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Seasonal variations of nonmethane hydrocarbons in rural New England: Constraints on OH concentrations in northern midlatitudes

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Abstract. Concentrations of C_2–C_6 hydrocarbons are reported at Harvard Forest in Central Massachusetts (42.54°N, 72.18°W; elevation, 340 m), measured at 45-min intervals from August 1992 through July 1994. The seasonal cycle of background concentrations for anthropogenic alkanes (ethane, propane, butane, isobutane, pentane, and hexane) and acetylene could be cleanly extracted from the ~900 measurements each month. Background concentrations exhibited seasonal maxima in winter and minima in summer. The phase of the seasonal cycle for each species reflected its rate of reaction with OH: The faster the reaction, the earlier the peak in winter, and the more rapid the decline in spring. Winter:summer ratios for hydrocarbons more reactive than propane were similar, implying a summer:winter ratio for OH of 9 ± 2 at northern midlatitudes. The annual cycle for ethane provides a measure of the mass-weighted annual mean OH concentration at northern midlatitudes, $7(\pm 3.5) \times 10^5 cm^{-3}$, as simulated by using a three-dimensional chemical tracer model.

1. Introduction

Most anthropogenic hydrocarbons are removed from the atmosphere primarily by reaction with OH. At northern midlatitudes, rates for removal vary markedly with season, while emissions are largely invariant. Seasonal variations in rates for long-range transport play a relatively minor role in the observed seasonal cycles. Hence the seasonal cycles for background concentrations of hydrocarbons provide a unique measure of OH concentrations averaged over midlatitudes.

This paper presents measurements of C_2–C_6 hydrocarbons at Harvard Forest in Central Massachusetts (42.54°N, 72.18°W; elevation, 340 m), obtained at 45-min intervals for 2 years. The data are analyzed to derive monthly mean background concentrations and to determine emission ratios for U.S. regional anthropogenic sources. Emission ratios are found to be consistent with the National Acid Precipitation Assessment Program (NAPAP) inventory. Background concentrations are consistent with previous observations from remote locations obtained at lower temporal resolution [*Jobson et al.*, 1994; *Blake and Rowland*, 1986; *Penkett et al.*, 1993; *Rudolph et al.*, 1989; *Singh et al.*, 1988; *Singh and Salas*, 1982; *Lightman et al.*, 1990; *Tille et al.*, 1985]. Observed annual cycles are analyzed by using photochemical models in order to constrain the annual mean and seasonal cycle for concentrations of hydroxyl radical in the northern midlatitude troposphere.

2. Experiment

Automated in situ measurements of C_2–C_6 nonmethane hydrocarbons (NMHCs) were obtained simultaneously at two altitudes, 24 and 29 m (2 and 7 m above the forest canopy) by using cryogenic concentration and gas chromatography as described by *Goldstein et al.* [1995]. Data were normally downloaded at 6-day intervals, although the system could operate continuously for more than 2 weeks unattended. Air was drawn through Teflon tubing from the inlets through nafion dryers (Perma Pure Products) to remove most of the water vapor, then through Ascarite II (Thomas Scientific) to remove CO_2, O_3, and residual H_2O. Samples (400 cm^3 STP) were collected over 10-min periods at 87°K on dual traps of 0.030-inch ID stainless steel tubing, then injected into a gas chromatograph with dual PLOT GS-Alumina 30-m Megabore capillary columns (J&W Scientific) and flame ionization detectors (FID) (Hewlett Packard 5890 series II). The null concentration gradient was determined by sampling from the same level every fifth run.

Concentrations were determined by using relative response factors [*Ackman*, 1964, 1968; *Dietz*, 1967] referenced to neohexane (Scott-Marrin, NIST traceable ±2%), an internal standard added by dynamic dilution to every sample. The overall accuracy of the system was estimated to be better than ±18% for all the C_2–C_6 hydrocarbons based on accuracy attributed to the neohexane standard,

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flow measurements for the dynamic dilution system, and relative response factors. Instrument precision was approximately 2% at 1 ppbv, 5% at 0.5 ppbv, 10% at 0.2 ppbv, and 20% for concentrations less than 0.1 ppbv, as determined by the variance between the dual measurements taken from the same level. The minimum detectable concentration for all compounds was 0.01 ppbv. Measurements have continued to the present time. Other continuous measurements at Harvard Forest include concentrations of CO, CO_2, O_3, NO_x, NO_y, H_2O, rain composition, wind speed and direction, temperature, and fluxes of sensible heat, latent heat, O_3, NO_y, and CO_2 by eddy correlation [*Wofsy et al.*, 1993].

3. Results

The influence of OH on hydrocarbon seasonal cycles was examined by distinguishing background concentrations from pollution events and identifying compounds with nearly aseasonal emissions in northern midlatitudes. Data for ethane and acetylene are shown in Figure 1 for

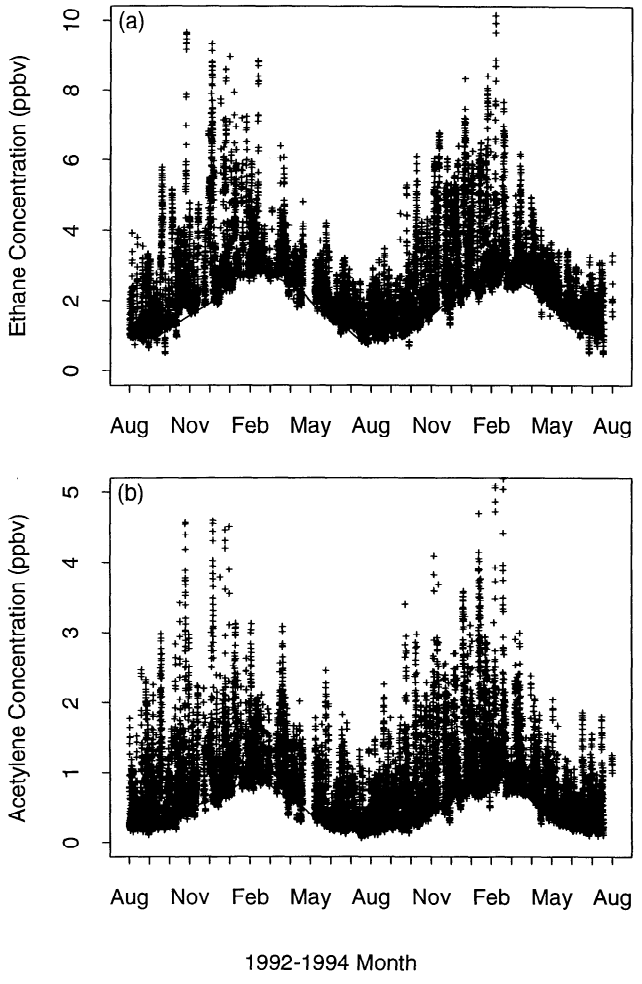

Figure 1. (a) Ethane and (b) acetylene concentrations measured at 45-min intervals above Harvard Forest from August 1992 to July 1994. A line is drawn through the running 0.1 quantile of the data in 30-day intervals, identifying the seasonally changing background concentration.

