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Emissions of ethene, propene, and *I*-butene by a midlatitude forest

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Abstract. Measurements of nonmethane hydrocarbon concentrations and gradients above Harvard Forest (42°32' N, 72°11' W) are reported for January through December 1993, along with inferred whole-ecosystem emission rates for ethene, propene, and *I*-butene. Emissions were calculated using a micrometeorological technique where the ratio of observed CO₂ fluxes and gradients were multiplied by the observed hydrocarbon gradients. Average emissions of ethene, propene, and *I*-butene during summer were 2.63, 1.13, and 0.41 × 10¹⁰ molecules cm⁻² s⁻¹, respectively. Emission of these olefins was correlated with incident solar radiation, implying a source associated with photosynthesis. In the northeastern United States, summertime biogenic emissions of propene and *I*-butene exceed anthropogenic emissions, and biogenic emissions of ethene contribute approximately 50% of anthropogenic sources. Our measurements suggest that terrestrial biogenic emissions of C₂-C₄ olefins may be significant for atmospheric photochemistry.

Introduction

Ozone concentrations in the northeastern United States are believed to be sensitive to emission rates of biogenic nonmethane hydrocarbons (NMHC) [Fehsenfeld *et al.*, 1992; McKeen *et al.*, 1991; Rosell *et al.*, 1991; Sillman *et al.*, 1990]. Uncertainties in rates of these emissions introduce large uncertainty in assessments of control strategies for air pollution, for example, in defining the relative benefits of reductions in emissions of anthropogenic NMHC versus NO_x (NO + NO₂). Moreover, peroxy acetyl nitrate (PAN) and other organic nitrates, formed as by-products of oxidation of NMHCs, can facilitate transport of NO_x precursors into the global troposphere where photochemical ozone production is highly efficient.

Most measurements of terrestrial biogenic NMHC emissions have focused on isoprene and terpenes which are widely believed to be the most important for atmospheric chemistry [Zimmerman, 1979; Winer *et al.*, 1989; Singh and Zimmerman, 1992; Fehsenfeld *et al.*, 1992]. Ethene, a plant hormone of interest to plant physiologists, has also been studied in detail. Sawada and Totsuka [1986] estimated that 74% of the total global emission of ethene (35.4 TgC yr⁻¹) was from natural sources, 89% from terrestrial ecosystems (78% from vegetation and 22% from soils), and 11% from aquatic ecosystems. They estimated average ethene emissions for temperate deciduous forests during the growing season of 2.2 × 10¹⁰ molecules cm⁻² s⁻¹. Emissions of light olefins

(including ethene, propene, and *I*-butene) have been detected from vegetation and in a variety of forested environments [Zimmerman *et al.*, 1988; Khalil and Rasmussen, 1992; Bonsang *et al.*, 1987; Isadorov *et al.*, 1985]. However, global budgets of propene and *I*-butene have been reported to be dominated by the ocean, biomass burning, and fuel combustion [Singh and Zimmerman, 1992].

In this paper we report observations using an automated instrument to measure NMHC concentrations continuously at two altitudes above a temperate deciduous forest in Massachusetts, emphasizing ethene, propene, and *I*-butene. The fluxes of these biogenic NMHCs from the forest were calculated by similarity using the observed concentration gradient and concurrent measurements of fluxes and gradients for CO₂. We present diurnal and seasonal variations of biogenic emissions of ethene, propene, and *I*-butene, and we assess the regional significance of these emissions.

Experiment

Site

Harvard Forest is located in Petersham, Massachusetts (42° 32' N, 72°11' W; elevation 340 m), 100 km west of Boston, Massachusetts and 100 km northeast of Hartford, Connecticut. There is a highway ≈ 5 km to the north and a secondary road ≈ 2 km to the west. The site is accessible by a dirt road which is closed to public traffic. Measurements were made from a 30-m tower, erected in May 1989, extending 9 m above the forest canopy. Instruments were housed in a temperature controlled shack located 15 m east of the tower.

The forest is 50 to 70 years old, predominantly red oak, with red maple, sugar maple, beech, yellow and white birch, black spruce, hemlock, and white and red pine. The total deciduous leaf area index was 4.0 (oak, maple, beech, and

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birch contributed 2.0, 1.0, 0.5, and 0.5, respectively) in 1992, as measured by collecting leaves in litter traps surrounding the tower. The terrain is moderately hilly (relief \approx 30 m), but there is no evidence of anomalous flow patterns that would make eddy-flux measurements at this site unrepresentative [Moore *et al.*, 1996], and the local energy budget is balanced to within 10% [Goulden *et al.*, 1996].

Continuous measurements of C2-C6 NMHCs were made simultaneously at 45-min intervals 2 and 7 m above the forest canopy commencing July 22, 1992. Other trace gas concentrations and meteorological variables have been measured continuously at this site since 1990, including CO, CO₂, O₃, NO_x, NO_y, H₂O, rainfall, wind speed, wind direction, temperature, and eddy correlation fluxes of sensible heat, latent heat, O₃, NO_y, and CO₂ [Wofsy *et al.*, 1993].

Flux-Gradient Similarity Method

Direct measurements of fluxes of ethene, propene, and 1-butene by eddy correlation are not currently possible, because eddy correlation requires concentration measurements more rapid than the timescale for the turbulent eddies that carry the flux (1-1000 s at Harvard Forest). Instead, we use a similarity approach for determining these fluxes for a whole forest, based on other quantities for which we have both concentration data and direct measurements of flux. The trace gas flux (F) is assumed to be proportional to the time-averaged concentration gradient (dC/dz) above the forest for intervals longer than the time scale for the slowest significant turbulent events,

$$F=K dC/dz, \quad (1)$$

where K is the exchange coefficient for the averaging interval. Denmead and Bradley [1985] reported that K (as defined above) for sensible heat and water vapor were nearly identical above a 40-year-old pine forest canopy. In this paper we compute K using measurements of flux from eddy correlation observations along with observed concentration gradients for CO₂, H₂O, and sensible heat and take the product with the hydrocarbon gradient to define the hydrocarbon flux. The hydrocarbon fluxes derived using similarity with different quantities are in generally good agreement as discussed below.

