

Measurement and interpretation of isoprene fluxes and isoprene, methacrolein, and methyl vinyl ketone mixing ratios at the PROPHET site during the 1998 Intensive

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[1] Mixing ratios of isoprene, methyl vinyl ketone (MVK), and methacrolein (MACR) were determined continuously during an 8-day period in the summer of 1998 at a rural forested site located within the University of Michigan Biological Station (UMBS). The measurements were obtained as part of the Program for Research on Oxidants: Photochemistry, Emissions, and Transport (PROPHET) study. Fluxes of isoprene were concurrently measured at a nearby tower (AmeriFlux, located 132 m north-northeast of the PROPHET tower). Following the study, 1-km-resolution emission estimates were derived for isoprene within a 60-km radius of the tower using forest density estimates (Biogenic Emissions Inventory System (BEIS3) model). Measured isoprene fluxes at the site compared well with modeled isoprene fluxes when using BEIS3 and a detailed leaf litter-fall data set by tree species from the UMBS site. Mean midday (1000–1400 LT) mixing ratios for isoprene, MACR, and MVK were 1.90 ± 0.43 , 0.07 ± 0.01 , and 0.14 ± 0.04 ppbv, respectively. Median midday mixing ratios of these compounds were 1.96 ± 0.26 , 0.06 ± 0.02 , and 0.10 ± 0.02 ppbv, respectively. Ratios of the isoprene oxidation products to isoprene are understood in the context of previous laboratory and field measurement studies of these compounds and a simple consecutive reaction scheme model. Results of the model indicate that the air masses studied represented relatively fresh emissions with a photochemical age of measured isoprene between 3.6 and 18 min, which is significantly less than the photochemical lifetime of isoprene ($\tau = 45$ min at $[\text{OH}] = 3.35 \times 10^6$ molecules cm^{-3}). Thus a large portion of the isoprene that reaches the manifold has not had time to react completely with OH, yielding lower than expected ratios based on model calculations that do not explicitly take this into account. A rapid decrease in isoprene mixing ratios was observed soon after sunset, followed by a slower decay throughout the rest of the night. Emission maps were generated indicating that isoprene fluxes are highest in the immediate vicinity of the tower compared to the surrounding area of the site. Thus vertical diffusion and advection from the surrounding region are postulated to cause the observed initial rapid decrease in isoprene at the site. The second isoprene decay may be due to chemistry and/or dynamics, but the effects cannot be separated with the available data. **INDEX TERMS:** 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0394 Atmospheric Composition and Structure: Instruments and techniques; **KEYWORDS:** isoprene, photochemistry, emissions, transport, methacrolein, methyl vinyl ketone

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1. Introduction

[2] The primary objectives of the Program for Research on Oxidants: Photochemistry, Emissions and Transport (PROPHET) have been discussed by Carroll *et al.* [2001]. The PROPHET site is located within the University of Michigan Biological Station (UMBS) in a relatively remote, highly forested region near the northern tip of the lower peninsula of Michigan. Although occasionally strongly impacted by anthropogenic emissions, it has been shown that biogenic compounds play an important role in the atmospheric volatile organic compound (VOC) chemistry at the site [Carroll *et al.*, 2001; Hurst *et al.*, 2001; Sumner *et al.*, 2001]. The most prevalent biogenically emitted VOC was isoprene. Mixing ratios for isoprene and its oxidation products, methacrolein (MACR) and methyl vinyl ketone (MVK), were measured each half hour for 8 days. Flux measurements of isoprene were made at the AmeriFlux tower, which was located 132 m north-northeast of the PROPHET tower.

Table 1. Rate Constants for Isoprene, MVK, and MACR^a

Compound	$k_{O_3}^b$	k_{OH}^b	k_{NO_3}	k_{Cl}^c
Isoprene	1.28E-17	1.10E-10	6.16E-12 ^b	4.0E-10
MVK	4.56E-18	1.88E-11	<6E-16 ^d	2.2E-10
MACR	1.14E-18	3.35E-11	3.30E-15 ^d	2.4E-10

^a Units are $\text{cm}^3 \text{molecules}^{-1} \text{sec}^{-1}$.

^b Values are taken from *Carter and Atkinson* [1996].

^c Values are taken from J. Orlando et al., Rate coefficients and mechanisms of the reaction of Cl-atoms with a series of unsaturated hydrocarbons under atmospheric conditions, manuscript in preparation, 2001.

^d Values are taken from *Finlayson-Pitts and Pitts* [2000, and references therein].

[3] On a global scale the emission rate of isoprene is estimated to be 503 Tg yr^{-1} [*Guenther et al.*, 1995], easily dwarfing any other VOC. Isoprene is highly reactive toward the hydroxyl (OH) radical, ozone (O_3), the nitrate radical (NO_3), and chlorine atoms (Cl) (Table 1). Studies continue on the contribution of isoprene toward oxidant cycles and the formation of O_3 . It has been established that there is a nonlinear relationship between ozone formation and its two primary precursors, nitrogen oxides (nitric oxide (NO) and nitrogen dioxide (NO_2)) and VOCs. Two different states relevant to O_3 formation in the troposphere have been identified. Under conditions in which there is a large abundance of VOCs relative to NO_x the state is referred to as NO_x limited. In this state, O_3 formation increases with increasing NO_x and is relatively independent of changes in VOC concentration. The other state exists when there is an abundance of NO_x and is called VOC limited. In this case, O_3 formation decreases with increasing NO_x but increases with increasing VOCs. As isoprene is processed (oxidized) in the troposphere, it has the potential of playing an important role in tropospheric ozone formation. In more remote forested regions of central and eastern North America where the availability of NO_x is limited, ozone formation is limited despite the abundance of biogenic VOCs such as isoprene. However, in rural, urban, or suburban areas that are impacted by anthropogenic emissions of NO_x , isoprene has a potentially very large impact in forming ozone [*Chameides et al.*, 1997; *Starn et al.*, 1998; *Stroud et al.*, 2001]. In order to more fully understand the role that isoprene plays, it is important to understand the isoprene oxidation cycle not only in a laboratory context but also in a real-world context: specifically, processes that lead to the availability of peroxy radicals which participate directly in the conversion of NO to NO_2 and thus in ozone formation. The PROPHET site represents a relatively remote forested environment and may normally be considered NO_x limited, but it can be impacted on occasion by air masses originating in the industrialized corridors of the midwestern United States.

[4] There have been a number of laboratory studies designed to examine the isoprene oxidation cycle. *Carter and Atkinson* [1996], for example, studied the OH-isoprene reaction in a reaction chamber under NO_x -rich conditions. *Myoshi et al.* [1994] studied this reaction both in the presence and in the absence of NO_x . The reaction was followed in time, and a number of primary, secondary, and so on, reaction products were observed. The major primary reaction products observed in these studies are MVK, MACR, and formaldehyde. However, except for the *Myoshi et al.* [1994] study with no NO_x , these experiments were conducted with relatively high initial mixing ratios of isoprene and NO_x . A number of field studies have also been conducted during the past decade to study the processing of isoprene in rural [e.g., *Pierotti et al.*, 1990; *Martin et al.*, 1991; *Montzka et al.*, 1993, 1995; *Goldan et al.*, 1995; *Biesenthal et al.*, 1997, 1998; *Helmig et al.*, 1998; *Makar et al.*, 1999] and urban or near-urban environments [e.g., *Stroud et al.*, 2001; *Riemer et al.*, 1994, 1998; *Starn et al.*, 1998; *Nouaime et al.*, 1998]. Comparisons with expected results based on laboratory studies have been made [e.g., *Montzka et al.*, 1993; *Stroud et*

al., 2001]. The combination of laboratory and field work forms a critical component in the development of an understanding of the isoprene oxidation mechanism with the underlying goal of its accurate representation in computer models and hence an understanding of its relevance to ozone formation. These investigations are particularly relevant to the issue of air pollution control strategies as rural areas become more populated. In particular, these studies help to determine the conditions under which it is useful to control VOCs (e.g., VOC limited environments) and the conditions under which this will have little effect.

[5] The chemical processing of isoprene occurs both during the day and at night. During the day, because of the high value for k_{OH} , $ISOP[OH]$ (Table 1), OH is responsible for the majority of the chemical processing of isoprene. At night, under typical conditions, O_3 processing becomes relatively more important as OH is reduced to low levels. If sufficient NO_2 and O_3 are present, NO_3 may play a significant role in isoprene oxidation [*Starn et al.*, 1998]. Chlorine is expected to play a significant role only in the daytime in locations with a significant source of molecular chlorine [*Finlayson-Pitts and Pitts*, 2000].

[6] We measured isoprene, MACR, and MVK from 5 August through 13 August as part of the 1998 PROPHET Intensive at the UMBS site in northern Michigan. Unique to this study was that a full suite of chemical [*Tan et al.*, 2001; *Carroll et al.*, 2001] and meteorological [*Carroll et al.*, 2001] measurements were recorded, and isoprene fluxes were measured concurrently at a nearby tower [*Westberg et al.*, 2001]. (The reader is referred to *Cooper et al.* [2001] for an overview of the meteorological and transport conditions that prevailed during the experiment.) Additionally, 1-km-resolution emission estimates for isoprene were made for a radius extending 60 km from the tower. The chemical measurements included OH and hydroperoxyl (HO_2) [*Tan et al.*, 2001], allowing an opportunity to study isoprene photochemistry in a relatively well characterized environment.

[7] A surprising observation was that the typical observed nighttime OH radical concentrations were higher than predicted from two independent photochemical models [*Tan et al.*, 2001; *Sillman et al.*, 2002]. Coincident with this observation was the rapid decrease in isoprene soon after sunset. These results are discussed in detail by *Faloona et al.* [2001], *Sillman et al.* [2002], and *Hurst et al.* [2001]. We recorded diurnal measurements of isoprene and its oxidation products simultaneously every 30 min. The measurements are interpreted in the context of their oxidation by OH, O_3 , and NO_3 and in the context of the prevailing meteorology. We investigated whether these measurements and their ratios offer insight into the oxidation mechanisms operative at the site during this study.