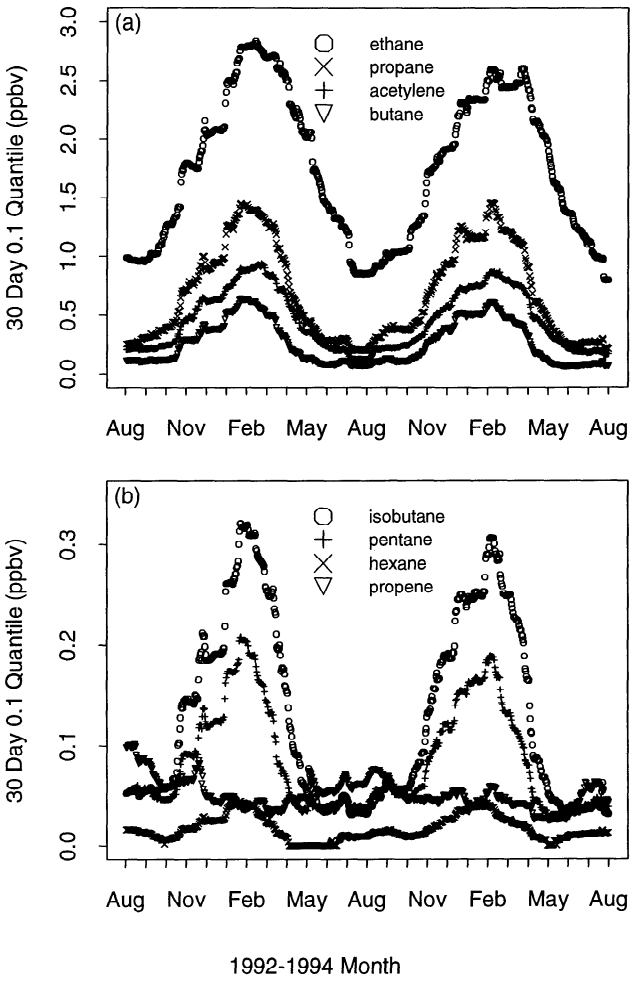

Figure 2. Background concentrations from August 1992 to July 1994 defined as the running 0.1 quantile of the data in 30-day intervals for (a) ethane, acetylene, propane, and butane and (b) isobutane, pentane, hexane, and propene.

August 1992 through July 1994. Background concentrations are clearly delineated by the lower envelope of the points, brought out by the line indicating monthly 0.1 quantiles. The annual cycles of background concentrations for ethane, acetylene, propane, butane, isobutane, pentane, hexane, and propene, defined as the 0.1 quantile of the data filtered in 30-day intervals, are shown in Figure 2.

Figure 3 shows 2 months of ethane data on standard cumulative probability axes, with lines drawn through the 0.1, 0.2, 0.3, 0.4, and 0.5 quantiles. The 0.1-0.3 quantiles are unaffected by pollution events or by occasional low values, which appear in some cases to result from stratospheric intrusions (high O_3, low H_2O). The value inferred for "background" is consequently insensitive to the particular quantile selected, lending confidence to the procedure.

Figure 4 shows scatterplots of simultaneous data for ethane, propane, isobutane, butane, pentane, and hexane, plotted against acetylene, for the same 2 months. The correlations observed in these scatterplots represent the signature of pollution inputs, as air with variable amounts of dilution, but consistent ratios among primary pollutants, is sampled at the site. Emission ratios measured at Harvard

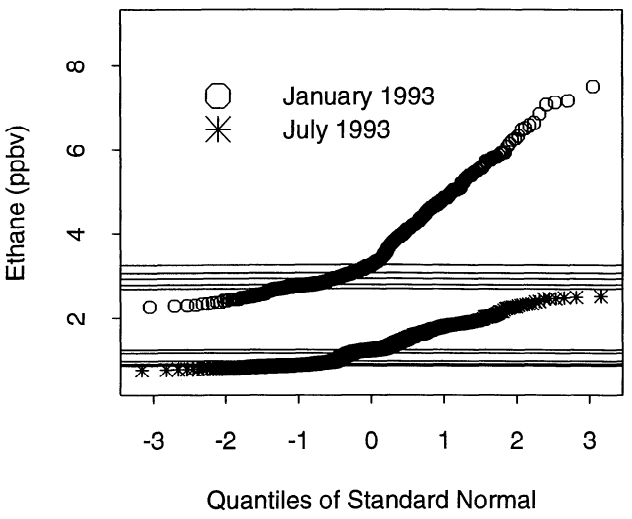

Figure 3. Ethane concentrations for the months of July 1993 and January 1993 plotted on standard cumulative probability axes, with lines drawn through the 0.1, 0.2, 0.3, 0.4, and 0.5 quantiles. Pollution episodes are clearly separated from background data.

Forest relative to acetylene (Table 1a) are reported as the mean ($\pm 1\sigma$) slope (line fit assumed uncertainty in both coordinates [*Press et al.*, 1992]) of summer months (June, July, August) and winter months (December, January, February) for 2 years of data.

Absolute emissions of hydrocarbons in North America (predominantly from automobiles) do not vary significantly with season, according to the 1985 NAPAP emission inventory. (New regulations in the clean air act amendments of 1990 required the use of oxygenated fuels during the winter (beginning in 1992) in most CO nonattainment areas including much of the northeastern United States. The projected effect of this legislation was a 15% reduction in hydrocarbon emissions [*The Oxygenated Fuels Association*, 1994].)

Observations of emission ratios for ethane and propane at Harvard Forest (Figure 4) show evidence for at least two sources, one associated with little or no acetylene that is observed more often in winter. Observations show essentially no seasonality for isobutane, slightly higher butane emissions in winter, and significantly higher pentane and hexane emissions in summer.

Table 1b summarizes monthly 0.1, 0.25, 0.5, and 0.9 quantiles for ethane, acetylene, propane, isobutane, butane, pentane, and hexane from August 1992 to July 1994. Background ethane concentrations at Harvard Forest are consistent with observations at clean air sites in northern midlatitudes [*Jobson et al.*, 1994; *Penkett et al.*, 1993; *Blake and Rowland*, 1986; *Rudolph et al.*, 1989; *Singh et al.*, 1988; *Singh and Salas*, 1982; *Lightman et al.*, 1990; *Tille et al.*, 1985], as expected from its long lifetime (38 days in summer, 450 days in winter). Background concentrations of shorter-lived gases (butanes, pentane, hexane) are more spatially variable, especially in summer, and generally slightly higher at Harvard Forest than at remote sites.

Markedly different seasonal patterns are evident for compounds with predominantly anthropogenic sources (ethane, acetylene, propane, butane, isobutane, pentane, and hexane), which have minima in summer and maxima in winter, compared to species with strong biogenic summertime sources (e.g., propene; see Figure 2 and *Goldstein* [1994]), which peak in summer. Higher concentrations were observed at the lower inlet for isoprene, ethene, propene, and 1-butene, supporting the view that the anomalous seasonal variations for these reactive species reflect biogenic sources in the forest environment [*Goldstein*, 1994].