Measurements

Air was drawn continuously at 10 L min⁻¹ through 3/8 inch OD Teflon tubes from two inlets (24 and 29 m) on a 30-m tower. Samples for analysis were extracted from the inlet lines through tees at the instrument and passed through nafion dryers (Perma Pure Products) and Ascarite II (Thomas Scientific) traps to remove O₃, CO₂, and H₂O. Samples were cryogenically preconcentrated on dual traps (40 ml min⁻¹ of air for 10 min onto a bare 1/16 inch OD stainless steel tube) and injected into a gas chromatograph with dual flame ionization detectors (Hewlett Packard 5890 series II). Chromatographic separation was accomplished using 30-m PLOT GS-Alumina Megabore capillary columns (J & W Scientific). Every fifth pair of samples was taken from the same altitude (29 m) through separate tubes (by switching a valve near the inlet of the 24-m sampling line) in order to determine the NULL for the observed concentration gradient. The measurement system could operate continuously and unattended for more than 2 weeks, although data were

normally downloaded at 6-day intervals. Concentrations were determined using relative response factors [Ackman, 1964, 1968; Dietz, 1967] referenced to an internal neohexane standard (Scott-Marrin, National Institute of Standards and Technology traceable \pm 2%) added to every sample by dynamic dilution.

The accuracy of the system was estimated to be better than \pm 18% for hexane and for hydrocarbons eluting before hexane, based on the cumulative uncertainty of the neohexane standard, measurements of standard addition flows, the integrity of individual compounds in the sampling and analysis process, and relative response factors. Measurement precision was approximately 3% at 1 ppbv, 5% at 0.5 ppbv, 10% at 0.2 ppbv, and 20% for concentrations less than 0.1 parts per billion by volume (ppbv), as determined by the variance between measurements taken from the same level every fifth injection. The detection limit for these compounds was approximately 0.01 ppbv.

Compounds eluting after hexane (including isoprene, hexenes, benzene, and toluene) suffered systematic losses in the analytical system. Standard additions of isoprene to air samples showed that isoprene recovery was linearly dependent on the amount of water vapor in the air and nonlinearly dependent on the amount of isoprene added (recovery decreased with decreasing concentration). Isoprene data could not be corrected reliably, and the system was changed in 1995 to eliminate isoprene losses in the trap. For further details see Goldstein *et al.* [1995a].

The analytical system was checked for contamination daily by running zero-air blanks. No ethene, propene, or 1-butene was observed. The Teflon sampling tubes were checked for contamination and memory effects by introducing zero-air at the sample inlets on top of the tower on July 12, 1993. Three measurements were made over a 2.5-hour period. Small quantities of ethene and 1-butene were measured in the top level (30 and 25 parts per trillion by volume (pptv) respectively), and 1-butene was measured in the lower level (30 pptv), indicating some memory for these compounds. No memory was observed for propene at either level. The influence of memory effects and systematic differences between the response of the dual analysis system (3%-7%) were eliminated from the gradient data by linearly interpolating the NULL gradient measured every fifth run onto the timeline of the gradient measurements and subtracting from the measured gradients.

Ethene was used as a reagent in an instrument measuring ozone at the site. The effluent from this instrument (30% ethene at 1 L min⁻¹) was vented approximately 30 m southeast of the tower. Prevailing winds were from the southwest, northwest, and north, nevertheless, reagent ethene was occasionally detected by the NMHC instrument as indicated by single-point enhancements in the time series. Contaminated measurements were removed for the gradient determination by eliminating observations where the concentration was above 0.8 ppbv, which also eliminated time periods for large pollution events. Correlations observed between ethene gradients selected in this way and gradients for 1-butene and propene support the validity of the selection criteria (see below).

Gradients for concentrations of CO₂ and H₂O, and for air temperature, were measured simultaneously with the hydrocarbon gradients. Concentration differences for CO₂ and H₂O were measured using a differential infrared gas

analyzer (LICOR 6262), with air from 29 m passed through the reference cell and air from 24 m through the sample cell. The gradient measurements were zeroed after every sampling period by filling both cells with air from 29 m. Instrument gain was determined by addition of CO₂ and dry air to the flow from 29 m. Pressure broadening and dilution corrections to the CO₂ concentration due to the presence of water vapor were made according to the instrument manufacturer's specifications. The standard deviations of the zero gradient measurements were determined by comparing the NULL gradient measured every fifth sampling period (when hydrocarbon NULL gradients were determined) to the zero measurement directly following that period. The standard deviation in the zero measurements for CO₂ and H₂O (0.18 ppm and 42 ppm, respectively) was of the order of 20% of the mean midday gradients (-0.9 ppm CO₂ and 190 ppm H₂O). Flux determinations were not attempted when observed gradients were very small, that is, within 1 standard deviation of zero. Water vapor gradient measurements were also discarded when the inlet filters on top of the tower became wet after rain events. The CO₂ fluxes and gradients and all the NMHC measurements are reported as mole fractions relative to dry air at a common temperature, avoiding the need for density corrections due to fluxes of sensible heat or H₂O [Webb *et al.*, 1980].

Temperature gradients were measured using copper-constantin bare fine wire thermocouples (44 gage), placed 1 m south of the tower at both 29 and 24 m. Significant radiation loading occurred during the daytime, making the differences between two thermocouples at the same level similar in magnitude to the temperature gradient between the levels (0.1°C-0.2°C). The temperature measurements worked well at night (1700 to 0800 LT), with the standard deviation between two thermocouples at the same level of 0.04°C, compared to standard deviations of 0.12 °C during the daytime (0800 to 1700 LT). Accurate gradients could be measured over Harvard Forest for CO₂ more often than for temperature or H₂O owing to radiation loading on the thermocouples and to the wetting of sample inlet filters. Therefore hydrocarbon fluxes reported here were calculated using similarity with CO₂.