2. Experiment

[8] All measurements, except for isoprene flux, were recorded at the PROPHET tower, which is located at 45.55873°N , 84.71455°W within the UMBS property. The isoprene flux measurements were recorded at the AmeriFlux tower, which is located 132 m north-northeast of the PROPHET tower but is also within the UMBS property. UMBS comprises 9000 acres of mixed forest with the major tree species represented by red maple, sugar maple, paper birch, beech, white pine, bigtooth aspen, quaking aspen, and red oak. The dominant isoprene source at this site is *Populus tremuloides* (quaking aspen). The average canopy height at the site was ~ 20 m. The local vegetation was homogeneous around both towers. Air was drawn into the PROPHET laboratory through an inlet positioned ~ 12 m above the forest canopy via a 5-cm-diameter Pyrex glass manifold. A 160 sL s^{-1} blower was attached to the end of the manifold, yielding a residence time in the manifold of 1–2 s. The fast isoprene sensor (FIS) [*Guenther and Hills*, 1998; *Westberg et al.*, 2001], used to record isoprene fluxes, sampled at a height of 31 m through a 1.3-cm polyvinyl chloride

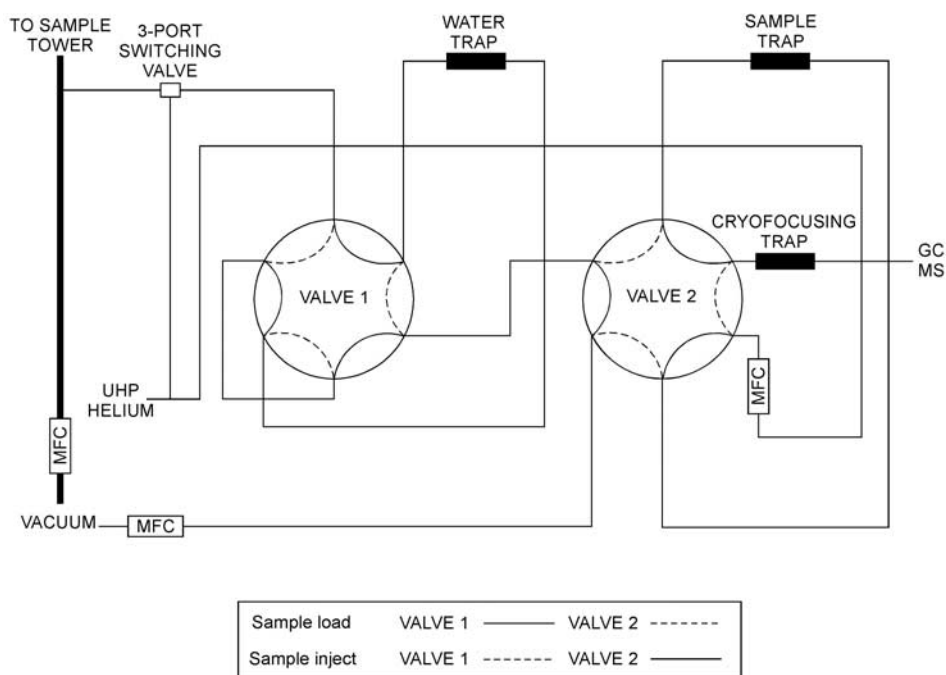


Figure 1. Schematic diagram of sampling system used to measure isoprene, MACR, and MVK. Samples were collected each half hour.

(PVC) pipe, with a sample line residence time of 4 s. *Carroll et al.* [2001] give a full description of the site and the suite of analytical measurements taken during the 1998 study.

[9] A fully automated gas chromatography/mass spectroscopy (GC/MS) instrument was used during the study to measure mixing ratios of isoprene, MVK, and MACR. The system consisted of a custom-built three-stage trap preconcentration device and an HP 5890 Series II GC/HP 5973 MS system. The cooling medium for the traps was provided by passing dry nitrogen gas through copper coils immersed in a Dewar of liquid N₂. The cooled N₂ gas was then passed through a heat exchanger containing the traps to effect cooling. The desired temperature was maintained by controlling the flow of N₂ gas through the heat exchanger.

[10] Ambient air was drawn from a port on the high-velocity glass manifold and into the preconcentration system (Figure 1). The sampling rate was held at 50 cm³ min⁻¹ for 6 min, yielding a total air sample of 300 cm³. The sample was passed through the first-stage trap, a 12 × 0.3175 cm perfluoroalkoxy (PFA) Teflon tube maintained at -20°C to remove water from the sample. It was then passed into the second stage, which consisted of a 12 × 0.3175 cm outside diameter Silcosteel[®] tube filled with silanized glass wool and maintained near -130°C. Here, the compounds of interest were initially trapped. A valve was switched, the trap was heated to 150°C, and helium carrier gas swept the compounds of interest to the third cryofocusing trap, which was a 10-cm piece of megabore (0.53 mm inside diameter) tubing maintained at -186°C. The cryofocuser was then rapidly heated to 120°C, transferring the compounds of interest to the head of a 60-m, 0.25-mm inside diameter, HP-624 column. The GC oven was held initially at 35°C for 2 min, temperature programmed at a rate of 25°C min⁻¹ until the oven reached 190°C, and then held at 190°C for 11 min, giving a total chromatographic run time of 20 min. Carrier gas flow rate was maintained at 6 mL min⁻¹ using the electronic pressure control feature of the HP GC. Although we report only isoprene, MVK, and MACR here, 41 compounds, from acetaldehyde through the terpenes, were separated and detected twice each hour. Laboratory tests conducted before the experiment

indicated that there were no transfer losses of MVK, MACR, or isoprene throughout a relative humidity range of 5–95%.

[11] The specificity is excellent with this type of analysis because compounds are separated chromatographically and the ions detected are specific to the compound whose retention time is known. Single-ion monitoring MS was utilized for quantitation, giving excellent sensitivity. For isoprene, mass to charge ratio $m/z = 67$ was used. For MVK and MACR, $m/z = 70$ was used giving, for all compounds, a limit of detection of <5 pptv.

[12] The GC/MS system was calibrated daily with the National Center for Atmospheric Research (NCAR) standards and with a dynamic dilution system. Standards were prepared gravimetrically in passivated aluminum cylinders (Luxfer) by established techniques [*Apel et al.*, 1998, 2001]. Standards were prepared in a range of 100 ppbv to 1 ppmv and were dynamically diluted with clean zero air to low pptv to ppbv levels. The standards were referenced to National Institute of Standards and Technology (NIST) standards for isoprene and propane Standard Reference Material 1601 by GC/flame ionization detector using previously determined relative sensitivities. Purdue University also measured isoprene, MVK, and MACR during the study. The isoprene standard used by the Purdue University group was cross-calibrated with the NCAR standard during the study, and agreement to within 5% was found [*Barket et al.*, 2001]. *Barket et al.* [2001] report on an intercomparison of isoprene measurements taken at the site during this study; satisfactory agreement was found between all measurements groups. MVK and MACR standards were calibrated against NIST butane/benzene standards using the effective carbon number response determined by *Apel et al.* [1998]. The standards were found to be stable over the course of the experiment.

[13] The FIS-99 (information available at www.hills-scientific.com) was deployed jointly by Washington State University and NCAR. The FIS has been used to monitor real-time isoprene concentrations in both cuvette [*Monson et al.*, 1991, 1992] and boundary layer flux studies [*Guenther and Hills*, 1998; *Bowling et al.*, 1998; *Westberg et al.*, 2001]. Direct fluxes are obtained with the FIS using the eddy covariance technique, utilizing a cross

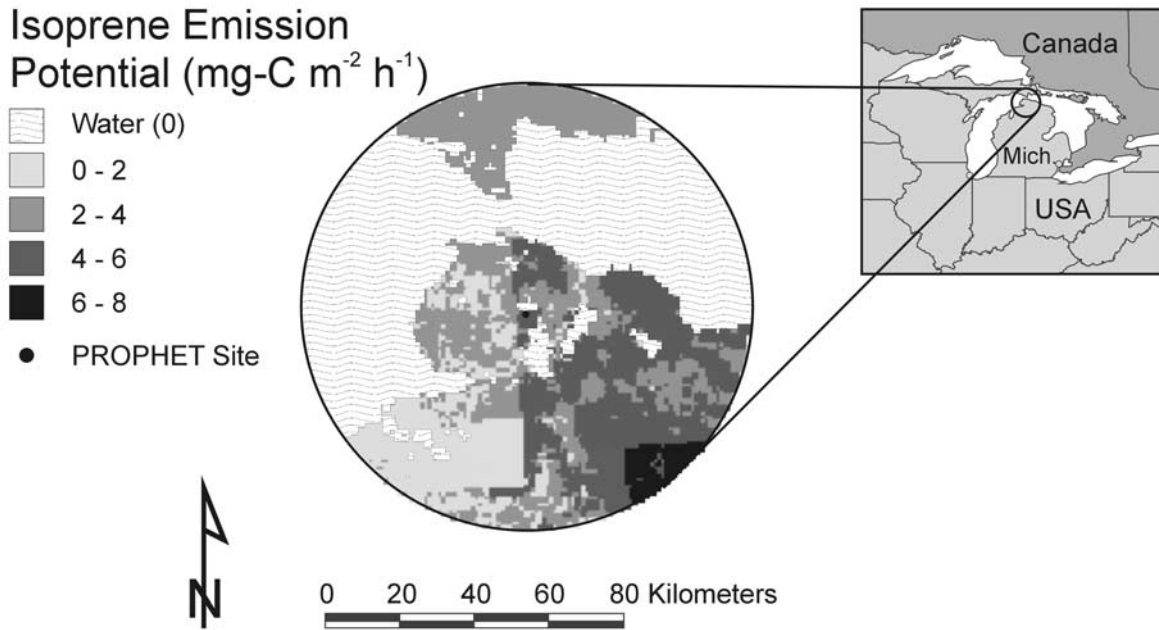


Figure 2. Isoprene emissions map with 1-km resolution, based on BEIS3 of the area within a 60-km radius of the site. The PROPHET site is in the center of the map.

correlation between the vertical wind speed fluctuations, measured using a sonic anemometer, and isoprene mixing ratio fluctuations measured by the FIS [Dabberdt *et al.*, 1993; Guenther and Hills, 1998; Westberg *et al.*, 2001]. Descriptions of the instrument as it

was deployed in this study are given by Barkert *et al.* [2001] and Westberg *et al.* [2001].

[14] During PROPHET 1998 the FIS was in ambient measurement mode 23 hours each day and in calibration mode for 1 hour per

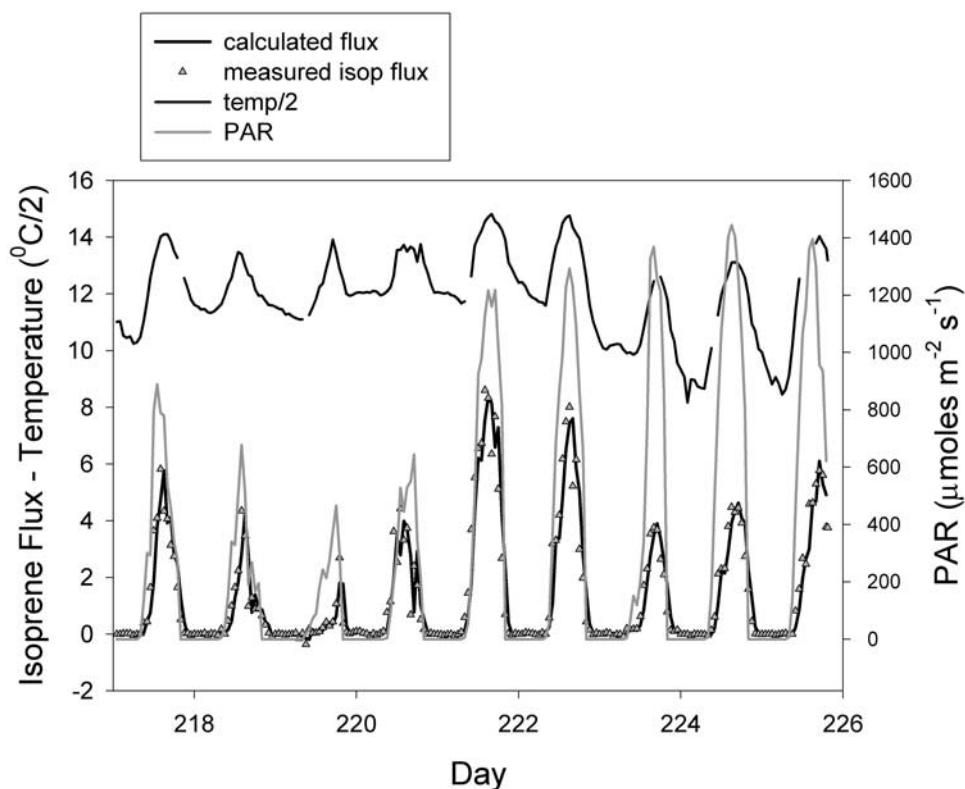


Figure 3. Measured flux (FIS) versus calculated flux based on known isoprene emitting species at the site. PAR and temperature are also shown. Units for isoprene flux are $\text{mg C m}^{-2} \text{h}^{-1}$.

