

Exchange of short-chain monocarboxylic acids by vegetation at a remote tropical forest site in Amazonia

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[1] As part of the project LBA-EUSTACH (European Studies on Trace gases and Atmospheric Chemistry as a contribution to the Large-Scale Biosphere-Atmosphere experiment in Amazonia), the exchange of formic acid and acetic acid between vegetation and the atmosphere was investigated in the wet-to-dry season transition and the dry-to-wet season transition periods in 1999 in Rondônia, Brazil. Direct exchange measurements on the branch level mainly exhibited uptake of formic acid and acetic acid for all plant species in both seasons, although diel, seasonal, and interspecies variations were observed. Even though other physiological and physico-chemical parameters may have contributed, the uptake of organic acids was found to be primarily a function of the ambient atmospheric mixing ratios. The linear dependence suggests a bidirectional exchange behavior of the plants and calculated deposition velocities ($0.17\text{--}0.23\text{ cm s}^{-1}$), compensation point mixing ratios ($0.16\text{--}0.30\text{ ppb}$), and potential emission rates under purified air conditions ($0.013\text{--}0.031\text{ nmol m}^{-2}\text{ s}^{-1}$) are discussed. Vertical profile measurements in and above the primary forest canopy further strengthened the assumption that the forest is rather a sink than a source for organic acids. The generally lower mixing ratios observed within the canopy were indicative of an uptake by vegetation and/or the soil surface. Continuous measurements of the ambient atmospheric mixing ratios at the canopy top revealed strong diel variations in both seasons and a marked seasonality with higher mixing ratios during the dry season, both being mirrored in the variation of observed uptake rates of the plants. High atmospheric concentrations during the dry season were attributed to biomass burning. During the wet season, when biomass burning activity was low, indirect emission by the vegetation, i.e., photochemical oxidation of primarily emitted biogenic reactive hydrocarbons, was assumed to dominantly contribute to the atmospheric burden of the organic acids. The high degree of correlation between atmospheric formic acid and acetic acid indicated that similar atmospheric processes were affecting their mixing ratios.

INDEX TERMS: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 1615 Global Change: Biogeochemical processes (4805)

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1. Introduction

[2] Carboxylic acids are important and ubiquitous chemical constituents in all biogeochemical compartments like soil, hydrosphere, biosphere and the global atmosphere. They contribute a large fraction to the atmospheric mixture

of volatile organic compounds (VOC) (for recent review, see *Chebbi and Carlier* [1996], *Khare et al.* [1999], and *Kesselmeier and Staudt* [1999]). Formic acid and acetic acid are usually the dominant species found in the highest mixing ratios, though other organic acid species have been observed [*Likens et al.*, 1983; *Norton et al.*, 1983; *Kawamura et al.*, 1985; *Kawamura and Kaplan*, 1986; *Andreae et al.*, 1987; *Hofmann et al.*, 1997]. Earlier measurements by *Andreae et al.* [1988] and *Talbot et al.* [1990] obtained during the ABLE-2 campaign in the central Amazon have demonstrated the dominant impact of formic acid and acetic acid in contributing to the acidity of the precipitation in this area. These oxygenated volatile organic compounds therefore hold important implications with regard to the precip-

