Isoprene and monoterpene emissions of Amazônian tree species during the wet season: Direct and indirect investigations on controlling environmental functions

U. Kuhn,[1] S. Rottenberger,[1] T. Biesenthal,[1,4] A. Wolf,[1] G. Schebeske,[1] P. Ciccioli,[2] E. Brancaleoni,[2] M. Frattoni,[2] T. M. Tavares,[3] and J. Kesselmeier[1]

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[1] As part of the project LBA-EUSTACH (European Studies on Trace gases and Atmosphere Chemistry as a contribution to the Large-Scale Biosphere-Atmosphere experiment in Amazonia), we examined the diel pattern of isoprenoid exchange in the wet season of 1999 at a remote field site in Rondônia, Brazil. The emission pattern of two tree species in a secondary forest was investigated by means of a dynamic branch enclosure system and was compared on the basis of climatological variables like temperature and light and physiological parameters such as assimilation, transpiration, and stomatal conductance. While the species *Hymenaea courbaril* was found to be a strong isoprene emitter, *Apeiba tibourbou* was found to exclusively emit monoterpenes and no isoprene. Species-related standard emission factors calculated on a carbon basis were 45.4 $\mu g\ g^{-1}\ h^{-1}$ (24.9 nmol $m^{-2}\ s^{-1}$) for isoprene and 3.6 $\mu g\ g^{-1}\ h^{-1}$ (0.75 nmol $m^{-2}\ s^{-1}$) for monoterpene emission, representing a nontrivial carbon loss by the plants of 1.8% and 0.1% C relative to the net carbon assimilation on a daily basis. About 90% of the total monoterpene emission from *A. tibourbou* was comprised of sabinene, α-pinene, β-pinene, myrcene, and limonene, in decreasing quantity. Despite the difference in isoprenoid emission composition, the diel emission pattern of both tree species reacted similarly toward the environmental conditions, fluctuating light and temperature, indicating that closely related metabolic controls were involved in the actual emission. Both isoprene emission and monoterpene emission exhibited a light saturation curve similar to CO_2 assimilation. No isoprenoid emission was found during nighttime. The strong light dependence of the monoterpene emission by *A. tibourbou* suggests that this tree species does not store monoterpenes but emits them immediately upon production. The diel pattern of both the isoprene and the monoterpene emission could be adequately simulated by current isoprene algorithms. The ambient air mixing ratios of isoprenoids were clearly dominated by isoprene, with peak values of 8 ppb inside the main canopy. Vertical gradients of ambient air mixing ratios in and above a primary rain forest site illustrated the emission of isoprene by the main canopy dependent upon light and temperature but were also indicative of a potential sink at the forest floor. For monoterpenes, corresponding gradients could hardly be resolved, reflecting observed ambient air mixing ratios more than an order of magnitude lower than for isoprene. Nevertheless, a strong diel cycle of short-lived monoterpene compounds like α-pinene was found in the primary as well as in the secondary forest site, which further strengthens our finding of a strong light dependence of biogenic monoterpene emission even on a larger scale. Our findings to some extent question the applicability of the commonly used monoterpene emission algorithm to the tropics. A strong light dependence of biogenic monoterpene emissions may, if generalized for tropical tree species in common, have a strong impact on estimated global flux rates for tropical regions. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition

[1]Biogeochemistry Department, Max Planck Institute for Chemistry, Mainz, Germany.
[2]Instituto sull' Inquinamento Atmosferico del C.N.R., Rome, Italy.
[3]Instituto de Química, Universidade Federal da Bahia, Salvador, Brazil.
[4]Now at Indoor Environment Program, National Research Council of Canada, Ottawa, Canada.

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1. Introduction

[2] Vegetation emits many reactive volatile organic compounds (VOCs) which have a major controlling influence on the atmospheric chemistry of the boundary layer over the Amazon, particularly during the wet season when pyrogenic sources are minimal [e.g., *Jacob and Wofsy*, 1988; *Fehsenfeld et al.*, 1992; *Kesselmeier and Staudt*, 1999]. Among VOCs, isoprene and monoterpenes play a central role in influencing the oxidative capacity of the atmosphere and were predicted to have a particularly strong impact on tropical regions [*Guenther et al.*, 1999]. In terms of reactivity, isoprene dominates the daytime chemistry of OH and is even more important than CO. Depending upon the nitric oxide (NO_x) concentration range, VOC oxidation may lead to either production or consumption of tropospheric ozone [*Chameides et al.*, 1992]. Such a threshold level is especially relevant for remote regions like the tropical rain forests, due to the relatively low NO_x concentration levels observed [*Gut et al.*, 2002a; *Rummel et al.*, 2002]. The impact of short-lived VOCs extends over the entire troposphere due to the formation of longer lived intermediates like carbon monoxide, organic nitrates, peroxyacetylnitrates (PAN), atmospheric aerosol and various carbonyl and carboxyl compounds [*Kesselmeier et al.*, 2000, 2002; *Poisson et al.*, 2000], the latter representing a large fraction of acidity in precipitation in remote areas [*Keene et al.*, 1983; *Andreae et al.*, 1988; *Kuhn et al.*, 2002]. Through their influence on the atmospheric oxidative balance, greenhouse gas concentration, and the formation of aerosols, VOCs may play an important role in climate forcing. Furthermore, the emission of VOCs represents a nontrivial carbon loss to the plant and is thus also the subject of current research concerning the implications for the global atmospheric carbon budget. The magnitude and relative abundance of volatile organic compounds are highly dependent on plant species distribution and environmental conditions. It is common knowledge that the primary short-term controls over isoprene production are light and temperature. Studies on temperate plants have shown that isoprene emission is a function of light intensity which approximates a rectangular hyperbola, similar to the photosynthesis versus light relationship, and depends on temperature according to enzyme activation kinetics [*Guenther et al.*, 1993; *Guenther*, 1997]. In contrast, the emission of monoterpenes is generally assumed to show minor dependence on light but to increase exponentially with temperature. In most cases studied so far, monoterpene-producing plants accumulate pools of monoterpenes and store them in specialized structures like resin ducts, glandular trichomes or related structures [*Gershenzon and Croteau*, 1991]. Due to their low vapor pressure, the instantaneous emission of monoterpenes from these pools is governed only by leaf temperature and the effect of leaf temperature on the vapor pressures of individual monoterpenes [*Tingey et al.*, 1991; *Monson et al.*, 1995]. Algorithms developed to describe the dependencies of isoprene and monoterpenes on light and/or temperature [*Guenther et al.*, 1993] have been incorporated into global emission inventories [*Guenther et al.*, 1995]. Even though these model results suggest that the tropics are the most important regions for the production of biogenic VOCs, field measurements in these areas are rare and flux estimates of VOCs have high uncertainties, especially for tropical regions. Despite its enormous dimensions and its impact on global emissions, little is known about the release of VOCs from the Amazônian rain forest (or other tropical rain forest vegetation), and what is known is mainly focused on isoprene alone [*Zimmerman et al.*, 1988; *Lerdau and Keller*, 1997; *Keller and Lerdau*, 1999]. Due to the insufficient database, we still largely depend on modeling to estimate the abundance and fate of isoprenoids in the tropical atmosphere. But as these models were based on algorithms developed for extratropical plants, they may not accurately simulate emissions in tropical areas. VOC emission rates do not only depend on instantaneous light and temperature, but also on the growth environment of the plants and the leaf developmental stage [*Kuzma and Fall*, 1993; *Harley et al.*, 1994; *Wildermuth and Fall*, 1998]. Furthermore the isoprenoid emission activity was found to be variable in phylogenetically separated oak species [e.g., *Kesselmeier et al.*, 1998; *Loreto et al.*, 1998; *Csiky and Seufert*, 1999]. All North American oaks were high isoprene emitters, but many European oak species do not emit isoprene at all. Instead some of them emit monoterpenes, which were found to respond in a light dependent manner [*Staudt and Seufert*, 1995; *Staudt et al.*, 1997; *Bertin and Staudt*, 1996; *Bertin et al.*, 1997; *Loreto et al.*, 1996a, 1996b; *Ciccioli et al.*, 1997; *Seufert et al.*, 1997; *Street et al.*, 1997; *Kesselmeier et al.*, 1996, 1997, 1998; *Csiky and Seufert*, 1999]. Following the same line of interpretation, the isoprene emissions in tropical regions have been reported to be correlated with successional ecosystem patterns [*Klinger et al.*, 1998]. The authors report peak emissions in early stages of woodland succession (savanna ecosystem), and declining emission rates in later successional forest development (rain forest ecosystem). This points to potential dissimilarities in plant response to environmental conditions in different ecosystems. It may be that the VOC emission behavior may not be specific to the particular plant species (or genus), but rather be a result of the environmental position it is in (or has developed in). Plant species that occupy a particular niche might behave in a similar fashion, like a functional group. Considering all these different relations on the microscalar and macroscalar physiological and environmental controls raises questions regarding the application of emission algorithms which are based on measurements of temperate tree species to tropical vegetation [*Guenther et al.*, 1995]. These and other questions highlight the need for field data in tropical areas, especially if taking into account that tropical vegetation is considered to have the major impact on global emission strength, but