4. Discussion

We initially examine these data, using a simple model, representing the extratropical troposphere as a single box to illustrate the seasonal cycles of hydrocarbon concentrations associated with variation of OH. The model equation is

$$\frac{dC}{dt} = P - k[OH]C, \tag{1}$$

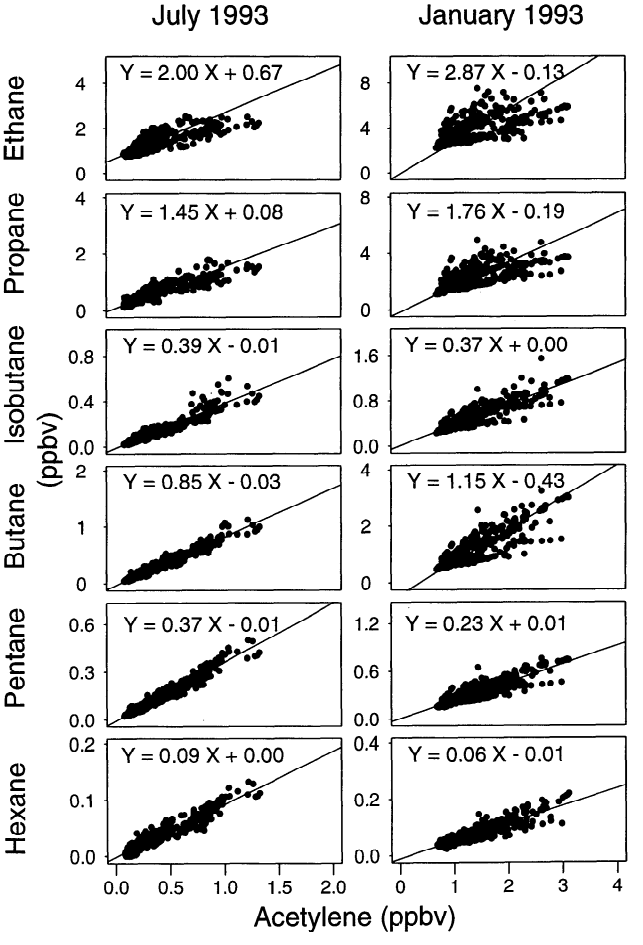

Figure 4. Ethane, propane, butane, isobutane, pentane, and hexane are plotted against acetylene for July and January 1993. The correlations indicate the signature of pollution inputs.

Table 1a. Mean Hydrocarbon Emission Ratios Versus C_2H_2 ($\pm\sigma$) Pollution Episodes at Harvard Forest

Alkane/C2H2	Summer	Winter	NAPAP (MA)[a]	NAPAP (US)[b]
Ethane	1.80±0.24	2.51±0.50	1.1	1.9
Propane	1.26±0.11	1.56±0.26	0.2	1.1
Butane	0.80±0.06	1.05±0.13	...	1.3
Isobutane	0.38±0.03	0.42±0.08	...	0.33
Pentane	0.37±0.03	0.23±0.02	...	0.34
Hexane	0.10±0.01	0.07±0.01	...	0.29

Summer includes June, July, and August. Winter includes December, January, and February
[a] NAPAP (MA), Massachussets emission ratios. From NAPAP [1985].
[b] NAPAP (US), U.S. emission ratios. From *Middleton and Stockwell* [1990].

where the model assumes that the tracer (C) is emitted at a constant rate (P) and removed solely by reaction with OH (with rate coefficient k; see Table 2) with all quantities averaged over northern midlatitudes. We adopt an expression for OH at northern midlatitudes given by

$$OH = 7 \times 10^5 \, [1 - \beta \cos (2\pi t / 365)] \qquad (2)$$

where 7×10^5 is a value characteristic of annual mean OH for midlatitudes [cf. *Spivakovsky et al.*, 1990], β is an adjustable parameter such that $(1-\beta)/(1+\beta)$ is the winter/summer ratio for OH concentrations, and t is in Julian days. The global calculations of *Spivakovsky et al.* [1990] indicate that $\beta \simeq 0.8$ at midlatitudes. Since solutions to (1) and (2) are proportional to P, the influence of emission rate can be eliminated by examining seasonal variations relative to the annual mean (relative seasonal variation, $c = C/\langle C \rangle_{annual}$ [cf. *Spivakovsky et al.*, 1990]).

The relative seasonal variations of hydrocarbons calculated by the simple model and observed at Harvard Forest show similar behavior (Figure 5). The phase of the seasonal cycle for each species reflects its rate of reaction with OH: The faster the reaction, the earlier the peak in winter, and the more rapid the decline in spring.

The shortest-lived species reach steady state even in winter,

$$C = \frac{P}{k[\mathrm{OH}]} . \qquad (3)$$

The winter:summer ratio for concentrations of hydrocarbons with aseasonal emission rates is equal to the summer:winter ratio for OH. If we assume that acetylene emissions are aseasonal, but emissions of the other hydrocarbons are not, we can determine the summer:winter OH ratio from

$$\frac{\mathrm{OH}_{sum}}{\mathrm{OH}_{win}} = \left[\frac{C_{win}}{C_{sum}}\right]\left[\frac{P_{sum}}{P_{win}}\right] \qquad (4)$$

using the empirical seasonal emission ratios in Table 1a.

To determine which hydrocarbons might reach steady state in both summer and winter, we adopt more realistic loss frequencies (Figure 6) calculated by using OH from a three-dimensional (3-D) model [*Spivakovsky et al.*, 1990] averaged from 32° to 56°N from the ground to 100 mbar (lowest seven model layers) weighted by mass of the atmosphere [*Prather and Spivakovsky*, 1990],

$$\langle k(T)\,\mathrm{OH}\rangle = \frac{\int \mathrm{k(T)\ OH}\ (x,y,p)\, f(x,y,p)\, dm}{\int f(x,y,p)\, dm} \qquad (5)$$

where $k(T)$ is the temperature dependent reaction rate coefficient, f is the mixing ratio by mass of the hydrocarbon species (assumed constant for this analysis), and dm is the mass element equal to $dx\,dy\,dp$. The corresponding lifetimes for selected hydrocarbons in summer and winter are shown in Table 2. The concentration of OH stays near its peak summer value for approximately 70 days, and the hydrocarbons (except possibly ethane) have sufficient time to reach a steady state value in summer; during winter, OH stays near its minimum for approximately 105 days, allowing time for hydrocarbons with lifetimes less than or equal to propane to accumulate to steady state concentrations.

Figure 7 shows winter:summer ratios for hydrocarbons versus reaction rate with OH; results indicated by the line were obtained by using the simple box model (equations (1) and (2)). The box model results illustrate that the rate of increase of winter:summer ratio for hydrocarbons decreases with k, and this feature is due solely to the seasonality of OH. Furthermore, isobutane, butane, and pentane, which essentially reach steady state in both summer and winter, have ratios within 10% of each other. Observed winter:summer ratios at Harvard Forest for both 1992-1993 and 1993-1994 are also shown (data for hexane were not used because the summer minimum was below our detection limit). The correction for seasonality in emission rate (equation (4)) has been applied to hydrocarbons which meet the steady state conditions defined above (isobutane, butane, and pentane), but it is not appropriate for longer-lived species.

The results in Figure 7 imply $\mathrm{OH}_{sum}/\mathrm{OH}_{win} = 9\pm2$. Calculations using OH fields from the 3-D model give mean values 1.5×10^6 for summer (Julian days 160-230), 0.15×10^6 for winter (Julian days 315-55) averaged over northern midlatitudes, i.e. $\mathrm{OH}_{sum}/\mathrm{OH}_{win} = 10$, in good agreement with this analysis (in the model box representing Harvard Forest, OH = 1.6×10^6 for summer and 0.13×10^6 for winter).

