correlation coefficient, chemical reactivity, and ratioing were developed and applied to these data. The results show that anthropogenic VOCs from automobile exhaust appeared to be dominant at Mammoth Cave National Park, and at Cove Mountain, Great Smoky Mountains National Park, but other sources were also important at Big Meadows, Shenandoah National Park. Correlation and ratio analysis based on chemical reactivity provides a basis for source-receptor relationship. The most abundant ambient VOCs varied both in concentration and order depending on park and year, but the following VOCs appeared on the top 10 list for all three sites: isoprene (6.3 to 18.4 ppbv), propane (2.1 to 12.9 ppbv), isopentane (1.3 to 5.7 ppbv), and toluene (1.0 to 7.2 ppbv). Isoprene is naturally emitted by vegetation, and the others are produced mainly by fossil fuel combustion and industrial processes. 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 contributions to ozone formation.

1. Introduction

Hydrocarbons play a key role as a precursor to ozone and other atmospheric photochemical oxidant formation. Since the passage of the 1970 Clean Air Act Amendments (CAAA), regulatory efforts to comply with the 0.12 ppm National Ambient Air Quality Standard for ozone have proved inadequate [National Research Council (NRC), 1991; Dimitriadis, 1989]. Ozone nonattainment continues to be a problem, especially in the southeast United States, and is attributed to excessive amounts of biogenically emitted volatile organic compounds (VOCs) such as isoprene [Trainer *et al.*, 1987; Chameides *et al.*, 1988; NRC, 1991]. The situation in rural areas where ozone concentrations are high is even less clear. Although biogenic VOCs can be high in heavily forested areas, the relative contribution of ozone from local production versus transport of ozone is still a question. The literature on VOCs in the troposphere [Hagerman *et al.*, 1997; Carter, 1996; Lawrimore *et al.*,

1995; Andronache *et al.*, 1994; Boudries *et al.*, 1994; Jobson *et al.*, 1994; Chameides *et al.*, 1992] is helpful, but not specific for the areas of interest. The expectation from previous studies is that the rural areas described in this paper are NO_x-limited for the formation of ozone.

In order to further investigate impacts of hydrocarbons and transported pollutants on air quality in rural areas, the National Park Service (NPS) is currently acquiring ambient data that includes intermittent hydrocarbon samples and continuous measurements of O₃, NO_y, NO, SO₂, and CO in the three parks. In this study, 3 years of data (1995–1997) are examined for the summer (June through September) maximum photochemical activity period. We (1) provide high-quality QA/QC data for an observational based analysis and for use by modelers, (2) develop appropriate techniques to identify sources of rural VOCs, (3) use correlation and ratio analysis based on chemical reactivity to provide a basis for source-receptor relationship, (4) compare the composition of VOCs at different sites, (5) analyze the contribution of rural VOCs using propylene-equivalent concentrations to ozone formation potential, especially in relation to isoprene, (6) evaluate relative

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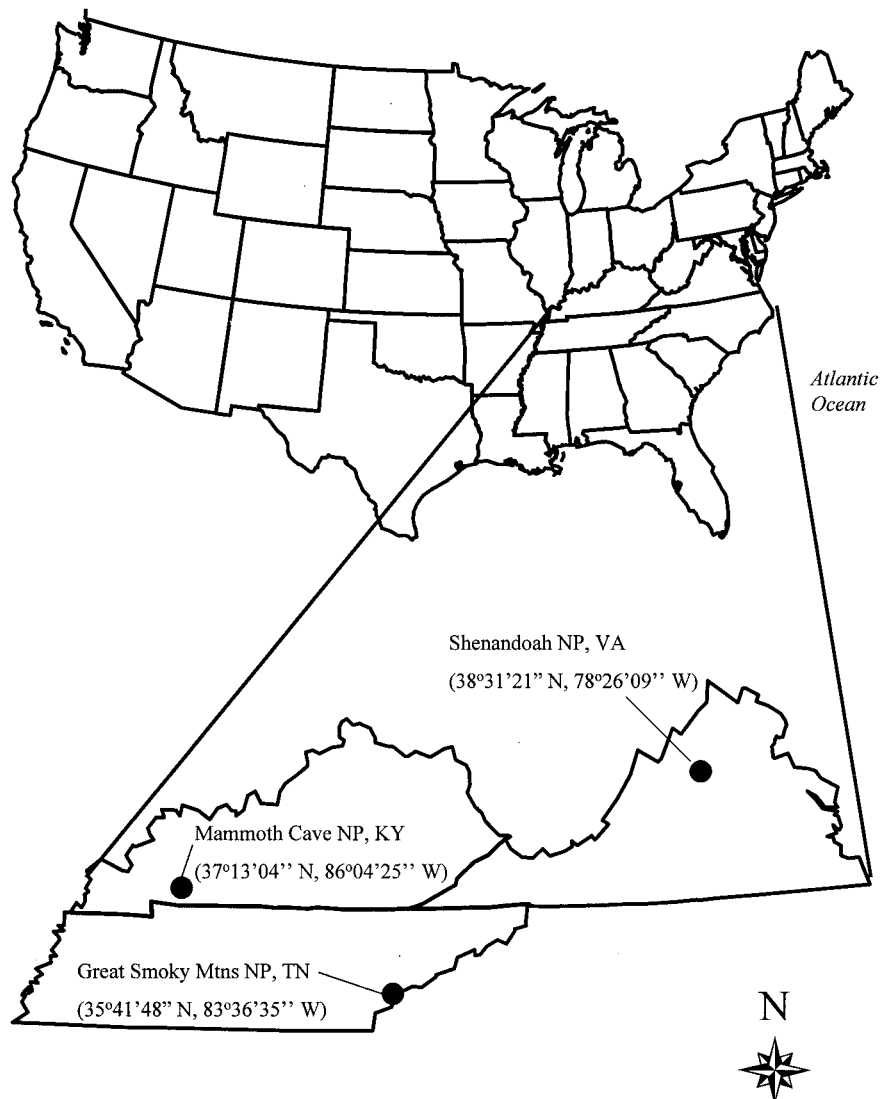


Figure 1. Map of sampling sites.

contributions of different classes of VOCs to the total concentration and ozone formation potential, and (7) examine the relationship between isoprene concentrations and temperature.

2. Experiment

Ambient air samples for determination of VOCs were collected in canisters at three enhanced monitoring sites (Figure 1) in the southeast United States. In addition, ozone, nitrogen oxides, carbon monoxide, sulfur dioxide, and meteorological parameters were measured. The northernmost location, Shenandoah National Park, Big Meadows site (SHEN), is in rural Virginia at 1073 m elevation in a clearing along a ridge (38°31'21"N, 78°26'09"W). The other two sites are rural locations in the Great Smoky Mountains National Park at Cove Mountain (GRSM), Tennessee, elevation 1243 m (35°41'48"N, 83°36'35"W) and at Mammoth Cave National Park (MACA), Kentucky, elevation 219 m (37°13'04"N, 86°04'25"W). Each site is part of the NPS gaseous-pollutant monitoring network. All the three sites are located within heavily forested areas with either a clearing for the site itself or a tower above the trees.

The dominant tree species at MACA and SHEN include oaks and hickories; and at GRSM they include maple, buckeye, birch, beech, spruce, poplar, pine, oak, and hemlock. A small relocation of the MACA site occurred during mid July 1997.

Ambient air samples were collected in stainless steel electropolished canisters using an automated pump. In 1995, inlet tubing was 19 mm OD Teflon tubing at SHEN, and 19 mm OD nickel tubing at the other two sites, and the inlet was at 10 m. In 1996 and 1997, inlet tubing was changed to Teflon at all sites, and the inlet was raised to 13 m at SHEN. One-hour integrated sampling was used, and only samples collected during 1200 to 1300 local time (LT) were used in this study. After collection, the samples were returned to the University of Miami, Rosenstiel School of Marine and Atmospheric Science (RSMAS) for analysis. The analytical system used for this study was an upgraded version of the system described in detail by *Farmer et al.* [1994]. Basically, the system consisted of a modified Entech model 7000 concentrator, with cryotrapping and cryofocusing capabilities. Ambient air samples were pulled through a cryotrap, containing glass beads and Chromasorb A, held at -180°C . The compounds retained in the cryotrap were

then transferred through a drying column to a second mixed bed sorbent trap [Riemer *et al.*, 1998]. This second trap was then desorbed, and the trapped compounds were transferred to the cryofocuser. At the end of the transfer the cryofocuser was flash heated to 100°C, and the gas chromatographic run was started. The gas chromatograph was a Hewlett-Packard 5890 Series II with flame ionization detection. Standards, both for retention time and quantification, were run routinely, and four internal standards were added to every chromatographic run to verify performance of the analytical system. Identification of the target compounds was confirmed by mass spectrometer analysis. On the basis of previous studies of ambient air [Bernardo-Bricker *et al.*, 1995] and replicate analysis performed during this study, the method detection limit is 0.10 parts per billion carbon (ppbc), with an uncertainty of $\pm 20\%$. Any target compounds not detected in the sample above 0.10 ppbc were reported as not detected (ND) and were not included in any statistical analysis.

3. Analysis and Discussion

3.1. Measurements of Speciated Hydrocarbons

3.1.1. Concentration and distribution. Tables 1a–1c summarize the statistics of compounds that belong to the 55–56 Photochemical Assessment Monitoring Stations (PAMS) target compounds (α,β -pinenes and limonene are also included due to their relative importance in rural areas) [Lewis *et al.*, 1998] detected at each site, where total nonmethane hydrocarbon compounds (TNMHC) is the total of these compounds. At the bottom of this table, totals are given for broad classes of compounds based on their sources, where BTEX is the total of benzene, toluene, ethylbenzene, and xylenes (m, o, p). AROMATICS include all other benzene-based compounds. TOT-AROM is the sum of BTEX and AROMATICS. ANTH-HC is anthropogenic hydrocarbons, here defined as all the hydrocarbons except those classically considered biogenic (isoprene, α , β -pinenes, and limonene). NAT-HC is the biogenic fraction including isoprene, α , β -pinenes, and limonene. Only data collected in June through September are summarized. Sampling dates used for the analysis are listed at the bottom of each table.

On the basis of the data (Table 2) at each site, isoprene, propane, isopentane, and ethane were all among the top 10 most abundant compounds, although the order differed at each site. Compared with five PAMS sites in the northeast United States, where isopentane, toluene, propane, ethane, n-butane, m,p-xylene, and n-pentane are among the most abundant species [Environmental Protection Agency (EPA), 1997], the top 10 most abundant species and their sequence changed dramatically in these parks, even though three of these relatively stable species, isopentane, propane, and ethane, remained most abundant at these sites. At MACA, isoprene is the dominant compound with mean concentrations of 15.64 ± 8.30 ppbv (1995), 22.80 ± 16.39 ppbv (1996), and 11.74 ± 13.74 ppbv (1997). At GRSM, in 1995 and 1997, isoprene is dominant with mean concentrations of 15.20 ± 8.15 ppbv (1995) and 18.35 ± 12.28 ppbv (1997). At GRSM, in 1996, 1,2,4-trimethylbenzene is dominant with mean concentration of 16.65 ± 3.94 ppbv, followed by isoprene with mean concentration of 10.25 ± 8.75 ppbv. TNMHC at MACA and GRSM for 1995–1997 is in the range 36.15 ± 9.83 ppbv to 64.79 ± 23.67 ppbv. By contrast, at SHEN, the 1995 data show anomalous behavior with isopentane, n-pentane, and α -pinene

being dominant although most likely contaminated by local sources, so the sampling pattern was changed in 1996 as described above. Even so, isoprene with mean concentration of 17.03 ± 9.27 ppbv seems reasonable. In 1996, propane (12.88 ± 11.39 ppbv), n-butane (7.14 ± 6.46 ppbv), and toluene (6.62 ± 6.0 ppbv) show concentrations greater than isoprene (6.26 ± 4.43 ppbv). In 1997, isoprene (10.09 ± 9.95 ppbv) is dominant, followed by propane (6.42 ± 2.75 ppbv). TNMHC is about 10% higher at SHEN than at the other two sites, with mean concentration in the range 64.44 ± 30.38 ppbv (1997) to 72.08 ± 39.35 ppbv (1996). This suggests that SHEN is influenced by sources different from those at MACA and GRSM, even when the 1995 data are excluded. This problem is discussed in detail in the following sections.

Figure 2 gives fractional contributions of various classes of hydrocarbons to the total hydrocarbons at the three sites. Figure 3 provides the variations of total VOCs and different classes of hydrocarbon at each site with year (it should be noted that the number of observations is limited in some years at some locations; there are 10 observations at MACA in 1996 and 1997 and at GRSM in 1997). At MACA (Figures 2a–2c) and GRSM (Figures 2d–2f) the fractional contribution of ALKENES to the total is similar, largest in 1997 (17% for MACA and 19% for GRSM) and lowest (4% for both) in 1996, and the contributions in 1995 are also similar (7% for MACA and 8% for GRSM). The contribution of ALKANES at MACA was relatively stable for the 3 years (from 40% to 44%), but at GRSM it changes from 31% (1996) to 40% (1997). In fact, as Figure 3 shows, ALKANES at GRSM increases year by year from 1995 to 1997, but remains relatively stable at MACA. The contribution of TOT-AROM at MACA also remains relatively stable (10 to 14%) in 1996 and 1997. At GRSM it is similar in 1995 and 1997, but in 1996 stands high by a large margin and is the largest contribution to the total. This is because in this year there were continuously high concentrations of 1,2,4-trimethylbenzene (16.61 ± 3.94 ppbv); this problem is discussed further in the following sections. NAT-HC varies over a larger range at both locations. This is because NAT-HC varies with temperature, light intensity, and vegetation. In general, ANTH-HC at GRSM and MACA show similar behavior in both concentration and distribution, suggesting that these two parks are under the same regional influence as ANTH-HC. However, the situation is different at SHEN. For the reason mentioned above for the 1995 data for this site, here the concentration and distribution for only 1996 and 1997 data are discussed. As Figures 2g and 2h show, ALKANES are dominant in both years (61% in 1996 and 53% in 1997), followed by TOT-AROM (~21%). ALKENES at SHEN are almost the same in both concentration and contribution to the total in both years. As Figure 3 shows, all the groups are quite consistent over 2 years. Compared with those at MACA and GRSM, the concentrations of ALKANES and TOT-AROM are significantly higher, but ALKENES and NAT-HC are lower at SHEN. This signifies that SHEN was under different influence of anthropogenic hydrocarbon sources than MACA and GRSM.

