

# Automated In-Situ Monitoring of Atmospheric Non-Methane Hydrocarbon Concentrations and Gradients

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**Abstract.** A fully automated system measuring C<sub>2</sub>–C<sub>6</sub> hydrocarbon concentrations and vertical gradients was installed at Harvard Forest in Petersham, Massachusetts, using a gas chromatograph with dual flame ionization detectors and cryogenic sample preconcentration. Measurements were made simultaneously at two heights above the forest canopy at forty five minute intervals, continuously from July 1992 to the present. Data for concentration gradients were combined with CO<sub>2</sub> flux measured by eddy correlation to determine the rates of production of biogenic hydrocarbons by the forest.

**Key words:** Hydrocarbons, biogenic emission, automated.

## 1. Introduction

An automated Environmental Measurement Station (EMS) was established at Harvard Forest (Petersham, Massachusetts) in 1989 (Wofsy *et al.*, 1993) to study the chemistry of the atmosphere, and the exchange of trace gases between the atmosphere and mid-latitude forests. Fluxes of CO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O, NO<sub>y</sub>, momentum and sensible heat were measured continuously between the forest and atmosphere using the eddy correlation method, along with ambient concentrations of CO, CO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O, NO<sub>x</sub>, NO<sub>y</sub>, and CH<sub>4</sub>, and physical environmental parameters such as wind speed and direction, temperature, relative humidity, radiation, and barometric pressure. The system described in this paper complements these measurements by monitoring ambient concentrations and vertical gradients of C<sub>2</sub>–C<sub>6</sub> non-methane hydrocarbons (NMHCs).

Automated in-situ measurements allow determination of NMHC concentrations free of the artifacts often associated with storage in canisters (Singh *et al.*, 1988; Blake *et al.*, 1992), and provide a true temporal ensemble of data with resolution from hours to years. Automated instruments for in-situ NMHC analysis have

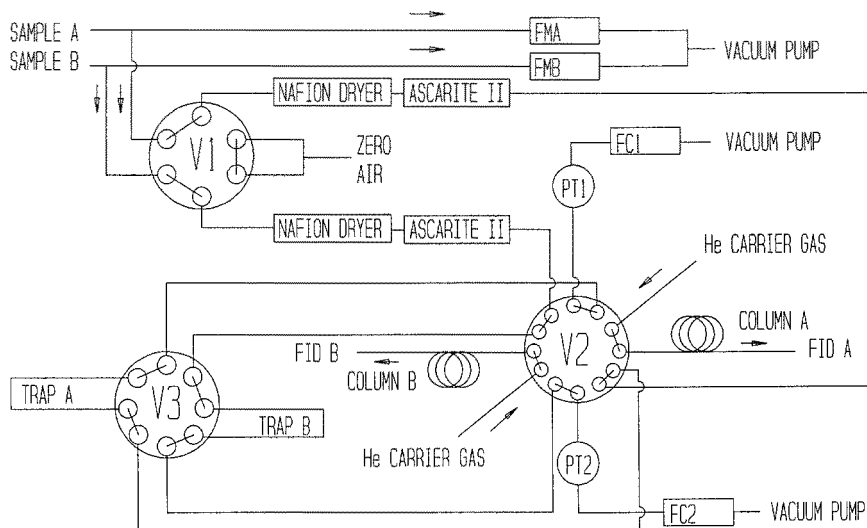


Fig. 1. Schematic diagram of the hydrocarbon measurement system. Air is drawn from above the forest canopy at  $\sim 10$  s/m, and 40 sccm are sampled from this flow.  $\text{H}_2\text{O}$ ,  $\text{O}_3$ , and  $\text{CO}_2$  are removed from the sample with the Nafion Dryer and Ascarite II. The sample is then preconcentrated in the cryogenic trap, injected into the chromatographic column, and detected with the flame ionization detector (FID). Symbols are: FC, flow controller; FM, flow meter; V, valve; PT, pressure transducer; TRAP, cryogenic preconcentration trap.

been described previously by Rudolph *et al.* (1990), and Martinez (1992), and commercial instruments are available. All cryogenically preconcentrate samples, separate species by Gas Chromatography (GC), and detect with Flame Ionization or Photo Ionization Detectors (FID or PID). The instrument described here measures hydrocarbon gradients in-situ at a remote site, using minimal quantities of cryogen in order to allow unattended operation for up to two weeks between visits.

## 2. Pretreatment, Preconcentration, and Chromatographic Separation

Figures 1–3 show schematic diagrams of the system. Removal of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{O}_3$  from samples is required for in-situ hydrocarbon analysis. Following Donahue (1991), most of the  $\text{H}_2\text{O}$  was removed by passing the sample through a Nafion dryer (Perma Pure Products, Inc.), and  $\text{CO}_2$  and  $\text{O}_3$  were removed to undetectable concentrations using Ascarite II (Thomas Scientific) (Figure 1). The hydrocarbons in 400 ml (STP) of air are cryogenically preconcentrated using a custom cryotrap described below.

