

# Monoterpene emissions from rubber trees (*Hevea brasiliensis*) in a changing landscape and climate: chemical speciation and environmental control

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## Abstract

Emissions of biogenic volatile organic compounds (VOCs) have important roles in ecophysiology and atmospheric chemistry at a wide range of spatial and temporal scales. Tropical regions are a major global source of VOC emissions and magnitude and chemical speciation of VOC emissions are highly plant-species specific. Therefore it is important to study emissions from dominant species in tropical regions undergoing large-scale land-use change, for example, rubber plantations in South East Asia. Rubber trees (*Hevea brasiliensis*) are strong emitters of light-dependent monoterpenes. Measurements of emissions from leaves were made in the dry season in February 2003 and at the beginning of the wet season in May 2005. Major emitted compounds were sabinene,  $\alpha$ -pinene and  $\beta$ -pinene, but  $\beta$ -ocimene and linalool also contributed significantly at low temperature and light. *Cis*-ocimene was emitted with a circadian course independent of photosynthetic active radiation (PAR) and temperature changes with a maximum in the middle of the day. Total isoprenoid VOC emission potential at the beginning of the wet season ( $94 \mu\text{g g dw}^{-1} \text{h}^{-1}$ ) was almost two orders of magnitude higher than measured in the dry season ( $2 \mu\text{g g dw}^{-1} \text{h}^{-1}$ ). Composition of total emissions changed with increasing temperature or PAR ramps imposed throughout a day. As well as light and temperature, there was evidence that assimilation rate was also a factor contributing to seasonal regulating emission potential of monoterpenes from rubber trees. Results presented here contribute to a better understanding of an important source of biogenic VOC associated with land-use change in tropical South East Asia.

**Keywords:** atmospheric chemistry, biogenic VOC, climate change, *Hevea brasiliensis*, land-use change, monoterpene emission, regional VOC flux, Xishuangbanna

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## Introduction

Emissions of biogenic volatile organic compounds (BVOCs) from vegetation have been studied for more than two decades, because they have an important role in tropospheric chemistry by contributing to the photo-

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chemical production of ozone and secondary particle formation (Fehsenfeld *et al.*, 1992). Although there is a growing body of literature contributing to our knowledge of tropical BVOC flux in Amazonia (e.g. Helmig *et al.*, 1998; Kesselmeier *et al.*, 2002; Greenberg *et al.*, 2004; Harley *et al.*, 2004), and in tropical Africa (e.g. Serca *et al.*, 2001; Greenberg *et al.*, 2003; Otter *et al.*, 2003), there is still a paucity of research on BVOC flux in tropical Asia, with only a few reports from India (e.g. Padhy & Varshney, 2005), and limited work based in the tropical Yunnan province of south China (e.g. Klinger *et al.*, 2002; Baker *et al.*, 2005; Wang *et al.*, 2005a, b). The tropical region of SE Asia is of particular importance

because it is subject to very rapid and large-scale land-use change, with plantations of species such as *Hevea brasiliensis* (rubber) replacing primary tropical forests.

In this study, detailed measurements were made of monoterpene emissions from *H. brasiliensis* growing at Xishuangbanna Tropical Botanic Gardens. The Xishuangbanna Prefecture is located in SW China, in the Yunnan province, just within the tropical zone and *H. brasiliensis* is an important and often dominant species in this region. BVOC emissions are highly dependent on vegetation cover (plant species composition and dominance) (Guenther *et al.*, 1995, 2006; Lerda & Slobodkin, 2002). Thus, large-scale land-cover changes from primary rainforests to rubber tree plantation, and from rubber plantation to other plantation crops (e.g. oil palm) are likely to result in regional BVOC emission pattern changes, which in turn might contribute to changes in regional air quality and climate in these tropical areas. Previous leaf level measurements have indicated that rubber trees are strong monoterpene emitters (Klinger *et al.*, 2002). More recently, Baker *et al.* (2005) estimated that typical wet season day-time average monoterpene fluxes from *H. brasiliensis* plantations are  $\sim 10$  times higher than from typical mixed tropical forest (or non-forest) landscapes [ $2.0$  vs.  $0.2 \text{ mg(C) m}^{-2} \text{ h}^{-1}$ ]. These conclusions were drawn from integrated canopy-scale measurements of BVOC flux on a tower in a small rubber plantation, and from some leaf-level measurements.

The emission rates of most BVOC increase with temperature exponentially up to an optimum, by increasing the rate of biosynthetic pathways, raising the BVOC vapour pressure, and decreasing the resistance of emission pathway (Loreto *et al.*, 1996). However, there are differences in the response depending on the compound volatility and biochemistry (Peñuelas & Llusià, 1999a). Irradiance influences long-term BVOC pool size by providing biosynthetic energy, regulating the synthesis and controlling growth (Langenheim, 1994). Moreover, on a short-time scale of minutes and hours, irradiance influences the emissions of non-stored BVOC such as isoprene and terpenes that need photosynthetic products for their biosynthesis (Kesselmeier *et al.*, 1996; Loreto *et al.*, 1996; Bertin *et al.*, 1997; Peñuelas & Llusià, 1999a,b; Llusià & Peñuelas, 2000). There is often no instantaneous light influence on terpene emissions for terpene-storing species (Peñuelas & Llusià, 1999b; Llusià & Peñuelas, 2000), even though a part of the emission may be derived from recently synthesized terpenes (Kesselmeier & Staudt, 1999). However, limited light dependency of monoterpene emissions from stored pools in Mediterranean species has been reported (Owen *et al.*, 2002). Monoterpene emissions from tropical rainforests have generally been consid-

ered as only temperature dependent (e.g. Guenther *et al.*, 1995), but there are now some reports of light-dependent monoterpene emissions from tropical canopies (e.g. Kuhn *et al.*, 2002, 2004; Rinne *et al.*, 2002; Otter *et al.*, 2003; Karl *et al.*, 2004) and previous research has indicated that rubber trees have a strong trend of light dependency of monoterpene emission (Klinger *et al.*, 2002; Baker *et al.*, 2005). Here, we present in detail for the first time the chemical speciation and temperature and light dependencies of monoterpene emissions from rubber trees. We show that strong diurnal factors other than temperature and light affect emissions of some compounds, and that physical properties of some emitted compounds are likely to play an important role.

## Materials and methods

### Study site

The study site was located in Xishuangbanna Tropical Botanical Garden (XTBG), Chinese Academy of Sciences, SW China ( $21^{\circ}55'25''\text{N}$ ,  $101^{\circ}16'05''\text{E}$ ), where the mean annual temperature is  $21.6^{\circ}\text{C}$ , the mean annual precipitation is about 1500 mm, and the average relative humidity is 86%. There is distinct alternation of dry and wet seasons over the year. The dry season is from November to April, the beginning of the wet season occurs in May, while the full wet season is from June to October with 75% of the yearly rainfall. Our field research was conducted during the dry season from late February to early March of 2003, and at the start of the wet season during May 2005. The experimental plants were rubber trees (*H. brasiliensis* Muell.-Arg.), growing at the edge of a 30-year-old rubber/tea-mixed plantation, and therefore, receiving sun on the sampled branches. Two trees were sampled in the dry season, and three trees at the start of the wet season. Full-grown leaves were sampled on branches which were part of the main canopy, but which had bent naturally to near-ground level. To bring them within operating distance of the leaf cuvette, the branches were secured and anchored with rope and pegs in the ground. Sampling height was at about 2 m on leaves which received sun for a large part of the day, and were considered to be representative of conditions nearer the top of the canopy. The relatively small standard errors of the means for much of the emission and physiology data indicate reasonably low variability between the sampled leaves, and provides further evidence that the leaves were representative of the healthy, sun-lit leaf population for that plantation.