Approximately 9000 pairs of measurements were made for each hydrocarbon compound, more than 75% of all 45 min intervals during the 12 months of data reported here. Gaps in the data occurred during the summer of 1993 owing to a lightning strike which disabled the sonic anemometer (August 9-September 7), a broken gas chromatographic capillary column (April 22-May 4), intermittent computer failures (April 2-May 7), and a broken sampling pump (June 7-12). Shorter gaps were due to occasional power failures and routine maintenance of the instruments.

Hydrocarbon Flux Error Analysis

Uncertainty in the hydrocarbon fluxes can arise from issues with the validity of the flux-gradient technique, systematic measurement errors, and random measurement errors. In the following discussion the random and systematic errors are evaluated separately. Random errors are assessed by propagating the standard deviations of the gradient and eddy flux measurements through the hydrocarbon flux calculation. Systematic errors are assessed by examining the validity of the flux-gradient similarity method as used at Harvard Forest and the potential for systematic measurement errors.

Individual hydrocarbon flux calculations have random errors associated with each of the measurements used to calculate the flux. Hydrocarbon fluxes are determined by similarity with CO₂ using the equation,

$$F_{hc} = F_c(g_{hc}/g_c) \quad (2)$$

where F is flux, g is gradient, and hc and c refer to hydrocarbon and CO₂, respectively. Assuming that errors in F_c , g_{hc} , and g_c are random and independent, the absolute standard deviation (σ) for a determination of F_{hc} can be calculated from [Skoog, 1985]:

$$\sigma_{F_{hc}} = F_{hc} [(\sigma_{F_c}/F_c)^2 + (\sigma_{g_c}/g_c)^2 + (\sigma_{g_{hc}}/g_{hc})^2]^{1/2} \quad (3)$$

Values for each of these terms are given in Table 1 for typical daytime summer conditions. Under these conditions the coefficient of variation ($\sigma_{F_{hc}}/F_{hc}$) for flux determinations of ethene, propene, and *I*-butene is 48%, 60%, and 76%, respectively.

Random errors will vary with ambient conditions including magnitude of the flux, atmospheric stability, and absolute hydrocarbon concentrations. Most of the uncertainty is associated with quantifying gradients of CO₂ and hydrocarbons above the forest. When fluxes are small or air above the canopy is being vigorously mixed, the gradients are small and harder to quantify. Precision of the hydrocarbon gradient measurement is a function of the absolute concentration thus uncertainties increase when ambient concentrations increase (owing to biogenic emission or regional pollution). We have averaged the gradient and flux data to minimize random errors while examining diurnal cycles, forcing factors, seasonality of emissions, and relative emissions in the following discussion.

Systematic errors in the flux-gradient similarity assumption could occur if the distribution of the sources and sinks for these scalars are inhomogeneous in the footprint of the tower, if exchange occurs at significantly different heights in the forest or if mesoscale circulations strongly affect observed concentration gradients. The magnitude of these systematic errors is extremely difficult to evaluate. We checked the validity of our similarity assumption by comparing exchange coefficients determined from CO₂ fluxes and gradients with those determined from H₂O and sensible heat. There could be additional systematic errors if the distribution of the sources and sinks for CO₂, H₂O, and sensible heat were significantly different from the distribution of the hydrocarbon sources.

Table 1. Olefin Flux Random Error Analysis

Variable	Units	Ethene	Propene	1-Butene
F_c	10^{13} molecules $\text{cm}^{-2} \text{s}^{-1}$	-104	-104	-104
σ_{F_c}	10^{13} molecules $\text{cm}^{-2} \text{s}^{-1}$	16	16	16
g_c	ppm	-0.87	-0.87	-0.87
σ_{g_c}	ppm	0.18	0.18	0.18
g_{hc}	ppbv	0.059	0.029	0.014
$\sigma_{g_{hc}}$	ppbv	0.024	0.016	0.008
F_{hc}	10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$	7.1	3.5	1.7
$\sigma_{F_{hc}}$	10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$	3.4	2.1	1.3

F , flux; σ , standard deviation; g , gradient; c , CO₂; and hc , hydrocarbon; ppbv, parts per billion by volume.

Figure 1a is a plot of K derived from CO_2 versus K derived from H_2O (slope is 1.07 ± 0.03 (1 standard error) and $R^2=0.68$). Figure 1b is a plot of K derived from CO_2 versus K derived from sensible heat during the night (2200 to 0400 LT), when no solar radiation loading problems were apparent (slope is 1.12 ± 0.06 (1 standard error) and $R^2=0.61$). There is significant statistical uncertainty in individual exchange coefficients derived from CO_2 , H_2O , and sensible heat, owing mostly to random errors inherent in measuring small concentration gradients. Outliers generally occurred when fluxes were relatively large and the gradients were small, inducing large errors in K .

Values of K calculated from these three sets of measurements agree very well, however, within $12 \pm 10\%$ (90% confidence interval from slope standard error), when the data are aggregated and averaged. Systematic errors which effect eddy flux measurements of H_2O , CO_2 , and sensible heat equally (such as errors in wind measurements) would not be accounted for by this comparison but are expected to be less than 10% based on closure of the energy budget [Goulden *et al.*, 1996]. Hence the sum of systematic errors for hydrocarbon fluxes due to deviations from similarity and to

CO_2 flux and gradient measurements should not exceed 20% for midday summer fluxes.