Penkett et al. [1993] observed concentrations of alkanes over the Atlantic Ocean off the coast of Ireland

Table 1b. 1992-1994 Monthly 0.1, 0.25, 0.5, and 0.9 Quantile Hydrocarbon Concentrations

Species	Quantile	August 1992	September	October	November	December	January 1993	February	March	April	May	June	July
Ethane	0.10	0.969	1.025	1.406	1.751	2.079	2.690	2.800	2.578	2.281	1.678	1.327	0.858
Ethane	0.25	1.045	1.195	1.826	1.904	2.291	2.846	2.907	2.771	2.540	1.817	1.421	0.934
Ethane	0.50	1.277	1.389	2.249	2.198	2.775	3.242	3.118	3.014	2.709	2.188	1.580	1.227
Ethane	0.90	2.598	2.949	3.971	4.456	6.348	5.233	4.115	3.973	3.260	3.006	2.174	1.867
Acetylene	0.10	0.219	0.221	0.332	0.555	0.637	0.842	0.929	0.717	0.549	0.287	0.205	0.127
Acetylene	0.25	0.267	0.266	0.468	0.680	0.741	0.943	1.011	0.842	0.668	0.353	0.253	0.162
Acetylene	0.50	0.402	0.393	0.714	0.888	0.937	1.212	1.206	1.040	0.810	0.463	0.334	0.243
Acetylene	0.90	1.103	1.312	1.706	1.534	1.939	2.103	1.746	1.840	1.294	1.124	0.834	0.674
Propane	0.10	0.272	0.332	0.506	0.804	0.961	1.367	1.378	1.056	0.621	0.353	0.277	0.208
Propane	0.25	0.409	0.449	0.769	1.002	1.158	1.564	1.530	1.246	0.880	0.429	0.370	0.280
Propane	0.50	0.597	0.651	1.219	1.391	1.542	1.908	1.754	1.487	1.064	0.653	0.535	0.461
Propane	0.90	1.515	1.718	2.489	3.003	4.130	3.282	2.383	2.129	1.409	1.276	1.105	0.972
Butane	0.10	0.117	0.114	0.174	0.292	0.387	0.578	0.569	0.365	0.190	0.092	0.089	0.075
Butane	0.25	0.168	0.150	0.321	0.409	0.485	0.684	0.658	0.489	0.298	0.137	0.129	0.098
Butane	0.50	0.253	0.265	0.570	0.613	0.683	0.845	0.794	0.632	0.407	0.214	0.200	0.167
Butane	0.90	0.856	1.013	1.791	1.693	2.203	1.888	1.524	1.432	0.944	0.783	0.639	0.531
Isobutane	0.10	0.055	0.053	0.089	0.149	0.192	0.296	0.288	0.196	0.093	0.040	0.042	0.034
Isobutane	0.25	0.082	0.069	0.154	0.214	0.232	0.338	0.330	0.247	0.160	0.058	0.064	0.046
Isobutane	0.50	0.124	0.130	0.257	0.278	0.318	0.416	0.408	0.323	0.225	0.086	0.104	0.079
Isobutane	0.90	0.387	0.456	0.735	0.756	0.896	0.772	0.659	0.645	0.443	0.442	0.302	0.225
Pentane	0.10	0.060	0.047	0.064	0.093	0.125	0.184	0.168	0.082	0.044	0.038	0.039	0.041
Pentane	0.25	0.079	0.064	0.104	0.132	0.154	0.218	0.200	0.124	0.070	0.054	0.058	0.052
Pentane	0.50	0.116	0.106	0.170	0.192	0.209	0.261	0.243	0.168	0.106	0.082	0.090	0.079
Pentane	0.90	0.408	0.437	0.516	0.450	0.568	0.484	0.380	0.341	0.249	0.312	0.313	0.228
Hexane	0.10	0.017	0.008	0.011	0.020	0.027	0.042	0.033	0.013	0.000	0.003	0.006	0.009
Hexane	0.25	0.022	0.014	0.021	0.030	0.034	0.050	0.041	0.021	0.009	0.009	0.012	0.014
Hexane	0.50	0.032	0.026	0.037	0.049	0.047	0.060	0.056	0.032	0.016	0.015	0.019	0.022
Hexane	0.90	0.093	0.099	0.121	0.110	0.127	0.120	0.094	0.080	0.047	0.069	0.071	0.058
Ethane	0.10	0.920	1.039	1.298	1.812	2.202	2.345	2.569	2.485	2.125	1.573	1.214	0.985
Ethane	0.25	1.151	1.192	1.539	1.989	2.539	2.503	2.717	2.653	2.276	1.703	1.329	1.172
Ethane	0.50	1.434	1.467	1.849	2.782	3.072	2.849	3.027	2.888	2.600	1.941	1.446	1.508
Ethane	0.90	2.213	2.303	3.471	5.079	5.232	5.561	5.095	3.876	3.320	2.600	2.177	2.318
Acetylene	0.10	0.214	0.232	0.314	0.502	0.719	0.755	0.859	0.750	0.457	0.286	0.188	0.192
Acetylene	0.25	0.292	0.305	0.407	0.625	0.823	0.878	0.967	0.817	0.521	0.335	0.226	0.257
Acetylene	0.50	0.436	0.416	0.558	0.866	1.030	1.174	1.164	0.909	0.694	0.426	0.363	0.372

Table 1b. (continued)

Species	Quantile	August 1993	September	October	November	December	January 1994	February	March	April	May	June	July
Acetylene	0.90	0.954	1.127	1.514	1.965	2.158	2.406	2.031	1.696	1.198	0.811	0.795	0.854
Propane	0.10	0.308	0.388	0.456	0.828	1.218	1.163	1.333	1.120	0.602	0.336	0.246	0.265
Propane	0.25	0.493	0.521	0.643	1.034	1.342	1.404	1.514	1.212	0.757	0.429	0.308	0.452
Propane	0.50	0.711	0.752	0.895	1.583	1.736	1.738	1.749	1.395	1.002	0.570	0.553	0.677
Propane	0.90	1.324	1.459	2.190	3.147	3.382	3.538	3.378	2.128	1.522	1.157	1.109	1.201
Butane	0.10	0.104	0.108	0.158	0.319	0.510	0.510	0.547	0.421	0.168	0.078	0.067	0.082
Butane	0.25	0.168	0.181	0.256	0.423	0.601	0.597	0.639	0.488	0.237	0.104	0.099	0.161
Butane	0.50	0.279	0.275	0.403	0.821	0.896	0.804	0.782	0.611	0.410	0.187	0.212	0.264
Butane	0.90	0.721	0.862	1.511	1.979	2.119	1.888	1.987	1.344	0.821	0.538	0.559	0.631
Isobutane	0.10	0.049	0.054	0.084	0.165	0.245	0.252	0.289	0.218	0.085	0.043	0.036	0.039
Isobutane	0.25	0.082	0.088	0.126	0.209	0.290	0.294	0.330	0.252	0.119	0.055	0.050	0.082
Isobutane	0.50	0.132	0.131	0.194	0.371	0.398	0.386	0.390	0.310	0.193	0.097	0.107	0.134
Isobutane	0.90	0.365	0.452	0.706	0.845	0.864	0.869	0.982	0.651	0.405	0.285	0.309	0.314
Pentane	0.10	0.055	0.051	0.057	0.103	0.152	0.164	0.166	0.109	0.044	0.027	0.034	0.044
Pentane	0.25	0.081	0.083	0.085	0.131	0.192	0.190	0.194	0.131	0.066	0.041	0.051	0.068
Pentane	0.50	0.127	0.128	0.136	0.238	0.264	0.250	0.232	0.162	0.109	0.071	0.105	0.112
Pentane	0.90	0.362	0.402	0.455	0.551	0.551	0.533	0.492	0.347	0.263	0.229	0.268	0.294
Hexane	0.10	0.014	0.012	0.011	0.021	0.035	0.039	0.031	0.022	0.008	0.005	0.011	0.012
Hexane	0.25	0.021	0.022	0.018	0.029	0.047	0.048	0.039	0.028	0.015	0.013	0.016	0.020
Hexane	0.50	0.034	0.036	0.031	0.057	0.068	0.068	0.058	0.038	0.029	0.024	0.033	0.034
Hexane	0.90	0.106	0.114	0.122	0.15	0.155	0.15	0.126	0.107	0.091	0.073	0.085	0.090

Concentrations are given in ppbv.

