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Anthropogenic emissions of nonmethane hydrocarbons in the northeastern United States: Measured seasonal variations from 1992–1996 and 1999–2001

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[1] Harvard Forest, a rural site located in central Massachusetts downwind of major urban-industrial centers, provides an excellent location to observe a typical regional mixture of anthropogenic trace gases. Air that arrives at Harvard Forest from the southwest is affected by emissions from the U.S. east coast urban corridor and may have residual influence from emissions in the upper Ohio Valley and Great Lakes region farther to the west. Because of its relatively long distance from large individual emission sources, pollution plumes reaching the site are a homogenized mixture of regional anthropogenic emissions. Concentrations of C_2-C_6 hydrocarbons along with CO and NO_y were measured nearly continuously from August 1992 through July 1996 and from June 1999 through November 2001. By correlating observed concentrations to acetylene, which is almost solely produced during combustion, we are able to detect seasonal trends in relative emissions for this series of trace gases. Seasonal changes in *n*-butane and *i*-butane emissions may largely be influenced by different gasoline formulations in late spring and summer. Shifts in evaporation rates due to the annual temperature cycle could induce a seasonal pattern for *n*-pentane, *i*-pentane and *n*-hexane emissions. Emissions of ethane and propane lack clear seasonality relative to acetylene emissions and also correlate less with acetylene than other gases, indicating that emissions of these two gases are strongly influenced by sources not associated with fuel combustion. Changes in the observed correlations of CO_2 and CO relative to acetylene are consistent with published changes in the estimated emissions of CO_2 and CO over the past decade, though variability in the observations makes it difficult to precisely quantify these changes.

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1. Introduction

[2] Anthropogenic emissions of trace gases influence the Earth's atmosphere at the local, regional and global scales. Chemically active species such as nonmethane hydrocarbons (NMHCs), carbon monoxide (CO) and nitrogen oxides ($NO_x = NO + NO_2$) combine in the presence of sunlight to produce ozone (O_3), higher oxides of nitrogen ($NO_y = NO_x + NO_3 + 2N_2O_5 + HNO_3$ + peroxyacetyl nitrate (PAN) + other organic nitrates + aerosol nitrates) and secondary aerosols, which affect human and ecosystem health as well as Earth's climate. Urban sources of NMHCs, CO and nitrogen oxides are predominantly anthropogenic. Over the past decades, implementation of emission control regulation and technology has aimed at significantly reducing these emissions in the United States. Hydrocarbon, NO_x and CO sources include fuel combustion in both mobile and stationary sources, biomass burning, and a variety of residential/industrial point sources. Additional sources for hydrocarbons include evaporation of fuels and solvents. CO is also formed secondarily in the atmosphere from the oxidation of primary hydrocarbons, which can contribute to summer CO concentrations [*Seinfeld and Pandis*, 1998].

[3] In this study, we present the seasonality of C_2-C_6 (ethane, propane, *n*-butane, *i*-butane, *n*-pentane, *i*-pentane and *n*-hexane) hydrocarbons, NO_y and CO as measured at Harvard Forest with roughly hourly measurements over nearly 6 years. We investigate the relative emissions of these compounds by analyzing the seasonality of the monthly orthogonal slope utilizing the reduced major axis technique of their linear correlations to acetylene, as previously done by *Goldstein et al.* [1995a] but for a longer time period and with finer temporal resolution. Acetylene is used because it is a reliable tracer for anthropogenic emissions that is almost solely derived from combustion [*Blake*, 2005]. In addition, because of year-round relatively constant fossil fuel use and

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the absence of acetylene in the headspace vapor of gasoline and diesel fuels, it is assumed for this analysis that the emission rate of acetylene is relatively constant throughout the year. However, acetylene emissions are not uniform among different combustion sources and significant differences in combustion processes or seasonality in biomass burning could induce seasonal shifts in acetylene emissions. All of the reported gases correlate reasonably well with acetylene at this rural site because the high-concentration anthropogenic pollution events observed here generally homogenize emissions from the large upwind urban regions rather than being indicative of individual local sources [e.g., *Moody et al.*, 1998]. Seasonal shifts in mixing height and other meteorological conditions affect the seasonal patterns of absolute concentration, but the influence of mixing and dilution that equally affect all species do not change the correlation slopes. Changes in the degree of oxidation due to variations in transport time and concentrations of oxidants will of course alter the monthly slopes of these gases with respect to acetylene, and these issues are addressed with more detail in discussing the observations. Finally, we examine the evidence for changes in emissions of carbon dioxide (CO_2), CO, and NO_x relative to acetylene over the 6 years of reported observations.

2. Methods

[4] Harvard Forest is located in Petersham, Massachusetts (42.54°N, 72.18°W) at an elevation of 340 m. It is remote from major cities with Boston, Massachusetts approximately 100 km to the east and Hartford, Connecticut 100 km to the southwest. There is a secondary road 2 km to the west and a highway 5 km to the north. The site itself is accessible by a dirt road that is closed to public vehicle traffic. Maps and additional details of the measurement site are presented by *Goldstein et al.* [1995b] and *Munger et al.* [1996]. Other continuous measurements at Harvard Forest include concentrations of CH_4 [*Shipham et al.*, 1998], CO, CO_2, O_3, NO_x, NO_y, H_2O, rain composition, wind speed, wind direction and temperature, as well as fluxes of sensible heat, latent heat, O_3, NO_y and CO_2 by eddy covariance [*Munger et al.*, 1996; *Wofsy et al.*, 1993].

[5] Automated in situ measurements of C_2-C_6 hydrocarbons were obtained from 29 m above ground (7 m above forest canopy) every 45 min using cryogenic concentration and gas chromatography. Air samples were drawn through Teflon tubing from the inlet and conditioned with a nafion dryer (Perma Pure Products) to remove H_2O, then with 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 a trap of 0.030-inch ID stainless steel tubing, then injected into a gas chromatograph with a PLOT GS-Alumina 30-m Megabore capillary column (J&W Scientific) and flame ionization detector (Hewlett Packard 5890 series II). Concentration for all NMHCs was determined by using relative response factors referenced to neohexane (Scott-Marrin, NIST traceable ±2%), which was added by dynamic dilution to every sample as an internal standard at low ppbv mixing ratios. The overall accuracy of the hydrocarbon system is estimated to be better than ±18% with a minimum detectable concentration of 0.01 ppbv for all C_2-C_6 hydrocarbons. T cision is approximately 2% at 1 ppbv, 5% at 0.5 ppbv, 10% at 0.2 ppbv and 20% for mixing ratios below 0.1 ppbv.

[6] The NO_y measurements are presented in detail by *Munger et al.* [1996]. Concentration of NO_y was determined by reduction to NO by H_2 on gold catalyst at the sample inlet and quantification by O_3-chemiluminescence. Estimated accuracy limited by absolute accuracy of the standards and flow measurements is within ±6% with a minimum detectable concentration of 0.05 ppbv and precision of 4%. The instrument response was determined by standard addition of NO in N_2 every 4 to 6 hours and maintained in the range of 0.25 to 0.75 pptv per count. The NO standard was calibrated against archived standards from the National Institute of Standards and Technology. CO was analyzed using a gas-filter correlation infrared absorption spectrometer that was modified by inclusion of sample drying over an approximately −20°C cold trap and frequent zeroing using an oxidizing catalyst. Analytical accuracy and precision are both approximately 10 ppbv or 10% of the measured value. Minimum detection limits are around 50 ppbv, which is always well below values observed in ambient air at the site. CO_2 mixing ratios were determined using Licor 6251 after ambient air was treated with a Nafion dryer followed by a −20°C cold trap [*Goulden et al.*, 1996]. The instrument response factors were determined 4–6 times per day by calibration with a pair of standards, which are accurate to 0.1 ppmv or better. The Licor 6251 sequentially sampled from 8 inlets to determine a CO_2 profile. Only data from inlet at 29 m above ground are used for this analysis. A second analyzer for measuring CO_2 eddy fluxes (Licor 6262) sampled continuously at high flow rate from an inlet at 29 m. The gain of the eddy CO_2 analyzer was determined by standard additions 4 to 5 times per day. Absolute calibration of the eddy CO_2 analyzer is achieved by least squares fit of the observed signal from the eddy CO_2 analyzer to the simultaneously measured concentration from the CO_2 profile analyzer sampling from the same height. Reported hourly concentrations are a combination of data from both analyzers. The overall uncertainty of the calculated concentrations based on the standard error of the calibration coefficients is ±0.5 ppmv.

