Long-term isoprene flux measurements above a northern hardwood forest

Shelley Pressley, Brian Lamb, Hal Westberg, Julia Flaherty, and Jack Chen
Department of Civil and Environmental Engineering, Washington State University, Pullman, Washington, USA

Christoph Vogel
University of Michigan Biological Station, University of Michigan, Pellston, Michigan, USA

Received 12 October 2004; revised 17 December 2004; accepted 13 January 2005; published 2 April 2005.

[1] We report continuous whole canopy isoprene emission fluxes from a northern hardwood forest in Michigan for the 1999–2002 growing seasons. The eddy covariance fluxes of isoprene, CO_2, latent heat, and sensible heat are presented along with an analysis of the seasonal and year-to-year variations. Measurements were made in collaboration with the AmeriFlux site located at the University of Michigan Biological Station (UMBS) and the Program for Research on Oxidants: PHotochemistry, Emissions, and Transport (PROPHET). In general, isoprene emissions increased throughout the day with increasing temperature and light levels, peaked at midafternoon, and declined to zero by night. There were significant variations from one 30-min period to the next, and from one day to the next. Average midday isoprene fluxes were 2.8, 3.2, and 2.9 mg C m^{-2} h^{-1} for 2000 through 2002, respectively. Insufficient data were available to include 1999. Last frost and full leaf out were significantly later in 2002 compared to the other years; however, total accumulated isoprene emissions for each year varied by less than 10%. Fully developed isoprene emissions occurred between 400 and 500 heating degree days, roughly half those required at other sites. Using long-term net ecosystem exchange measurements from the UMBS∼Flux group, isoprene emissions represent between 1.7 to 3.1% of the net carbon uptake at this site. Observations for 2000–2002 were compared with the BEIS3 emission model. Estimates agree well with observations during the midsummer period, but BEIS3 overestimates observations during the spring onset of emissions and the fall decline in emissions. This work provides a unique long-term data set useful for verifying canopy scale models and to help us better understand the dynamics of biosphere-atmosphere exchange of isoprene.

Citation: Pressley, S., B. Lamb, H. Westberg, J. Flaherty, J. Chen, and C. Vogel (2005), Long-term isoprene flux measurements above a northern hardwood forest, *J. Geophys. Res.*, *110*, D07301, doi:10.1029/2004JD005523.

1. Introduction

[2] Isoprene (2-methyl-1,3-butadiene) is one of the most reactive naturally emitted hydrocarbons, and it is one of the most abundant biogenic hydrocarbon species found over forested environments. Isoprene, along with other biogenic hydrocarbons, plays an important role in tropospheric chemistry at regional and global scales, and improved quantification of the biospheric source strength is crucial for photochemical modeling applications. The primary removal mechanism for isoprene from the troposphere is oxidation by hydroxyl radicals (HO), ozone (O_3) and nitrate radicals. Isoprene oxidation products (alkyl peroxy radicals RO_2) will preferentially react with anthropogenic nitric oxides (NOx = NO + NO_2) leading to increased levels of O_3 and other reactive species involved in the production of photochemical smog [*Fehsenfeld et al.*, 1992; *Andreae and Crutzen*, 1997; *Atkinson*, 2000]. Various photochemical model studies have shown that biogenic emissions have the potential to markedly influence atmospheric photochemistry by contributing to the production of carbon monoxide (CO) and O_3 concentrations, in addition to altering the tropospheric lifetime of methane (CH_4) [*Jiang et al.*, 2003; *Poisson et al.*, 2000; *Wang and Shallcross*, 2000].

[3] Isoprene is produced via the novel glyceraldehyde phosphate/pyruvate pathway [*Lichtenthaler et al.*, 1997], and its biosynthesis is associated with the carboxylation process in the leaf chloroplast [*Sharkey and Yeh*, 2001]. The final step of isoprene synthesis involves a membrane bound, light activated enzyme isoprene synthase [*Silver and Fall*, 1991; *Wildermuth and Fall*, 1996]. Changes in isoprene emission have been shown to correlate with changes in the activity of isoprene synthase [*Monson et al.*, 1992; *Kuzma and Fall*, 1993], thus linking isoprene emissions to availability of light and hence photosynthetic activity [*Sharkey et*

0148-0227/05/2004JD005523

al., 1991]. However, isoprene synthesis and emission will continue (through the stomata) even when stomata are closed due to increased vapor pressures within the leaf [*Fall and Monson*, 1992]. Two environmental variables that affect isoprene emission are temperature and photosynthetic photon flux density (PPFD). Other factors also affect the rate at which a particular leaf will emit isoprene. These include the leaf environment (Sun versus shade) [*Harley et al.*, 1996], leaf phenology [*Harley et al.*, 1994], and historical temperatures [*Geron et al.*, 2000], among others. Theories currently used to explain the reason for production and emission of isoprene include thermal tolerance or protection from short periods of high temperatures [*Singsaas et al.*, 1997], an antioxidant role to protect intercellular areas from harmful oxidants such as O_3 [*Loreto and Velikova*, 2001], and a pathway for removing excess carbon [*Logan et al.*, 2000]. Needless to say, our understanding of the function of isoprene is incomplete, but the role isoprene plays in atmospheric chemistry is well understood.

[4] Isoprene emissions from vegetation have been measured from various environments using techniques ranging from leaf and branch enclosures [*Zimmerman*, 1979; *Lamb et al.*, 1985; *Monson et al.*, 1994] to whole canopy measurements using micrometeorological techniques [*Baldocchi et al.*, 1995; *Guenther et al.*, 1996a, 1996b; *Goldstein et al.*, 1998]. Isoprene emission rates are known to depend on temperature and light and to go to zero at night, they change as a function of height within the canopy [*Harley et al.*, 1996], and there is a seasonal switch which controls emissions that appears to be a function of the number of growing days after the last frost [*Monson et al.*, 1994; *Geron et al.*, 2000].

[5] In this paper, we describe results of growing season isoprene emission studies at the Program for Research on Oxidants: PHotochemistry, Emissions and Transport (PROPHET) site [*Carroll et al.*, 2001]. This study is a continuation of measurements made at this site beginning in 1997 [*Westberg et al.*, 2001] and continuing through 2002. These data provide one of the longest records of isoprene emissions from any ecosystem, and they provide an invaluable record for studying long-term controls over isoprene emissions. Concurrent work during the summers of 2000 and 2001 include the PROPHET 6-week intensive measurement campaigns, the continuous operation of an AmeriFlux tower focusing on CO_2 flux measurements [*Schmid et al.*, 2003], and the operation of a smaller instrumented tower focusing on transport and turbulence within and above the canopy [*Villani et al.*, 2003].

[6] The primary objective of this work is to present the long-term isoprene flux measurements along with the biosphere-atmosphere exchange of energy (momentum, sensible heat, and latent heat) and CO_2. Discussions regarding the eddy covariance technique and the inherent uncertainties are presented, along with a brief description of the daily and annual isoprene flux observations. The response of isoprene to temperature, light, and phenology is presented, and the performance of the current U.S. Environmental Protection Agency (USEPA) biogenic emission model (BEIS3) is evaluated for isoprene emissions at this site. Because observations of isoprene differ from the models, and there is variability in isoprene fluxes that cannot be explained with current biogenic emission models, long-term observations may help us to better understand the dynamics of these differences.

2. Site Description

[7] Measurements were made from the University of Michigan Biological Station (UMBS)∼Flux tower (part of the AmeriFlux program) [*Baldocchi et al.*, 2001] located near Pellston, Michigan (45°30′N, 84°42′W). The secondary successional hardwood forest contains a mix of bigtooth aspen (*Populus grandidentata* Michx.), quaking aspen (*P. tremuloides* Michx.), beech (*Fagus grandifolia* Ehrh.), paper birch (*Betula papyrifera* Marsh.), maple (*Acer rubrum* L., *A. saccharum* Marsh.) and red oak (*Quercus rubra* L.), with an understory component of young eastern white pine (*Pinus strobus* L.) and bracken fern (*Pteridium aquilium*) [*Schmid et al.*, 2003]. Douglas Lake is located 1 km to the north and Burt Lake 3.5 km to the southeast. The fetch is relatively flat with a maximum change in elevation of 20 m over 1 km distance in any direction from the tower. Approximately 130 m to the southeast of the UMBS∼Flux tower is the PROPHET tower, used for studying regional atmospheric chemistry. A more detailed description of the PROPHET program and the site is provided by *Carroll et al.* [2001]. The average canopy height (h_c) is 22 m, and measurements were made at the 31 m height of the UMBS∼Flux tower ($1.4h_c$). In 2002 the flux system was moved to the PROPHET tower, and measurements were made at the 32 m height ($1.5h_c$). Footprint analysis for each year, using a model developed by *Hsieh et al.* [2000], indicates that the typical daytime fetch (unstable conditions) that encompasses 90 to 95% of the measured flux extends approximately 100–200 m from the tower. The model was run using a zero plane displacement height, $d = 0.75*h_c = 16.5$ m, and a roughness height of $z_0 = 0.4$ m. Aspen and red oak are the primary isoprene emitters and account for approximately 69% of the total biomass within a 1 km radius of the UMBS∼Flux tower. Measurements were conducted each year (1999–2002) from roughly mid-May through the end of September at which time leaf senescence occurred, and isoprene emissions became effectively zero.