Table 2. Hydrocarbon Reaction Rates with OH and Lifetimes

Species	OH Rate Coefficient k cm^{3}s^{-1} [a]	Lifetime (Summer) days	Lifetime (Winter) days
Ethane	$1.42\times10^{-17}T^2$ exp(-462/T)	38	450
Acetylene	9.4×10^{-12} exp(-700/T)	10	116
Propane	$1.50\times10^{-17}T^2$ exp(-44/T)	7.9	87
Isobutane	$1.04\times10^{-17}T^2$ exp(277/T)	3.6	37
Butane	$1.51\times10^{-17}T^2$ exp(190/T)	3.4	36
Pentane	$2.10\times10^{-17}T^2$ exp(223/T)	2.2	23
Hexane	1.35×10^{-11} exp(-262/T)	1.5	15

OH and temperature used for calculating lifetimes: summer, 1.5×10^6cm^{-3} OH, 276 K; winter, 0.15×10^6cm^{-3} OH, 264 K.
[a] From *Atkinson* [1989].

and obtained notably higher winter:summer ratios for shorter-lived hydrocarbons (e.g., butane and pentane) than those at Harvard Forest. In winter, concentrations of these gases were similar over the North Atlantic and at Harvard Forest, while in summer, concentrations were lower over the Atlantic, suggesting that these hydrocarbons were oxi-

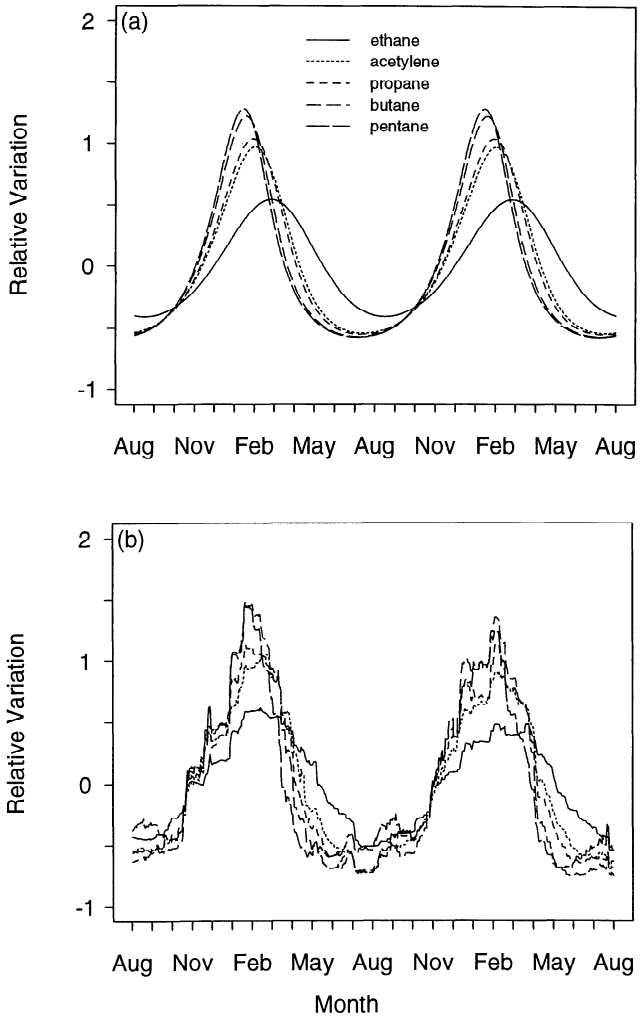

Figure 5. Relative seasonal variations of ethane, acetylene, propane, isobutane, butane, and pentane (a) calculated from the simple box model and (b) measured at Harvard Forest from August 1992 to July 1994.

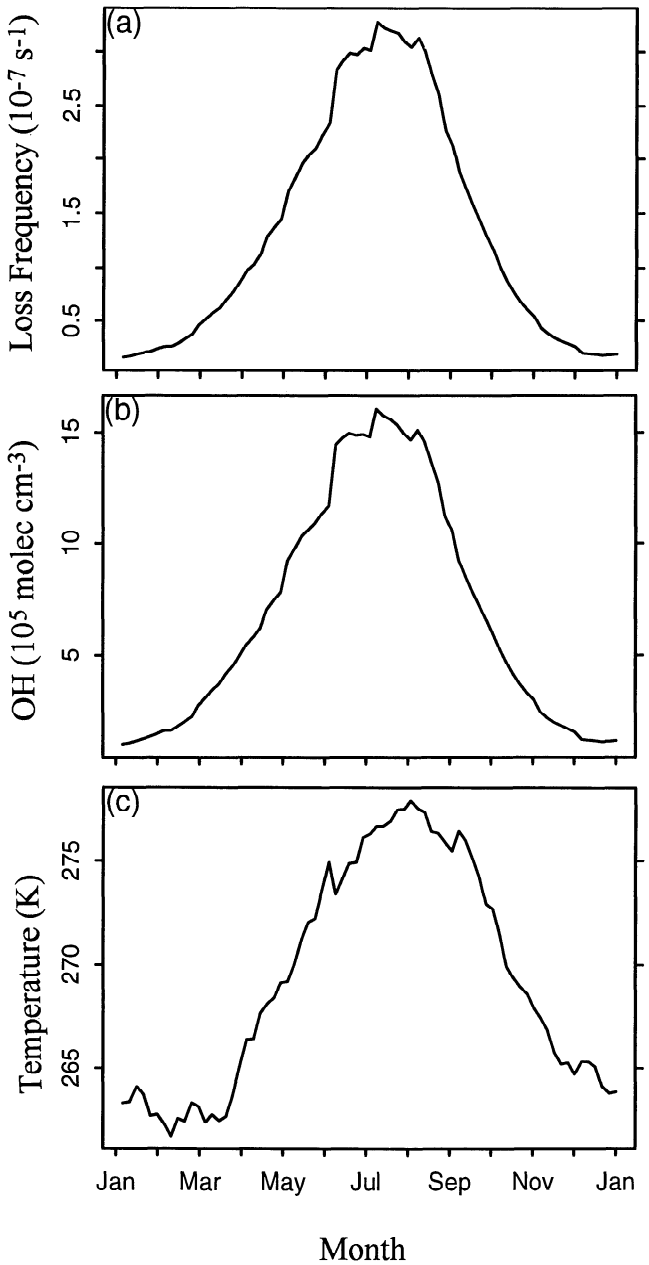

Figure 6. (a) Loss frequency of ethane averaged from 32°N to 56°N and 1000 to 100 mbar from the 3D OH [*Spivakovsky et al.*, 1990] and temperature [*Hansen et al.*, 1983] fields, and the corresponding seasonal cycles of (b) OH and (c) temperature.