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itation chemistry in the tropics. However, both acids occur primarily in the gas phase and commonly exhibit a well-defined seasonal cycle with higher mixing ratios in the growing season. Despite their extensive distribution, the atmospheric sources and sinks of formic acid and acetic acid are not well characterized. Both have primary and secondary sources. Potential sources include direct anthropogenic emissions like automobile exhaust [Kawamura *et al.*, 1985; Talbot *et al.*, 1988], but carbon isotopic composition analysis of formic acid samples from a rural and semiremote area in Denmark [Glasius *et al.*, 2000] indicate that 80–100% of formic acid stem from biogenic VOC emitted from terrestrial sources. Reported natural sources are emission from biomass burning [Talbot *et al.*, 1988; Hartmann, 1990], dry soils [Sanhueza and Andreae, 1991], oceans [Graedel and Weschler, 1981], plants (see below), and—for formic acid—formicine ants [Graedel and Eisner, 1988; Johnson and Dawson, 1993], and secondary formation in the atmosphere by oxidation of natural reactive hydrocarbons [Sanhueza *et al.*, 1996a; Poisson *et al.*, 2000]. The atmospheric chemistry of organic acids is far from being well understood. Kinetic studies have confirmed the formation of both acids in the reaction of ozone with olefins like ethene, propene, and butene, which are ubiquitous in the atmosphere but are predominantly anthropogenic in origin [Calvert and Stockwell, 1983; Atkinson, 1990; Horie and Moortgat, 1991; Neeb *et al.*, 1997b; Khare *et al.*, 1999]. The reaction of the respective short-chain aldehydes with OH or peroxides is also discussed as a secondary source of formic acid and acetic acid [Chameides and Davis, 1983; Jacob, 1986; Moortgat *et al.*, 1989; Chebbi and Carlier, 1996]. However, the lack of correlation between the organic acids and peroxide species led Talbot *et al.* [1996] argue against a significant source from permutation reactions of peroxy radicals. On the other hand a good correlation with isoprene in the diel course of concentrations in the field suggests this biogenic alkene to be the main atmospheric precursor of formic acid [Sanhueza *et al.*, 1996a]. This finding is in good agreement with model results [Jacob and Wofsy, 1988] and laboratory results on the reaction of isoprene with ozone [Neeb *et al.*, 1997b]. According to Horie *et al.* [1994], any alkene with terminal double bounds (most prominently isoprene, ethene and some terpenes) is capable of forming HCOOH. The sources for CH₃COOH, on the other hand, are even more vague. Like for formic acid, the ozonolysis of methylvinylketone as well yields acetic acid [Poisson *et al.*, 2000]. Atmospheric oxidation of isoprenoids can also produce CH₃COOH and another potential source is the decomposition of peroxyacetyl nitrate (PAN) [Niki *et al.*, 1985; Moortgat *et al.*, 1989; Madronich *et al.*, 1990]. The aqueous phase in clouds and rain are rather a net sink than a source for both acids [Jacob and Wofsy, 1988; Sanhueza *et al.*, 1992; Lelieveld and Crutzen, 1991; Keene *et al.*, 1995]. Neither monocarboxylic acid photolyses in the troposphere due to their spectral absorption in the range of 180–240 nm [Calvert and Pitts, 1966] and gas phase oxidation is rather slow, i.e., the lifetime of formic acid for the reaction with OH radicals is >10 days [Dawson and Farmer, 1988; Sanhueza *et al.*, 1996a]. Due to their very limited chemical transformation, the removal of carboxylic acids from the atmosphere is assumed to be largely due to wet and dry deposition [e.g.,

Chebbi and Carlier, 1996]. In that respect carboxylic acids are one of the terminal products of the photooxidation of hydrocarbons from the planetary boundary layer and have to be accounted for when discussing the role of hydrocarbon emission in the global carbon budget.

[3] Numerous VOC species are directly emitted into the atmosphere by the leaves of many plant species, especially by trees. Whereas most earlier publications emphasize the importance of isoprene and monoterpenes, more recent studies report about the release of oxygenated volatile organic hydrocarbons by vegetation in considerable amounts [Fehsenfeld *et al.*, 1992; Guenther *et al.*, 1995; Kesselmeier and Staudt, 1999]. Direct emission of formic acid and acetic acid were found by various exchange measurements on trees [Talbot *et al.*, 1990; Kesselmeier *et al.*, 1997a, 1997b, 1998; Gabriel *et al.*, 1999; Martin *et al.*, 1999; Staudt *et al.*, 2000; Kesselmeier, 2001]. During field investigations in the Mediterranean area, Staudt *et al.* [2000] found emission during daytime, but net acid deposition during the early morning hours and evening. Crop plant species (corn, pea, barley and oat), however, did not emit organic acids, but deposition was found when low mixing ratios of organic acids were provided in oxidant-free air [Kesselmeier *et al.*, 1998]. As part of the Large-scale biosphere-Atmosphere experiment in Amazonia (LBA-EUSTACH), see Andreae *et al.* [2002], we examined the exchange of organic acids between tropical vegetation and the atmosphere with different methodological approaches. Measurements were carried out in the end of the wet and the end of the dry season 1999 at a remote site in the southwestern part of the Amazon basin in Rondônia, Brazil, in order to improve our understanding of the role of the tropical rain forest in the exchange of formic acid and acetic acid. Enclosure measurements on the branch level gave insight into the exchange behavior of different plant species directly on the plant surface, while ambient air and profile measurements inside and above the canopy were carried out to assess exchange on a larger scale.