[8] Both towers are accessed via an unimproved driveway and gravel footpath off of Bryant Road (east of the site). The UMBS∼Flux tower has a triangular cross section with a large base at the bottom (5.1 m sides) that tapers to 1.8 m sides at 30.5 m in height, and steel grid work platforms every 6 m. An interior ladder provides access to the top of the tower, and a shelter at the base of the tower houses data acquisition equipment and other instruments [*Schmid et al.*, 2003]. The PROPHET tower is a 31 m high walk-up scaffolding tower, rectangular in shape with 1.5 by 1.8 m platforms and a small laboratory at the base of the tower that houses the sampling equipment [*Carroll et al.*, 2001].

3. Measurements and Calculations

[9] Eddy covariance flux measurements of isoprene, sensible heat, latent heat, CO_2 and momentum were made within the surface boundary layer. Environmental param-

eters such as air temperature, relative humidity (RH), net radiation (R_n), PPFD, short wave radiation, rain, and atmospheric pressure were also monitored by the UMBS∼Flux group. The data acquisition system for the eddy covariance data was a fast response (10 Hz) system, which stored 30-min data files for processing off-line. The environmental parameters were stored via a series of Campbell data loggers (Campbell Scientific, Inc., Logan, UT) at various temporal resolutions (ranging from 1 s to 10 min averages) [*Schmid et al.*, 2003].

3.1. Eddy Covariance Measurements

[10] Wind speed and temperature were measured using an ATI sonic anemometer (K-configuration) aligned toward the northwest. An open-path infrared gas analyzer [*Auble and Meyers*, 1992] (IRGA) mounted 0.5 m from the sonic measured CO_2 and H_2O mixing ratios. The IRGA was calibrated for CO_2 mixing ratios approximately every 2 weeks (Scott-Marrin, Riverside, CA, 290 and 402 ppm CO_2 in N_2). The H_2O channel was calibrated using pressure, temperature and RH measured simultaneously with nearby sensors. A 1.27 cm (I.D.) Teflon sampling line mounted 0.2 m from the sonic array drew air to the ground for analysis via a fast isoprene sensor (FIS, Hills Scientific, Inc.). The FIS is a total alkene analyzer using a chemiluminescent technique with a fast response time (0.4 s) [*Hills and Zimmerman*, 1990]. Due to low concentrations of other alkenes at the site and a low relative response of the FIS to these alkenes, the interference for isoprene measurements is negligible (see *Westberg et al.* [2001] for more details). The detection limit when operating the instrument at 10 Hz is 0.5 ppbv isoprene with 20% uncertainty. Calibrations were performed using a dynamic dilution of isoprene (Scott-Marrin, 6.09 ppm ±2% isoprene in N_2) at a minimum of once per day to determine the zero and the slope, or sensitivity (photon counts per ppbv isoprene per time). In 2002 the FIS was upgraded with automated calibration capabilities, so calibrations were performed approximately every 7 hours or about 3 times per day. The FIS sensitivity varied slightly, with standard deviations of 27%, 25%, 28% and 19% for years 1999–2002, respectively. There was no discernable trend or drift with the FIS zero for any year. *Guenther and Hills* [1998] reported that instrument noise is primarily high frequency, random noise that is relatively independent of mixing ratio.

[11] The processing of the 10 Hz data was done for each 30-min period using the following approach: (1) calibration coefficients were applied, and the raw (10 Hz) data were converted from the digital signal into scientific units; (2) correlations of the vertical wind component (w) and the isoprene mixing ratio were calculated for a range of times (τ) (midday periods only) and the τ corresponding to the maximum correlation for each 30-min period were averaged to determine the daily lag time between the sonic signal and the fast isoprene sensor located on the ground (lag times ranged between 9–14 s); (3) hard spikes were removed from the raw data including errors from instrumentation and interference from weather such as rain; (4) coordinate rotation was performed on the 3 wind components to orient u in the mean wind direction [*Kaimal and Finnigan*, 1994] (5) Reynolds decomposition, based on a recursive filter technique with a running mean of 3-min, was used to compute averages and standard deviations for each variable; (6) soft-spikes were removed from the w component (vertical) of wind based on the magnitude of the standard deviation and the length of the spike as explained by *Schmid et al.* [2000]; (7) the means were removed from each variable creating the prime quantities; (8) instantaneous fluxes were calculated (taking into account appropriate lag times previously determined) as $w'c'$ where c is the scalar (or u' in the case of momentum); (9) 30-min average fluxes were determined for momentum, sensible heat, latent heat, CO_2, and isoprene; (10) the isoprene, CO_2, and latent heat fluxes were corrected for the effects of density fluctuations as described by *Webb et al.* [1980]; and lastly, (11) isoprene flux was corrected for the high-frequency loss due to transport through the sampling line using a ratio of the unfiltered heat flux to the low-pass-filtered heat flux [*Kaimal and Finnigan*, 1994; *Massman*, 2000; *Massman and Lee*, 2002].

3.2. Flux Uncertainties

[12] Systematic errors are consistent overreadings or underreadings of fluxes, and some examples of those associated with the eddy covariance method include: (1) sensor separation between the sonic and scalar measurements, (2) underpredicted nighttime fluxes due to drainage flow, (3) inadequate sensor response or flow distortion, (4) damping of high frequency fluctuations due to travel through a sample line, and (5) incorrect processing of fluxes.

[13] Filtering effects due to the path length of the sonic and the IRGA were assumed negligible and there were no spectral corrections applied to these signals. This assumption is based on the fact that the filtering effect due to path length is much smaller than the filtering effect due to a recursive filter provided that the height of the sensor above the surface level is much greater than the path length [*Massman and Lee*, 2002]. Cospectra of $w'T'$ (sensible heat flux), $w'H_2O'$ (latent heat flux), and $w'c'$ (CO_2 flux) were compared and their shapes were all similar with the expected slope of −7/3 [*Kaimal and Finnigan*, 1994] (data not shown but similar to Figure 2 in *Westberg et al.* [2001]). It was also assumed that the separation distance between sonic and IRGA contributed minimal flux loss (possible phase shifts) to the CO_2 and latent heat fluxes. Phase differences are small for relatively low frequencies, but they can be important for larger frequencies. For all years considered in this report, the horizontal separation distance between the IRGA and the sonic was 0.5 m. Based on work done by *Kristensen et al.* [1997], for a ratio of displacement (D) to measurement height (z), where D/z = 0.5/31 = 0.02, the measured flux is 98% of the "true" flux. Thus there were no frequency loss corrections applied to other fluxes except isoprene. The power density cospectra for $w'I'$ (isoprene flux) exhibited a similar shape as that presented in *Westberg et al.* [2001] with a cutoff frequency of ∼0.7 Hz. By integrating the area under the curve for a typical 30-min midday period and an idealized cospectrum, uncorrected 30-min averaged isoprene fluxes are approximately 17% low due to high frequency losses. A similar analysis done on the corrected isoprene flux (using the ratio of unfiltered heat flux to the low-pass-filtered heat flux) shows the correction increases the measured flux by

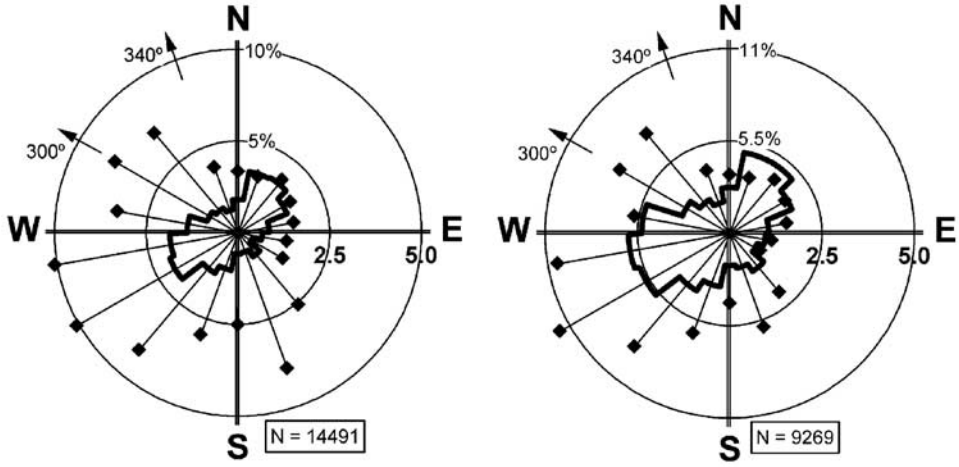

Figure 1. Polar plots of 30-min averaged isoprene fluxes (shown by black line, mg C m^{-2} h^{-1}) and the fraction of total wind (indicated by diamond points) sorted into 20° sectors for all years (1999–2002). Polar plot on the left is all data; polar plot on the right is only data with u* > 0.3 m s^{-1}. Sonic anemometer mounted at 300° in 1999–2001 and at 340° in 2002.