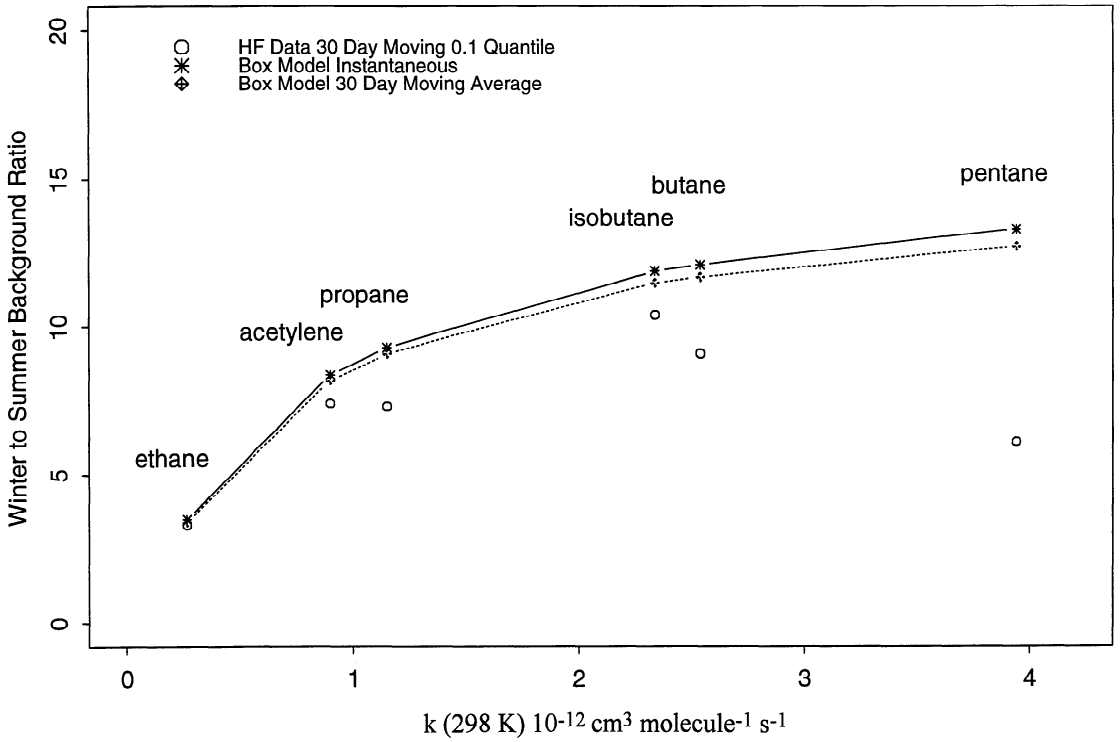

Figure 7. Winter maximum to summer minimum concentration ratios of ethane, acetylene, propane, isobutane, butane, and pentane versus their reaction rate with OH taken from 2 years of Harvard Forest measurements (maximum and minimum are defined from the 0.1 quantile of the data filtered in 30-day intervals shown in Figure 2). Simulations using the simple box model (equations (1) and (2)) are indicated by the line. The Harvard Forest data for isobutane, butane, and pentane are corrected for seasonality in emissions (equation (4)).

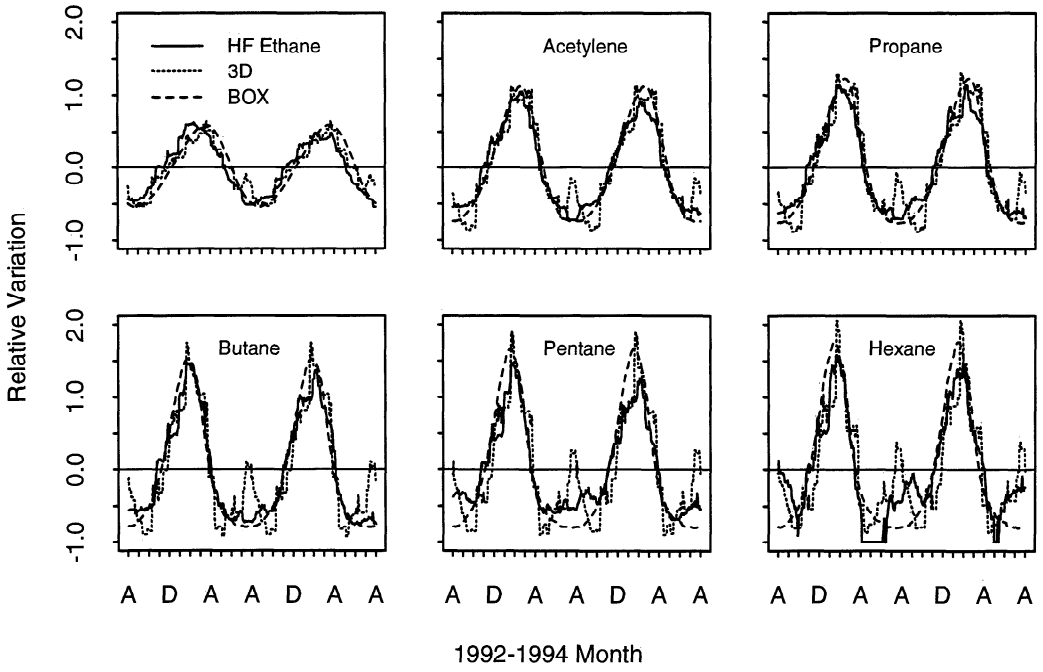

Figure 8. Relative seasonal variations measured at Harvard Forest are shown with the box model (using loss frequencies calculated from 3D model) and 3D model simulations for ethane, acetylene, propane, butane, pentane, and hexane, supporting the view that OH chemistry determines the relative seasonal cycles of hydrocarbons at this site.

dized in transit across the Atlantic during summer. Hence concentrations of short-lived hydrocarbons at Harvard Forest in summer reflect steady state balance between regional emissions and OH concentrations, but over the Atlantic, concentrations are affected by rates of transport from source regions. Penkett's values are affected also by operational constraints: Summertime measurements are near the detection limit and therefore have large uncertainties, and there are relatively few measurements, making it difficult to identify maxima and minima.

Penkett et al. [1993] interpreted deviations between iso- and normal alkane data as implying significant rates for hydrocarbon reactions with NO_3. If reaction with NO_3 were important, there would be preferential loss of iso- over normal paraffin isomers, particularly in winter. The ratio of emissions for butanc:isobutanc is about 2 at Harvard Forest (Table 1a) and also in London [*Penkett et al.*, 1993]. The ratio of background concentrations for these butanes is also ≈2 in winter (639 and 322 pptv at Harvard Forest and 405 and 193 pptv over the North Atlantic, respectively), apparently inconsistent with significant reaction of isobutane with NO_3. The butane and isobutane background concentrations in summer were 70 and 31 pptv (ratio of ≈2) at Harvard Forest and were 25 and 47 pptv (ratio of ≈0.5) over the North Atlantic [*Penkett et al.*, 1993]. This low ratio over the North Atlantic in summer could reflect an additional oceanic source of isobutane in summer, or there could have been experimental problems associated with the recovery of very low concentrations from the flasks.