[7] The flow rate of the internal standard being dynamically diluted into the NMHC instrument was maintained at 7–8 mL min^{-1} from 1992 through 1995, but experienced a gradual decline due to drift in a pressure regulator starting in early 1996 leveling off around 1–2 mL min^{-1} by 2001. The low flow rates were inaccurate because they were outside the range of the initial pressure to flow calibration, approaching the measurement resolution of the flow transducers. This led to errors in the calculated response factors used to compute hydrocarbon mixing ratios from peak areas. The mixing ratio from the initial data reduction was adjusted on the basis of an updated pressure-flow relationship spanning a wider range of pressures. The corrected mixing ratios for 1996, 1999 and 2001 were consistent with the 1992–1995 data in terms of "background" mixing ratios defined at Harvard Forest as the 10th percentile of the mixing ratio for a given time period. For the first six months of 2000 when the flow of internal standard was at its lowest during the entire measurement period, the computed response factors were not reliable. Instead, we assumed that the detector sensitivity remained constant and computed the mixing ratios for only this time

period by using a constant response factor based on an average value from 1996, when the pressure drift was mild and the response factors were still relatively stable. We computed mixing ratios using the constant response factor for all of 1996–2001 data and found that the mean difference from these mixing ratios and those derived from an explicit calculation of the response factor was 0.02 ± 0.07 ppbv, which demonstrates that the assumption of constant response factors has not biased the results. Because all reported NMHC mixing ratios are based on responses relative to the neohexane internal standard, ratios of individual NMHC to one another, which are the focus of this paper, are unaffected by any errors in the computed or assumed response factor. Any error in the computed response factors contributes uncertainty in the slopes of CO, NO_y and CO_2 relative to acetylene and limits our ability to quantify any long-term trends in emissions of these species relative to one another.

[8] Additionally, about 750 samples with extremely low mixing ratios of ethane (more than half ppbv lower than the defined background), which is a symptom of inadequate cooling of the cryotrap dewar were excluded from the data set. Long-term data sets will inevitably have gaps, which occur because of routine instrument calibrations and periodic shutdowns due to sensor malfunctions, lightning strikes, power failures, etc. There is a 3-year data gap between July 1996 and June 1999 when the measurements were deliberately stopped for instrument repair, but remained shut down for nearly 3 years because of limited personnel. The NMHC data set reported here includes approximately 43,000 data points for each compound over approximately 6 years of measurements over nearly a 10-year period.

3. Results

[9] Figure 1a shows the mixing ratios in ppbv of acetylene for the entire measurement period from August 1992 through November 2001. A seasonal oscillation of the "background" concentration, defined at Harvard Forest as the monthly 0.1 quantile [*Goldstein et al.*, 1995a], is apparent in these data (Figure 1b) and has been well documented for NMHCs at other sites throughout the Northern Hemisphere [*Swanson et al.*, 2003, and references therein]. This oscillation, which remains essentially unchanged during the entire measurement period, is mainly due to seasonally changing atmospheric lifetimes from photochemical oxidation by hydroxyl (OH) radicals [*Goldstein et al.*, 1995a]. Above the seasonally changing background concentration, pollution plumes are evident. The magnitude of these pollution events also changes seasonally because of variations in boundary layer depths and thus dilution rates, as well as oxidation rates to some extent.

[10] Air parcels arriving at Harvard Forest during periods with southwesterly winds generally contain higher concentrations of NMHCs, NO_y, CO and CH_4 than air parcels arriving from other directions. Figure 2 shows mixing ratios of acetylene, NO_y, CO and CH_4 from the southwest (180–270°) and from the other combined wind directions (>270° and <180°) in 1994, as an example of what is observed for a typical year. This site experiences a much higher frequency of winds from the northwest and southwest than the other directions. The southwesterly winds are associated with transport from the east rban corridor integrating over

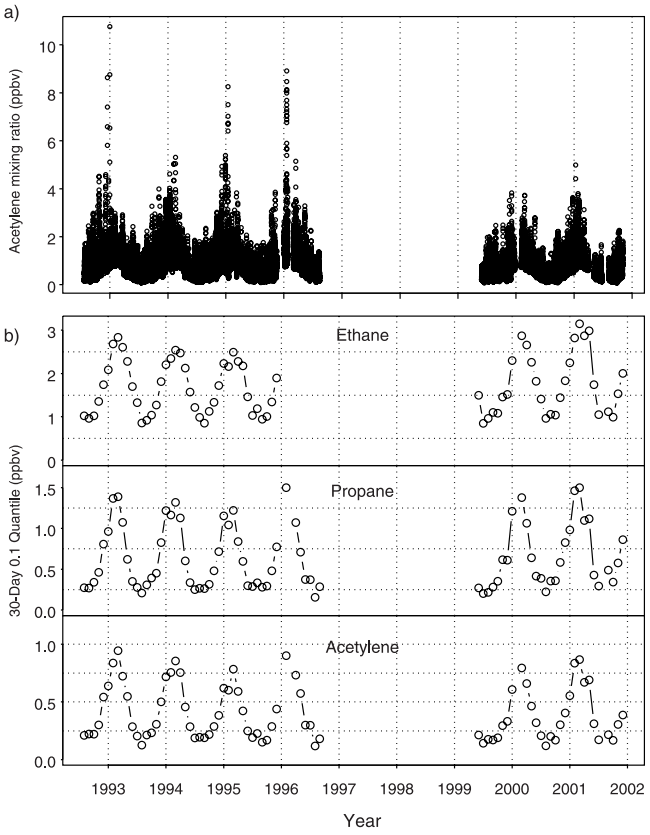

Figure 1. (a) Mixing ratio (ppbv) of acetylene measured at 45-min intervals above Harvard Forest from August 1992 to November 2001. (b) Background mixing ratios defined as the 10th percentile of the data in 30-day intervals for (top) ethane, (middle) propane and (bottom) acetylene.

numerous anthropogenic sources while winds from the northwest are usually less polluted because of fewer anthropogenic emission sources, rapid transport and subsidence from origins in northern Canada [*Moody et al.*, 1998]. Furthermore, transport pattern to the measurement site varies seasonally with prevalent winds from the southwest during summer and a higher occurrence of northwesterly winds during winter [*Shipham et al.*, 1998].

[11] Regardless of wind directions, time of day, or season, enhancements of acetylene over the seasonally changing background concentration were well correlated to enhancements of other observed anthropogenically emitted trace gases. For instance, Figure 3 shows ethane, propane, *n*-butane, *i*-butane, *n*-pentane, *i*-pentane, *n*-hexane, CO, CO_2, CH_4 and NO_y plotted against acetylene in June (Figure 3a) and December (Figure 3b) of 1993 and 1994. High correlation coefficients between species imply they are emitted from the same or colocated sources and are mostly affected by processes that act on both species together. Moreover, there is relatively little variability between the 1993 and 1994 slopes relative to acetylene (Figure 3) as well as between other years (not shown), with the exception of NO_y in the summer which is discussed below. Variability in emissions or mixing of air with different extents of oxidation or deposition would degrade the correlations. The minimum r^2 values for monthly correlations from 1992 through 2001 for *n*-butane, *i*-butane,