19%. Thus we feel this technique does an adequate job of correcting for high frequency losses due to tube attenuation and instrument response.

[14] Flux measurements made during periods of atmospheric stability, and flux measurements collected during periods when the mean wind passes through the tower have a higher level of uncertainty and in some cases may not be reliable. One tool used to filter reasonable flux measurements from those with higher uncertainties is the value of the friction velocity (u*, m s^{-1}). When the atmosphere is stable (typically during night time periods), u* values can be quite low (i.e., <0.3 m s^{-1}) which indicates generally calm or low winds, and low turbulence. Between 33 and 39% of the recorded flux data each year had u* values < 0.3 m s^{-1}. Almost all of these periods were at night. Measurements of eddy covariance fluxes during these periods can be very uncertain, and for H, LE, and CO_2 fluxes, this should be considered. However, the emission rate of isoprene is effectively zero at night. The first graph in Figure 1 shows a polar plot of the fraction of winds sorted by 20° sectors over all four years, and the second plot presents only the data with u* > 0.3 m s^{-1}. The same figure presents the average isoprene flux contributed from each 20° sector. Winds were predominantly from the west, and most of the time the source footprint for isoprene fluxes was to the west of the tower, with some contribution from the NE.

[15] It is also important to orient the sonic anemometer (and other sensors) to minimize interference from the tower structure. In 1999–2001 the sonic was oriented northwest at 300°, in 2002 the orientation was 340°. On average, about 24% of the time winds blew through the tower (between 75° and 165° for 1999–2001 and between 115° and 205° in 2002). Data corresponding to low u* values and to winds from behind the tower were left in the data set so as to not introduce a bias, since these data points typically are low value isoprene fluxes.

[16] To estimate the overall uncertainty in flux measurements, we can identify the uncertainties associated with each measurement (i.e., isoprene concentration, temperature, wind speed, etc.), and combine those with the errors associated with the theoretical assumptions inherent in the eddy covariance technique. Uncertainty associated with the sonic wind speed and temperature is 5%, for the CO_2 and H_2O fluxes the instrument uncertainty is 10%, and for isoprene concentrations the uncertainty is 20% (for 10 Hz operation). Combining these errors with estimates of the errors associated with the eddy covariance technique, we estimate that the uncertainty associated with H is ~20%, and for CO_2 and LE the uncertainty is ~30%. These are for daytime fluxes, and it is expected that uncertainties are probably greater for nighttime fluxes of H, LE, and CO_2. The maximum estimated uncertainty related to isoprene fluxes is on the order of 40%. Currently, the uncertainty in biogenic emission estimates is 50% or more [*Guenther et al.*, 2000; *Geron et al.*, 1997].

3.3. Environmental Measurements

[17] At the UMBS~Flux site, total vegetative area index (VAI) was measured periodically at over 30 locations on 6 transects using a LiCor LAI-2000 (Li-Cor Inc., Lincoln, NE) sensor, with full sky reference measured at the top of the tower. Figure 2 presents the evolution of VAI for each year between 1999 and 2002. Surveys were conducted to determine timing of bud break and fraction of foliation expansion for each species on-site. The vertical lines in Figure 2 represent full leaf out (>90%) for the two dominant isoprene emitting species (red oak and bigtooth aspen). As seen in the figure, leaf out during years 1999–2001 was fairly consistent (between 22 May (Day of Year (DOY) 142) and 1 June (DOY 152)); however, leaf out in 2002 was delayed until 18 June (DOY 169). Total VAI for 2002 was also greater than the other three years with a peak at 3.7 m^2 m^{-2} compared to 3.2–3.5 m^2 m^{-2}.

[18] Meteorological parameters were monitored continuously by the UMBS~Flux group, and all measurements were from the 46 m level of the UMBS~Flux tower. Above canopy R_n was recorded using an REBS Q*7.1 (REBS, Inc., Seattle, WA) net radiometer, PPFD (0.4–0.7 μm) was

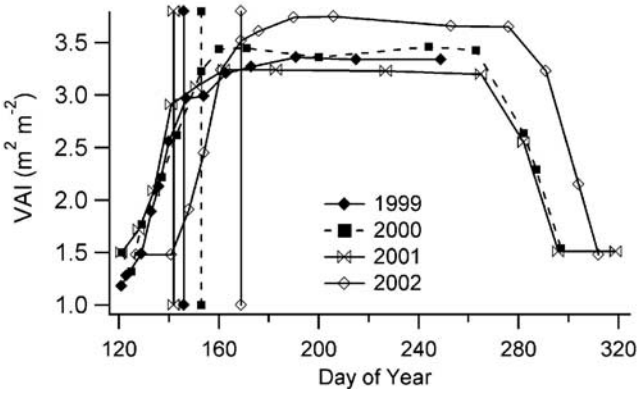

Figure 2. Evolution of total vegetative area index (VAI) (m^2 m^{-2}) over the growing seasons of 1999 to 2002. Vertical lines indicate the date of full leaf out (>90%) for red oak and bigtooth aspen combined. Note the delayed leaf out in 2002.

measured using a Li-Cor LI-190SZ quantum sensor, and short wave radiation (0.4–1.1 μm) was measured using a Li-Cor LI-200SA pyranometer. Rainfall was recorded using a Texas Electronics (model TR-525-M) tipping bucket, and a Rotronic probe (Rotronic Instrument Corp., Huntington, NY, model HPO-43) measured RH and temperature. Details regarding the UMBS∼Flux system setup can be found in *Schmid et al.* [2003] and *Curtis et al.* [2002].

3.4. Biogenic Emission Inventory System (BEIS3) Model

[19] Photochemical models used to predict tropospheric O_3 concentrations, particulate matter (PM), and other atmospheric pollutants require accurate estimates of biogenic emissions. The Biogenic Emission Inventory System 3 (BEIS3) is the current USEPA model for simulating all biogenic emissions, including isoprene [*Pierce et al.*, 2002]. Using the Biogenic Emission Land Dataset (BELD3) [*Kinnee et al.*, 1997], and isoprene emission rates at standard temperature and PPFD levels, BEIS3 estimates normalized biogenic emissions at the desired spatial and temporal (typically hourly) resolution. With above canopy meteorological inputs, the normalized emissions are adjusted for ambient temperature and light levels using the Guenther algorithm [*Guenther et al.*, 1993]. BEIS3 has also been implemented into the Sparse Matrix Operator Kernel Emissions (SMOKE) model [*Pierce et al.*, 2002] and the Community Multiscale Air quality Modeling System (CMAQ) [*Pierce et al.*, 2002]. This makes biogenic emis-

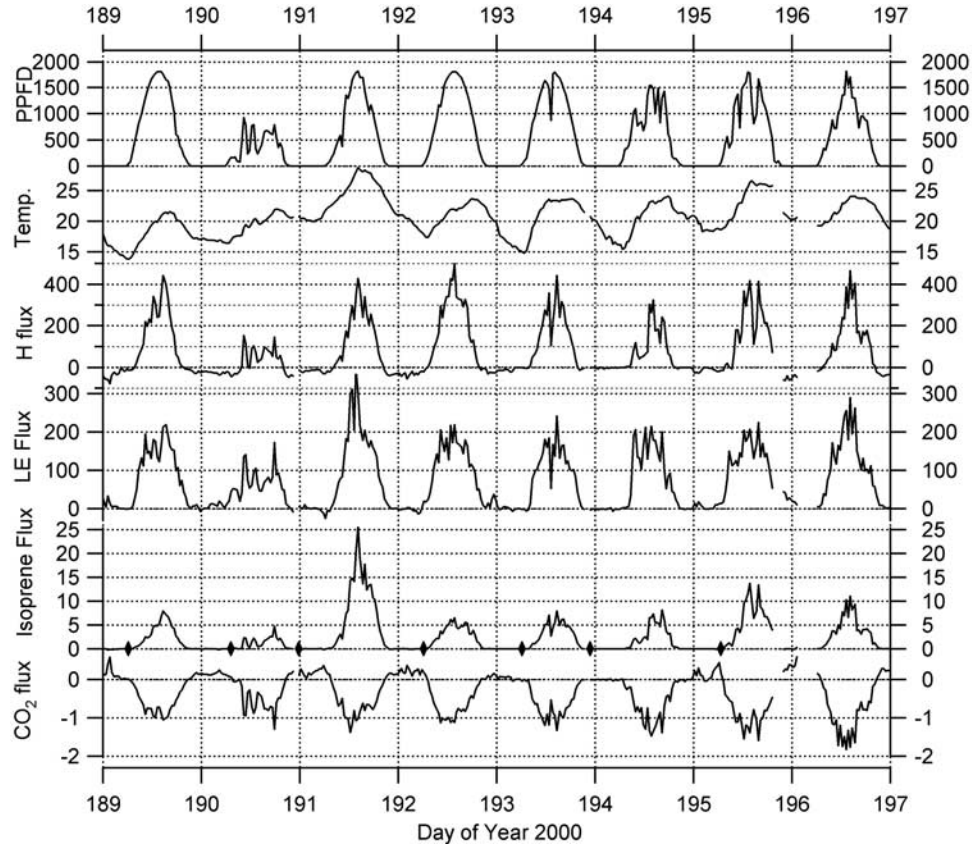

Figure 3. An example of typical 30-min averaged fluxes beginning 7 July 2000 (DOY 189) through 14 July 2000 (DOY 196). From the top, traces represent PPFD (μmol m^{-2} s^{-1}), ambient temperature (°C), sensible heat flux (H: W m^{-2}), latent heat flux (LE: W m^{-2}), isoprene flux (mg C m^{-2} h^{-1}), and CO_2 flux (mg m^{-2} s^{-1}). Diamond markers indicate FIS calibrations, and missing data indicate rain events.

