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Eddy covariance measurement of isoprene fluxes

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Abstract. A system has been developed to directly measure isoprene flux above a forest canopy by eddy covariance using the combination of a fast response, real-time isoprene sensor and sonic anemometer. This system is suitable for making nearly unattended, long-term, and continuous measurements of isoprene fluxes. Isoprene detection is based on chemiluminescence between isoprene and reactant ozone, which produces green light at 500 nm. The sensor has a noise level (1σ) of 450 pptv for a 1-s integration which is dominated by random high-frequency noise that does not significantly degrade eddy covariance flux measurements. Interference from the flux of other compounds is primarily due to the emission of monoterpenes, propene, ethene, and methyl butenol and the deposition of methacrolein and methyl vinyl ketone. The average total interference for North American landscapes in midday summer is estimated to be about 5% for emissions and -3% for deposition fluxes. In only a few North American landscapes, where isoprene emissions are very low and methyl butenol emissions are high, are interferences predicted to be significant. The system was field tested on a tower above a mixed deciduous forest canopy (Duke Forest, North Carolina, U.S.A.) dominated by oak trees, which are strong isoprene emitters. Isoprene fluxes were estimated for 307 half-hour sampling periods over 10 days. Daytime fluxes ranging from 1 to 14 mg C m^{-2} h^{-1} were strongly correlated with light and temperature. The daytime mean flux of 6 mg C m^{-2} h^{-1} is similar to previous estimates determined by relaxed eddy accumulation by *Geron et al.* [1997] at this site. Nighttime fluxes were near zero (0.01 ± 0.03 mg C m^{-2} h^{-1}).

1. Introduction

Isoprene (2-methyl-1,3-butadiene) emission from vegetation is the largest known flux of a reactive hydrocarbon to the atmosphere [*Guenther et al.*, 1995]. Isoprene is often the most abundant nonmethane hydrocarbon in rural and remote atmospheric boundary layers and influences atmospheric chemistry even in urban areas [*Fehsenfeld et al.*, 1992]. Understanding the factors controlling isoprene emission is an important step toward improving regional and global numerical chemistry and transport models. Vertical turbulent isoprene fluxes above forest canopies have been measured using a variety of techniques including relaxed eddy accumulation, surface layer gradients and mixed-layer gradients [*Guenther et al.*, 1996a]. These methods rely on assumptions that are often reasonable but can result in large errors in some cases [*Dabberdt et al.*, 1993]. Another disadvantage is that all of these methods rely on gas chromatographic (GC) techniques that are labor intensive and usually require samples to be stored and transported. Errors arising from sample handling can be minimized by incorporating an automated GC into the flux system, but the result is a system that is complex and difficult to maintain for extended periods.
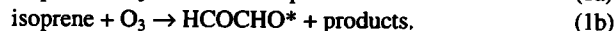
The eddy covariance method determines the flux directly by measuring the covariance of chemical mixing ratio with vertical wind currents. *Dabberdt et al.* [1993] discuss the advantages of this method and suggest that this flux measurement technique be used where practical and feasible. Eddy covariance has not previously been applied to the measurement of isoprene fluxes because no suitable sensor has been available. The method imposes three critical constraints on a chemical measurement system. A measurement method supporting an eddy covariance measured flux should have a response time of less than 1 s, be specific for the compound whose flux is being determined, and have sufficient sensitivity for the targeted flux rate. These three constraints have limited the application of eddy covariance to a small suite of gases including H_2O, CH_4, CO, CO_2, O_3, NO, NO$_x$, N_2O, and SO_2.

We have developed a fast isoprene sensor (FIS) which meets the above criteria and which we recently applied toward the eddy covariance measurement of isoprene flux from a forest canopy. *Hills and Zimmerman* [1990] originally developed the ozone-induced chemiluminescence analyzer for isoprene and recognized its potential for eddy covariance measurements. This sensor has been used for enclosure measurements of isoprene fluxes in laboratory [*Hills et al.*, 1992; *Guenther et al.*, 1991] and field studies [*Guenther et al.*, 1996b]. The FIS described in this paper is based on the original design but has been upgraded, enabling its application to eddy covariance measurements in a field environment. In this paper we describe recent FIS modifications, discuss existing limitations, and present field measurements of isoprene fluxes.

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2. Experimental Procedure

2.1. Fast Isoprene Sensor

The fast isoprene system is based on the chemiluminescence reaction between a primary alkene and ozone. This reaction produces electronically excited formaldehyde and glyoxal:

$$\text{isoprene} + O_3 \rightarrow \text{HCHO*} + \text{products} \tag{1a}$$
$$\text{isoprene} + O_3 \rightarrow \text{HCOCHO*} + \text{products.} \tag{1b}$$

Upon relaxation to the ground state, both species emit green light:

$$\text{HCHO*} \rightarrow \text{HCHO} + h\nu \ (\lambda=490 \text{ nm}) \tag{2}$$

$$\text{HCOCHO*} \rightarrow \text{HCOCHO} + h\nu \ (\lambda=550 \text{ nm}). \tag{3}$$

The process is extremely sensitive because the chemiluminescence appears against a near-zero background and because photon detectors can detect and count individual photons [Ridley and Howlett, 1974; Birks, 1989; Schorran et al., 1994]. Hills and Zimmerman [1990] demonstrated that the number of photons detected is linearly proportional to isoprene mixing ratio.