have been the least investigated to date. A better understanding of the environmental controls of VOC release and a better description of the exchange processes on different spatial and temporal scales is essential. Field measurements in South America, during LBA and other studies, are used to improve the characterization of hydrocarbon emission from tropical rain forests. In this study enclosure measurements were carried out to examine the exchange behavior of different plant species at the branch level, while ambient air and profile measurements inside and above the canopy assessed the exchange on a larger scale.

2. Method

2.1. Sampling Sites and Periods

[3] Measurements were performed in a relatively well preserved ecological reserve 100 km north of Ji-Paraná in the state of Rondônia, southwest Amazônia, Brazil. The area is covered predominantly by primary tropical rain forest (*Floresta Ombrofila Aberta*). The site experiences a mean annual rainfall of 1600 mm and has a pronounced dry season between June and August, while the wettest periods are between December and April [*Gash et al.*, 1996]. For further details, see *Andreae et al.* [2002]. The campaign was carried out at the end of the wet season in April/May 1999, representative for background conditions without the influence of biomass burning. Dynamic branch enclosure (cuvette) measurements were conducted by means of a mobile 10 m scaffolding tower at the top of a secondary forest canopy close to the Reserva Biológica Jarú (RBJ) camp site (10°08′43″S, 62°54′27″W, 107 m asl), an facility of IBAMA (Instituto Brasileiro de Meio Ambiente e Recursos Naturais Renovaveis). The campsite is in the middle of a 1 km^2 square of secondary forest surrounded by primary forest. Two deciduous tree species were investigated by cuvette measurements: *Hymenaea courbaril* L. var. (common name: Jatoba; family name: Caesalpinaceae), ranging from tropical dry to wet through subtropical dry to wet forest life zones [*Duke*, 1978] and *Apeiba tibourbou* (common name: Pente de Macaco; family name: Tiliaceae), with principal occurrence in secondary but also in primary rain forest [*Lorenzi*, 1998]. All measurements presented here were carried out on mature leaves. Vertical profile measurements of isoprenoids were conducted on a 52 m micrometeorological scaffold tower erected in 1991 at a primary forest site (RBJ tower A, 10°04′55″S, 61°55′48″W, 110 m asl [*Gash et al.*, 1996]). The mean canopy height was 32 m, although single emergent trees reached up to 45 m height. Under a relatively open stem space up to 20 m, a palm-rich understory of a few meters height was found. The maximum leaf area density was at 25 m, while the total leaf area index (LAI) was about 5.5 [*Andreae et al.*, 2002]. The fetch of the forest site was only limited to the southwest, where the Machado River ran (distance ~400 m). Profiles within and above the canopy were obtained by sampling simultaneously at three heights (1, 25 and 46 m above ground level).

2.2. Sampling Procedure and Chemical Analysis

[4] Two different sampling/analysis systems were used to analyze the isoprenoids. Quantification was routinely achieved using a thermal desorption GC/FID system. On an event basis a GC/MS system was used to qualitatively confirm the measurement results. For the GC/FID system (Autosystem XL (with ATD400 Thermal Desorber), Perkin Elmer, Germany), samples were collected by drawing air through fused silica-lined stainless steel cartridges (89 mm length, 5.33 mm I.D., Silicosteel, Restek, USA) packed with sequential adsorbent beds of 180 mg Tenax TA 60/80 (35 m^2/g, Alltech, Deerfield, IL, USA) followed by 130 mg Carbotrap 1 (90 m^2/g, Lara s.r.l., Rome, Italy). For subsequent analysis, two capillary columns connected in series were used (Supelco SPB-5, 30 m length, 0.25 mm I.D., 0.25 μm film thickness and Hewlett Packard HP-1, 30 m length, 0.25 mm I.D., 0.25 μm film thickness) (see *Kesselmeier et al.* [2002]). In addition to isoprene, the monoterpenes that were targeted in the GC/FID analyses were as follows: α-pinene, β-pinene, sabinene, limonene, myrcene, α-phellandrene, α-terpinene, 3-carene, γ-terpinene, and p-cymene. The sample flow rate was 100 mL min^{-1}. Two different sample volumes were used: for analysis of isoprene only 0.8 liters (8 min sampling period) were collected to prevent breakthrough problems, while for the monoterpenes a sample volume of 4.0 liters (40 min sampling period) was used to improve the detection limit. Ozone scrubbers consisting of multiple plies of MnO_2-coated copper mesh (Type ETO341FC003, Ansyco, Karlsruhe, Germany) within a Teflon tube were used to remove ozone from all ambient sampling streams to avoid possible ozone interference. Airflow during the sampling procedure was continuously monitored using electronic mass flow controllers. The Teflon (PFA) inlet lines for both the vertical gradient measurements in the primary forest and the enclosure measurements in the secondary forest were 5 m in length. Sample air was continuously drawn through the sampling lines, which were heated above ambient temperatures (to ~40°C) to avoid condensation and absorptive losses. Field blanks were regularly collected during the study, with about 1 blank cartridge for every 10 real samples. The detection limit of this method was estimated as the greater of the variability in the blank levels (at the 95% confidence level) and a chromatographic peak ~3 times the noise for each compound, and was typically ~30 ppt for isoprene and <10 ppt for monoterpenes (with some variation among individual compounds). Three identical automatic sampling units (made in-house) were used to control the collection of air samples. Tests performed during the study with ambient air samples showed that there was no bias between the different sampling units. These three units were typically used for the collection of samples from the branch cuvette, the reference cuvette, and the ambient air simultaneously (see next section) or, similarly, at 3 different tower heights in profile measurements. Before each branch enclosure experiment, a series of air samples was collected from both empty cuvettes and ambient air at the same time; the resulting air concentrations from the 3 samples were indistinguishable within the analytical uncertainties for the compounds of interest (~10% RSD). This indicated both good agreement between the different automatic sampling units and that the cuvette systems were not introducing any biases to the measurements. The error of the individual concentration measurements was calculated by an error propagation of the analytical error and the error of the mass flow, respectively. Typical uncertainties were ~10% for isoprene at 1 ppb, and ranged from ~5–30% at 100 ppt for monoterpenes, depending on the individual monoterpene

peak resolution and blank variability. For the GC/MS system (HP 5890 with HP 5970B mass selective detector, Hewlett Packard, USA), isoprenoids were collected using glass cartridges (160 mm length, 3 mm I.D.) packed with 118 mg Carbopack C (12 m^2/g, Supelco, Bellefonte, USA), 60 mg Carbograph 1 (90 m^2/g, Lara s.r.l., Rome, Italy), and 115 mg Carbograph 5 (560 m^2/g, Lara s.r.l., Rome, Italy) in sequential beds [*Brancaleoni et al.*, 1999]. Sample flow rate was 250 mL min^{-1} and the sample volume was 5.0 liters. For details on the subsequent analysis technique using a silica capillary column (50 m length, 0.32 mm I.D., chemically bonded for mass spectroscopy, 0.4 μm film thickness, Chrompack, Middelburg, Netherlands), see *Ciccioli et al.* [1993] and *Kesselmeier et al.* [2002].