Table 1. Climate and Phenology Comparison for Years 1999–2002

	1999	2000	2001	2002
Avg. air temp,[a] °C	18.0	16.3	17.7	17.0
Avg. soil temp,[a] 2cm, °C	16.1	14.7	15.7	14.0
Avg. PPFD,[a] W m^{-2}	113	108	100	97
Cum. Rain,[a] mm	300	466	239	318
Last frost[b]	18 April (108)	19 April (110)	18 April (108)	18 May (138)
Budbreak - aspen	8 May (128)	8 May (129)	8 May (128)	5 June (156)
Budbreak - red oak	5 May (125)	8 May (129)	3 May (123)	22 May (142)
Full Leaf out (>90%)	16 May (146)	1 June (153)	22 May (142)	18 June (169)

[a]The average air temperature, soil temperature, PPFD, and cumulative rainfall were determined only for 123 days from 1 May through 31 August (DOY 121–243).
[b]The last frost is the last day in spring when the 21 m air temperature < 0.5°C.

sion inventory development more integrated with the latest photochemical models.

4. Results

[20] Measurements were made continuously each year from roughly mid-May through mid-October. Minor interruptions were caused by instrument calibrations, data transfer, weather events (i.e., rain), and routine sensor maintenance. There were some larger data gaps due to instrument failures. In 1999, a light-leak in the FIS developed slowly over the course of the summer, which ultimately resulted in unreliable isoprene emissions for most of the summer. Data acquisition problems delayed the start date in 2001 until after the onset of isoprene emissions, and the flux system was turned off earlier than expected in the fall (mid-September) due to computer problems. In 2002, the IRGA was not operational for approximately 4 weeks from early July to early August, at which point a replacement IRGA was installed. Combining all four years, there was on average 133 days of measurements resulting in an average of 4130 half-hour periods of data each year. Approximately 12% of the data each year was discarded due to sensor malfunction during extreme weather conditions (i.e., rain or power outages). Sensor calibration and sensor repair/maintenance (not including the FIS light leak) accounted for 3–9% of unusable 30-min periods. If data gaps due to sensor calibration or maintenance exceeded 15 min, then the entire 30-min period was considered a missing observation. Overall, approximately 21% of the data used to determine the energy and CO_2 fluxes was discarded. Of the data required to generate isoprene fluxes, approximately 31% was discarded due to operational problems (again, not including the 1999 light leak).

4.1. Seasonal Course of Energy and Isoprene Fluxes

[21] Eight typical days of measurements are shown in Figure 3. The figure presents PPFD (μmol m^{-2} s^{-1}), ambient temperature (°C), H and LE (W m^{-2}), isoprene flux (mg C m^{-2} h^{-1}), and CO_2 flux (mg m^{-2} s^{-1}) beginning on 7 July 2000 (DOY 189). The diamonds indicate FIS calibration events, and data gaps indicate rain events. All the fluxes show a diurnal profile, with isoprene fluxes and the energy fluxes (H + LE) highly correlated with PPFD and temperature. For example, day 190 was cloudy with relatively low temperatures (18–22°C midday), consequently neither sensible heat flux nor latent heat flux reached 200 W m^{-2}, and isoprene flux was less than 5 mg C m^{-2} h^{-1} all day. On the next day (191), temperatures increased by 10°C, sensible and latent heat fluxes doubled (~400 W m^{-2}), and isoprene fluxes quintupled (25.5 mg C m^{-2} h^{-1}). The peak isoprene emission for the year in 2000 occurred on this day, and it illustrates the large variation in isoprene fluxes that can occur from one day to the next. These examples show how closely linked isoprene is with environmental parameters (temperature and PPFD) and consequently the energy fluxes (H and LE). Another example can be seen by studying days 192–195. The diel temperature profiles for days 192, 193 and 194 were practically identical, and as expected isoprene fluxes for those 3 days were fairly consistent. Temperatures increased by almost 5°C on day 195 and isoprene fluxes followed suit by doubling in magnitude. Variations from one 30-min period to the next were also quite high for all of the flux measurements, as seen in the ''sawtooth'' shapes. Similar patterns and shapes can be seen in the day-to-day fluxes each year.

[22] The measurements (PPFD, temperature, LE, H, and isoprene flux) during each year are summarized in Table 1 and presented in Figure 4. This figure presents the daily average of each measurement (the dark line) along with the daily maximum and minimum (shaded bars) for all sampling days in 1999–2002. Due to incomplete measurements in 1999, the following discussion focuses on years 2000–2002 only. Daily average isoprene fluxes for 2000–2002 ranged from 1.1 to 1.4 mg C m^{-2} h^{-1}, and average midday (10:00 a.m. to 4:00 p.m.) isoprene fluxes were 2.8, 3.2 and 2.9 mg C m^{-2} h^{-1} for 2000–2002, respectively (Table 2). Peak emissions occurred on 9 July 2000 (25.5 mg C m^{-2} h^{-1} DOY 191), 9 August 2001 (18.3 mg C m^{-2} h^{-1} DOY 221) and 1 July 2002 (13.3 mg C m^{-2} h^{-1} DOY 182). Year 2001 was the warmest and the driest of the three years, with approximately half of the rainfall compared to 2000. This is probably the reason that the highest average isoprene flux occurred in 2001 (1.4 mg C m^{-2} h^{-1}). For comparison, eight days of relaxed eddy accumulation (REA) fluxes were measured in 1997 from the PROPHET tower and the isoprene flux measurements peaked near 12 mg C m^{-2} h^{-1}. In 1998, both eddy covariance and REA flux measurements were collected from the UMBS~Flux tower over a span of 5 weeks, and peak levels approached 11.0 mg C m^{-2} h^{-1} [*Westberg et al.*, 2001].

[23] For years 2000 and 2002 in particular, there is a gradual increase of isoprene emissions, then during the middle of the summer, variations in isoprene are linked to variations in temperature and light, and in the late summer/