*Field sampling*

A leaf cuvette (LCpro, ADC Bioscientific Ltd, Hoddesdon, UK) was adapted for sampling VOC emissions, by introducing a sampling port in the gas line exiting the cuvette. Before each measuring campaign, the leaf cuvette had been serviced and checked, and was in optimal working order. A charcoal filter was fitted to the inflow of the leaf cuvette to remove ambient BVOCs and ozone. This had the effect of elevating the ambient CO<sub>2</sub> concentrations by about 50 ppm on average, but this was fairly consistent for all emission samples. While this is a little higher than the average ambient (CO<sub>2</sub>), there are several reports of high (CO<sub>2</sub>) between 1 and 5 m from a tropical forest floor during the morning and later in the afternoon (e.g. Buchmann *et al.*, 1997; Culf *et al.*, 1999). Rosenstiel *et al.* (2003) found that increasing CO<sub>2</sub> concentrations reduces canopy isoprene emission and decouples isoprene emissions from photosynthesis, however, they worked with concentrations of 800 and 1200 ppm, which is far higher than the concentrations that the sampled leaves experienced in the investigation reported here (~400 ppm). Using a charcoal trap to clean inflowing air might result in upper-limit emission measurements because purified air can result in a higher concentration gradient of emitted compound between leaf air space and ambient air. But in nature, wind or high ozone concentrations reacting with emitted products would also increase monoterpene concentration gradients. We consider that natural factors affecting concentration gradients of emitted compounds are complex and variable, and that concentration gradients of emitted compounds resulting from using a charcoal filter are likely to be matched in nature with reasonable frequency.

Inter-comparison experiments performed during the first field campaign suggested that BVOC emissions measured using this cuvette system were comparable with those measured using a LiCOR system (Geron *et al.*, 2006). The leaf cuvette was installed on a leaf and left to equilibrate for 45 min before VOC samples were taken. Flow rate through the cuvette was ~300 mL min<sup>-1</sup>, and the sampled leaf area was 6.25 cm<sup>2</sup>. Sample cartridges were filled with 100 mg Carbotrap and 200 mg Tenax and conditioned for 15 min at 300 mL min<sup>-1</sup> in a flow of helium. Cartridges prepared this way have been used in our laboratory for many years, and are always very consistent in their adsorbent properties. A cartridge was fitted to the cuvette outlet port, and air from the cuvette drawn through it at 100–120 mL min<sup>-1</sup>. This range of flow rates ensured that only cuvette air was sampled, and was not contaminated with outside air. Samples were taken for 10–20 min, and the cartridges were stored in a refrigerator until returned to

Lancaster, UK, for analysis using gas chromatography with mass selective detection (GC-MS). To assess changes in sample compound content during storage and transport, three conditioned sample tubes were injected with a standard monoterpene mixture of 10 different commonly occurring compounds. A further three tubes were injected with gaseous isoprene standard. These tubes were capped and transported to the field site alongside the conditioned tubes for sampling. They were exposed to ambient conditions in the field for a day, stored with sampled tubes in a refrigerator during the field work, and were subject to the same processes of return transport and storage before analysis as the samples. The transported standards were analysed after the samples to represent a worst-case scenario of delay before analysis. Overall, there was between 0.1% and 10.4% more of each compound in the transported standard tubes compared with freshly injected standards, but differences were not significant, due to variability in different batches of diluted standards. In addition, a sample was taken from an empty leaf cuvette each day to give a blank value which was subtracted from emission samples.

*Sample strategy*

Three types of field experiment were performed: (1) a course of BVOC emission potential (Epot) measurements. Epot is defined as emission rate at a standard temperature (30 °C) and photosynthetic active radiation (PAR; 1000 μmol m<sup>-2</sup> s<sup>-1</sup>). Several consecutive measurements were made from two trees (one leaf each) in the dry season, and from three trees (one leaf each) at the start of the wet season. Each leaf was installed in the leaf cuvette at the beginning of the sampling day, and remained there throughout the day. Maximum Epot values were calculated as the mean of four emission measurements made at standard conditions between 11:00 and 14:00 local time (Table 1); (2) an investigation of the effect of increasing PAR on BVOC emissions throughout the day. PAR was increased in steps from 0 to 1760 μmol m<sup>-2</sup> s<sup>-1</sup> (dry season – 0, 300, 600, 800, 1050, 1200, 1400, 1650 and 1780 μmol m<sup>-2</sup> s<sup>-1</sup>; wet season – 0, 104, 218, 452, 905 and 1740 μmol m<sup>-2</sup> s<sup>-1</sup>), equilibrating for 45 min after setting a new PAR level, and keeping temperature constant at 30 °C ('PAR ramp'); and (3) an investigation of the effect of increasing temperature on BVOC emissions throughout the day. Temperature was increased in steps from 20 to 40 °C (dry season – 24, 29, 30, 34, 37, 40, 29 °C; wet season – 20, 25, 30, 35, 40, 43 °C), equilibrating for 45 min after setting a new temperature level, keeping PAR constant at 1000 μmol m<sup>-2</sup> s<sup>-1</sup> ('temperature ramp'). Humidity was sustained at ambient values

**Table 1** Emission potentials ( $\pm$  SE) from *Hevea brasiliensis* estimated from four samples taken in the middle of the day (11:00–14:00)

	Boiling point (K)	$K_{OH}$ (298 K)* $\times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Emission potential ( $\mu\text{g g dw}^{-1} \text{ h}^{-1}$ )				
			Dry season		Start of wet season		
			Tree 1	Tree 2	Tree 1	Tree 2	Tree 3
sabinene	437	117	1.9 $\pm$ 0.1	1.4 $\pm$ 0.1	43 $\pm$ 14	65 $\pm$ 7	67 $\pm$ 4
$\alpha$ -pinene	428	54	0.2 $\pm$ 0.0	0.2 $\pm$ 0.0	7.1 $\pm$ 0.7	6.9 $\pm$ 0.8	6.9 $\pm$ 0.5
$\beta$ -pinene	436	79	0.2 $\pm$ 0.0	0.1 $\pm$ 0.0	6.8 $\pm$ 2.2	6.7 $\pm$ 1.7	9.5 $\pm$ 0.7
<i>cis</i> -ocimene	373	252			4.3 $\pm$ 2.3	9.3 $\pm$ 3.1	5.9 $\pm$ 2.8
limonene	448	171			6.2 $\pm$ 0.8	1.6 $\pm$ 0.9	3.0 $\pm$ 0.4
$\alpha$ -terpinene	447	363			5.5 $\pm$ 4.4	0.2 $\pm$ 0.1	0.3 $\pm$ 0.2
$\gamma$ -terpinene	455	177			8.0 $\pm$ 5.4	0.3 $\pm$ 0.2	0.6 $\pm$ 0.2
cineole	450	11 <sup>†</sup>			3.4 $\pm$ 0.3	2.9 $\pm$ 0.9	1.0 $\pm$ 0.2
$\alpha$ -terpineole	490	190 <sup>‡</sup>			3.5 $\pm$ 3.1	0.3 $\pm$ 0.1	0.5 $\pm$ 0.1
myrcene	440	215			2.8 $\pm$ 0.3	1.9 $\pm$ 0.4	1.7 $\pm$ 0.9
$\alpha$ -thujene	425	<sup>§</sup>			1.8 $\pm$ 0.5	0.7 $\pm$ 0.2	0.9 $\pm$ 0.2
$\alpha$ -phellandrene	448	313			0.3 $\pm$ 0.3	0.0 $\pm$ 0.0	0.1 $\pm$ 0.1
$\beta$ -ocimene	373	252			0.0 $\pm$ 0.0	0.5 $\pm$ 0.3	0.4 $\pm$ 0.2
linalool	469	159 <sup>¶</sup>			0.0 $\pm$ 0.0	0.1 $\pm$ 0.1	0.1 $\pm$ 0.0
Total MT <sup>  </sup>			2.3 $\pm$ 0.1	1.7 $\pm$ 0.2	93 $\pm$ 5.4	96 $\pm$ 13	98 $\pm$ 7.0

\*Seinfeld & Pandis (2006).