2. Measurements and Methods

2.1. Sampling Sites and Periods

[4] Measurements were performed in a relatively well preserved ecological reserve 100 km north of Ji-Parana in the state of Rondônia, southwest Amazonia, Brazil. The area is covered by seasonally dry tropical rain forest (*Floresta ombrofila aberta*). The site has a pronounced dry season between June and August, while the wettest periods are between December and April. For further details, see Andreae *et al.* [2002].

[5] Two campaigns were carried out, one at the wet-to-dry season transition period in April/May 1999, representative for background conditions without the influence of biomass burning (afterward named wet season); the other at the dry-to-wet transition period in September/October 1999, associated with high biomass burning activity (afterward named dry season). Dynamic branch enclosure (cuvette) measurements and most of the ambient air measurements were conducted on a mobile 10m scaffolding tower at the top of a secondary forest canopy close to the Jaru biological reserve camp site (10°08'43''S, 62°54'27''W, 107 m asl). The camp site is in the middle of a 1 km² of secondary

forest surrounded by primary forest. On the southwest side of the camp the Machado River gave access to the camp by boat. Three different tree species were investigated by cuvette measurements: *Hymenaea courbaril* L. var. (common name: Jatoba), ranging from tropical dry to wet through subtropical dry to wet forest life zones [Duke, 1978], *Apeiba tibourbou* (common name: Pente de Macaco), with principal occurrence in secondary but also in primary rain forest [Lorenzi, 1998], and *Sorocea guilleminiana* (common name: Jaca-branca, Jaca-brava). All measurements presented here were carried out on mature leaves in both seasons. Maturity was defined as the point when leaves reached full size, grew fully turgid and became dark green. *Hymenaea* and *Apeiba* are deciduous trees with a leafless period within the dry season whereas *Sorocea* is an ever-green broad-leaved species.

[6] Vertical profile measurements of carboxylic acids were conducted on a 52 m micrometeorological scaffold tower erected 1991 in a primary forest site (RBJ tower A, 10°04'55"S, 61°55'48"W, 110 mas l) [Gash et al., 1996]. The mean canopy height was 32 m, with maximum density at 25 m. Under a relatively open stem space up to 20 m a palm-rich understory of a few meters height was found. Single jutting trees reached up to 45 m height, the leaf area index was about 5.5 (for vertical LAI distribution, see Andrea et al. [2002]). The fetch of the forest site was only limited to the southwest, where the Machado River ran in about 400 m distance. Profiles within and above the canopy were obtained by sampling simultaneously at three heights above ground level (1, 25, and 46 m) during the wet season and at four heights (1, 25, 44, and 51 m) during the dry season. Unfortunately the measurements at the end of the dry season were influenced by repeated rainfall events during the sampling periods, not representative for the weather conditions typically prevailing during the dry season. Profile measurements were conducted during daytime only, between 1100 and 1600 h local time.

2.2. Sampling Procedure and Chemical Analysis

[7] The organic acids were sampled by cryogenic cotrapping with atmospheric water vapor. Tests in our laboratory proved that losses of formic acid and acetic acid were negligible and the efficiency of this method is 100% [Hofmann et al., 1997]. Glass coils were emerged in ethanol cooled to -70°C. Air was sampled at a flow rate of about 5 L min⁻¹ through 5 m of 0.25 inch Teflon inlet tubing. Airflow was continuously monitored during sampling using electronic mass flowmeters. Teflon filters (Zefluor, 2 µm pore size, 47 mm diameter) housed in Teflon inline filter holders were used to remove particulate matter from the sample air stream. Individual sample collection intervals were 30 min during the wet season, and were increased to 40 min during the dry season, because of the lower air humidity in this period. With a sample time of 30 min the total sample air volume was about 150 L. The resulting liquid sample mass was determined gravimetrically, and was typically ~4 mL. Immediately after collection, the samples were spiked with 0.5% of chloroform to prevent microbial decomposition of the organic acids and stored at -18°C until chemical analysis. Analysis was normally performed within 2 days