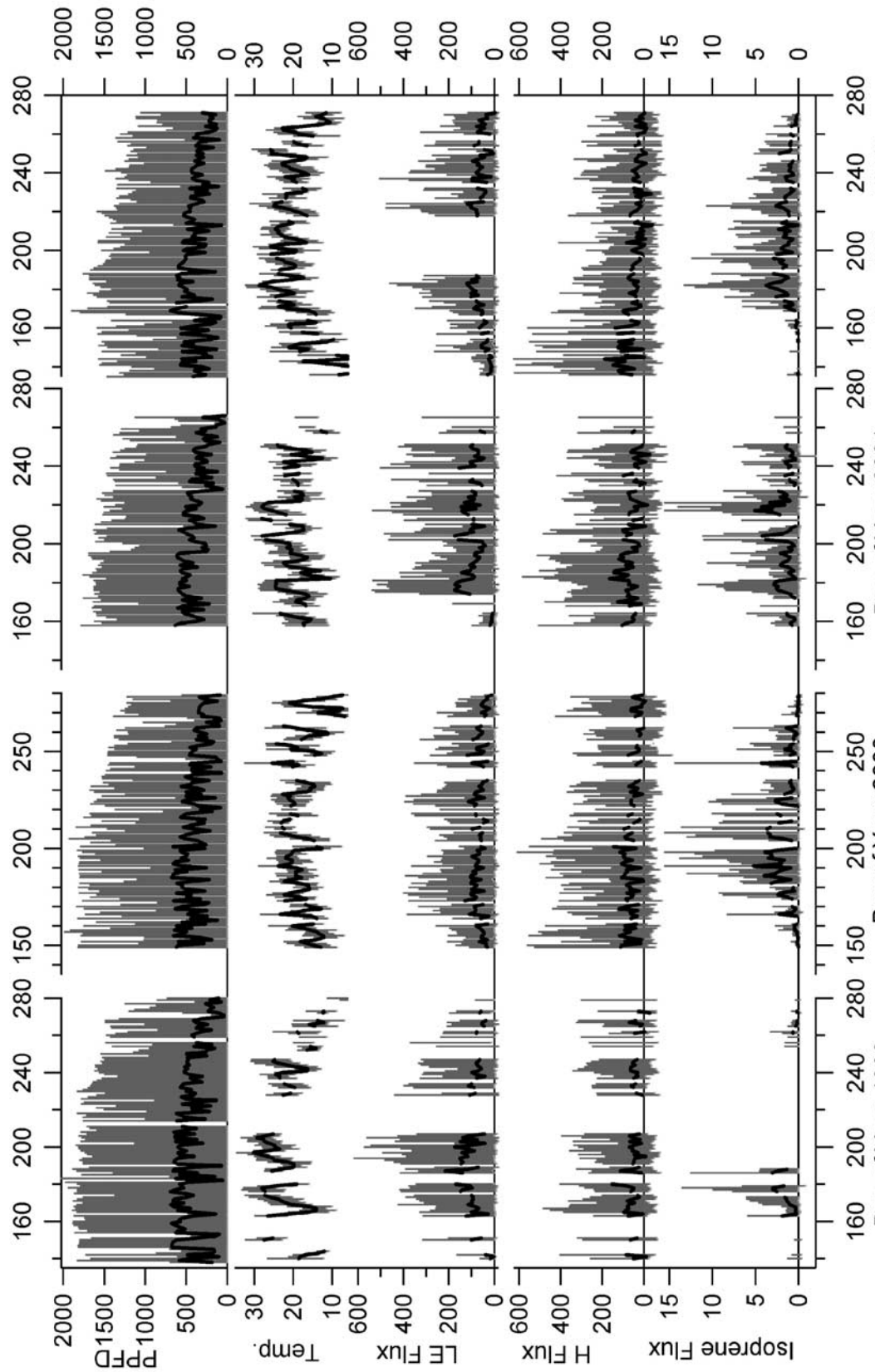

Figure 4. Daily average PPFD (μmol m^{-2} s^{-1}), ambient temperature (°C), latent heat flux (LE: W m^{-2}), sensible heat flux (H: W m^{-2}), and isoprene flux (mg C m^{-2} h^{-1}) indicated by dark traces. Range (maximum and minimum) of daily values indicated by gray colored bars.

Table 2. Isoprene Emission Annual Characteristics and Heating Degree-Day (°D) Benchmarks

	1999	2000	2001	2002
Budbreak bigtooth aspen	230°D	240°D	244°D	193°D
Budbreak red oak	188°D	240°D	181°D	26°D
Full Leaf out (>90%)	438°D	507°D	437°D	406°D
Earliest isoprene detection	10 June (161)	31 May (152)	NA	9 June (160)
Fully developed emissions	13 June (164)	6 June (158)		13 June (164)
Max. F_{iso}, mgC m^{-2} h^{-1}	14.7	25.5	18.3	13.3
Avg. F_{iso}, mgC m^{-2} h^{-1}	NA	1.2	1.4	1.1
Avg. Midday F_{iso}, mgC m^{-2} h^{-1}	NA	2.8	3.2	2.9
Cum. Isoprene,[a] mgC m^{-2} (*n*)	NA	2699 (3601)	2487(3637)	2454 (3780)

[a]Cumulative isoprene fluxes for 6 June (DOY 158) through 21 September (DOY 265) in mg C m^{-2}, and (*n*) number of 30-min periods included in sum.

early fall there is a gradual decline in emissions. There is insufficient data in 1999 and 2001 to see the complete seasonal pattern. The onset of isoprene emissions and fully developed emission rates are discussed in the next section. Regardless of when isoprene emissions begin, however, the cumulative isoprene emissions for each year appear to remain fairly consistent. Cumulative isoprene emissions are shown in Figure 5. The annual cumulative total isoprene emissions are presented in Table 2. The average cumulative isoprene emission for days 158–265 during years 2000–2002 is 2547 ± 133 mg C m^{-2}. The variation between each year is less than 10%. The cumulative isoprene emissions may be slightly underestimated due to (1) not including the period during which isoprene emissions are gradually increasing (pre-day 158), and (2) missing observational data. For 2000 and 2002 (the years which we have observations during the spring/early summer), including all available observations only increased the cumulative emissions by 1%. If we assume these are annual isoprene emissions, and based on the long-term measurements of net ecosystem exchange (NEE) reported by *Schmid et al.* [2003], isoprene emissions account for 1.7% in 2000 and 3.1% in 2001 of the net carbon uptake (net ecosystem production (NEP) for 2000 = 160, and NEP for 2001 = 80 g C m^{-2}). The fraction of carbon emitted as isoprene is typically between 0.1 and 3% for most sites, and it has been reported at 2% in 1995 for the Harvard forest (annual isoprene emission = 4.2 g C m^{-2}, NEP = 220 g C m^{-2}) [*Goldstein et al.*, 1998].

4.2. Onset of Isoprene Emissions

[24] Isoprene emission rates are typically delayed from bud break for up to 2–4 weeks in some cases, and most plants do not reach their fully developed emission rates (basal emission rate) until full leaf development and expansion [*Monson et al.*, 1994; *Fuentes et al.*, 1999]. Several methods for estimating the onset of isoprene emissions as a function of phenology for modeling purposes have been proposed including growing days [*Monson et al.*, 1994], effective temperature sum [*Hakola et al.*, 1998, 2000], and heating degree-days (H°D) [*Geron et al.*, 2000]. Heating degree-days are measured using the cumulative average daily temperature (°C) since the last spring frost. Table 1 summarizes the dates of the phenological stages, and Table 2 summarizes the associated heating degree-days. The last spring frost occurred between days 108 and 110 for years 1999–2001, with bigtooth aspen budbreak following approximately 20 days later when 230–244°D was reached. Red oak budbreak was much more variable from year-to-year. Full leaf out (>90%) for both species, and the onset of isoprene emissions, occurred approximately 40 days after the last frost when heating-degree days reached between 437–507°D. These three years (1999–2001) appear to be the average, while 2002 was quite different. The last spring frost in 2002 was one month later than the previous years, yet full leaf out and fully developed isoprene emissions occurred 26–31 days after last frost at approximately 406°D. In comparison, 1000°D was required to reach fully developed isoprene emissions from white oak (*Q. alba* L.) at the Duke Forest in North Carolina [*Geron et al.*, 2000], and 1050°D was needed at Harvard Forest [*Goldstein et al.*, 1998].

4.3. Energy Budget

[25] One simple tool that may indicate systematic errors in a flux measurement system is to balance the surface energy budget by comparing total energy input into the system with the sum of energy output from the system: $R_n - S - G - Q = LE + H$. Where R_n is net radiation, S is the rate of change of heat storage (air and biomass) between

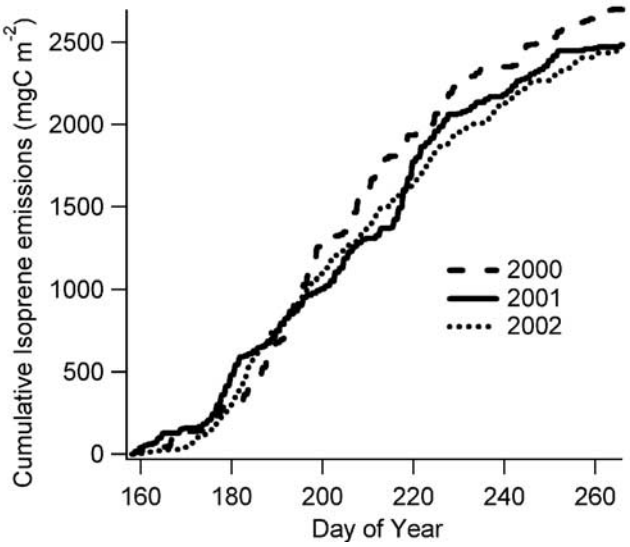

Figure 5. Cumulative isoprene emissions for years 2000–2002 in mg C m^{-2} beginning on day 158 (6 or 7 June) through day 265 (21 or 22 September). Long dashed line (2000, *n* = 3601), solid black line (2001, *n* = 3637), and short dashed line (2002, *n* = 3780).