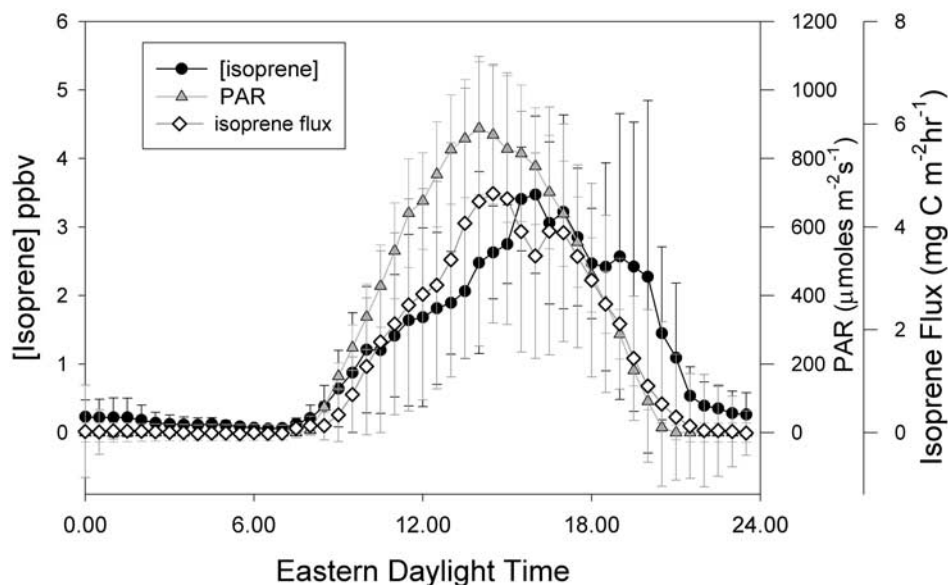


Figure 4. Average measured isoprene mixing ratios during the study. Isoprene flux and PAR are also shown. Error bars represent the spread in measurements in terms of standard deviation.

day. In calibration mode, inlet air is directed through a platinum catalytic converter maintained at 380°C which removes >99.9% of ambient isoprene [Guenther and Hills, 1998]. Instrument zero is recorded for 10 min followed by a series of dynamically generated isoprene standards. The standards (0–30 ppbv) were generated using a built-in dynamic dilution system that adds a mass-flow controlled stream of an isoprene standard (6-ppm nominal isoprene in ultra-high-purity N₂, ±3% primary analysis, Scott-Marrin Corp.) to the sample flow. The isoprene standard was periodically calibrated against NIST propane, Standard Reference Material 1601.

3. Results

3.1. Isoprene Emission Model

[15] The methods discussed by Guenther *et al.* [2000] were applied to estimate biogenic fluxes of isoprene along with 31 other VOCs and carbon monoxide (CO). These methods form the basis for the BEIS3 model [Guenther *et al.*, 2000]. The growing season peak forest canopy coverage is derived from the 1-km forest density estimates of Zhu and Evans [1994] for the area within a 60-km radius of the PROPHET flux tower. The forest cover is apportioned into species-level foliage quantities as a function of basal area, which is calculated from the plot-level forest inventory data for this area using methods described by Geron *et al.* [1994]. Isoprene emission rates, standardized for photosynthetically active radiation (PAR) values of 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ and leaf temperatures of 30°C, are assumed to be 70 $\mu\text{g-C (g-foliar dry mass)}^{-1} \text{h}^{-1}$ for *Quercus* and *Populus* (oak and aspen), 14 $\mu\text{g-C g}^{-1} \text{h}^{-1}$ for *Picea* (spruce), and 0.1 $\mu\text{g-C g}^{-1} \text{h}^{-1}$ for the other genera found at the site [Guenther *et al.*, 1994].

[16] The empirical algorithms of Guenther *et al.*, [1994] were used to adjust emission rates to ambient PAR and temperature conditions. The PAR correction factor changes vertically through the canopy in the manner illustrated by Guenther *et al.*, 2000, [Figure 1]. Direct beam and diffuse fractions of measured total above-canopy PAR and sunlit/shaded fractions of leaf area were estimated using the techniques described by Guenther *et al.* [1995]. Exponential decay algorithms were applied to reduce diffuse PAR and specific leaf weight at lower levels within forest canopies [Geron *et al.*, 1994]. The seasonal peak leaf area index estimate of

3.5 $\text{m}^2 \text{m}^{-2}$ measured at the UMBS site was used in the model simulations since the study was performed during the period of maximum leaf area development.

[17] The dominant isoprene source at this site is *Populus tremuloides* (quaking aspen). Leaves of this species exhibit a high degree of leaf flutter, even under conditions of low wind speed. Stomatal conductance and transpiration from this species are also quite high in comparison to other species such as oak or maple. For these reasons we assumed that leaf temperatures are closely coupled to ambient air temperature. We further altered the model to incorporate the use of heating degree day estimates [Monson *et al.*, 1994; Geron *et al.*, 2000] to simulate the initiation and increase in springtime isoprene emission and use of nighttime temperature to initiate late summer decline. The leaf age activity factors, ratio of current to peak foliar density, and escape efficiency factors described by Guenther *et al.* [2000] were incorporated here. These factors have minimal effect on net estimated flux ($\sim -5\%$) since the study period corresponds to the time of peak active leaf area for forests in this region.

[18] An emission map was generated from the data within a 60-km radius of the PROPHET site (Figure 2). The PROPHET tower, indicated by a dot in the middle of Figure 2, is located in a very high emission source area. Emission estimates at the site can be compared to isoprene fluxes measured at the site with the FIS. Figure 3 shows the comparison between actual measured flux and emissions estimated from BEIS3 using local biomass density and leaf area estimates by species determined from 1998 litter-fall data collected within a 60-m radius of the AmeriFlux tower where the FIS fluxes were measured. PAR and above-canopy temperature are given as well. The model estimates are in excellent agreement with measured fluxes. The model replication of the observed diurnal isoprene emission pattern demonstrates satisfactory performance of the Guenther *et al.* [1994] algorithms in simulating light and temperature effects. The agreement in peak daytime fluxes indicates that the basal emission factors and canopy environment adjustments are also representative of this site. These local isoprene emission fluxes and model estimates are higher than the estimates based on the land use composition of the surrounding area, indicating that the local forest is a strong source of isoprene, at least twice that of the immediate surrounding area. This is verified by the Forest Inventory and Analysis plot-level forest composition

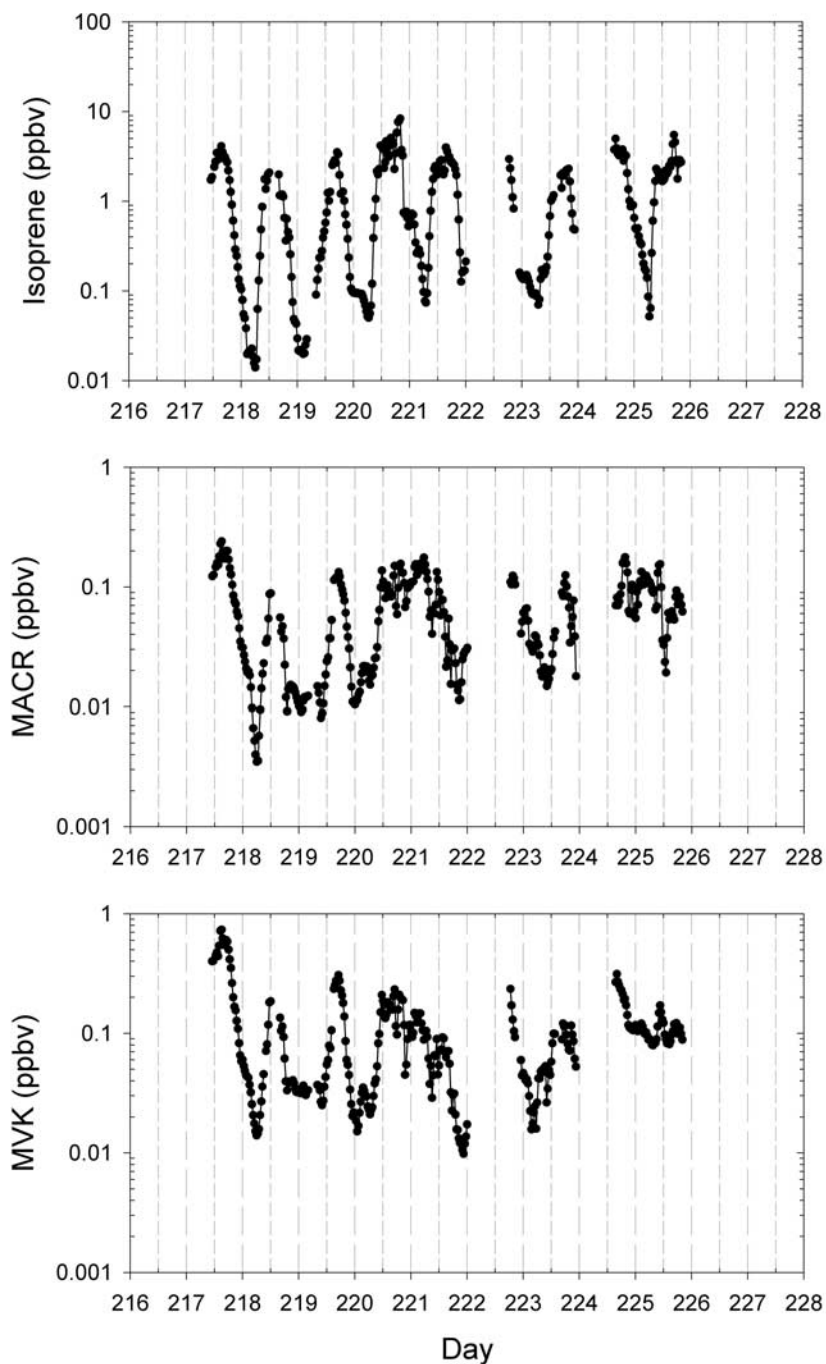


Figure 5. Time series plots for (top) isoprene, (middle) MACR, and (bottom) MVK.

that is estimated for this region. The most recent information may be found at <http://www.fs.fed.us/ne/fia/>.