The FIS is an extension of earlier work [Hills and Zimmerman, 1990] and represents several generations of improvements aimed at making the instrument faster, more sensitive, and more stable, while simultaneously reducing its size and weight. The instrument shown schematically in Figure 1 is

currently housed in a small case and weighs 20 kg. The ozonizer, ozone monitor, and isoprene standard reside outside the FIS case. Details of specific improvements are presented below.

2.1.1. Atmospheric pressure operation. The most significant change since development of the original instrument is the modification of the sensor to operate at ambient pressure. Unlike most chemiluminescence sensors, the FIS can operate at atmospheric pressure with only a small (<20%) quenching of chemiluminescence. The O_3/O_2 mixture is forced into the 39-mL mirror-finished stainless steel reaction cell at 0.8 STP L min^{-1} (SLPM). The oxygen source can be either a high-pressure cylinder or an oxygen generator with a pump. Simultaneously, a small diaphragm pump (UN05, KNF Neuberger) pulls in sample air and directs it to the reaction cell at 4.2 SLPM. The ratio of O_3/O_2 mixture to sample air was chosen to provide the minimum O_3 required to react with nearly all of the isoprene during the cell residence time. Chemiluminescence occurs in a 39-mL mirror-finished stainless steel reaction cell before exiting into the catalytic chamber. The residence time in the reaction zone is 0.47 s.

2.1.2. Photon counting. Chemiluminescence systems typically produce very weak light intensities (hundreds to thousands of photons per second). For this reason, photon counting is used by the FIS to eliminate the noise associated with the photomultiplier tube (PMT) and electrometer configuration of the original instrument developed by Hills and Zimmerman [1990]. The FIS uses a commercial photon detector (HC134, Hamamatsu), which houses the PMT and provides the necessary
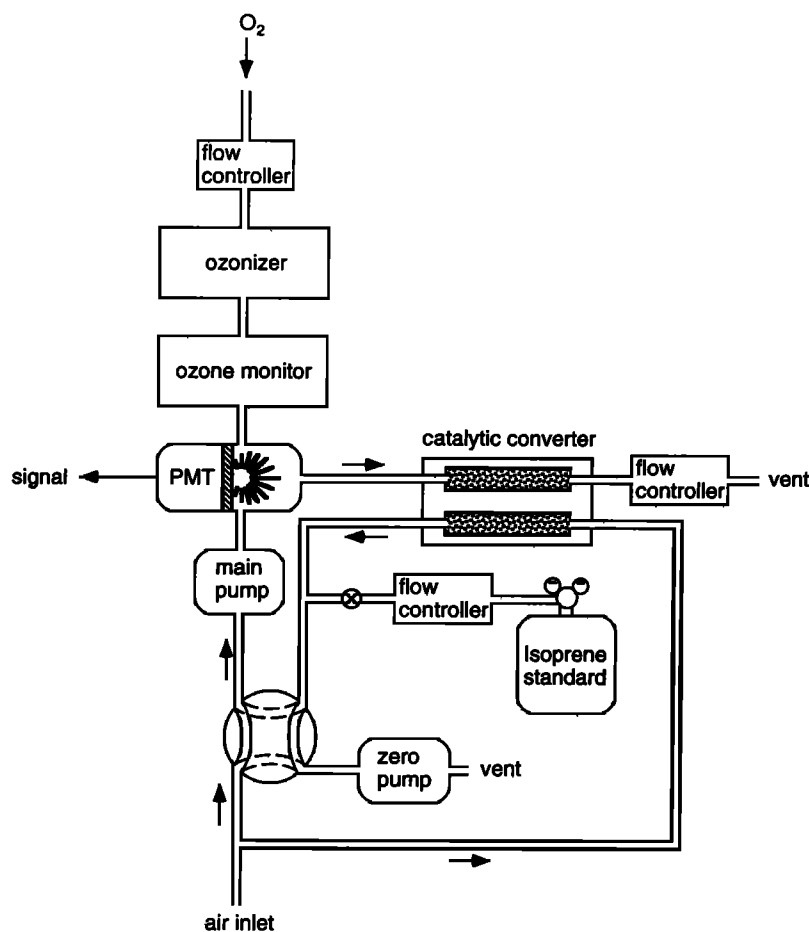

Figure 1. Schematic of the fast isoprene sensor. PMT stands for photomultiplier tube.

high voltage, pulse amplification, discrimination, and conversion to RS-232 output.

2.1.3. Catalytic converter. A two-channel catalytic converter is used in the FIS to destroy unreacted ozone exiting the reaction cell and to provide an instrument zero by scrubbing ambient isoprene. Each channel consists of a 10-cm length of 0.75 inch (1.9 cm) OD stainless steel tubing, containing alumina beads coated with platinum (23,211-4, Aldrich). At a converter temperature of 450°C, >99% of the ozone exiting the reaction cell is destroyed. A second channel scrubs isoprene from inlet air and can be directed into the reaction cell to provide isoprene-free air to which an isoprene standard (6.28 ppmv in N_2, Scott Marin Corporation) can be added, providing a calibration standard of the sensor.

2.1.4. Temperature control. Baseline drift of the FIS is dominated by the temperature sensitivity of the PMT photocathode. An increase in temperature causes electrons to be emitted by the photocathode which add to the PMT dark current. Thus temperature changes of several degrees Celsius give rise to hundreds of photon counts per second. The FIS is expected to face large diurnal temperature swings, and for this reason the PMT housing was temperature controlled to maintain a constant 36.0°C. The sample inlet tube (Figure 1) was heated to 60°C primarily to boost the kinetics of reaction (1).