3.1.2. Variation with date. Figures 4a–4c give the variation of concentrations of three major anthropogenic groups with date at each site for each year. The three groups are ALKANES, ALKENES, and TOT-AROM. In 1995 all three sites were sampling sites for Southern Oxidants Study (SOS) Nashville Intensive, with sampling dates continuous from June 20 to July 25 at MACA and GRSM, and from July 14 to July

Table 1a. Summary of Hydrocarbon Concentrations at Mammoth Cave National Park, Kentucky^a

Compound	1995				1996				1997							
	Mean	Median	s.d.	Minimum	Maximum	Minimum	Mean	Median	s.d.	Maximum	Minimum	Mean	Median	s.d.	Maximum	Minimum
Ethene	1.244	0.536	2.876	ND	12.564	ND	0.720	0.691	0.389	1.451	ND	0.427	0.366	0.230	0.814	0.120
Acetylene	0.822	0.660	1.022	ND	4.447	ND	0.607	0.622	0.271	1.026	ND	0.522	0.551	0.107	0.659	0.295
Ethane	2.328	0.965	2.550	ND	8.412	ND	5.647	6.099	3.231	9.089	ND	3.660	3.867	1.386	5.700	1.634
Propene	0.454	0.414	0.160	0.210	0.972	0.210	0.439	0.422	0.234	0.803	ND	3.794	2.788	1.969	7.807	2.106
Propane	3.346	2.680	3.167	ND	14.621	ND	4.196	4.060	2.474	7.908	ND	2.987	2.515	1.432	5.715	1.419
Isobutane	1.566	0.565	4.807	0.164	27.762	0.164	0.736	0.729	0.461	1.378	ND	1.907	1.808	1.449	4.555	ND
1-Butene	0.142	0.099	0.205	ND	0.839	ND	0.163	0.119	0.214	0.747	ND	0.409	0.302	0.106	0.302	ND
n-Butane	1.889	1.328	1.474	0.445	7.001	0.445	1.777	1.707	1.215	3.850	ND	0.919	0.527	0.985	2.965	ND
<i>trans</i> -2-Butene	0.006	ND	0.036	ND	0.206	ND	ND	ND	ND	0.833	ND	0.381	0.249	0.325	1.114	0.113
<i>cis</i> -2-Butene	0.148	ND	0.292	ND	1.463	ND	0.083	ND	0.263	0.833	ND	1.328	0.751	1.390	4.192	ND
3-Methyl-1-butene	0.004	ND	0.025	ND	0.141	ND	ND	ND	ND	0.833	ND	0.193	0.211	0.199	0.593	ND
Isopentane	1.907	1.335	1.615	0.521	7.534	0.521	5.686	3.043	8.483	29.776	2.128	1.660	0.160	2.190	5.706	ND
1-Pentene	0.561	ND	2.053	0.367	9.564	0.367	0.188	0.125	0.238	0.833	ND	0.201	0.109	0.226	0.550	ND
n-Pentane	1.153	0.801	1.010	0.367	5.367	0.367	0.928	0.884	0.345	1.632	0.503	0.950	0.495	0.495	1.676	0.330
Isoprene	15.637	14.375	8.297	2.274	44.467	2.274	22.802	19.494	16.388	64.594	8.489	11.736	4.387	13.743	41.711	0.224
<i>trans</i> -2-Pentene	0.036	ND	0.141	ND	0.714	ND	0.094	ND	0.142	0.397	ND	0.196	0.087	0.269	0.774	ND
<i>cis</i> -2-Pentene	0.015	ND	0.075	ND	0.419	ND	ND	ND	ND	ND	ND	0.175	0.145	0.167	0.489	ND
2-Methyl-2-butene	0.111	ND	0.188	ND	0.746	ND	ND	ND	ND	ND	ND	0.118	0.087	0.135	0.370	ND
4-Methyl-1-pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.830	0.133	1.417	4.033	ND
Cyclopentane	0.077	ND	0.121	ND	0.520	ND	0.117	0.125	0.092	0.271	ND	0.179	0.170	0.179	0.449	ND
2-Methylpentane	0.423	0.330	0.331	ND	1.422	ND	2.770	2.891	1.737	6.181	0.315	2.714	2.585	1.113	4.876	1.175
3-Methylpentane	0.413	0.274	0.403	ND	1.983	ND	0.786	0.741	0.380	1.335	0.300	1.780	1.624	1.552	5.381	0.271
n-Hexane	0.440	0.349	0.408	ND	1.800	ND	0.474	0.404	0.223	0.854	0.184	0.431	0.382	0.210	0.773	0.167
<i>cis</i> -3-Hexene	0.117	0.118	0.093	ND	0.300	ND	0.354	0.272	0.270	1.040	0.112	0.206	0.146	0.195	0.712	ND
Methylcyclopentane	0.205	0.190	0.173	ND	0.509	ND	0.333	0.192	0.471	1.634	ND	0.249	0.224	0.164	0.604	ND
2,4-Dimethylpentane	0.083	ND	0.133	ND	0.502	ND	0.158	0.052	0.260	0.824	ND	0.294	0.352	0.231	0.631	ND
Benzene	1.021	0.861	0.407	0.447	2.031	0.447	0.914	0.896	0.230	1.365	0.571	0.628	0.652	0.181	0.874	0.374
Cyclohexane	0.092	ND	0.202	ND	1.090	ND	0.202	0.163	0.254	0.860	ND	0.231	0.239	0.129	0.441	ND
2,3-Dimethylpentane	0.127	0.080	0.232	ND	1.253	ND	0.383	0.396	0.374	1.250	ND	0.286	0.328	0.208	0.588	ND
Heptane	0.219	0.184	0.211	ND	1.080	ND	0.458	0.142	0.871	2.924	0.075	0.148	0.147	0.083	0.256	ND
Methylcyclohexane	0.119	0.075	0.184	ND	0.778	ND	0.413	0.416	0.248	0.780	ND	0.269	0.273	0.240	0.626	ND
2,3,4-Trimethylpentane	0.424	0.365	0.384	ND	1.272	ND	0.369	0.256	0.326	1.174	ND	0.444	0.452	0.204	0.829	0.223
Toluene	1.396	0.963	1.745	0.472	10.453	0.472	0.935	0.899	0.508	2.192	0.463	1.282	1.115	0.537	2.410	0.603
n-Octane	0.129	0.107	0.105	ND	0.344	ND	0.061	0.032	0.091	0.292	ND	0.139	0.122	0.051	0.215	0.082
Ethylbenzene	0.250	0.210	0.104	0.106	0.593	0.106	0.381	0.329	0.189	0.764	0.212	0.232	0.186	0.119	0.418	0.102
m-Xylene	0.439	0.398	0.213	0.142	1.098	0.142	0.472	0.412	0.178	0.819	0.296	0.662	0.492	0.475	1.409	0.193
p-Xylene	0.194	0.169	0.168	ND	0.924	ND	ND	ND	ND	0.403	ND	0.071	ND	0.094	0.229	ND
Styrene	0.137	0.106	0.143	ND	0.463	ND	1.924	1.158	1.452	5.482	0.940	1.757	1.743	0.440	2.566	1.110
o-Xylene	0.652	0.668	0.162	0.281	0.968	0.281	0.471	0.378	0.314	1.196	0.094	0.554	0.566	0.106	0.681	0.353
Nonane	0.092	ND	0.262	ND	1.484	ND	0.057	0.000	0.094	0.294	ND	0.310	0.253	0.166	0.602	0.120
Isopropylbenzene	0.055	0.030	0.060	ND	0.162	ND	0.037	0.000	0.079	0.192	ND	0.044	0.064	0.038	0.083	ND
n-Propylbenzene	0.895	0.734	0.572	0.186	2.392	0.186	1.640	1.009	1.502	5.133	0.505	1.128	1.073	0.344	1.609	0.727
1,3,5-Trimethylbenzene	0.125	0.062	0.223	ND	1.169	ND	0.113	0.082	0.141	0.403	ND	0.056	0.073	0.052	0.142	ND
1,3,5-Trimethylbenzene	0.100	ND	0.182	ND	0.808	ND	ND	ND	ND	ND	ND	0.008	ND	0.026	0.081	ND
b-Pinene	0.333	0.226	0.442	ND	1.850	ND	1.336	1.239	1.151	4.157	ND	1.221	0.613	1.243	3.166	ND
1,2,4-Trimethylbenzene	0.204	0.176	0.195	ND	0.636	ND	3.862	3.268	1.859	7.146	0.911	1.621	1.544	0.607	3.074	1.004
n-Decane	1.129	0.264	2.648	ND	14.004	ND	0.277	0.146	0.338	1.130	0.070	0.678	0.672	0.220	1.033	0.270

Limonene	1.323	0.449	2.035	10.059	ND	0.564	0.392	0.622	2.239	0.054	0.545	0.530	0.139	0.753	0.303
Undecane	4.704	0.856	8.394	38.384	ND	0.590	0.398	0.591	1.866	ND	0.695	0.659	0.213	1.156	0.327
TNMHC	47.29	42.98	20.53	97.34	15.30	64.52	57.13	18.32	97.59	48.81	58.01	52.35	35.89	192.05	ND
Class totals															
ALKANES	20.866	15.151	14.132	58.934	6.158	26.419	26.179	9.440	46.119	13.775	20.931	19.424	7.935	37.168	13.351
ALKENES	3.662	2.145	3.907	15.071	0.610	2.649	2.520	0.641	3.633	1.772	8.420	6.490	4.960	20.000	3.803
AROMATICS	0.622	0.696	0.515	1.624	ND	5.936	5.190	2.853	11.860	2.018	3.486	3.473	3.871	4.997	2.427
BTEX	3.951	3.199	2.189	13.905	2.001	3.174	2.758	1.202	5.959	1.920	3.430	3.048	1.179	5.681	2.013
PINENES	2.551	1.422	2.752	13.870	0.186	3.540	2.354	2.859	9.969	0.739	2.894	2.885	1.240	4.621	1.029
TOT-AROMATICS	4.573	3.899	2.456	14.854	2.001	9.110	7.916	3.779	17.818	4.500	6.916	6.038	1.681	9.513	5.380
ANTH-HC	29.101	22.343	18.395	83.894	9.952	38.178	37.738	12.111	65.920	23.024	36.267	33.536	13.997	66.681	23.674
NAT-HC	18.189	17.619	9.142	50.356	2.459	26.342	21.997	18.936	74.563	9.227	14.630	7.272	14.581	44.834	1.254
Sampling dates	June 19, 1995	June 26, 1995	July 4, 1995	July 16, 1995	July 23, 1995	July 18, 1996	Aug. 29, 1996				June 27, 1997	Aug. 20, 1997			
	June 20, 1995	June 27, 1995	July 5, 1995	July 17, 1995	July 24, 1995	July 22, 1996	Sept. 9, 1996				July 3, 1997	Aug. 26, 1997			
	June 21, 1995	June 28, 1995	July 6, 1995	July 18, 1995	July 25, 1995	Aug. 5, 1996	Sept. 23, 1996				July 19, 1997	Sept. 1, 1997			
	June 22, 1995	June 29, 1995	July 8, 1995	July 19, 1995	July 26, 1995	Aug. 7, 1996					July 21, 1997				
	June 23, 1995	June 30, 1995	July 10, 1995	July 20, 1995		Aug. 8, 1996					Aug. 2, 1997				
	June 24, 1995	July 1, 1995	July 11, 1995	July 21, 1995		Aug. 13, 1996					Aug. 8, 1997				
	June 25, 1995	July 3, 1995	July 15, 1995	July 22, 1995		Aug. 19, 1996					Aug. 14, 1997				

^aUnits are in ppbv. ND, not detected; s.d., standard deviation.

28 at SHEN (save a few interrupts due to failed sampling or analysis). In 1996 and 1997, samples were collected roughly once every 6 days at all three sites, with some exceptions. Despite a small relocation during 1997 at MACA, it does not seem to affect the proceeding discussion.

Let us first compare the variations for the three sites (Figures 4a–4c). The three hydrocarbon groups generally follow almost the same variation pattern with date. Among the three sites, MACA and GRSM have much in common in terms of the variation patterns for all the three groups in 3 years. For example, in 1995 the variation at both sites is more drastic than that in the other 2 years, especially for ALKENES. If we compare ALKENES with TOT-AROM for the 1995 data, the following pattern exists: prior to June 28, the concentrations of ALKENES are less than those of TOT-AROM; after June 29, both concentrations are almost the same. In 1996 both ALKANES and ALKENES peak, and TOT-AROM drops, around August 8 at both sites except that the concentrations of TOT-AROM are generally higher at GRSM. In 1997 both sites experience relative smooth variations for the three groups, and the concentrations of ALKENES are persistently higher than those in the other 2 years (the concentrations fluctuate around the 10 ppbv gridline, and most values are larger than those of TOT-AROM on the same date). From the above analysis we can conclude that anthropogenic compounds at MACA and GRSM varied similarly with date. This indicates that the two parks might have been influenced by the same hydrocarbon sources. From the topological locations (Figure 1) of these two parks, we may conclude that these two parks were under the same regional influence with regard to anthropogenic hydrocarbons.

In general, the variation pattern of all three groups at SHEN (Figure 4c) differs from that at the other parks. For all 3 years, ALKANES have the largest concentrations (except in 1995 when the suspicious compounds, isopentane and n-pentane, are taken out from the calculation of ALKANES in Figure 4c (top)), TOT-AROM has the second largest, and ALKENES have the least. In 1995, TOT-AROM has higher concentrations than that in the other 2 years, but the variation trend is the same as that for other groups. Compared with MACA and GRSM, the most significant characteristic of SHEN is that the concentrations of TOT-AROM are higher through all 3 years, and the concentrations of ALKENES are on the same level. This indicates that the anthropogenic sources of hydrocarbons at SHEN must have been different from those at MACA and GRSM.

3.2. Identification of Anthropogenic Hydrocarbons and Their Sources

Usually hydrocarbons in the atmosphere are classified as anthropogenic or biogenic, according to their origin. Traditionally, paraffins and aromatics are regarded as anthropogenic, and isoprene, pinenes, limonene, etc. are regarded as biogenic. Although this classification may be too arbitrary, since some paraffins and aromatics may also be produced by biogenic processes [Hewitt, 1999], in the following discussion we abide by this traditional classification and deal only with anthropogenic hydrocarbons.

3.2.1. Analysis of correlation coefficient between individual compounds and ANTH-HC. There are a very large number of different hydrocarbons in the atmosphere, and even the most advanced analytical techniques still have problems identifying each individual compound. For some compounds, coe-

Table 1b. Summary of Hydrocarbon Concentrations at Great Smoky Mountains National Park, Tennessee^a