<sup>†</sup>Corchnoy & Atkinson (1990).

<sup>‡</sup>Wells (2005).

<sup>§</sup>No data available.

<sup>¶</sup>Hoffmann *et al.* (1997).

<sup>||</sup>All compounds, including ocimene and linalool (see text).

within the cuvette. For the temperature and PAR ramps, one tree (one leaf) was investigated in the dry season, and three trees (one leaf each) were investigated at the start of the wet season.

### BVOC analysis

Emission samples were analysed using GC-MSD. Sample cartridges were thermally desorbed using a Perkin Elmer (Waltham, MA, USA) Turbomatrix Automatic Thermal Desorption unit, connected via a heated transfer line to a Perkin Elmer TurboMass Gold GC-MSD. The two-stage desorption programme first heated the sample cartridges at 280 °C for 6 min in a stream of purified helium gas at 30 mL min<sup>-1</sup>. During this primary desorption process, VOCs were desorbed from the sample cartridge and were cryo-focussed in a Tenax-TA cold trap held at -30 °C. After primary desorption, the cold trap was flash heated to 300 °C and held for 5 min for secondary desorption of compounds from the cold-trap via a heated transfer line at 200 °C, onto an Ultra-2 capillary column (50 m  $\times$  0.22 mm id  $\times$  1.05  $\mu$ m film thickness, Hewlett Packard, Varian Inc., CA, USA) for separation. The GC oven was initially held at 40 °C for 2 min, before heating to 160 °C at a rate of 4 °C min<sup>-1</sup>. The temperature was then increased further

at a rate of 45 °C min<sup>-1</sup> to 300 °C, which was held for 10 min. Identification of the individual monoterpenes were confirmed via comparison of retention time and similarity of fragmentation patterns of individual monoterpene standards, using the Wiley (John Wiley and Sons, NY, USA) and NIST Mass Spectral Libraries in conjunction with the TURBOMASS software (TURBOMASS Version 4.4.0.014; PerkinElmer Instruments). Quantification for each compound was achieved by comparison with standard compounds, and was based on the abundances of ion 93 (*m/z*). Those compounds for which standards were not available were quantified by the ratio of their ion 93 abundance compared with  $\alpha$ -pinene (Greenberg *et al.*, 2004).

### The 'G93' algorithm and statistical analyses

Guenther *et al.* (1993, 1995) developed the widely used algorithm ('G93') for predicting isoprene and monoterpene emissions from vegetation, based on leaf temperature and PAR.

$$\text{Emission\_rate} = \text{Epot} * C_T * C_L, \quad (1)$$

$$C_L = (\alpha * C_{L1} * L) * (1 + (\alpha^2 * L^2))^{-0.5}, \quad (2)$$

$$C_T = \left\langle \exp \left[ C_{T1} * (T - T_s) * (R * T_s * T)^{-1} \right] \right\rangle * \left\langle 1 + \exp \left[ C_{T2} * (T - T_{\max}) * (R * T_s * T)^{-1} \right] \right\rangle^{-1}, \quad (3)$$

where  $E_{pot}$  = emission potential at 30 °C and 1000  $\mu\text{mol m}^{-2}\text{s}^{-1}$  PAR,  $T_{\max}$  = 314 K and  $R$  = 8.314  $\text{J K}^{-1}\text{mol}^{-1}$ .  $L$  is the flux of PAR ( $\mu\text{mol m}^{-2}\text{s}^{-1}$ ) and  $T_s$  is the leaf temperature at standard condition (303 K for this study). Guenther *et al.* (1993) empirically derived the constants  $\alpha$  = 0.0027  $\text{m}^2\text{s}\mu\text{mol}^{-1}$ ,  $C_{L1}$  = 1.066,  $C_{T1}$  = 95 000  $\text{J mol}^{-1}$ ,  $C_{T2}$  = 230 000  $\text{J mol}^{-1}$  from experiments with a limited number of species. At standard conditions of 1000  $\mu\text{mol m}^{-2}\text{s}^{-1}$  PAR and 303 K,  $(C_L * C_T)_{\text{std}} = 1$ .

Because monoterpene emissions from *H. brasiliensis* are light dependent, it was assumed that the G93 algorithm would be a suitable tool for predicting monoterpene emissions from this species. This has been successfully applied for light-dependent monoterpene emitting tropical tree species (Kuhn *et al.*, 2002, 2004).

## Results

### *Physiological response of H. brasiliensis to PAR and temperature ramps*

In both dry and wet seasons, at constant PAR (1000  $\mu\text{mol m}^{-2}\text{s}^{-1}$ ) and temperature (30 °C), assimilation decreased during the course of the sampling day until ~17:00 hours, with signs of increase again towards 18:00 hours (Figs 1a and b). Assimilation rates in the dry season were at least half those measured at the beginning of the wet season at equivalent times of day. During PAR ramp experiments, assimilation rates increased from negative  $\text{CO}_2$  uptake at 0  $\mu\text{mol m}^{-2}\text{s}^{-1}$  PAR, to ~1.5  $\mu\text{mol m}^{-2}\text{s}^{-1}$  at 600  $\mu\text{mol m}^{-2}\text{s}^{-1}$  PAR, and ~6  $\mu\text{mol m}^{-2}\text{s}^{-1}$  at 2000  $\mu\text{mol m}^{-2}\text{s}^{-1}$  PAR (dry season and beginning of the wet season, respectively). As PAR was increased further, there were no further significant changes in assimilation rates in the dry season, but there was a slight decline at the beginning of the wet season (Figs 1c and d). During the increasing temperature ramp in both dry and wet seasons,