2.2. Eddy Covariance Flux System

Field flux experiments were conducted in June 1996 within the Duke University Research Forest (35°58'25"N, 79°06'05"W) near Chapel Hill, North Carolina, U.S.A. Previous isoprene flux studies at this site and general site characteristics are given by *Geron et al.* [1997]. The forest is a bottomland deciduous hardwood mix dominated by oaks (*Quercus* spp.), hickories (*Carya* spp.), sweetgum (*Liquidambar styraciflua*), yellow poplar (*Liriodendron tulipifera*), and red maple (*Acer rubrum*).

The eddy covariance flux system was deployed on a 42-m walk-up tower that is surrounded by flat terrain for about a kilometer in all directions. The mean canopy height of the trees surrounding the tower is about 30 m. *Geron et al.* [1997] demonstrated that this site is suitable for measuring vertical turbulent fluxes. Our measurements of individual energy fluxes confirm their conclusion that surface energy balance, within about 20%, can be obtained at this site.

The flux system consisted of a three-dimensional (3-D) sonic anemometer, several fast response chemical sensors, a portable computer and custom-designed software. Vertical and horizontal wind velocities and sonic temperature were estimated with a 3-D sonic anemometer (Solent model 1012L, Gill Instruments) positioned at the end of a 2-m horizontal boom facing into the prevailing wind direction (225°) at a height of 42 m. Fast response chemical measurements included isoprene (the FIS described above), CO_2 and H_2O (LI-6262, LICOR), and ozone (95-08-21, GFAS).

The ozone sensor was attached to the horizontal boom about 0.6 m behind the sonic array so that airflow near the sonic was not disturbed. Sample air for each of the closed path systems (FIS and LI-6262) was pulled through individual 3-m length (4 mm I.D.) Teflon tubing with the inlets attached to the back of the sonic array. The FIS and LI-6262 were placed on the tower at a height of 40 m, with the ozonizer at 38 m. Ozone produced by the ozonizer as the FIS reactant was about 4% of the total O_2 and was measured using a custom built UV absorption meter. The CO_2, H_2O, and ozone measurements will be described elsewhere.

Additional components of the energy balance equation were measured with a net radiometer (REBS Q6) positioned above the canopy and heat flow transducers (REBS HFT-3) and soil thermocouples (Campbell Scientific 107B) positioned at soil depths between 5 and 10 cm. Digital data streams from both the sonic anemometer and the FIS were acquired at 20.8 Hz using a portable computer and stored on a removable 270-Mb disk.

Instantaneous flux is given as the product of the instantaneous fluctuations (deviation from the mean) of vertical wind velocity, w', and the chemical mixing ratio, c',

$$F = w'c'. \tag{4}$$

The integral of F over time is the time-averaged vertical eddy covariance flux. Fluxes were calculated for 30-min intervals from (4) after removal of the linear trend. Coordinate rotations were applied to the raw data to set the mean vertical wind velocity to zero. The raw isoprene data were shifted to account for the transit time in the tubing and the analyzer. A lag time of 0.87 s was estimated by determining the lag time that resulted in the maximum covariance for most 30-min periods. This value is in close agreement with that calculated from the volume of the tubing, the flow rate through the tubing, and the lag time of the analyzer. Corrections for density fluctuations [e.g., *Webb et al.,* 1980] were not applied, since pressure and temperature fluctuations were assumed to be damped in the tubing and analyzer, and the water vapor correction was negligible.

Spectra and cospectra were calculated for vertical wind velocity, isoprene mixing ratio and sonic temperature with a standard fast Fourier transform routine that included logarithmic smoothing. A comparison of these spectra, discussed in Section 3, indicated that using the raw isoprene and vertical wind speed covariance could lead to an underestimate in the isoprene flux due to the lack of a high-frequency contribution. The cospectral similarity approach (see *Hicks and McMillen* [1988]) was used to estimate the deviation from the actual isoprene flux. We used sonic temperature fluxes calculated from the 20.8-Hz raw data and fluxes calculated after applying a low-pass filter to simulate the response characteristics of the FIS. The resulting correction term (the ratio of the raw heat flux to the low-pass heat flux) was typically between 1 and 1.15 and was applied to the raw isoprene and vertical wind speed covariance to estimate the actual isoprene flux.

A data logger (CR10, Campbell Scientific) sampled additional sensors on a nearby tower at a rate of 0.5 Hz and stored 30-min standard deviations and averages. Quantum sensors (LI-190SA, LI-COR) were used to measure above canopy photosynthetically active radiation (PAR) fluxes. Wind direction and speed were measured with a prop-vane anemometer (05305-5, R.M. Young), and mean temperature and humidity were measured with a Vaisala HMP35C probe.