Compound	1995				1996				1997						
	Mean	Median	s.d.	Minimum	Maximum	Mean	Median	s.d.	Minimum	Maximum	Mean	Median	s.d.	Minimum	Maximum
Ethene	0.656	0.639	0.623	ND	2.259	0.549	0.534	0.261	0.959	0.115	0.677	0.666	0.243	1.016	0.261
Acetylene	0.708	0.519	0.777	ND	3.464	0.653	0.582	0.318	1.136	0.256	0.953	0.990	0.413	1.556	0.300
Ethane	3.024	3.035	2.679	ND	9.227	4.415	3.919	1.767	9.125	2.683	3.322	3.045	1.214	6.037	1.866
Propene	0.666	0.555	0.377	0.322	1.709	0.466	0.348	0.468	1.944	0.238	4.312	4.891	1.548	5.578	1.642
Propane	2.086	1.945	1.335	0.095	4.502	2.817	2.163	1.586	6.811	1.146	2.358	2.012	0.760	3.628	1.478
Isobutane	0.382	0.325	0.190	0.117	0.842	0.922	0.467	1.587	5.897	0.148	0.983	0.895	0.427	1.811	0.492
1-Butene	0.163	0.151	0.169	ND	0.708	0.063	0.084	0.051	0.144	ND	0.026	ND	0.057	0.161	ND
n-Butane	0.944	0.859	0.423	0.357	1.830	1.155	1.199	0.629	2.577	0.223	1.266	1.363	0.337	1.643	0.604
<i>trans</i> -2-Butene	0.010	ND	0.034	ND	0.121	ND	ND	ND	ND	ND	0.681	0.907	0.479	1.182	ND
<i>cis</i> -2-Butene	0.049	ND	0.068	ND	0.197	ND	ND	ND	ND	ND	2.100	2.431	1.066	3.203	0.228
3-Methyl-1-butene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.345	0.369	0.212	0.766	ND
Isopentane	1.298	1.091	0.591	0.512	2.612	2.315	2.275	1.219	4.886	0.302	4.049	4.133	2.146	8.887	1.045
1-Pentene	0.026	ND	0.052	0.143	0.078	0.074	0.074	0.042	0.161	0.042	0.379	0.379	0.388	1.211	0.364
n-Pentane	0.556	0.474	0.213	0.248	1.080	0.703	0.643	0.472	1.882	0.149	1.757	1.255	2.054	7.531	0.364
Isoprene	15.204	13.992	8.147	3.928	31.116	10.248	7.198	8.745	24.390	1.031	18.385	16.360	12.279	39.270	2.057
<i>trans</i> -2-Pentene	ND	ND	ND	ND	ND	0.054	ND	0.109	0.301	ND	0.387	0.380	0.219	0.726	ND
<i>cis</i> -2-Pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.223	0.224	0.217	0.540	ND
2-Methyl-2-butene	0.044	ND	0.102	ND	0.309	0.007	ND	0.023	0.081	ND	0.278	0.327	0.118	0.418	ND
4-Methyl-1-pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.226	ND	0.296	0.666	ND
Cyclopentane	0.018	ND	0.087	ND	0.415	0.081	0.022	0.118	0.372	ND	0.292	0.317	0.147	0.494	ND
2-Methylpentane	0.350	0.265	0.390	ND	1.649	0.793	0.340	1.083	3.484	ND	3.311	3.594	1.702	5.922	0.592
3-Methylpentane	0.295	0.253	0.321	ND	1.428	0.603	0.510	0.676	2.326	ND	2.052	2.297	1.159	3.479	0.339
n-Hexane	0.254	0.268	0.145	ND	0.604	0.313	0.277	0.115	0.492	0.141	0.473	0.466	0.165	0.753	0.164
<i>cis</i> -3-Hexene	0.125	0.084	0.134	ND	0.474	0.140	0.139	0.082	0.252	ND	0.366	0.338	0.234	0.869	ND
Methylcyclopentane	0.071	ND	0.120	ND	0.434	0.096	0.092	0.057	0.200	ND	0.231	0.207	0.120	0.391	ND
2,4-Dimethylpentane	0.030	ND	0.092	ND	0.373	0.073	0.034	0.113	0.390	ND	0.310	0.290	0.153	0.632	0.126
Benzene	1.023	0.913	0.415	0.478	2.247	0.735	0.724	0.129	0.977	0.547	0.802	0.867	0.253	1.182	0.330
Cyclohexane	0.130	ND	0.333	ND	1.503	0.071	ND	0.108	0.260	ND	0.420	0.445	0.125	0.574	0.125
2,3-Dimethylpentane	0.071	ND	0.107	ND	0.425	0.337	0.343	0.246	0.826	ND	0.509	0.502	0.212	0.811	0.152
Heptane	0.142	0.160	0.133	ND	0.358	0.128	0.116	0.061	0.224	ND	0.178	0.151	0.099	0.321	ND
Methylcyclohexane	0.049	ND	0.103	ND	0.367	0.420	0.409	0.263	0.843	ND	0.324	0.335	0.079	0.434	0.166
2,3,4-Trimethylpentane	0.365	0.134	0.485	ND	1.708	0.189	0.214	0.141	0.387	ND	0.311	0.279	0.083	0.444	0.217
Toluene	1.214	0.871	0.991	0.468	4.912	2.109	0.781	4.230	15.493	0.389	1.682	1.709	0.723	2.916	0.543
n-Octane	0.151	0.074	0.236	ND	1.051	0.083	0.072	0.081	0.292	ND	0.151	0.165	0.080	0.258	ND
Ethylbenzene	0.316	0.289	0.132	0.137	0.626	0.289	0.269	0.137	0.526	ND	0.376	0.400	0.139	0.561	0.125
m-Xylene	0.559	0.502	0.252	ND	1.074	0.413	0.346	0.365	1.471	0.119	0.963	0.914	0.384	1.506	0.239
p-Xylene	0.296	0.281	0.170	ND	0.815	0.026	ND	0.048	0.121	ND	0.016	ND	0.051	0.162	ND
Styrene	0.188	0.110	0.231	ND	0.731	1.228	1.158	0.408	2.004	0.539	1.880	1.809	0.465	2.802	1.224
o-Xylene	0.973	0.963	0.336	0.459	1.622	0.268	0.203	0.197	0.836	0.059	0.552	0.516	0.244	1.053	0.227
Nonane	0.377	ND	0.711	ND	2.495	0.094	0.105	0.065	0.185	ND	0.282	0.241	0.112	0.452	0.154
Isopropylbenzene	0.091	0.074	0.111	ND	0.418	0.024	ND	0.045	0.123	ND	0.029	ND	0.039	0.088	ND
a-Pinene	1.105	1.042	0.370	0.562	1.972	0.668	0.557	0.469	1.738	ND	1.527	1.584	0.731	2.559	0.406
n-Propylbenzene	0.082	ND	0.147	ND	0.488	0.081	0.095	0.056	0.173	ND	0.086	0.103	0.053	0.138	ND
1,3,5-Trimethylbenzene	0.027	ND	0.064	ND	0.220	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
b-Pinene	0.256	0.253	0.184	ND	0.665	1.025	1.032	0.661	2.208	ND	1.343	1.419	0.429	1.855	0.678

1,2,4-Trimethylbenzene	0.145	ND	0.255	1.138	ND	16.646	15.612	3.939	26.173	9.749	1.061	0.889	0.508	2.371	0.628
n-Decane	0.414	0.285	0.380	1.509	ND	0.077	0.057	0.077	0.220	ND	0.685	0.537	0.445	1.584	0.256
Limonene	0.462	0.460	0.304	1.322	ND	0.181	0.107	0.260	0.938	ND	0.394	0.363	0.184	0.821	0.211
Undecane	0.756	0.515	0.784	2.976	0.092	0.283	0.255	0.202	0.800	ND	1.471	0.766	1.324	3.957	0.320
TNMHC	36.151	35.278	9.830	62.274	19.098	51.920	53.143	12.938	68.874	24.823	64.789	64.262	23.666	101.120	25.175
Class totals															
ALKANES	11.762	11.372	4.421	21.447	5.264	15.967	15.402	6.592	26.642	4.991	24.737	25.754	7.655	37.769	14.006
ALKENES	2.448	2.161	1.461	6.806	0.604	2.010	1.845	0.869	4.441	1.074	10.955	12.523	4.037	14.367	2.631
AROMATICS	0.534	0.477	0.462	1.731	ND	17.979	17.152	4.072	28.099	10.894	3.057	3.008	0.751	4.285	2.031
BTEX	4.381	4.095	1.758	9.969	2.283	3.841	2.441	4.383	17.434	1.271	4.392	4.284	1.583	7.184	1.627
PINENES	1.823	1.796	0.592	3.418	0.891	1.875	1.791	1.042	3.687	ND	3.264	3.247	0.715	4.344	2.414
TOT-AROMATICS	4.914	4.522	2.157	11.700	2.435	21.820	20.140	5.923	35.804	13.735	7.449	7.372	2.046	11.469	4.067
ANTH-HC	19.124	17.727	6.430	34.528	10.691	39.798	38.801	10.271	64.218	23.792	43.140	44.865	12.140	57.506	20.703
NAT-HC	17.027	15.647	8.220	32.017	5.113	12.123	8.803	9.368	26.160	1.031	21.649	19.397	12.697	43.614	4.471
Sampling dates	June 20, 1995	June 25, 1995	July 1, 1995	July 11, 1995	July 22, 1995	July 22, 1995	July 22, 1996	Aug. 12, 1996	Sept. 23, 1996		June 27, 1997	July 27, 1997			
	June 21, 1995	June 26, 1995	July 2, 1995	July 12, 1995	July 23, 1995	July 29, 1995	Aug. 19, 1996	Sept. 30, 1996			July 3, 1997	Aug. 2, 1997			
	June 22, 1995	June 27, 1995	July 3, 1995	July 15, 1995	July 24, 1995	Aug. 5, 1996	Aug. 26, 1996				July 9, 1997	Aug. 8, 1997			
	June 23, 1995	June 29, 1995	July 6, 1995	July 19, 1995	July 24, 1995	Aug. 7, 1996	Aug. 30, 1996				July 15, 1997	Aug. 14, 1997			
	June 24, 1995	June 30, 1995	July 10, 1995	July 21, 1995	July 24, 1995	Aug. 8, 1996	Sept. 19, 1996				July 21, 1997	Aug. 20, 1997			

^aUnits are in ppbv.

lution and misidentification are unavoidable. Nevertheless, compounds such as propane, isopentane, benzene, and toluene are thought to be precisely identifiable and quantifiable, and the validity of other compounds in the same data set can be checked against these compounds.

Henry *et al.* [1994] first suggested that the matrix of scatterplots of all compounds versus acetylene be used as a diagnostic tool to screen a data set. However, acetylene is one of the most challenging compounds to measure, and its concentration may be suspect in some cases. Lewis *et al.* [1998] further suggested using total nonmethane organic compounds (TNMHC) instead of acetylene to make a scatterplot matrix for all the identified PAMS target compounds. The basis of this method is that, if hydrocarbons in the atmosphere come from one dominant source or if the source composition is relatively stable over time, then the major constituent should have a linear relationship with TNMHC. For example, in an urban atmosphere, automotive exhaust dominates TNMHC, and the source composition is relatively stable since all sources are close to the affected atmosphere. One would expect compounds in urban areas, especially those that come primarily from vehicles, to be highly correlated with TNMHC, just as isopentane shows a very good relationship in their example. However, this expectation holds only where TNMHC source composition is stable. As far as rural atmosphere is concerned, TNMHC may arise from two or more major sources. Furthermore, source composition varies with wind direction and speed because most TNMHC components may have been transported from other areas. If the above method is used, one may expect that a well-behaved scatterplot cannot be obtained. Furthermore, in some cases the correlation between isoprene (the dominant biogenic compound) and TNMHC may be better than that between isopentane and TNMHC. Therefore the scatterplot method cannot be applied directly to the analysis of rural hydrocarbon data. In addition, the scatterplot method can result in a false conclusion. For example, if one compound dominates TNMHC, since TNMHC also includes this compound, this compound is guaranteed to have a well-behaved scatterplot. The problem here is that the individual compound is a member of the total; that is, there is no independent variable in the plot.

In order to avoid the above problems a different strategy is adopted in this study. Instead of showing a scatterplot matrix, Tables 3a–3c list statistically significant (except some of the most abundant compounds) correlation coefficients between individual compounds and ANTH-HC in descending order at each site for all 3 years. For calculations of the correlation coefficient for one compound, the concentration of this compound is subtracted from the total concentration of ANTH-HC. In other words, the correlation coefficient for one specific compound represents the correlation between this compound and all other anthropogenic compounds in consideration as a whole. If we consider ANTH-HC as the background anthropogenic hydrocarbons at a location, the correlation coefficient of one specific compound with ANTH-HC can be used as a measure to see whether this compound is a persistent component of ANTH-HC. On the other hand, if one compound has high mean concentration, but low correlation coefficient, then either this compound might have been contaminated during the process of sampling and/or analysis or the ANTH-HC influencing this location might have different compositions at different times.

For convenience of comparison, Table 4 lists the fingerprints

Table 1c. Summary of Hydrocarbon Concentrations at Shenandoah National Park, Big Meadows, Virginia^a

Compound	1995					1996					1997				
	Mean	Median	s.d.	Maximum	Minimum	Mean	Median	s.d.	Maximum	Minimum	Mean	Median	s.d.	Maximum	Minimum
Ethene	1.941	2.047	1.382	4.119	ND	0.968	0.836	0.298	1.769	0.586	0.697	0.786	0.304	1.185	0.093
Acetylene	2.222	0.636	3.913	15.125	ND	0.663	0.611	0.231	1.062	0.332	0.571	0.528	0.181	1.017	0.284
Ethane	4.476	4.015	3.652	16.427	ND	4.495	4.054	1.185	7.148	3.034	4.156	3.968	1.898	8.843	1.595
Propene	1.705	1.135	2.366	10.863	ND	1.153	0.431	1.919	6.141	0.249	0.423	0.421	0.168	0.756	0.127
Propane	3.693	3.597	2.282	8.111	ND	12.881	10.187	11.387	47.166	1.743	6.421	6.450	2.747	11.198	2.303
Isobutane	1.433	1.513	0.935	3.205	0.363	3.535	2.512	3.192	12.383	0.254	1.829	1.851	0.832	3.238	0.592
1-Butene	0.413	0.205	1.005	4.466	ND	0.144	0.102	0.119	0.434	ND	0.152	0.113	0.143	0.491	ND
n-Butane	8.065	1.231	22.452	92.604	ND	7.142	5.521	6.459	26.402	0.638	3.328	3.136	1.441	5.735	1.114
<i>trans</i> -2-Butene	0.032	ND	0.076	0.247	ND	ND	ND	ND	ND	ND	0.025	ND	0.069	0.240	ND
<i>cis</i> -2-Butene	0.133	ND	0.317	0.955	ND	0.062	ND	0.246	0.985	ND	0.057	ND	0.104	0.278	ND
3-Methyl-1-butene	0.041	ND	0.120	0.498	ND	0.044	ND	0.108	0.369	ND	0.053	ND	0.152	0.592	ND
Isopentane	491.493	429.500	372.203	1114.7	18.273	5.470	2.519	9.146	38.098	0.662	2.744	2.390	1.434	5.434	0.910
1-Pentene	0.422	0.338	0.425	1.764	ND	0.403	0.187	0.656	2.648	ND	1.089	0.883	0.975	2.637	ND
n-Pentane	118.280	114.456	79.757	256.95	5.846	2.296	0.827	4.384	17.717	ND	1.527	0.559	2.770	9.422	0.257
Isoprene	17.033	17.645	9.272	43.361	3.185	6.259	6.810	4.438	14.203	ND	10.085	6.470	9.954	33.012	0.365
<i>trans</i> -2-Pentene	0.257	ND	0.861	3.748	ND	0.289	0.221	0.310	0.758	ND	0.335	0.239	0.411	1.190	ND
<i>cis</i> -2-Pentene	0.269	ND	0.773	3.238	ND	0.009	ND	0.037	0.148	ND	0.142	ND	0.267	0.705	ND
2-Methyl-2-butene	0.386	0.193	0.665	2.367	ND	0.034	ND	0.090	0.346	ND	0.177	ND	0.296	0.895	ND
4-Methyl-1-pentene	0.056	ND	0.242	1.057	ND	ND	ND	ND	ND	ND	0.158	ND	0.324	1.051	ND
Cyclopentane	0.824	0.922	0.555	1.645	ND	0.286	ND	0.421	1.239	ND	0.187	ND	0.271	0.863	ND
2-Cyclopentane	3.266	3.314	2.897	9.054	0.194	0.811	0.419	1.114	4.152	0.166	3.086	2.628	2.292	7.434	0.404
3-Methylpentane	0.611	0.342	0.730	2.514	ND	1.086	1.148	0.572	2.179	ND	0.596	0.466	0.443	1.386	0.404
n-Hexane	0.530	0.464	0.273	1.286	0.223	0.480	0.450	0.232	1.147	0.170	0.402	0.351	0.216	0.996	0.181
<i>cis</i> -3-Hexene	0.526	0.473	0.342	1.153	ND	0.025	ND	0.055	0.162	ND	0.272	0.190	0.289	0.996	ND
Methylcyclopentane	0.331	0.184	0.501	1.782	ND	0.149	0.160	0.159	0.529	ND	0.193	0.160	0.179	0.680	ND
2,4-Dimethylpentane	0.203	ND	0.277	0.819	ND	0.058	ND	0.082	0.216	ND	0.193	0.120	0.224	0.686	ND
Benzene	1.930	1.752	1.560	7.560	0.502	0.969	1.001	0.176	1.261	0.678	0.968	0.720	0.439	1.720	0.466
Cyclohexane	0.230	0.216	0.191	0.716	ND	0.115	ND	0.189	0.497	ND	0.183	0.161	0.213	0.679	ND
2,3-Dimethylpentane	0.708	0.256	0.853	2.483	ND	0.365	0.327	0.444	1.750	ND	0.489	0.380	0.339	1.302	ND
Heptane	0.586	0.575	0.356	1.063	ND	0.168	0.140	0.099	0.376	ND	0.177	0.177	0.126	0.493	ND
Methylcyclohexane	0.735	0.323	2.061	9.155	ND	2.368	2.217	1.835	5.688	ND	1.954	1.809	0.639	3.173	1.150
2,3,4-Trimethylpentane	1.100	0.736	0.966	3.141	ND	0.294	0.057	0.415	1.209	ND	0.237	0.245	0.214	0.582	ND
Toluene	7.165	6.527	4.878	17.316	0.709	6.623	4.923	6.001	22.556	0.798	3.827	3.808	1.789	6.980	1.187
n-Octane	5.313	4.089	5.189	20.159	0.105	0.136	0.117	0.134	0.397	ND	0.221	0.220	0.150	0.511	ND
Ethylbenzene	4.180	2.964	2.932	11.787	0.450	0.871	0.786	0.449	1.820	0.347	0.794	0.704	0.381	1.711	0.307
m-Xylene	6.515	5.847	3.205	13.094	1.625	2.109	1.820	1.334	4.989	0.718	1.913	1.637	0.957	4.070	0.833
p-Xylene	3.629	1.650	4.478	17.043	ND	0.025	ND	0.102	0.406	ND	0.201	ND	0.255	0.676	ND
Styrene	6.889	5.809	5.221	17.584	0.396	1.968	1.982	0.973	4.255	0.737	2.007	1.483	1.490	6.558	0.858
o-Xylene	7.367	7.549	2.787	12.254	1.778	1.905	1.737	0.889	4.127	0.905	1.201	1.127	0.343	1.904	0.750
Nonane	5.145	3.245	5.481	20.546	ND	0.222	0.193	0.198	0.692	ND	3.337	2.763	2.014	6.831	0.740
Isopropylbenzene	1.885	1.787	1.358	3.959	0.173	0.087	0.094	0.087	0.244	ND	1.833	1.985	1.055	4.731	0.118
a-Pinene	30.067	29.353	24.679	82.381	1.379	1.356	1.146	0.873	3.854	0.344	1.833	1.985	1.055	4.169	0.484
n-Propylbenzene	1.236	1.046	0.919	3.018	0.118	0.160	0.161	0.144	0.470	ND	0.450	0.416	0.250	0.977	ND
1,3,5-Trimethylbenzene	0.554	0.340	0.594	2.428	ND	0.038	ND	0.105	0.338	ND	0.217	0.259	0.144	0.389	ND
b-Pinene	2.359	1.797	2.619	9.763	ND	1.184	0.977	0.854	3.025	0.263	0.719	0.711	0.354	1.411	0.172