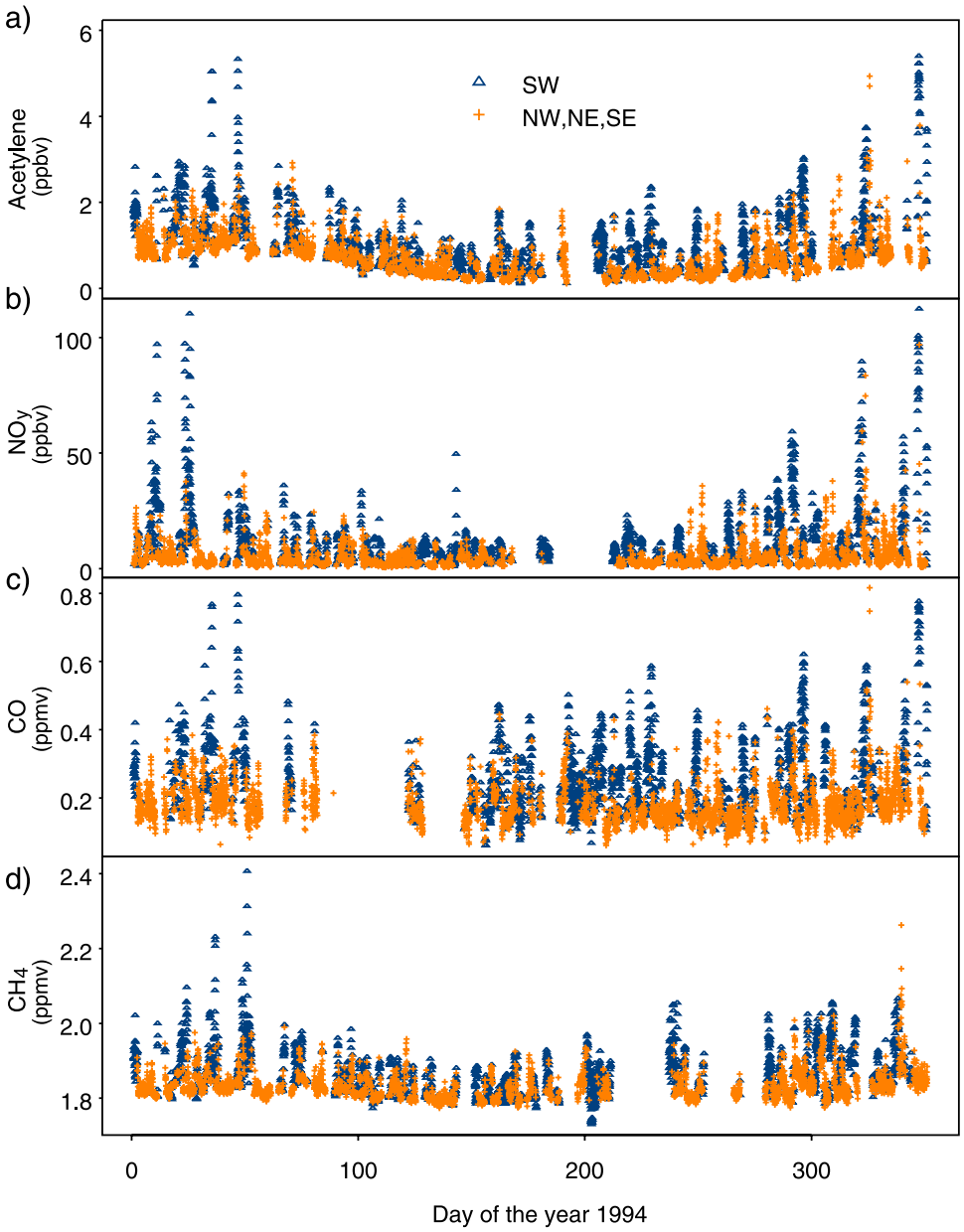

Figure 2. Mixing ratios of (a) acetylene, (b) NO_y, (c) CO and (d) CH_4 for 1994, parsed by southwest (180°–270°) and northwest, northeast and southeast wind directions combined (<180° and >270°).

n-pentane, *i*-pentane and *n*-hexane are 0.42, 0.67, 0.51, 0.62 and 0.53, respectively, while ethane and propane correlations to acetylene are generally lower than that of the other NMHCs for reasons discussed below. Slopes relative to acetylene are included in the analysis for all NMHCs, CO and NO_y in months with at least 150 correlation data points (five measurements per day). For NMHCs, at most six out of the possible 61 monthly correlation slopes relative to acetylene were excluded because of sparse monthly data, while for CO and NO_y 25 monthly slopes for each species were excluded. Additionally, four *n*-hexane, five CO and five NO_y monthly slopes had r^2 values less than 0.40 indicating a poor correlation to acetylene which would not be representative of anthropogenic pollution events focused in this study and were excluded in the following analysis. We use the r^2 value as a criterion to exclude monthly slopes in which variance in a species' mixing ratio is not explained by variations in acetylene.

[12] The remainder of this paper focuses on the seasonality of emissions of ethane, propane, *n*-butane, *i*-butane, *n*-pentane, *i*-pentane, *n*-hexane, CO and NO_y and interannual changes in emissions of CO_2, CO, and NO_y by analyzing their monthly orthogonal slopes with respect to acetylene.

4. Discussion

[13] One method of estimating regional emissions, in order to assess the accuracy of regional emission trends and inventories, is to measure the relative enhancements of trace gases in pollution plumes downwind of major urban-industrial centers. Tracking the enhancements relative to CO_2 emissions would be ideal because anthropogenic CO_2 emis-

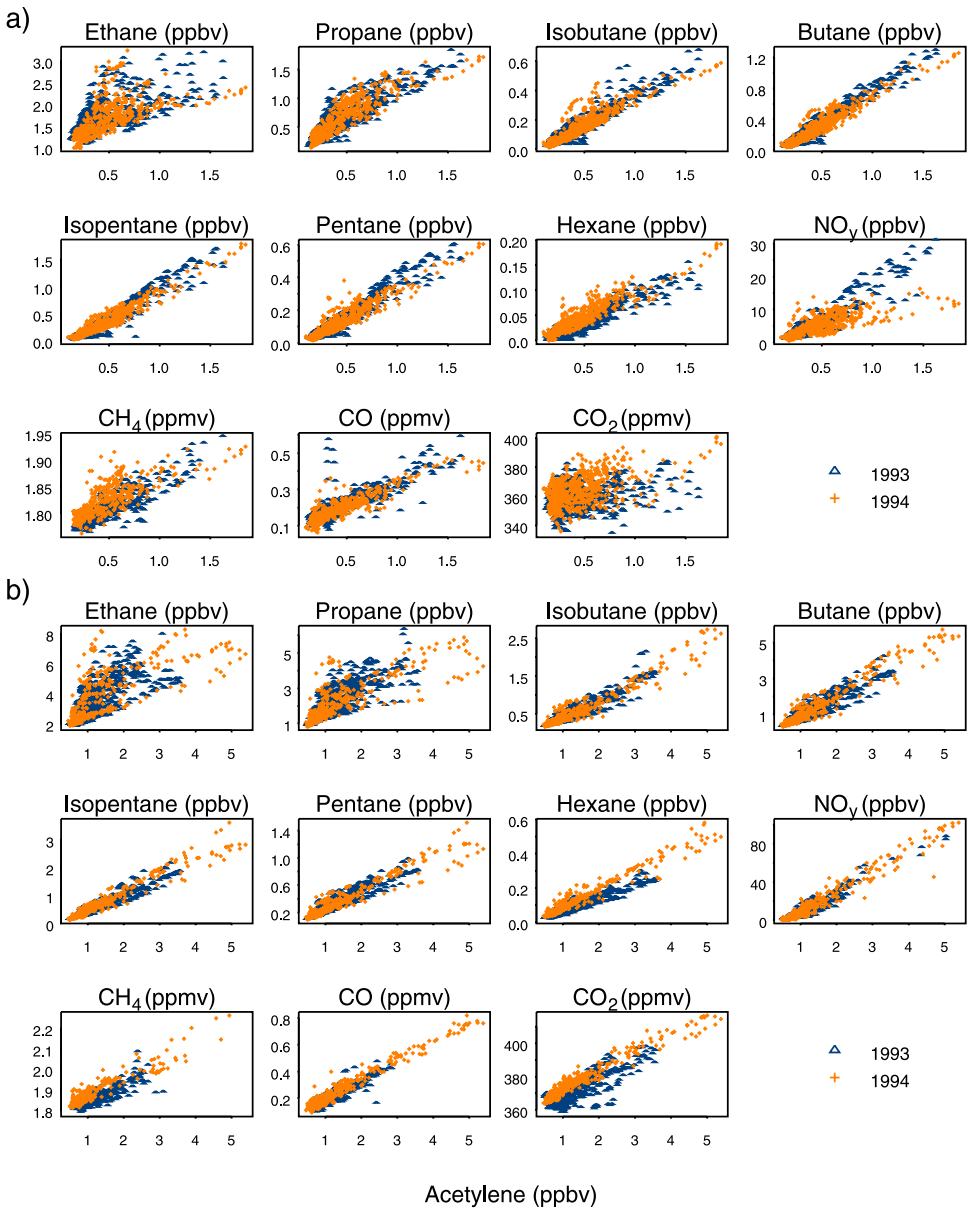

Figure 3. Ethane, propane, *n*-butane, *i*-butane, *n*-pentane, *i*-pentane, *n*-hexane, NO_y, CO, CO_2 and CH_4 plotted against acetylene (a) in June and (b) in December of 1993 and 1994.

sions are well constrained by fuel sales data. However, variations in CO_2 concentrations at the measurement site are dominated by photosynthesis and respiration of the surrounding forests during the growing season. There is a poor correlation between CO_2 and acetylene in the summers of 1993 and 1994 (Figure 3a), as well as in other years (not shown). Hence emission ratios of primary pollutants with respect to CO_2 can only be estimated from these data in wintertime. Another good tracer for anthropogenic emissions is acetylene, which as mentioned earlier is emitted almost solely as a by-product of combustion. The covariance of NMHCs, CO and NO_y to acetylene concentrations offers an insight into the seasonality of their emissions assuming that the seasonal variation in the acetylene emissions is small.