after sampling. Organic acids were quantified in the aqueous phase by an ion-exchange chromatographic system, equipped with a Dionex Ion Pac AS 11, 4 mm column, a Dionex anion micromembrane suppressor (model ASRS-1) and a conductivity detector [Hofmann et al., 1997; Gabriel et al., 1999]. The detection limit of this method depends on the absolute humidity of the ambient air and was typically better than 10 ppt for both acids with an overall accuracy of better than 11%. During the wet season campaign tests were performed to avoid potential O₃ oxidation artifacts in the liquid water solution accumulated in the glass coils during the sampling procedure. With relatively low O₃ mixing ratios in the wet season (never exceeding 20 ppb), we simultaneously collected samples using the normal inlet line and another which included an ozone scrubber (multiple plies of MnO₂-coated copper mesh (Ansyco, Karlsruhe, Germany)) in front of the Teflon filter. We did not detect any significant difference between the two approaches, and concluded there were no adsorption or desorption effects for the acids on the ozone scrubber. Accordingly we collected all samples (including the ambient air measurements) through this ozone scrubber to prevent O₃ oxidation artifacts during the sampling procedures, especially with much higher O₃ mixing ratios during the dry season. Ambient ozone mixing ratios measurements were carried out using a photometric ozone analyzer (Model 1003, Dasibi Environmental Corporation, Glendale, Calif.) with an estimated precision of ±3 ppb and a detection limit of 2 ppb.

2.3. Branch Enclosure and Ambient Air Measurements

[8] An open, dynamic (flow-through) cuvette system [Kesselmeier et al., 1998] flushed with ambient air was used for the gas exchange measurements on various tree branches at about 8 m height. The distal end of a branch was loosely 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 L) consisted of a cylindrical Teflon bag that was supported by an external frame. Previous studies demonstrated that the applied Teflon film (FEP) shows no interference with trace gases tested such as organic acids [Schäfer et al., 1992], monoterpenes and isoprene [Kesselmeier et al., 1996], and reduced sulfur compounds [Kuhn et al., 2000] and is fully light permeable in the spectral range of 300–900 nm. 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 better than once every 2 min. The air inside the chambers was well mixed by a Teflon propeller driven by a magnetically coupled motor attached outside. 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. 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).

[9] The cuvettes were operated by pumping ambient air through the cuvette system using four membrane pumps (Vakuubrand, Germany). The application of ozone scrubbers in the air supply of the cuvettes was required to prevent the secondary formation of carboxylic acids by ozonolysis of primarily emitted reactive hydrocarbons like isoprene inside the cuvettes [Neeb *et al.*, 1997a]. Thus, each of the pump exits was equipped with a MnO₂ ozone scrubber (Ansyco, Karlsruhe, Germany) and the airflow from all four pumps were subsequently merged together before being branched to both cuvettes in order to provide identical input mixing ratios. Even though all inner surfaces of the pumps were Teflon, this procedure increased the mixing ratios of acids in the air supply as compared to the normal ambient conditions, especially for formic acid during the wet season, when ambient air mixing ratios were very low, resulting in an two- to three-fold increase in extreme cases. This artificial increase is considered by using the reference cuvette concentrations as described below. Tests were conducted by sucking ambient air through the empty cuvettes instead of pumping, which showed that the cuvettes themselves did not contribute to the concentration increase of the acids. Furthermore, we regularly tested both cuvettes being empty (i.e., before installing a branch) and did not find any significant blank problem. To obtain all information on the prevailing conditions, we always made three measurements simultaneously: one of ambient air, one of the reference cuvette, and one of the branch cuvette.