1,2,4-Trimethylbenzene	3.399	1.962	2.991	8.591	0.155	0.856	0.839	0.428	1.666	0.236	1.619	1.557	0.631	2.559	0.424
n-Decane	5.025	3.820	4.200	16.545	0.688	0.475	0.292	0.426	1.669	0.109	2.131	1.956	1.167	4.287	0.473
Limonene	6.300	2.619	7.010	25.601	0.097	0.199	0.171	0.191	0.775	ND	0.234	0.224	0.185	0.605	ND
Undecane	5.925	5.451	4.376	13.918	0.639	0.850	0.753	0.646	1.844	ND	0.436	0.271	0.434	1.175	ND
TNMHC	766.882	724.427	524.66	1629.5	67.634	72.084	63.047	39.352	163.028	32.340	64.436	60.285	30.38	129.483	26.278
Class totals															
ALKANES	657.97	597.04	471.72	1440.0	33.64	43.681	34.717	28.554	110.939	14.758	33.828	31.955	15.217	66.712	13.659
ALKENES	8.40	7.07	6.88	31.60	1.57	3.795	3.120	2.084	8.843	1.939	4.152	4.128	2.330	9.644	1.608
AROMATICS	13.96	15.16	9.91	31.82	0.97	3.108	2.915	1.392	5.566	1.121	4.679	4.453	2.084	10.134	1.917
BTEX	30.79	29.91	16.35	69.03	7.20	12.502	10.660	8.007	32.394	4.292	8.904	8.596	3.549	14.400	4.231
PINES	38.73	35.05	32.22	111.50	2.49	2.740	2.692	1.252	5.554	1.035	2.787	2.792	1.381	5.795	0.719
TOT-AROMATICS	44.75	42.46	25.83	100.85	8.17	15.610	13.491	9.051	36.874	5.922	13.583	12.744	5.376	24.534	6.147
ANTH-HC	711.1	674.5	497.0	1526.8	43.4	63.085	51.092	37.620	153.308	22.778	51.564	47.988	21.698	92.382	23.131
NAT-HC	55.8	44.6	34.5	131.4	15.6	8.998	9.789	4.818	16.458	1.035	12.871	9.704	10.942	37.101	1.089
Sampling dates	July 14, 1995	July 22, 1995	July 28, 1995	Sept. 18, 1995		July 2, 1996	Aug. 7, 1996				June 4, 1997	July 3, 1997	Aug. 8, 1997		
	July 16, 1995	July 23, 1995	Aug. 1, 1995			July 8, 1996	Aug. 13, 1996				June 6, 1997	July 9, 1997	Aug. 14, 1997		
	July 17, 1995	July 24, 1995	Aug. 7, 1995			July 16, 1996	Aug. 19, 1996				June 9, 1997	July 15, 1997	Aug. 20, 1997		
	July 18, 1995	July 25, 1995	Aug. 13, 1995			July 20, 1996	Aug. 25, 1996				June 15, 1997	July 21, 1997	Aug. 26, 1997		
	July 19, 1995	July 26, 1995	Aug. 19, 1995			July 26, 1996	Aug. 31, 1996				June 21, 1997	July 27, 1997	Aug. 2, 1997		
	July 20, 1995	July 27, 1995	Aug. 25, 1995			Aug. 1, 1996	Sept. 6, 1996				June 27, 1997	Aug. 2, 1997			

^aUnits are in ppbv.

of nonmethane hydrocarbons of major anthropogenic sources. Most of the hydrocarbons listed in Tables 1a–1c are listed here. The values in the table are the weight percent of each component of the total nonmethane organic compounds. Eight major sources modified from *Fujita et al.* [1995] are included.

At the location of a source the correlation coefficient of any component emitted by this source should be equal to one regardless of component reactivity because no reaction has taken place. However, assuming that the dilute effect of air is the same for all components, then the ANTH-HC of the air mass contains increasingly fewer reactive compounds after the air mass is transported some distance because the more reactive hydrocarbons are removed at a faster rate than the less reactive ones during transport. Thus, if two compounds with different reactivity are emitted at the source, initially both should show similar correlation with ANTH-HC; yet the farther the air mass moves away from the source, the worse the correlation of the more reactive one with ANTH-HC is relative to that of the less reactive one. Therefore, through cross-examination of the correlation coefficient and the mean concentration of one compound, when compared with the fingerprints of hydrocarbons in major sources, one can infer the data validity of major components, source contribution, and air mass age.

As expected, Tables 3a–3c indicate that some aromatics and alkanes, which are considered to be anthropogenic compounds, have higher correlation coefficients with ANTH-HC than do biogenic compounds. However, the correlation coefficients of isoprene with ANTH-HC are near zero or negative because isoprene is not a member of ANTH-HC. When one compares Table 2 with Table 3a for MACA, in 1995 most of the anthropogenic compounds listed in Table 2 do not show significant correlation with ANTH-HC except toluene (0.6089), isopentane (0.5159), and propane (0.3872). The same situation exists for 1996 data: among all the abundant anthropogenic compounds, only styrene (0.8806) significantly correlates with ANTH-HC. However, styrene is suspected to coelute with another compound, and so its concentration is unreliable. However, the 1997 data show a different view, in which propene, ethane, 2-methylpentane, 3-methylpentane, and isopentane show significant correlation with ANTH-HC (from 0.6035 for ethane to 0.9001 for isopentane; the correlation coefficient for propane, 0.5659, is just beyond the significant value: 0.576 at 5% significant level for a degree of freedom of 10). This may suggest that the anthropogenic hydrocarbon sources that affected MACA in 1995 and 1996 are more complex than those in 1997 during the sampling period. Some compounds, such as ethylbenzene, toluene, and n-hexane, persistently show higher correlation coefficients through all 3 years, even though their concentration might be comparatively lower than others. In Table 3a the obvious feature is that in 1997, as opposed to previous years, some alkene compounds such as *cis*-2-butene, propene, and ethene show strong correlation with ANTH-HC. In fact, the mean concentration of propene is also significantly large (3.794 ppbv), making it the most abundant anthropogenic compound (Table 2) in 1997. Considering that the lifetimes of these alkene compounds in the atmosphere are less than 1 day [Warneck, 1988], one may conclude that the major anthropogenic hydrocarbon sources that affect the site in 1997 are closer to the site than they are in the previous years. In Table 4, propene is emitted mainly by two sources: automobile exhaust and liquefied petroleum gas. If automobile exhaust is the major source in 1997, then ethene should show a higher mean con-

Table 2. Most Abundant Compounds in Concentration at Each Site^a

1995		1996		1997	
Compound	Mean	Compound	Mean	Compound	Mean
<i>Mammoth Cave National Park</i>					
isoprene	15.637	isoprene	22.802	isoprene	11.736
undecane	4.704	isopentane	5.686	propene	3.794
propane	3.346	ethane	5.647	ethane	3.660
ethane	2.328	propane	4.196	propane	2.987
isopentane	1.907	1,2,4-trimethylbenzene	3.862	2-methylpentane	2.714
n-butane	1.889	2-methylpentane	2.770	isobutane	1.907
isobutane	1.566	styrene	1.924	3-methylpentane	1.780
toluene	1.396	n-butane	1.777	styrene	1.757
limonene	1.323	a-pinene	1.640	isopentane	1.660
ethene	1.244	b-pinene	1.336	1,2,4-trimethylbenzene	1.621
<i>Great Smoky Mountains National Park</i>					
isoprene	15.204	1,2,4-trimethylbenzene	16.646	isoprene	18.385
ethane	3.024	isoprene	10.248	propene	4.312
propane	2.086	ethane	4.415	isopentane	4.049
isopentane	1.298	propane	2.817	ethane	3.322
toluene	1.214	isopentane	2.315	2-methylpentane	3.311
a-pinene	1.105	styrene	1.228	propane	2.358
benzene	1.023	n-butane	1.155	<i>cis</i> -2-butene	2.100
o-xylene	0.973	b-pinene	1.025	3-methylpentane	2.052
n-butane	0.944	isobutane	0.922	styrene	1.880
undecane	0.756	toluene	0.901	n-pentane	1.757
<i>Shenandoah National Park</i>					
isopentane	491.493	propane	12.881	isoprene	10.085
n-pentane	118.280	n-butane	7.142	propane	6.421
a-pinene	30.067	toluene	6.623	ethane	4.156
isoprene	17.033	isoprene	6.259	toluene	3.827
n-butane	8.065	isopentane	5.470	nonane	3.337
o-xylene	7.367	ethane	4.495	n-butane	3.328
toluene	7.165	isobutane	3.535	2-methylpentane	3.086
styrene	6.889	methylcyclohexane	2.368	isopentane	2.744
m-xylene	6.515	n-pentane	2.296	n-decane	2.131
limonene	6.300	m-xylene	2.109	styrene	2.007

^aUnits are in ppbv.

centration than propene because of its higher emission rate. However, the mean concentration of propene is ~10 times higher than that of ethene at both locations. Therefore liquefied petroleum gas must constitute a higher component of the ANTH-HC sources in 1997 at MACA and GRSM than that in other years.

The situations at GRSM are very similar to those at MACA, albeit with some subtle differences. In 1996, 1,2,4-trimethylbenzene is the most abundant compound (mean concentration of 16.65 ppbv in Table 2), but it does not correlate with ANTH-HC at all. Unless 1,2,4-trimethylbenzene can be produced by a biogenic process like isoprene (unlikely), its concentration is suspect. The same problem shows up at MACA as well in both 1996 and 1997: it is among the top 10 most abundant compounds, but its correlation with ANTH-HC both years is not significant. Therefore the data for 1,2,4-trimethylbenzene in this data set cannot be used.

The situations at SHEN are quite different. First, most of the abundant anthropogenic compounds in Table 2 also have large correlation coefficients in Table 3c. Exceptions include n-butane in 1995, isopentane, ethane, and methylcyclohexane in 1996, and styrene in 1997. Second, if we ignore the problematic 1995 data temporarily, and compare the 1996 and 1997 data in Table 3c top down, most of the compounds that show upper high correlation coefficients in 1996 show high coefficients in 1997 as well. This means that the compositions of the

anthropogenic hydrocarbon sources that affected SHEN are very similar in 1996 and 1997. In fact, if isopentane and n-pentane, the most problematic compounds in 1995, are excluded, many other compounds in 1995 also resemble the other 2 years' data. This signifies that the ANTH-HC sources that affect SHEN are consistent for the 3 years studied. Even though toluene has significantly higher mean concentrations persistently in all 3 years compared with its concentration at other sites, since it highly correlates with ANTH-HC at this site, the validity of toluene concentration is not suspect.

Next, let us examine the correlation coefficients of some selected compounds. First, let us compare isopentane with propane in Tables 3a–3c. At MACA and GRSM the correlation coefficients of isopentane are always larger than those of propane in all 3 years. At SHEN, due to the problem of isopentane mentioned above for 1995, we ignore the 1995 data. The correlation coefficients of propane are always larger than that of isopentane in 1996 and 1997; but in the other two sites the correlation coefficients are always lower in all 3 years. Second, let us look at benzene versus toluene. At MACA and SHEN the correlation coefficients of toluene are always larger than those of benzene, but at GRSM the relationship is reversed. As Table 4 shows, propane comes mainly from natural gases (CNG, GNG, and LPG), but isopentane comes mainly from automotive exhaust, liquid gasoline, and gasoline vapor. If automotive exhaust is the major source at a location, then

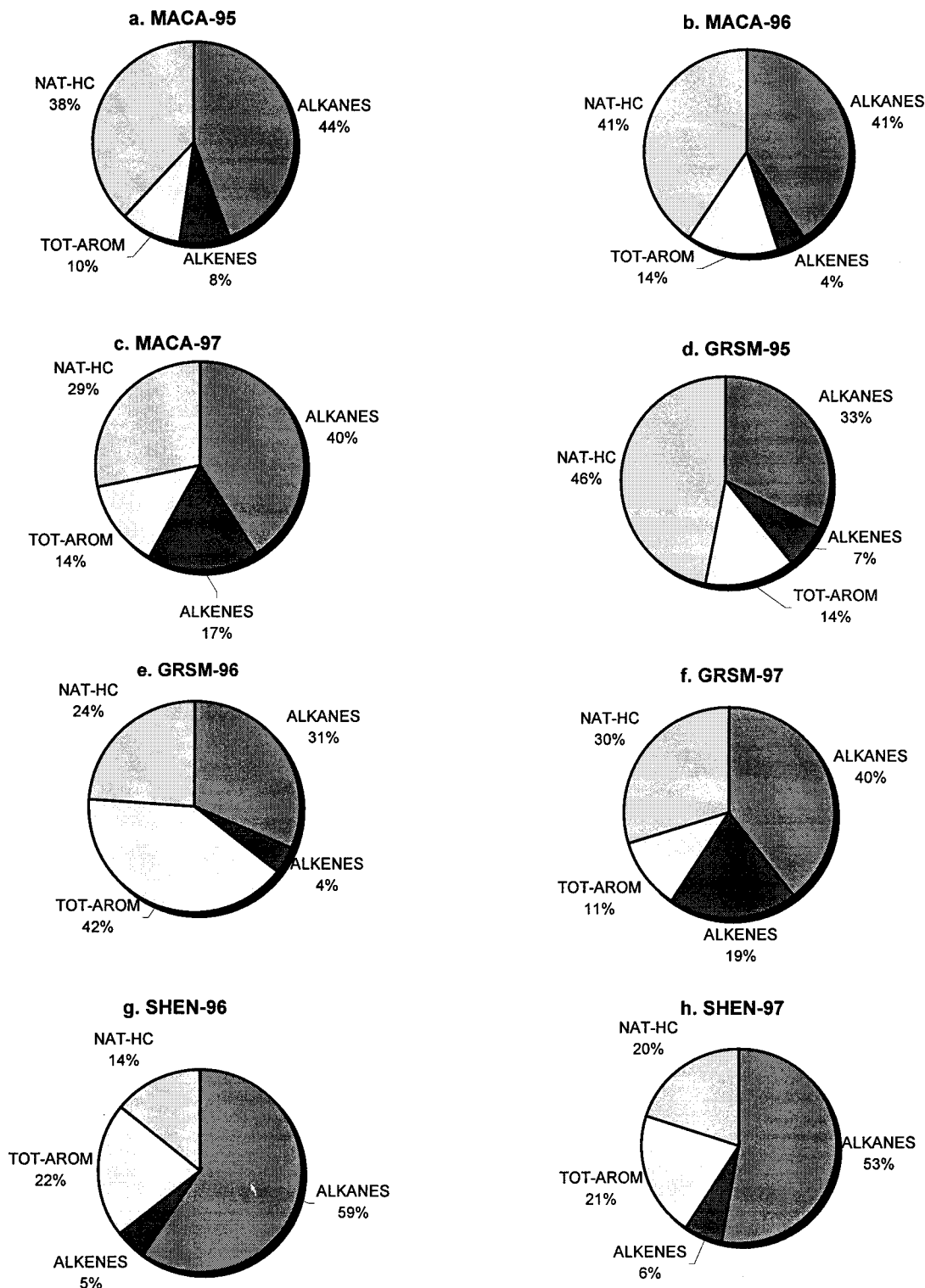


Figure 2. Fractional contribution by ppbv concentration of various classes of hydrocarbons to the total.

