Title
Wet and dry season ecosystem level fluxes of isoprene and monoterpenes from a southeast Asian secondary forest and rubber tree plantation

Journal
Atmospheric Environment, 39(2)

ISSN
1352-2310

Authors
Baker, B
Bai, JH
Johnson, C
et al.

Publication Date
2005

DOI
10.1016/j.atmosenv.2004.07.033

Available online at www.sciencedirect.com
SCIENCE DIRECT®
Atmospheric Environment 39 (2005) 381–390
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

Wet and dry season ecosystem level fluxes of isoprene and monoterpenes from a southeast Asian secondary forest and rubber tree plantation

Brad Baker[a,*], Jian-Hui Bai[b], Curtis Johnson[a], Zhong-Tao Cai[a], Qing-Jun Li[c], Yong-Feng Wang[c], Alex Guenther[d], Jim Greenberg[d], Lee Klinger[e], Chris Geron[f], Rei Rasmussen[g]

[a]*South Dakota School of Mines and Technology, Rapid City, SD 57701, USA*
[b]*Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China*
[c]*Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, Yunnan 666303, China*
[d]*National Center for Atmospheric Research, Boulder, CO 80303, USA*
[e]*Institute of Noetic Sciences, Petaluma, CA 94952, USA*
[f]*Environmental Protection Agency, Research Triangle Park, NC 27711, USA*
[g]*Oregon Graduate Institute, Beaverton, OR 97006, USA*

Received 26 February 2004; accepted 27 July 2004

Abstract

Canopy scale fluxes of isoprene and monoterpenes were investigated in both wet and dry seasons above a rubber tree (*Hevea brasiliensis*)/secondary tropical forest in the Yunnan province of southwestern China. Drought conditions were unusually high during the dry season experiment. The eddy covariance measurement technique was used to measure isoprene fluxes, while monoterpene fluxes were modeled based on leaf level emission measurements. Maximum observed isoprene fluxes occurred during the wet season and daytime average fluxes were about 1 mg C $m^{-2} h^{-1}$. Dry season fluxes were much lower with a daytime average of 0.15 mg C $m^{-2} h^{-1}$. Wet season isoprene fluxes compare quite well with isoprene fluxes observed from other tropical forests. Monoterpene fluxes came, almost entirely, from *Hevea brasiliensis*, which is a light-dependent monoterpene emitter. Modeled wet season total monoterpene fluxes were about 2 mg C $m^{-2} h^{-1}$ (average for the daytime), and in the dry season were undetectable. Extreme drought conditions, and the drought deciduous nature of *Hevea brasiliensis* may be the cause of the low dry season fluxes.

Keywords: Isoprene; Monoterpenes; Biogenic volatile organic compounds; Eddy covariance; Hevea brasiliensis

1. Introduction

It has been well established that globally, vegetation emits large quantities of volatile organic compounds (VOCs) to the atmosphere (Guenther et al., 1995, 2000). It has also been shown that emissions of biogenic VOCs play a significant role in both regional and global atmospheric chemistry (Trainer et al., 1987; Roberts et al., 1998; Guenther et al., 1999). Biogenic VOC emissions are more than a factor of 7 higher than anthropogenic VOC emissions (Guenther et al., 1995),

*Corresponding author. CSUS, Department of Chemistry, 6000 J Street, Sacramento, CA 95819-6032, USA.

1352-2310/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2004.07.033

and biogenic VOCs tend to be more reactive on average than anthropogenic VOCs (Atkinson and Arey, 2003). Some effects that biogenic VOCs have on atmospheric chemistry and composition include, the production of ozone and carbon monoxide, reductions in OH radical, changes in aerosol composition, and contribution to carbon cycling. Global biogenic VOC emission models indicate that 44% of global biogenic VOC emissions to the atmosphere are isoprene (2-methyl-1,3,-butadiene), and that monoterpenes make up 11% of global biogenic VOC emissions (Guenther et al., 1995). Emissions of isoprene are controlled by both light and temperature at the leaf level over short time periods (Guenther et al., 1991,1993). Monoterpene emissions are usually dependent solely on temperature (Guenther et al., 1991, 1993), but in limited cases, have been found, very similarly to isoprene, to depend on light as well (Staudt and Seufert, 1995; Kesselmeier et al., 1996; Klinger et al., 2002). Over longer time periods, isoprene and monoterpene emissions may show variations depending on factors such as: light environment, leaf developmental stage, water and nitrogen availability, and exposure to various pollutants, including CO_2 (Fuentes et al., 2000; Rosenstiel et al., 2003).

According to global models, tropical forests account for the majority of isoprene and monoterpene emissions (Guenther et al., 1995; Potter et al., 2001), and therefore, exert a large influence on the atmospheric chemistry of the lower latitudes (Guenther et al., 1999). High biogenic VOC emissions from the tropics stem from year-around growing seasons and high biodiversity, which guarantees at least several isoprene and/or monoterpene emitters in an ecosystem containing hundreds of different plant species. Although daily maximum tropical forest emissions of biogenic VOCs at any given time may be quite low compared to maximum emissions from mid-latitude deciduous forests, annual emissions will most likely be much higher from tropical forests due to the tropical climate. Due to these high annual emissions and influence on global atmospheric chemistry, it is very important to understand tropical biogenic VOC emission patterns.