The largest potential for systematic error in the hydrocarbon gradient is most likely associated with the NULL gradient correction. The existence of nonzero NULL gradients appears to reflect memory in the tubing, and frequent measurements of the NULL gradient are crucial to correct for both these memory effects and for any systematic differences between the dual analysis systems. We have tried to minimize systematic errors by carefully correcting for nonzero NULL gradients. Mean daytime (1000 to 1500 LT, June 1 to October 31) hydrocarbon gradients were 0.045, 0.024, and 0.012 ppbv, including mean NULL gradient corrections of -0.014, -0.005, and 0.000 ppbv, for ethene, propene, and *I*-butene, respectively. The maximum systematic error due to the NULL gradient corrections is therefore 30% for midday mean summer fluxes, based on the ratio of the NULL gradient correction to the corrected gradient. The total systematic error associated with the mean daytime hydrocarbon fluxes should not exceed 50%, and our analysis suggests that it may be considerably smaller (~20%).

Results and Discussion

First, we provide evidence from several different sets of observations for summertime biogenic emissions of ethene, propene, and *I*-butene. Next, we examine diurnal flux cycles and evaluate which environmental forcing factors are most important. Finally, we assess the significance of biogenic emissions of these olefins, comparing the observed fluxes to those reported for regional anthropogenic sources.

Evidence of Biogenic Emissions

Evidence of summertime biogenic emissions of ethene, propene, and *I*-butene is apparent in scatter plots of ambient concentrations versus acetylene (a tracer of anthropogenic emissions) in January and July 1993 (Figure 2). Variations of the olefin concentrations are closely correlated with acetylene in January, indicating their anthropogenic emission ratio. In July the correlations with acetylene were weak, particularly for propene and *I*-butene, owing to biogenic emissions and possibly to faster loss rates in summer. Scatter plots of propene versus acetylene (Figure 3) for all the months of 1993 show that significant biogenic emissions occurred from May to September. The impact on "background" concentrations (defined as times when acetylene is below its 0.2 quantile in 30 day periods) of these olefins is shown by comparing their relative seasonal variations with those of butane, pentane, and hexane (Figure 4), compounds of dominantly anthropogenic origin. Normalized seasonal variations of hydrocarbons with predominantly anthropogenic sources, and with lifetimes shorter than propane, are nearly identical at Harvard Forest [Goldstein *et al.*, 1995b]. Concentrations of propene and *I*-butene are anomalously high in summer owing to the influence of local biogenic sources for these compounds. Ethene reaches its highest concentrations in winter, but its relative seasonal variation is not as pronounced as for butane, pentane, and hexane, also owing to the influence of seasonal biogenic emissions.

Diurnal and Seasonal Fluxes

A 2-day sequence of data for concentrations of hexane, *I*-butene, propene, and ethene (at 29 m), the raw gradient

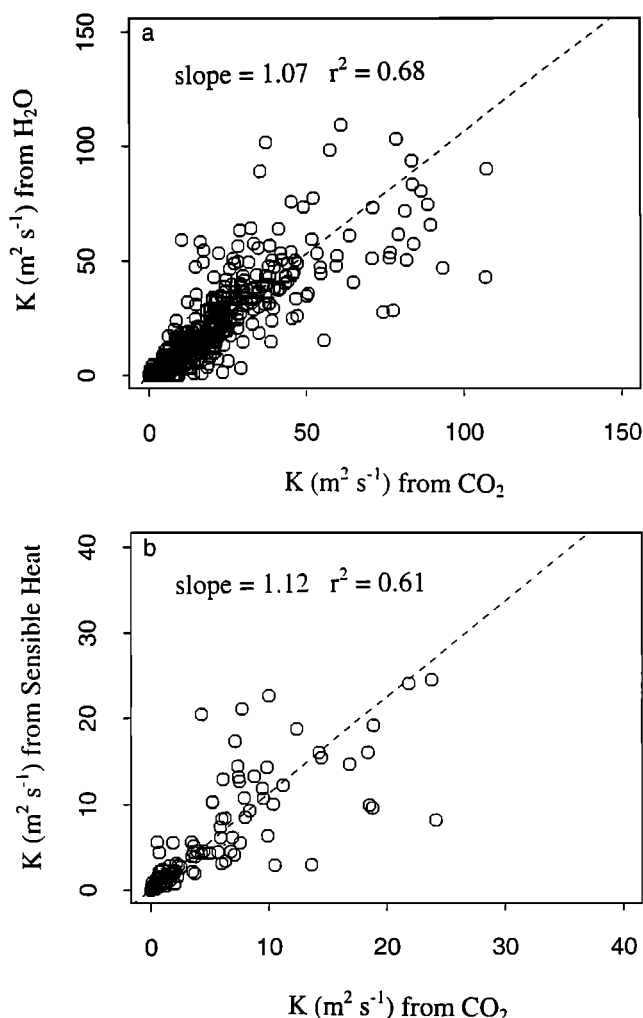


Figure 1. Exchange coefficient (K) calculated from the measured flux and gradient of CO_2 and (a) H_2O and (b) sensible heat (nighttime data only owing to radiation loading problems on temperature sensors during the day).