2.3. Branch Enclosure and Ambient Air Measurements

[5] An open, dynamic (flow-through) cuvette system [*Kesselmeier et al.*, 1998; *Kuhn et al.*, 2002] flushed with ambient air was used for the gas exchange measurements on the branch level. The distal end of a branch was mounted into one of two enclosures. An identical but empty reference cuvette was operated simultaneously. Each of the cylindrical cuvettes of 60 cm in height and 40 cm in diameter (volume ~75 liters) consisted of a cylindrical Teflon bag which was supported by an external frame. With a constant flow rate (Q) of about 40 L min^{-1} through the cuvettes, a complete exchange of the air within the cuvettes was achieved in less than two minutes. The air inside the chambers was mixed by a Teflon propeller driven by a magnetically coupled motor attached outside [*Kuhn et al.*, 2000]. The aerodynamic resistance inside the enclosures was 30 s m^{-1}, indicating well-mixed conditions [*Gut et al.*, 2002b]. Air temperature within the cuvettes was continuously recorded by Teflonized microthermocouples (0.005″, Chromel–Constantan, Omega, UK). Leaf temperatures were measured at the top and at the bottom of the leaves by attaching the same type of thermocouples to the leaves, which indicated that the leaf surface temperatures were somewhat higher than the air temperature inside the enclosure, although average differences were small (0.5–2.0°C). Photosynthetically active radiation (PAR) was measured with a LICOR quantum sensor (Model SB 190, LICOR, USA) positioned outside the chamber. Relative humidity was monitored with a combined temperature/relative humidity probe (Model Rotronics YA-100F, Walz, Germany). All continuously measured parameters were stored as 5-min averages on a data logger (Model 21X, Campbell Scientific Inc., UK).

[6] The cuvettes were operated by pumping ambient air through the cuvette system using four Teflon membrane pumps (Vakuubrand, Germany). Teflon filters (Zefluor, 2 μm pore size, 47 mm diameter) housed in Teflon inline filter holders were used to remove particulate matter from the ambient air stream. To avoid potential ozone artifacts, ozone scrubbers (multiple plies of MnO_2-coated copper mesh, Type ETO341FC003, Ansyco, Karlsruhe, Germany) were installed in front of the Teflon inlet filters. The use of ozone scrubbers in the air supply of the cuvettes was required to prevent chemical conversion of the primary emitted VOCs inside the cuvettes [*Neeb et al.*, 1997]. As all inner surfaces of the pumps were Teflon, this procedure did not alter the mixing ratios of isoprenoids in the air supply from the normal ambient conditions. Previous studies demonstrated that the applied Teflon film (FEP) showed no interference with monoterpenes and isoprene [*Kesselmeier et al.*, 1996], and that it is fully light permeable in the spectral range of 300–900 nm. However, we always made three measurements simultaneously: one of ambient air, one of the reference cuvette, and one of the branch cuvette to check potential contamination problems by the cuvette system.

[7] Quantification of CO_2 (assimilation/respiration) and H_2O (transpiration) exchange was achieved using a standard infrared dual-channel gas analyzer (Model 6262, LICOR, Lincoln, NE, USA) operated in the differential mode. The analyzer was maintained in an insulated, temperature controlled box at 40°C to prevent signal fluctuations due to temperature effects as well as water condensation inside the instrument due to the high relative humidity. Furthermore, all tubing downstream of the cuvette was insulated and heated above ambient temperature to about 40°C. For determination of the trace gas flux, air samples were taken continuously from inside of both cuvettes for isoprenoid analysis (0.1 L min^{-1}) and for the CO_2/H_2O-analyzer (1 L min^{-1}). The gas exchange rates (F) were calculated according to equation (1) from the measured concentration difference between the cuvettes ($\Delta c = c_{sample} - c_{ref}$), the chamber flush rate (Q) and the enclosed leaf area and/or dry weight (A), respectively.

$$F = \Delta c \cdot \frac{Q}{A} \tag{1}$$

[8] For the error calculation of the exchange rates, an error propagation method was used integrating the calculated error of each individual concentration measurement, the error of the mass flow, and the leaf area, respectively [*Kesselmeier et al.*, 1997; *Kuhn et al.*, 1999]. Stomatal conductance was calculated according to *Pearcy et al.*'s [1989] study. Projected leaf area and leaf dry weight were determined at the end of the experiments. Leaf area was measured by a calibrated scanner system (ScanJET IICX with DeskSCAN II, both Hewlett Packard, USA, and SIZE 1.10, Müller, Germany), and dry weight was determined using a microbalance (PM 400, Mettler-Toledo, Germany) after drying the leaves in a ventilated oven (90°C) for two days. Enclosed leaf areas were 0.25 m^2 for *H. courbaril* and 0.26 m^2 for *A. tibourbou*. For further recalculation the following mean specific leaf weights (g leaf dry weight per m^{-2} leaf area) may be applied: 90 g m^{-2} for *A. tibourbou* and 118.5 g m^{-2} for *H. courbaril*, respectively.

2.4. Application of Light and Temperature Algorithm

[9] Leaf temperature and light intensity are the primary driving forces for vegetation emissions. In emission inventories, the instantaneous emission rates for monoterpenes are calculated by multiplying a standard emission factor with an exponential function depending only on temperature [see *Tingey et al.*, 1991; *Guenther et al.*, 1991, 1993], while the emission of isoprene is calculated by multiplying a standard emission factor (E_S) (the emission rate under standard light and standard temperature conditions) with functions of both a temperature dependency (C_T) and light dependency (C_L) [*Guenther et al.*, 1991, 1993; *Guenther*, 1997]:

$$E = E_S \cdot C_T \cdot C_L \tag{2}$$

where E is the isoprene emission rate at the current leaf temperature T (K) and PAR intensity L (μmol m^{-2} s^{-1}), and

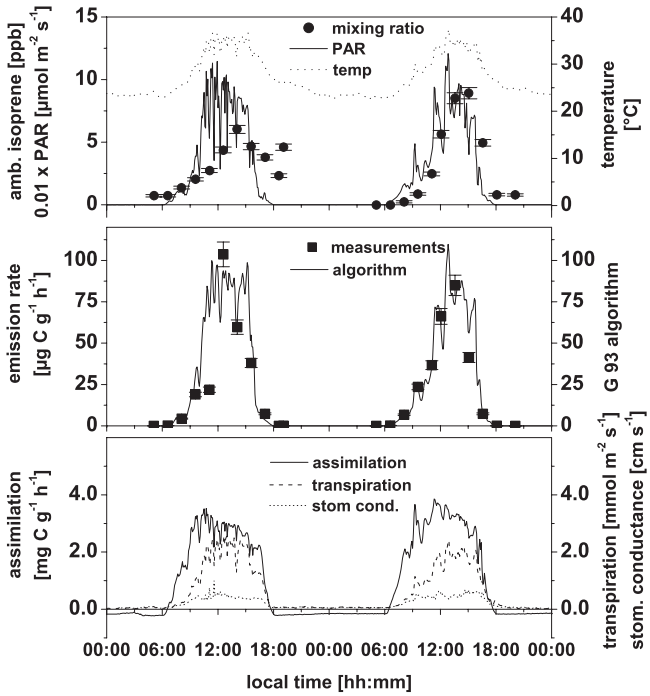

Figure 1. Diel pattern of observed isoprene emission rates from *H. courbaril* on 8–9 May 1999 together with meteorological data of photosynthetic active radiation (PAR), leaf temperature (temp), and the ambient air isoprene mixing ratios, plus physiological data of assimilation, transpiration, and calculated stomatal conductance (stom. cond.). Measured emission rates are presented together with the diel course predicted by the G93 algorithm for isoprene in the middle diagram. Error bars are calculated by an error propagation method for the absolute (ambient) and the difference (enclosure) measurements, respectively (see text).