[10] Quantification of CO₂ (respiration/assimilation) and H₂O (transpiration) exchange was achieved using a standard infrared dual-channel gas analyzer (Model 6262, LICOR, Lincoln, NE, USA) in the differential mode. It 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. Furthermore, all tubing downstream of the cuvette was insulated and heated above ambient temperature to about 35°C.

[11] For determination of the trace gas flux, air samples were taken continuously from inside of both cuvettes for acid analysis (5 L min⁻¹) and for the CO₂/H₂O analyzer (1 L min⁻¹). The gas exchange rates (F) were calculated according to equation (1) from the measured concentration difference ($\Delta c = c_{\text{sample}} - c_{\text{ref}}$), the chamber flush rate (Q) and the enclosed leaf area (A).

$$F = \Delta c \cdot \frac{Q}{A} \quad (1)$$

[12] For the calculation of the exchange error, an error propagation method was used [Kesselmeier *et al.*, 1997a, 1997b; Kuhn *et al.*, 1999]. Exchange rates obtained with the enclosure techniques may not be extrapolated directly to the natural (undisturbed) field situation, as chamber measurements generally cause an alteration of the trace gas mixing ratio adjacent to the leaves. For a quantitative description of this effect and for comparing measurements with different methods, the concept of the deposition velocity is used [see, e.g., Hicks *et al.*, 1987]. Deposition fluxes are assumed to be

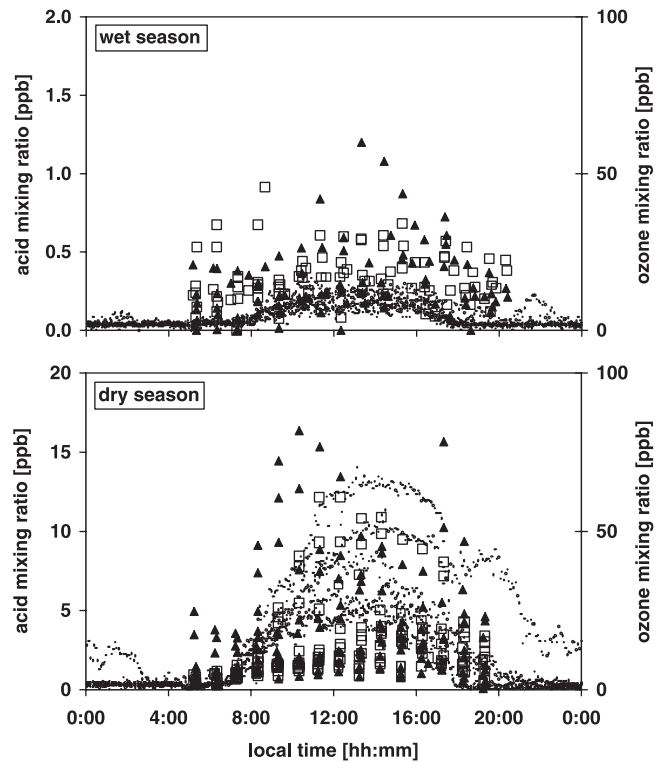


Figure 1. Diel cycles of formic acid (solid triangles), acetic acid (open squares), and ozone (dots) mixing ratios during the wet season ($n = 92$) and the dry season ($n = 148$) measured at canopy top. Note: The acid scale is enlarged one order of magnitude in the dry season.

proportional to the ambient air concentration (c) and are therefore normalized to the so-called deposition velocity (v_d):

$$v_d = \frac{F}{c} \quad (2)$$

[13] Stomatal conductance was calculated according to *Pearcy et al.* [1989]. 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 for 2 days. Enclosed leaf areas were between 0.1 and 0.25 m². For further recalculation the following mean specific leaf weights (g leaf dry weight per m⁻² leaf area) may be applied: 90 and 70 g m⁻² for *Apeiba* and 118.5 and 80 g m⁻² for *Hymenaea*, in the wet and the dry season, respectively, and 92 g m⁻² for *Sorocea* (investigated in the dry season only).