3. Results and Discussion

3.1. FIS Sensitivity

A typical calibration plot is shown in Figure 2. The instrument is linear ($R=0.997$) with a sensitivity (slope of the plot) of 98 photon counts per second per ppbv isoprene. The intercept of the plot, 556 photon counts per second, is the sum of the PMT dark current and light produced via the decomposition of ozone on the reaction cell surface
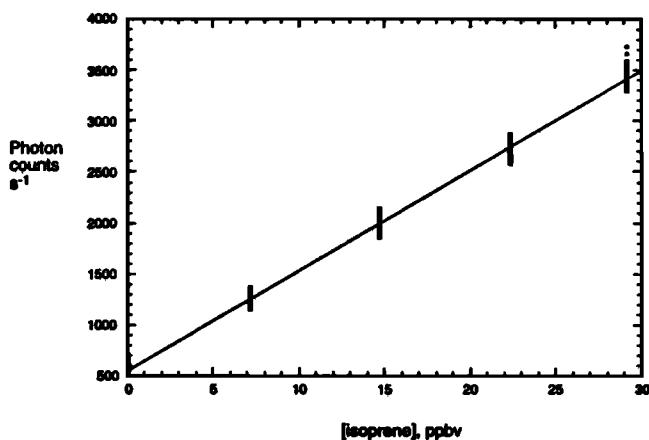
$$O_3 + \text{stainless steel} \rightarrow 3/2\, O_2 + h\nu. \tag{5}$$
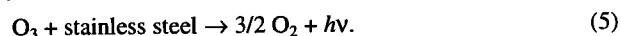
Figure 2. Calibration data for FIS sensor. Sample flow = 3.46 SLPM, O_2 flow rate = 0.80 SLPM, ozone partial pressure = 25 Torr, sampling rate = 1 Hz, time at each mixing ratio ~45 s, slope = 98.2 photons s^{-1}/(ppbv isoprene)$^{-1}$, intercept = 556 photons s^{-1}, $R = 0.997$.

Calibrations were performed 2-3 times each day. Daily mean calibration factors have a standard deviation of 4.8% and do not exhibit a trend over the course of the 10-day experiment. Lack of significant drift indicates that unattended operation of the FIS is feasible for at least this length of time.

Instrument noise is primarily high-frequency, random noise and is relatively independent of mixing ratio. At a sampling rate of 20 Hz, the 1σ (one standard deviation) noise level is equivalent to about 2 ppbv. This is reduced to 140 pptv at 0.1 Hz (equivalent to a 10-s integration). The high-frequency noise does not significantly influence the eddy covariance flux measurements that are averaged over 30-min periods.

3.2. Response Time and Attenuation

Figure 3 shows a plot of photon counts per 0.1 s as a function of time as an isoprene standard is introduced into the FIS inlet. As the data points are recorded every 0.1 s, we conclude that the response time for >95% of full signal change is about 0.5 s. This corresponds closely to the calculated reaction cell residence time of 0.47 s. Alternatively, an instrument response time of about
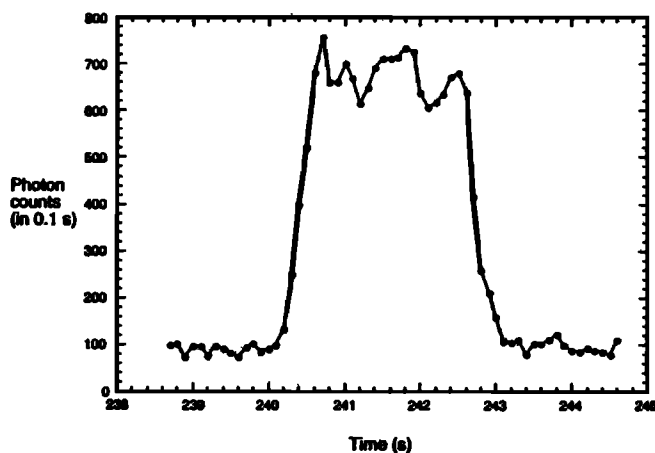

Figure 3. Response time characteristics for FIS sensor. Flow rates and ozone mixing ratio match those of Figure 2.

0.35 s is estimated using an exponential fit to the data shown in Figure 3. Memory effects due to adsorption or desorption of isoprene on tubing and cell walls are minimal and do not significantly influence the response time. These response time estimates indicate that this system should be capable of resolving isoprene fluctuations of 1 Hz and less.

Lenschow and Raupach [1991] showed that scalar mixing ratio fluctuations could be significantly attenuated while passing through sample tubing. They demonstrate that the frequency f_0 above which significant attenuation occurs is

$$f_0 = n_0 \, U \, (r \, X)^{-0.5} \tag{6}$$

where n_0 is a normalized frequency which can be estimated from the Reynolds number, U is the velocity in the tubing, r is the radius of the sample tubing, and X is the distance traveled in the sample tubing. The velocity (6.3 m s^{-1}), tubing diameter (4 mm), and length of tubing (3 m) we used resulted in f_0 of about 2 Hz. *Lenschow and Raupach* [1991] note that the frequency f_0 can be greatly increased by having turbulent flow in the sample tubing rather than the laminar flow (Re=1500) that resulted from the configuration we used. However, our analysis indicates that even with laminar flow, the ability of this system to resolve isoprene fluctuations is limited by the response time of the instrument rather than by attenuation in the inlet tubing.

3.3. Selectivity

Characterizing and limiting interference is a significant challenge for an isoprene eddy covariance system. Although there are chemiluminescence reactions between ozone and other trace gases, selective ozone-induced chemiluminescence instruments are possible since systems can be designed that respond only to a limited range of wavelengths [*Birks*, 1989]. *Hills and Zimmerman* [1990] measured the response of the FIS to 15 compounds including two inorganic species and representatives of a range of organic categories including organosulfur, alkane, alkene, alkyne, alcohol, ketone, aldehyde, and cyclic organic species. We have extended this list, shown in Table 1, with three additional compounds: methacrolein (MAC), methyl vinyl ketone (MVK), and 2-methyl-3-buten-2-ol (MBO).