E_S is the emission rate at standard temperature T_S (303 K), and standard PAR intensity (1000 µmol m^{-2} s^{-1}). The scaling factors C_T and C_L are defined by the functions:

$$C_T = \frac{\exp\frac{c_{T1}\cdot(T-T_s)}{R\cdot T_S\cdot T}}{0.961+\exp\frac{c_{T2}\cdot(T-T_m)}{R\cdot T_S\cdot T}} \quad (3)$$

$$C_L = \frac{\alpha\cdot c_{L1}\cdot L}{\sqrt{1+\alpha^2\cdot L^2}} \quad (4)$$

where R is the gas constant, and c_{T1}, c_{T2}, T_m, α, and c_{L1} are empirical coefficients derived by applying nonlinear best fit procedures from measurements on temperate plant species. In order to force $C_T \cdot C_L$ equal to 1 at standard conditions, the 1 in the denominator of C_T of earlier versions [*Guenther et al.*, 1993, 1995] was replaced by 0.961 [*Guenther*, 1997]. The species-specific standard emission factor E_S can either be measured under standard conditions (PAR of 1000 µmol m^{-2} s^{-1} and temperature of 30°C), or, like here, estimated from the slope of the linear regression between $C_T \cdot C_L$ (from equations (3) and (4)) and the experimentally determined emission rates at light intensity L and temperature T. While the light and temperature functions account for short-term variations of the emission rate, changes in the standard emission factor can account for interspecific variation, long-term adaptations such as the plant developmental stage, or even for entirely different ecosystem types [*Guenther et al.*, 1995; *Monson et al.*, 1995; *Bertin et al.*, 1997; *Staudt et al.*, 1997; *Klinger et al.*, 1998]. Temperature and light conditions that a leaf has been exposed to during the previous hours to days appear to significantly influence emissions, but this has not been well characterized [*Harley et al.*, 1997; *Sharkey et al.*, 1999]. In a modified version, *Guenther et al.* [1999] used slightly modified algorithms and a third scaling factor (C_A) is added to account for leaf age and past environmental conditions or phenology.

3. Results

3.1. Branch Enclosure Measurements

[10] The direct exchange measurements were carried out over a period of several days each, allowing for an adaptation time (after enclosing a branch) of at least one day before the respective exchange measurements. Weather conditions during these measuring periods were rather cloudy, reflected by relatively low intensities and short-term fluctuations of PAR, quite characteristic for wet season conditions.

3.1.1. Diel Isoprenoid Emission Pattern

[11] The diel patterns of the isoprenoid emission rates of *H. courbaril* and *A. tibourbou* are given in Figures 1 and 2, respectively, in conjunction with meteorological data of PAR, leaf temperature and the ambient air isoprenoid mixing ratios, plus the physiological data of assimilation, transpiration and stomatal conductance. In Figure 2 the relative contributions of the five most dominant individual monoterpene compounds to the overall emission composition are also specified. Each of the two plots shows the course of two consecutive days of investigation. The observed net assimilation and transpiration rates indicated a typical diel pattern of plant physiological processes as a function of light intensity and temperature. The maximum daytime carbon assimilation rates of sunlit leaves of *H. courbaril* and *A. tibourbou* at the canopy top were very similar on a leaf area basis, and only slightly different when compared on a dry weight basis, with values of 10.5 µmol m^{-2} s^{-1} (3.9 mgC g^{-1} h^{-1}) and 10.0 µmol m^{-2} s^{-1} (4.9 mgC g^{-1} h^{-1}), respectively. In contrast, the composition of the emitted VOCs of the two tree species differed completely. While *H. courbaril* emitted only isoprene and no monoterpenes (Figure 1), the species *A. tibourbou* was found to emit exclusively monoterpenes and no isoprene (Figure 2). On a carbon basis, monoterpene emissions by *A. tibourbou* were about one order of magnitude lower than the isoprene emissions by *H. courbaril*. However, strong similarities were observed in the diel pattern of isoprenoid emission of both tree species. Emission of both isoprene and monoterpenes was negligible during nighttime, increased through the morning with increasing air temperature and light, reached a peak in the afternoon coinciding with the peaks in leaf temperature and light, and then declined in the afternoon. Maximum isoprenoid emission rates on a carbon basis were 104 µgC g^{-1} h^{-1} (57 nmol m^{-2} s^{-1}) for isoprene from *H. courbaril* and 6.2 µgC g^{-1} h^{-1} (1.3 nmol m^{-2} s^{-1}) for the sum of monoterpenes emitted from *A. tibourbou*. The calculated standard emission factor E_S on a carbon

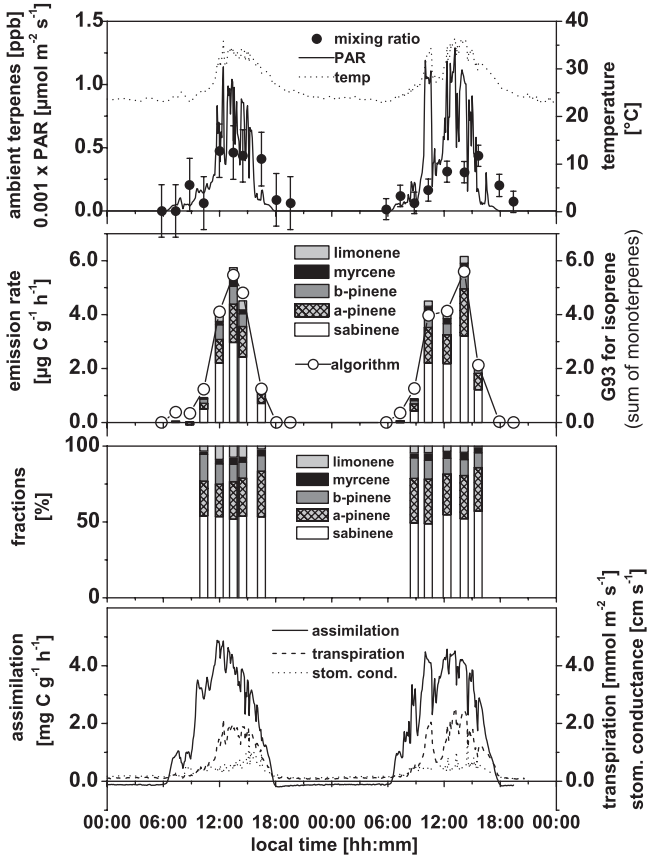

Figure 2. Diel pattern of the five dominantly emitted monoterpenes from *A. tibourbou* on 4–5 May 1999 together with meteorological data of photosynthetic active radiation (PAR), leaf temperature (temp), and the ambient air mixing ratios of the sum of monoterpenes, plus physiological data of assimilation, transpiration, and calculated stomatal conductance (stom. cond.). Measured emission rates are presented together with the course predicted for monoterpenes (using the G93 algorithm for isoprene) in the upper middle diagram. In the lower middle diagram, the relative proportions (%) of the five dominantly emitted monoterpene compounds are shown. Error bars are calculated by an error propagation method for the absolute (ambient) and the difference (enclosure) measurements, respectively (see text).

basis (μgC g^{-1} h^{-1}), i.e., the emission rate normalized to standard light (1000 μmol m^{-2} s^{-1}) and temperature (30°C), was 45.4 for isoprene emission from *H. courbaril* and 3.6 for monoterpene emission from *A. tibourbou*. Generally about 90% of the total monoterpenes emitted from *A. tibourbou* was comprised of sabinene, α-pinene, β-pinene, myrcene and limonene (in order of abundance). While the total sum of monoterpenes showed a clear diel cycle, the relative proportion of composition (in average: 53 ± 2% sabinene, 27 ± 3% α-pinene, 12 ± 2% β-pinene, 4 ±1% myrcene, and 4 ±2% limonene) did not change significantly during the day, i.e., was independent of light intensity (Figure 2). The remaining fraction investigated, but not accounted for in our calculations, was composed of camphene, α-phellandrene, α-terpinene, p-cymene, and γ-terpinene.