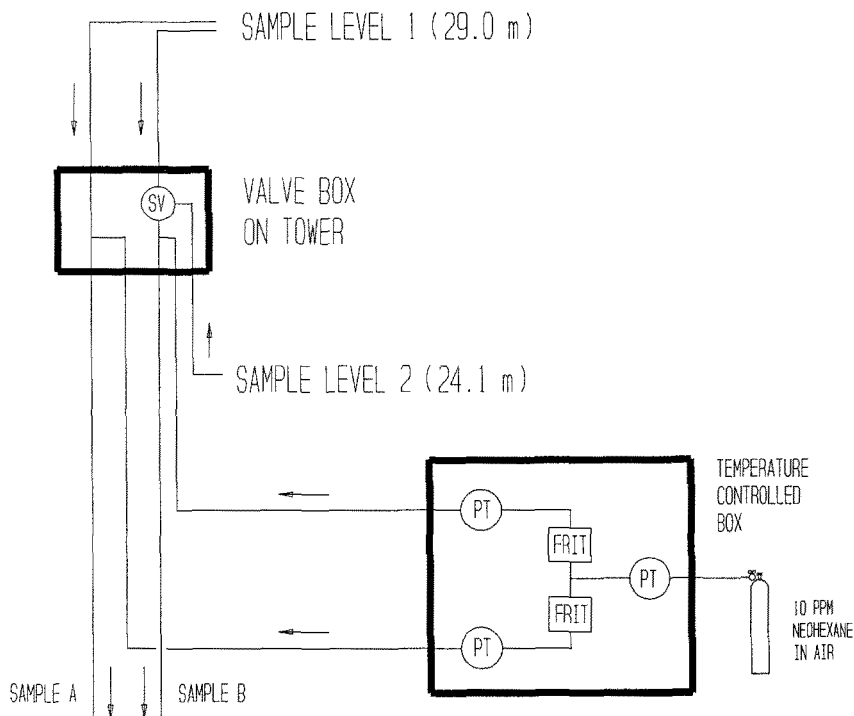


Fig. 2. Schematic diagram of the air sampling system with addition of neohexane as an internal standard. Sample A is always taken from the 29 m level. Sample B is normally taken from the 24 m level. Every fifth sampling period sample B is taken from the 29 m level by actuating a three way solenoid valve (SV) on the tower, providing a measurement of systematic differences between the two channels. Neohexane is added to every sample by continuously flowing  $\sim 7$  sccm into the sampling lines, creating a concentration of  $\sim 7$  ppbv. Neohexane flow is controlled by pressure gradients across stainless steel frits which are housed in a temperature controlled box.

### 3. Hydrocarbon Sampling System

Two samples are drawn at approximately 10 liters per minute continuously through 3/8" OD Teflon tubes from inlets at heights of 24 and 29 m on the tower (2 and 7 m above the forest canopy) (Figure 2). A 10 ppmv neohexane standard (Scott–Marrin, certified NIST traceable  $\pm 2\%$ ) is added continuously to each sample stream at 7 sccm near the sample inlet. The neohexane internal standard is used to quantify concentrations of all the hydrocarbons by applying relative response factors (RRF) adapted from Ackman (1964), and to provide a time reference for peak identification by relative retention time (RRT) (see below). Sample A is always taken from the 29 m level and sample B is taken simultaneously from 24 m, or on every 5th run from 29 m by actuating a three way solenoid valve on the tower. Simultaneous measurements from the same level define any systematic differences between the two channels. The flow rate through the pretreatment and preconcentration devices is 40 sccm, taken from each main sample line through valve 1. Samples flow

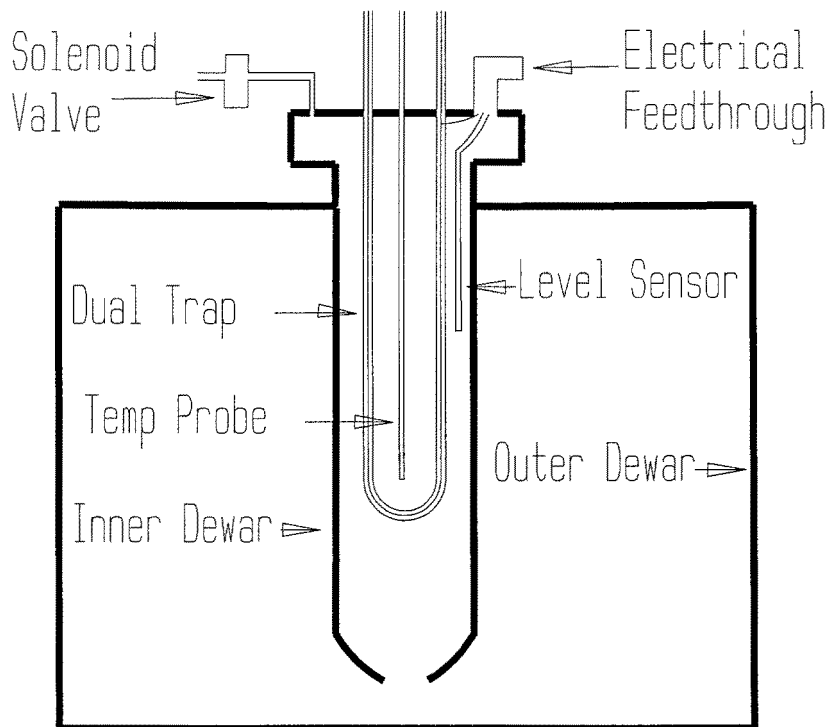


Fig. 3. Schematic diagram of the cryogenic trap. See text for details.

through valves 2 and 3 to the cryotrap for 10 minutes, then the traps are isolated until analysis time by switching valve 3. Sample flows A and B are maintained by flow controllers (MKS Instruments) 1 and 2, and pressures are monitored by transducers (Mediamate) 1 and 2, respectively. The samples are drawn through this system with diaphragm vacuum pumps (KNF Nueberger, Inc.). Sample pressures during preconcentration are 450–500 Torr.

After the samples have been preconcentrated, the traps are heated to  $-60^{\circ}\text{C}$  (45 seconds) to desorb the C<sub>2</sub> hydrocarbons under zero flow conditions, thus avoiding the need to cryofocus them. Valves 2 and 3 are then switched, allowing carrier gas to flow through the cryotrap and carry the samples into the GC. After the valves are switched, heating continues to  $70^{\circ}\text{C}$  (additional 60 seconds) to assure desorption of higher molecular weight compounds.

Zero-air (Aadco Zero-Air Generator) is introduced through valve 1 in place of ambient air every 30th run in order to check for hydrocarbon contamination. Zero-air is also used to flush the cryotrap while heating the trap to  $160^{\circ}\text{C}$  to remove any residual sample between runs.

The flows of neohexane standard are controlled by maintaining a pressure gradient across stainless steel frits (Mott Metallurgical), while measuring the upstream and downstream pressures (Mediamate pressure transducers). The frits were cali-

brated with a flow controller (MKS) which was in turn calibrated using a known volume and a pressure transducer (MKS).