5. Three-Dimensional Model

The effects of transport and chemistry together were simulated by using a global 3-D chemical transport model (CTM) with both 4×5 degree and 8×10 degree resolution. The CTM uses transport fields from the general circulation model (GCM) developed at the Goddard Institute for Space Studies [*Hansen et al.*, 1983], as described by *Prather et al.* [1987] and *Jacob et al.* [1987], and has been used previously to study interhemispheric exchange using chlorofluorocarbons (CFCs) [*Prather et al.*, 1987] and ^{85}Kr [*Jacob et al.*, 1987], convection using ^{222}Rn [*Jacob and Prather*, 1990], and tropospheric OH using CH_3CCl_3 [*Spivakovsky et al.*, 1990]. We ran the model for hydrocarbons, using the OH fields of *Spivakovsky et al.* [1990] and fossil fuel combustion (aseasonal) and biomass burning (seasonal) as hydrocarbon sources, with emissions distributed geographically as for CO by J. A. Logan (personal communication, 1994). The simulations for hydrocarbons showed no significant effects from biomass burning for the box containing Harvard Forest. All results are presented in terms of relative variation in order to eliminate influence of the absolute magnitude of the source and as 30-day filtered 0.1 quantiles, consistent with the presentation of the Harvard Forest Data.

The relative variations of ethane, acetylene, propane, butane, pentane, and hexane from the 8×10 model box in which Harvard Forest is located are shown in Figure 8. The similarity of Harvard Forest data with both box and 3-D models (Figure 8) supports the view that OH chemistry determines the observed seasonal cycles of background concentrations for hydrocarbons at this site.

The spatial variance of background hydrocarbon seasonal cycles, according to the 4x5 model, is shown in Figure 9. Results are plotted for the Harvard Forest Box, the boxes to the north (8°) and east (10°), and a box over the North Atlantic (8°N, 50°E) for both ethane and butane. The relative amplitude in the Harvard Forest box is significantly smaller than that in boxes to the north and east, and over the Atlantic for butane, but not for ethane, reflecting the relatively uniform distribution of background ethane concentrations over the hemisphere. The more

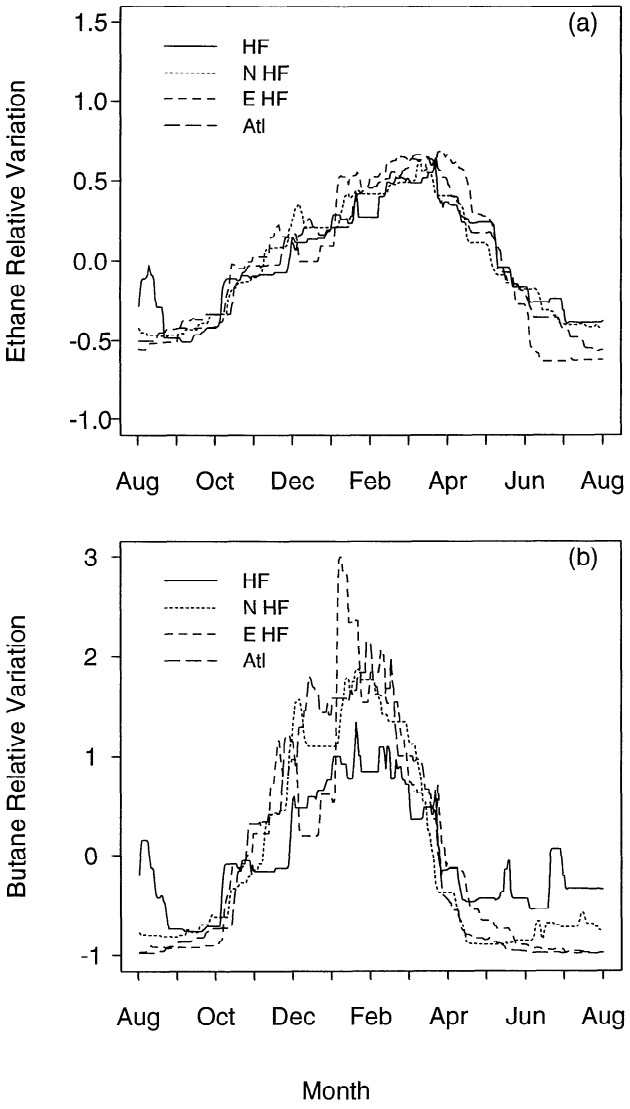

Figure 9. Spatial variance of hydrocarbon relative seasonal variation as simulated by the 3D chemical tracer model (4×5 resolution). Results are plotted for the Harvard Forest box, the boxes to the north (8°) and east (10°), and a box over the North Atlantic (8°N, 50°E) for (a) ethane and (b) butane.

remote sites exhibit larger winter:summer ratios for the most reactive hydrocarbons because in summer, significant losses occur in transit to remote areas (as discussed above in relation to *Penkett et al.* [1993]). The consistency of ethane relative amplitude between different locations in northern midlatitudes is confirmed by comparison with other measurements of time series for ethane [*Penkett et al.*, 1993; *Blake and Rowland*, 1986]. Ethane is therefore a good tracer for analysis of hemispheric mean OH.

Model OH [*Spivakovsky et al.*, 1990] was evaluated by using observed seasonal cycles for ethane. Simulations with model OH multiplied by 0.5, 1.0, and 1.5, and with annually averaged (aseasonal) OH, are shown in Figure 10. The aseasonal run (Figure 10a) indicates that the seasonal cycle for ethane is not produced by seasonal variations of transport rates. The data agree best with unmodified fields of OH and appear to be bounded by ±50%. Results for ethane are similar if the simple box model is used (Figure 10b), reflecting the weak influence of transport on seasonal cycles. There is a small phase shift between the ethane data and the models. This shift could reflect some seasonality

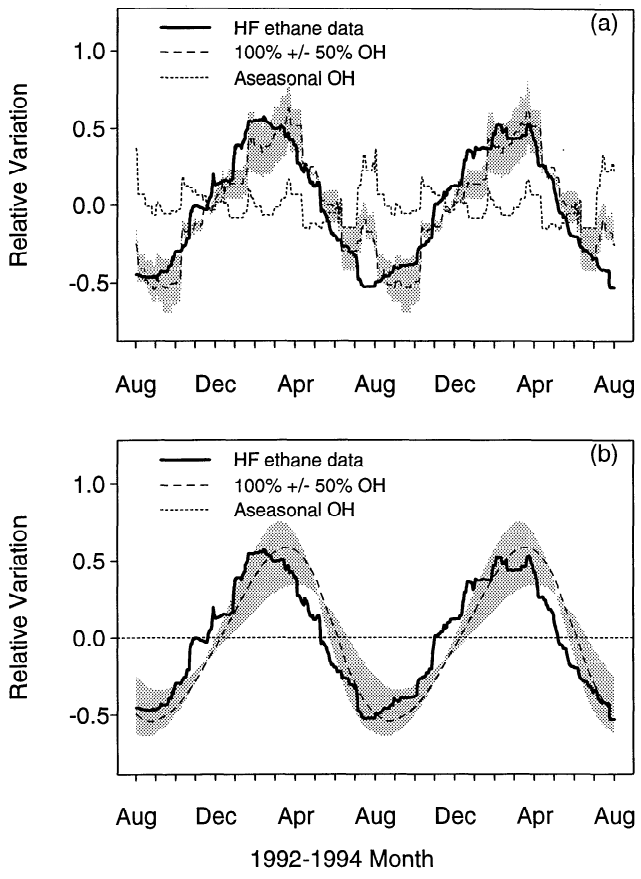

Figure 10. Simulations of sensitivity of ethane relative seasonal variation to changes in absolute OH concentration (50%, 100%, 150%) using the (a) 8x10 model and (b) simple box model (using loss frequency calculated from the 3D model), compared with Harvard Forest data. Simulations with annually averaged (aseasonal) OH are indicated by the dotted line.

in ethane emissions, with higher emissions in fall and winter. Results for butane are insensitive to OH concentrations, as expected from the discussion above. There is almost no difference between the ×1 and ×1.5 runs, with slightly smaller relative variation for the ×0.5 run.