3.1.2. Light and Temperature Dependence of Isoprenoid Emission

[12] In Figure 3 the isoprene emission from *H. courbaril* and the monoterpene emission from *A. tibourbou*, respectively, are plotted versus the corresponding light intensities (PAR). The emission rates were normalized to standard temperature (30°C) by dividing by the temperature correction factor C_T (equation (3)) to better illustrate the dependence on light intensity and to allow better comparison between the response of isoprenoid emission from both tree species. Due to the weather conditions prevailing during our measurements, i.e., typical for wet season conditions, the examined range of light and temperature were somewhat restricted. Although the database is small, the striking feature of Figure 3 is the indication that both the isoprene emission of *H. courbaril* and the monoterpene emission of *A. tibourbou* exhibited the same strong response to light, i.e., no emission in the dark, an increase at low intensities and approaching a saturation at higher PAR. The isoprene and monoterpene synthesis and emission was closely related to photosynthesis, as their light dependencies appeared to reflect that of photosynthetic activity, also shown in Figure 3. This is even more evident for the monoterpene emission (Figure 3, lower

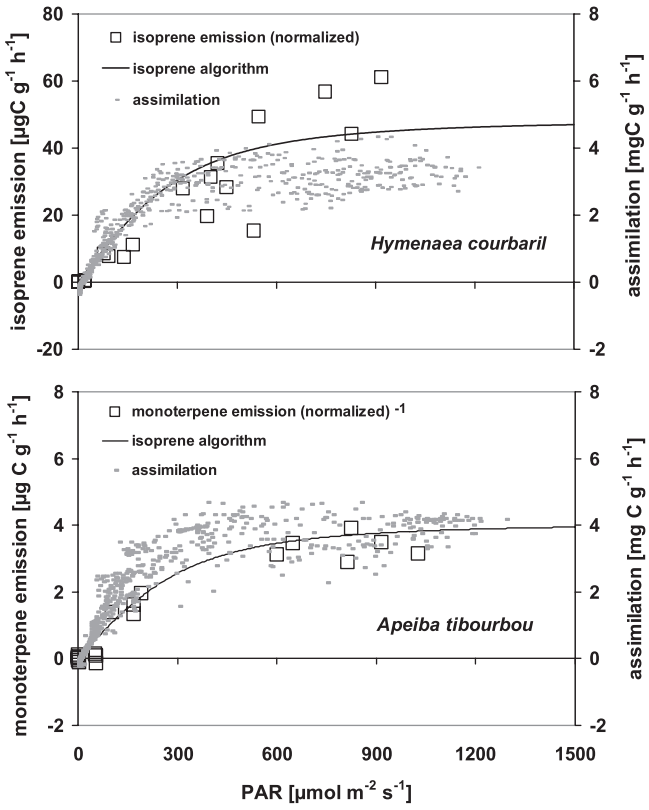

Figure 3. Response of photosynthesis and isoprene emission from *H. courbaril* (upper diagram) and monoterpene emission from *A. tibourbou* (lower diagram) to the corresponding light intensities (PAR). The solid lines indicate the dependence on light predicted by the G93 algorithm for isoprene. The measured emission rates were normalized to standard temperature (30°C) by dividing by the temperature correction factor C_T (see equation (3)).

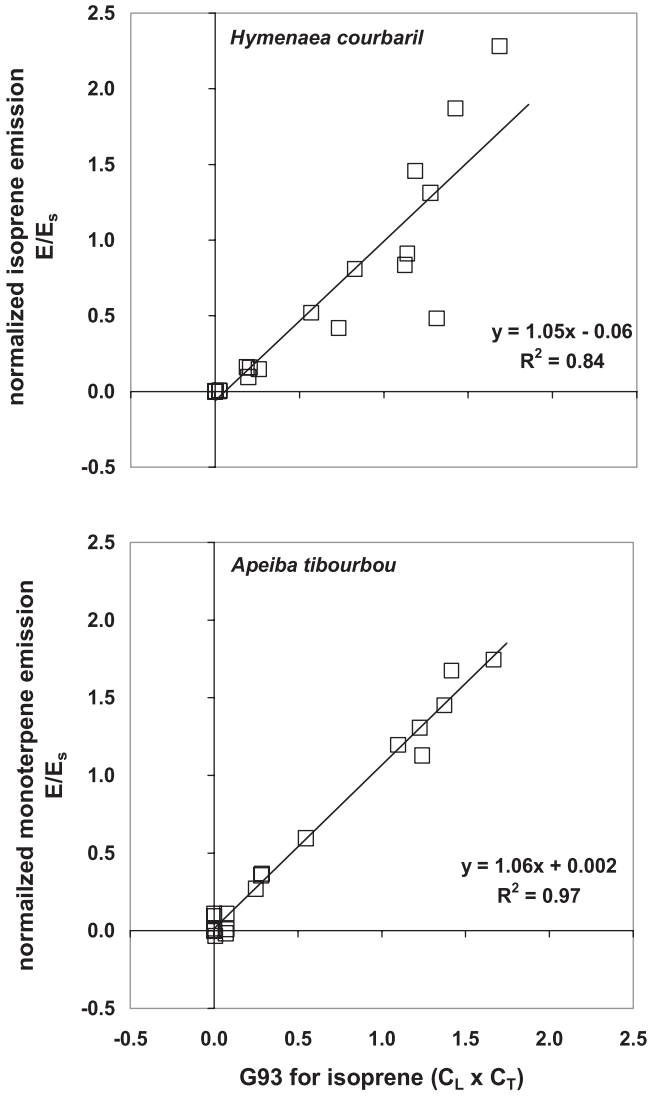

Figure 4. Comparison of observed normalized isoprenoid emission rates (E/E_s, see equation (3)) and the emission predicted by the G93 algorithm for isoprene. The linear regression analysis indicates that the isoprene algorithm predicts the monoterpene emission of *A. tibourbou* (R^2 = 0.97, lower diagram) even better than the isoprene emission of *H. courbaril* (R^2 = 0.84, upper diagram).

diagram) as it saturated with increasing light at levels as low as 500 μmol m^{-2} s^{-1}, similar to CO_2 assimilation, which itself showed similar response to light for both tree species.

[13] Production and emission of isoprene are closely related and are understood to be light and temperature dependent. Monoterpenes in contrast, although synthesized during the photoperiod, are normally stored prior to emission and most investigations on monoterpene emitters did not find an instantaneous influence of light on the direct emission. We did not observe monoterpene release under dark conditions, and the function of the light dependence for isoprene emissions (G93, see chapter 2.4) was found to be quite robust to predict the monoterpene emissions of *A. tibourbou*. In fact, according to the linear regression analysis of normalized observed flux rates versus the G93 algorithm shown in Figure 4, the isoprene algorithm was found to better represent the monoterpene emission of *A. tibourbou* (R^2 = 0.97) than the isoprene emission of *H. courbaril* (R^2 = 0.84).

[14] The dependence on temperature in the range investigated, between 23 and 36°C, showed a constant increase of isoprenoid emission for both species (data not shown). The question of whether or not these functions reveal an optimum at about 40°C for isoprene emission, as proposed by *Guenther et al.* [1993], or for monoterpene emission, as it was observed for some monoterpenes in laboratory experiments on *Quercus ilex* by *Staudt and Bertin* [1998], could not be resolved due to the relatively narrow temperature range as was observed during this study.

3.1.3. Loss of Organic Carbon by Isoprenoid Emission

[15] VOC emissions represent a nontrivial carbon loss to the plant, as biosynthesis of isoprene and monoterpenes is based on photosynthetically fixed carbon [e.g., *Harley et al.*, 1999; *Kesselmeier et al.*, 1998]. Even though both the emission of isoprenoids and the assimilation of CO_2 showed a comparable diel pattern at first glance, the instantaneous relative C-loss by isoprenoid emission during the course of the day also exhibited a distinct diel pattern (Figure 5). The highest values were found around noon reaching 3.7% for *H. courbaril* and 0.16% for *A. tibourbou*. The daily integrated values (relative to NPP, net primary production on a daily basis, including nighttime respiration) were

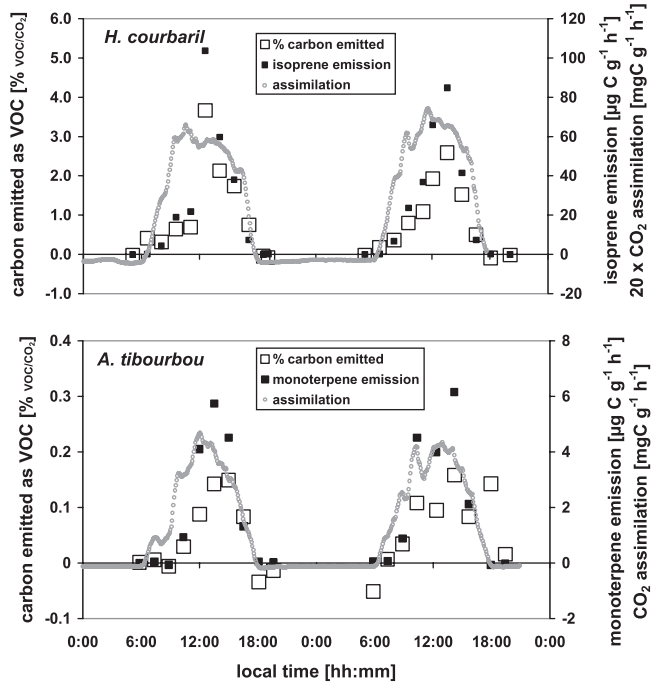

Figure 5. Diel course of carbon loss due to isoprene emission from *H. courbaril* (8–9 May 1999; upper diagram) and monoterpene emissions from *A. tibourbou* (4–5 May 1999; lower diagram) per carbon assimilated by photosynthesis. For comparison, the respective isoprene and monoterpene emission rates and the photosynthetic activity are also plotted.