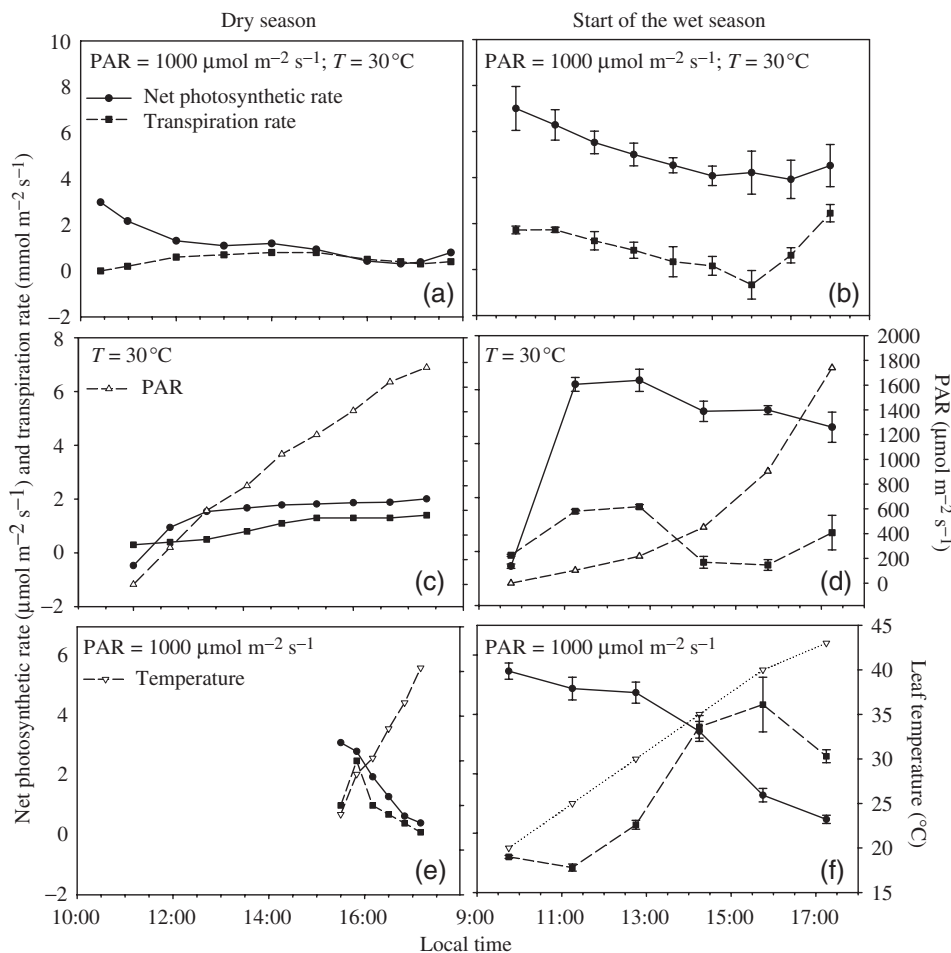


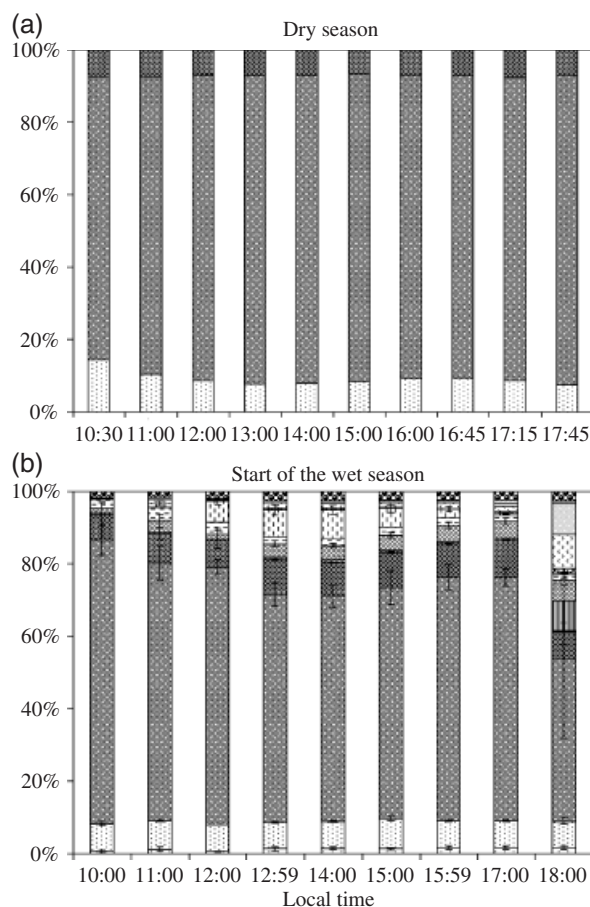
Fig. 1 Net photosynthetic and transpiration rates for *Hevea brasiliensis* during constant diurnal conditions, PAR and temperature ramps.

assimilation rates decreased continuously and almost ceased at temperatures  $> 40^{\circ}\text{C}$  (Figs 1e and f).

Transpiration rate in the dry season was extremely low, ranging between 0 and  $1\text{ mmol m}^{-2}\text{ s}^{-1}$  with a small mid-day peak in conditions of constant PAR ( $1000\ \mu\text{mol m}^{-2}\text{ s}^{-1}$ ) and temperature ( $30^{\circ}\text{C}$ ) (Figs 1a and b). At the beginning of the wet season, transpiration rate started at  $2\text{ mmol m}^{-2}\text{ s}^{-1}$  at the beginning of the day, and declined until late afternoon ( $\sim 16:00$  hours), recovering in the early evening. In the dry season, transpiration rate increased from 0.3 to  $1.4\text{ mmol m}^{-2}\text{ s}^{-1}$  during the PAR ramp from 0 to  $\sim 1000\ \mu\text{mol m}^{-2}\text{ s}^{-1}$ , then remained more or less constant as PAR increased further to  $1760\ \mu\text{mol m}^{-2}\text{ s}^{-1}$  (Fig. 1c). At the beginning of the wet season, transpiration rate increased from  $\sim 0$  to  $\sim 1.75\text{ mmol m}^{-2}\text{ s}^{-1}$  as PAR increased from 0 to  $400\ \mu\text{mol m}^{-2}\text{ s}^{-1}$ , then decreased at higher PAR values later in the day, matching the small decrease in assimilation rate at the same time of day (Fig. 1d). During the temperature ramp, dry season transpiration rates declined as temperature increased above  $30^{\circ}\text{C}$  (Fig. 1e). At the beginning of the wet season, transpiration rate increased from  $\sim 0$  to  $\sim 4\text{ mmol m}^{-2}\text{ s}^{-1}$  with increasing temperatures to  $40^{\circ}\text{C}$ , but decreased at the highest temperature of  $43^{\circ}\text{C}$  (Fig. 1f).

*Absolute emission potentials and contribution of different monoterpenes to emission profiles from H. brasiliensis at constant temperature and PAR*

Epot for total monoterpene compounds was between  $2.0 \pm 0.1$  and  $2.3 \pm 0.1\ \mu\text{g g}^{-1}\text{ h}^{-1}$ , based on measurements from two trees in the dry season, and between  $93 \pm 5.4$  and  $98 \pm 7.0\ \mu\text{g g}^{-1}\text{ h}^{-1}$ , based on measurements from three different trees at the start of the wet season (Table 1). The main emitted monoterpene compounds from *H. brasiliensis* were  $\alpha$ -pinene, sabinene, and  $\beta$ -pinene (Figs 2a and b). These contributed  $8.4 \pm 0.2\%$ ,  $84.4 \pm 0.2\%$  and  $7.2 \pm 0.1\%$  (respectively,  $\pm$  SE%) to total emissions in the dry season, and  $7.5 \pm 0.1\%$ ,  $64.3 \pm 2.9\%$ , and  $8.5 \pm 0.5\%$  (respectively,  $\pm$  SE%) to total emissions at the beginning of the wet season. In the dry season, negligible concentrations of other compounds were detected (Fig. 2a), but at least 13 other monoterpene compounds were detected in emissions at the beginning of the wet season (Fig. 2b). In both seasons, the relative contribution of different compounds to total emissions measured at constant temperature ( $30^{\circ}\text{C}$ ) and PAR ( $1000\ \mu\text{mol m}^{-2}\text{ s}^{-1}$ ) changed slightly during the day. In the dry season, the contribution of  $\alpha$ -pinene decreased from 14.4% to a minimum of 7.7% in the middle of the day, while that of sabinene increased from 78.1% to a maximum of 85.1%. The contribution of  $\beta$ -pinene did not change significantly throughout the day (Fig. 2a).