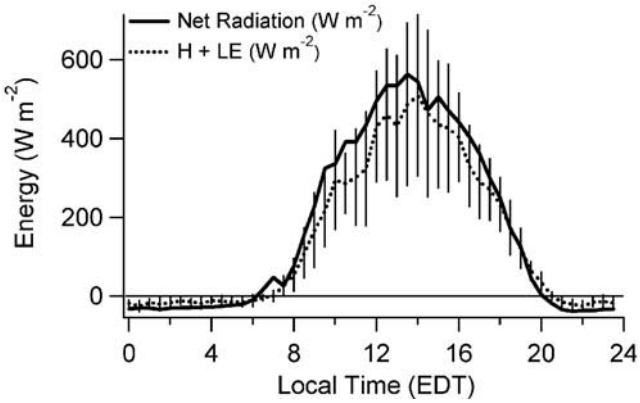

Figure 6. Energy balance for days shown in Figure 2, 7–14 July 2000 (DOY 189–196). Solid black line is net radiation in W m^{-2}, and dashed line is the sum of eddy covariance measurements of latent (LE) plus sensible heat (H) flux (W m^{-2}). Variations of H and LE between each day are shown by the vertical bars, which represent ±1 standard deviation.

the ground level and the measurement height, G is the soil heat flux, Q is the sum of all additional energy sources and sinks, (i.e., photosynthesis), and LE and H are latent and sensible heat flux, respectively. Soil heat flux was not available for analysis, Q is typically neglected as a small term, and over long time periods S is approximately zero. The average diel course of net radiation typically exceeds the sum of H and LE by 50–100 W m^{-2} during the middle of the day, while at night the outgoing radiation is greater (in magnitude) than the sum of H and LE by about 20 W m^{-2} (Figure 6). For each year, the ordinary least squares (OLS) regression between 30-min average H+LE versus R_n was performed using all of the available data [*Massman and Lee*, 2002; *Wilson et al.*, 2002]. For all four years, results indicated that the energy fluxes were less than the available energy by 10–30%. The slopes of the OLS regressions for each year were 0.81, 0.81, 0.85, and 0.75 for years 1999–2002, respectively. Soil heat flux and canopy storage were not included in this analysis, and based on *Wilson et al.* [2002], including canopy storage can increase the slope on average by 7%, and including soil heat flux can increase the slope on average by 3%. Overall, the energy balance results for 1999–2002 compare quite well with results from other eddy covariance flux sites [*Su et al.*, 2004; *Wilson et al.*, 2002] which can indicate the general soundness of a system and the associated methods of analysis [*Schmid et al.*, 2003].

4.4. Comparison With BEIS3

[26] Isoprene emissions were estimated using the BEIS3 model for years 2000–2002. BEIS3 biogenic emissions from the 1 km grid from the BELD3 database that encompassed the site were compared to the observational data. For all model runs, hourly observational meteorological data including above canopy temperature (K), atmospheric pressure (Pa), and short-wave radiation (W m^{-2}) were used to drive the BEIS3 model. Originally, the default emission factors and BELD3 1 km resolution land classifications were employed; however, isoprene observations were 2–3 times larger than those predicted. Based on these results, the land use data were modified to better reflect the species present at UMBS. Land use categories were set to zero for all species except the two dominant isoprene emitters, Populus and Northern Red Oak. Based on biomass density data from the UMBS∼Flux group, 76% and 24% were assumed for the proportion of Populus and Northern Red Oak, respectively. The BEIS3 emission factor table was also

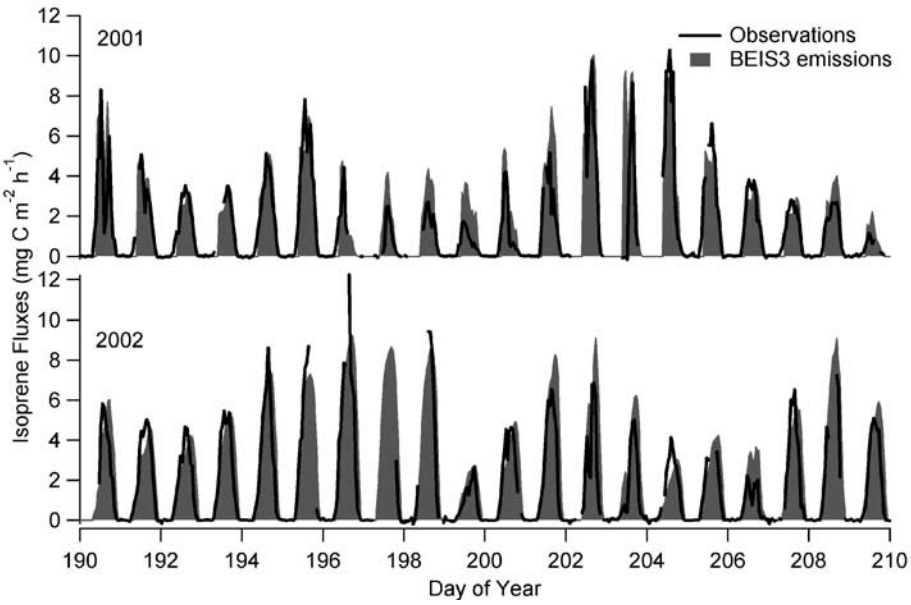

Figure 7. Measured isoprene fluxes (solid black line) versus BEIS3 predicted isoprene emissions (shaded areas) for days 9 July (DOY 190) through 28 July (DOY 209) for 2001 (top graph) and 2002 (bottom graph). Thirty-minute observational data were averaged to create hourly data for comparison with BEIS3.

Table 3. Model Evaluation Statistics for BEIS3 Versus Observations for the Days Indicated in the Table During Years 2000–2002[a]

	2000	2001	2002
Days included	165–265	160–250	170–255
Mean bias, mg C m^{-2} h^{-1}	−0.68	0.46	0.24
Mean error, mg C m^{-2} h^{-1}	1.69	1.25	1.08
Fractional bias, %	12	13	9
Fractional error, %	65	43	31
Normalized mean square error (all days)	1.5	0.62	0.95

[a]Note: $Mean\ Bias = \frac{1}{N}\sum_{i=1}^{N}(Cm - Co)$, $Mean\ Error = \frac{1}{N}\sum_{i=1}^{N}|Cm - Co|$, $Fractional\ Bias = \frac{1}{N}\sum_{i=1}^{N}\frac{(Cm - Co)}{\left(\frac{Co + Cm}{2}\right)}$, $Fractional\ Error = \frac{1}{N}\sum_{i=1}^{N}\frac{|Cm - Co|}{\left(\frac{Co + Cm}{2}\right)}$, and $Normalized\ Mean\ Square\ Error = \frac{\overline{(Co_i - Cm_i)^2}}{\overline{Co}\ \overline{Cm}}$, where Co is magnitude of the observation and Cm is the modeled or predicted magnitude.

modified with a biomass density of 183 g m^{-2} (compared to the default value of 375 g m^{-2}), and an LAI of 4 instead of 5 m^2 m^{-2}. These two values reflect the total isoprene emitting biomass, since all other land use categories were set to zero. The default BEIS3 standard emission factors for Populus and Northern Red Oak were used (70 μg C g^{-1} h^{-1}). All three years were simulated using these same land use and biomass data. Previous work with BEIS3 isoprene emission estimates for this site is presented in *Apel et al.* [2002]. In that study, measured isoprene fluxes were compared to BEIS3 estimates for a period in 1998. Similarly, the biomass density was modified based on local measurements, and an LAI of 3.5 m^2 m^{-2} was used in lieu of the BEIS3 default values [*Apel et al.*, 2002]. Model results presented in that study are very similar to the results presented here for 2000 through 2002.

[27] With the site-specific biomass data, BEIS3 does a good job of estimating isoprene emissions over all three years. Model results for 20 days in 2001 and 2002 are shown in Figure 7, compared to the measured isoprene fluxes. As shown, the model slightly tends to overestimate emissions for most days (i.e., DOY 197 through 201, 2001), with the exception of days where observed isoprene fluxes are quite large and the predicted emissions are typically less than those observed (i.e., DOY 195 and 196, 2002). Model statistics were determined for all three years and they are summarized in Table 3. The gradual increase of emissions early during the measurement period and the decline of emissions during leaf senescence are not captured correctly by BEIS3, as the version of BEIS3 used in this study (version 3.09) did not include any seasonal adjustments. Therefore the model statistics reported in Table 3 are for midsummer days only when the basal emission rate is assumed to be fairly constant. Results for mean bias indicate that on average BEIS3 slightly overestimates observations for 2001 and 2002, yet BEIS3 slightly underestimates measured isoprene fluxes in 2000. Mean errors range from 1.08 to 1.69 mg C m^{-2} h^{-1}, with BEIS3 predictions for 2002 having the lowest mean error. Fractional bias and fractional errors are also reported, with the lowest fractional error reported for 2002 (31%) and the highest fractional error during 2000 (65%).

[28] For the midsummer period (days 158–265), when observational isoprene flux data are available, the BEIS3 cumulative isoprene emissions are 2087, 2771, and 3854 mg C m^{-2} for 2000–2002, respectively. This corresponds to a difference of −23%, +11%, and +57% between the observations (Table 2) and BEIS3 predictions for 2000–2002, respectively. The large overpredictions in 2001 and 2002 could be due to the BEIS3 inability to model the decline in observational emissions late in the season when temperatures are still somewhat elevated; however, this does not explain the BEIS3 underprediction for 2000. The variation among the three years using the BEIS3 predictions is also much greater than the variations in observations. The average BEIS3 isoprene accumulation (for all periods) is 3550 ± 982 mg C m^{-2}, with the difference between 2000 and 2002 almost 60%. We have no explanation for this phenomenon. The fraction of net carbon uptake emitted as isoprene for 2001 increases with the BEIS3 estimate to 4.2%, which is probably an overestimate.