Table 1. Relative Response Factors for Isoprene and Other Compounds

Compound	Relative Response Factor[a]
Isoprene	1.0
Propene	1.0
Methyl vinyl ketone	0.40
Methacrolein	0.25
2-methylpropenal	0.19
Ethene	0.15
2-methyl-3-buten-2-ol	0.15
Dimethyl sulfide	0.12[b]
3-butene-2-one	0.12
Acetylene	0.050
Hydrogen sulfide	0.041
α-pinene	0.036
β-pinene	0.039
NO	0.025
Acetaldehyde	0.00027
1-butanol	0.00027
Benzene	0.000052
Cyclohexane	0

[a]Relative to isoprene
[b]0.54 in the absence of Corning GC-475 filter.

Table 2. Estimated Interferences From all Compounds Known to Respond to the Eddy Covariance Isoprene Flux System for Typical North American Forests

Compounds	North American average	Southern[a] Hardwoods	Southern[b] Conifers	Rocky[c] Mountain Conifers	Western[d] Conifers
Monoterpenes	1.2	0.16	0.8	1.7	6.8
Propene	1.5	0.14	0.4	0.9	3.1
Ethene	0.4	0.04	0.1	0.3	0.9
2-methyl-3-buten-2-ol	2.2	0.04	1.0	37	169
Methacrolein	-1.3	-1.3	-1.3	-1.3	-1.3
Methyl vinyl ketone	-2	-2	-2	-2	-2
DMS and other compounds	0.2	0.03	0.1	0.2	0.6
Total emission interference	5.5	0.1	2.4	40	180
Total deposition interference	-3.3	-3.3	-3.3	-3.3	-3.3
Total flux interference	2.2	2.9	0.9	37	177

Flux interferences are expressed as percentages of the isoprene flux that would be measured by the eddy covariance system and are based on the fluxes predicted for midday in July by A.B.Guenther et al. (submitted to *Atmospheric Environment*, 1998) and the relative responses listed in Table 1.

[a] 35% oaks, 25% hickory, 15% sweetgum, 15% maples and 10% loblolly pine.

[b] 63% loblolly pine, 18% slash pine, 12% oaks, 4% hickory and 3% sweetgum.

[c] 61% lodgepole pine, 12% ponderosa pine, 8% fir, 8% douglas-fir, 7% aspen and 4% spruce.

[d] 90% ponderosa pine, 8% maple and 2% oaks.

Propene is the only compound tested that has a response similar to that of isoprene. The responses of MAC and MVK, both of which are isoprene oxidation products, are 25% and 40%, respectively, of the isoprene response. MBO, dimethyl sulfide (DMS), ethene, 3-butene-2-one, and 2-methylpropenal all have responses that are between 12% and 19% of the isoprene response. The response of DMS is about a factor of five higher in the absence of an optical filter. Acetylene, hydrogen sulfide, NO, α-pinene and β-pinene responses were each between 2.5 and 5%. All other tested compounds had responses that were less than 0.05% of the response of isoprene.

Estimates of the interference associated with these compounds, shown in Table 2, are based on the July average fluxes for North America and the relative responses listed in Table 2. Emissions of isoprene, monoterpenes, ethene, propene, butene, methylbutenol, DMS, NO and other biogenic compounds were estimated by A.B. Guenther et al. (Natural emissions of volatile organic compounds, carbon monoxide and oxides of nitrogen from North America, submitted to *Atmospheric Environment*, 1998). The estimated deposition fluxes of MAC and MVK assume a deposition velocity of 0.5 cm s^{-1} and an ambient mixing ratio that is based on the isoprene flux. The total average emission interference for North America (5.5% of the isoprene flux) is dominated by contributions from propene, MBO and monoterpenes. The deposition of MVK and MAC result in an estimated interference of -3.3%. The net interference is about 2%. Table 2 demonstrates that even in a landscape dominated by southern U.S. conifers, where 88% of the trees are monoterpene emitters (pines, hickories, and sweetgum) and only 15% are isoprene emitters (oaks and sweetgum), the total interference from all compounds is only a few percent of the isoprene flux. The only landscapes expected to have a significant midday interference are those with high MBO emissions and low isoprene emissions. Nighttime flux interferences are relatively large as a result of near-zero isoprene emissions in the dark.

3.4. Eddy Covariance Isoprene Flux Measurements

A positive correlation between isoprene mixing ratio and vertical wind speed was observed above the forest canopy during

daytime hours and is illustrated in Figure 4. The spectra and cospectra shown in Figure 5 demonstrate the expected frequency distribution for sonic temperature T and vertical wind speed w in an unstable surface layer. The corresponding variance or covariance normalizes all spectra and cospectra. Isoprene (C) spectra closely follow sonic temperature at frequencies less than 1 Hz but deviate at higher frequencies as expected due to the limited response time of the FIS. The bottom panel of Figure 5 shows that the wC cospectrum deviates from the wT cospectrum
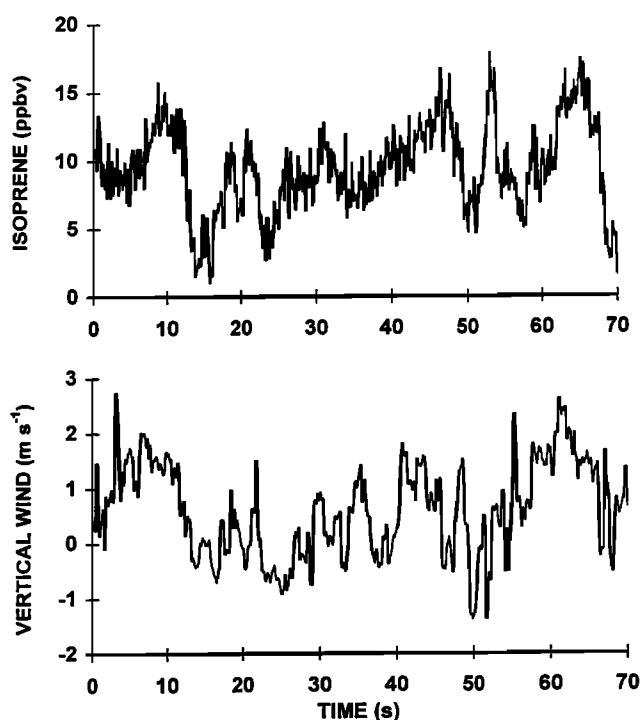