**Fig. 2** Percent contribution of monoterpene compounds to total emissions throughout the day under constant conditions of PAR and temperature (a) single measurements each hour in the dry season (b) mean  $\pm$  SE each hour ( $n=3$ ) at the start of the wet season.

□  $\alpha$ -thujene; □  $\alpha$ -pinene; ■ camphene; ■ sabinene; ■  $\beta$ -pinene; ■  $\alpha$ -phellandrene; ■  $\alpha$ -terpinene; ■ limonene; □ cineole; □ *cis*-ocimene; ■  $\beta$ -ocimene; □  $\gamma$ -terpinene; ■ ocimene-2; □  $\alpha$ -terpineole; □ linalool; ■ myrcene.

At the beginning of the wet season,  $\alpha$ -pinene, sabinene, and  $\beta$ -pinene did not change significantly from early morning to the middle hours of the day. However, the contribution of *cis*-ocimene to total emissions increased from  $0.1 \pm 0.1\%$  to  $9.7 \pm 1.6\%$  (Fig. 2b). For most compounds, the relative contributions of different compounds to total emissions were constant between replicate plants (Fig. 2), but there was some intra-specific variability in emission potentials of sabinene,  $\alpha$ -terpinene, limonene, and  $\gamma$ -terpinene at the beginning of the wet season (Table 1).

*Time course of monoterpene emissions throughout the day at approximately constant temperature and PAR*

Although leaf cuvette temperature and PAR were set to  $30^{\circ}\text{C}$  and  $1000\ \mu\text{mol m}^{-2}\text{ s}^{-1}$ , respectively, high ambient

temperatures affected the control on the leaf cuvette, and so it was impossible to sustain 30 °C precisely throughout a sampling day (Fig. 3a). Even when temperature was more successfully sustained at a constant value, total monoterpene emissions were not constant throughout the day (Figs 3b and c, start of the wet season). At the start of the wet season, emissions were low but very variable (with high SE) at the beginning of the day when the weather was overcast and cloudy (in spite of constant PAR and temperature in the cuvette; Fig. 3b). Once emissions had reached the full potential for the day, emission rates were more or less sustained, at least until the last sample was taken at about 18:00 hours. All of the individual emitted monoterpenes followed this pattern of emissions throughout the day, except *cis*-ocimene, which showed a distinct diurnal trend which was not influenced by temperature or PAR (Fig. 3c).

#### Contribution of different monoterpenes to emission profiles from *H. brasiliensis* during PAR ramps

There was no large change in monoterpene emission profiles for *H. brasiliensis* as PAR was changed throughout the sampling day during the dry season, possibly because absolute emission rate was considerably lower than at the start of the wet season, with few compounds emitted above the detection limit of the sampling and analytical systems (Fig. 4a). However, the emission

profile changed considerably during the PAR ramp experiments at the start of the wet season (Fig. 4b). At low PAR,  $\beta$ -ocimene made its largest contribution ( $39 \pm 3.3\%$ ), but this decreased with increasing PAR in the middle hours of the day to  $13 \pm 1.5\%$ , recovering to  $23 \pm 2.2\%$  at the highest PAR values at the end of the day. Meanwhile, the dominant emitted compound (*sabinene*) made a lower contribution to total emissions at the beginning of the experimental day when cuvette PAR was low ( $33 \pm 3.7\%$ ), rising to a maximum contribution in the middle of the day ( $51 \pm 3.6\%$ ), when cuvette PAR was mid-range, to decrease again at the end of the sampling day to  $32 \pm 3.9\%$  when cuvette PAR values were highest. Linalool made its lowest contribution at the start of the sampling day ( $5.3 \pm 0.7\%$ ), but as cuvette PAR increased, the relative contribution of linalool to total emissions also increased to  $31 \pm 3\%$ .

#### Contribution of different monoterpenes to emission profiles from *H. brasiliensis* during temperature ramps

There was no great change in monoterpene emission profiles for *H. brasiliensis* during the temperature ramp experiment in the dry season (Fig. 5a). However, at the start of the wet season, changes in emission profiles during the temperature ramp experiments were similar to the changes during the PAR ramps (Fig. 5b). At low temperatures,  $\beta$ -ocimene made its largest contribution