#### 4. Cryotrap

The cryotrap design (Figure 3) was adapted from that of Rudolph *et al.* (1990) to minimize cryogen consumption, a critical parameter due to the remote location of the site. A 50 l dewar is pressurized to 22 psi using a pressure relief valve, increasing the liquid nitrogen temperature from 77 to 84 K. This change in temperature (boiling point) eliminates the possibility of condensing liquid oxygen inside the sample trap (note the sample pressure cannot exceed 1 atm because the sample is pulled through the trap). Inside the large dewar is a smaller dewar with a hole in the bottom. The top of the inner dewar has ports for sample tubes, a temperature probe, a solenoid valve which opens to the atmosphere, and an electrical feedthrough for the level sensors and heater. The heater is an insulated nichrome wire wrapped around the two 1/16" OD stainless steel trapping tubes (0.03" ID). During sample concentration, a level controller (Andonian Cryogenics, LLA-450) opens and closes the solenoid valve on top of the inner dewar to keep the traps immersed to a constant depth. Immersion depth is therefore consistent from run to run, regardless of the amount of liquid in the reservoir dewar. During sample desorption and trap purge, the heater is turned on and the solenoid valve is closed, increasing the pressure in the inner dewar and forcing the cryogen into the main dewar while volatilizing the hydrocarbons in the sampling tube. This cryotrap uses less than 0.1 l per pair of samples, 10 to 30 times less than commercially available devices for cryogenic preconcentration.

#### 5. Sample Analysis

The GC (Hewlett Packard 5890 series II) uses a four stage temperature program as follows: 35 °C for 4 min, 12 °C min<sup>-1</sup> to 100 °C, 9 °C min<sup>-1</sup> to 200 °C, then hold at 200 °C for 15.6 min. Helium is used as the carrier gas with a flow rate of 4 ml min<sup>-1</sup>. 0.53 mm × 30 m PLOT GS-Alumina columns (J + W Scientific) are used.

The response factor (RF<sub>n</sub>) of the FID's is determined according to the equation:

$$RF_n = (FI_n/FI_a)([\text{neohexane}]/\text{peak area})$$

FI<sub>n</sub> is the flow of neohexane standard (sccm), FI<sub>a</sub> is the flow of ambient air sample (sccm), [neohexane] is the concentration of the neohexane standard, and peak area is the integrated area of the neohexane peak. Relative response factors for individual hydrocarbons (RRF<sub>i</sub>) are calculated using the equation (Ackman, 1964, 1968):

$$RRF_i = [(mass\%C_i * \#C_i)/(mass\%C_n * \#C_n)][RF_n],$$

where

$$\text{mass}\%C_i = 100\%(\#C_i * 12.011) / (\#C_i * 12.011 + \#H_i * 1.008),$$

#C and #H refer to the number of carbon and hydrogen atoms in the hydrocarbon molecule respectively.

Values for  $RF_n$  were stable over the measurement time period (July 1992–January 1993, 5000 samples at each level) with a relative standard deviation of 3%. This variation is due to errors in flow measurements and slight changes in the instruments environmental conditions such as temperature.

Peak identification was made using Scott Gas standard mixtures. Each standard mixture was analyzed a minimum of four times on each column and detector by standard addition to zero-air spiked with neohexane. A relative retention time (RRT) was calculated for each compound on each column:

$$RRT_i = \text{Retention time}_i / \text{Retention time}_n.$$

Standard additions of each standard mix were also made periodically to real air samples at the field site in order to confirm the peak identifications and individual compound integrity in the analysis system. Compounds listed in Table I were determined to be separable, identifiable and quantifiable on a routine basis.

Zero-air is analyzed at least once per day to check for hydrocarbon contamination in the measurement system. There has been contamination of t-2-butene (< 70 ppt) and isobutene (< 40 ppt) from the Nafion dryer. In July and August 1992 there was propene contamination (< 20 ppt) which diminished with time and disappeared by September 1992. In July 1993, the Teflon sampling tubes were checked for contamination and memory effects by analyzing zero-air which was introduced at the sample inlets on top of the tower. Three measurements were taken over a 2.5 h period. Isoprene was measured in the first sample (11 pptv in top, 13 pptv in lower level), but was not detected in the second or third sample, indicating a small memory effect. In all three samples, Ethene and 1-butene were measured in the top level (30 and 25 pptv respectively), and 1-butene was measured in the lower level (30 pptv) indicating some consistent contamination from the sampling tubes for these compounds. No other significant contamination has been found.

## 6. Automation

Automation of the hydrocarbon measurement system is accomplished through a combination of HP Chemstation software and a Campbell Scientific CR10 datalogger. The HP software has the capability of creating a sequence of methods for the GC. Each method can control the GC temperature program, and up to four electronic events. These events are used to control valves, the cryotrap heater, and the level control solenoid on the cryotrap.

The datalogger (CR10) with a multiplexer (AM416, Campbell Scientific) is used to record signals from the pressure transducers, temperature probes, flow meters,

TABLE I. Mean ratios and standard deviations of same level measurements for hydrocarbons which are separable, identifiable and quantifiable\*

Hydrocarbon	Mean ratio B/A	Standard deviation	Median concentration
ethane	1.03	0.03	2.074 (ppbv)
ethene <sup>a</sup>	1.02	0.12	0.526
propane	1.03	0.03	1.007
propene	1.01	0.19	0.118
isobutane	1.02	0.05	0.243
butane	1.03	0.04	0.447
acetylene	1.03	0.04	0.674
t-2-butene <sup>b</sup>	0.87	0.30	0.061
1-butene	1.00	0.21	0.066
cyclopentane	0.99	0.11	0.061
isobutene <sup>c</sup>	1.04	0.15	0.064
2-methylbutane	1.03	0.03	0.301
pentane	1.03	0.05	0.169
1,3-butadiene	1.07	0.13	0.059
propyne	1.01	0.14	0.061
3-methyl-1-butene <sup>d</sup>	–	–	–
t-2-pentene	1.05	0.12	0.058
2-methyl-2-butene	1.05	0.12	0.059
cyclohexane	1.03	0.09	0.073
methylcyclopentane	1.01	0.05	0.058
hexane	0.95	0.10	0.079

\* Data from January 1, 1993 to December 31, 1993 were used for these calculations. Concentrations below 0.05 pptv were not used due to the low precision of data so close to the detection limit.