the correlation for isopentane should be better than that for propane. On the basis of the above argument we qualitatively conclude that at MACA and GRSM automotive exhaust makes a larger contribution than it does at SHEN. Benzene and toluene are emitted mainly by automobile exhaust and gasoline, and in these sources the two compounds are always produced together. Another major source of toluene is solvent

emissions, especially from industrial coating (Table 4). If the major sources are automobile exhaust and gasoline, the correlation coefficients of both compounds should be similar. In fact, in most cases, both significantly correlate with ANTH-HC. However, because of the filter effect of the atmosphere, their correlation and relative concentration change. For example, the lifetime of benzene is over 5 times greater than that of

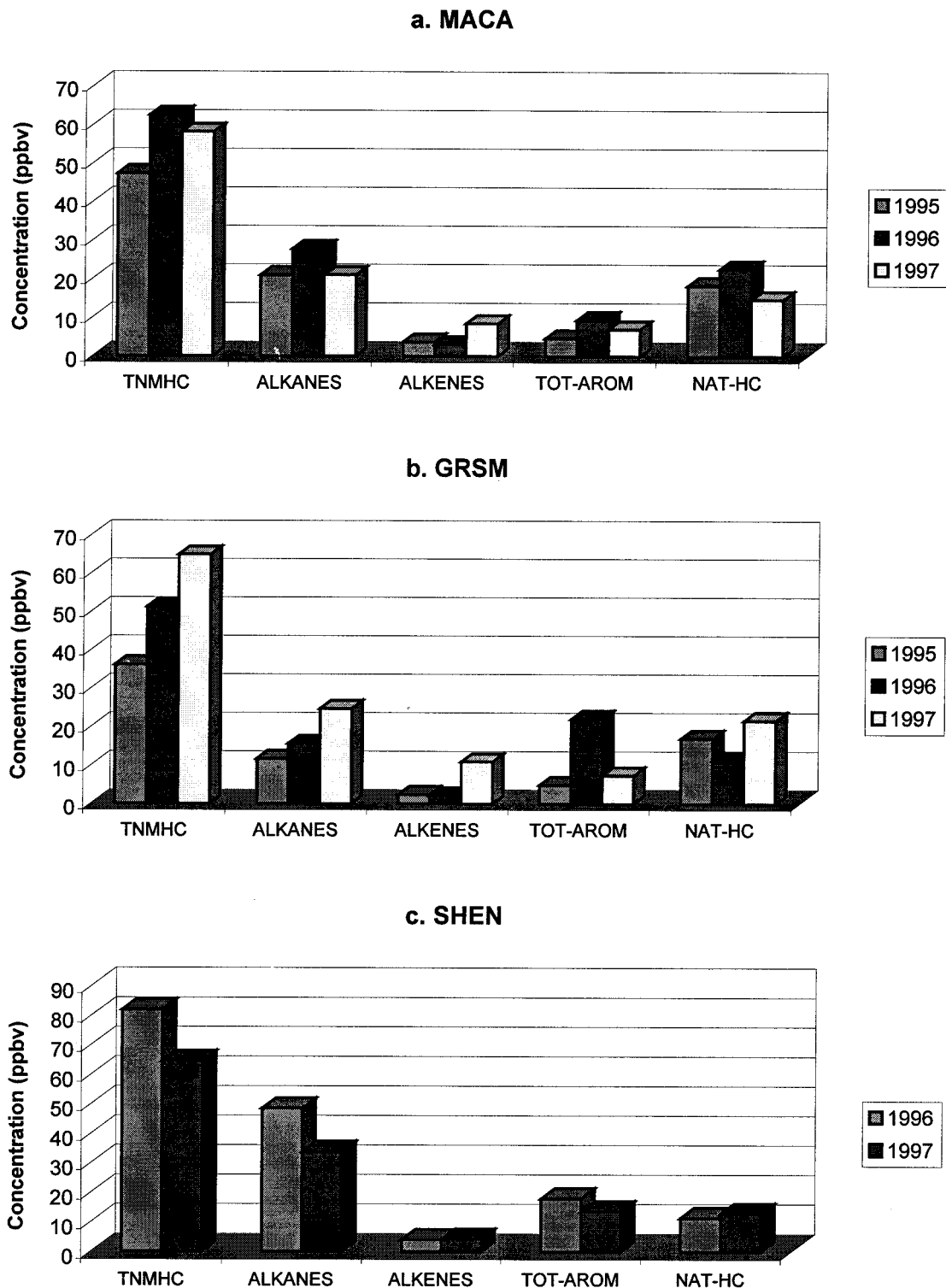


Figure 3. Variations of different classes of hydrocarbons at each site with year: (a) Mammoth Cave National Park; (b) Great Smoky Mountains National Park; (c) Shenandoah National Park.

toluene [Warneck, 1988]. Near the source, because toluene has a larger emission rate than does benzene, its correlation with ANTH-HC is better than that of benzene, and this is the case at MACA and SHEN. When the air mass travels some distance, as argued above, the correlation of toluene with ANTH-HC becomes worse than that of benzene, and this is the case at GRSM. The larger correlation coefficients and higher

mean concentrations of toluene at SHEN compared with benzene strongly signify that there is a large contribution of solvent source.

On the basis of the above analysis the following preliminary conclusions emerge: (1) MACA and GRSM are affected by the same regional anthropogenic hydrocarbon sources, and the age of air mass is older at GRSM than at MACA. (2) In addition

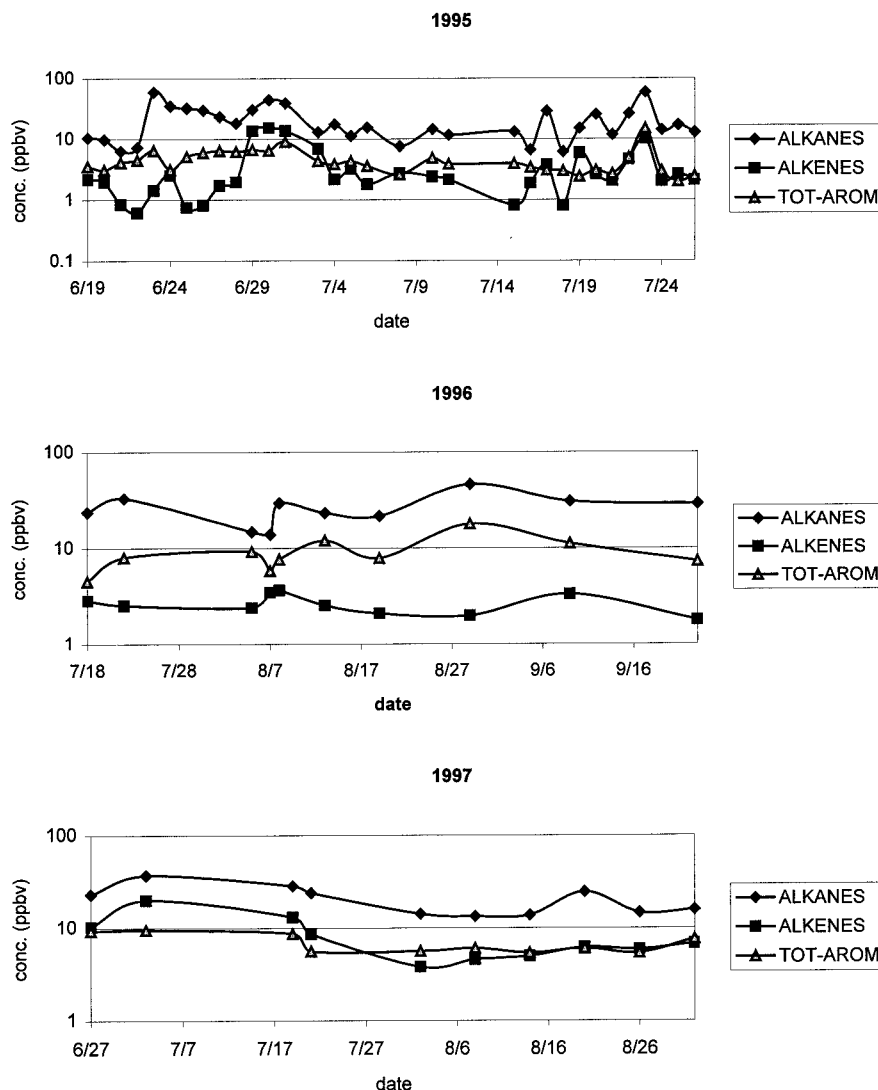


Figure 4a. Variation of HC group concentrations with date at MACA.

to automobile exhaust, contributions from other sources are suggested. The 1997 data at MACA and GRSM suggest a local contribution from liquefied petroleum gas. Data for 3 years at SHEN suggest significant contribution from solvent to the anthropogenic hydrocarbons.

3.2.2. Correlation and ratio analysis based on chemical reactivity. In order to further investigate the source composition of hydrocarbons and to differentiate between local and transported sources, the correlation coefficients between some compounds and the ratio of their concentrations were examined. Because of the filter effect of the atmosphere mentioned above, during long-range transport the correlation and concentration ratio between each other change. If two compounds are produced by local automobile exhaust, a large correlation coefficient (approaching 1) is expected between them, and the ratio of their concentrations is close to the ratio of their emissions. If they are transported from a remote location, the correlation coefficient is expected to be less, and the ratio of their concentrations is expected to be other than unity.

Since benzene and toluene are emitted together by automobile exhaust and gasoline, and are the major sources for anthropogenic hydrocarbons in urban areas, these two com-

pounds are analyzed first. Assuming that the sole sink for benzene and toluene is the reaction with OH and both reactions are first order, then the reaction rates can be expressed as

$$d[\text{ben}]/dt = -k_{\text{OH}}^{\text{ben}}[\text{ben}]$$

$$d[\text{tol}]/dt = -k_{\text{OH}}^{\text{tol}}[\text{tol}].$$

Solving, we can get

$$\ln [\text{ben}] - \ln [\text{ben}]_0 = -k_{\text{OH}}^{\text{ben}}t \quad (1)$$

$$\ln [\text{tol}] - \ln [\text{tol}]_0 = -k_{\text{OH}}^{\text{tol}}t. \quad (2)$$

Letting $r = [\text{ben}]/[\text{tol}]$, $r_0 = [\text{ben}]_0/[\text{tol}]_0$, (1)–(2), we have

$$r = r_0 \exp((k_{\text{OH}}^{\text{tol}} - k_{\text{OH}}^{\text{ben}})t) \quad (3)$$

where

[ben] concentration of benzene at time t ;
 [tol] concentration of toluene at time t ;
 [ben]₀ initial concentration of benzene;
 [tol]₀ initial concentration of toluene.

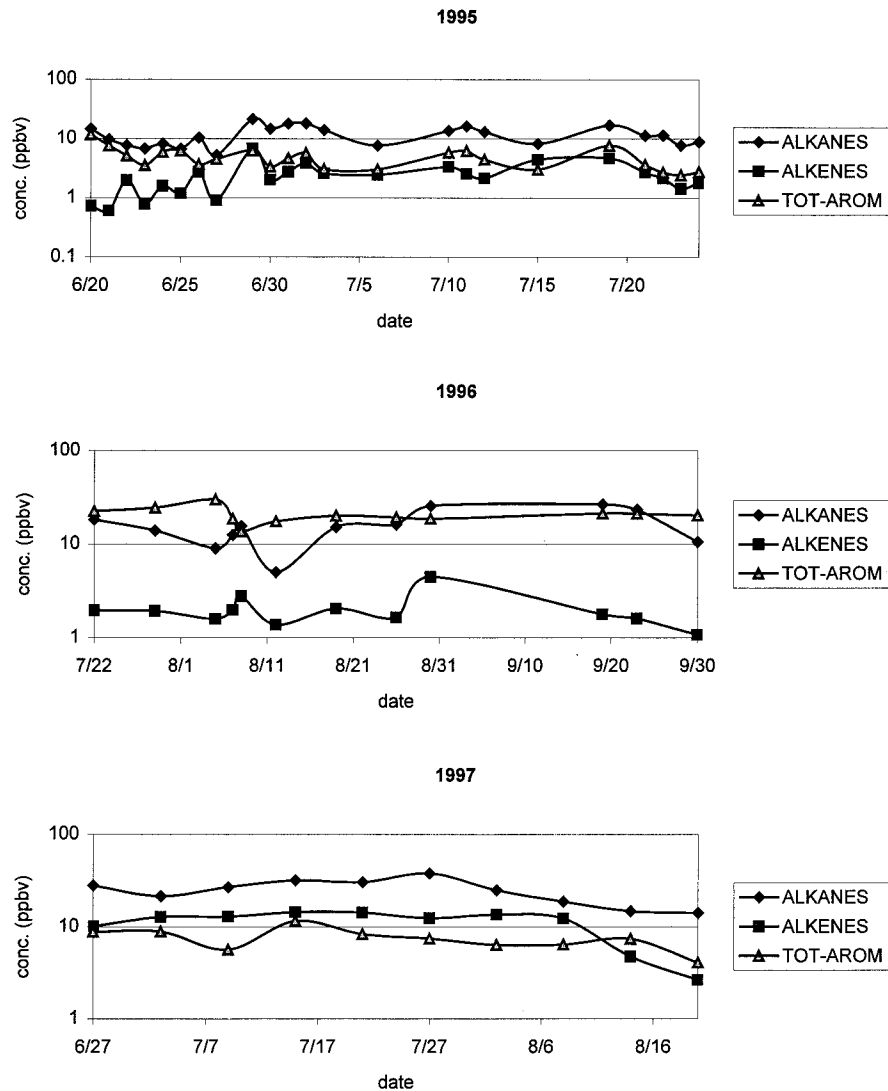


Figure 4b. Variation of HC group concentrations with date at GRSM.

Using (3), we plot the variation of benzene to toluene with time for three different anthropogenic sources (Table 4) in Figure 5. If benzene and toluene come from any of these three sources, then the ratio should be within the upper and lower curves (the literature reveals some discrepancies between fingerprints of hydrocarbons; here the ratio can be viewed only as a rough estimate). Table 5 lists the benzene/toluene ratio at all three sites for the 3 years. At MACA and GRSA the mean values are 0.505 to 1.139, all within the upper and lower curves. The mean value from several U.S. cities [Warneck, 1988; Spicer *et al.*, 1996; Sexton and Westberg, 1984] is about 0.400, similar to the gasoline vapor line in Figure 5. If hydrocarbons are transported from surrounding cities, then average transport time at these two locations is from several to 40 hours. Note that the transport time in Figure 5 corresponds to transport during active photochemical processes at daytime; the actual transport time may be much longer than estimated here. At both locations the average ratios in 1995 and 1996 are almost 2 times larger than those in 1997, suggesting that local AHTH-HC sources contribute more heavily in 1997 than in the other two years. However, the ratios at SHEN are all small, some even lower than the initial value from any of the three

sources mentioned above. Even assuming a fresh urban ratio of 0.400, on average the ratio at SHEN is about 7% lower in 1995 and about 30% lower in 1996 and 1997. Assuming a moderately aged air mass (as the case in 1996 at GRSM), then the ratio at SHEN is more than 50% lower than the assumed values in any of the years concerned. This can be explained only by contribution from another source that emits large amounts of toluene, such as solvent. Of course, benzene and toluene concentrations may be the combined result of local and distant sources, which is difficult to deconvolute with the methods suggested here.