Figure 4. An 80-s trace (0.25-s average) of isoprene mixing ratio and vertical wind velocity w above the forest canopy beginning at 1200 local standard time (LST) on June 22, 1996.
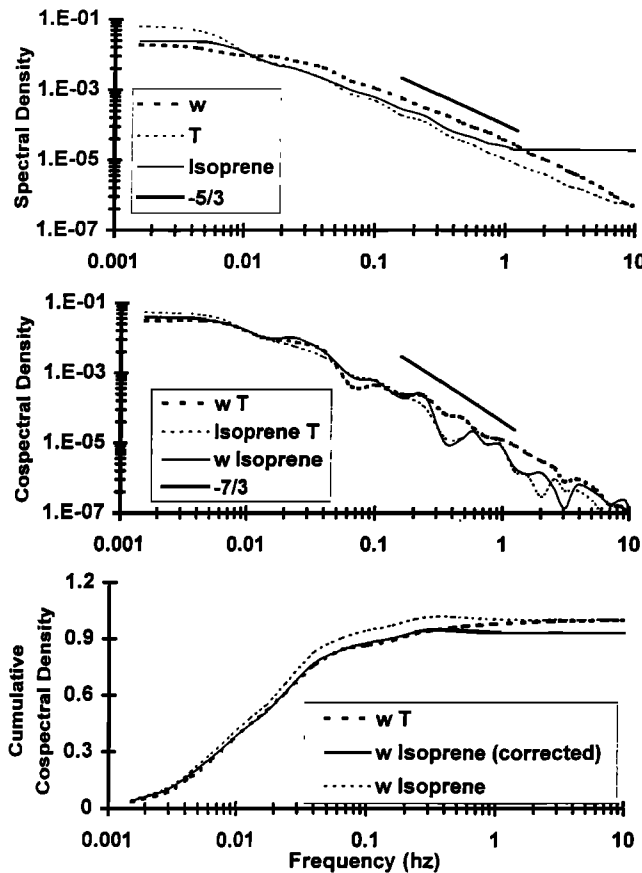
Figure 5. Isoprene, vertical wind velocity (w), and sonic temperature (T) spectra and cospectra normalized by the corresponding variance or covariance for a 30-min period beginning at 1200 LST on June 22, 1996.

when normalized by the raw wC covariance but agrees well (at lower frequencies) when normalized by the wC covariance corrected by the cospectral similarity term (the ratio of raw wT covariance to low-pass wT covariance).

Figure 6 demonstrates that isoprene fluctuations follow the same pattern as other trace gases (ozone, CO_2, water vapor) and virtual temperature. Vertical trace gas transport from the forest canopy is initiated by downdrafts that occur every 200 to 300 s. This behavior is typical of forest canopies [*Paw U et al.*, 1995]. The downdrafts bring relatively low isoprene mixing ratios into the canopy and are followed by a slow upward venting of isoprene rich air that is buoyant due to the heated canopy. As a result of this long timescale for vertical transport, an extremely fast detector is not needed to measure eddy covariance fluxes. The cospectra shown in Figure 5 indicate that about 90% of the isoprene flux is associated with frequencies of <0.1 Hz. Similar cospectra were observed for the other trace gases and temperature.

Eddy covariance measurements of 30-min average isoprene fluxes for a 2.5-day period are illustrated in Figure 7. The observed isoprene fluxes range from near zero at night to about 14 mg C m^{-2} h^{-1}. Days 172 and 174 were characterized by variable cloudiness during midday, while day 173 represents clear skies. This is illustrated in Figure 7 by the lower and more variable PAR fluxes on the two cloudy days. Figure 7 demonstrates that the isoprene emission variations observed with

the eddy covariance system follow the general pattern predicted by the *Guenther et al.* [1995] canopy model. The model incorporates the influence of PAR and temperature and accounts for variations due to different isoprene source regions, since on average, we observed fluxes that were 50% higher when winds were from the west (225° to 315°) than for other wind directions. This had little effect on the model predictions shown in Figure 7, since winds were consistently from the west except between 1000 and 1400 local standard time (LST) on day 172. Figure 7 demonstrates that both model and observed fluxes tend to increase with PAR after sunrise with a maximum in early afternoon followed by a relatively rapid decrease in the evening. There is a strong correlation between isoprene fluxes, PAR, and temperature.