[14] The observed slopes are affected by the extent of reaction during transport from the emission source to the measurement site. Correlation slopes relative to acetylene underpredict regional emission ratios for gases more reactive than acetylene (propane, *i*-butane, *n*-butane, *i*-pentane, *n*-pentane and *n*-hexane) and overpredict the emission ratios for gases less reactive than acetylene (ethane and CO). Table 1 lists the summer and winter photochemical lifetimes of these species at the Harvard Forest latitude. Higher OH concentrations in the summer speed up chemical reactions and allow greater differential loss of the most reactive gases. During winter when OH concentration at the Harvard Forest latitude is about 1/10 of that in summer [*Goldstein et al.*, 1995a], the measurements approach a chemically inert case where atmospheric chemical loss timescales are long compared to atmospheric-mixing times [*McKeen and Liu*, 1993], as well as to typical transport times of air plumes traveling from regional sources to the measurement site.

Table 1. Hydrocarbon Reaction Rates With OH and Lifetimes[a]

Species	OH Rate Coefficient,[b] k cm^3 s^{-1}	Lifetime (Summer), days	Lifetime (Winter), days
Ethane	$1.49 \times 10^{-17} T^2 \exp(-499/T)$	42	608
Acetylene	$9.4 \times 10^{-12} \exp(-700/T)$	10	142
Propane	$1.65 \times 10^{-17} T^2 \exp(-87/T)$	8.5	114
i-butane	$1.17 \times 10^{-17} T^2 \exp(213/T)$	4.0	51
n-butane	$1.81 \times 10^{-17} T^2 \exp(114/T)$	3.7	48
n-pentane	$2.52 \times 10^{-17} T^2 \exp(158/T)$	2.3	29
i-pentane[c]	3.6×10^{-12} @298 K	2.6 (298 K)	···
n-hexane[d]	$2.54 \times 10^{-14} T \exp(-112/T)$	1.7	21
CO[e]	$(1 + 0.6P_{atm})1.5 \times 10^{-13}$	32	386

[a]OH [*Goldstein et al.*, 1995b] and temperature used for calculating lifetimes: summer, 1.5×10^6 cm^{-3} OH, 276 K; winter, 0.15×10^6 cm^{-3} OH, 264 K.
[b]*Atkinson and Arey* [2003].
[c]Data available only at 298 K.
[d]Acceptable temperature range is 292–962 K.
[e]*DeMore et al.* [1994].

More recent analyses suggest the winter to summer ratio is closer to 1/20 [*Spivakovsky et al.*, 2000], however, the difference is negligible since both values result in winter lifetimes of species much longer than typical transport times. Consequently, correlation slopes measured at Harvard Forest (Table 2) during winter are used to quantify regional emission ratios but could still be underestimates for the most reactive trace gases.

[15] Figure 4 shows the relative slopes, RS, with respect to acetylene, which are defined as the difference between the monthly correlation slope S_i and the mean annual slope $\bar{S}$ over the mean annual slope:

$$RS = \frac{(S_i - \bar{S})}{\bar{S}} \quad (1)$$

As apparent from Figure 4, seasonal changes in alkane correlation slopes with respect to acetylene can be grouped into three general categories: (1) ethane and propane, (2) *n*-butane and *i*-butane and (3) *n*-pentane, *i*-pentane and *n*-hexane. Trace gases in each category exhibit similar emission trends throughout the year in slopes relative to acetylene, suggesting they share common or colocated sources. The observed seasonality for trace gases in each category is discussed in the following sections.

[16] The observed correlation slopes are the result of relatively homogeneous combinations of local and regional sources and are affected by chemical loss, particularly in the summer. Oxidation by OH, the dominant process removing alkanes and acetylene from the atmosphere, increases by about a factor of 10 from winter to summer at the Harvard Forest latitude, which reduces the hydrocarbon lifetimes accordingly. However, the impact of differential oxidation rates on the relative loss for a pair of trace gases emitted together can be calculated from the difference in their reaction rate constants:

$$\frac{C_1(t)}{C_2(t)} = \frac{C_1(t_0)}{C_2(t_0)} \exp((k_2 - k_1) \cdot OH \cdot t) \quad (2)$$

The colored (blue and red) dotted lines in Figure 5 represent expected slopes from seasonally changing oxidation rates while assuming a constant emission rate, which was estimated to be the mean of all December and January slopes relative to acetylene measured at Harvard Forest. Deviation from the pattern imposed by differential oxidation would indicate that emissions are varying seasonally.

4.1. Emissions and Their Seasonality Relative to Acetylene: C_2-C_6 NMHCs

4.1.1. Ethane and Propane

[17] Ethane and propane enhancements are typically correlated to acetylene, but occasionally occur independently, particularly in pollution plumes arriving at the site from the northwest. For instance, Figure 6a shows that during southwesterly winds on day 200 of 1993 the enhancement of ethane mixing ratios was accompanied by similar enhancements of the other trace gases including acetylene, CO, NO_y and CH_4. However, on day 201 when the winds shifted to the northwest the magnitude of the ethane concentration was comparable to that of the previous day, while the enhancements of the other trace gases were at most half the magnitude experienced during southwest winds. Earlier in the same year on day 41 (Figure 6b) when the winds shifted to the northwest

Table 2. Winter (December–February) Slopes (ppbv/ppbv ± Standard Error) Relative to Acetylene Measured at Harvard Forest

Species	1992–1993	1993–1994	1994–1995	1995–1996	1999–2000	2000–2001	Mean ± Standard Deviation
Ethane (NW)	2.42 ± 0.2	2.35 ± 0.4	2.44 ± 0.2	na[a]	2.37 ± 0.4	3.46 ± 0.2	2.61 ± 0.5
Ethane (SW, SE, NE)	1.31 ± 0.13	1.94 ± 0.2	1.52 ± 0.3	na[a]	1.86 ± 0.4	2.16 ± 0.2	1.76 ± 0.3
Propane (NW)	1.82 ± 0.2	1.93 ± 0.3	1.76 ± 0.2	1.56 ± 0.8	1.65 ± 0.3	2.53 ± 0.15	1.87 ± 0.3
Propane (SW, SE, NE)	1.06 ± 0.10	1.33 ± 0.13	1.08 ± 0.15	1.22 ± 0.2	1.25 ± 0.2	1.45 ± 0.16	1.23 ± 0.15
n-butane	1.18 ± 0.08	0.97 ± 0.09	1.02 ± 0.08	1.09 ± 0.11	0.81 ± 0.13	0.93 ± 0.07	1.00 ± 0.13
i-butane	0.43 ± 0.02	0.42 ± 0.03	0.43 ± 0.03	0.59 ± 0.06	0.50 ± 0.09	0.52 ± 0.03	0.48 ± 0.07
i-pentane	0.57 ± 0.04	0.54 ± 0.04	0.58 ± 0.03	0.59 ± 0.04	0.45 ± 0.03	0.47 ± 0.02	0.53 ± 0.06
n-pentane	0.27 ± 0.02	0.24 ± 0.02	0.24 ± 0.012	0.27 ± 0.010	0.20 ± 0.014	0.22 ± 0.015	0.24 ± 0.03
n-hexane	0.070 ± 0.003	0.075 ± 0.003	0.11 ± 0.003	0.080 ± 0.002	0.16 ± 0.005	0.081 ± 0.002	0.10 ± 0.03

[a]Insufficient data.