Modeled estimates of tropical biogenic VOC emissions tend to be based on little data. Global biogenic VOC emissions estimated by Guenther et al. (1995) are dependent on only 22 field studies and tropical rainforest emissions are based solely on ambient isoprene and monoterpene concentrations measured during one field study (Zimmerman et al., 1988). Potter et al. (2001) used the emission factors derived by Guenther et al. (1995) and did not include any additional field data. More detailed modeling studies have focused on specific regions such as Central Africa (Guenther et al., 1999), North America (Guenther et al., 2000), or China (Klinger et al., 2002). Guenther et al. (1999) made improvements to past modeling efforts and utilized more current and extensive data describing both species specific isoprene emissions and biomass characterization for the Central African tropical region. To explain the higher ecosystem level isoprene fluxes measured during the dry season versus the wet season as reported by Serça et al. (2001), they accounted for higher leaf temperature during the dry season due to decreased stomatal conductance. The same phenomena might be responsible for high ambient isoprene concentrations observed at the end of the dry season relative to wet season concentrations at a site near Ji-Paraná (Kesselmeier et al., 2002) and near Santarém (Trostdorf et al., 2004), in the Amazon. Seasonal variations in biogenic VOC emissions from tropical forests can have a large influence on the amount of biogenic VOCs in the atmosphere, and therefore, a large influence on atmospheric chemistry.

In addition to understanding biogenic VOC emissions from native tropical vegetation, land use change is also an important factor in the tropics that can lead to changes in biogenic VOC emission patterns. When primary or even secondary forests are cleared and land is utilized for crops or agriforest plantations, significant changes in emission patterns may result. To verify, and to better predict tropical biogenic VOC emissions and their influences on atmospheric chemistry there is a great need for additional field measurements of leaf level and ecosystem level biogenic VOC fluxes from tropical landscapes.

This paper describes ecosystem level fluxes of isoprene and monoterpenes above a tropical *Hevea brasiliensis* plantation with a secondary tropical forest understory located in southwestern China. *Hevea brasiliensis*, is native to the tropical forests on South America, and was brought to southeast Asia for economic development. The sap of *Hevea brasiliensis* is used to produce natural latex rubber. China is home to approximately 1.3 billion people and has experienced average annual economic growth of 9.6% over the past 20 years (The World Bank, 2001). As the standard of living and population in China continues to rise, the potential for deterioration in urban and rural air quality increases, caused by a combination of anthropogenic pollutants and natural emissions. The 1.7×10^5 ha of land planted with *Hevea brasiliensis* cover approximately 9% of the land area in the Xishuangbanna region, and represent 16% of the area planted with rubber trees in China (Summary of National Economic Statistics of Xishuangbanna Dai Nationality Prefecture (2002); Statistics Bureau of Xishuangbanna Dai Nationality prefecture, 2003). Several other studies have described biogenic VOC emissions from China and Southeast Asia. Bai et al. (1995) estimated total biogenic isoprene and monoterpene emissions from China to be $8.3\,\mathrm{Tg\,C\,yr^{-1}}$ based on branch enclosure measurements of 9 common tree species found in China. Klinger et al. (2002) used the Guenther et al. (1995) model to estimate emissions from China, and improved regional flux estimates by screening 386 species of plants from 52

different field sites for biogenic VOC emissions. They estimated emissions of isoprene, monoterpenes, and other VOCs to be 4.1, 3.5, and 13 Tg C yr^{-1} respectively. Steiner et al. (2002) used satellite data to determine current land cover and compared present-day biogenic VOC emissions with pre-disturbed vegetation emissions in east Asia. They estimated that biogenic isoprene and monoterpene emissions had decreased by 31% and 40%, respectively, due to conversion of forests to agriculture. The study described in this paper represents the first ecosystem level biogenic VOC flux measurements reported from any ecosystem in continental Asia.

2. Experiment

2.1. Field site

The study site was located within the boundary of the Xishuangbanna Tropical Botanical Gardens (XTBG), which is sponsored by the Chinese Academy of Sciences, in the Yunnan province of southwestern China. This region receives average annual precipitation of 156 cm; 80% of this falls during the May through October wet season. Average annual temperature at the XTBG is 21.4 °C. The specific field site used for this study was located at 21°55′25″N, 101°16′5″E and at an elevation of 587 m above sea level. The local vegetation was dominated by *Hevea brasiliensis Muell.-Arg.*, or rubber tree, which made up the forest canopy, and was approximately 25 m high. The *Hevea brasiliensis* forest extended approximately 100 m in all directions, and was planted and cultivated for economic development purposes. The understory vegetation consisted of a mixture of agricultural plants such as *Camellia sinensis var.assamica (Masters) Kitamura* (tea plant), and many native plants. In particular, plants from the family *Palmae* (palms) and *Thelypteridaceae* (ferns) were common. The terrain was relatively flat to the north and south, which were the dominant wind directions, and sloped upwards several degrees to the east. Ecosystem level measurements were made from a 30 m tall triangular tower located in this forest. A lightly used access road ran north and south approximately 70 m to the west of the tower. The Luosuo river, a major tributary to the Mekong river, ran north and south approximately 200 m to the west of the tower. Two measurement campaigns took place. The first was in July of 2002 (8–18 July) during the wet season, and the second was in late February/early March of 2003 (22 February – 3 March) during the dry season.

2.2. Biogenic VOC flux measurements

All flux instrumentation was located 30 m above ground level, approximately 5 m above the top of the canopy. The flux tower was supplied with 220 V line power. Above canopy ecosystem level fluxes of isoprene were measured using the eddy covariance technique. Wind speed, in the u, v, and w directions, and virtual temperature were measured by a sonic anemometer (Applied Technologies, Boulder, CO). Ambient isoprene concentrations were measured using a fast isoprene system (FIS) (Hills Scientific, Boulder, CO) (Hills and Zimmerman, 1990). A detailed description of the FIS system and how it can be used to measure fluxes of isoprene by eddy covariance is given by Guenther and Hills (1998). The inlet for the FIS system was 1.5 m long. Calibrations were performed several times daily using a NIST-traceable compressed gas standard (Apel-Riemer Environmental, Denver, CO) containing 10 parts per million by volume (ppmv) isoprene diluted to several parts per billion by volume (ppbv) by the built-in calibration system aboard the FIS. Serial data from both the sonic anemometer and FIS were collected at 10 Hz on a portable computer. One-minute averages of photosynthetically active radiation (PAR) (Li-Cor, Lincoln, NE) and ambient temperature (Campbell Scientific, Logan, UT) were also recorded. During the dry season measurements, problems with analog data acquisition required the use of PAR and temperature data that was collected at a weather station located in a clearing about 500 m north of the tower.