The diurnal variation in the 30-min average isoprene flux, temperature and PAR for all 307 sampling periods is shown in Figure 8. The daily maximum was typically between 11 and 14 mg C m^{-2} h^{-1} and always occurred after the solar zenith as a result of the continued increase in temperature between 1200 and 1600 LST. Fluxes between 6 and 14 mg C m^{-2} h^{-1} were observed between 1200 and 1500 LST and were associated with temperatures between 28 and 33°C and PAR fluxes between 1200 and 1900 µmol m^{-2} s^{-1}. Isoprene fluxes in the morning (700 to
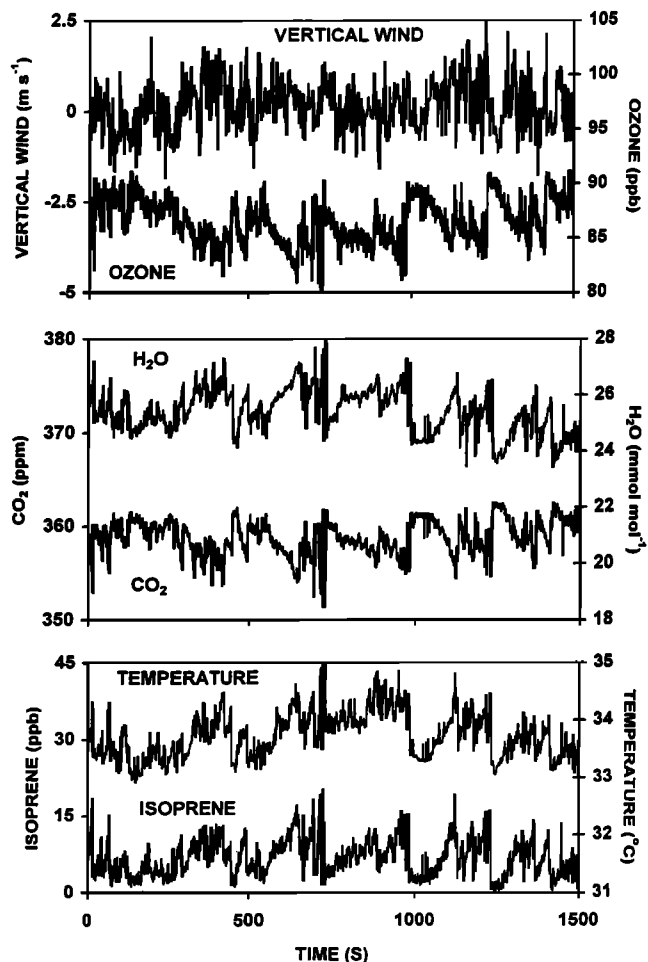

Figure 6. A 30-min trace (1-s average) integrated vertical wind speed (m s^{-1}), ozone (ppb), CO_2 (ppm), H_2O (mmol mol^{-1}), sonic temperature (°C), and isoprene (ppb) above the forest canopy beginning at 1200 LST on June 22, 1996.

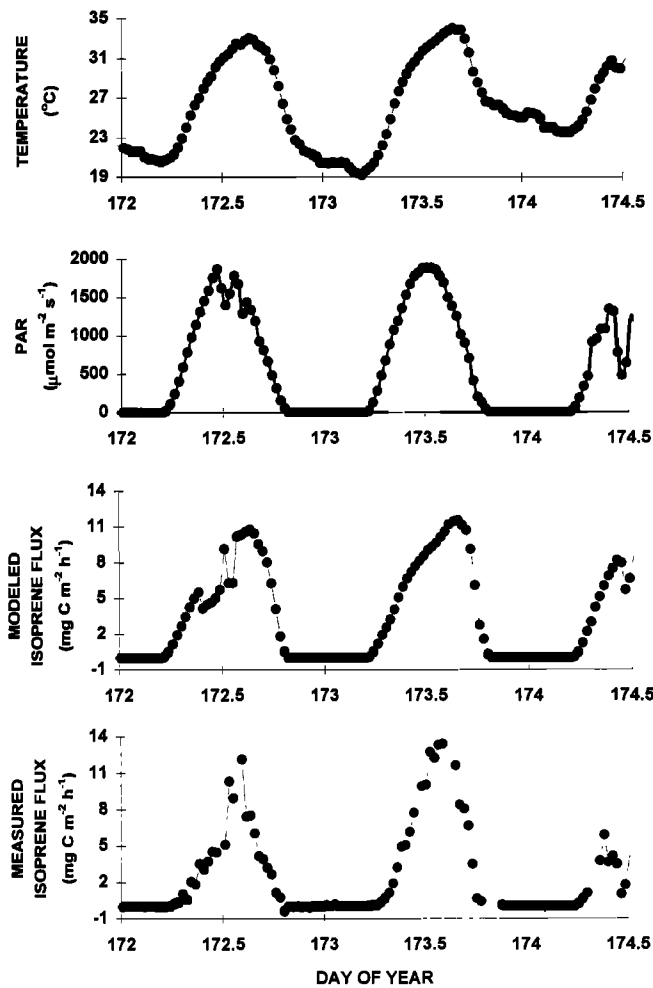## 4. Summary and Conclusions

An above-canopy isoprene flux measurement system has been developed based on the eddy covariance method. Previous investigators used a variety of indirect flux measurement techniques to estimate above-canopy isoprene fluxes. Isoprene detection is based on the chemiluminescence reaction between isoprene and ozone, which produces electronically excited products that emit light upon relaxation to the ground state. The system provides a direct measurement of isoprene flux and is suitable for relatively long term, nearly unattended, operation.