<sup>a</sup> Occasional contamination from another instrument on site.

<sup>b</sup> Blank problems in A (< 70 ppt) and B (< 30 ppt).

<sup>c</sup> Blank problems in A (< 40 ppt) and B (< 40 ppt).

<sup>d</sup> Concentration was never above 0.05 ppbv.

and flow controllers. The signals are read at 1 Hz and saved as 15 s averages. A file containing this data is downloaded from the CR10 to the computer's hard disk at the beginning of each GC run. The CR10 is also used to switch the tower solenoid for same level sampling every 5th run.

Duration of the automated measurements is limited by the capacity of the cryotrap, which holds enough liquid nitrogen for more than two weeks of continuous analysis. In practice, data are downloaded at six day intervals and the cryotrap is refilled at twelve day intervals.

## 7. Data Reduction and Analysis

For the chromatogram analysis to be relatively quick and routine, the factors that effect the retention times of the hydrocarbons must be rigorously controlled. Therefore, the room that contains the GC is maintained at  $18 \pm 2$  °C. In addition, all of the flow meters, flow controllers, frits, pressure transducers, and valves are housed in a temperature controlled box at  $38 \pm 0.3$  °C to minimize factors that may contribute to drift of system response.

Each six day data set contains about 380 chromatograms and requires approximately 3–4 h of data reduction and analysis. Two types of files are recorded for each sample: A raw data file from the GC detector, and a file of information collected on the datalogger. The raw data files are integrated using the HP Chemstation 3365 series II software, which creates ASCII files of peak identification and peak area information.

The information in the datalogger and peak identification files is synthesized into a matrix of time vs. concentrations, flows, pressures, temperatures, and response factors using an Splus (StatSci) batch job which:

- (1) Converts flows, pressures, time, and temperatures to proper units and time averages.
- (2) Calculates  $RF_n$ ,  $RRF_i$ , and concentration for each hydrocarbon.
- (3) Creates a vector of time, concentrations, flows, temperatures, etc.
- (4) Adds the vector to the overall matrix as a new row.
- (5) Continues to the next sample run and repeats steps 1 through 4.

These data matrices are the final data format. Each six day data set contains approximately 20 MB of raw data, and 200 KB of final data, both archived on 8 mm videocassettes.

## 8. Detection Limits, Accuracy, and Precision

Detection limits are approximately 0.01 ppbv for each compound. The accuracy of each measurement is limited by the flow measurements, neohexane standard, integrity of the individual compound in the sampling and analysis process, and knowledge of the RRF. The MKS flow meters have a stated accuracy of  $\pm 0.8\%$ , and the standard flow through the frits has been calibrated to  $\pm 3\%$ . The neohexane standard is certified NIST traceable  $\pm 2\%$  (Scott–Marrin). The integrity of individual compounds in the sampling and analysis process has been assessed by making standard additions to real air samples both above the forest canopy near the inlet, and below the canopy near the instrument. For example, standard additions of unsaturated hydrocarbons (Figure 4) at concentrations ranging from a few hundred pptv to 10 ppbv show excellent recovery and linearity for ethene, acetylene, propene, 1-butene, and 1-pentene, but poor recovery of 1-hexene (mean background concentrations during standard addition tests were 485 pptv, 478 pptv, 105 pptv, 32 pptv, below detection limit, and below detection limit, respectively). The



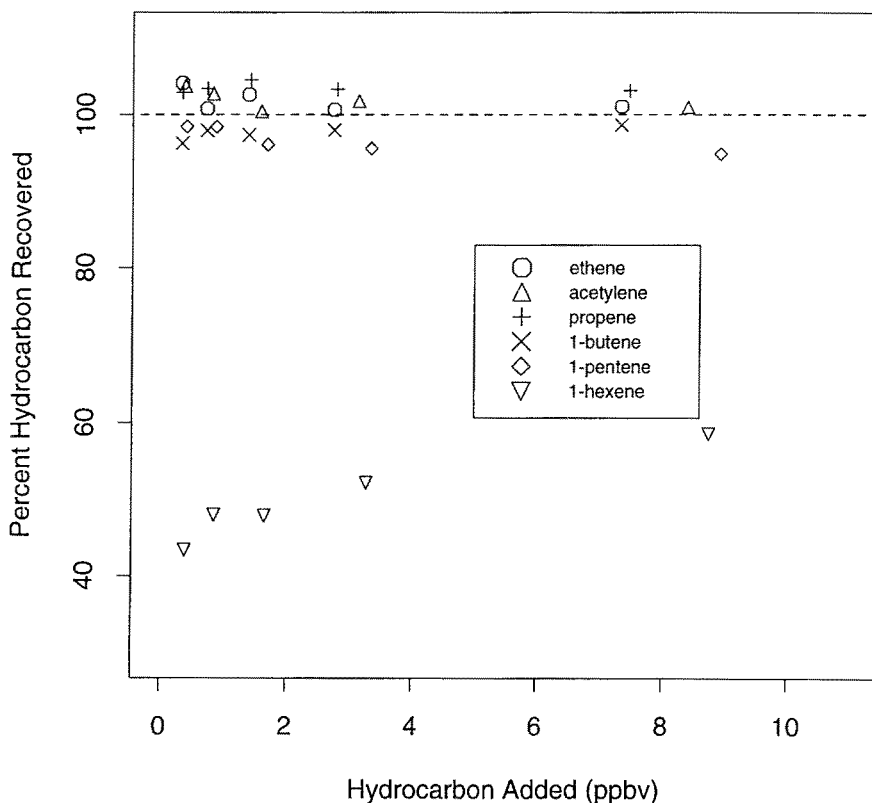


Fig. 4. Percent hydrocarbon recovered for standard additions of alkenes and acetylene to real air samples.