3.2. Mixing Ratios of Isoprene and Its Oxidation Products

[19] Figure 4 shows the averaged diurnal profile for isoprene along with the measured PAR. Also shown is the isoprene flux measurement taken at the AmeriFlux tower. As a consequence of the two major factors controlling isoprene emission (i.e., PAR and temperature) and the fact that the sampling inlet was located close to the canopy top, isoprene concentrations rose steadily during the daytime until a maximum concentration was reached. This is in line with a number of previous studies that indicate that isoprene

was being produced more rapidly than it was being destroyed from the time it was emitted until the time it was detected. This is despite the fact that isoprene reacts very rapidly with the OH radical (Table 1), which implies a relatively short time between emission and detection. Isoprene concentrations fell rapidly at night during this study [Hurst *et al.*, 2001], and on several nights it attained very low concentrations (20 pptv). The change in isoprene concentration at night may be attributable to a number of different factors: cessation of isoprene production, nighttime oxidant chemistry, changing boundary layer height, deposition [Cleveland and Yavitt, 1997], and advection of air masses low in isoprene concentrations. This behavior is the subject of papers by Hurst *et al.* [2001], Faloon *et al.* [2001], and Sillman *et al.* [2002]. Hurst *et al.* [2001]

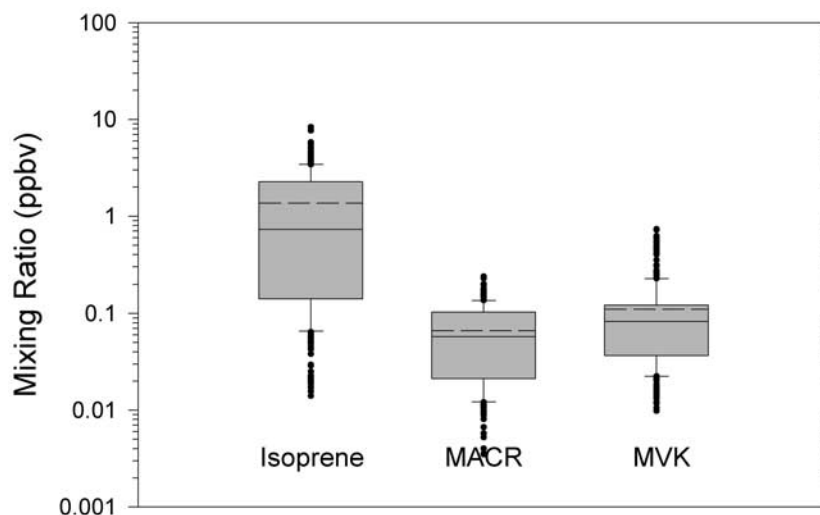


Figure 6. Box and whisker plot of isoprene, MACR, and MVK.

and Faloona *et al.* [2001] ascribe the behavior largely to nighttime oxidant chemistry, while Sillman *et al.* [2002] ascribe it largely to meteorological processes. This behavior will be addressed further in section 4.

[20] The relationship between isoprene and its oxidation products has been discussed in several papers [e.g., Martin *et al.*, 1991; Montzka *et al.*, 1993, 1995; Goldan *et al.*, 1995; Biesenthal *et al.*, 1998; Stroud *et al.*, 2001]. According to laboratory measurements [Carter and Atkinson, 1996], formaldehyde, MVK, and MACR are primary first-generation reaction products from isoprene oxidation by OH and O₃. MVK is the favored product of the OH reaction (1.4/1), whereas MACR is the favored product of the O₃ reaction (2.4/1). MVK and MACR also react with OH and O₃ (Table 1). During the day, isoprene is thought to be chemically removed primarily by OH. At night, isoprene is thought to be chemically removed primarily by O₃ and NO₃, if present. Isoprene reaction with NO₃ produces little MACR and MVK [Kwok *et al.*, 1996]. If isoprene is the predominant source of MVK and MACR, as it should be in this rural environment, a relationship is expected between mixing ratios of isoprene and these species as well as between the species themselves.

[21] Figure 5 shows time series plots for isoprene, MACR, and MVK measurements obtained during the study. Discontinuities in the plots indicate that no data were available for those time periods. Figure 6 shows a box and whisker plot of these data. The median value is represented by a solid line, and the mean is represented by a dashed line. The edges of the box are the 25th and 75th percentiles, and the edges of the whisker line represent the 10th and 90th percentiles. Over the entire 8-day study, median mixing ratios (day and night) for isoprene, MACR, and MVK were 0.73, 0.06, and 0.08 ppbv, respectively. Mean mixing ratios (day and night) were 1.36, 0.07, and 0.11 ppbv, respectively. Mean midday mixing ratios (1000–1400 LT) for isoprene, MACR, and MVK were 1.90 ± 0.43 , 0.07 ± 0.01 , and 0.14 ± 0.04 ppbv, respectively. Median midday ratios of these compounds were 1.96 ± 0.26 , 0.060 ± 0.02 , and 0.10 ± 0.02 ppbv, respectively.

[22] Figure 7 shows the averaged diurnal profiles of MACR and MVK. On average, MVK is higher in the daytime than at night, whereas MACR is only slightly higher in the daytime. Both species show a decrease during the night to low pptv levels. This is consistent with rural canopy studies of Montzka *et al.* [1993] and Biesenthal *et al.* [1998] and is in contrast with a recent study conducted in an urban-area clearing [Stroud *et al.*, 2001]. The fact that MVK mixing ratios are higher than MACR mixing ratios during the daytime reflects the higher yield of MVK from OH-driven isoprene chemistry and the higher reaction rate of MACR

with OH. During the daytime the boundary layer mixing heights increase, and at night the mixing height decreases. Thus MVK and MACR should be diluted into a relatively larger volume during the day and concentrated into a smaller volume during the night. Unlike isoprene, which is produced within the forest and enters the mixed layer at the bottom, MVK and MACR are produced in a larger volume of the mixed layer. MVK and MACR have significantly longer lifetimes than isoprene and, as a result, are influenced by isoprene emissions over a broader area. In canopy studies such as this, where the sampling inlet is located very close to the isoprene emitters, the importance of the boundary layer height is limited in the daytime.

[23] Chemical processing of these species is expected to be very limited at night because of the low rate constants with O₃ (Table 1). Therefore it might be expected that when the nocturnal boundary layer is formed, mixing ratios of MVK and MACR would rise and, from a purely chemical viewpoint, would remain at high levels during the night. Although this is what was observed in the Stroud *et al.* [2001] study, this is not what is observed here or in the rural canopy studies of Montzka *et al.* [1995] and Biesenthal *et al.* [1998]. A one-dimensional (1-D) Lagrangian model for atmospheric transport and photochemistry was developed by Sillman *et al.* [2002] to interpret measurements made at the site. Although the model overpredicts measured MACR and MVK, it does predict that there can be a significant influence from transport on MACR and MVK when depleted air impacts the site from the west (Lake Michigan). This would lead to lower values of both MVK and MACR at night. It is likely that a combination of transport, vertical diffusion, and, to a lesser extent, nighttime deposition and chemistry plays an important role in the diurnal behavior of these compounds.

[24] Figure 8 shows the averaged diurnal profiles of (MVK + MACR)/isoprene. The average ratio of (MVK + MACR)/isoprene for this study was 0.4, although throughout the daylight hours the ratio is 0.12 (with a ninetieth percentile value of 0.25 and a tenth percentile value of 0.05) and climbs to nearly 2.0 during the night. The nighttime ratio is consistent with previous studies. The daytime ratio is lower than previous studies and lower than would be predicted by the Sillman *et al.* [2002] model. This will be addressed in more detail in section 4. This ratio is dependent upon atmospheric mixing, distance from isoprene emitters, and the prevailing oxidant chemistry, including the concentration of NO_x [Myoshi *et al.*, 1994; Yokouchi, 1994; Biesenthal *et al.*, 1998]. Following the initial attack of isoprene by the OH radical, peroxy radicals are formed. Different pathways may be followed by the isoprene peroxy radicals based upon the relative availability of NO compared to peroxy radicals. Under low-NO conditions, the

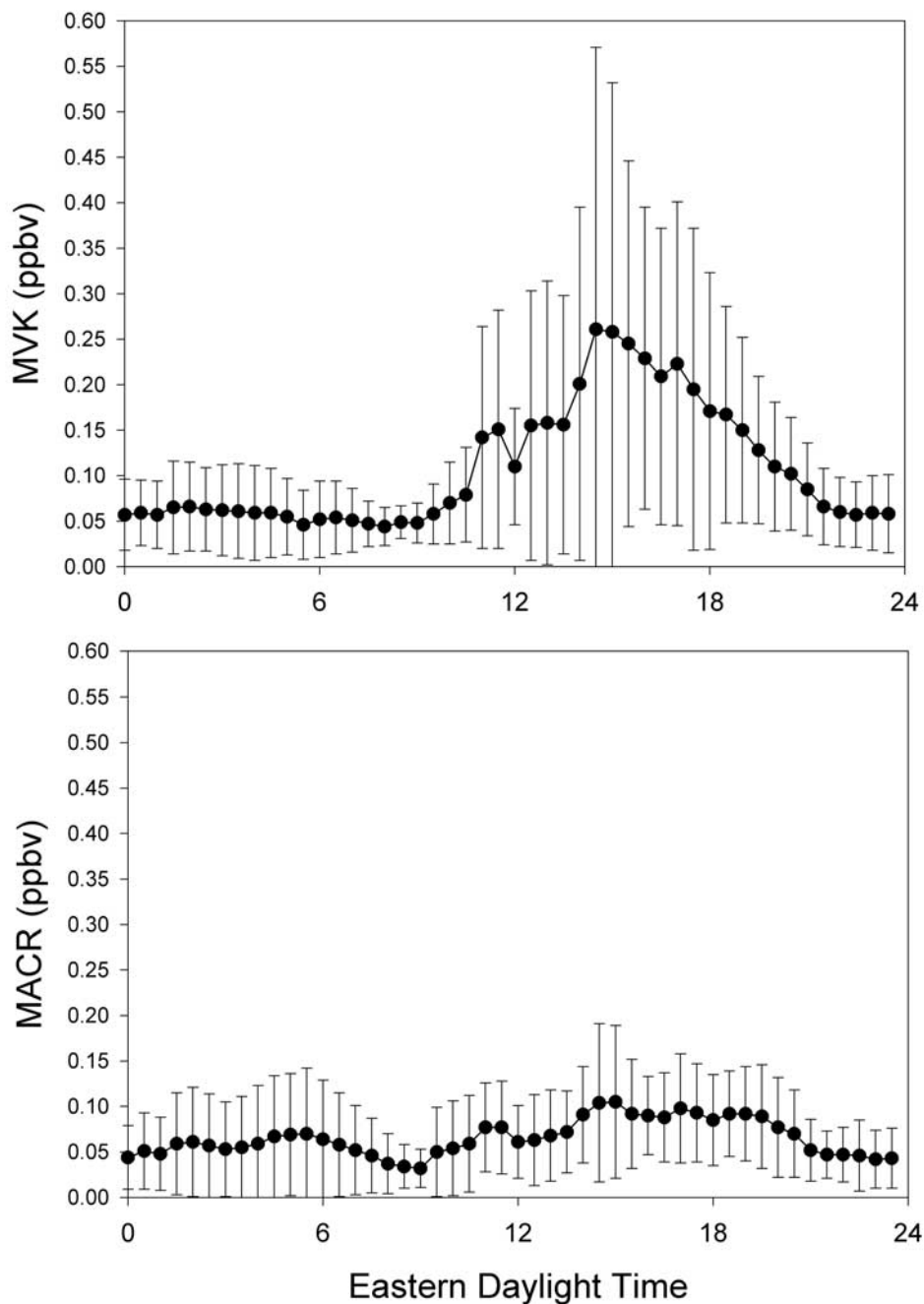


Figure 7. Average diurnal profiles of (top) MVK and (bottom) MACR during the study.