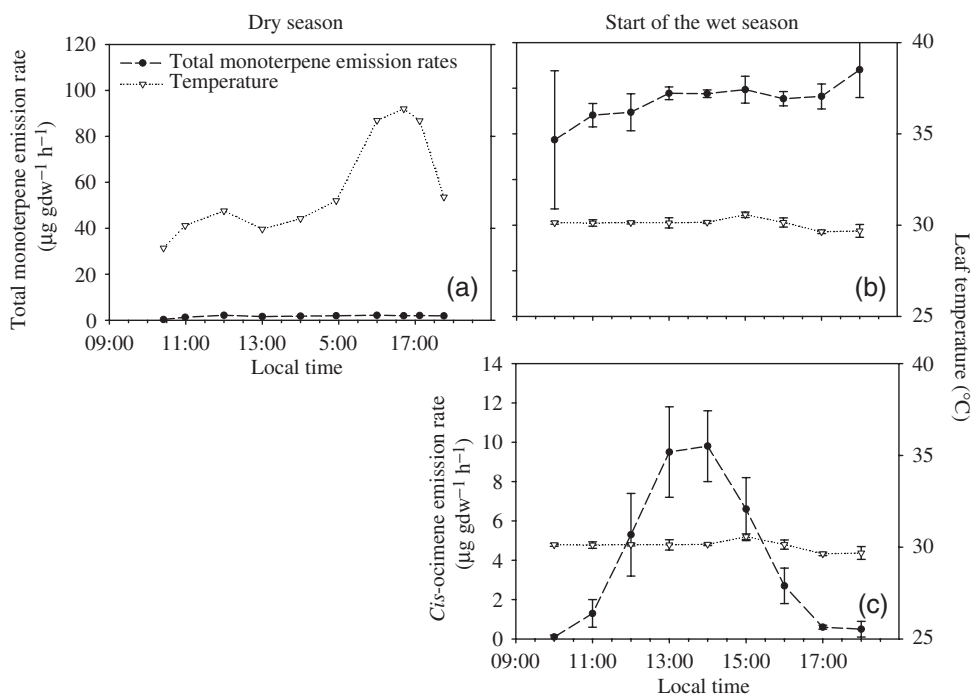
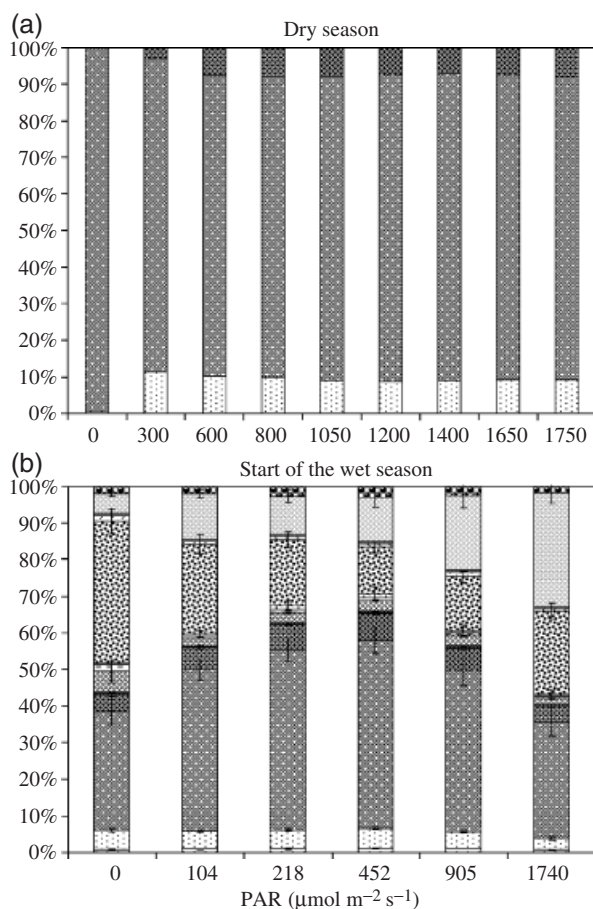
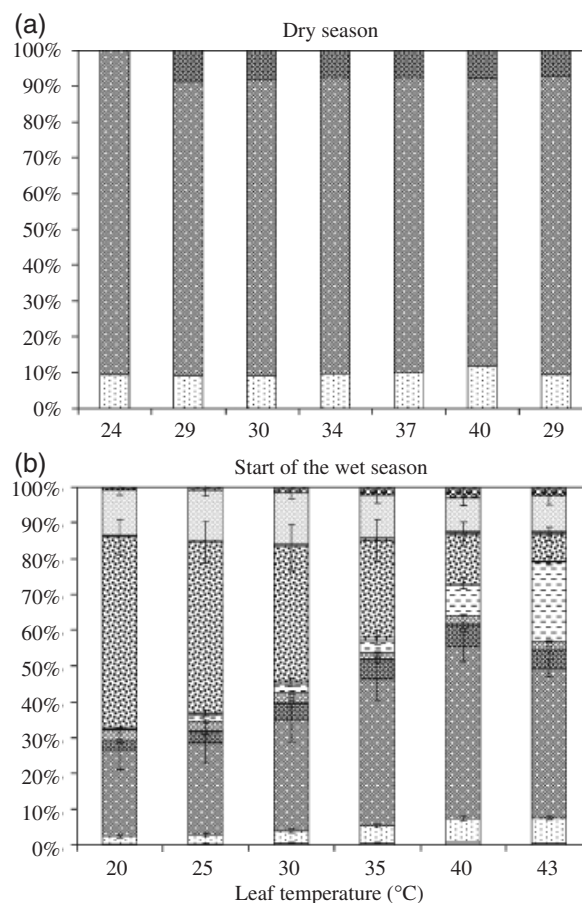


Fig. 3 Diurnal course of monoterpene emissions at constant PAR =  $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ ;  $n = 1$  dry season;  $n = 3$  wet season.



**Fig. 4** Changes in monoterpene emissions profiles from *Hevea brasiliensis* with increasing PAR (a) single measurements each hour in the dry season (b) mean  $\pm$  SE each hour ( $n = 3$ ) at the start of the wet season.  $\square$   $\alpha$ -thujene;  $\square$   $\alpha$ -pinene;  $\blacksquare$  camphene;  $\blacksquare$  sabinene;  $\blacksquare$   $\beta$ -pinene;  $\blacksquare$   $\alpha$ -phellandrene;  $\blacksquare$   $\alpha$ -terpinene;  $\blacksquare$  limonene;  $\blacksquare$  cineole;  $\blacksquare$  *cis*-ocimene;  $\blacksquare$   $\beta$ -ocimene;  $\blacksquare$   $\gamma$ -terpinene;  $\blacksquare$  ocimene-2;  $\blacksquare$   $\alpha$ -terpineole;  $\blacksquare$  linalool;  $\blacksquare$  myrcene.

( $53 \pm 4.9\%$ ), which decreased to  $7.5 \pm 1.8\%$  as temperature increased throughout the day. Sabinene again made a lower contribution ( $24 \pm 5.5\%$ ) to total emissions at the beginning of the experimental day when cuvette temperature was low, rising to a maximum contribution ( $48 \pm 4.1\%$ ) later in the day at higher temperatures, only decreasing a small amount at the end of the sampling day. The pattern of linalool contributions varied between replicates, generally starting with a contribution to total emissions of  $\sim 10\%$  which decreased as the temperature increased. Cineole contributions were non-existent at low temperatures but as cuvette temperature increased, cineole emissions appeared, and their relative contributions increased to a maximum of  $22 \pm 0.7\%$  at the end of the day.



**Fig. 5** Changes in monoterpene emissions profiles from *Hevea brasiliensis* with increasing temperature (a) single measurements each hour (b) mean  $\pm$  SE each hour ( $n = 3$ ).  $\square$   $\alpha$ -thujene;  $\square$   $\alpha$ -pinene;  $\blacksquare$  camphene;  $\blacksquare$  sabinene;  $\blacksquare$   $\beta$ -pinene;  $\blacksquare$   $\alpha$ -phellandrene;  $\blacksquare$   $\alpha$ -terpinene;  $\blacksquare$  limonene;  $\blacksquare$  cineole;  $\blacksquare$  *cis*-ocimene;  $\blacksquare$   $\beta$ -ocimene;  $\blacksquare$   $\gamma$ -terpinene;  $\blacksquare$  ocimene-2;  $\blacksquare$   $\alpha$ -terpineole;  $\blacksquare$  linalool;  $\blacksquare$  myrcene.

#### Comparing G93 algorithm predictions with emissions of individual compounds from *H. brasiliensis* during PAR and temperature ramps

The G93 predictions (i.e.  $C_T$  and  $C_L$ ) compared variably with individual compounds' emissions (normalized to 1 for the emission measured at  $30^\circ\text{C}$  and  $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ ) (Fig. 6). In the dry season,  $\alpha$ -pinene PAR-dependent emissions followed the general trend of G93 predictions, but were overestimated by the G93 parameters (Fig. 6a). Emissions of the other emitted compounds, sabinene and  $\beta$ -pinene were too low to demonstrate significant dependency on PAR. Similarly, G93 parameters over-estimated temperature dependency of  $\alpha$ -pinene emissions during the dry season. Emissions peaked at  $33^\circ\text{C}$  then declined at higher