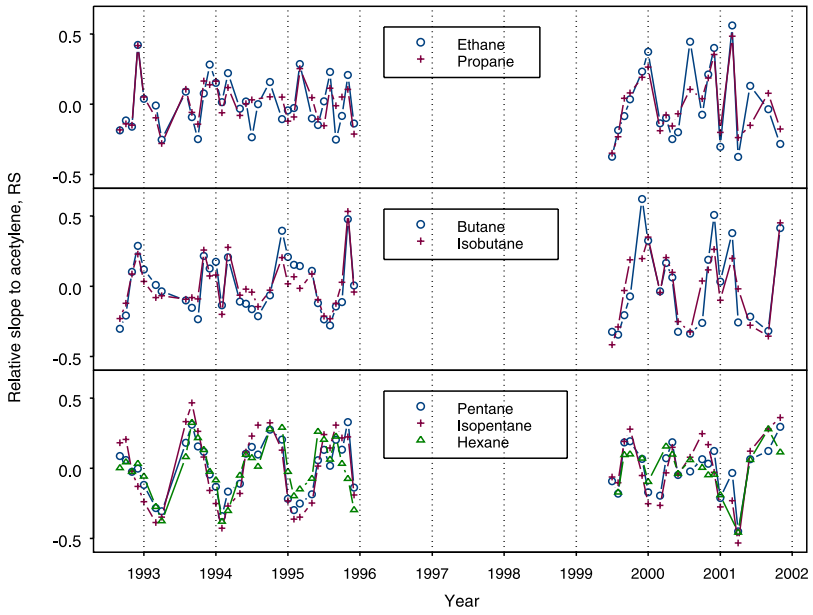

Figure 4. Slopes relative to acetylene for the entire measurement period. Vertical lines indicate 1 January of each calendar year. Ethane and propane data measured during NW winds are excluded.

there was an immediate increase in the ethane and propane mixing ratios of about 6 and 4 ppbv, respectively, which was not at all coincident with the other gases including CO whose summer photochemical lifetime (Table 1) is comparable to that of ethane's. Such events, which were observed in all seasons throughout the measurement period, indicate two things: (1) the presence of relatively local sources of ethane and propane northwest of the site and (2) emission sources of CH_4, acetylene and CO that are fewer in number, less frequent, weaker in strength and/or more distant to the site from the northwest than from other directions.

[18] Figure 7 shows ethane plotted against acetylene, CH_4, CO and propane for the entire measurement period from August 1992 through November 2001, with the exception of CH_4 measurements (from P. M. Crill, downloaded from ftp://ftp.as.harvard.edu/pub/nigec/UNH_Crill/methane/) which are available through December 1994. The depressed slopes of the correlation of ethane to acetylene, CH_4 and CO arriving from the northwest provide additional evidence of the relatively sparse sources of these gases compared to those for ethane and propane in that direction. Furthermore, the slope of propane to ethane remains fixed around 0.70 regardless of wind directions, which is somewhat higher than the propane to ethane slope of 0.59 ± 0.10 measured in Summit, Greenland [*Swanson et al.*, 2003] and comparable to the median propane to ethane concentration ratio of 0.67 determined from a study of 39 different U.S. cities [*Seila et al.*, 1989].

[19] The regional emission ratios represented by the wintertime (December–February) slopes relative to acetylene measured at Harvard Forest (Table 2) also show that the ratios of propane to ethane slopes are similar for air plumes from the northwest (ranging from 0.70 to 0.82) to those excluding the northwest winds (0.67 to 0.81), which is a strong indication that ethane and propane are emitted by sources nearly identical in mixture from the northwest as elsewhere in the region. Ethane and prop opes relative to acetylene from

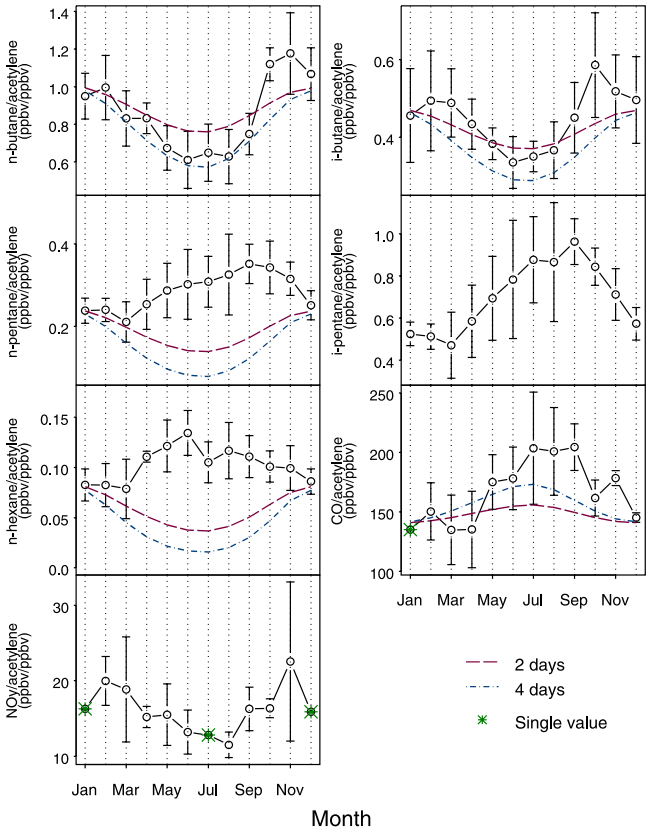

Figure 5. Mean of the monthly slopes (ppbv/ppbv) for *n*-butane, *i*-butane, *n*-pentane, *i*-pentane, *n*-hexane, CO and NO_y relative to acetylene. The error bars indicate the standard deviation of the mean of each month. Colored dotted lines represent the expected slopes after 2 (red) and 4 (blue) days of photochemical aging. The precise reactivity of *i*-pentane is unavailable.

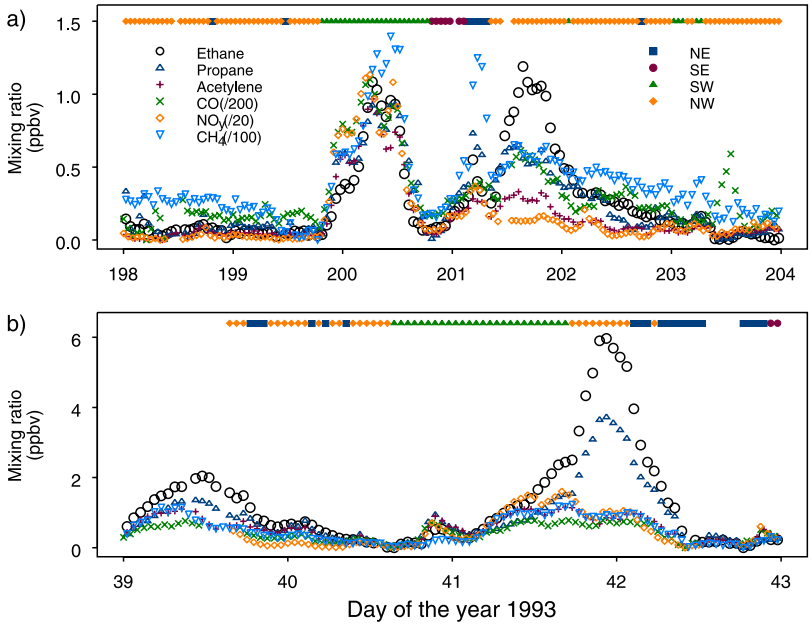

Figure 6. Mixing ratios of ethane, propane, acetylene, CO, NO_y and CH_4 plotted alongside wind directions for a few typical days in (a) summer and (b) winter of 1993. All mixing ratios are subtracted by their minimum values in the time periods shown. Mixing ratios of CO, NO_y and CH_4 are normalized by 200, 20 and 100, respectively.

the northwest (Table 2) are also much higher than those from the other combined wind directions, which suggests both a closer proximity of ethane and propane sources to the site and sparse sources of acetylene and the other reported NMHCs, CO, NO_y, and CH_4 from the northwest.

[20] The dominant source of ethane and propane remains a mystery. We considered biomass burning and liquefied natural gas (LNG), but their propane to ethane ratios are not consistent. Low ratios ranging from 0.3 to 0.5 are associated with biomass burning while those approaching 1 signify LNG [*D. R. Blake et al.*, 1996; *N. J. Blake et al.*, 1996]. Although trace gas enhancements due to extensive fires from as far away as Quebec, Canada have been previously observed at the Harvard Forest site [*DeBell et al.*,

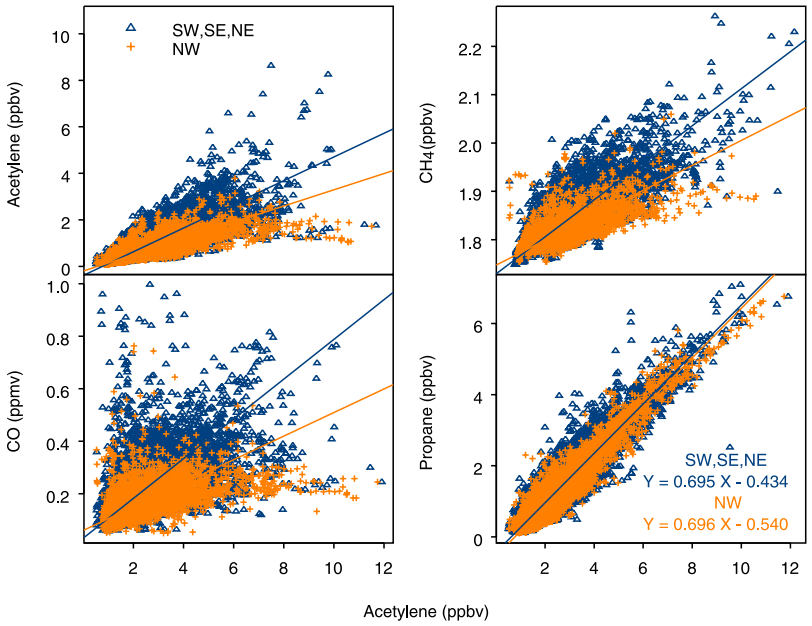

Figure 7. Acetylene, methane, CO and propane plotted against ethane, parsed by wind directions; NW versus the combined SW, SE and NE. Acetylene, CO, propane and ethane data encompass hourly measurements from August 1992 to November 2001, while methane data are only available up through December 199