2.3. Ambient concentration measurements

Air samples were collected on 5 days during the wet season, and 2 days during the dry season to determine ambient concentrations of monoterpenes above the forest canopy. In addition to the primary flux tower described previously, ambient air samples were also collected from the top of a second tower, 55 m high, 1 km to the southeast, and outside of the *Hevea brasiliensis* forest. This tower was surrounded by secondary tropical forest, and under normal conditions of southerly winds, air passing by this tower was not influenced by emissions from the *Hevea brasiliensis* trees upwind. Samples were collected on solid adsorbent cartridges packed with 130 mg of Tenax, and 90 mg of Carbosieve S-III. Samples were pulled through cartridges using a 2 L gas-tight syringe (Hamilton, Reno, NV). Cartridges were prepared before the experiment and stored before and after sampling in order to reduce sample losses and blank values as described by Helmig (1996). Sampled cartridges were returned to the laboratory for analysis and analyzed as described by Greenberg et al. (1999), except that a gas chromatograph (GC), containing a DB-624 column (J&W Scientific, Folsom, CA), with a flame ionization detector (FID) was used for this study. Daily calibrations of the GC-FID were performed using a compressed gas standard containing several ppmv of each: α-pinene, β-pinene,

limonene, and 3-carene (Apel-Riemer Environmental, Denver, CO). The standard was diluted for analysis by mixing hydrocarbon free air using mass flow controllers, and then sampled onto adsorbent cartridges to simulate field conditions. The precision of repeated standard analysis for each of the listed monoterpenes was better than 5%. Several samples were analyzed by GC-MS (mass spectroscopy) to positively identify monoterpenes present in the samples.

2.4. Biomass characterization

During the wet season, biomass was characterized by running eight radial transects out from the measurement tower. Each transect was 100 m long and consisted of 10 separate 10×10 m plots in which detailed biomass characterization was carried out as described by Helmig et al. (1999). Estimates of biomass density for trees (trunk diameter at 1.5 m > 4 cm) were then made using the allometric equations described by Geron et al. (1994). Biomass density for shrubs and grasses and overall leaf area index (LAI) were determined based on observations made by Klinger et al. (2002) at this site. In addition, upward looking hemispherical photos were taken for each plot during both the wet and dry seasons, in order to determine the change in LAI between the two seasons (Leblanc et al., 2002).

3. Results and discussion

3.1. Foliar Biomass

Transect data indicated that 437 different plant species were present in the area within 100 m from the tower. The major species was *Hevea brasiliensis,* which made up an estimated 61% of the total foliar biomass. Average overall foliar biomass density was estimated to be 526 g m^{-2}. This is likely to be a lower limit, since temperate allometric functions were applied. Trees accounted for 431 g m^{-2}, and other vegetation accounted for 95 g m^{-2}. The LAI for the site was reported as 5.2 m^2 m^{-2} by Klinger et al. (2002). *Hevea brasiliensis* trees are drought deciduous, and under the exceptionally arid conditions as experienced at the XTBG during recent dry seasons, the *Hevea brasiliensis* trees lose a large percentage of their leaves. From hemispherical photos, it was estimated that there was a 30% average drop in LAI between the wet and dry seasons, giving a dry season LAI of 3.6 m^2 m^{-2}. A visual inspection of the vegetation suggested that most of this loss was due to the *Hevea brasiliensis* trees.

Klinger et al. (2002) screened 246 species of plants in the Xishuangbanna region for light-dependent VOC emissions (assumed to be isoprene) and for stored VOC emissions (assumed to be terpenes) using a simple hand-held leaf cuvette and photoionization detector (Klinger et al., 1998). Emissions were assigned as high, medium, or low, and rough emission potentials were assigned for each category. For 26 of these species, a more sophisticated leaf cuvette was used (with PAR and temperature monitoring capability) and cuvette samples were collected on adsorbent cartridges for later analysis in the laboratory and determination of more precise emission capacities. Owen et al. (2004, Volatile organic compound (VOC) emissions from three commercially important tropical tree genera growing at Xishuangbanna Tropical Botanic Gardens, Yunnan, China, manuscript in preparation) made detailed leaf level emission measurements of 47 plant species located within XTBG for isoprene and monoterpenes. Many of these were also found near the measurement tower.

Measurements from the two studies (Klinger et al., 2003; Owen et al., 2004) were used to scale leaf level emissions to the canopy level (described in a following section). Of the 437 species of plants identified in the transects, 104 were screened for isoprene and monoterpene emissions. This represented 82% of the total estimated foliar biomass. From those leaf level data and the biomass characterization, it is estimated that 75% of total isoprene emissions came from only 4 species that made up only 3% of the total foliar biomass. These 4 species were all significant emitters of isoprene (> 25 μg C gdw^{-1} h^{-1}; gdw = gram dry weight of green leaf material). Isoprene emissions came from both the forest canopy (41%) and from understory vegetation (59%). Monoterpene emissions came almost exclusively from the *Hevea brasiliensis* trees (> 99%). This demonstrates how the cultivation of monodominant plantation forests can drastically change regional emission patterns. Table 1 lists the plant species found near the tower that contributed most to canopy level isoprene and monoterpene fluxes.