3. Results

3.1. Ambient Air Mixing Ratios

[14] Figure 1 shows the diel variations of the ambient atmospheric mixing ratios of formic acid and acetic acid during the branch exchange measurements in both field experiments in the wet and the dry season 1999. In both seasons we observed relatively low mixing ratios before sunrise and after sunset (nighttime), and maximum levels

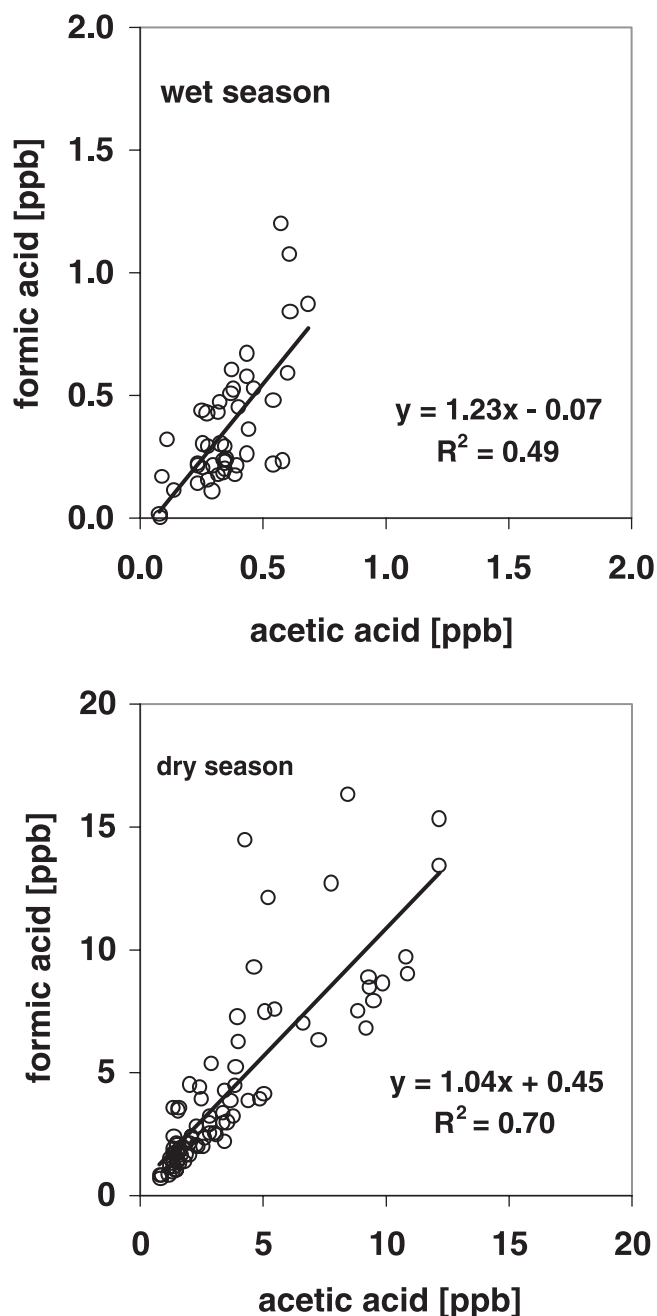


Figure 2. Correlation between HCOOH and CH₃COOH in the wet season and the dry season measured at canopy top.

during daytime. The diel cycle of formic acid is more pronounced than for acetic acid, probably owing to the high mixing ratios of isoprene observed at the same site during daytime [Kesselmeier *et al.*, 2002a], which is thought to be the dominant chemical precursor of formic acid [Sanhueza *et al.*, 1996b]. The ambient concentration ranges of the organic acids also exhibited a strong seasonal difference. For comparison only daytime values under well mixed daytime conditions were used, since they are more representative of the boundary layer background mixing ratios than the nighttime values. Higher mixing ratios were found during the dry season compared to the wet season. The average daytime (0900–1700 h) atmospheric mixing ratios for formic acid and acetic acid were 0.38 ± 0.30 ppb ($n =$

92) and 0.36 ± 0.17 ppb ($n = 92$) during the wet season and 4.17 ± 3.68 ppb ($n = 148$) and 3.58 ± 2.95 ppb ($n = 148$) during the dry season, respectively. The daytime values were statistically different ($P = 0.01$) to the nighttime values, except for acetic acid in the wet season. The total observed ranges for formic acid and acetic acid were 0–1.35 and 0–0.83 ppb in the wet season and 0–16.4 and 0–12.2 ppb in the dry season, respectively.