Table 3. Composition (Mass %) of Headspace Vapor of Gasoline

Species	Regular Gasoline Berkeley, California, Summer 1995[a]	Regular Gasoline, San Francisco, California, May 1999[b]	Regular Gasoline Houston, Texas, Aug–Sep 2000[c]	Regular Gasoline Near Fort McHenry Tunnel, Maryland, Summer 1992[d]	Regular Gasoline Near Tuscarora Mountain Tunnel, Pennsylvania, Summer 1992[d]
Acetylene	...	...	...	...	...
Ethane	...	...	0.05	...	...
Propane	0.49	0.04	0.10	0.53	0.56
n-butane	9.35	7.42	5.06	17.65	11.19
i-butane	3.04	0.77	1.01	3.27	2.55
n-pentane	10.39	14.15	6.12	8.77	9.1
i-pentane	36.59	24.12	23.20	27.87	27.37
n-hexane	2.10	4.30	2.50	1.64	1.76

[a] *Kirchstetter et al.* [1999].
[b] *Harley et al.* [2000].
[c] Data provided by G. R. McGaughey and R. A. Harley [*McGaughey et al.*, 2000].
[d] *Gertler et al.* [1996].

2004], these events are not frequent. Furthermore, biomass burning would also emit significant quantities of acetylene and CO, while LNG is composed mainly (≈95% by volume) of CH_4, none of which are clearly consistent with our observations. Leakage from domestic LPG usage is unlikely because liquid propane contains very little ethane (≈2% by vol.). Moreover, there is no annually repeating seasonal pattern observed in the monthly orthogonal slopes of ethane and propane relative to acetylene, even when measurements are segregated by wind directions. This is likely due to multiple different sources of ethane and propane throughout the region including natural gas, biomass burning, landfills, etc. each contributing significantly enough to nullify any apparent seasonal pattern, and not due to a single dominant source emitting both gases constantly throughout the year.

4.1.2. n-Butane and i-Butane

[21] Emission sources of *n*-butane and *i*-butane are predominantly anthropogenic including combustion, evaporation of fossil fuels and the production and refining of petroleum, all of which emit varying quantities of *n*-butane and *i*-butane. However, a previous study by *Parrish et al.* [1998], which analyzed 11 different data sets of tropospheric NMHCs measured in continental North America, concluded that the *i*-butane to *n*-butane geometric mean ratio should range from 0.4 to 0.6. The reason for this observation is that emissions from the various butane sources in a region mix rapidly in comparison to the lifetimes of the butanes (summer ≈ 4.0 d, winter ≈ 50 d) as well as to average transport times of air parcels en route to measurement sites [*Parrish et al.*, 1998]. The *i*-butane to *n*-butane ratios of winter slopes relative to acetylene observed at Harvard Forest (Table 2) fall within this expected range with the exception of the 1992–1993 and 1999–2000 winters, which exhibit ratios of 0.36 ± 0.03 and 0.62 ± 0.15, respectively. Deviations from the expected *i*-butane to *n*-butane ratio may be explained by varying source strengths and their proximity to the measurement site.

[22] *n*-butane and *i*-butane emissions relative to acetylene exhibit a strong seasonal pattern with amplitudes greater than what could be expected from OH oxidation. The correlation slopes relative to acetylene increase in the fall (September–October) by 50 and 30% for *n*-butane and *i*-butane, respectively, and drop by 25 and 20% for *n*-butane and *i*-butane, respectively, throughout the spring and early summer (April–June) in Figure 5. These seasonal changes in slopes likely reflect the mandated changes in gasoline volatility [*U.S. Congress*, 1990], which is measured as Reid vapor pressure (RVP) in pounds per square inch (psi). The U.S. EPA under the Clean Air Act Amendments of 1990 established a two-phase reduction in summertime gasoline volatility in an effort to curb motor vehicle emissions of volatile organic compounds (VOCs), a main contributor of ground-level ozone, during the high smog season. Phase II, which was implemented in 1992 capped the RVP at 9.0 psi (7.8 psi in some states) from 1 May (refineries) or 1 June (retail outlets/wholesale purchasers) through 15 September. The summertime RVP standard is generally achieved during gasoline production by reducing the amount of butanes in the fuel blend and thereby in the headspace vapor (Table 3), and/or by adding other less volatile components. Specific details regarding gasoline production could not be obtained and would likely vary depending on manufacturer.

[23] For *n*-butane and *i*-butane, emissions from January until August–September are consistent with what is expected solely from changing oxidation rates (equation (2), as discussed previously). The mean of these monthly observed slopes lies close to the dotted lines, which represent the expected slopes following 2 and 4 days of photochemical reaction assuming emissions were constant at wintertime values (red and blue dotted lines denote 2 and 4 days, respectively). This might suggest that the observed decline in summer *n*-butane and *i*-butane slopes relative to acetylene is entirely due to their relative oxidation rates and not due to changes in gasoline volatility. However, it is possible that a steeper decrease in slopes during summer is not observed because it is offset by evaporative sources of butanes in the summer when *n*-butane and *i*-butane are present in the headspace vapor of gasoline in quantities as high as 18 and 3% by mass, respectively (Table 3). We expect volatile species present in significant quantities in gasoline to exhibit seasonal emission trends reflecting that of ambient air temperature, as observed for *n*-pentane, *i*-pentane and *n*-hexane (discussed in the next section). This trend, however, is not observed for the butanes and if the observed decrease in *n*-butane and *i*-butane slopes relative to acetylene is indeed due to the summertime RVP restriction, it suggests an approximate 60 and 50% decrease in *n*-butane and *i*-butane content in gasoline, respectively, from winter to summer assuming a 50% winter to summer increase in the slopes of the butanes relative to acetylene as observed for *n*-pentane

Table 4. Winter (December–February) and Summer (June–August) Correlation Slopes (ppbv/ppbv ± Standard Error) of NO_y and CO Relative to Acetylene and Seasonal Change %

	NO_y			CO		
Winter/Summer	Winter Slope	Summer Slope	% Change Winter to Summer	Winter Slope	Summer Slope	% Change Winter to Summer
1992–1993/1993	17.1 ± 1.1	21.0 ± 1.3	22.9 ± 1.6	133 ± 5.1	232 ± 6.8	74.7 ± 3.2
1993–1994/1994	22.1 ± 2.4	10.6 ± 1.0	−52.3 ± 6.1	161 ± 6.6	229 ± 13	41.8 ± 2.2
1994–1995/1995	18.7 ± 0.7	13.2 ± 0.8	−29.4 ± 1.3	146 ± 2.8	221 ± 9.9	51.2 ± 1.7
1999–2000/2000	20.1 ± 2.2	13.0 ± 0.6	−35.6 ± 4.0	158 ± 7.1	239 ± 16	50.9 ± 3.1
2000–2001/2001	17.7 ± 0.6	12.5 ± 1.2	−29.3 ± 1.5	118 ± 5.3	197 ± 12	66.6 ± 4.0

due to increased evaporation. However, hydrocarbon content data in the liquid phase and headspace of gasoline was available only for summertime. The two different deadlines for the early summer RVP standard, 1 May and 1 June (depending on purchaser) could also contribute to the weaker-than-expected decrease in slopes during the summer months. However, in October when gasoline RVP is no longer restricted by summertime standards, substantial increases in *n*-butane and *i*-butane slopes relative to acetylene are consistently observed.