3.2. Above canopy isoprene fluxes

Isoprene fluxes were determined from 10 Hz vertical wind and ambient isoprene concentration data using the eddy covariance method. Before calculating half-hour fluxes, the three-dimensional wind data was rotated to acquire a zero mean in the vertical direction, and the linear trend in the isoprene concentrations were removed. Any timing offset between the chemical and vertical wind data was accounted for by shifting the chemical data set relative to the vertical wind data until a maximum covariance was reached. This shift was consistently about 0.2 s for this experiment. The fluxes were then determined by

$$F_i = \bar{w}'\bar{c}', \quad (1)$$

where F_i is the instantaneous isoprene flux averaged over a half-hour period, and w' and c' are the instantaneous

Table 1
Summary of major isoprene and monoterpene emitters within 100 m of the flux tower. The top known isoprene emitters, in terms of contribution to total canopy isoprene emissions are listed; accounting for 90% of the total isoprene emission potential. Only one species accounted for over 99% of total canopy monoterpene emissions

	Family	Species	% of total biomass[a]	% of total emissions[b]	Emission Rate[c]	Reference[d]
Isoprene	Palmae	*Calamus gracilis*	0.92	29	146	Owen et al., (2004)
	Poaceae	*Dendrocalamus colastachyus*	0.78	25	70.0	Klinger et al., (2002)
	Moraceae	*Ficus langkokensis*	0.85	11	29.7	Klinger et al., (2002)
	Moraceae	*Ficus maclellandii* v *rhodafolia*	0.32	10	69.0	Klinger et al., (2002)
	Euphorbiaceae	*Hevea brasiliensis*	61	4	0.17	Klinger et al., (2002)
	Tiliaceae	*Microcos nervosa*	0.20	3	32.6	Klinger et al., (2002)
	Moraceae	*Ficus racemosa*	0.12	3	50.0	Owen et al., (2004)
	Moraceae	*Ficus auriculata*	0.04	3	139	Klinger et al., (2002)
	Thelypteridaceae	*Cyclosorus parasiticus*	0.01	2	284	Owen et al., (2004)
Monoterpenes	Euphorbiaceae	*Hevea Brasiliensis*	61	99	25.0	Klinger et al., (2002)

[a]Calculated based on the biomass characterization of the 8 radial transects laid out from the tower.
[b]Calculated based on the percent biomass for the species and the measured emission potential.
[c]Emission rates are reported in units of μg C $gdw^{-1} h^{-1}$ and were measured at or near 30 °C and 1000 PAR (see the listed reference for details).
[d]The reference was used to obtain the leaf level emission potential listed in the table.

deviations of the vertical wind velocity and isoprene concentration from the mean. The overbars indicate 30-min averages for these quantities. Above canopy isoprene fluxes for both the wet and dry seasons are shown in Fig. 1a. Fig. 1b shows temperature and PAR data for the wet season, indicating the light and temperature dependence of isoprene emissions. Above canopy daytime isoprene fluxes during the wet season averaged about 1 mg C $m^{-2} h^{-1}$. Maximum fluxes were over 4 mg C $m^{-2} h^{-1}$. Dry season daytime fluxes averaged about 0.15 mg C $m^{-2} h^{-1}$ and maximum fluxes reached 0.6 mg C $m^{-2} h^{-1}$. Maximum wet season PAR was just over 2500 μmol $m^{-2} s^{-1}$ at midday during cloudless periods; although, during the wet season, it was uncommon to have cloudless skies. During the dry season, maximum PAR values dropped to just over 1500 μmol $m^{-2} s^{-1}$ and the presence of clouds was uncommon. Maximum temperatures between 30 and 35 °C were similar during both the wet and dry seasons. Minimum temperatures diverged considerably with wet season nighttime temperatures normally reaching 25 °C and dry season nighttime temperatures regularly below 15 °C. The large difference in nighttime temperatures may have had an effect on the seasonal emission capacity of different plants.

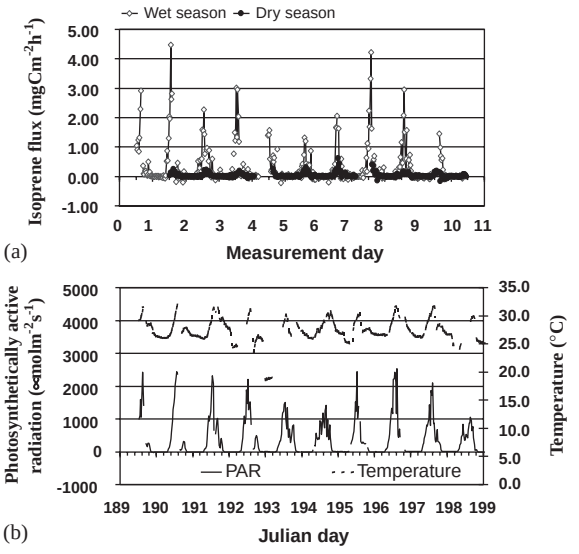

Fig. 1. Comparison of wet and dry season above canopy isoprene fluxes from the *Hevea brasiliensis*/secondary tropical forest (1a). Dry season isoprene fluxes were significantly lower than those for the wet season. Diurnal measurements of light and temperature for the wet season are shown (1b) to demonstrate the light and temperature dependence of isoprene emissions.

3.3. Modeled isoprene fluxes

Canopy scale isoprene and monoterpene emissions were scaled up from biomass characterization and leaf level measurements described earlier using the Global Biosphere Emissions and Interactions System (GLO-BEIS) model framework explained by Guenther et al.