isoprene-peroxy radicals have an increased probability of reacting with other peroxy radicals, leading to lower yields of MVK and MACR and altered ratios of these products [Myoshi *et al.*, 1994; Biesenthal *et al.*, 1998]. Figure 9 shows the average NO and NO_x levels at the site during the period of this study [Thornberry *et al.*, 2001]. On the basis of the PROPHET data presented and modeled by Tan *et al.* [2001] the isoprene peroxy radicals have roughly an equal probability of reacting with HO₂ as they do with NO; this probability is a contributing factor to the low ratios of (MACR + MVK). Despite this, the measurements reported here are lower than expected based on previous results, especially relative to NO_x [Biesenthal *et al.*, 1998]. However, there have been few previous studies in which the manifold inlet was situated directly above vegetation consisting mostly of isoprene emitters. The Montzka *et al.* [1993, 1995] studies were done above a pine plantation; the

manifold was close to the canopy but the majority of the canopy was pine (a nonemitter of isoprene), so it is likely that more mixing and chemistry, relative to this study, could occur with isoprene and oxidation products before entering the sampling system. The Biesenthal *et al.* [1998] study was done in a clearing; their ratios probably would have been substantially lower if they were sampling directly above a canopy. The Yokouchi [1994] study was done in a flat plane area of a local city with surrounding scattered farms and forests, which allowed for relatively complete mixing of the compounds from the time of emission until the time of detection.

[25] Figure 10 shows the averaged diurnal ratio of MVK to MACR. This ratio has been discussed in several papers [e.g., Stroud *et al.*, 2001; Montzka *et al.*, 1993; Starn *et al.*, 1998]. The diurnal average ratio observed here appears to closely follow that

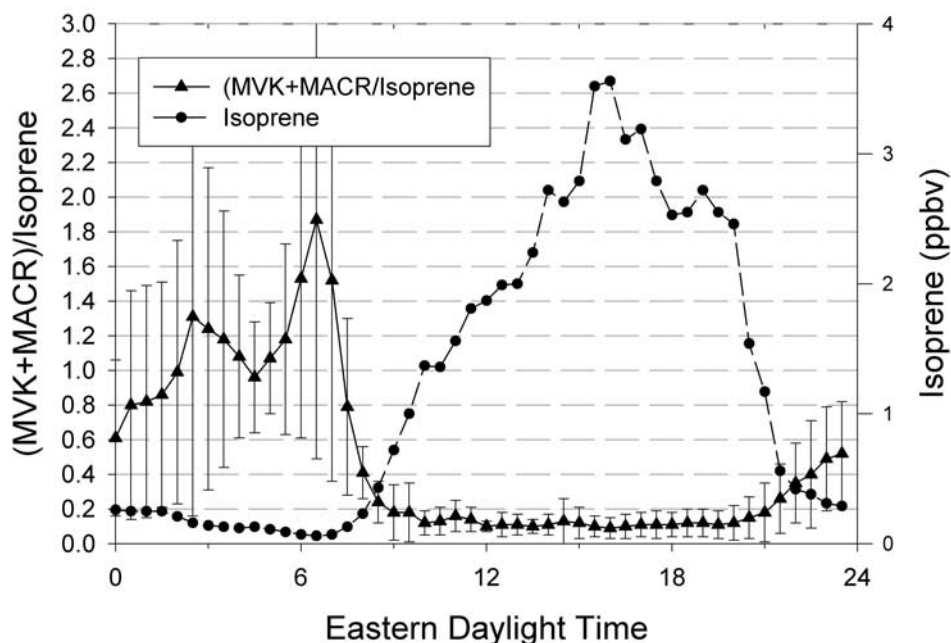


Figure 8. Diurnal plot of the ratio (MVK + MACR)/isoprene. Also shown is the coincident average isoprene mixing ratio. Bars indicate the range of measurements in 1 standard deviation.

observed by *Montzka et al.* [1993] and *Stroud et al.* [2001]. The ratio, on average, increases during the day to values greater than 2/1 and decreases during the nighttime hours to ~1. This ratio is understood to arise chiefly from the significant role that OH plays in the processing of isoprene and these reaction products. As indicated earlier, the daytime oxidation of isoprene by OH yields an [MVK]/[MACR] ratio of ~1.4. The MACR formed in this reaction reacts faster with OH than does the MVK (Table 1), and hence the ratio of the lifetimes of these species increases during the daytime as OH increases. As OH begins to decrease, the ratio of the lifetimes decreases leading to lower ratios of [MVK]/[MACR].

The lifetime ratio of MVK/MACR during the daytime at $OH = 3.35 \times 10^6$ (average measured daytime OH during this study) and $O_3 = 50$ ppbv is ~2.2. A 1-D model of *Montzka et al.* [1993] run over the full diurnal cycle for their study showed a maximum ratio during the day of ~2.0. Normally, at night, oxidation of isoprene by O_3 becomes more important as OH decreases or goes to zero. Processing of isoprene by only O_3 yields an [MVK]/[MACR] ratio of ~0.4 [*Carter and Atkinson*, 1996]. However, this low value is not normally expected to be reached during the night because of the slow reaction of isoprene with O_3 (the $1/e$ lifetime of isoprene with respect to O_3 at $O_3 = 50$ ppbv is 18 hours) and the residual

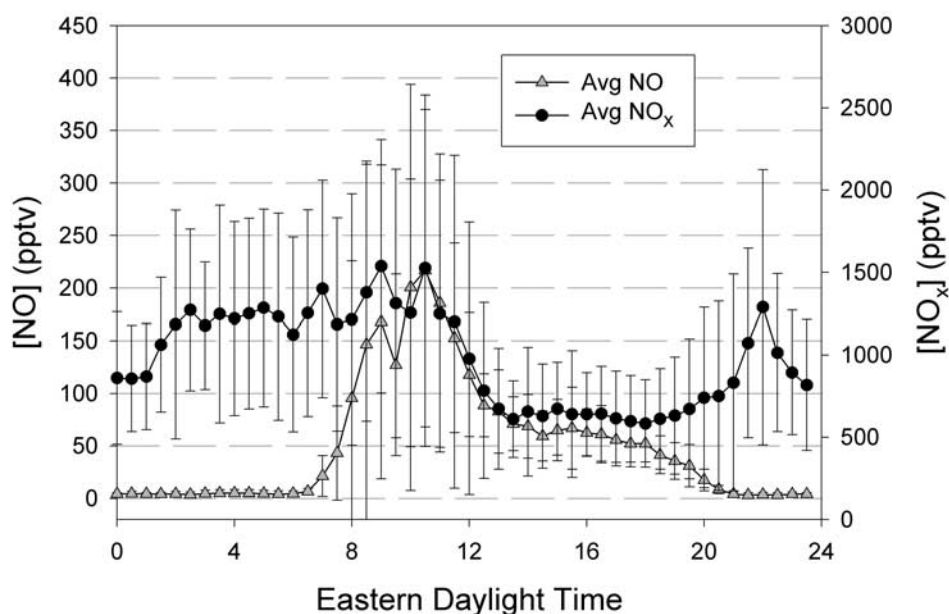


Figure 9. Plot of NO and NO_x during the time period of discussed measurements. Bars indicate the range of measurements in 1 standard deviation.

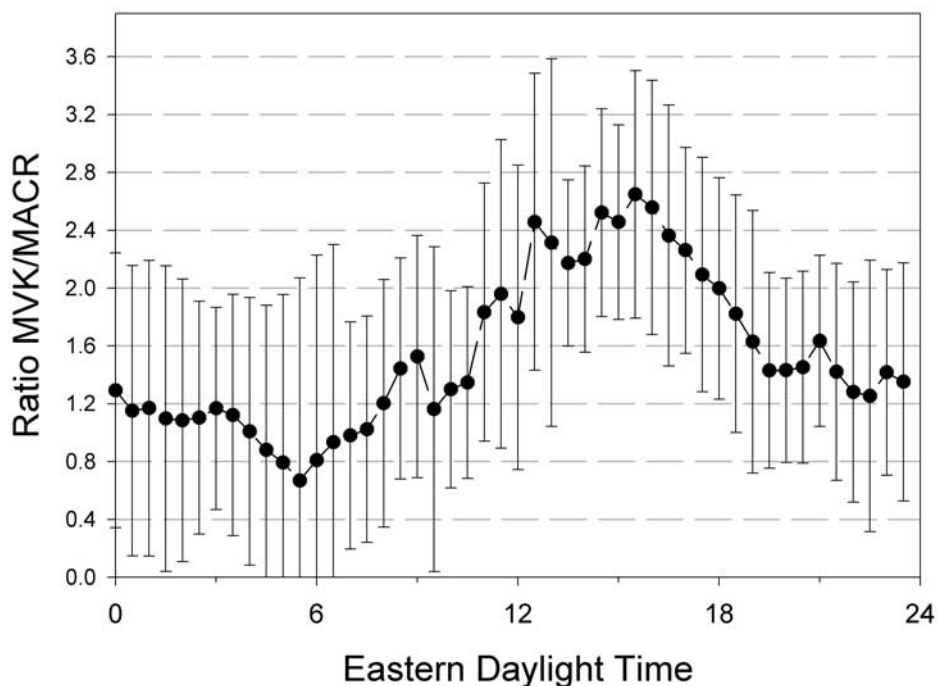


Figure 10. Average ratio for each half hour of MVK/MACR during the study.

MVK and MACR present at the end of the day as a result of OH chemistry. The 1-D model of *Montzka et al.* [1993] showed, indeed, that the nighttime ratio reached a minimum of ~ 1.0 before sunrise. It is clear from our data that at times the ratio fell below this value, particularly during the 0000 to 0600 LT time period, but the average data trend is consistent with expected results.

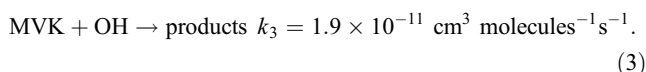
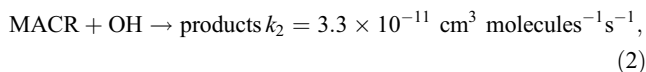
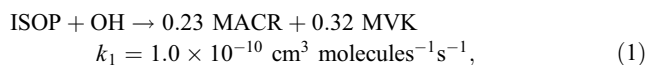
[26] Figure 11 shows the daytime and nighttime data for MACR versus MVK. The daytime data are represented by circles, and the nighttime data are represented by triangles. The top plot shows all the data. The dashed line is the 1/1 line, and the solid line is the 2/1 line. It is clear that most of the data fall within the boundaries of these two lines. If we eliminate data from the first 2 days of the study in which air came from the east, where the air traverses over local lakes, nearly all of the data fell close to within these two lines (bottom plot). This point will be revisited in section 4.