percentage of 1-hexene recovered increased with the amount added. Compounds eluting earlier than hexane (including hexane) all had excellent recovery. Compounds eluting later than hexane including isoprene, hexenes, heptane, benzene, and toluene all showed systematic losses in the instrument. Significant efforts were made to understand the systematic losses of isoprene because it is a very important biogenically emitted hydrocarbon. Standard additions of isoprene to real air samples were done during winter, spring, summer, and fall. The fraction recovered depended linearly on the water vapor content of the ambient air, and nonlinearly on the absolute amount of isoprene added (recovery decreased with decreasing concentration). Thus, determinations of isoprene concentrations and fluxes from this data are highly uncertain. Other researchers have encountered similar problems with isoprene recovery when trapping samples on bare stainless steel tubing (R. Arnts, personal communication).

Relative response factors were verified on our system to better than  $\pm 10\%$ , consistent with work of other researchers (Ackman, 1964, 1968; Dietz, 1967). The overall accuracy of this analytical system is therefore estimated to be better than

$\pm 18\%$  for all the C2–C6 hydrocarbons which elute before hexane. Participation in the Nonmethane Hydrocarbon Intercomparison Experiment [Apel *et al.*, 1994] confirmed our hydrocarbon identifications and proved our accuracy to be within 10% of NIST values for each compound reported (ethane, ethene, propane, propene, isobutane, butane, acetylene, isopentane, pentane, and hexane).

The dual measurement capability of this instrument provides an excellent opportunity to assess the precision of the hydrocarbon measurements using ambient air samples. Mean concentration ratios and their standard deviation are reported (Table I) for one full year of data (January 1–December 31, 1993). These data show that instrument precision is a function of concentration with  $1\sigma$  approximately: 3% at 1 ppbv, 5% at 0.5 ppbv, 10% at 0.2 ppbv, and 20% for concentrations less than 0.1 ppbv.

## 9. Chromatograms

An example chromatogram is shown in Figures 5a–b for a sample collected on January 14, 1993 (note the different scales on the time and detector response axes). The concentrations of ethane, pentane, and propyne were 4.37, 0.609, and 0.101 ppbv, respectively, indicating fairly polluted air; 70% of the peaks were identified. When clean tropospheric air was being analyzed, approximately 80% of the peaks were identified, and the ethane concentration was  $\sim 2.5$  ppbv at this time of year.

## 10. Data from Harvard Forest

In order to illustrate the application of this system, three examples of Harvard Forest NMHC data are given. The first shows a two day sequence (22–23 June, 1993) of propene concentrations at each level, the concentration gradient between the two levels, the concentration gradient and flux of CO<sub>2</sub>, and the propene fluxes calculated by similarity with CO<sub>2</sub> (Figure 6a–e). Propene concentrations are shown at both 24 and 29 meters. Every fifth run both samples were taken from 29 meters (NULL gradient) and are indicated with distinct symbols. The gradient data was corrected by linearly interpolating the NULL gradient and subtracting it from the measured gradient. Propene fluxes are calculated by similarity with CO<sub>2</sub>, using the equation:

$$\Phi_{\text{pro}} = \Phi_{\text{CO}_2} (\delta[\text{propene}] / \delta[\text{CO}_2]),$$

where  $\Phi_{\text{pro}}$  is propene flux,  $\Phi_{\text{CO}_2}$  is CO<sub>2</sub> flux measured by eddy correlation (Wofsy *et al.*, 1993),  $\delta[\text{propene}]$  is the propene concentration gradient and  $\delta[\text{CO}_2]$  is the CO<sub>2</sub> concentration gradient measured by a differential infrared gas analyzer (LICOR). The similarity calculation of flux assumes there are no sources or sinks of either CO<sub>2</sub> or propene between the two sample inlets (both above the canopy). Gradients indicating emission from the forest have also been observed for

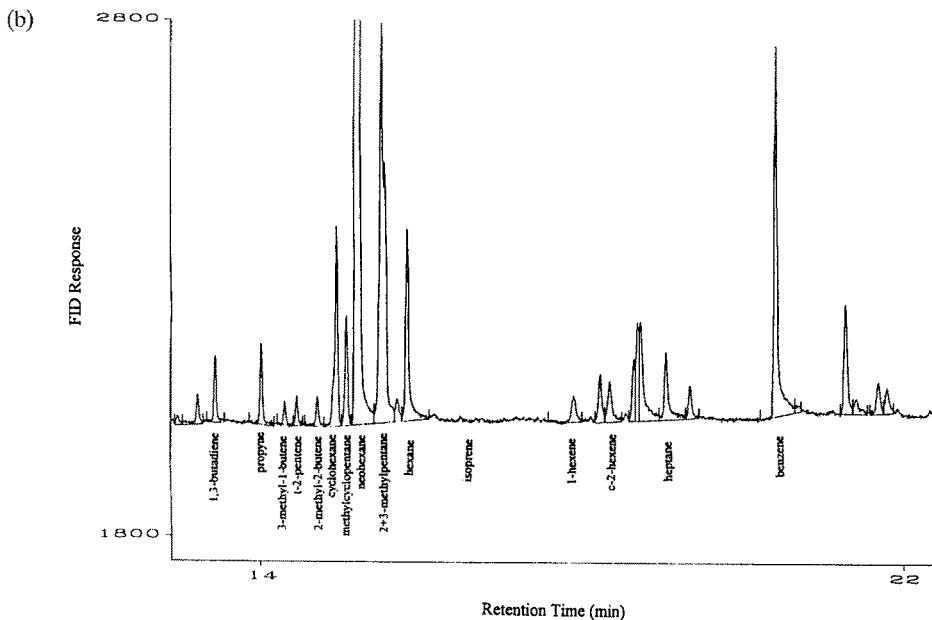
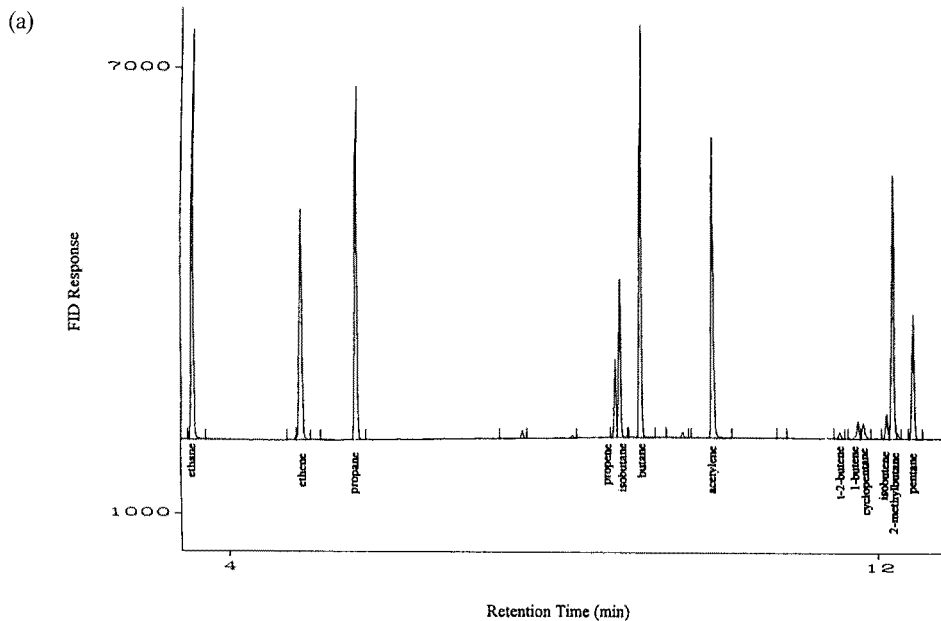