Field tests at a mixed hardwood site within the Duke Forest in North Carolina demonstrate that the system is capable of accurately estimating isoprene fluxes at a site with significant isoprene emission. Daytime (800 to 1600 LST) fluxes ranged from 1 to 14 (mean=6.2) mg C m^{-2} h^{-1}, which is similar to the

Figure 7. Comparison of 30-min average above-canopy ambient temperature, photosynthetically active radiation (PAR), modeled isoprene flux, and isoprene flux measured by the eddy covariance flux system for a 60-hour period.

1200 LST) and evening (1500 to 2000 LST) ranged from 0.2 to 7 mg C m^{-2} h^{-1}. Isoprene fluxes of 0.01±0.03 mg C m^{-2} h^{-1} were observed at night (2000 to 400 LST).

Geron et al. [1997] have used a relaxed eddy accumulation (REA) flux measurement system to measure isoprene fluxes at the site we used to evaluate the eddy covariance isoprene flux system. The REA system was not operating during the June 1996 deployment of our eddy covariance system, but it is useful to compare our measurements with the REA fluxes reported for this site in summer 1994. The 19 daytime REA isoprene fluxes reported by *Geron et al.* [1997] range from 1 to 13 mg C m^{-2} h^{-1}. Their mean measured flux of 5.7 mg C m^{-2} h^{-1} was associated with a mean PAR of 1410 μmol m^{-2} s^{-1} and mean temperature of 27.8 °C. Our measurements made between 800 and 1600 LST are associated with a similar mean PAR (1390 μmol m^{-2} s^{-1}) and slightly higher mean temperature (29.4 °C). The corresponding mean flux of 6.2 mg C m^{-2} h^{-1} is in good agreement with the REA fluxes. In addition to a similar mean and range, both studies display the same general diurnal pattern. *Geron et al.* [1997] report that their REA flux measurements were in good agreement with model estimates based on detailed site specific enclosure measurements, biomass density, and species composition data.
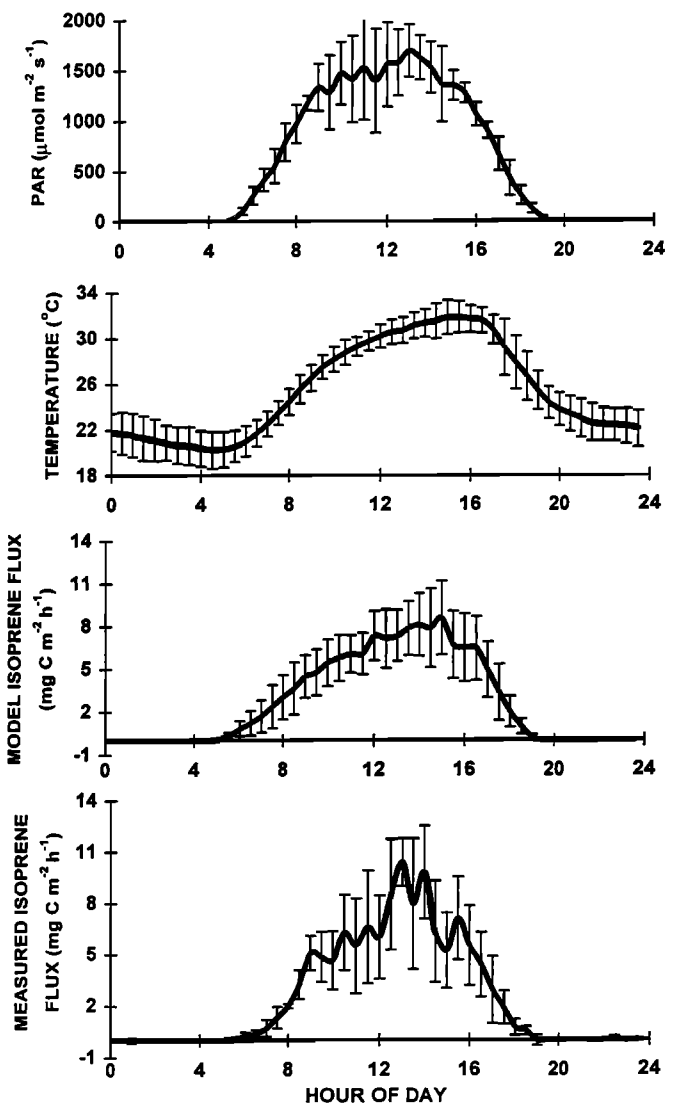

Figure 8. Diurnal pattern of 30-min average, above canopy ambient temperature, photosynthetically active radiation (PAR), modeled isoprene flux, and isoprene flux measured by the eddy covariance flux system. The mean (solid line) and standard deviation (vertical line with horizontal bars) represent 307 sampling periods from the 10-day study.

relaxed eddy accumulation measurements reported by *Geron et al.* [1997] for this site. Isoprene fluxes at night were low, $0.01\pm.03$ mg C m^{-2} h^{-1}, as is expected for light dependent emissions. The observed diurnal variations closely follow model predictions.

Care must be taken when using this system to estimate nighttime fluxes or at locations with relatively large fluxes of other alkenes. Midday interference from fluxes of compounds other than isoprene is estimated to be less than 5% for most North American landscapes. Future work will be directed at reducing this interference.

The system can run in a hands-off mode for days at a time and provide continuous flux measurements with much less effort than other systems, which require samples to be collected and then analyzed by gas chromatographic methods. A medical oxygen generator (MK5, Nidek) which produces 95% pure O_2 from ambient air has recently been used with the FIS at a remote field site and is of great benefit for long-term measurements and studies at remote field sites.

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