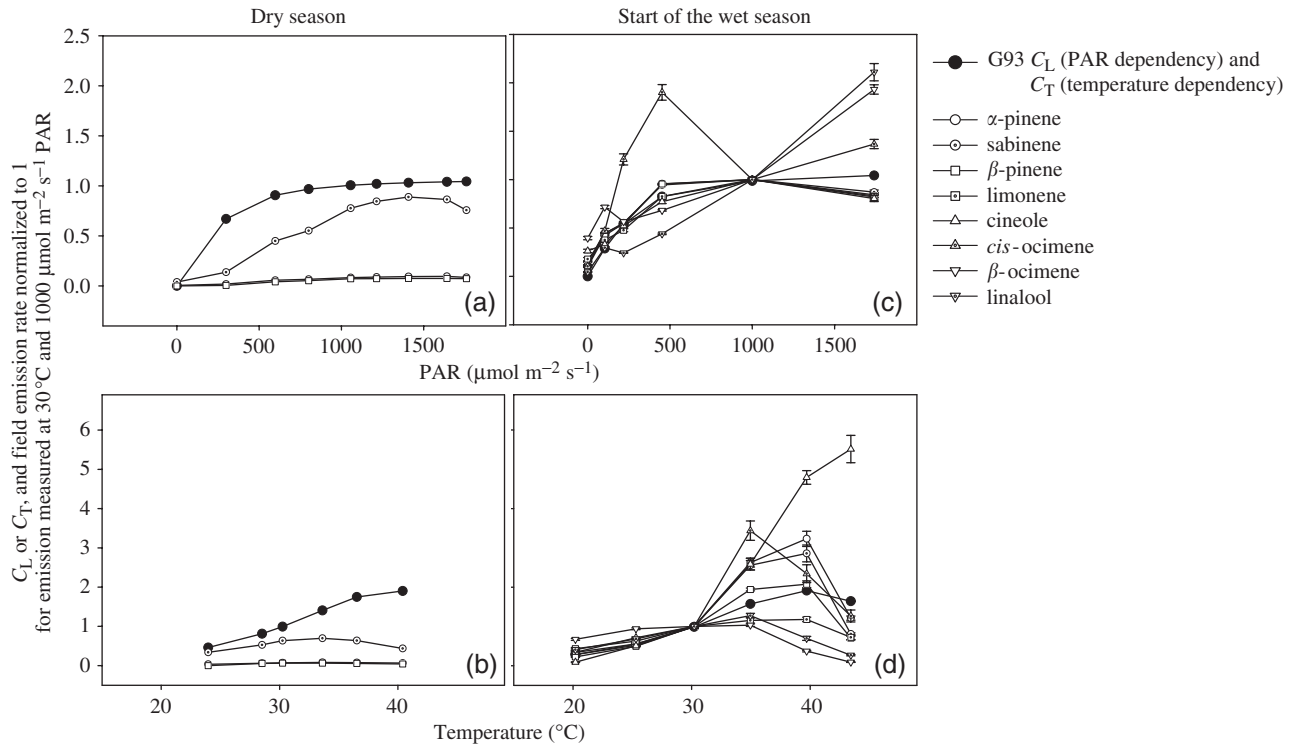


Fig. 6 Performance of G93 algorithm for predicting emissions of individual isoprenoid VOCs from *Hevea brasiliensis*.

temperatures (Fig. 6b). At the beginning of the wet season, the G93 parameters predicted PAR dependency of  $\alpha$ -pinene, sabinene, and  $\beta$ -pinene emissions reasonably well, but emissions all started to decrease at 1800  $\mu\text{mol m}^{-2} \text{s}^{-1}$  PAR. Emissions of *cis*-ocimene were not well described by G93 PAR parameterization and were probably more strongly controlled by other factors (Fig. 6c). Linalool and  $\beta$ -ocimene continued to increase with increasing PAR and did not plateau in the way that G93 predicts. Temperature dependency at the beginning of the wet season varied for different compounds (Fig. 6d). There was a lower temperature peak for *cis*-ocimene,  $\beta$ -ocimene, and linalool and a strong continuing increase of cineole emissions with increasing temperature. The other compounds temperature dependency were better described by the G93 algorithm, although reached higher peaks than predicted (Fig. 6d).

## Discussion

### Leaf level variability in monoterpene emissions

The total monoterpene emission potential estimate was high for the start of the wet season (94  $\mu\text{g g}^{-1} \text{dw h}^{-1}$ ; i.e. 83  $\mu\text{g C g}^{-1} \text{dw h}^{-1}$ ), around three times the value reported by Klinger *et al.* (2002) and which was used by Baker *et al.* (2005). This is possibly because our Epot

value was estimated from measurements of emissions from *H. brasiliensis* over a period of a whole day, from three different trees, at the beginning of the wet season when the trees were physiologically active after relief of drought conditions. It is likely, though not proven in this study, that such high Epot values are typical only for these conditions, and are not sustained for the duration of the wet season. Staudt & Bertin (1998) found that emissions of light-dependent monoterpenes from *Quercus ilex* were higher by a factor of 10 (on a dry leaf weight basis) during early leaf development, compared with emissions from mature leaves. Lower emission rates of monoterpenes from *Apeiba tibourbou* were also found in the dry season at an Amazonian site (Kuhn *et al.*, 2004). However, differences in emissions between dry and wet season at the Amazon site were not as large as those reported here, possible because the difference in water availability was not as extreme as at Xishuangbanna. Because emissions were much lower in the dry season, many compounds were below the detection limit, and the emission profile consisted of only few compounds. The low emission rates were accompanied by low transpiration and photosynthesis rates, indicating that the canopy in the dry season may well have been senescent.

The increase and decrease of *cis*-ocimene emissions during the day in constant conditions of light and temperature within the cuvette suggests that the diur-

nal pattern these emissions might have been under circadian control. Proof of true circadian control would require more detailed laboratory investigations similar to those carried out by Dudareva *et al.* (2005), showing circadian control of monoterpene emissions from snapdragon flowers (Dudareva *et al.*, 2005), by Wilkinson *et al.* (2006), showing clear circadian control of isoprene emissions from oil palm leaves, and by Loivamaki *et al.* (2007) who showed that isoprene synthase in grey poplar leaves is also under Circadian control. Circadian control of *cis*-ocimene emissions from *H. brasiliensis* might act via substrate supply, or via synthase enzyme production or activity [see Wilkinson *et al.* (2006) and Loivamaki *et al.* (2007) for a fuller discussion of the circadian control of isoprene emissions].

Generally, monoterpenes are emitted from stored pools, and emissions depend on temperature dependent vaporization from these pools, although physicochemical properties of individual compounds can affect the underlying mechanisms governing the passage of molecules from the storage location to the exterior of the leaf (Niinemets *et al.*, 2004). Over the last 15 years, emissions of instantaneously synthesised monoterpenes have been discovered and investigated, firstly for Mediterranean oak species (Staudt & Seufert, 1995), and subsequently for other species (Owen *et al.*, 2002). This type of monoterpene emission is rather like isoprene emission, depending upon PAR and temperature, and reasonably well described by the algorithm of Guenther *et al.* (1995). However, relatively little is known about changes in relative composition of monoterpene emissions in changing light and temperature conditions. In this study, changes in emission composition during PAR and temperature ramps were observed only at the start of the wet season, probably because emissions were much higher and with a more varied composition compared with the dry season (Figs 5 and 6). These changes were probably not related to whole plant responses to natural diurnal rhythms because they were not observed at constant PAR and temperature throughout the day. The emission patterns observed for standard emission potentials throughout the day were probably due to different physicochemical properties of the different compounds associated with factors other than light and temperature, [e.g. humidity (Niinemets *et al.*, 2004)]. There may be other explanations for changes in relative composition of emissions, including constitutive diurnal rhythms in compound production.

Relative chemical speciation did not change a lot during temperature and PAR ramps in the dry season, possibly because the compounds whose contributions changed most in the wet season were not observed in the emissions during the dry season. It is also possible that while the large wet season emissions are mostly

from instantaneously synthesised (non-stored) sources, the small dry-season emissions are from small residual stored pools, and are masked by instantaneous emissions in the wet season.

Absolute emissions often increased and then decreased with increasing PAR and temperature. This indicates that above a certain level of light (or temperature) emissions are inhibited. In the light and temperature ramp experiments, measurements and high light and temperature conditions were at the end of the sampling day, so these emission patterns might also be an artefact of an underlying circadian control, where emissions would decrease whatever the level of light intensity or temperature.