(1999). Measured light and temperature data, measured biomass density and LAI, and measured leaf level emissions of isoprene and monoterpenes that were available for local vegetation were used for the model calculations. Fig. 2 shows the correlation between modeled and measured isoprene fluxes for (a) the wet season, and (b) the dry season. The model correlates well ($r^2 = 0.67$) with measured isoprene fluxes during the wet season; however, under predicts isoprene emissions by about a factor of 4 (slope = 0.27). Dry season isoprene fluxes are not as well correlated with predicted fluxes ($r^2 = 0.36$) and measured dry season fluxes are under predicted by a factor of 2 (slope = 0.49) by the model. Measured isoprene fluxes are particularly high relative to model predictions at higher measured flux values. This is particularly evident for the wet season. In addition to differences in PAR and temperature, the model also takes into account the 30% reduction in LAI that was observed between the wet and dry seasons. However, most of this reduction was due to the drought deciduous nature of the *Hevea brasiliensis* trees, which are only low isoprene emitters. One might expect higher isoprene emissions when the *Hevea brasiliensis* trees do not have leaves, due to an increased openness in the canopy, allowing more light to reach the isoprene-emitting understory. The discrepancy between the measured and modeled isoprene fluxes may be explained by the fact that only a few species of trees that represent a small percentage of the total biomass are responsible for the majority of the isoprene flux (Table 1). Any errors in the leaf level emission data, which could be due to drought conditions during the dry season, or the biomass estimations for these isoprene emitting plant species, has the potential to have a large effect on the accuracy of the modeled fluxes. In such a situation, it is not surprising to have such a discrepancy between the measurements and the model. There is also the possibility that additional isoprene emitters were present around the tower in areas that were not covered by the vegetation transects, or that a significant amount of the 18% of the foliar biomass that was not screened for emissions were isoprene emitters; and therefore, these emissions would not be accounted for in the model.

Correlations of the sensible heat flux with the isoprene flux are also shown on Figs. 2a and b. Sensible heat flux correlated better with isoprene fluxes than the modeled

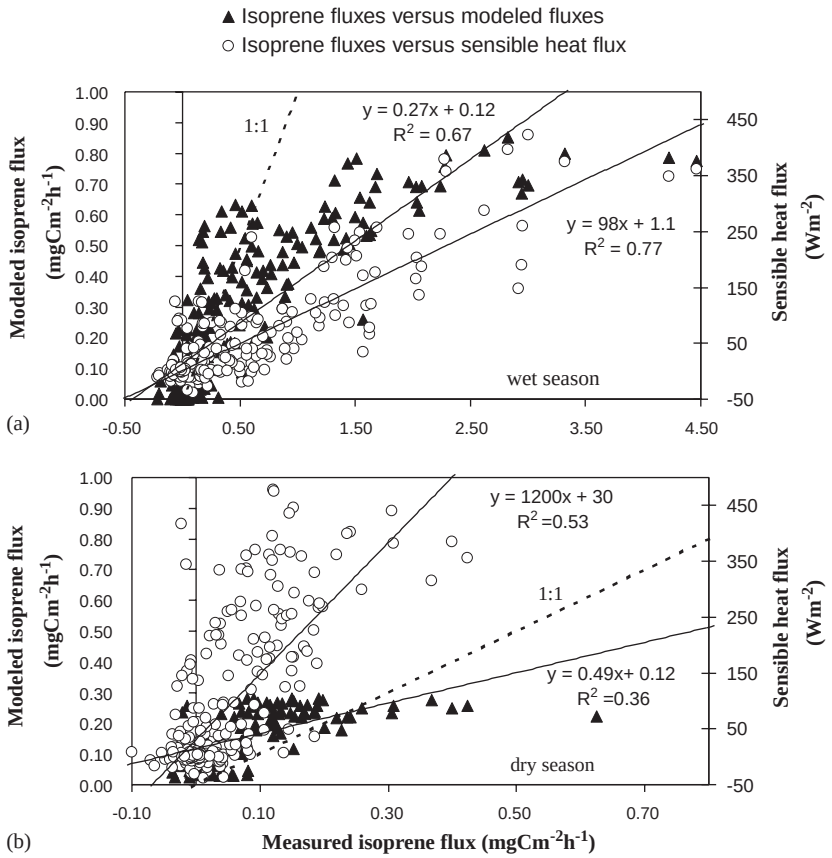

Fig. 2. Correlation between modeled isoprene fluxes and sensible heat fluxes with measured isoprene fluxes for the wet season (2a) and the dry season (2b). A 1:1 line is shown for the modeled versus measured isoprene fluxes.

fluxes in both the wet and dry seasons. This is most likely due to the model's inability to replicate the temperature and light environment within the canopy (Rinne et al., 2002). There is a factor of 12 increase in the slope between the wet and dry season for the correlation between sensible heat flux and isoprene flux. The slope for the wet season (98 Wmg $C^{-1} h^{-1}$) agrees well with the slope between sensible heat and isoprene flux given by Rinne et al. (2002) for isoprene fluxes in an Amazonian rainforest, also during the wet season.