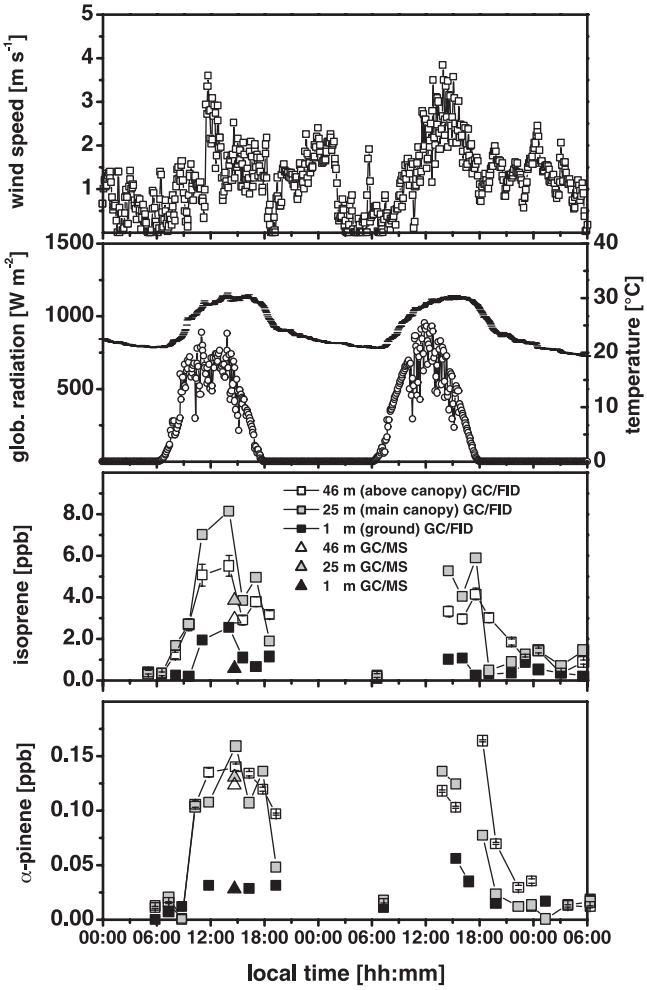

Figure 6. Diel course of vertical profiles of isoprene and α-pinene observed during two consecutive days (17–18 May, 1999) in and above a primary rainforest site in Rondônia, Brazil. Measurements were conducted on a 52 m micrometeorological scaffold tower erected 1991 (10°04′55″S, 61°55′48″W, 110 m asl). The mean canopy height was 32 m. Measured heights were at the ground level (1 m), the crown region (25 m, at maximum leaf area density), and above the canopy (46 m). Meteorological data of light intensity (glob. rad.: open circles), temperature, and windspeed were measured at 50 m. Two sampling and analytical systems (squares: GC/FID, analyzed at the Max Planck Institute for Chemistry, Mainz; triangles: GC/MS, analyzed at the Instituto sull' Inquinamento Atmosferico del C.N.R., Rome) were used independently and showed good agreement. Error bars shown for the 46 m samples are calculated according to an error propagation method.

substantial for *H. courbaril* (1.8%) and only of minor impact for *A. tibourbou* (0.1%).

3.2. Canopy Concentration Profiles

[16] In addition to the enclosure studies, we examined the vertical distribution of isoprenoids in and above the forest canopy to gain insight into the behavior of this ecosystem as a whole. The diel course of isoprenoid mixing ratios during two consecutive days (17–18 May 1999) at the ground level (1 m), the crown region (25 m, at the highest LAI density), and above the canopy (46 m) are shown in Figure 6, together with light intensity, temperature and wind speed at 50 m. The two sampling methods and analytical systems (see chapter 2.2) were used independently, and showed good agreement (indicated by the squares, i.e., GC/FID analysis, and triangles, i.e., GC/MS analysis for isoprene and α-pinene in Figure 6). Unfortunately, the first half of the second day could not be investigated due to power problems. However, in general both diel courses revealed the same pattern for isoprene and for α-pinene, representative for monoterpenes. Throughout the photoperiod the highest isoprenoid mixing ratios were found in the upper crown region of the forest canopy (25 m) and intermediate values were consistently found above the canopy (46 m). Consistently very low values, however, were always found near the ground (1 m). In general the ambient air mixing ratios of isoprenoids were clearly dominated by isoprene, with peak values of 8 ppb inside the main canopy, comparable to mixing ratios that were regularly found in the wet season close to the top of the nearby secondary forest site [*Kesselmeier et al.*, 2002]. The gradient between the two uppermost profile heights clearly demonstrates that the leaf canopy was a source of isoprene, as soon as the isoprene production was activated by sunlight. In contrast to isoprene, the vertical gradients of the monoterpenes did not show consistent significant differences between the two uppermost heights. Monoterpene flux rates were too small to be resolved by the gradient method, reflected also by total monoterpene concentrations about one order of magnitude lower than isoprene. Nevertheless a distinct diel cycle of α-pinene mixing ratios was observed for all heights with very low concentrations during night and peak values during daytime, following the diel course of light intensity. α-pinene, with a chemical lifetime less than 3 h (assuming an average daytime OH radical mixing ratio of $2 \cdot 10^6$ molecules cm^{-3}) [e.g., *Crutzen and Gidel*, 1983; *Atkinson*, 2000], may be depleted nearly as soon as the source ceases, and the diel cycle of ambient mixing ratios suggests a light dependent source for monoterpenes, especially if taking into account the small diel variation in ambient temperature of about 10°C (Figure 6).

[17] Especially for isoprene, an interesting feature was found shortly before sunset on both days. At 1700 and 1730 h on 17 and 18 May, respectively (see Figure 6), a significant short-term concentration increase was observed for the uppermost two heights which can not be explained by the patterns of light intensity and temperature alone. Shortly afterward, directly after sunset, at 1830 and 1900 h, respectively, the concentration at the crown region (25 m) decreased extremely quickly, falling to lower values than those found above the canopy at the same time.

4 Discussion

4.1. Enclosure Measurements

[18] With the branch enclosure approach we were able to provide compound specific and reproducible data on isoprenoid fluxes, allowing separation of the environmental control parameters. All exchange measurements were accompanied by an assessment of the respective physiological and micrometeorological parameters. The daytime assimilation rates of sunlit leaves of *H. courbaril* and *A.*

tibourbou, ranging between 4 and 5 mgC g^{-1} h^{-1}, were comparable to each other and agree well with the mean rates for various other tropical tree species found in Costa Rica, Australia, Cameroon, Malaysia, and Brazil (for details, see *Kuhn et al.* [2002]). Assimilation rates seem to correspond more to the respective environment rather than to the particular tree species. Species that occupy a particular ecological niche seem to behave in a similar fashion with respect to their physiology, like a functional group [*Körner*, 1993]. In our study the light dependence of both isoprene and monoterpene emission appeared to resemble that of photosynthesis (Figure 3). However, while for *H. courbaril* the emission of isoprene represented a nontrivial loss of photosynthetically fixed organic carbon of 1.8% on a daily basis, thereby corresponding to the range of carbon loss of strong isoprenoid emitters reported in the literature [e.g., *Sharkey et al.*, 1996; *Street et al.*, 1996; *Kesselmeier et al.*, 1997, 1998], the carbon loss by monoterpene emission from *A. tibourbou* was an order of magnitude smaller.