4.1.3. n-Pentane, i-Pentane, and n-Hexane

[24] Emissions of *n*-pentane, *i*-pentane and *n*-hexane relative to acetylene also show strong seasonality. Figure 5 shows that the slopes with respect to acetylene of these trace gases increase by approximately 50, 80 and 35% for *n*-pentane, *i*-pentane and *n*-hexane, respectively, from January to September. This is opposite the cycle that would be expected if reactivity was the dominant factor in determining the observed slopes. Slopes simulating year-round constant emissions where reactivity is the only variable are represented by the red and blue dotted lines in Figure 5. The seasonal cycle of these observed slopes is similar to the seasonal trend in ambient air temperature, suggesting that this seasonal pattern may be affected by temperature-dependent evaporation. Evaporative emissions would contain mostly the more volatile alkanes and would not include acetylene since acetylene is absent in the liquid form and headspace vapor of gasoline. These observations may suggest a significant contribution from evaporative or unburned gasoline emissions to the total hydrocarbon emissions from the region, especially since measured slopes in the summer of the more volatile species underestimate actual emissions because of faster chemical losses of the more reactive species during transport to Harvard Forest. Nontailpipe evaporative sources include hot-soak emissions, diurnal emissions, resting loss, refueling loss and running loss, all of which could account for up to 35% of the total motor vehicle NMHC emissions [*Pierson et al.*, 1999]. In addition, the seasonality of *n*-hexane with respect to acetylene is less pronounced compared to that of *n*-pentane and *i*-pentane, which is likely due to its relatively shorter atmospheric lifetime and smaller composition in the headspace vapor of gasoline (Table 3). It is also important to note that the *n*-hexane reaction rate is currently only available at 292 K and above.

4.2. Emissions and Their Seasonality Relative to Acetylene: CO and NO_y

[25] Concentrations of ambient NMHCs, CO, NO_y and NO_x are at their maximum in the winter and minimum in the summer. Anthropogenic emissions of CO and NO_x are estimated to be relatively constant throughout the year with less than 10% seasonal variation [*U.S. National Acid Precipitation Assessment Program*, 1991] since relatively constant transportation-related fuel consumption is the dominant source for urban emissions of both gases [*U.S. Environmental Protection Agency* (*U.S. EPA*), 2005]. However, Figure 5 shows strong seasonality in the slopes of both CO and NO_y relative to acetylene. CO is enhanced while NO_y, which includes NO_x and all its oxidative products, is depleted relative to acetylene in the summer months.

[26] Oxidation by OH is the dominant (80–90%) process removing CO [*Novelli et al.*, 1992] as well as acetylene from the atmosphere. Because the lifetime of acetylene is shorter than the CO lifetime by a factor of three, a 13 to 27% increase in the CO slopes relative to acetylene is expected because of their difference in oxidation rates in midsummer conditions after two to four days, respectively, according to equation (2). The exact magnitude of change in the observed slopes will depend on the behavior of background concentrations and mixing of air parcels with different photochemical ages. Clearly, though, the CO slopes relative to acetylene will overestimate the actual regional emission ratio in summertime to some extent because CO reacts slower with OH than does acetylene.

[27] The average increase from winter (December–February) to summer (June–August) in the CO slopes relative to acetylene observed at Harvard Forest between 1992 and 2001 is 57% ± 13% (Table 4), which exceeds by 38 ppbv/ppbv (September) the expected amplitude change in CO slope relative to acetylene after 4 days of differential oxidation if CO and acetylene emissions were aseasonal (Figure 5). Secondary CO formation during the summer months when OH oxidation is rapid may contribute to the enhancement of CO relative to acetylene in anthropogenic pollution plumes. *Chin et al.* [1994] estimated that 9% of the summer CO source in the boundary layer of the eastern United States is due to oxidation of anthropogenic hydrocarbons. An upper limit to secondary CO formation derived from the total hydrocarbon to acetylene ratios [*Seila et al.*, 1989] by assuming a complete conversion of every carbon atom to CO is 33 CO per acetylene (ppbv/ppbv). However, a recent study [*Aumont et al.*, 2005] reports that only 20 to 30% of the available carbon in a primary hydrocarbon such as heptane oxidizes all the way to either CO or CO_2 after 5 days, even though essentially none of the parent compound heptane remains in the atmosphere. This is not enough CO from secondary formation to account for the enhanced CO slopes relative to acetylene observed at Harvard Forest.

[28] Forest fires during the summer months may also contribute to enhanced CO [*Wotawa and Trainer*, 2000].

High CO to acetylene emission ratios observed in smoke plumes (from 256 to 480) [*Friedli et al.*, 2001; *Laursen et al.*, 1992; *Nance et al.*, 1993; *Radke et al.*, 1991; *Wofsy et al.*, 1992] would raise CO slopes relative to acetylene during the peak periods of forest fires in the late summer and early fall months. However, signals of biomass burning at Harvard Forest were not clearly evident from the propane to ethane ratios (discussed earlier). Seasonality in acetylene emissions (lower emission rates during summer) could also account for the large winter to summer increase in slopes.

[29] Oxidation of biogenic hydrocarbons (mainly isoprene and terpenes) also contributes to secondary CO formation. *Chin et al.* [1994] estimate roughly 20% of the summer CO source in the eastern U.S. boundary layer is due to secondary formation from biogenic hydrocarbons (isoprene). However, secondary biogenic CO should not correlate with acetylene because the major sources of biogenic hydrocarbons are not colocated with anthropogenic sources. Similarly, oxidation of CH_4 contributes to the overall CO background mixing ratio and should not be enhanced in pollution plumes and therefore in the slopes relative to acetylene. Reductions in the correlation coefficients between CO and acetylene and increased standard errors on the CO slopes relative to acetylene during the summer months (Table 4) are consistent with contributions from secondary biogenic CO formation and perhaps additional sources of CO with very different ratios to acetylene.

[30] The NO_y correlation slopes relative to acetylene observed at Harvard Forest are generally lower in the summer than in winter (Figure 5) reflecting the higher NO_x oxidation and deposition rates in the summer months. The characteristic (*e*-folding) time for NO_x oxidation ranges from 0.3 days in the summer to about 1.5 days in winter at Harvard Forest [*Munger et al.*, 1998]. Subsequent deposition (dry or wet) of HNO_3 and other oxidized nitrogen species is rapid for all seasons. The oxidation (homogeneous + heterogeneous + organic pathways) and subsequent deposition of total nitrogen decreases by about 39% from summer (June–August) to winter (December–February) at Harvard Forest [*Munger et al.*, 1998, Table 1], which is largely due to the decline in winter OH concentration. The average winter-to-summer decrease in the NO_y slopes relative to acetylene observed in this study is about 25% ± 28% (Table 4). The large margin of error is due to unusually high NO_y to acetylene slopes observed for many months in 1993, which may have been caused by slow deposition due to lack of precipitation and/or anomalous NO_x emissions. However, excluding the 1992–1993 winter and summer data yields an average winter-to-summer NO_y to acetylene slope decrease of 37% ± 11%, which is in agreement with what was reported by *Munger et al.* [1998].

[31] As noted above, relative oxidation of acetylene may affect its slope with CO. However, only about 0.7 and 3.5 days are required to oxidize approximately 90% of NO_x in summer and in winter, respectively [*Munger et al.*, 1998]. In those same amounts of time (assuming summer OH concentration of 1.5×10^6 cm^{-3}, winter OH concentration of 0.15×10^6 cm^{-3}), only about 6.7% and 3% of acetylene would be oxidized by OH radicals in summer and in winter, respectively, which is not enough to detract from its suitability as a tracer for NO_y losses.

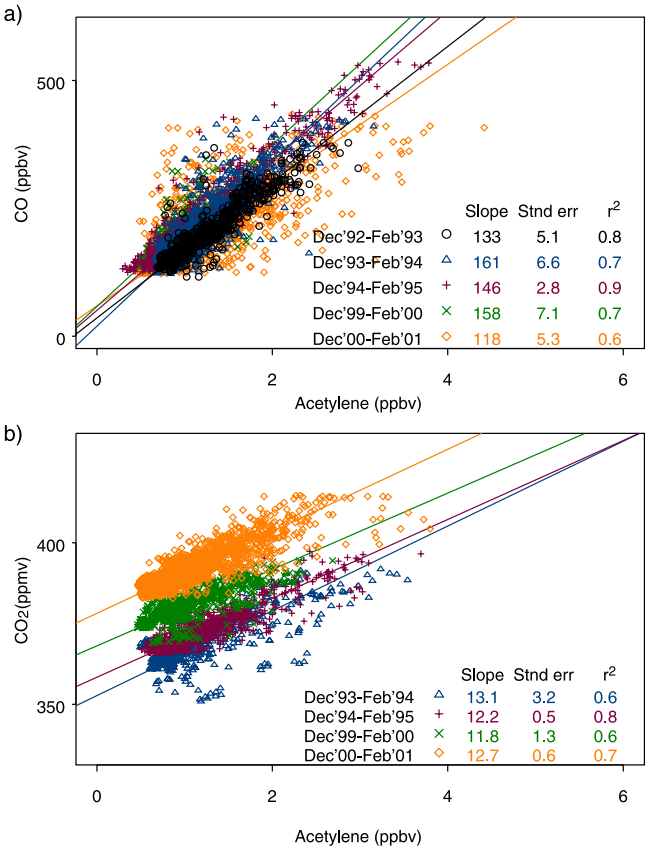

Figure 8. (a) CO and (b) CO_2 plotted against acetylene for the winter months (December to February). CO and CO_2 winter mixing ratios greater than two standard deviations from their median (less than 5% of the data for each winter) were excluded in order to offset local pollution effects during shallow inversion layers.