Table 6 lists the correlation coefficients between benzene and toluene and between toluene and *m,p*-xylene for all three sites in the 3 years. The correlation coefficients between toluene and *m,p*-xylene are more consistent than those between benzene and toluene because each has similar sources and reactivity. The correlation coefficients between benzene and toluene are highest on average at MACA, followed by GRSM, then SHEN. This may reflect the source compositions and the age of the air mass at each location. The same conclusion can be reached as for the concentration variation of selected compounds; that is, MACA and GRSM might reflect similar re-

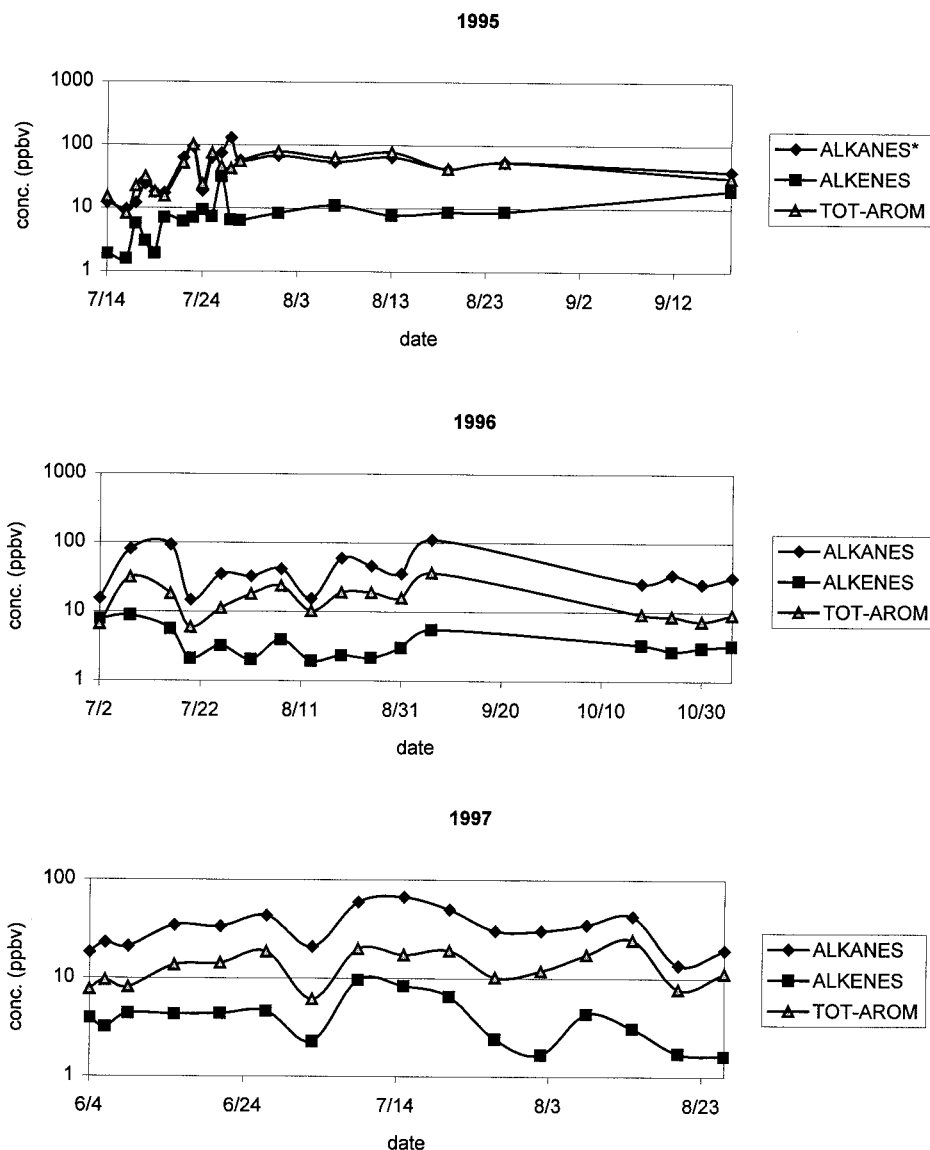


Figure 4c. Variation of HC group concentrations with date at SHEN. (Asterisk indicates that for the alkanes group in 1995, isopentane and n-pentane are not included.)

gional influence with regard to ANTH-HC, with the impact on MACA being the stronger. The poor correlation at SHEN indicates that benzene and toluene have different origin, at least for some portion.

Assuming chemistry processes to be the only sink for hydrocarbons, the relationship between some principal components can be further evaluated [Parrish *et al.*, 1992; Rudolph *et al.*, 1990]. Here we select isopentane, benzene, and toluene for analysis. Again, it is assumed that these compounds react only with OH in atmosphere and that all reactions are first order. The following relationship obtains

$$\ln ([\text{iso}]/[\text{ben}]) = s'_0 + (k_{\text{OH}}^{\text{ben}} - k_{\text{OH}}^{\text{iso}})t \quad (4)$$

$$\ln ([\text{tol}]/[\text{ben}]) = s_0 + (k_{\text{OH}}^{\text{ben}} - k_{\text{OH}}^{\text{tol}})t \quad (5)$$

where iso is isopentane and $s'_0 = \ln ([\text{iso}]_0/[\text{ben}]_0)$, $s_0 = \ln ([\text{tol}]_0/[\text{ben}]_0)$ are the initial ratios for toluene/benzene and isopentane/benzene, respectively (called source factors).

After rearrangement, from (4) and (5) we obtain the following expression:

$$\ln ([\text{iso}]/[\text{ben}]) = C + \{(k_{\text{OH}}^{\text{ben}} - k_{\text{OH}}^{\text{iso}})/(k_{\text{OH}}^{\text{ben}} - k_{\text{OH}}^{\text{tol}}) - k_{\text{OH}}^{\text{tol}}\} \ln ([\text{tol}]/[\text{ben}]) \quad (6)$$

where $C = s'_0 - s_0(k_{\text{OH}}^{\text{ben}} - k_{\text{OH}}^{\text{iso}})/(k_{\text{OH}}^{\text{ben}} - k_{\text{OH}}^{\text{tol}})$ is a constant determined by the source factors and reaction coefficients.

The coefficient in (6) is $\{(k_{\text{OH}}^{\text{ben}} - k_{\text{OH}}^{\text{iso}})/(k_{\text{OH}}^{\text{ben}} - k_{\text{OH}}^{\text{tol}}) - k_{\text{OH}}^{\text{tol}}\}$, which is 0.3654 under standard atmospheric conditions (298°K and 1 atm). Plotting the relationship between $\ln ([\text{iso}]/[\text{ben}])$ and $\ln ([\text{tol}]/[\text{ben}])$, we should get a line with slope of 0.3654, and intercept C determined by the source factors s_0 and s'_0 . For example, under standard atmospheric conditions, for automobile exhaust, $C = -0.24$, for gasoline, $C = 2.43$, and for gasoline vapor, $C = 1.88$. Figures 6a to 6c are plotted using the actual data from the three monitoring sites. Slopes vary from 0.3303 at MACA to 0.3822 at GRSM, showing good

Table 3a. Correlation Coefficients Between Individual Compound and ANTH-HC in Decreasing Order at MACA^a

Compound	1995	Compound	1996	Compound	1997
ethylbenzene	0.7688	toluene	0.8957	n-butane	0.9474
cyclohexane	0.7047	styrene	0.8806	<i>cis</i> -2-butene	0.9228
heptane	0.6896	n-octane	0.8789	3-methyl-1-butene	0.9201
methylcyclopentane	0.6666	2,4-dimethylpentane	0.8719	toluene	0.9166
3-methyl-1-butene	0.6522	n-decane	0.8430	isopentane	0.9001
n-octane	0.6327	2,3,4-trimethylpentane	0.8184	3-methylpentane	0.8749
2-methylpentane	0.6167	n-hexane	0.8164	ethylbenzene	0.8568
toluene	0.6089	nonane	0.7912	propene	0.8413
n-hexane	0.6025	n-propylbenzene	0.7821	n-octane	0.8408
1-butene	0.5837	benzene	0.7726	m-xylene	0.8317
o-xylene	0.5350	ethylbenzene	0.7716	b-pinene	0.8296
1,2,4-trimethylbenzene	0.5250	isopropylbenzene	0.7623	2-methylpentane	0.8033
isopentane	0.5159	m-xylene	0.7560	n-pentane	0.7865
methylcyclohexane	0.4928	cyclohexane	0.7131	methylcyclohexane	0.7860
2,4-dimethylpentane	0.4784	undecane	0.7089	n-hexane	0.7793
benzene	0.4758	o-xylene	0.6749	ethene	0.7688
n-propylbenzene	0.4757	1-butene	0.6510	1,3,5-trimethylbenzene	0.7628
cyclopentane	0.4694	limonene	0.6411	nonane	0.7360
isopropylbenzene	0.4480	1-pentene	0.6338	benzene	0.6985
m-xylene	0.4270	isopentane	0.1847	undecane	0.6984
limonene	0.4155	propane	-0.2891	heptane	0.6699
p-xylene	0.3874	isoprene	-0.8895	ethane	0.6035
propane	0.3872			propane	0.5659
isoprene	0.1377			isoprene	-0.4278

^aHere the concentration of the individual compound is subtracted from the concentration of ANTH-HC (the same in Tables 3a and 3b).

agreement with the theoretical value. Because OH radicals are generated by photochemical processes in the atmosphere, the above result means that the major pathway for destruction of these compounds in atmosphere is by photochemical processes. The intercepts in Figures 6a and 6b, small negative values, indicate that MACA and GRSM have similar sources: principally, for the three compounds studied, automobile exhaust. From the C values and intercepts above, the contribution from automobile exhaust can be estimated. Assuming that the contribution of automobile exhaust is equal to x , the contribution from gasoline and gasoline vapor is equal to $1 - x$,

and, since the C values of gasoline and gasoline vapor are similar and so can be averaged, the following holds:

$$C_{\text{auto}}x + C_a(1 - x) = \text{intercept} \quad (7)$$

where C_{auto} is the C value of automobile exhaust; C_a is the average C value of gasoline and gasoline vapor, and intercept is taken from Figures 6a to 6c.

Plugging in the C values and intercepts from Figures 6a to 6b, the calculated contribution of automobile exhaust for the three compounds studied at MACA and GRSM is all over 90%, assuming that the three sources are the only possible

Table 3b. Correlation Coefficients Between Individual Compound and ANTH-HC in Decreasing Order at GRSM

Compound	1995	Compound	1996	Compound	1997
n-pentane	0.8210	methylcyclohexane	0.8160	3-methylpentane	0.8626
p-xylene	0.7099	1-pentene	0.7226	benzene	0.8285
isopentane	0.7023	isopentane	0.6989	n-hexane	0.8274
benzene	0.6931	heptane	0.6603	2-methylpentane	0.8249
2-methylpentane	0.6713	cyclohexane	0.6218	ethene	0.8198
2,4-dimethylpentane	0.6680	nonane	0.5872	ethylbenzene	0.8069
ethene	0.6302	propane	0.5533	<i>cis</i> -2-butene	0.8020
n-butane	0.5711	n-hexane	0.5490	propene	0.7978
2,3-dimethylpentane	0.5465	n-propylbenzene	0.5319	n-octane	0.7726
n-propylbenzene	0.5136	benzene	0.3626	toluene	0.7694
1-pentene	0.4820	toluene	0.3336	cyclohexane	0.7678
<i>trans</i> -2-butene	0.4699	isoprene	-0.7748	a-pinene	0.7644
n-hexane	0.4693			m-xylene	0.7600
3-methylpentane	0.4217			isopentane	0.7446
propene	0.4180			methylcyclohexane	0.7420
methylcyclopentane	0.4002			cyclopentane	0.7313
toluene	0.2162			methylcyclopentane	0.7282
propane	0.1927			<i>trans</i> -2-butene	0.7045
isoprene	-0.8113			acetylene	0.6479
				2,3-dimethylpentane	0.6413
				<i>trans</i> -2-pentene	0.6217
				<i>cis</i> -3-hexene	0.5964
				propane	0.4276
				isoprene	-0.3203

Table 3c. Correlation Coefficients Between Individual Compound and ANTH-HC in Decreasing Order at SHEN

Compound	1995	Compound	1996	Compound	1997
isopropylbenzene	0.9804	<i>trans</i> -2-butene		isobutane	0.9282
n-pentane	0.9694	isobutane	0.9457	toluene	0.9109
n-propylbenzene	0.9622	ethylbenzene	0.9246	n-butane	0.9060
isopentane	0.9567	toluene	0.9228	n-decane	0.8928
cyclopentane	0.9268	m-xylene	0.8897	propane	0.8845
styrene	0.9235	cyclohexane	0.8804	limonene	0.8824
isobutane	0.9114	n-octane	0.8555	isopropylbenzene	0.8771
m-xylene	0.9044	n-propylbenzene	0.8498	<i>cis</i> -3-hexene	0.8685
heptane	0.9018	n-butane	0.8495	a-pinene	0.8454
<i>cis</i> -3-hexene	0.8586	a-pinene	0.8469	1,2,4-trimethylbenzene	0.8454
ethylbenzene	0.8502	limonene	0.8282	4-methyl-1-pentene	0.8113
a-pinene	0.8349	heptane	0.7915	n-propylbenzene	0.8037
n-decane	0.8334	nonane	0.7890	benzene	0.8013
undecane	0.8127	propane	0.7793	nonane	0.7981
o-xylene	0.7805	ethene	0.7787	methylcyclopentane	0.7980
p-xylene	0.7689	n-decane	0.7733	n-octane	0.7837
2,3,4-trimethylpentane	0.7682	isopropylbenzene	0.7652	ethane	0.7427
n-octane	0.7616	2,4-dimethylpentane	0.7577	n-hexane	0.7422
nonane	0.7488	undecane	0.7227	2,3-dimethylpentane	0.7328
toluene	0.7472	n-hexane	0.6642	m-xylene	0.7265
1,3,5-trimethylbenzene	0.7354	2,3,4-trimethylpentane	0.6551	cyclohexane	0.7231
ethene	0.7338	methylcyclopentane	0.6328	o-xylene	0.6941
limonene	0.6658	1-pentene	0.6282	heptane	0.6908
propane	0.6204	2,3-dimethylpentane	0.5986	propene	0.6824
cyclohexane	0.6126	benzene	0.4944	isopentane	0.6753
b-pinene	0.5783	isopentane	0.2890	cyclopentane	0.6462
2-methylpentane	0.5370	isoprene	0.0112	n-pentane	0.6348
n-hexane	0.5283			2-methylpentane	0.6346
1,2,4-trimethylbenzene	0.5200			2,4-dimethylpentane	0.6334
benzene	0.4241			<i>cis</i> -2-pentene	0.5602
isoprene	-0.0158			1-pentene	0.5505
				isoprene	0.2485

ones. If the above equation were used to estimate the automobile contribution at SHEN, however, the result might be incorrect, since there might be a large contribution for toluene from another source that had no contribution to isopentane and benzene (Table 4).

3.3. Biogenic Hydrocarbons

Since all the samples were collected during summertime, as argued above, the average isoprene concentrations at all sites are very high. This is consistent with other reports of seasonal dependence of isoprene levels [Fuentes *et al.*, 2000; Hagerman

et al., 1997; Rasmussen and Khalil, 1988]. Isoprene emissions are directly related to plant growth period and sunlight intensity. The dependence of \log [isoprene] on temperature has been well established by several authors as well as by this work. The regression equations between isoprene (in ppbv) and temperature ($^{\circ}\text{C}$) are given below

$$\ln(\text{isoprene}) = 0.2451 \times \text{temp} - 2.9775 \quad (\text{SHEN}) \quad (8)$$

$$R^2 = 0.7558$$

$$\ln(\text{isoprene}) = 0.2389 \times \text{temp} - 3.3301 \quad (\text{GRSM}) \quad (9)$$

$$R^2 = 0.4602$$

$$\ln(\text{isoprene}) = 0.2443 \times \text{temp} - 4.5057 \quad (\text{MACA}) \quad (10)$$

$$R^2 = 0.6119.$$

Note that even though the three sites are at three different locations (Figure 1), the relationship between isoprene concentration and temperature is very similar, as shown by the regression coefficients and intercepts.