Guenther et al. (1999) predicted that dry season isoprene emissions might be higher than those in the wet season under similar conditions of temperature due to lower stomatal conductance during the dry season, causing higher leaf temperatures. This has been supported by canopy level isoprene flux data from central Africa (Serça et al., 2001), and ambient concentration data from the Amazon basin (Kesselmeier et al., 2002; Trostdorf et al., 2004). The data presented here does not agree with this other data. Reductions in both isoprene and monoterpene emissions have been observed as a response to severe drought. Sharkey and Loreto (1993) have shown, measuring isoprene emissions from individual kudzu leaves, that water stress will at first lead to an increase, and then under severe stress, a reduction in isoprene emissions. Núñez et al. (2002) observed a reduction in light-dependent monoterpene emissions from *Quercus ilex* that was a result of high ambient temperature and low relative humidity. Owen et al. (2004) observed similar emission patterns from some of the plants located at the XTBG. In the studies by Sharkey and Loreto (1993), and Owen et al. (2004), a dramatic reduction in carbon assimilation was observed along with reductions in isoprene emissions. Unfortunately, no ecosystem level carbon assimilation measurements were made concurrently with isoprene flux measurements, so it is impossible to confirm if the forest was suffering the same extreme water stress conditions that some of the individual leaf level emission measurements suggest; however, this scenario is likely.

3.4. Above canopy monoterpene concentrations

Leaf level measurements have shown that *Hevea brasiliensis* is a strong light-dependent monoterpene emitter (Klinger et al., 2002; Owen et al., 2004). The major monoterpene emission from *Hevea brasiliensis* is sabinene (Owen et al., 2004). In order to account for all monoterpene emissions, GC-FID chromatograms were integrated over the entire region of the chromatogram where monoterpenes elute. Four of the major peaks in this region were identified by comparison with the standard gas described previously; all of the major peaks in this region followed the same diurnal pattern as the four identified monoterpenes. Nonetheless, by integrating over the entire region without identifying each individual peak, an unknown overestimation of the ambient concentrations has been introduced. Above canopy monoterpene concentrations are only reported for the wet season since ambient monoterpene measurements for the dry season commonly resulted in monoterpene concentrations below detection limits (about 60 parts per trillion by volume (pptv) for any individual monoterpene and a 2 L sample). These low concentrations during the dry season infer an extremely low flux for the monoterpenes at that time, which is consistent with the loss of the *Hevea brasiliensis* leaves during the dry season. Alternatively, low monoterpene concentrations may have been due to elevated ozone concentrations during the dry season, possibly from regional biomass burning. However, without measurements of ozone at this field site, it is impossible to be conclusive.

Fig. 3 shows average ambient monoterpene concentrations over the *Hevea brasiliensis* forest for a five-day period, along with ambient concentrations over the second, upwind tower. In addition, half-hour average ambient isoprene concentrations for the same five-day period, measured by the FIS system, are also shown for comparison. The diurnal pattern in the ambient monoterpene concentrations is indicative of a light-dependent flux of monoterpenes, with higher daytime concentrations, similar to the pattern of isoprene. Afternoon concentrations of monoterpenes drop off faster than those of isoprene. This may be due to losses of monoterpenes on the adsorbent cartridge because of reactions with ozone on the adsorbent material, or afternoon transport of isoprene from areas of higher isoprene emissions. Monoterpene concentrations at the second upwind tower, that was not in the vicinity of *Hevea brasiliensis* trees, show a constant, and lower daytime monoterpene concentration.

3.5. Modeled monoterpene fluxes

Above canopy monoterpene fluxes were modeled using the same algorithm as for modeled isoprene fluxes. Only wet season monoterpene fluxes are considered, since our dry season ambient monoterpene measurements indicate extremely low monoterpene concentrations and presumably extremely low fluxes. Low monoterpene fluxes during the dry season are assumed to be a result of the drought deciduous nature of the light-dependent monoterpene emitting *Hevea brasiliensis*. Modeled total monoterpene fluxes corresponding to the five-day period that ambient air samples were collected are shown in Fig. 4. Modeled fluxes peak at about 4 mg $C\,m^{-2} h^{-1}$.

The modeled above canopy monoterpene fluxes reported here are considerably higher than those observed at other tropical forests. Rinne et al. (2002) reported α-pinene fluxes (representing half of observed monoterpenes) on the order of 0.1 mg $C\,m^{-2} h^{-1}$. High

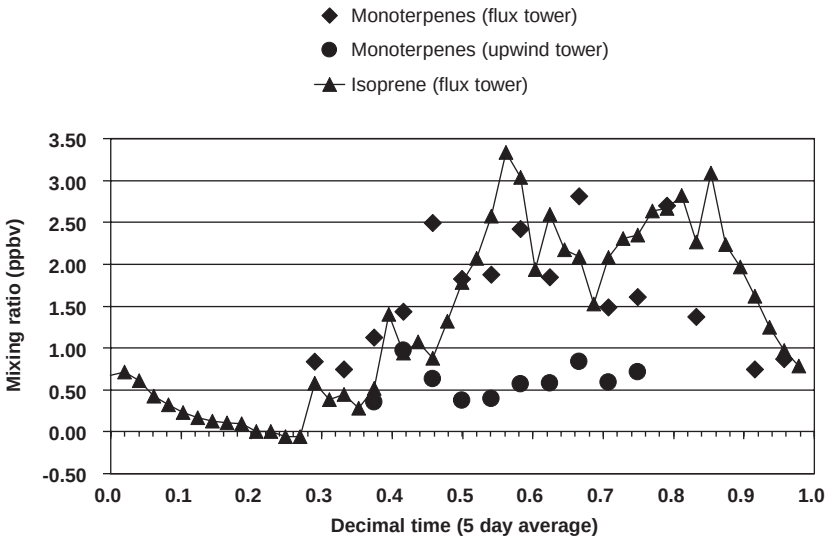

Fig. 3. Ambient concentrations of isoprene and total monoterpenes at the flux tower and ambient total monoterpene concentrations at an upwind tower. The data represents the average concentrations from five days of measurements.