4. Discussion

4.1. Isoprene, MACR, and MVK Mixing Ratios

[27] Studies of mixing ratios of isoprene and products have been conducted in a number of very different environments with a number of different physical sampling arrangements as may be found in the references to previous studies. Enhanced values of the (MVK + MACR) to isoprene ratio are expected in sampling situations where the air mass has aged under high- NO_x conditions. It was shown in section 3.2 that during this study we were in a relatively low NO_x regime and this may contribute to lower ratios. However, there may be a much larger factor contributing to this ratio. As recently pointed out by *Stroud et al.* [2001], the ratios of MACR/isoprene and MVK/isoprene yield useful information on the photochemical age of measured isoprene in an air mass. In the present study, the isoprene emitters were located 12 m directly below the sampling inlet. Hence the levels should be dominated by fresh, local emissions, and low ratios are expected. It is possible to quantify the expected ratios and to compare them with actual data. Following *Stroud et al.* [2001], an expression for the time rate of change in the MACR/isoprene and MVK/isoprene ratios may be derived as a function of $[\text{OH}]$, the rate coefficients, and the time

available for processing. A consecutive reaction scheme, in which isoprene (ISOP) and the reaction products MVK and MACR react with OH [*Carter and Atkinson, 1996*], is shown by



[28] These branching ratios were obtained under NO_x -rich conditions and may not strictly hold, although, as we shall see, it appears to be a reasonably good approximation for the daytime data in this study. Solving the consecutive reaction scheme, the following expressions may be derived assuming a pseudo-first-order reaction (OH constant):

$$[\text{MACR}]/[\text{ISOP}] = [0.23 k_1 (1 - \exp(k_1 - k_2)[\text{OH}]_{\text{Avg}}^t)] / (k_2 - k_1) \quad (4)$$

$$[\text{MVK}]/[\text{ISOP}] = [0.32 k_1 (1 - \exp(k_1 - k_3)[\text{OH}]_{\text{Avg}}^t)] / (k_3 - k_1). \quad (5)$$

[29] This expression is purely chemical and does not include any mixing processes that may affect the ratio during transport. We may construct a plot of these ratios against each other, assuming the average measured daytime (0900–1600 LT) OH mixing ratio of $3.35 \times 10^6 \text{ molecules cm}^{-3}$, and superimpose the measured daytime ratios. This plot is shown in Figure 12. Considering

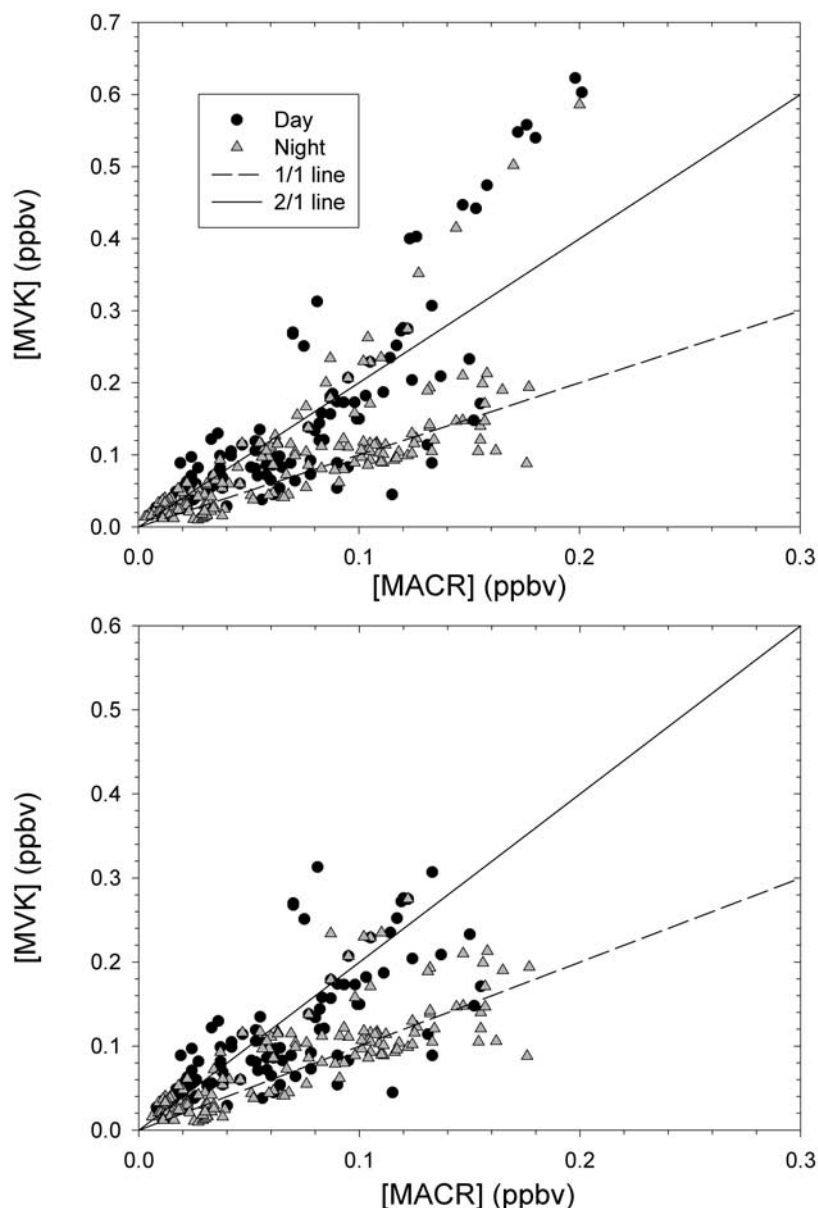


Figure 11. (top) Day and nighttime correlations of MVK and MACR. Shown also are the 1/1 line and the 2/1 line. (bottom) Same correlations but with the first 2 days eliminated from the data set. The eliminated days show winds out of the east and southeast.

the uncertainties, the data fit the predicted line quite well. The experimental data lie somewhat above the predicted line, similar to data obtained by *Montzka et al.* [1995] in a canopy experiment analyzed by *Stroud et al.* [2001]. Isoprene photochemical ages at the inlet may be estimated by comparing the measured ratios versus the derived trend line. The bulk of the data correspond to isoprene photochemical ages between 3.6 and 18 min, with the average near 6 min. In contrast, *Stroud et al.* [2001] derived an isoprene photochemical age of 40 min for their data in an urban clearing site impacted by isoprene emissions. The predicted line depends on the OH mixing ratio used in (4) and (5). As indicated above, we used the measured [OH] at the site [*Tan et al.*, 2001], but there is uncertainty associated with this because OH can vary considerably over short spatial scales. As indicated above, mixing is not taken into consideration.

[30] An estimate of the timescale for vertical diffusion may be derived and compared to the results above. As detailed by

Lenschow [1995], vertical fluxes of conserved quantities can be considered constant in the surface layer (approximately the lower 10% of the depth of the atmospheric boundary layer). A characteristic timescale τ for diffusion of a trace gas from the surface to a height z may be specified in terms of the turbulent eddy diffusivity, K :

$$\tau = z^2/K, \quad (6)$$

where

$$K \cong ku_*z. \quad (7)$$

Here, k is von Karmen's constant, and u_* is the friction velocity. It follows that

$$\tau = z/(ku_*). \quad (8)$$

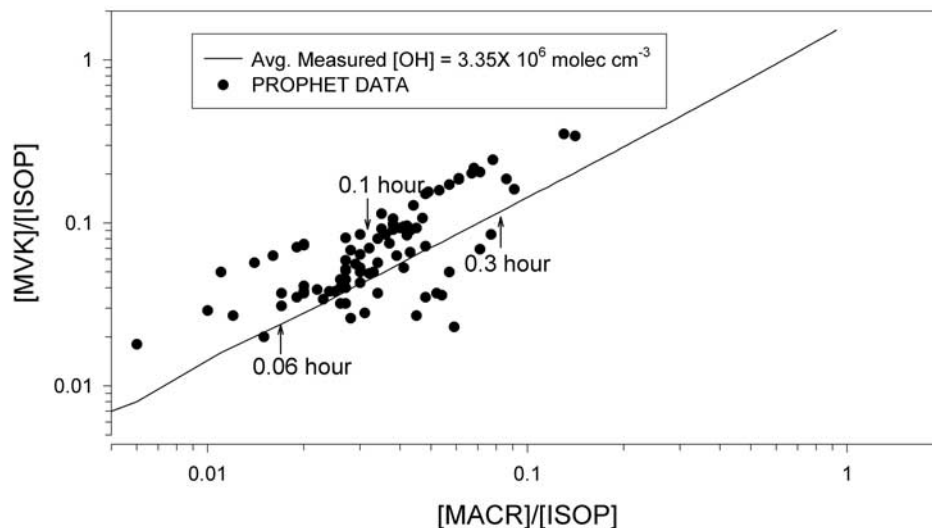


Figure 12. Plot of the measured ratios of MVK/isoprene versus MACR/isoprene and the calculated ratio based on a consecutive reaction scheme model.

[31] The value of k is ~ 0.38 . For our experiments the height from the top of the canopy to the inlet, z , was 12 m, and the average value of u_* during this experiment was 0.15 m s^{-1} . This yields a value, τ , of 3.5 min, which essentially represents a lower limit because it neglects any horizontal diffusion or diffusion from below the top of the canopy. This value is nearly identical to the timescale derived from (4) and (5).

[32] Recall that the isoprene flux data and the isoprene mixing ratio diurnal trends follow one another closely. This indicates that isoprene is being created and detected more quickly than it is being destroyed, which is what we should expect in an environment with this sampling arrangement showing that fresh emissions are being detected. We should be able to further investigate the validity of this hypothesis through ratios of the isoprene oxidation products. Recall from (1) that in the processing of isoprene by OH in the daytime, the branching ratio favors MVK over MACR by 1.4 to 1.

Further processing of the air mass by OH yields ratios higher than 1.4 to 1 because of the faster reaction of MACR by OH compared with MVK by OH (Table 1). Indeed, we saw in Figure 11 that the ratios can be >2 . However, a close look at the data reveals that most of the daytime ratios fall significantly below 2. Figure 13 shows a plot of the data of MACR versus MVK in which the highest values of MVK have been removed from the data set (where [MVK] is $>0.3 \text{ ppbv}$, 11% of the data). The slope of this line, which encompasses 89% of the data, is 1.35 with an r^2 value of 0.6. This supports the argument that for the majority of the data points, fresh emissions of isoprene were being sampled and that the MVK and MACR had not been processed significantly. These data, along with the data shown in Figure 11, show consistency with the NO_x -rich derived laboratory kinetic experiments.