Compare these with the similar equations reported by Hagerman *et al.* [1997] and Jobson *et al.* [1994] (transformed from the original publication in accordance with current units):

$$\ln(\text{isoprene}) = 0.1294 \times \text{temp} - 1.5644 \quad (11)$$

$$R^2 = 0.53 \quad (\text{Hagerman et al.})$$

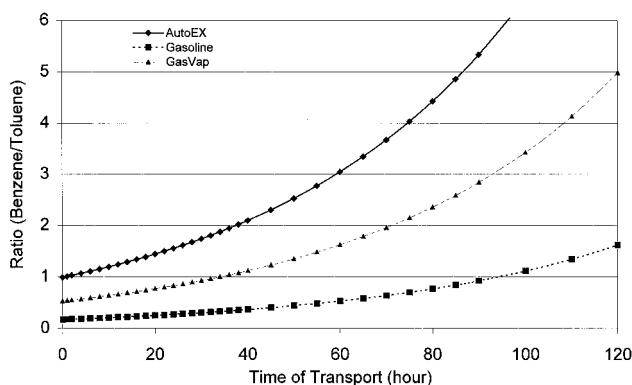


Figure 5. Variations of benzene to toluene ratio with time for different sources ($K_{\text{ben}}^{\text{OH}} = 1.2 \times 10^{-12} \text{ cm}^3/\text{molecule s}$, $K_{\text{tol}}^{\text{OH}} = 6.4 \times 10^{-12} \text{ cm}^3/\text{molecule s}$, $[\text{OH}] = 1 \times 10^6 \text{ molecules/cm}^3$ [Warneck, 1988]).

Table 4. Source Profile (Weight Percent of Nonmethane Organic Gas) of Major Nonmethane Hydrocarbons From Common Anthropogenic Sources^a

Compound	AutoEx	Gasoline	GasVap	CNG	GNG	LPG	Solvent1	Solvent2
Ethene	7.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetylene	2.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ethane	3.11	0.00	0.00	69.40	15.80	4.10	0.00	0.00
Propene	3.30	0.00	0.01	0.00	0.00	5.10	0.00	0.00
Propane	0.40	0.01	0.56	21.30	25.20	90.40	0.00	0.00
1-Butene	0.72	0.02	0.34	0.00	0.00	0.00	0.00	0.00
n-Butane	5.91	1.31	11.19	3.10	14.60	0.00	0.00	0.00
<i>trans</i> -2-Butene	0.45	0.12	0.91	0.00	0.00	0.00	0.00	0.00
<i>cis</i> -2-Butene	0.67	0.13	0.91	0.00	0.00	0.00	0.00	0.00
Isopentane	4.31	7.38	27.37	0.70	0.00	0.00	0.00	0.00
1-Pentene	0.22	0.47	1.53	0.70	6.20	0.00	0.00	0.00
n-Pentane	2.73	3.21	9.10	0.00	6.20	0.00	0.00	0.00
Isoprene	0.31	0.07	0.18	0.00	0.00	0.00	0.00	0.00
<i>trans</i> -2-Pentene	0.30	1.15	3.04	0.00	0.00	0.00	0.00	0.00
<i>cis</i> -2-Pentene	0.26	0.63	1.63	0.00	0.00	0.00	0.00	0.00
Cyclopentane	0.22	0.33	0.59	0.00	0.00	0.00	0.00	0.00
2-Methylpentane	3.43	3.27	4.48	0.30	2.90	0.00	0.00	0.00
3-Methylpentane	1.71	1.97	2.38	0.10	1.50	0.00	0.00	0.00
n-Hexane	1.67	1.77	1.76	0.40	1.80	0.00	38.71	0.00
Methylcyclopentane	0.64	1.14	1.00	1.00	2.60	0.00	0.00	0.00
2,4-Dimethylpentane	0.66	0.00	0.00	0.00	0.00	0.00	0.00	2.32
Benzene	5.98	1.23	1.01	0.00	0.00	0.00	0.00	0.00
Cyclohexane	0.15	0.27	0.17	0.00	0.00	0.00	38.71	0.68
2,3-Dimethylpentane	1.01	1.14	0.56	0.00	0.00	0.00	0.00	0.00
Heptane	0.62	1.02	0.38	0.20	1.20	0.00	0.00	3.96
Methylcyclohexane	0.29	0.42	0.14	0.10	2.20	0.00	0.00	4.91
2,3,4-Trimethylpentane	1.10	1.69	0.40	0.00	0.00	0.00	0.00	0.00
Toluene	7.12	8.48	2.26	0.00	0.00	0.00	9.67	51.57
n-Octane	0.38	0.54	0.08	0.00	1.00	0.00	0.00	0.00
Ethylbenzene	2.42	1.77	0.24	0.00	0.00	0.00	8.04	0.68
<i>m,p</i> -Xylene	5.69	5.71	0.76	0.00	0.00	0.00	4.86	0.00
Styrene	0.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>o</i> -Xylene	1.88	2.54	0.29	0.00	0.00	0.00	0.00	0.00
Nonane	0.15	0.22	0.02	0.00	0.00	0.00	0.00	0.00
Isopropylbenzene	0.14	0.19	0.02	0.00	0.00	0.00	0.00	0.00
<i>n</i> -Propylbenzene	0.32	0.66	0.07	0.00	0.00	0.00	0.00	0.00
1,3,5-Trimethylbenzene	0.61	1.37	0.13	0.00	0.00	0.00	0.00	0.00
1,2,4-Trimethylbenzene	1.65	3.88	0.40	0.00	0.00	0.00	0.00	0.00
<i>n</i> -Decane	0.15	0.20	0.02	0.00	0.00	0.00	0.00	0.00

^aModified from Fujita *et al.* [1995]. Note: AutoEx, vehicle exhaust; GasVap, gasoline vapor; CNG, commercial natural gas; GNG, geogenic natural gas; LPG, liquefied petroleum gas; SOL-1, architectural coatings-composite solvent, MEDS 196; SOL-2, industrial coatings-solvent based, MEDS 783.

$$\ln(\text{isoprene}) = 0.1635 \times \text{temp} - 1.6142 \quad (12)$$

$$R^2 = 0.61 \quad (\text{Jobson et al.}).$$

The equations in this study have higher regression coefficients and lower intercepts, which means that isoprene concentration increases more rapidly with temperature increase than in previous studies.

In order to make further comparisons, linear regressions for log [isoprene] versus $1/T$ (T is absolute temperature, kelvin) for the three locations were also performed. The slopes were

−8852 (GRSM), −9018 (SHEN), and −9318 (MACA); the intercepts were 31.03 (GRSM), 31.60 (SHEN), and 32.15 (MACA). In contrast, Young *et al.* [1997] produce similar equations for “Old Aspen” (where the dominant vegetation is aspen trees) with slopes of -7800 ± 900 and intercepts of 27 ± 3 . Taking the slope as $-E_a/R$ (R is the gas constant, 0.008314 kJ/mol), the calculated activation energies E_a for this study are 73.60 kJ/mol (GRSM), 74.96 kJ/mol (SHEN), and 77.99 kJ/mol (MACA). These are about 15% higher than Young *et al.*'s results (65 ± 8 kJ/mol) at Old Aspen, but closer to the results

Table 5. Statistics of Benzene to Toluene Ratios at Three Sites for 3 Years^a

	MACA			GRSM			SHEN		
	1995	1996	1997	1995	1996	1997	1995	1996	1997
Mean	0.979	1.139	0.530	1.092	0.850	0.505	0.372	0.272	0.282
Median	0.922	1.181	0.515	1.074	0.816	0.529	0.257	0.183	0.261
s.d.	0.379	0.441	0.165	0.578	0.381	0.086	0.323	0.220	0.121
Maximum	2.055	1.957	0.803	2.492	1.582	0.611	1.521	0.850	0.630
Minimum	0.058	0.539	0.344	0.297	0.045	0.376	0.068	0.056	0.137

^aUnits are in ppbv.

Table 6. Coefficients of Determination Between Benzene and Toluene, Toluene and m,p-Xylene at Three Sites for 3 Years

R^2	MACA			GRSM			SHEN		
	1995	1996	1997	1995	1996	1997	1995	1996	1997
ben/tol	0.7561	0.8350	0.4222	0.1116	0.2107	0.8536	0.0588	0.3067	0.4990
tol/m,p-xyl	0.3707	0.5356	0.8000	0.3825	0.4474	0.8065	0.3638	0.9040	0.6688

of *Guenther et al.* [1996] for isoprene production by isoprene synthase and for emission of isoprene from leaves (95 kJ/mol).

As in the relationship of $\log[\text{isoprene}]$ to $1/T$, the slopes yield the activation energy for isoprene emission from vegetation. Similarly, the slopes in the relationship of $\log[\text{isoprene}]$ to T yield the temperature sensitivity of the vegetation in releasing isoprene. The difference in slope between locations may reflect the different mixtures of vegetation types. Upon interpolation the intercepts in the relationship of $\log[\text{isoprene}]$ to T yield the log concentrations of isoprene at $T = 0^\circ\text{C}$, which may reflect the background concentration of isoprene to some extent.

It should be pointed out that the relationship between isoprene and temperature is affected by many other factors in addition to the mixture of vegetation types, such as atmosphere conditions, including height of the boundary layer, vertical mixing, and turbulence in the atmosphere. Two of the sampling sites in this study are at elevations over 1000 m, another is at

elevation of 219 m; atmospheric conditions may differ from those in previous studies where samples were taken at low elevations.

Assuming that isoprene reacts only with OH and O_3 , the lifetime of isoprene in atmosphere $\tau_{\text{isoprene}} = (k_{\text{OH}}[\text{OH}] + K_{\text{O}_3}[\text{O}_3])^{-1}$. At $\text{OH} = 1.0 \times 10^6$ molecules cm^{-3} and $\text{O}_3 = 1.0 \times 10^{12}$ molecules cm^{-3} at 850 mbar and 298°K at the three sites, $\tau_{\text{isoprene}} = 10,526$ s = 2.9 hours. The flux of isoprene can be estimated by the following:

$$F_{\text{isoprene}} = C_{\text{isoprene}} \frac{pM}{RT} \frac{\text{PBL}}{\tau_{\text{isoprene}}} 10^{-3} \quad (13)$$

where F_{isoprene} is isoprene flux ($\text{mg m}^{-2} \text{h}^{-1}$), C_{isoprene} is isoprene concentration (ppbv), p is air pressure (mbar), M is molecular weight of isoprene (68), T is the absolute air temperature, PBL is the mixing height (km), and $R = 0.08314$ mbar $\text{m}^3 \text{K}^{-1} \text{mol}^{-1}$.

The mean concentrations of isoprene are 11.13 ppbv at SHEN, 14.61 ppbv at GRSM, and 16.73 ppbv at MACA. Assuming 1.0 km mixing height, this results in isoprene fluxes of $9.0 \text{ mg m}^{-2} \text{h}^{-1}$ at SHEN, $11.8 \text{ mg m}^{-2} \text{h}^{-1}$ at GRSM, and $13.5 \text{ mg m}^{-2} \text{h}^{-1}$ at MACA at midday in summer. *Geron et al.* [1997] report isoprene fluxes above canopy level at various locations, with mean values from 0.08 to $10.57 \text{ mg m}^{-2} \text{h}^{-1}$ for surface layer and 2.15 to $7.8 \text{ mg m}^{-2} \text{h}^{-1}$ for mixed layer. *Goldstein et al.* [1998] report, for summer 1995 at Harvard Forest, 24-hour average emissions of isoprene from June through October of $1.32 \text{ mg m}^{-2} \text{h}^{-1}$ with mean midday mixing ratio of 4.4 ppbv at 24 m above canopy level. According to *Guenther et al.* [2000] all the three locations are in the region with July emission rate of isoprene in the range of 130 to $250 \text{ mg C m}^{-2} \text{d}^{-1}$. When conversion of unit is made, our results are higher but still reasonable given the differing time of day and various assumptions. However, according to the different vertical profiles of isoprene reported by *Guenther et al.* [1996], using the measured surface layer concentration to estimate the assumed 1.0 km mixed layer fluxes, our results may be overly high.

The pinenes that include the naturally emitted compounds α -pinene, β -pinene, and limonene have relatively constant concentrations at each site. At MACA, average pinene concentrations range from 2.55 to 3.54 ppbv; at GRSM they range from 1.82 to 3.26 ppbv; at SHEN they range from 2.74 to 2.78 ppbv (1995 data are not included, because of the extremely high concentration of α -pinene in that year). These compounds are produced mainly by conifers, and they are very reactive in atmosphere with lifetimes less than a few hours [*Warneck*, 1988]. Concentrations of even these compounds are lower than isoprene during summer. Unlike isoprene, which is produced only in summer, these compounds can be produced throughout the year, and may play an important role in atmospheric chemistry during other seasons in rural areas.

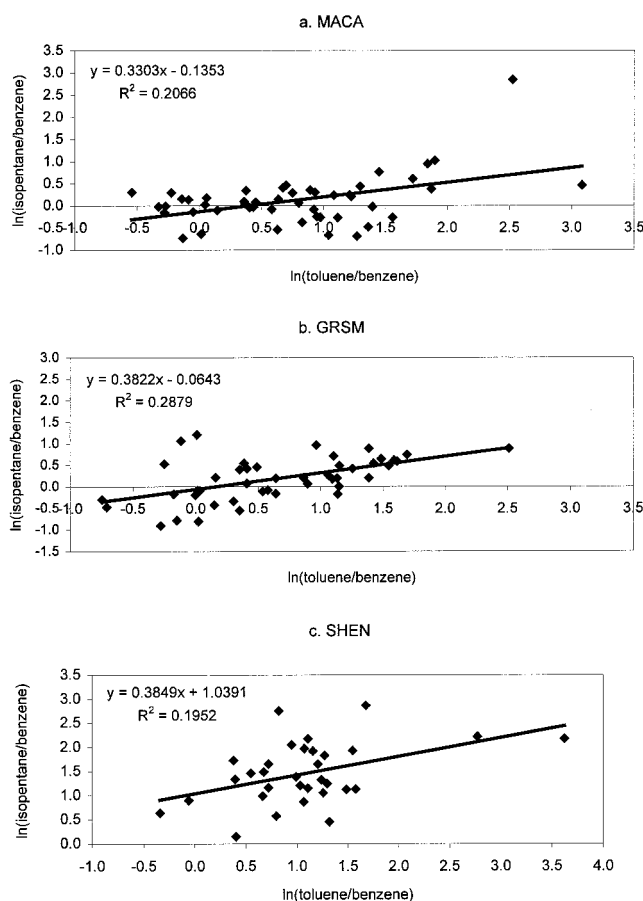
**Figure 6.** Relationship between $\ln(\text{isopentane/benzene})$ and $\ln(\text{toluene/benzene})$.