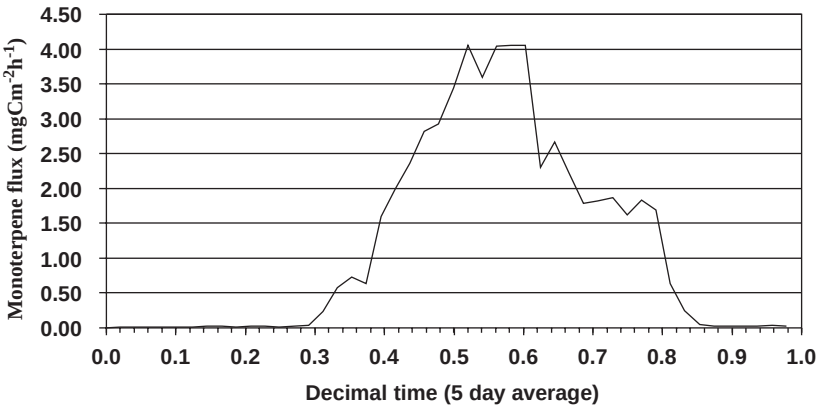

Fig. 4. Modeled total monoterpene fluxes, based on the scaling up of leaf level monoterpene flux measurements. The data represents averages over a 5-day period.

emission capacities for monoterpenes, on the order of 3.0 mg C $m^{-2} h^{-1}$, have been reported for some African savanna ecosystems (Otter et al., 2002). It is not surprising that the high monoterpene emissions reported here are not typical of natural tropical forests. The monodominant *Hevea brasiliensis* forest is not naturally occurring, and under natural conditions, *Hevea brasiliensis* would simply represent one high monoterpene emitter in the midst of many low emitting trees; resulting in a forest with moderate monoterpene emissions. The high monoterpene emissions reported here stress the importance of understanding human induced changes in land use and management over time with respect to biogenic VOC emissions, since these changes, even on a small scale, can have potentially large impacts on regional emissions.

4. Conclusions

Seasonal above canopy isoprene and monoterpene fluxes have been reported for a mixed plantation/secondary tropical forest in southwestern China. Wet season above canopy isoprene fluxes agree quite well in magnitude to above canopy isoprene fluxes observed from other tropical forests. Wet season fluxes were much higher for both isoprene and monoterpenes relative to the dry season. This does not agree with reported data

from other tropical forests, which indicate that dry season fluxes should be higher due to higher leaf temperatures; however, the extreme drought conditions that were present during the dry season in southwestern China may account for this discrepancy. More frequent seasonal flux measurements are needed to characterize the large fluctuations in ecosystem level fluxes that are observed. In addition, future measurements should include carbon dioxide and water vapor exchange, as well as soil moisture, in order to get a better picture of the overall condition of the vegetation, and for a more accurate comparison to leaf level emissions. Wet season monoterpene emissions were unusually high due to the dominance of one species of tree, *Hevea brasiliensis*, in the forest canopy. This species is a high emitter of light dependent monoterpenes. The dominance of this one tree species, which was planted for agricultural purposes, highlights the effects that land use change can have on biogenic VOC emissions.

Acknowledgements

This work was funded by an NSF International Program supplement to NSF Grant ATM-0131785 to B. Baker. The authors would like to thank Chong-Jiang Zhao for help in collecting transect data, and Wen-Jie Liu and Jianwei Tang for access to the flux tower used in this investigation. The flux tower is sponsored by the Chinese Ecosystem Research Network. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

References

Atkinson, R., Arey, J., 2003. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. Atmospheric Environment 37, S197–S219.

Bai, Y., Li, J., Liang, B., Zhao, M., Tang, X., 1995. Natural hydrocarbon compounds emitted from vegetation in China. Pure and Applied Chemistry 67, 1415–1419.

Fuentes, J.D., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J.W., Ciccioli, P., Lamb, B., Geron, C., Gu, L., Guenther, A., Sharkey, T.D., Stockwell, W., 2000. Biogenic hydrocarbons in the atmospheric boundary layer: A review. Bulletin of the American Meteorological Society 81, 1537–1575.

Geron, C.D., Guenther, A.B., Pierce, T.E., 1994. An improved model for estimating emissions of volatile organic compounds from forests in the eastern United States. Journal of Geophysical Research 99, 12773–12791.

Greenberg, J.P., Guenther, A., Zimmerman, P., Baugh, W., Geron, C., Davis, K., Helmig, D., Klinger, L.F., 1999. Tethered balloon measurements of biogenic VOCs in the atmospheric boundary layer. Atmospheric Environment 33, 855–867.

Guenther, A.B., Monson, R.K., Fall, R., 1991. Isoprene and monoterpene emission rate variability: observations with eucalyptus and emission rate algorithm development. Journal of Geophysical Research 96, 10799–10808.

Guenther, A.B., Zimmerman, P.R., Harley, P.C., Monson, R.K., Fall, R., 1993. Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses. Journal of Geophysical Research 98, 12609–12617.

Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. Journal of Geophysical Research 100, 8873–8892.

Guenther, A.B., Hills, A.J., 1998. Eddy covariance measurement of isoprene fluxes. Journal of Geophysical Research 103, 13145–13152.

Guenther, A., Baugh, B., Brasseur, G., Greenberg, J., Harley, P., Klinger, L., Serça, D., Vierling, L., 1999. Isoprene emission estimates and uncertainties for the Central African EXPRESSO study domain. Journal of Geophysical Research 104, 30625–30639.

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

Helmig, D., 1996. Artifact-free preparation, storage and analysis of solid adsorbent sampling cartridges used in the analysis of volatile organic compounds in air. Journal of Chromatography 732, 414–417.