[15] The linear correlation between HCOOH and CH₃COOH presented in Figure 2 indicates that similar atmospheric processes are affecting their mixing ratios. The regression analysis gives a slope corresponding to a formic acid/acetic acid ratio of 0.85 for the wet season and 1.06 for the dry season, respectively. The diel cycle of the concentration ratio is shown in Figure 3. During the wet season only a small variation is visible. Values above 1 demonstrate the predominance of formic acid during late afternoon, while values below 1 before sunrise and after sunset indicate a dominance of acetic acid. In the dry season, subject to biomass burning activity and a 10-fold higher concentration range, a predominance of acetic acid may also be visible after sunset, but in the morning, a predominance of formic acid is apparent, mainly owing to very low acetic acid values (see Figure 1).

3.2. Canopy Concentration Profiles

[16] We examined the vertical distribution of gaseous HCOOH and CH₃COOH and the interspecies relationship vertically through the forest canopy in an attempt to gain

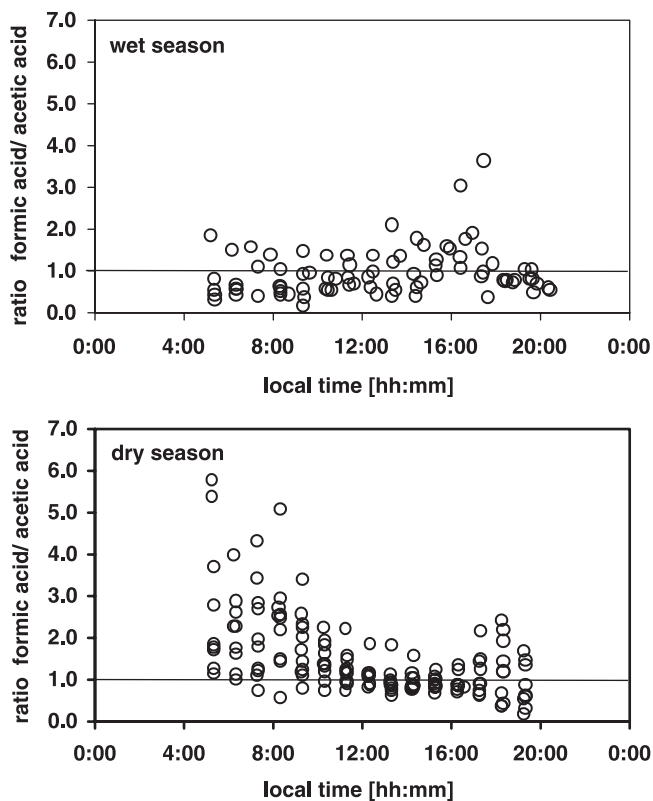


Figure 3. Diel variation of the HCOOH/CH₃COOH ratio in the wet season and the dry season measured at canopy top. Values were skipped if the mixing ratio of either acid was below detection limit.