Fig. 5. Chromatogram for a 400 STP ml sample collected on 14 January 1993.

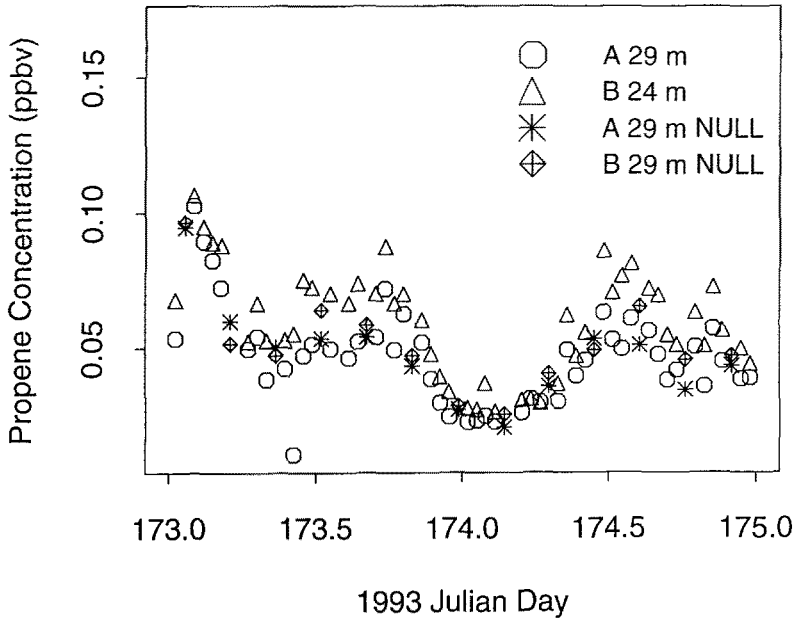


Fig. 6a.

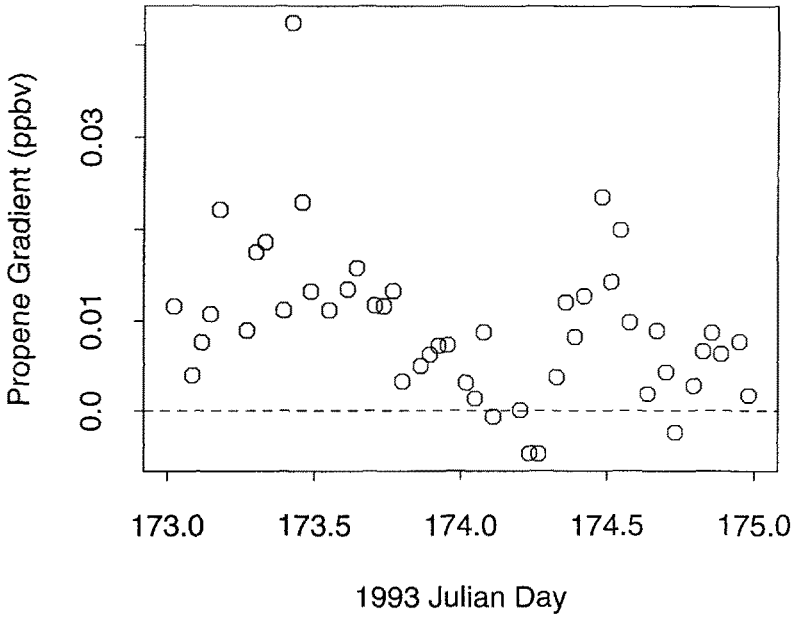


Fig. 6b.