#### *Photosynthesis and transpiration rates, and carbon balance*

Overall, physiology parameter values reflected normal diurnal rhythms and the trees' responses to imposed changes in PAR and temperature. Generally, assimilation and transpiration decreased when PAR or temperature reached stressful levels, or when the normal diurnal rhythm of the whole tree was experiencing ambient stressful levels of PAR and/or temperature. During the course of emission measurements at constant temperature and PAR, emissions represented a loss of assimilated carbon of between 0.3% and 2.0%. During the PAR and temperature ramp experiments, emissions represented a loss of assimilated carbon of between 0% and 4.7%, and between 0.1% and 22%, respectively. These losses are similar to those reported for isoprene emissions from *Hymenaea courbaril* in Amazonia (up to 3.5%, Kuhn *et al.*, 2004), and from the tropical species *Mangifera indica* (up to 4.4%, Harley *et al.*, 2004). However, Kuhn *et al.* (2004) found lower carbon loss due to light-dependent monoterpene emissions from the tropical species *A. tibourbou* (0.1%). The higher ratios reported here are due to low photosynthesis rates rather than high emission rates. At the beginning of the PAR ramp, when respiration rates exceeded assimilation rates in the dark, carbon was lost as monoterpene emissions at up to 7% of the rate of carbon loss in respiration.

While there was no strong relationship between emission rates and assimilation rates over a period of a few days, lower emission rates in the dry season were accompanied by lower assimilation rates (Fig. 1). These data support the findings of Kuhn *et al.* (2004) for light-dependent monoterpene emissions from *A. tibourbou* growing in the Amazonian tropical forest. However, Kuhn *et al.* (2004) found higher isoprene emission rates from *H. courbaril* at the end of the dry season, compared with emission rates measured at the end of the wet season. Serca *et al.* (2001) also report a lower isoprene flux, but a stronger uptake of CO<sub>2</sub>, by a forest canopy at

a tropical forest site in the Republic of Congo at the end of the wet season compared with measurements at the beginning of the wet season. It is likely that climatic changes could affect isoprenoid emissions via the availability of photosynthate. However, other factors, such as developmental stage of the leaf may also explain the difference in isoprenoid emission potentials observed between seasons here.

#### Comparing field measurements with G93 model estimates

The behaviour of different compounds does not necessarily follow the G93 algorithm (Fig. 6), especially where the compounds are controlled by parameters other than light and temperature, (e.g. volatility, e.g. cineole, the ocimene compounds) and other circadian-related control (e.g. *cis*-ocimene; Fig. 3). Variability in response of different compounds to PAR and temperature contributed to the changing composition of total monoterpene emissions during the ramping experiments (Figs 4 and 5). Cineole emissions tended to continue increasing with increasing temperature up to 43 °C at the start of the wet season. The large relative emission of  $\beta$ -ocimene at low temperature may be due to its lower boiling point and higher volatility compared with other monoterpenes (Table 1; Fig. 5b; Niinemets *et al.*, 2004; Peñuelas & Llusià, 2004). In contrast, Staudt & Bertin (1998) found that *cis*- $\beta$ -ocimene emissions from *Q. ilex* were considerably higher at high temperatures (>40 °C). The relatively high contribution of  $\beta$ -ocimene to emissions at low PAR may be a result of lower dependency on PAR compared with the other emitted compounds (Fig. 4b). Indeed, it appeared only when the plants were undergoing PAR or temperature ramps, and does not contribute a major part of emissions measured at standard PAR (1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) and temperature (30 °C) throughout the day (Fig. 2b). Emissions of  $\beta$ -ocimene have also been observed in response to herbivory and mechanical wounding (e.g. Arimura *et al.*, 2000; Faldt *et al.*, 2003). While the leaves sampled here appeared to be intact and free from herbivores, emissions of  $\beta$ -ocimene may have been elicited as a response to mechanical stress after installing the cuvette on leaves sampled the previous day at constant conditions. Or the response might be due to light and/or temperature stress. Staudt & Bertin (1998) found that the light response of ocimene compound emissions from *Q. ilex* were too variable for successful prediction using the G93 algorithm, and that the contribution of these compounds to total monoterpene emissions from foliage depended on age of the foliage. Sabillon & Cremades (2001) observed trans-ocimene only in summer emissions from *Pinus pinea*.

#### Implications for atmospheric chemistry

Monoterpene emissions from vegetation take part in the chemistry of the atmosphere. The ocimene compounds and linalool are between two and 30 times more reactive than  $\alpha$ -pinene and  $\beta$ -pinene with the common atmospheric oxidising species OH, O<sub>3</sub> and NO<sub>3</sub> (Hoffmann *et al.*, 1997). In particular, rate constants with the OH radical ( $K_{\text{OH}}$  values) for linalool and ocimene compounds are at least an order of magnitude higher than for  $\alpha$ -pinene and  $\beta$ -pinene (Table 1). These higher rate constants result in much shorter atmospheric lifetimes for the ocimene compounds and linalool (e.g. 41 and 66 min, respectively, with the OH radical) than for  $\alpha$ -pinene and  $\beta$ -pinene (e.g. 194 and 132 min, respectively, with the OH radical) (Hoffmann *et al.*, 1997). Similarly, atmospheric lifetimes for the ocimene compounds and linalool in the presence of O<sub>3</sub> and NO<sub>3</sub> radicals were considerably shorter than for  $\alpha$ -pinene and  $\beta$ -pinene (Hoffmann *et al.*, 1997). Therefore, the varying contributions of different monoterpene compounds to total monoterpene emissions from *H. brasiliensis* may significantly affect the tropospheric chemistry in regions covered by extensive rubber tree plantation. Accounting for the relative contribution of each compound to total emissions (Fig. 2) and the individual  $K_{\text{OH}}$  values for each compound, the weighted average rate constant for monoterpene emissions from *H. brasiliensis* (Fig. 2) is 122  $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$  compared with 66.5  $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$  for emissions from a theoretical canopy consisting of 50%  $\alpha$ -pinene and 50%  $\beta$ -pinene. Higher rate constants of different emitted compounds, in turn, will affect the lifetimes of less reactive hydrocarbons (e.g. CH<sub>4</sub>, with possible implications for climate change). Therefore, it is useful to understand not only the controls and magnitude of total emissions from a canopy, but also the controls and magnitude of the individual components' emissions.

#### Concluding remarks

An analysis of monoterpene emissions from *H. brasiliensis* are presented for the first time in considerable detail, in terms of compound speciation, and PAR and temperature dependency. Major emitted compounds were sabinene,  $\alpha$ -pinene and  $\beta$ -pinene, with ocimene compounds and linalool contributing more significantly at high values of PAR and temperature, when PAR and temperature ramps were imposed on the normal diurnal cycle of environmental control. Emissions are strongly dependent on PAR.

Measurements suggest that large amounts of reactive monoterpene compounds are emitted by rubber tree canopies, especially at the beginning of the wet season, and that the compound speciation of monoterpene

emissions from *H. brasiliensis* can vary according to environmental conditions. Changes in rubber plantation area are likely to impact significantly on biogenic emissions of monoterpenes in tropical China. Because of their different reactivities with oxidising radicals, different speciations of monoterpene emissions are likely to have a profound effect on regional tropospheric chemistry.

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