Table 7. Comparison of Selected Anthropogenic Hydrocarbons Measured at Various Urban and Rural Sites^a

Compound	39 U.S. Cities ^b	Houston, Texas ^c	Raleigh, North Carolina ^c	Fraserdal, Canada ^c	Belfast, Maine ^c	NW England ^d	Centreville, Alabama ^e	Mammoth, Kentucky ^f	Cove Mtn, Tennessee ^f	Shenandoah, Virginia ^f
Ethene	25.0				2.3	1.9	0.71	0.8	0.63	1.2
Acetylene	13.9			0.16	<0.54	0.65	0.39	0.65	0.77	1.15
Ethane	29.4	12.5		2.05	4.7	19.9	2.32	3.88	3.59	4.38
Propene	9.0	5.7	0.63		0.58	4.8	0.85	1.56	1.81	1.09
Propane	28.7	17	11.72	0.28	2.4	12.6	3.18	3.51	2.42	7.66
Isobutane	17.9	8.20	0.74	0.034	0.6	1	0.93	1.4	0.76	2.27
n-Butane	48.7	16	2.47	0.07	2.4	1.3	1.79	1.53	1.12	6.18
Isopentane	53.6	13.40	5.16	0.05	1.2		2.59	3.08	2.55	4.11
n-Pentane	25.7	7.6	2.3	0.07	1.2	6	1.21	1.01	1.01	1.91
2-Methylpentane	17.8	3.3	1.53			<0.6	3.99	1.97	1.48	2.39
3-Methylpentane	3.0	2.5	0.84			<0.6	0.96	0.99	0.97	0.76
n-Hexane	13.1	3.3	1.04			6.1	0.81	0.45	0.34	0.47
cis-3-Hexene						<0.6	0.82	0.23	0.21	0.27
Benzene	13.7	3	1.42				0.66	0.85	0.85	1.29
Toluene	37.0	6.8	9.81				1.31	1.2	1.67	5.87

^aUnits were transformed from ppbC to ppbv from original publications.

^bParrish *et al.* [1998] (medium concentrations from 39 U.S. cities, data collected from 1984 to 1986).

^cLawrimore *et al.* [1995] (semiurban, surface, August 1993, 0500–0800 LT).

^dColbeck and Harrison [1985] (May–July 1983).

^eHagerman *et al.* [1997] (June–August 1993, 1200–1300 LT).

^fThis study (June–August 1995–1997, 1200–1300 LT. At Shenandoah for isopentane and n-pentane only, 1996 and 1997 data were used.

3.4. Hydrocarbon Reactivities With Hydroxyl Radical

The contribution of hydrocarbon compounds to the production of photochemical ozone in troposphere starts with their reaction with OH and O₃ in the complex photooxidation mechanism. For most hydrocarbons, OH is the most important reaction pathway. To estimate the reactivity of hydrocarbons, we use the propylene-equivalent concentration method proposed by Chameides *et al.* [1992]:

$$\text{propy-equiv}(j) = \text{conc}(j) \frac{k_{\text{OH}}(j)}{k_{\text{OH}}(\text{C}_3\text{H}_6)} \quad (14)$$

where 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 ppbv; *k*_{OH}(*j*) is the rate constant for the reaction between species *j* and OH; and *k*_{OH}(C₃H₆) is the rate constant for the reaction between OH and propylene.

Using this method and the rate constant for each compound with OH, propylene-equivalent concentrations were calculated. The dominant compound in propylene-equivalent concentration at each site for every year is always isoprene. The group contributions at each location for each year (for SHEN the 1995 data are not included) are shown in Figure 7. The values on the right top corner are total propylene-equivalent concentrations (hydrocarbon totals are calculated by first individually calculating the propylene-equivalent concentration for each hydrocarbon, then summing them). It turns out that at all sites for any year, NAT-HC in which isoprene is a dominant member is always the dominant hydrocarbon group in propylene-equivalent concentration and is 69 to 95% of the total. In contrast to the group contribution in ppbv, the contributions of ALKANES are 2 to 4% only at MACA and GRSM for all years and are ~10% at SHEN in 1996 and 1997. Contributions of ALKENES are smaller, ~2%, at MACA and GRSM in 1995 and 1996 but rise to ~15% in 1997. Contributions of ALKENES are consistent, 7% at SHEN in 1996 and 1997. Contributions of TOT-AROM vary from 1% at GRSM in 1995 to 13% at SHEN in 1996. In general, the contribution of

anthropogenic hydrocarbons in propylene-equivalent concentration at SHEN is larger (~30%) than at the other two locations. The contribution of anthropogenic hydrocarbons increases at MACA and GRSM in 1997 compared with the previous 2 years, especially for ALKENES. In fact, because ALKENES are the most reactive class among anthropogenic hydrocarbons, their presence in large quantity indicates a significant local anthropogenic source.

It must be pointed out that the propylene-equivalent method, or any other OH reactivity method, prioritizes individual compounds according to their reactions only with OH

Table 8. Comparison of Biogenic Hydrocarbons With Various Rural Sites^a

Location	Isoprene	a-Pinene	b-Pinene	Limonene
Raleigh, North Carolina ^b	2.36			
Brazil ^c	13.6	3.04		
Niwot Ridge, Colorado ^d	3.57	1.13		
Candor, North Carolina ^e	11.34	2.53	1.46	0.78
Centreville, Alabama ^f	23.97	1.8	1.53	0.27
Oak Grove, Mississippi ^f	12.68	3.05	3.42	0.71
Yorkville, Georgia ^f	11.11	0.8	2.32	0.52
Mammoth Cave National Park, Kentucky ^g	16.73	1.22	0.96	0.81
Great Smoky Mountains National Park, Tennessee ^h	14.61	1.1	0.87	0.35
Shenandoah National Park, Virginia ⁱ	11.13	1.59	0.95	0.22

^aUnits are in ppbv.

^bLawrimore *et al.* [1995] (surface, August 1993, 0500–0800 LT).

^cGreenberg and Zimmerman [1984] (surface, August and September 1979 and 1980).

^dGreenberg and Zimmerman [1984] (surface, August–September and November 1982).

^eHagerman *et al.* [1997] (June 1992 and 1993, 1200–1300 LT).

^fHagerman *et al.* [1997] (June–August 1993, 1200–1300 LT).

^gThis study (June–August, 1995–1997, 1200–1300 LT).

^hThis study (June–August, 1997, 1200–1300 LT).

ⁱThis study (June–July, 1995, 1200–1300 LT).

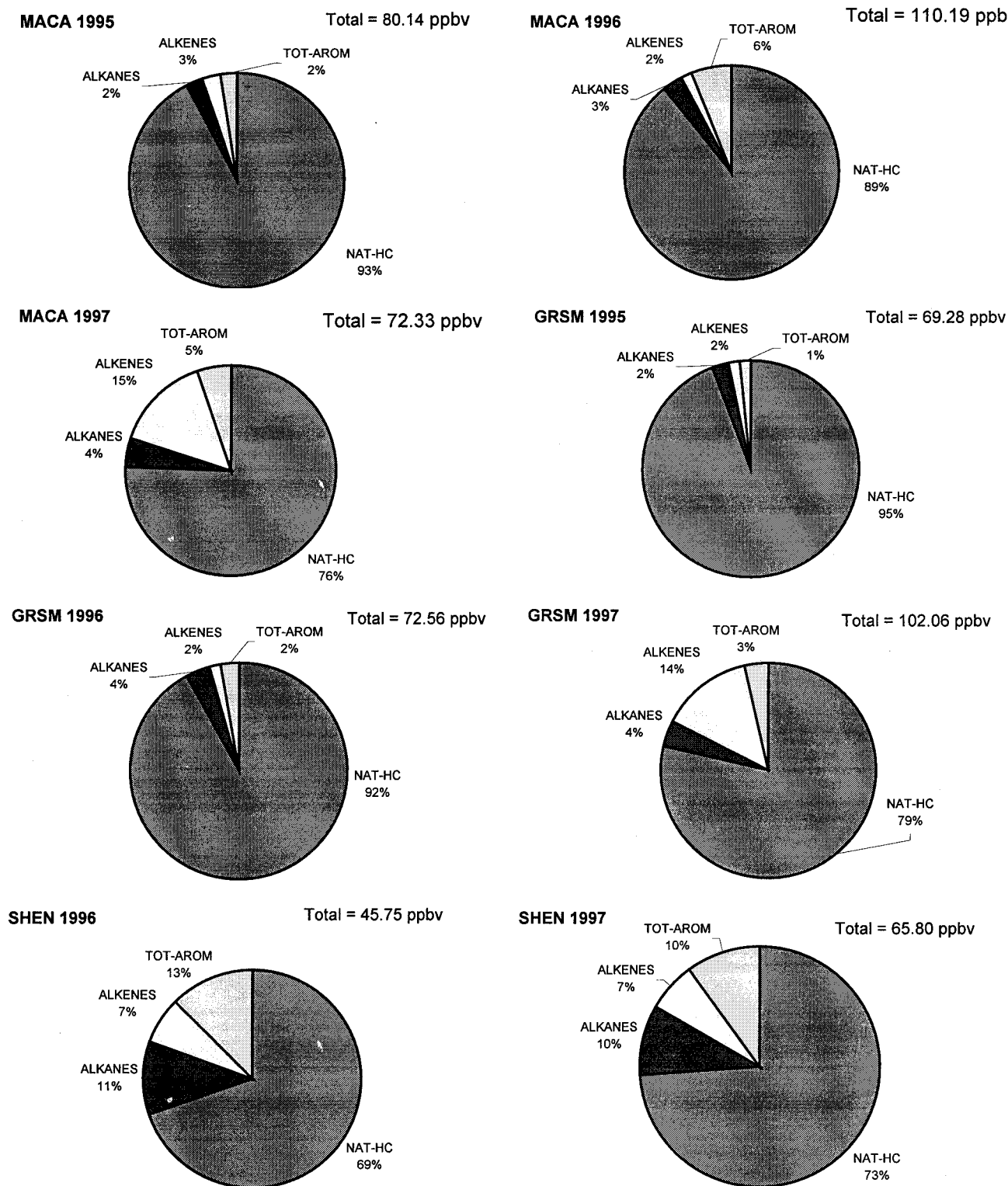


Figure 7. Class distribution in propylene-equivalent concentration (ppbv).

radicals. Nevertheless, this method, which builds the same basis for all the compounds in terms of their reactions with OH, presents a simple way to look at hydrocarbons in the domain of atmospheric chemistry and ozone formation. However, hydrocarbon reactions in atmosphere are very complex and depend on many factors including the availability of NO_x and the ozone level.

In order to take a look at the relationship between ozone levels and hydrocarbon concentrations, the correlation coefficients between ozone and NAT-HC and between ozone and ANTH-HC are calculated for each year at all three sites. At MACA in 1995 both NAT-HC and ANTH-HC do not correlate with ozone (the correlation coefficients are below significant value). In 1996 the correlation coefficient r between ozone

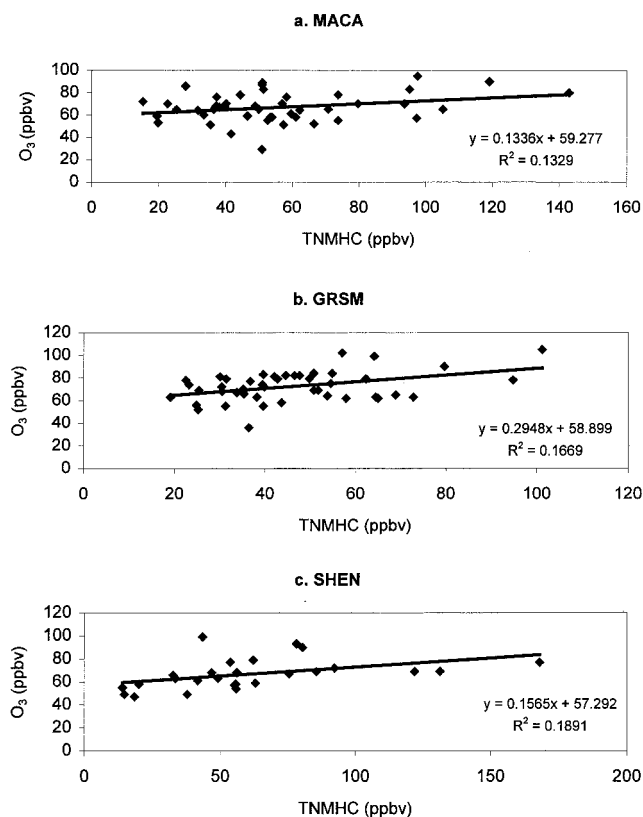


Figure 8. Relationship between TNMHC (ppbv in prop-equivalent concentration) and O_3 at each site.

and NAT-HC is 0.707, but ANTH-HC does not correlate with ozone. In 1997, because only six ozone results were obtained, and the concentration of NAT-HC was almost constant, no significant correlation can be obtained. At GRSM in all 3 years the correlation coefficients are not significant. At SHEN in 1996, ozone correlates with ANTH-HC ($r = 0.697$). In 1997 both NAT-HC and ANTH-HC do not correlate with ozone significantly. This analysis indicates that the relationship between ozone and hydrocarbons is very complex; ozone may be the combined result of both local production (mostly by reactions of NAT-HC compounds) and distant origin.

Figures 8a–8c give the relationship between the concentration of daily maximum O_3 and the propylene-equivalent concentration of TNMHC (ppbv) for the three sites. In Figures 8a and 8b all 3 years' data are used, but in Figure 8c, only the 1996 and 1997 data are used. All the three figures show a positive correlation, even though it is weak, between the concentrations of the daily maximum O_3 and the propylene-equivalent concentrations of TNMHC. This suggests that nonmethane hydrocarbons contribute positively to the local production of O_3 in the national parks.

3.5. Comparison of Hydrocarbons With Other Rural Sites During Summer

Tables 7 and 8 summarize selected anthropogenic and biogenic hydrocarbons measured during the summer at various urban, semiurban, and rural sites. In Table 7 the data from the first two columns (Columbus, Ohio, and Houston, Texas) are from urban areas, the data from the third column (Raleigh, North Carolina) are from a semiurban area, and the data from

the others are from rural and remote areas. As expected, Table 7 shows that the concentrations of anthropogenic compounds decrease from urban to semiurban to rural areas. The concentrations of anthropogenic compounds at MACA and GRSM are similar to those at other rural sites, but the situation at SHEN more closely resembles that of a semiurban area. Especially in terms of benzene and toluene, mean concentrations and the ratios between them are very similar at MACA and GRSM, and it seems that these two locations may be affected by similar anthropogenic sources.

Table 8 shows that biogenic compounds at all three sites had concentrations comparable to those at other locations, but concentrations of β -pinene appeared to be lower at the three sites in this study than at other locations. However, it must be pointed out that because biogenic compounds vary with season, temperature, plant variety, and density, it is difficult to evaluate their relationship at different locations.

4. Conclusions

The major components of anthropogenic VOCs in southeast U.S. high-elevation national parks are isopentane (1.3 to 5.7 ppbv) from automobile exhaust and related gasoline handling, toluene (1.0 to 7.2 ppbv) from automobile exhaust, related gasoline operations, and solvents, and propane (2.1 to 12.9 ppbv) from commercial natural gas. Isoprene (6.3 to 18.4 ppbv) from biogenic source is the most abundant compound in summer in these parks. Anthropogenic VOCs from automobile exhaust are dominant at Mammoth Cave National Park, and at Cove Mountain, Great Smoky Mountains National Park, while at Big Meadows, Shenandoah National Park, the source composition is complex and changed from 1995 to 1996. On average, anthropogenic VOCs at Mammoth Cave National Park and Cove Mountain, Great Smoky Mountains National Park, are influenced on a regional scale in 1995 and 1996, but result largely from local sources in 1997. At Big Meadows, Shenandoah National Park, all 3 years' data strongly indicate a large contribution from local sources. The major pathway for VOCs destruction is by chemical processes. In summer, upon conversion into propylene-equivalent concentration, biogenic components including isoprene, α -pinene, β -pinene, and limonene (of which 80% is isoprene) are 69% to 95% of the total propylene-equivalent concentration in all three parks from 1995 to 1997. In all three national parks, when converted into propylene-equivalent concentration, nonmethane hydrocarbons positively affect the daily maximum O_3 . Isoprene concentration correlates with ambient temperature as reported by other researchers. At the three locations the relationship between isoprene concentration and temperature is quite similar, but the concentrations are more than 50% higher than in previous studies. Estimated isoprene fluxes during midday in summer are $9.0 \text{ mg m}^{-2} \text{ h}^{-1}$ at SHEN, $11.8 \text{ mg m}^{-2} \text{ h}^{-1}$ at GRSM, and $13.5 \text{ mg m}^{-2} \text{ h}^{-1}$ at MACA. Both anthropogenic and natural VOCs concentrations are comparable with previous studies for other rural areas.

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