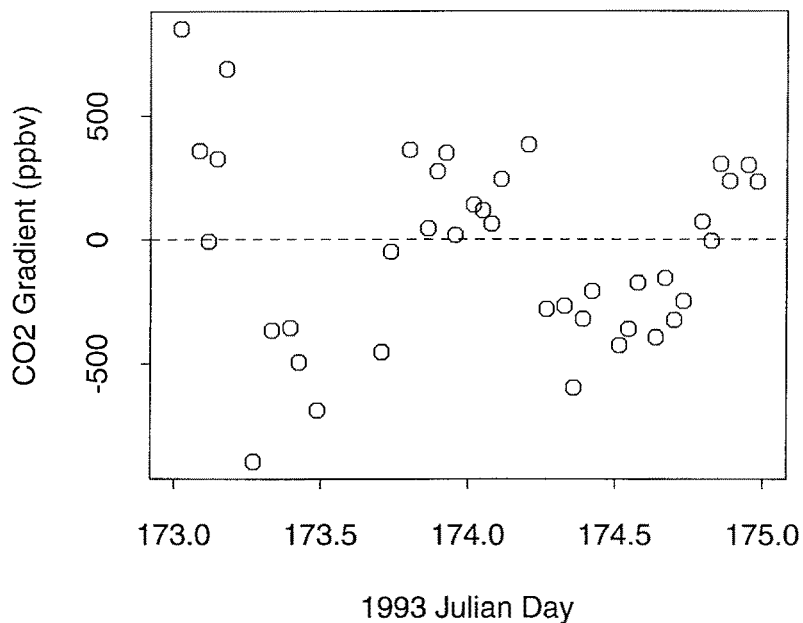


Fig. 6c.

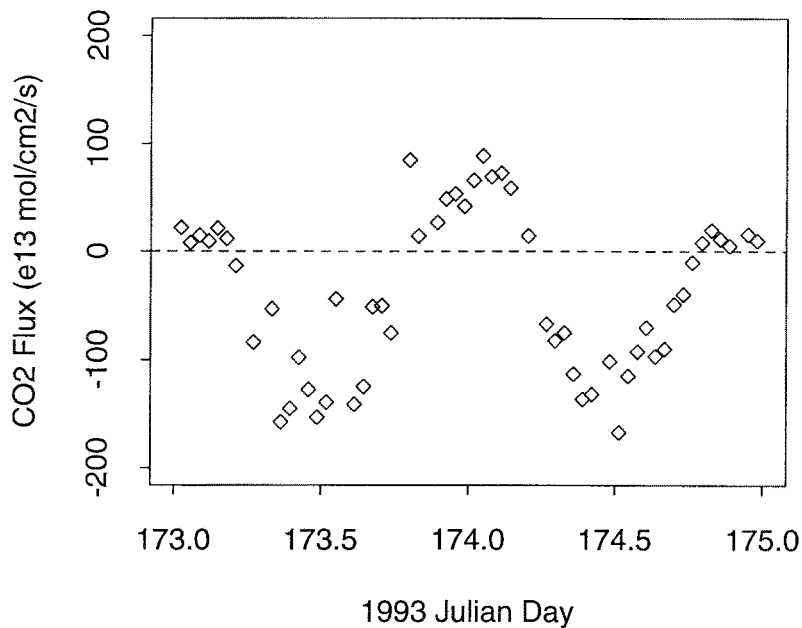


Fig. 6d.

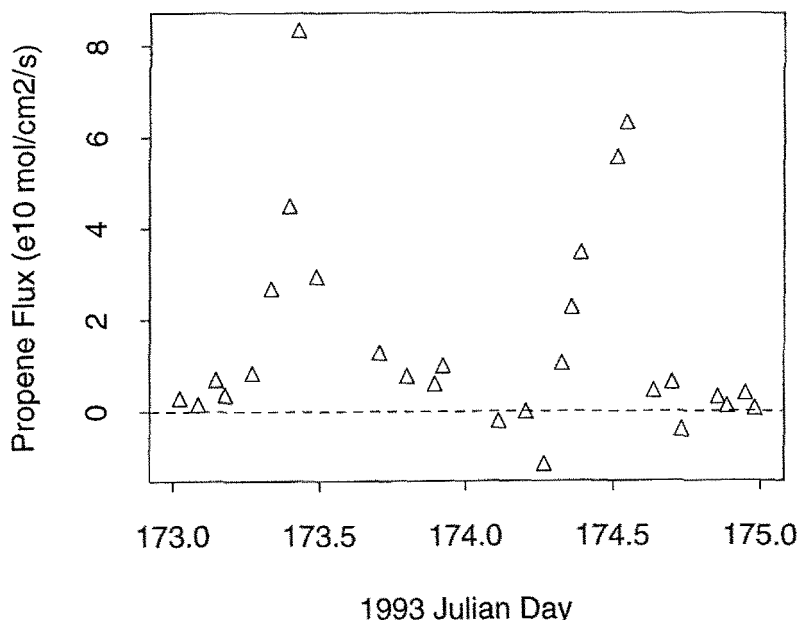


Fig. 6e.

Fig. 6. Two day sequence (22–23 June, 1993) of: (a) Propene concentrations at 29 and 24 m above the ground with the NULL gradient measured every fifth sample (shown with different symbols); (b) Propene gradient (24 m–29 m – NULL gradient); (c) CO<sub>2</sub> gradient; (d) CO<sub>2</sub> flux at 29 m; (e) Propene flux.

ethene and 1-butene, and the average emission ratio of ethene/propene/1-butene is approximately 4/2/1.

The second data set is a three day sequence (22–25 October, 1992) of ethane, propene, butane, and acetylene concentrations showing polluted and relatively clean air, as well as the transition between the two (Figure 7). Note the features during the pollution event on the morning and afternoon of Julian Day 298 where the enhancement of ethane relative to the other hydrocarbons changes dramatically indicating that there are at least two sources with different emission ratios contributing to this event.

The final data set is a one year time sequence of ethane concentrations from 1 August, 1992 to 31 July, 1993 (Figure 8). Seasonal changes in the background ethane concentrations as well as in the concentration enhancements due to anthropogenic pollution are evident. These seasonal changes, as well as the biogenic and anthropogenic NMHC emissions, will be addressed in detail elsewhere.