[32] Another factor that might contribute to the seasonal changes in the NO_y slopes relative to acetylene is NO_x emissions themselves. Stationary sources of NO_x, including the electric power industry, industrial processes and residential energy consumption, constituted 45% of the total NO_x budget in the eastern United States in 2004 [*U.S. EPA*, 2005] and may vary according to season because of greater heating/energy demands in winter and summertime NO_x emission control regulations, such as the NO_x Budget Program [*Ozone Transport Commission*, 1997]. Significant contributions from power plant NO_x reaching the site may account for the lower monthly correlations between NO_y and acetylene, which is nearly absent in power plant emissions. However, this program, which reduced summertime (1 May through 30 September) NO_x emissions from fossil fuel fired electric generating units, was first implemented in 1999. Moreover, as mentioned above the lifetime of NO_x is relatively short and rapid deposition diminishes the potential impact of distant power plant derived NO_x emissions.

4.3. Interannual Emission Trends Relative to Acetylene: CO_2, CO, and NO_y

[33] CO_2 and CO observations are shown in Figure 8 plotted against acetylene in the winter (December–February) months for the entire measurement period. The winter slopes

Table 5. U.S. CO and CO_2 Emission Estimates Reported in Thousand Metric Tons

Year	CO_2 Emissions[a]	% Change	CO Emissions[b]	% Change
1992	4823793	· · ·	140896	· · ·
1993	5104455	5.82	135901	−3.55
1994	5196341	1.80	133559	−1.72
1995	5198699	0.05	126777	−5.08
1996	5280044	1.56	128858	1.64
1997	5452575	3.27	117910	−8.50
1998	5502867	0.92	115380	−2.15
1999	5510593	0.14	114541	−0.73
2000	5605585	1.72	114467	−0.06
2001	na[c]	na[c]	106295	−7.14

[a] *Marland et al.* [2003].
[b] *U.S. EPA* [2005].
[c] Not available.

relative to acetylene provide a good approximation of regional emission ratios of CO and CO_2, since CO contribution from secondary production and CO_2 enhancements due to photosynthesis/respiration are both minor during the winter months.

[34] Although CO emissions in the United States have been decreasing in the past decade [*U.S. EPA*, 2005] (Table 5), largely in response to more stringent emission standards for vehicles, these reductions in vehicular CO emissions will likely be accompanied by reduced VOC emissions as well [*Parrish et al.*, 2002]. Indeed, correlation slopes of CO relative to acetylene during winter months (Figure 8) measured at Harvard Forest show no strong evidence of any long-term trend, although these winter slopes vary by as much as ±34% between years and exhibit considerable scatter. It is also notable that CO concentrations associated with low acetylene concentrations, which provide an estimate of background concentrations, have remained relatively unchanged over the measurement period as indicated by the overlap of winter data points near the intercepts (Figure 8). Background concentrations depend on anthropogenic and biomass burning sources throughout the northern hemisphere that are not affected by U.S. emission controls.

[35] A central assumption in our analysis is that acetylene is a suitable tracer of regional combustion emissions. Combustion efficiencies (hence CO_2 to acetylene ratios) vary widely among emission sources such as vehicles, power plants and domestic heating. Moreover, the total fossil fuel derived CO_2 emissions in the United States have increased over the past decade [*Marland et al.*, 2003] (Table 5). To check the consistency of the CO_2 to acetylene relationship over the measurement period we examine the correlation slopes of CO_2 relative to acetylene measured during the winter months (Figure 8). The 1992–1993 winter slope with respect to acetylene is not included because of insufficient overlap between the CO_2 and acetylene data during that winter. The computed slopes vary by less than ±8% and show little evidence of a consistent trend. The impact of rising background CO_2 is evident in the offset between years. Additionally, CO_2 concentrations vary widely across the range of observed acetylene concentrations, which may be due to the latitudinal gradients and seasonal trends in CO_2 concentrations for the northern hemisphere winter. Monthly CO_2 measurement data at various latitudes is available through the Climate M ng and Diagnostic Laboratory (http://www.cmdl.noaa.gov/ccgg/iadv/). Air masses arriving at Harvard Forest from different directions therefore can start with very different CO_2 concentrations.

[36] Anthropogenic emission of NO_x is also reported to have decreased significantly over the last decade [*U.S. EPA*, 2005]. However, as evident in Table 3 no clear trend in the winter NO_y to acetylene slopes is observed. A possible reason for the large variations in these slopes is that NO_y transport to the measurement site is a sensitive function of oxidation, deposition, precipitation and transport history of air plumes. Since interannual changes in the wintertime slopes vary by as much as ±23%, the trend in NO_x emissions may be difficult to detect from these data.

5. Conclusions

[37] We have presented the seasonal emission patterns of C_2-C_6 hydrocarbons, NO_y and CO relative to acetylene emissions as measured in rural New England. The site is downwind of major anthropogenic sources such as large cities/landfills and thereby captures the full mix of pollutant sources that are regionally significant. Measurements were taken every 45 min, which allowed us to utilize the monthly correlation slopes with respect to acetylene in order to approximate the seasonal emission patterns of these species for a large urban-industrial region, while taking into account their seasonally changing reactivities. Acetylene is used as the tracer for anthropogenic emissions since it occurs mainly via combustion and also on the basis that the seasonal variation in the acetylene emission rate is fairly small.

[38] Ethane and propane emissions relative to acetylene lack a clear seasonal pattern, likely because of contributions from numerous different source types including biomass burning, natural gas, landfills plus other minor sources in the region. Seasonal trends in *n*-butane and *i*-butane slopes relative to acetylene likely reflect the summertime (1 May/1 June to 15 September) gasoline volatility regulations [*U.S. Congress*, 1990] implemented to help reduce summertime vehicular emissions of some ozone precursors. Consequently, emissions of *n*-butane and *i*-butane relative to acetylene significantly increase from September to October at the end of the summertime regulation period. However, the observed decreases in the *n*-butane (25%) and *i*-butane (20%) slopes relative to acetylene during late spring and early summer are not as large as the increases in the fall (50 and 30% for *n*-butane and *i*-butane, respectively) and may be offset by evaporative sources of butanes during these warmer months. Emissions of *n*-pentane, *i*-pentane and *n*-hexane are likely driven by temperature-dependent evaporation. The slopes observed during summer for *n*-pentane, *i*-pentane and *n*-hexane relative to acetylene underpredict the actual emission ratio for the region since chemical losses of these species are much faster than the loss rate of acetylene, particularly in summertime. This is additional evidence that nontailpipe evaporative emission of unburned gasoline may be a significant source of light NMHCs to the regional atmosphere.

[39] The seasonal trend of NO_y correlation slopes relative to acetylene is mainly dependent on nitrogen oxidation and deposition during transport to the measurement site, with possible contributions from seasonally dependent stationary

emissions. Because the oxidation and subsequent deposition of NO_x is much faster in summer than in winter, correlation slopes relative to acetylene observed at Harvard Forest are much lower in the summer. For CO, secondary production due to anthropogenic hydrocarbon oxidation does not fully account for the large difference in the observed increase from winter to summer CO slopes relative to acetylene and that expected solely due to differential oxidation. It is likely that enhancements from forest fires contribute CO as well as acetylene. However, precisely quantifying the possible seasonal dependence of CO and acetylene emissions measured at Harvard Forest by focusing on the seasonally changing CO slopes relative to acetylene is difficult because of rapid loss of acetylene relative to CO in the summer months and because of difficulty in ascertaining precise photochemical ages of pollution plumes arriving at the site.

[40] CO_2 and CO slopes relative to acetylene have large interannual variability, but no consistent change over the measurement period. Although reported inventories indicate that CO and CO_2 emission rates have changed, their relative emissions to acetylene in the northeastern United States have not exhibited substantial changes. Increases in the average background CO_2 are apparent, but CO concentrations associated with clean air have not changed noticeably; regional emissions that contribute to peak levels may have dropped, but background concentrations depend on anthropogenic and biomass burning sources throughout the northern hemisphere.

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