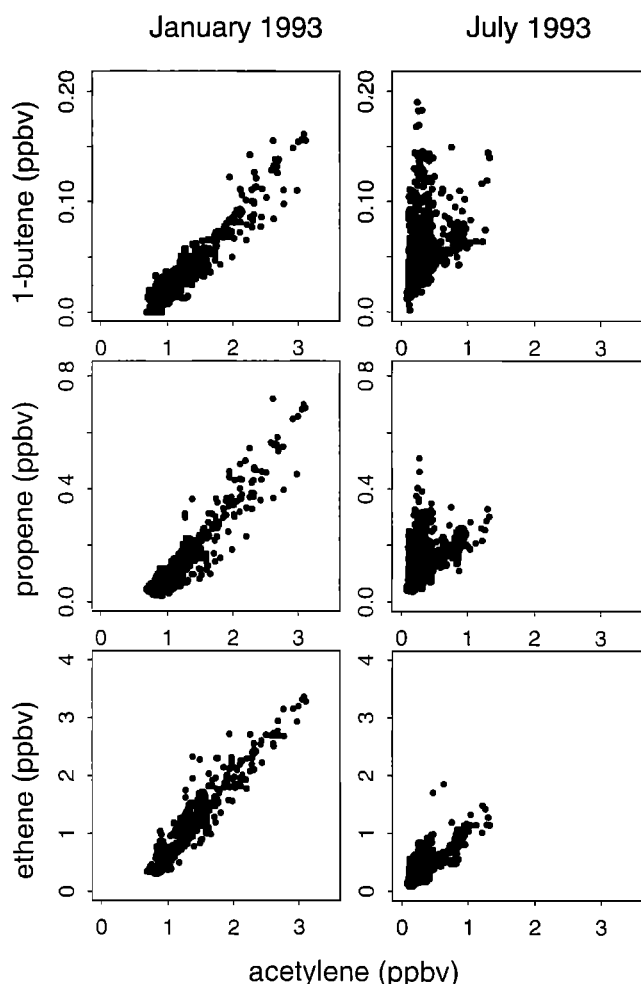


Figure 2. Concentrations of 1-butene, propene, and ethene versus acetylene concentration in January and July 1993. Acetylene is a tracer of anthropogenic hydrocarbon emissions with no significant terrestrial biogenic source. The signature of anthropogenic emissions is evident in January. The olefins, 1-butene, propene, and ethene, all have increased concentrations in July relative to acetylene owing to emission from the forest.

between the levels (24–29 m), and the NULL gradient (every fifth run) (Figures 5a–5d) reveals striking patterns (corrected gradient is raw minus NULL). Significant excess concentrations at the lower inlet were observed during the day for ethene, propene, and 1-butene, with much smaller gradients at night; corresponding diurnal cycles were observed in the mean concentrations. Gradients were not observed for any C2–C6 alkanes or for acetylene, indicating that these species were not emitted from the forest in observable quantity. The raw and NULL gradients for hexane are indistinguishable and essentially zero. The NULL gradients for 1-butene, propene, and ethene are measurable, correlating with the mean concentration. As discussed above, nonzero NULL gradients appear to reflect memory by the tubing, and we have tried to minimize systematic errors by carefully correcting for nonzero NULL gradients.

Fluxes of ethene, propene, and 1-butene during the growing season (June 1 to October 31, 1993) more closely followed the diurnal pattern of incident photosynthetically

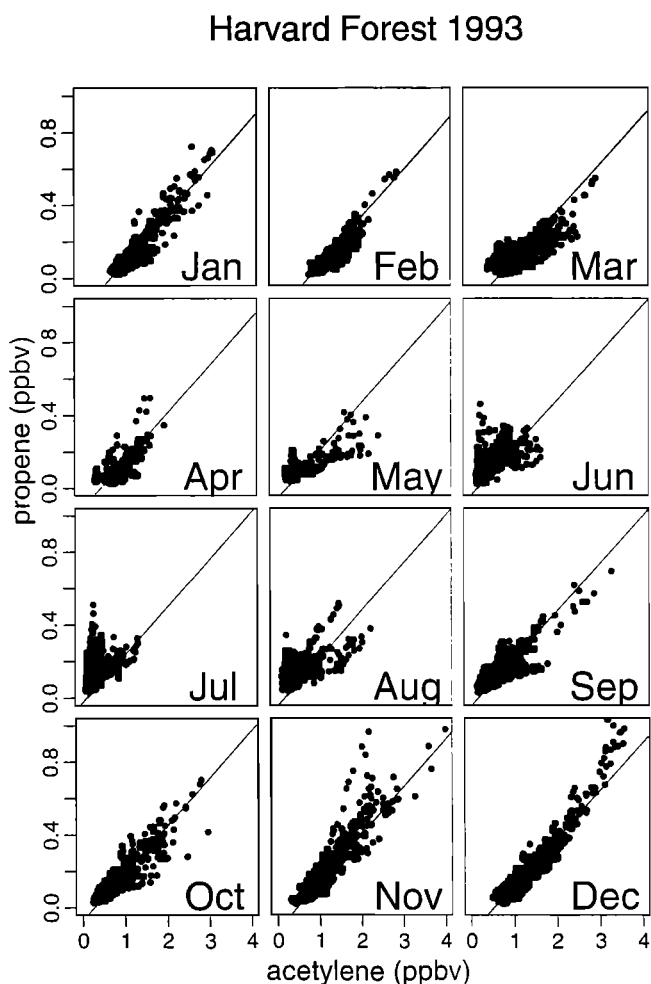


Figure 3. Propene versus acetylene concentration for all the months of 1993. The line in each scatter plot represents the slope of the January 1993 correlation.

active radiation (PAR) (measured above the canopy) than the cycle of air temperature (Figure 6). The 1-butene diurnal pattern was the least well defined, probably because its gradient was so close to the detection limit of the NMHC instrument. Fluxes of ethene, propene, and 1-butene increased linearly with light, presented as mean flux versus PAR in Figure 7 (R^2 is 0.93, 0.99, and 0.96, respectively and R^2 for nonaggregated data is 0.10, 0.19, and 0.09, respectively with $P < 0.0001$). The correlation between emissions of olefins and incident light suggests that forest vegetation was the main source of these olefins. Unfortunately, the observations lack the precision needed to define the role of secondary factors such as humidity or phenology.

Soil processes were probably negligible sources of ethene, propene, and 1-butene. If the olefins were coming from the soil, we would expect their emissions to be correlated with soil temperature and to continue at night. We observe large vertical concentration gradients above the forest at night for CO_2 , especially during stable mixing conditions, but not for the olefins. The nighttime gradient in CO_2 results predominantly from soil emissions. Hence we conclude olefin emissions from soils were not significant.