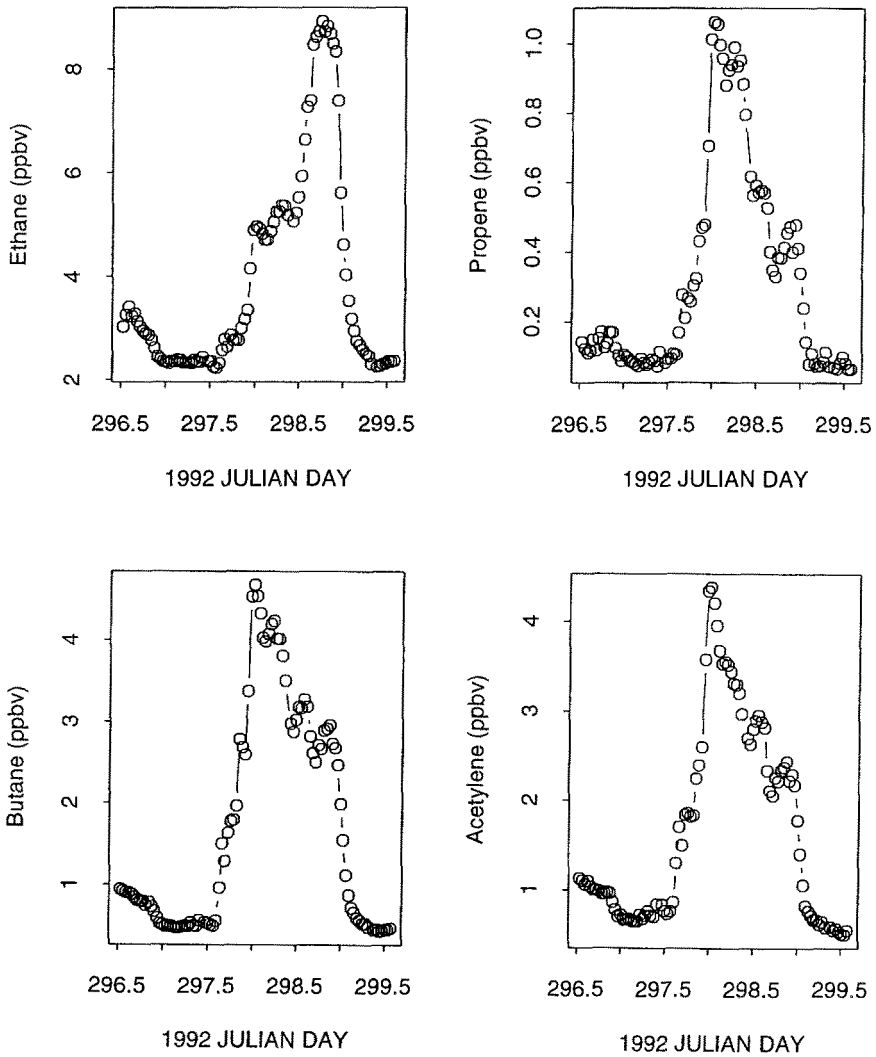


Fig. 7. Three day sequence (22–25 October, 1992) of ethane, propene, butane, and acetylene, showing both pollution events and relatively clean air.

## 11. Summary

Fully automated continuous measurements of hydrocarbon concentrations and vertical gradients have been implemented in a rural site in central Massachusetts starting in July 1992. The instrument can operate continuously for two weeks between site visits. Measurements are made at 45 min intervals. The detection limit is approximately 10 pptv. The simultaneous dual measurement capability of this instrument has facilitated an analysis of NMHC measurement precision for real air samples which can be expressed in terms of standard deviations of ambient

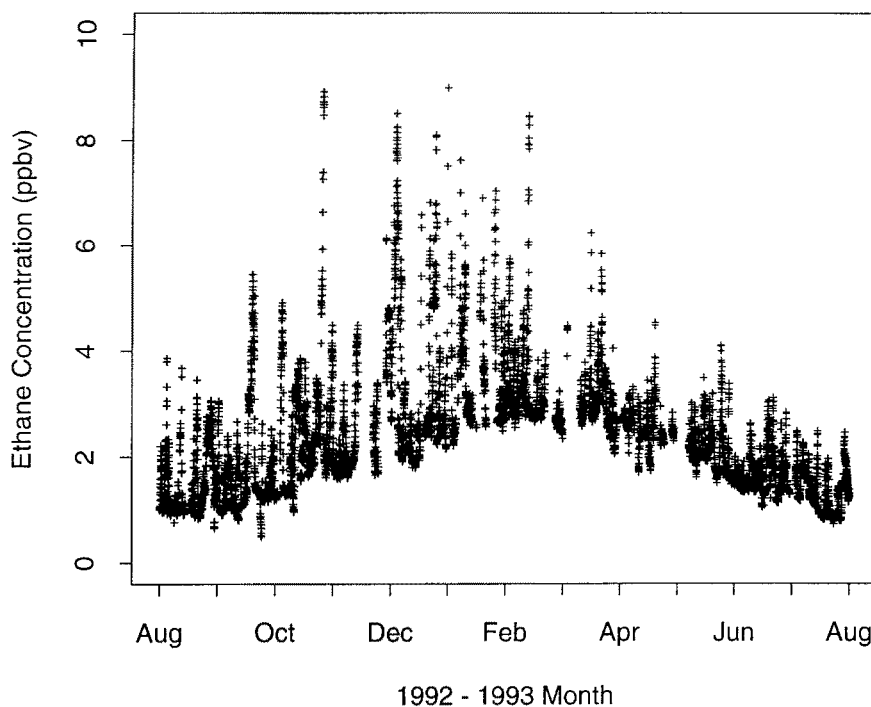


Fig. 8. Ethane concentrations measured at 45 min intervals from 1 August, 1992 to 31 July 1993. Seasonal cycles in the background concentration and in concentration enhancements due to anthropogenic pollution are evident.

concentrations: 3% at 1 ppbv, 5% at 0.5 ppbv, 10% at 0.2 ppbv, and 20% for concentrations less than 0.1 ppbv.

These NMHC measurements are part of an environmental monitoring station that includes measurements of many other trace atmospheric gas fluxes and concentrations as well as meteorological variables. The data being collected will help to improve understanding of NMHCs in terms of biogenic and anthropogenic emissions, seasonal cycles, and their effects on the chemistry of the troposphere.

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