[19] Even though model results suggest that the tropics are the most important global biogenic isoprenoid source [*Guenther et al.*, 1995], field measurements on tropical tree species in these areas are rare. Recent studies by *Guenther et al.* [1996a], *Lerdau and Keller* [1997], and *Keller and Lerdau* [1999] extended the range of ecosystems studied to include tropical savannas and tropical dry forest. In general it is problematic to compare branch level studies with leaf level studies because partly shaded leaves on the lower portion of a branch have a considerably lower emission rate than leaves that are in direct sunlight [*Guenther et al.*, 1996b]. As only 0.25 and 0.26 m^2 of leaf surface were enclosed in our branch enclosures, shading is not assumed to be an important issue, but let us consider our branch level results as a lower bound estimate if compared to leaf level experiments. Our calculated standard emission factor on the branch level found for isoprene emission from *H. courbaril* of 45.4 μgC g^{-1} h^{-1} (24.9 nmol m^{-2} s^{-1}) is comparable to the mean emission factor on the leaf level reported for a screening experiment on 15 isoprene-emitting tropical tree species (mean of 26.3 ± 9.5 nmol m^{-2} s^{-1}; range of 9–43) conducted by *Keller and Lerdau* [1999] in a semideciduous forest in Panama, and to the mean value of 35.3 ± 16.4 nmol m^{-2} s^{-1} reported by *Lerdau and Keller* [1997] for a tropical dry forest in Puerto Rico. The emission factor of monoterpenes from *A. tibourbou* of 3.6 μgC g^{-1} h^{-1} (0.75 nmol m^{-2} s^{-1}) was low as compared to the isoprene emission. A direct comparison with literature values is not possible due to the lack of field data for the tropics, although the low numbers appear consistent with the overall data sets for monoterpene emitters [e.g., *Kesselmeier and Staudt*, 1999].

[20] Our investigations on the two tropical tree species revealed that despite the different isoprenoid emission composition, the diel emission pattern of both tree species reacted similarly toward the environmental conditions of fluctuating light and temperature. Neither isoprene nor monoterpene emission was detectable during nighttime. Both isoprene and monoterpene emissions exhibited a light saturation curve similar to CO_2 assimilation, indicating that close metabolic pathways are involved (Figure 3). This is in accordance with recent findings that the isoprenoid production is based on a very close relationship to photosynthetic productivity [*Flesch and Rohmer*, 1988; *Lichtenthaler et al.*, 1997; *Schwender et al.*, 1997; *Lichtenthaler*, 1999]. In contrast, the temperature dependence is instead related to enzyme activation kinetics [*Monson et al.*, 1992; *Schnitzler et al.*, 1996]. Isoprene emission occurs essentially without a leaf reservoir. It is directly linked to its instantaneous production in the isoprene synthase reaction. Isoprene synthase is highly temperature-sensitive and the temperature response of isoprene emission parallels the temperature dependence of isolated isoprene synthase. Thus, the isoprene emission rate is directly under enzymatic control and accurately reflects the instantaneous rate of synthesis.

[21] It was significant to learn that the monoterpene emission of the tropical tree species *A. tibourbou* also exhibited a close relation to light. Monoterpenes are formed from photosynthesis intermediates and may share the same synthetic pathway with isoprene within plant plastids [*Loreto*, 1996a], thus monoterpene synthesis may be assumed to be light dependent, similar to isoprene. In contrast to isoprene, however, monoterpene-producing plants mostly accumulate pools of monoterpenes and store them in specialized structures like resin ducts, glandular trichomes or related structures [*Gershenzon and Croteau*, 1991]. Due to their low vapor pressures, instantaneous emission of monoterpenes from these pools is then governed only by leaf temperature and the effect of leaf temperature on the vapor pressures of individual monoterpenes, but not on light intensity [*Monson et al.*, 1995; *Fall*, 1999; *Kesselmeier and Staudt*, 1999]. A prominent exception to this behavior was found in the extensively examined oak species *Q. ilex* and other Mediterranean oak species, which emit large amounts of monoterpenes in a light-dependent manner, similar to isoprene [*Staudt and Seufert*, 1995; *Staudt et al.*, 1997; *Bertin and Staudt*, 1996; *Bertin et al.*, 1997; *Loreto et al.*, 1996a, 1996b, 1998; *Ciccioli et al.*, 1997; *Seufert et al.*, 1997; *Staudt and Bertin*, 1998; *Csiky and Seufert*, 1999; *Kesselmeier et al.*, 1996, 1997, 1998]. The close connection between photosynthesis related biosynthesis and emission was demonstrated in labeling experiments by *Loreto et al.* [1996a, 1996b]. Our investigations provide experimental evidence that for monoterpene emission from the tropical tree species *A. tibourbou* both light and temperature were involved in the short-term control of its emission. We interpret this behavior to result from the close association between emission and biosynthesis. The relative proportion of the individual monoterpenes did not change significantly during the day (Figure 2). All monoterpene emission ceased at night, which points to direct production of these compounds prior to emission and a lack of terpene storage pools in the leaves of *A. tibourbou*.

4.2 Vertical Profile Measurements

[22] Micrometeorological flux calculations by the vertical gradient concentration method give access to whole canopy fluxes, but often suffer from limitations like the interference of atmospheric chemical reactions along the gradient, the strong assumptions concerning the turbulent exchange coefficients and different footprint areas seen from the sensors placed at different heights. The diel courses of the ambient air mixing ratios at different heights in and above the canopy presented here were used to emphasize the environmental controls on both the isoprene and monoterpene emission (Figure 6). The vertical gradients of ambient air

mixing ratios gave some qualitative insights into the distribution of sinks and sources of a tropical rain forest canopy.

[23] The diel course of isoprene, with increased mixing ratios during the day, in general resembled the expected diel pattern of isoprene emission/production strength, which results from the combined effects of increasing sunlight and temperature as was also demonstrated by our enclosure measurements. The daytime mixed layer concentrations are controlled by a balance between emission from vegetation and reaction with OH, the main daytime sink. According to the investigations of *Zimmerman et al.* [1988] in the Amazon basin, approximately 95% of isoprene reacts with OH and 5% with O_3. The resultant chemical atmospheric lifetime of isoprene at noon was estimated to be about 3 hours. In a low NO_x environment as observed during our study [*Gut et al.*, 2002a; *Rummel et al.*, 2002], the concentration of OH decreases as the isoprene source increases, and consequently, the isoprene concentration in the upper canopy and above the canopy rises almost as the square of the source strength before noon [*Jacob and Wofsy*, 1988]. The rate of increase is reduced by increased turbulent mixing due to thermal convection as the day progresses. The meteorological effects of warmer temperature, increased light intensities and increased vertical mixing above the canopy and the effect of varying atmospheric oxidation as the day progresses act in concert, so that their individual effects cannot be determined from our data. When the day proceeded the mixing ratios declined at all heights, which suggests that the daytime source is reduced, followed by removal from the atmosphere during afternoon and at night. While the highest mixing ratios were continually found in the two uppermost heights, consistently very low values were found near ground (1 m), indicative of a low emission rates and/or a sink for isoprene. Due to the dense concentration of leaf area in the top of the canopy and the extreme height of the tropical forest, the lower canopy is to some extend decoupled from the atmosphere above [*Jacob and Bakwin*, 1991; *Lloyd et al.*, 1996; *Kruijt et al.*, 2000; *Gut et al.*, 2002b] and the transport out of, or into, the decoupled lower canopy depends on turbulent diffusion or on the occurrence of large-scale events (eddies), such as storms. As a result of absorption and scattering of light by vegetation, the upper third of a tropical forest canopy may reduce the incoming PAR more than 80% [Carswell et al., 2000] and light levels near the ground of many rain forests can be less than 1% of that reaching the top of the canopy, with a strong dependence on the Sun angle. The vegetation source for isoprenoids in this near ground layer is not only reduced due to a lower activation by light, but also by the substantially lower standard emission factors that are normally reported for leaves grown in the shade, as compared to sunlit leaves of the same species [*Sharkey et al.*, 1996; *Harley et al.*, 1997; *Seufert et al.*, 1997; *Bertin et al.*, 1997]. Moreover, a biologically mediated consumption of isoprene in forest soils, including tropical dry and moist soils in Puerto Rico and in Panama, respectively, was recently demonstrated by *Cleveland and Yavitt* [1997, 1998].