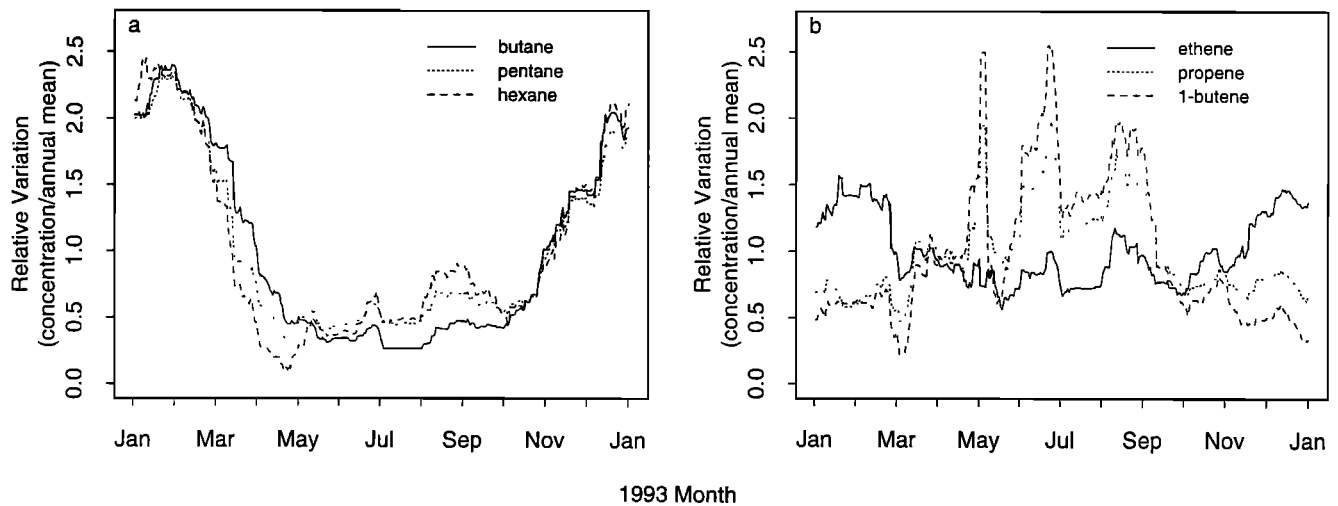


Figure 4. Relative seasonal variations of 1993 "background" concentrations of (a) butane, pentane, hexane, and (b) ethene, propene, and *I*-butene. Background is defined as the mean value when acetylene is below its 0.2 quantile in 30-day periods.

The seasonal trends of emissions of ethene, propene, and *I*-butene may be inferred from mean midday gradients (1000 - 1500 LT) observed over a 1-year period (Figure 8a). Emissions began in April or May and ended in October or November, a slightly longer period than was obvious from

Figure 3. Deciduous trees develop leaves in early May, this result provides evidence that coniferous trees contribute to emissions of these compounds.

We may compare observed gradients for ethene, propene, and *I*-butene directly to define relative rates of emission at

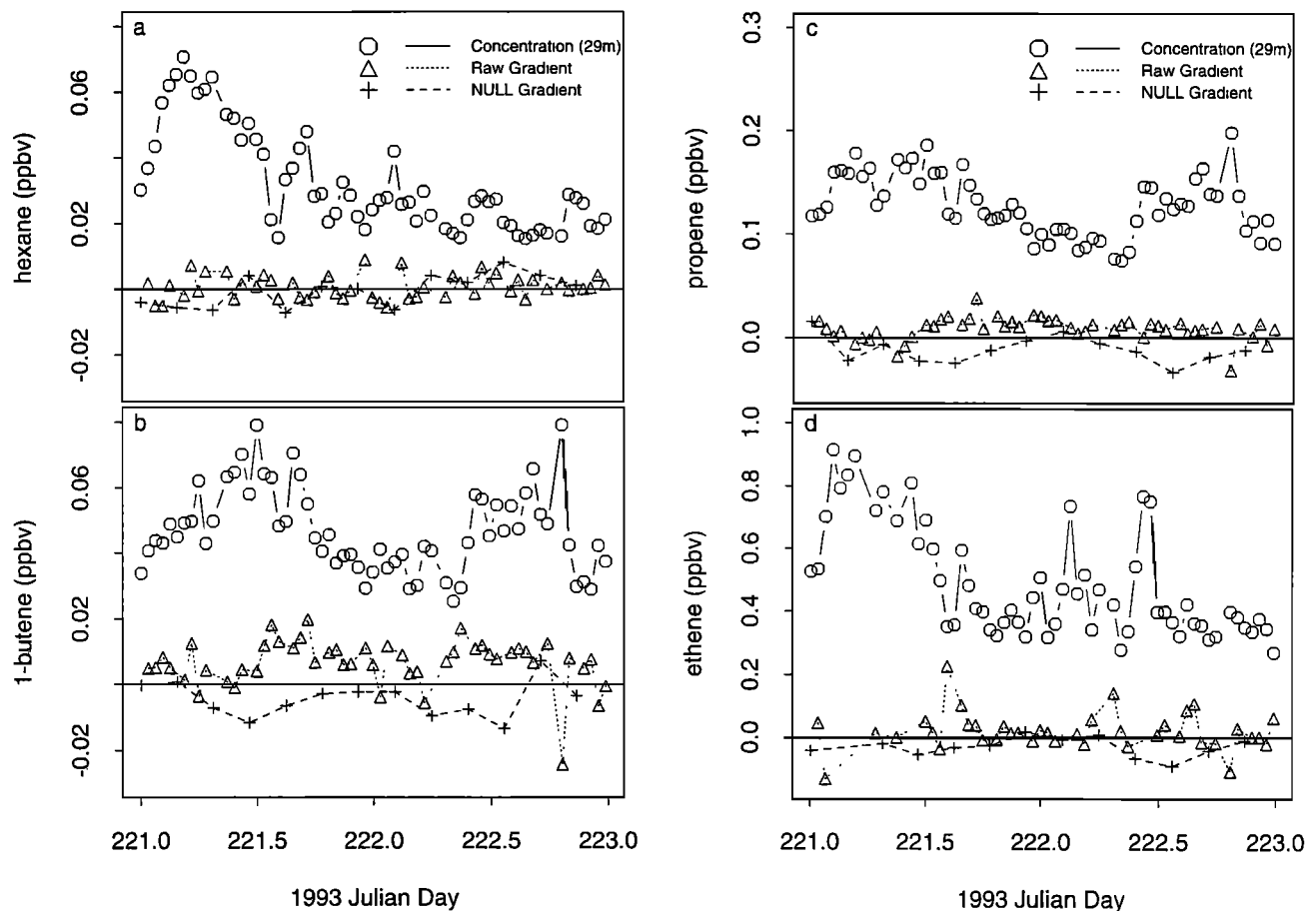


Figure 5. Concentration (at 29 m), raw gradient (29-24 m), and NULL gradient (every fifth run) measured above Harvard Forest on August 9 and 10, 1993 for (a) hexane, (b) *I*-butene, (c) propene, and (d) ethene. The corrected gradient equals the raw minus NULL gradients.