6. Conclusions

We have presented 2 years of continuous measurements of C_2–C_6 hydrocarbon concentrations in rural New England. Seasonal cycles of background NMHC concentrations can be cleanly extracted from measurements made with sufficient frequency at a rural site near an industrialized region. Background concentrations of hydrocarbons with predominantly anthropogenic sources (ethane, acetylene, propane, butane, pentane, and hexane) reach maxima in winter and minima in summer. The more rapid the rate for reaction with OH, the earlier the winter peak, and the faster the spring decline. Comparison with data in the literature indicates that the background concentration of ethane is evenly distributed in northern midlatitudes in all seasons, as is expected from its lifetime (38 days in summer, 450 days in winter), while background concentrations of more reactive gases (butanes, pentane, and hexane) are higher near source regions in summer and uniformly distributed in winter.

Hydrocarbon background seasonal cycles observed at Harvard Forest are regulated by balance between nearly aseasonal anthropogenic emissions and chemical loss by reaction with OH. The amplitude of the annual cycle for ethane background, relative to the annual mean, is a measure of absolute OH concentrations, while relative variations of species with lifetimes shorter than the lifetime of propane are sensitive only to the ratio of OH in different seasons. The data imply a summer:winter ratio for hydroxyl radical in the range 9 ± 2 at northern midlatitudes, and annual mean OH concentrations of $7\times10^5 cm^{-3}$ ± 50%.

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References

Ackman, R. G., Fundamental groups in the response of flame ionization detectors to oxygenated aliphatic hydrocarbons, *J. Gas Chromatogr.*, *2*, 173-179, 1964.

Ackman, R. G., The flame ionization detector: Further comments on molecular breakdown and fundamental group responses, *J. Gas Chromatogr.*, *6*, 497-501, 1968.

Atkinson, R., Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds, *J. Phys. Chem. Ref. Data Monogr., 1*, 1989.

Blake, D. R., and F. S. Rowland, Global atmospheric concentrations and source strength of ethane, *Nature, 321*, 231-233, 1986.

Dietz, W. A., Response factors for gas chromatographic analysis, *J. Gas Chromatogr., 1*, 68-71, 1967.

Goldstein, A. H., Non-methane hydrocarbons above a midlatitude forest: biogenic emissions and seasonal concentration variations, Ph.D thesis, Harvard Univ., Cambridge, Mass., 1994.

Goldstein, A. H., B. C. Daube, J. W. Munger, and S. C. Wofsy, Automated in-situ monitoring of atmospheric non-methane hydrocarbon concentrations and gradients, *J. Atmos. Chem., 21*, 43-59, 1995.

Hansen, J., G. Russel, D. Rind, P. Stone, A. Lacis, S. Lebedeff, R. Ruedy and L. Travis, Efficient 3-D global models for climate studies: Models I and II, *Mon. Weather Rev., 111*, 609-662, 1983.

Jacob, D. J., and M. J. Prather, Radon-222 as a test of convective transport in a general circulation model, *Tellus, 42B*, 118-134, 1990.

Jacob, D. J., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Atmospheric distribution of 85Kr simulated with a general circulation model, *J. Geophys. Res., 92*, 6614-6626, 1987.

Jobson, B. T., Z. Wu, and H. Niki, Seasonal trends of isoprene, C_2–C_5 alkanes, and acetylene at a remote boreal site in Canada, *J. Geophys. Res., 99*, 1589-1599, 1994.

Lightman, P., A. S. Kallend, A. R. W. Marsh, B. M. R. Jones, and S. A. Penkett, Seasonal variation of hydrocarbons in the free troposphere at mid-latitudes, *Tellus, 42B*, 408-422, 1990.

Middleton, P., and W. R. Stockwell, Aggregation and analysis of volatile organic compound emissions for regional modeling, *Atmos. Environ., 24A*, 1107-1133, 1990.

National Acid Precipitation Assessment Program, The 1985 NAPAP emissions inventory (version 2): Development of the annual data and modelers' tapes, *Rep. EPA-600/7-89-012a*, pp. 2-19, U.S. Environ. Prot. Agency, Washington, D. C., 1985, (available from Nat. Tech. Inf. Serv., Springfield, Va).

The Oxygenated Fuels Association, A new day is dawning for cleaner fuels: Benefits of a national oxygenated fuels policy, white paper, Washington D. C., 1994.

Penkett, S. A., N. J. Blake, P. Lightman, A. R. W. Marsh, P. Anwyl, and G. Butcher, The seasonal variation of nonmethane hydrocarbons in the free troposphere over the North Atlantic Ocean: Possible evidence for extensive reaction of hydrocarbons with the nitrate radical, *J. Geophys. Res., 98*, 2865-2885, 1993.

Prather, M. J., and C. M. Spivakovsky, Tropospheric OH and the lifetimes of hydrochlorofluorocarbons, *J. Geophys. Res., 95*, 18,723-18,729, 1990.

Prather, M. J., M. B. McElroy, S. C. Wofsy, G. Russell, and D. Rind, Chemistry of the global troposphere: Fluorocarbons as tracers of air motion, *J. Geophys. Res., 92*, 6579-6613, 1987.

Press, W. H., S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran: The Art of Scientific Computing*, 2nd ed., pp. 660-664, Cambridge Univ. Press., New York, 1992.

Rudolph, J., F. J. Johnen, A. Khedim, and G. Pilwat, The use of automated "on line" gaschromatography for the monitoring of organic trace gases in the atmosphere at low levels, *In. J. Environ. Anal. Chem., 38*, 143-155, 1989.

Singh, H. B., and L. J. Salas, Measurements of selected light hydrocarbons over the Pacific Ocean: Latitudinal and seasonal variations, *Geophys. Res. Lett., 9*, 842-845, 1982.

Singh, H. B., W. Viezee, and L. J. Salas, Measurements of selected C_2–C_5 hydrocarbons in the troposphere: Latitudinal, vertical, and temporal variations, *J. Geophys. Res., 93*, 15,861-15,878, 1988.

Spivakovsky, C. M., R. Yevich, J. A. Logan, S. C. Wofsy, M. B. McElroy, and M. J. Prather, Tropospheric OH in a three-dimensional chemical tracer model: An assessment based on observations of CH_3CCl_3, *J. Geophys. Res., 95*, 18,441-18,471, 1990.

Tille, K. J. W., M. Savelsberg, and K. Bachmann, Airborne measurements of nonmethane hydrocarbons over Western Europe: Vertical distributions, seasonal cycles of mixing ratios and source strengths, *Atmos. Environ., 19*, 1751-1760, 1985.

Wofsy, S. C., M. L. Goulden, J. W. Munger, S.-M. Fan, P. S. Bakwin, B. C. Daube, S. L. Bassow, and F. A. Bazzaz, Net exchange of CO_2 in a mid-latitude forest, *Science, 260*, 1314-1317, 1993.

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