[29] Predicted versus observed comparisons from other sites show similar results to those presented here. Overall model performance is reported in several papers in terms of normalized mean square error (NMSE) (equation presented in Table 3). Good model performance is indicated by NMSE < 0.4 and poor model performance is indicated by NMSE > 4 [*Lamb et al.*, 1996]. NMSE results for this northern Michigan site, including all available observational data, were 1.5, 0.62, and 0.95 for 2000–2002, respectively. *Lamb et al.* [1996] reports a range of NMSE of 0.4 to 1.3 for different versions of a canopy model compared to measurements made in a mixed deciduous forest near Oak Ridge, TN. *Geron et al.* [1997] reports NMSE values ranging from 0.44 to 1.06 for various modifications to the BEIS2 model compared to measured above canopy relaxed eddy accumulation fluxes at the Duke University Research Forest in NC. Lastly, gradient measurements of above canopy isoprene fluxes were compared to BEIS2 predictions at the Harvard Forest, with midday measurements typically exceeding model estimates by 40% [*Goldstein et al.*, 1998]. In summary, model predictions are still within 40–50% of observed fluxes, with the average fractional error for all three years at this site equal to 46%.

[30] The results presented here provide an excellent example of the progress made over the past 10 years in the development of the BEIS model. In most cases where isoprene measurements are collected, detailed biomass data is also collected. Thus the land use data in BEIS can be modified to match the location of the observations. Provided accurate land use data and vegetation emission factors, BEIS does a good job of accurately estimating isoprene emissions. Work has been done to improve land use data at the resolution needed for atmospheric modeling; however, based on the results presented here additional work in this area is needed.

5. Conclusions

[31] Canopy scale emissions of isoprene from a northern hardwood forest in Michigan were measured using the eddy covariance technique during the summer growing periods from 1999 through 2002. With the exception of 1999, fluxes of isoprene, CO_2, H and LE were measured almost continuously from mid-May through the end of September and provide an unprecedented long-term isoprene flux data set. Day-to-day variations in isoprene flux can be quite significant (factor of 5), yet the average daily isoprene flux for each year is quite consistent, with an overall variation of

30% (1.2, 1.4, and 1.1 mg C m^{-2} h^{-1}). The warmest and driest year, 2001, had the highest average midday isoprene flux (3.2 mg C m^{-2} h^{-1}), but the largest 30-min isoprene flux occurred in 2000 (25.5 mg C m^{-2} h^{-1}) when the 30-min averaged temperature was 28.8 °C and PPFD was 1810 W m^{-2}. Total cumulative isoprene emissions between years 2000–2002 were within 10% of each other, regardless of the differing phenological cycles each year. Last frost was delayed by roughly one month, and full leaf out was delayed by roughly 2.5 weeks in 2002, compared to the other 3 years. Isoprene emissions were fully developed in 1999 roughly 18 days after full leaf out, but in 2000 and 2002 isoprene emissions were fully developed shortly after leaf out (5 days in 2000) or before full leaf out (2002). Thus, for this site, isoprene emissions are fully developed between 400–500 °D, which is less than half the heating degree-days required at either the Duke Forest or the Harvard Forest.

[32] Based on our analysis of the long-term flux data, we find that there is variation from day-to-day that current biogenic emission models cannot completely simulate, and the seasonal onset and decline of isoprene emissions is also an important aspect that current models do not predict correctly. The use of heating degree days to estimate the onset of emissions may improve model estimates; however, as previously pointed out, the emissions appear to "turn on" at different times, possibly as a function of ecosystem development. Although daily variations in isoprene emissions can be quite large, it appears that annual variations are surprisingly small. Model results again show the strong dependence of isoprene on the environmental drivers (temperature and light), but there are obviously additional environmental parameters that affect isoprene emissions. Continued work in this area will improve our understanding of what drives isoprene emissions. Meanwhile, this long-term isoprene flux data set will be instrumental for further evaluation of canopy scale models that are used to generate emission inventories for regional photochemical models.

[33] **Acknowledgments.** This research is part of the PROPHET and UMBS∼Flux programs at the University of Michigan Biological Station. The authors wish to thank the National Science Foundation (NSF) and EPA for funding the research, and both the PROPHET and UMBS∼Flux teams for their expertise and the use of their tower and laboratory facilities. The NSF Integrated Graduate Education Research Training (IGERT) program administered by Western Michigan University and entitled Biosphere Atmosphere Research Training (BART); and the NSF Research Experience for Undergraduates (REU) Program provided support for this research. We would like to acknowledge the help provided by Grant Hatten as an REU. Support was also provided through a Boeing endowment to Washington State University. The UMBS∼Flux research was supported by the Office of Science (BER) Program, U.S. Department of Energy (DOE), and through its Midwest Regional Center of the National Institute for Global Environmental Change (NIGEC) under cooperative agreement DE-FC03-90ER61010. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the DOE.

References

Andreae, M. O., and P. J. Crutzen (1997), Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, *Science*, *276*, 1052–1058.

Apel, E. C., et al. (2002), Measurement and interpretation of isoprene fluxes and isoprene, methacrolein, and methyl vinyl ketone mixing ratios at the PROPHET site during the 1998 intensive, *J. Geophys. Res.*, *107*(D3), 4034, doi:10.1029/2000JD000225.

Atkinson, R. (2000), Atmospheric chemistry of VOCs and NO_x, *Atmos. Environ.*, *34*, 2063–2101.

Auble, D. L., and T. P. Meyers (1992), An open path, fast response infrared absorption gas analyzer for H_2O and CO_2, *Boundary Layer Meteorol.*, *59*, 243–256.

Baldocchi, D., A. Guenther, P. Harley, L. Klinger, P. Zimmerman, B. Lamb, and H. Westberg (1995), The fluxes and air chemistry of isoprene above a deciduous hardwood forest, *Philos. Trans. R. Soc. London., Ser. A*, *351*, 279–296.

Baldocchi, D., et al. (2001), FLUXNET: A new tool to study the temporal and spatial variability of ecosystem-scale carbon dioxide, water vapor and energy flux densities, *Bull. Am. Meteorol. Soc.*, *82*, 2415–2434.

Carroll, M. A., S. B. Bertman, and P. B. Shepson (2001), 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.

Curtis, P. S., P. J. Hanson, P. Bolstad, C. Barford, J. C. Randolph, H. P. Schmid, and K. B. Wilson (2002), Biometric and eddy-covariance based estimates of annual carbon storage in five eastern North American deciduous forests, *Agric. For. Meteorol.*, *113*, 3–19.

Fall, R., and R. Monson (1992), Isoprene emission rate and intercellular isoprene concentration as influenced by stomatal distribution and conductance, *Plant Physiol.*, *100*, 987–992.

Fehsenfeld, F., J. Calvert, R. Fall, P. Goldan, A. Guenther, and C. N. Hewitt (1992), Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry, *Global Biogeochem. Cycles*, *6*, 389–430.

Fuentes, J. D., D. Wang, and L. Gu (1999), Seasonal variations in isoprene emissions from a Boreal Aspen forest, *J. Appl. Meteorol.*, *38*, 855–869.

Geron, C., D. Nie, R. R. Arnts, T. D. Sharkey, E. L. Singsaas, P. J. Vanderveer, A. Guenther, J. E. Sickles, and T. E. Kleindienst (1997), Biogenic isoprene emission: Model evaluation in a southeastern United States bottomland deciduous forest, *J. Geophys. Res.*, *102*, 18,889–18,901.

Geron, C., A. Guenther, T. Sharkey, and R. R. Arnts (2000), Temporal variability in basal isoprene emission factor, *Tree Physiol.*, *20*, 799–805.

Goldstein, A. H., M. L. Goulden, J. W. Munger, S. C. Wofsy, and C. D. Geron (1998), Seasonal course of isoprene emissions from a midlatitude deciduous forest, *J. Geophys. Res.*, *103*, 31,045–31,056.

Guenther, A., and A. J. Hills (1998), Eddy covariance measurement of isoprene fluxes, *J. Geophys. Res.*, *103*, 13,145–13,152.

Guenther, A., P. R. Zimmerman, P. C. Harley, R. K. Monson, and R. Fall (1993), Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses, *J. Geophys. Res.*, *98*, 12,609–12,617.

Guenther, A., et al. (1996a), Isoprene fluxes measured by enclosure, relaxed eddy accumulation, surface layer gradient, mixed layer gradient, and mixed layer mass balance techniques, *J. Geophys. Res.*, *101*, 18,555–18,567.