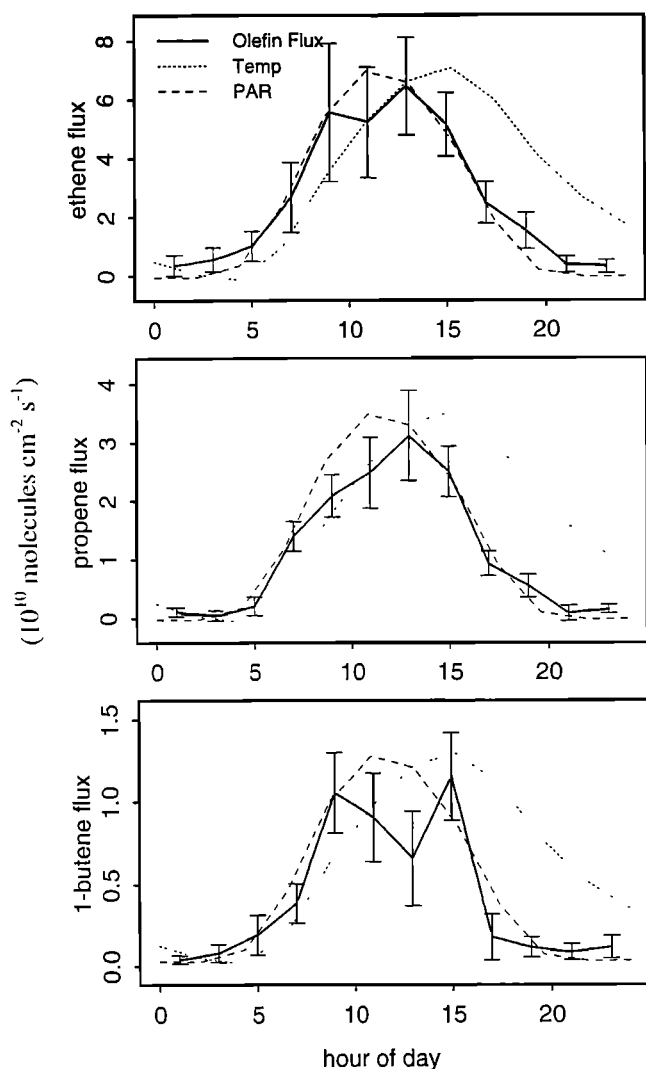


Figure 6. Average diurnal cycles for fluxes of ethene, propene, and 1-butene (\pm standard error) along with temperature and incident photosynthetically active radiation (PAR) (June 1 to October 31, 1993). Data was parsed into 2-hour time windows.

midday (4:2:1, Figure 8b) over the period June 1 to October 31, 1993, eliminating uncertainty due to the CO_2 and vertical wind measurements. The relative fluxes estimated by integrating mean diurnal fluxes measured over the same period (Figure 6), 2.63 , 1.13 , and 0.41×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$ respectively, are consistent with these values.

Biogenic Versus Anthropogenic Emissions in Massachusetts

Ethene, propene, and 1-butene have regional anthropogenic emissions due to the combustion of fossil fuel. The 1985 National Acid Precipitation Assessment Program (NAPAP) emission inventory indicates Massachusetts emissions for ethene and propene (1-butene is not included as a separate species in this inventory) to be 99% and 95% from mobile sources with total emissions of 638 and 55 million moles per year, respectively, equivalent to 5.7×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$ and 0.5×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$ if these sources were evenly distributed over the state. Comparing this number to summertime emissions at Harvard Forest, we

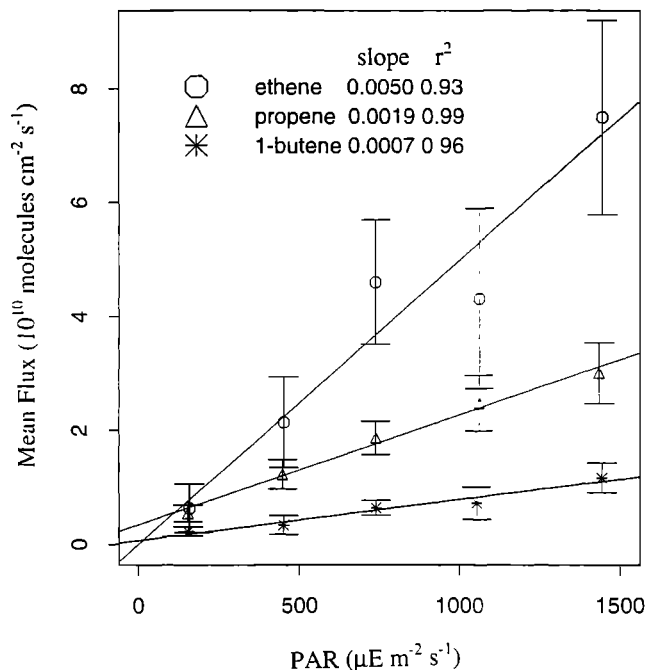


Figure 7. Mean flux (\pm standard error) of ethene, propene, and 1-butene as a function of incident PAR (June 1 to October 31, 1993). Data was parsed into PAR windows of $300 \mu\text{E m}^{-2} \text{s}^{-1}$. Standard errors of the slopes of the correlation's with PAR equal 0.0008, 0.0001, and 0.0001 for ethene, propene, and 1-butene, respectively.

find that biogenic emissions of ethene (2.63×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$) are about half the anthropogenic emission, while biogenic emissions of propene (1.13×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$) are twice as large as anthropogenic emissions. This interpretation is supported by the summertime enhancements shown in Figure 2.