[33] We may take a closer look at the data of Figure 11 in which high ratios of MVK/MACR are observed. The highest ratios were

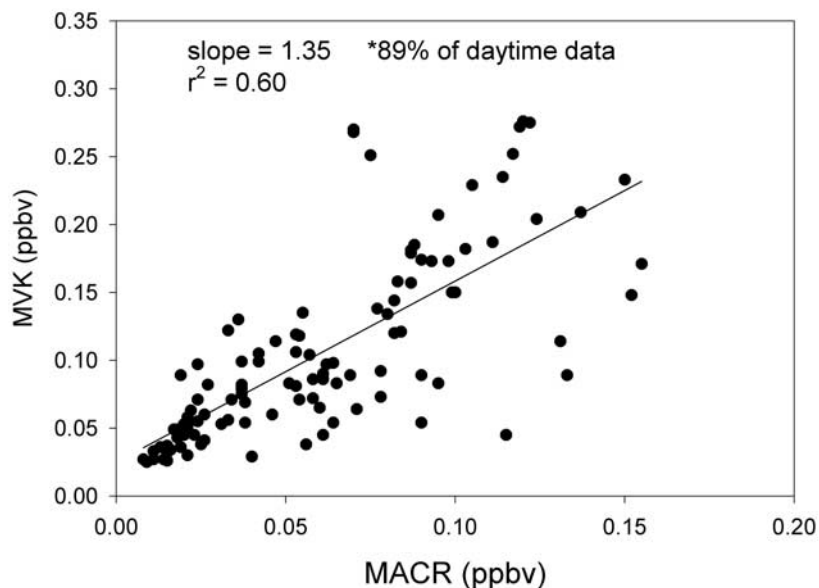


Figure 13. Plot of MVK versus MACR for data in which the highest mixing ratios of MVK ($>0.3 \text{ ppbv}$) and MACR have been eliminated.

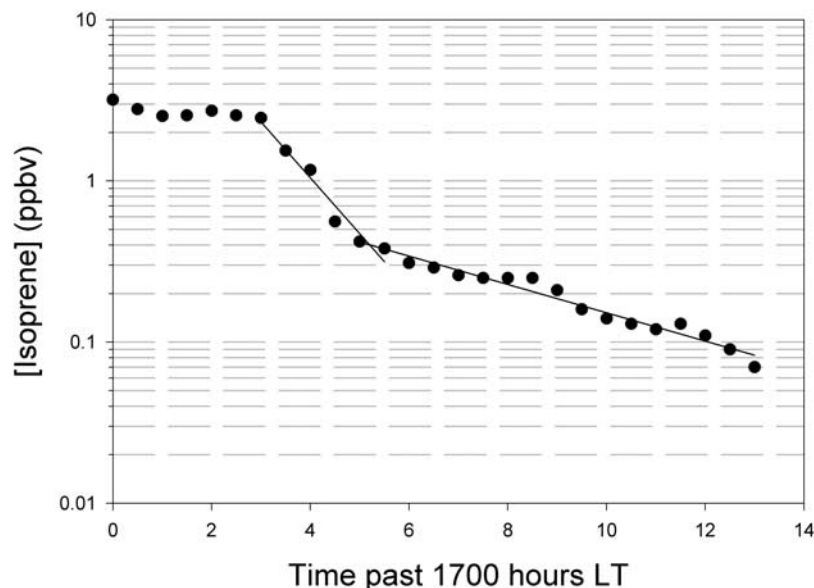


Figure 14. Average decay of isoprene during the study after 1700 LT.

observed over the first 2 days of the study when the wind was from the east and southeast. These were the only days in which the wind was from this direction. This air, originating in areas of high isoprene emission potential, had a high likelihood of passing over one of three lakes, Douglas, Burt, or Mullett, prior to arriving at the inlet. In the absence of fresh isoprene emissions the MVK/MACR ratio should increase to values >1.4 because of the higher reactivity of MACR compared to MVK. Mixing will also be slowed as the air parcel passes over the lakes because of reduced convective heating of the surface. At a wind speed of 2 m s^{-1} the air parcel may spend between 1 and 2 hours over the lake(s). This is enough time to significantly impact the ratio because the lifetimes of MACR and MVK are 2.5 and 4.5 hours, respectively, assuming $\text{OH} = 3.35 \times 10^6 \text{ molecules cm}^{-3}$. It should be noted, however, that this scenario does not, in itself, explain the highest observed ratios (~ 3).

4.2. Nighttime Behavior of Isoprene, MACR, and MVK

[34] During the 8-day period described here, isoprene decays very rapidly between 1930 and 2130 LT with an effective lifetime of ~ 0.75 hours. After 2130 LT the decay is much slower, with an effective lifetime of ~ 3.6 hours. These data are shown in Figure 14 for the average isoprene data observed during this study. This discussion centers on whether the data presented in this paper give us a clue as to what the dominant loss processes are at night. *Faloona et al.* [2001] present results indicating that there is sufficient OH, based on their measurements, to cause the rapid isoprene decay. On the other hand, *Sillman et al.* [2002] present modeling results that suggest that atmospheric dynamics plays the major role. There is merit to both arguments. This discussion focuses on new insight gained from this study.

[35] A sharp vertical gradient has been predicted [*Trainer et al.*, 1987] for isoprene throughout the mixed layer as a result of slow vertical mixing near the surface and rapid reaction with OH radicals. Since we are measuring fresh emissions near the bottom of the gradient, the volume directly above the sampling inlet contains less isoprene, and [isoprene] should decrease with height up to the top of the mixing volume. As noted by *Sillman et al.* [2002, and references therein], measurements have typically shown a gradient but often not a particularly steep one, with isoprene concentrations at 100–300 m less than isoprene concentrations just above the forest canopy but only by a factor of ~ 2 . After sunset a

decrease in isoprene concentrations measured at the inlet would be expected due to cessation of isoprene emissions and to mixing in of air from above. Indeed, the flux data (Figure 3) indicate that emissions come to a fairly rapid end each day after sunset. However, the expected net decrease during the night, based on previous observed “typical” gradients, is much less than the observations show (see Figure 5). For example, in the most extreme case, during Day 217 (Figure 5), isoprene concentrations decreased from a maximum of 4.1 ppbv to <20 pptv during the night. This rapid decrease to low concentrations has been the subject of a spirited debate between those supporting chemistry [*Hurst et al.*, 2001; *Faloona et al.*, 2001] and those supporting dynamics [*Sillman et al.*, 2002] as the major factor in the decay. A key factor, and a major contribution from the work described here, in qualitatively understanding the rapid isoprene decay after sunset is the accurate determination of the emission profiles from surrounding areas. In this paper, the latest emission estimates (BEIS3) were used (shown graphically in Figure 2). These estimates show clearly that the isoprene emissions at the site are much higher than emissions from any of the surrounding areas. As a result, air that is advected to the site from any direction will contain significantly less isoprene than the air in the direct vicinity of the inlet manifold. At average wind speeds of $2\text{--}3 \text{ m s}^{-1}$, air will be rapidly advected to the site from these areas. These processes occur soon after sunset and most likely account for the “first” decay of isoprene, although *Hurst et al.* [2001] present arguments that the initial decay involves both meteorological and chemical processes. The “second” decay may be more complex and almost certainly involves both chemical and meteorological processes. The reader is referred to papers by *Hurst et al.* [2001] and *Sillman et al.* [2002] for further discussion.

[36] Although the vertical profiling was limited during the study, profiles shown by *Hurst et al.* [2001] show a steep vertical gradient which is consistent with what would be expected from vertical mixing and advection from surrounding areas having significantly less isoprene emission based on the BEIS3 emission estimates.

[37] If the decays are caused by chemical processing, can we discern useful information from the isoprene reaction product data? It might be expected that during the initial decay, especially when there is some NO present (Figure 9) to help drive reaction (equation (1)) and during formation of the nocturnal boundary layer, there would be an increase in absolute concentrations of

MACR and MVK. This is not observed (Figure 7). However, as pointed out by Hurst *et al.* [2001], it is likely that vertical mixing, although less dramatic than for isoprene, contributes to the observed decreases in these species since their chemical lifetimes are significantly less than the timescale for vertical mixing in the boundary layer during the daytime. After the nocturnal boundary layer is formed, processing of isoprene by OH radicals leading to MACR and MVK should be more discernable, even in the absence of NO, because of the reduced boundary layer height. Myoshi *et al.* [1994] observed significant MVK and MACR under NO_x-free conditions, albeit in different relative yields (17% MVK and 22% MACR) than in the presence of NO. However, by this time, [isoprene] has already been significantly reduced, and increases in the absolute concentrations may not be discernable. Another contributing factor may be nighttime deposition of these species.

[38] Changes in the ratios of MVK to MACR can be observed during the daytime, and it might be expected that changes in the ratios could be observed at night if there is significant processing by OH radicals. In addition, these ratios are less dependent on mixing dynamics than their absolute concentrations. However, it may not be possible to discern the difference in processing of isoprene by OH (in the absence of NO [Myoshi *et al.*, 1994]) compared to O₃ because each will yield a higher ratio of MACR/MVK at night than during the day. For the second decay, if the oxidation is occurring due to NO₃, there will be no useful information in the MVK/MACR ratios. This is because the yield of these compounds from isoprene oxidation by NO₃ is similarly low for both compounds (~3.5% [Kwok *et al.*, 1996]).

5. Summary and Conclusions

[39] Isoprene and two of its initial reaction products, MACR and MVK, were measured each half hour at the rural forested PROPHET site from a glass manifold inlet situated 10 m directly above a forest canopy predominantly composed of isoprene emitters. Isoprene fluxes were concurrently measured at the nearby AmeriFlux site. Emissions profiles were constructed for a radius of within 60 km of the site. Calculated emissions were compared to the fluxes measured at the site. These data show that the PROPHET site is located in an isoprene-enriched area; isoprene emissions are significantly higher at the site than in surrounding areas.

[40] The location of the sampling manifold is shown to affect the measured ratios of MACR and MVK to isoprene. The photochemical lifetime of measured isoprene (i.e., the time between emission and measurement of isoprene (3.6–18 min)) is significantly less than the photochemical lifetime of isoprene ($t = 45$ min at $[OH] = 3.35 \times 10^6$ molecules cm⁻³). Thus a large portion of the isoprene that reaches the manifold has not had time to react completely with OH, yielding lower-than-expected ratios based on model calculations that do not explicitly take this into account. A contributing factor to the low ratios is the relatively low NO at the site, leading to lower product yield of MACR and MVK when processing isoprene with the OH radical.

[41] The rapid nighttime decay of isoprene has been discussed extensively by Hurst *et al.* [2001] and Sillman *et al.* [2002]. As a result of refined emissions estimates from this article and observations of the effect of sampling near the top of the canopy, vertical diffusion and advection from isoprene-poor areas are postulated to contribute significantly to the initial rapid decay of isoprene soon after sunset. If OH is a large contributing factor to the isoprene decay at night, it might be expected that important information could be gleaned from ratios of MVK to MACR. However, because of the low mixing ratios of NO encountered at this site during the night, the ratios yield little useful information, owing to the fact that NO_x-free oxidation of isoprene by OH is expected to

give a higher yield of MACR to MVK, which is qualitatively similar to what is expected from O₃ processing of isoprene.