Guenther, A., J. Greenberg, P. Harley, D. Helmig, L. Klinger, L. Vierling, P. Zimmerman, and C. Geron (1996b), Leaf, branch, stand and landscape scale measurements of volatile organic compound fluxes from US woodlands, *Tree Physiol.*, *16*, 17–24.

Guenther, A., C. Geron, T. Pierce, B. Lamb, P. Harley, and R. Fall (2000), Natural emissions of non-methane volatile organic compounds; carbon monoxide, and oxides of nitrogen from North America, *Atmos. Environ.*, *34*, 2205–2230.

Hakola, H., J. Rinne, and T. Laurila (1998), The hydrocarbon emission rates of tea-leafed willow (*Salix phylicifolia*), silver birth (*Betula pendula*) and European aspen (*Populus tremula*), *Atmos. Environ.*, *32*, 1825–1833.

Hakola, H., T. Laurila, J. Rinne, and K. Puhto (2000), The ambient concentrations of biogenic hydrocarbons at a northern European boreal site, *Atmos. Environ.*, *34*, 4971–4982.

Harley, P., M. E. Litvak, T. D. Sharkey, and R. K. Monson (1994), Isoprene emission from Velvet Bean-leaves—Interactions among nitrogen availability, growth photon flux-density, and leaf development, *Plant Physiol.*, *105*, 279–285.

Harley, P., A. Guenther, and P. Zimmerman (1996), Effects of light, temperature and canopy position on net photosynthesis and isoprene emission from Sweetgum (*Liquidambar Styraciflua*) leaves, *Tree Physiol.*, *16*, 25–32.

Hills, A. J., and P. R. Zimmerman (1990), Isoprene measurement by ozone-induced chemiluminescence, *Anal. Chem.*, *62*, 1055–1060.

Hsieh, C.-I., G. Katul, and T. Chi (2000), An approximate analytical model for footprint estimation of scalar fluxes in thermally stratified atmospheric flows, *Adv. Water Resour.*, *23*, 765–772.

Jiang, G., B. Lamb, and H. Westberg (2003), Using back trajectories and process analysis to investigate photochemical ozone production in the Puget Sound region, *Atmos. Environ.*, *37*, 1489–1502.

Kaimal, J. C., and J. J. Finnigan (1994), *Atmospheric Boundary Layer Flows: Their Structure and Measurement*, Oxford Univ. Press, New York.

Kinnee, E., C. Geron, and T. Pierce (1997), United States land use inventory for estimating biogenic ozone precursor emissions, *Ecol. Appl.*, *7*, 46–58.

Kristensen, L., J. Mann, S. P. Oncley, and J. C. Wyngaard (1997), How close is close enough when measuring scalar fluxes with displaced sensors?, *J. Atmos. Oceanic Technol.*, *14*, 814–821.

Kuzma, J., and R. Fall (1993), Leaf isoprene emissions rate is dependent on leaf development and the level of isoprene synthase, *Plant Physiol.*, *101*, 435–440.

Lamb, B., H. Westberg, E. Allwine, and T. Quarles (1985), Biogenic hydrocarbon emissions from deciduous and coniferous trees in the United States, *J. Geophys. Res.*, *90*, 2380–2390.

Lamb, B., et al. (1996), Evaluation of forest canopy models for estimating isoprene emissions, *J. Geophys. Res.*, *101*, 22,787–22,797.

Lichtenthaler, H. K., J. Schwender, A. Disch, and M. Rohmer (1997), Biosynthesis of isoprenoids in higher plant chloroplasts proceeds via a mevalonate-independent pathway, *FEBS Lett.*, *400*, 271–274.

Logan, B. A., R. K. Monson, and M. J. Potosnak (2000), Biochemistry and physiology of foliar isoprene production, *Trends Plant Sci.*, *5*, 477–481.

Loreto, F., and V. Velikova (2001), Isoprene produced by leaves protects the photosynthetic apparatus against ozone damage, quenches ozone products, and reduces lipid peroxidation of cellular membranes, *Plant Physiol.*, *127*, 1781–1787.

Massman, W. J. (2000), A simple method for estimating frequency response corrections for eddy covariance systems, *Agric. For. Meteorol.*, *104*, 185–198.

Massman, W. J., and X. Lee (2002), Eddy covariance flux corrections and uncertainties in long-term studies of carbon and energy exchanges, *Agric. For. Meteorol.*, *113*, 121–144.

Monson, R., C. Jaeger, W. Adams, E. Driggers, G. Silver, and R. Fall (1992), Relationships among isoprene emission rate, photosynthesis, and isoprene synthesis, as influenced by temperature, *Plant Physiol.*, *92*, 1175–1180.

Monson, R., P. C. Harley, M. E. Litvak, M. Wildermuth, A. B. Guenther, P. R. Zimmerman, and R. Fall (1994), Environmental and developmental controls over the seasonal pattern of isoprene emission from aspen leaves, *Oecologia*, *99*, 260–270.

Pierce, T., C. Geron, G. Pouliot, E. Kinnee, and J. Vukovich (2002), Integration of the Biogenic Emissions Inventory System (BEIS3) into the Community Multiscale Air Quality modeling system, paper presented at 25th Agricultural and Forest Meteorology Meeting, Am. Meteorol. Soc., Norfolk, Va.

Poisson, N., M. Kanakidou, and P. J. Crutzen (2000), Impact of non-methane hydrocarbons on tropospheric chemistry and the oxidizing power of the global troposphere: 3-dimensional modeling results, *J. Atmos. Chem.*, *36*, 157–230.

Schmid, H. P., C. S. B. Grimmond, F. Cropley, B. Offerle, and H.-B. Su (2000), Measurements of CO_2 and energy fluxes over a mixed hardwood forest in the midwestern United States, *Agric. For. Meteorol.*, *103*, 357–374.

Schmid, H. P., H.-B. Su, C. S. Vogel, and P. S. Curtis (2003), Ecosystem-atmosphere exchange of carbon dioxide over a mixed hardwood forest in northern lower Michigan, *J. Geophys. Res.*, *108*(D14), 4417, doi:10.1029/2002JD003011.

Sharkey, T. D., and S. S. Yeh (2001), Isoprene emission from plants, *Ann. Rev. Plant Physiol. Plant Mol. Biol.*, *52*, 407–436.

Sharkey, T. D., F. Loreto, C. F. Delwiche, and I. W. Treichel (1991), Fractionation of carbon isotopes during biogenesis of atmospheric isoprene, *Plant Physiol.*, *97*, 463–466.

Silver, G. M., and R. Fall (1991), Enzymatic synthesis of isoprene from dimethylallyl diphosphate in aspen leaf extracts, *Plant Physiol.*, *97*, 1588–1591.

Singsaas, E. L., M. Lerdau, K. Winter, and T. D. Sharkey (1997), Isoprene increases thermotolerance of isoprene-emitting species, *Plant Physiol.*, *115*, 1413–1420.

Su, H. B., H. P. Schmid, C. S. B. Grimmond, C. S. Vogel, and A. J. Oliphant (2004), Spectral characteristics and correction of long-term eddy-covariance measurements over two mixed hardwood forests in non-flat terrain, *Boundary Layer Meteorol.*, *110*, 213–253.

Villani, M. G., H. P. Schmid, H. B. Su, J. L. Hutton, and C. S. Vogel (2003), Turbulence statistics measurements in a northern hardwood forest, *Boundary Layer Meteorol.*, *108*, 343–364.

Wang, K. Y., and D. E. Shallcross (2000), Modeling terrestrial biogenic isoprene fluxes and their potential impact on global chemical species using a coupled LSM-CTM model, *Atmos. Environ.*, *34*, 2909–2925.

Webb, E. K., G. J. Pearman, and R. Leuning (1980), Correction of flux measurements for density effects due to heat and water vapor transfer, *Q. J. R. Meteorol. Soc.*, *106*, 85–100.

Westberg, H., B. Lamb, R. Hafer, A. Hills, P. Shepson, and C. Vogel (2001), Measurement of isoprene fluxes at the PROPHET site, *J. Geophys. Res.*, *106*, 24,347–24,358.

Wildermuth, M. C., and R. Fall (1996), Light-dependent isoprene emission-characterization of a thylakoid-bound isoprene synthase in Salix discolor chloroplasts, *Plant Physiol.*, *112*, 171–182.

Wilson, K., et al. (2002), Energy balance closure at FLUXNET sites, *Agric. For. Meteorol.*, *113*, 223–243.

Zimmerman, P. (1979), Determination of emission rates of hydrocarbons from indigenous species of vegetation in the Tampa/St. Petersburg Fla. area, *Rep. EPA-904/9-77-028*, U.S. Environ. Prot. Agency, Research Triangle Park, N. C.

J. Chen, J. Flaherty, B. Lamb, S. Pressley, and H. Westberg, Department of Civil and Environmental Engineering, Washington State University, Pullman, WA 99164-2910, USA. (spressle@wsunix.wsu.edu)

C. Vogel, University of Michigan Biological Station, University of Michigan, Pellston, MI 49769, USA.