Regional fossil fuel combustion sources for propene and 1-butene can also be scaled from the NAPAP ethene emissions using emission ratios measured during the winter at Harvard Forest (Figure 2), 20/4/1, which agree well with those determined from the NAPAP [1985] emission inventory for the whole United States, 19/4/1 [Middleton *et al.*, 1990]. Using these data and our measured ratio of 4/2/1 for forest vegetation emissions, we infer that combustion sources likely represent an even smaller fraction of regional emissions for 1-butene than for propene or ethene. The data show unambiguously that regional biogenic emissions of propene and 1-butene are larger than the regional anthropogenic sources in summer at Harvard Forest, despite proximity to a region with massive anthropogenic sources.

Enhanced atmospheric concentrations of ethene and propene have previously been observed in forested regions. Zimmerman *et al.* [1988] reported elevated levels of ethene and propene in the Amazon boundary layer over a tropical forest suggesting biomass burning as a likely source, although they noted that terrestrial or aquatic biogenic sources could have contributed. Greenberg *et al.* [1992] found significant increases in ethene, propene, and isoprene during upslope flow at Mauna Loa, Hawaii; they attributed the isoprene to island vegetation but the ethene and propene to local marine emissions. Our results suggest that significant enhancements of ethene and propene concentrations in these environments could be attributed to emissions from vegetation.

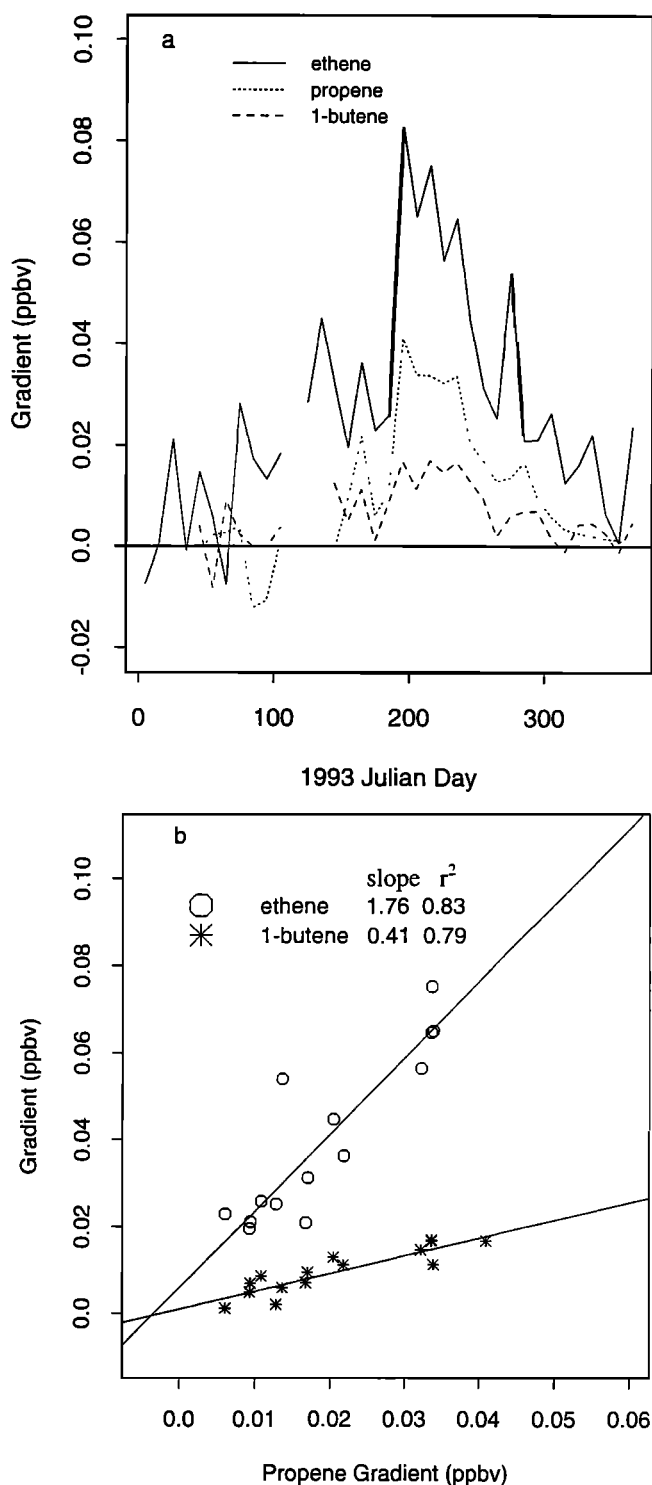


Figure 8. Ten day mean gradients (1000 - 1500 LT) of (a) ethene, propene, and 1-butene for 1993, and (b) ethene and 1-butene gradients versus propene gradient from June 10 to October 31. The slopes provide a good measure of relative midday fluxes 1.8 ± 0.22 (standard error) and 0.41 ± 0.06 for ethene and 1-butene, respectively, versus propene.

Conclusions

Emissions of propene and 1-butene by vegetation during summer exceed anthropogenic emissions in the northeastern United States, and emissions of ethene by vegetation contribute about 50% of anthropogenic sources. During

winter we observed dominant contributions from anthropogenic sources, and the NAPAP [1985] United States emission inventory accurately predicted observed emission ratios. Our measurements suggest that terrestrial biogenic emissions could provide a significant global source for two important reactive olefins, propene and 1-butene.

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