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References

- Apel, E., J. Calvert, J. Greenberg, D. Riemer, R. Zika, T. Kleindienst, W. Lonneman, K. Fung, and E. Fujita, Generation and validation of oxygenated organic carbon standards for the 1995 Southern Oxidants Study Nashville Intensive, *J. Geophys. Res.*, **103**, 22,281–22,294, 1998.
- Apel, E. C., T. Gilpin, A. Fried, and D. Riemer, Techniques for the standardization, validation, and measurement of targeted oxygenated trace gases which participate in tropospheric ozone formation, NCER-QA grant final report executive summary, U.S. Environ. Prot. Agency, Natl. Cent. for Environ. Res. and Qual. Assurance, Washington, D. C., April 2001.
- Barket, D., Jr., et al., Intercomparison of automated methodologies for determination of ambient isoprene during the PROPHET 1998 summer campaign, *J. Geophys. Res.*, **106**, 24,301–24,313, 2001.
- Biesenthal, T., Q. Wu, P. Shepson, H. Wiebe, K. Anlauf, and G. Mackay, A study of relationships between isoprene, its oxidation products, and ozone in the lower Fraser Valley, BC, *Atmos. Environ.*, **31**, 2049–2058, 1997.
- Biesenthal, T. A., J. W. Bottenheim, P. B. Shepson, S.-M. Li, and P. C. Brickell, The chemistry of biogenic hydrocarbons at a rural site in eastern Canada, *J. Geophys. Res.*, **103**, 25,487–25,498, 1998.
- Bowling, D., A. Turnipseed, A. Delany, D. Baldocchi, J. Greenberg, and R. Monson, The use of relaxed eddy accumulation to measure biosphere-atmosphere exchange of isoprene and other biological trace gases, *Oecologia*, **116**, 306–315, 1998.
- Carroll, M. A., S. B. Bertman, and P. B. Shepson, Overview of the Program for Research on Oxidants: Photochemistry, Emissions, and Transport (PROPHET) summer 1998 measurements intensive, *J. Geophys. Res.*, **106**, 24,275–24,288, 2001.
- Carter, W. P. L., and R. Atkinson, Development and evaluation of a detailed mechanism for the atmospheric reactions of isoprene and NO_x, *Int. J. Chem. Kinet.*, **28**, 497–530, 1996.
- Chameides, W. L., R. D. Saylor, and E. B. Cowling, Ozone pollution in the rural United States and the new NAAQS Policy Forum, *Science*, **276**, 916, 1997.
- Cleveland, C. C., and J. B. Yavitt, Consumption of atmospheric isoprene in soil, *Geophys. Res. Lett.*, **24**, 2379–2382, 1997.
- Cooper, O. R., J. L. Moody, T. Thornberry, M. Town, M. S. Town, and M. Carroll, PROPHET 1998 meteorological overview and air-mass classification, *J. Geophys. Res.*, **106**, 24,289–24,299, 2001.
- Dabberdt, W., D. Lenschow, T. Horst, P. Zimmerman, S. Oncley, and A. Delany, Atmosphere-surface exchange measurements, *Science*, **260**, 1472–1481, 1993.
- Faloon, I., et al., Nighttime observations of anomalously high levels of hydroxyl radicals above a deciduous forest canopy, *J. Geophys. Res.*, **106**, 24,315–24,333, 2001.
- Finlayson-Pitts, B., and J. N. Pitts, Jr., *Chemistry of the Upper and Lower Atmosphere*, pp. 180–213, Academic, San Diego, Calif., 2000.
- Geron, C. D., A. Guenther, and T. Pierce, An improved model for estimating emissions of volatile organic compounds from forests in the eastern United States, *J. Geophys. Res.*, **99**, 12,773–12,791, 1994.
- Geron, C. D., A. Guenther, T. D. Sharkey, and R. R. Arnts, Temporal variability in the basal isoprene emission factor, *Tree Physiol.*, **20**, 799–805, 2000.
- Goldan, P. D., W. C. Kuster, F. C. Fehsenfeld, and S. A. Montzka, Hydrocarbon measurements in the southeastern United States: The Rural Oxidants in the Southern Environment (ROSE) program 1990, *J. Geophys. Res.*, **100**, 25,945–25,963, 1995.
- Guenther, A., and A. Hills, Eddy covariance measurement of isoprene fluxes, *J. Geophys. Res.*, **103**, 13,145–13,152, 1998.
- Guenther, A., P. R. Zimmerman, and M. Wildermuth, Natural volatile organic compound emission rate estimates for U.S. woodland landscapes, *Atmos. Environ.*, **28**, 1197–1210, 1994.

- Guenther, A., et al., A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, **100**, 8873–8892, 1995.
- Guenther, A., C. D. Geron, T. Pierce, B. Lamb, P. Harley, and R. Fall, Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America, *Atmos. Environ.*, **34**, 2205–2230, 2000.
- Helmig, D., J. Greenberg, A. Guenther, and P. Zimmerman, Volatile organic compounds and isoprene oxidation products at a temperate deciduous forest site, *J. Geophys. Res.*, **103**, 22,397–22,414, 1998.
- Hurst, J. M., et al., Investigation of the nighttime decay of isoprene, *J. Geophys. Res.*, **106**, 24,335–24,346, 2001.
- Kwok, E. S. C., S. M. Aschman, J. Arey, and R. Atkinson, Product formation from the reaction of the NO₃ radical with isoprene and rate constants for the reactions of methacrolein and methyl vinyl ketone with the NO₃ radical, *Int. J. Chem. Kinet.*, **28**, 925–934, 1996.
- Lenschow, D. H., Micrometeorological techniques for measuring biosphere-atmosphere trace gas exchange, in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by P. Matson and R. Harriss, pp. 126–163, Blackwell Sci., Malden, Mass., 1995.
- Makar, P. A., J. D. Fuentes, D. Wang, R. M. Staebler, and H. A. Wiebe, Chemical processing of biogenic hydrocarbons within and above a temperate deciduous forest, *J. Geophys. Res.*, **104**, 3581–3603, 1999.
- Martin, R. S., H. Westberg, E. Allwine, L. Ashman, J. C. Farmer, and B. Lamb, Measurement of isoprene and its atmospheric oxidation products in a central Pennsylvania deciduous forest, *J. Atmos. Chem.*, **13**, 1–32, 1991.
- Monson, R., A. Hills, P. Zimmerman, and R. Fall, Studies of the relationship between isoprene emission rate and CO₂ or photon-flux density using a real-time isoprene analyzer, *Plant Cell Environ.*, **14**, 517–523, 1991.
- Monson, R., A. Hills, and R. Fall, *Methods for the Analysis of Isoprene from Leaves*, *Mod. Methods Plant Anal.*, vol. 13, edited by D. Czeschlik, Springer-Verlag, New York, 1992.
- Monson, R. K., P. Harley, M. E. Litvak, M. Wildermuth, A. Guenther, P. R. Zimmerman, and R. Fall, Environmental and developmental controls over the seasonal pattern of isoprene emission from aspen leaves, *Oecologia*, **99**, 260–270, 1994.
- Montzka, S. A., M. Trainer, P. D. Goldan, W. C. Kuster, and F. C. Fehsenfeld, Isoprene and its oxidation products, methyl vinyl ketone and methacrolein, in the rural troposphere, *J. Geophys. Res.*, **98**, 1101–1111, 1993.
- Montzka, S. A., M. Trainer, W. Angevine, and F. C. Fehsenfeld, Measurements of 3-methyl furan, methyl vinyl ketone, and methacrolein at a rural forested site in the southeastern United States, *J. Geophys. Res.*, **100**, 11,393–11,401, 1995.
- Myoshi, A., S. Hatakeyama, and N. Washida, OH radical-initiated photo-oxidation of isoprene: An estimate of global CO production, *J. Geophys. Res.*, **99**, 18,787–18,799, 1994.
- Nouaime, G., S. B. Bertman, C. Seaver, D. Elyea, H. Huang, P. B. Shepson, T. K. Starn, D. D. Riemer, R. G. Zika, and K. Olszyna, Sequential oxidation products from tropospheric isoprene chemistry: MACR and MPAN at a NO_x-rich forest environment in the southeastern United States, *J. Geophys. Res.*, **103**, 22,463–22,471, 1998.
- Pierotti, D., S. C. Wofsy, D. Jacob, and R. Rasmussen, Isoprene and its oxidation products: Methacrolein and methyl vinyl ketone, *J. Geophys. Res.*, **95**, 1871–1881, 1990.
- Riemer, D., P. Milne, C. Farmer, and R. Zika, Determination of terpene compounds and related species in semi-urban air by GC-MSD, *Chemosphere*, **28**, 837–850, 1994.
- Riemer, D., et al., Observations of nonmethane hydrocarbons and oxygenated volatile organic compounds at a rural site in the southeastern United States, *J. Geophys. Res.*, **103**, 28,111–28,128, 1998.
- Sillman, S., et al., Loss of isoprene and sources of nighttime OH radicals at a rural site in the U.S.: Results from photochemical models, *J. Geophys. Res.*, **107**, 10.1029/2001JD000449, 2002.
- Starn, T. K., P. B. Shepson, D. D. Riemer, R. G. Zika, and K. Olszyna, Nighttime isoprene chemistry at an urban-impacted forest site, *J. Geophys. Res.*, **103**, 22,437–22,447, 1998.
- Stroud, C. A., et al., Isoprene and its oxidation products, methacrolein and methyl vinyl ketone, at an urban forested site during the 1999 Southern Oxidants Study, *J. Geophys. Res.*, **106**, 8034–8046, 2001.
- Sumner, A. L., et al., A study of formaldehyde chemistry above a forest canopy, *J. Geophys. Res.*, **106**, 24,387–24,405, 2001.
- Tan, D., et al., HO_x budgets in a deciduous forest: Results from the PROPHET summer 1998 campaign, *J. Geophys. Res.*, **106**, 24,407–24,427, 2001.
- Thornberry, T. D., et al., Observations of reactive oxidized nitrogen and speciation of NO_y during the PROPHET summer 1998 intensive, *J. Geophys. Res.*, **106**, 24,359–24,386, 2001.
- Trainer, M., E. J. Williams, D. D. Parrish, M. P. Buhr, E. J. Allwine, H. H. Westberg, F. C. Fehsenfeld, and S. C. Liu, Models and observations of the impact of natural hydrocarbons on rural ozone, *Nature*, **329**, 705–707, 1987.
- Westberg, H., B. Lamb, R. Hafer, A. Hills, P. B. Shepson, and C. Vogel, Measurement of isoprene fluxes at the PROPHET site, *J. Geophys. Res.*, **106**, 24,347–24,358, 2001.
- Yokouchi, Y., Seasonal and diurnal variation of isoprene and its reaction products in a semirural area, *Atmos. Environ.*, **28**, 2651–2658, 1994.
- Zhu, Z., and D. L. Evans, U.S. forest types and predicted percent forest cover from AVHRR data, *Photogramm. Eng. Remote Sens.*, **60**(5), 525–531, 1994.

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