[24] Thus, the dominant processes involved in the observed vertical pattern are assumed to be the light-dependent direct emission by the upper canopy during daytime and the chemical decomposition and/or potential deposition to the ground in the lower canopy. Assuming a daytime source in the leaf canopy and a sink at the ground level, the pattern observed in the late afternoon can be attributed to boundary layer dynamics. Shortly before sunset a nocturnal boundary layer (NBL) develops above the canopy with stable meteorological conditions and the cessation of convective circulation. Induction of NBL formation leads to a stratification of the near canopy level [*Stull*, 1988]. Together with frequently low wind speed (Figure 6), this leads to a limited NBL height, i.e., the layer that is interacting with the surface through turbulent mixing. Simultaneously a significant short-term increase in isoprene concentrations was observed for the uppermost two heights. Isoprene has a very low light compensation point (i.e., is still emitted at low light intensities; see Figure 3, upper diagram) and quantities emitted below the inversion layer are confined to a much smaller air volume, resulting in a concentration increase in the air layer containing the active leaf canopy source. Shortly afterward, when light totally ceased, a sharp drop of the isoprene concentration in the crown region was observed. While during daytime the lower canopy is thermally stratified (stable conditions), during nighttime effective turbulent mixing occurs within the lower region of the canopy in tropical rain forests. This condition is assumed to be caused by cooling of the upper canopy during the night [*Kruijt et al.*, 2000]. Due to the cessation of isoprene emission in the dark, the uptake of isoprene on soil and/or plant surfaces may then govern the atmospheric fate of isoprene inside the entire canopy, leading to the observed rapid depletion at 25 m height. In the air layer above the canopy, however, the isoprene concentration decreased relatively slowly, which is backed up by investigations of *Rasmussen and Khalil* [1988], who found that the nocturnal concentrations in the mixed layer over the Amazon forest, far from the ground (>300 m AGL), were comparable to daytime mixing ratios at the same height, indicating that this compound is quite stable at night without the influence of photochemistry and interaction with ground surface. While the major chemical losses of isoprene in the daytime are through reactions with OH and ozone, nighttime atmospheric losses of isoprene are through reactions with ozone and the nitrate radical [*Atkinson*, 2000]. A very rapid depletion of isoprene in inside-canopy air of the Amazon rain forest has also been reported by *Jacob and Wofsy* [1988] and *Zimmerman et al.* [1988]. However, according to their model the chemical decomposition of isoprene alone (mainly nitrate radical reaction) could not account for such a rapid depletion [*Jacob and Wofsy*, 1988], which also suggested surface deposition processes to be active. Furthermore, *Valentini et al.* [1997] observed slight canopy isoprene deposition fluxes during nighttime conditions through vertical gradient and relaxed eddy accumulation (REA) measurements, indicative of an active sink inside the forest canopy. For monoterpenes we also consistently found lowest values near the ground, suggesting the same may be valid for monoterpenes. Interesting to mention in this context is that for other VOCs at our site, like organic acids [*Kuhn et al.*, 2002] and aldehydes [*Rottenberger et al.*, 2002] the mixing ratios decreased across all measured heights in and above the canopy during the whole day, indicating the deposition of these compounds into the forest canopy and/or the soil. The concept of the uptake of these

compounds by plants was also supported by direct exchange measurements.

[25] For monoterpenes no consistent vertical gradients between the crown region and above the canopy could be resolved, which indicates that positive biogenic fluxes other than isoprene were rather low, highlighting the dominant role of isoprene emission at that specific site. In general this reflects the low monoterpene emission rates found by our direct enclosure measurements for one specific tree species (*A. tibourbou*) and is consistent with ambient total monoterpene concentrations generally not exceeding 1 ppb, i.e., an order of magnitude lower than for isoprene at Brazilian rain forest sites [*Kesselmeier et al.*, 2000, 2002; *Rinne et al.*, 2002]. Biogenic monoterpene emissions contribute only to a minor extent to the atmospheric burden of VOC at this site. However, the similarity in the diel cycles of ambient air mixing ratios of monoterpenes and isoprene, as was observed at all heights, indicates that the controlling environmental functions of monoterpene emissions are similar to isoprene. Considering the low diel variation of temperature at that site suggests a strong light-dependence of monoterpene emissions on a larger scale. A nighttime emission of monoterpenes would have resulted in an increase of the ambient mixing ratio due to the development of the NBL. The finding of a strong depletion of α-pinene at night is in accordance with a cease of the emission source shown by our enclosure measurements, even though the small data set (i.e., for only one monoterpene emitter) can not yet be generalized. Very recently, light-dependent monoterpene emissions on a canopy scale have also been reported by *Rinne et al.* [2002], who applied an eddy accumulation technique at an Amazônian tropical rain forest site. Both the ambient concentration and the observed flux rates of α-pinene, which comprised approximately 50% of the total monoterpene concentrations at that site, were about one order of magnitude lower than for isoprene [*Rinne et al.*, 2002]. The reported concentration range as well as the environmental monoterpene emission controls was in good agreement with our data.

5. Conclusion

[26] Measurements reported here may help to improve the database of hydrocarbon emission rates from vegetation in tropical regions for future emission rate inventories and model testing. Mechanistic studies on the environmental controls of isoprenoid emission were achieved by application of enclosures. Environmental factors and mechanisms controlling the short-term behavior of monoterpene emission from *A. tibourbou* and isoprene emission from *H. courbaril* were found to be similar and involved both temperature and light. Our finding of a light dependence of the monoterpene emission by the tropical tree species *A. tibourbou* suggests that it does not store terpenes, but emits them immediately upon production. The strong diel cycle of ambient α-pinene mixing ratios in general resembled the behavior we observed in the enclosure measurements and further supports the concept of a light-dependence of biogenic monoterpene emission on a larger scale. Although the data set is small and only one monoterpene emitter was investigated during our study, our findings may indicate that the widely applied exponential function to model monoterpene emissions, which is only dependent on temperature [*Tingey et al.*, 1991; *Guenther et al.*, 1991, 1993, 1995], may not be applicable to predict the diel and seasonal variation of monoterpene emission in tropical areas. Most recent canopy flux measurements by *Rinne et al.* [2002] in the Amazon further strengthen this conclusion. A light dependent behavior of monoterpene emission, if common among tropical tree species, would have strong influence on the predicted temporal distribution of monoterpene emission as well as on the total amount of monoterpenes being emitted. If emission estimates using a temperature dependent algorithm are replaced with estimates based on light and temperature algorithms using the same standard emission rate, the daily integrated amount of monoterpene emissions would be reduced by two-thirds [*Rinne et al.*, 2002]. Generalization and upscaling of this behavior may prove to be crucial although difficult due to the vast biodiversity in tropical regions. Characterization of a whole ecosystem requires very large sample quantities to reduce uncertainties. For our site, monoterpenes were found to play a minor role compared to isoprene. Monoterpene mixing ratios were an order of magnitude lower than for isoprene and the gradients were too small to significantly indicate positive monoterpene fluxes. In contrast, the gradients found for isoprene evolving during daytime clearly indicated emission driven by the environmental controls of light and temperature. However, the vertical distribution inside and above the canopy during the course of the day revealed the complexity of the fate of primarily emitted VOC. The biogenic sources of isoprenoids in the main canopy, a possible biogenic sink at the ground, the loss of isoprenoids by chemical conversion and boundary dynamics must all be taken into account to explain the diel course in a natural forest canopy. Seasonal effects additionally may have an important impact on the canopy exchange processes. These and other objectives have to be addressed in more detail in future work.

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T. Biesenthal, J. Kesselmeier, U. Kuhn, S. Rottenberger, G. Schebeske, and A. Wolf, Biogeochemistry Department, Max Planck Institute for Chemistry, P.O. Box 3060, D-55020, Mainz, Germany. (kuhn@mpch-mainz.mpg.de)

E. Brancaleoni, P. Ciccioli, and M. Frattoni, Instituto sull' Inquinamento Atmosferico del C.N.R., Area d. Ricerca di Roma, Rome, Italy.

T. M. Tavares, Instituto de Química, Universidade Federal da Bahia, Salvador, Brazil.