Helmig, D., Klinger, L.F., Guenther, A., Vierling, L., Geron, C., Zimmerman, P., 1999. Biogenic Volatile Organic Compound Emissions (BVOCs) II. Landscape Flux Potentials from Three Continental Sites in the US. Chemosphere 38, 2189–2204.

Hills, A.J., Zimmerman, P.R., 1990. Isoprene measurement by ozone-induced chemiluminescence. Analytical Chemistry 62, 1055–1060.

Kesselmeier, J., Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Andreae, M.O., Ciccioli, P., Brancaleoni, E., Frattoni, M., Oliva, S.T., Botelho, M.L., Silva, C.M.A., Tavares, T.M., 2002. Concentrations and species composition of atmospheric volatile organic compounds (VOCs) as observed during the wet and dry season in Rondônia (Amazonia). Journal of Geophysical Research 107 D20, 8053.

Kesselmeier, J., Schaefer, L., Ciccioli, P., Brancaleoni, E., Cecinato, A., Frattoni, M., Foster, P., Jacob, V., Denis, J., Fugit, J.L., Dutaur, L., Torres, L., 1996. Emission of monoterpenes and isoprene from a Mediterranean oak species *Quercus ilex L.* measured within the BEMA (Biogenic Emissions in the Mediterranean Area) project. Atmospheric Environment 30, 1841–1850.

Klinger, L.F., Greenberg, J., Guenther, A., Tyndall, G., Zimmerman, P., M'Bangui, M., Moutsamboté, J.-M., Kenfack, D., 1998. Patterns in volatile organic compound emissions along a savanna-rainforest gradient in central Africa. Journal of Geophysical Research 103, 1443–1454.

Klinger, L.F., Li, Q.-J., Guenther, A.B., Greenberg, J.P., Baker, B., Bai, J.-H., 2002. Assessment of volatile organic

compound emissions from ecosystems of China. Journal of Geophysical Research 107.

Leblanc, S.G., Chen, J.M., Kwong, M., 2002. Tracing radiation and architecture of canopies (TRAC) manual version 2.1, Canada Centre for Remote Sensing, Natural Resources Canada, 25p.

Núñez, L., Plaza, J., Pérez-Pastor, R., Pujadas, M., Gimeno, B.S., Bermejo, V., García-Alonso, S., 2002. High water vapour pressure deficit influence on *Quercus ilex* and *Pinus pinea* field monoterpene emission in the central Iberian Peninsula (Spain). Atmospheric Environment 36, 4441–4452.

Otter, L.B., Guenther, A., Greenberg, J., 2002. Seasonal and spatial variations in biogenic hydrocarbon emissions from southern African savannas and woodlands. Atmospheric Environment 36, 4265–4275.

Potter, C.S., Alexander, S.E., Coughlan, J.C., Klooster, S.A., 2001. Modeling biogenic emissions of isoprene: exploration of model drivers, climate control algorithms, and use of global satellite observations. Atmospheric Environment 35, 6151–6165.

Rinne, H.J.I., Guenther, A.B., Greenberg, J.P., Harley, P.C., 2002. Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature. Atmospheric Environment 36, 2421–2426.

Roberts, J.M., Williams, J., Baumann, K., Buhr, M.P., Goldan, P.D., Holloway, J.S., Hübler, G., Kuster, W.C., McKeen, S., Ryerson, T.B., Trainer, M., Williams, E.J., Fehsenfeld, F.C., Bertman, S.B., Nouaime, G., Seaver, C., Grodzinsky, G., Rodgers, M., Young, V.L., 1998. Measurements of PAN, PPN, and MPAN made during the 1994 and 1995 Nashville Intensives of the Southern Oxidant Study: implications for regional ozone production from biogenic hydrocarbons. Journal of Geophysical Research 103, 22473–22490.

Rosenstiel, T.N., Potosnak, M.J., Griffin, K.L., Fall, R., Monson, R.K., 2003. Elevated CO_2 uncouples growth and isoprene emission in an agriforest ecosystem. Nature 421, 256–259.

Serça, D., Guenther, A., Klinger, L., Vierling, L., Harley, P., Druilhet, A., Greenberg, J., Baker, B., Baugh, W., Bouka-Biona, C., Loemba-Ndembi, J., 2001. EXPRESSO flux measurements at upland and lowland Congo tropical forest site. Tellus 53B, 220–234.

Sharkey, T.D., Loreto, F., 1993. Water stress, temperature, and light effects on the capacity for isoprene emission and photosynthesis of kudzu leaves. Oecologia 95, 328–333.

Staudt, M., Seufert, G., 1995. Light-dependent emission of monoterpenes by holm oak (*Quercus ilex L.*). Naturwissenschaften 82, 89–92.

Steiner, A., Luo, C., Huang, Y., Chameides, W.L., 2002. Past and present-day biogenic volatile organic compound emissions in East Asia. Atmospheric Environment 36, 4895–4905.

Trainer, M., Williams, E.J., Parrish, D.D., Buhr, M.P., Allwine, E.J., Westberg, H.H., Fehsenfeld, F.C., Liu, S.C., 1987. Models and observations of the impact of natural hydrocarbons on rural ozone. Nature 329, 705–707.

Trostdorf, C., Gatti, L., Yamazaki, A., Potosnak, M., Guenther, A., Martins, W., Munger, J., 2004. Seasonal cycles of isoprene concentrations in the Amazonian rainforest. Atmospheric Chemistry and Physics Discussions 4, 1291–1310.

Zimmerman, P., Greenberg, J., Westberg, C., 1988. Measurements of atmospheric hydrocarbons and biogenic emission fluxes in the Amazon boundary layer. Journal of Geophysical Research 93, 1407–1416.