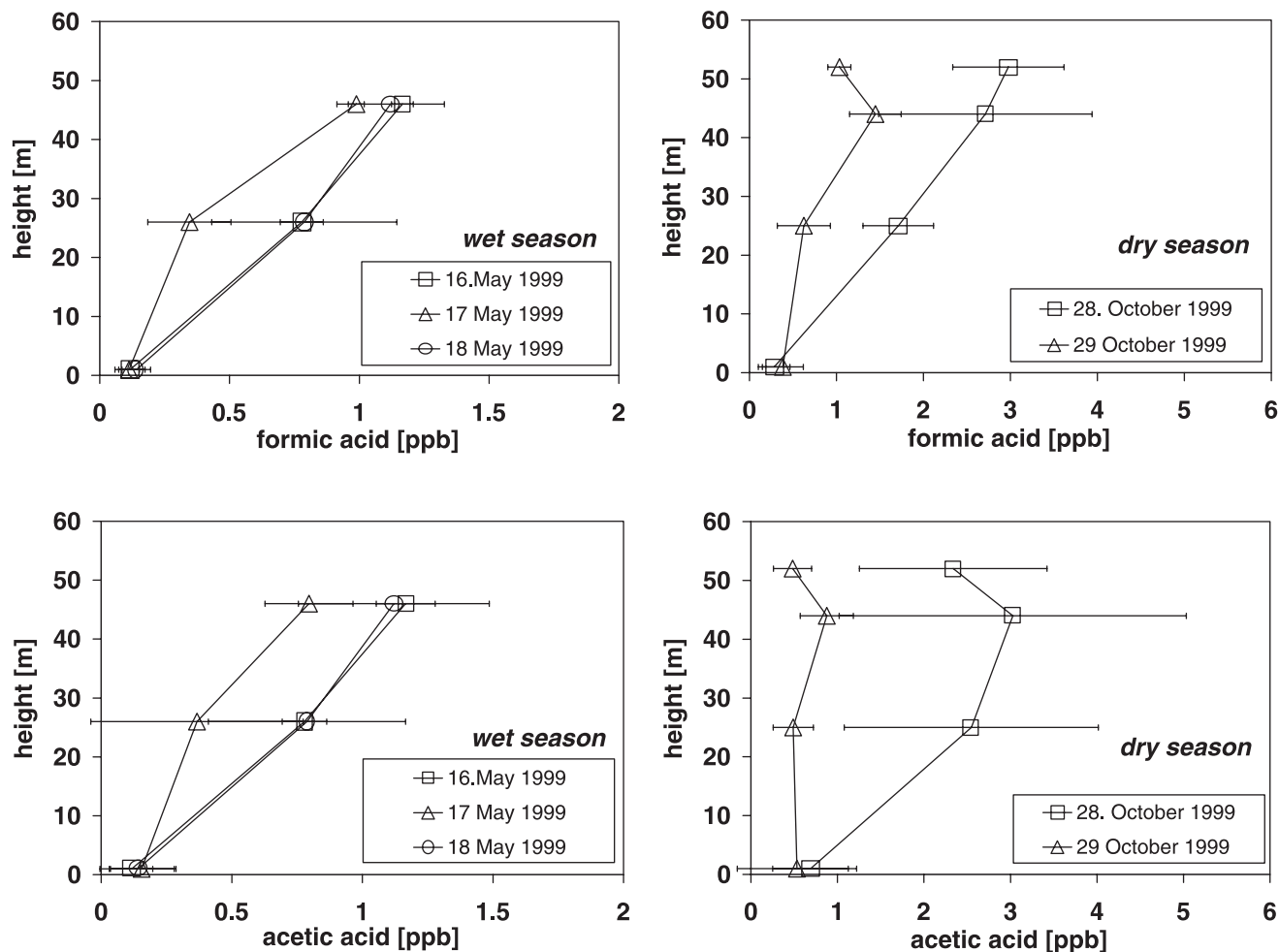


Figure 4. Mean daytime vertical profiles measured in and above the primary forest site in the wet season (left panels) and the dry season (right panels) in Rondônia, Brazil (mean $\pm 1\sigma$; $n = 3-6$). Note: The x-scale for the dry season is enlarged.

insight into the role of the canopy for the exchange of these acids on a larger scale. Mean daytime values for both seasons are shown in Figure 4. The wet season profiles (Figure 4, left panels) indicated gradients with consistently the highest mixing ratios at the uppermost level above the canopy (46 m), intermediate values in the grown region (25 m), and the lowest values near the ground (1 m) throughout the day for both acids. The measured concentrations did not exceed 2 ppb for either acid. This general shape of the wet season profiles was also found but less pronounced during the dry season. The concentrations measured in the dry season normally showed considerably higher values with a large scatter presumably due to frequent biomass burning activity even close to the site. Unfortunately the weather conditions during the 2 day sampling period shown in Figure 4 were not representative for typical dry season conditions. The transition to the wet season had already started, with interfering rainfall events. Heavy cloud cover and local intermittent rain events were observed during the sampling periods with relatively low and highly variable concentrations especially at the two highest levels above the canopy. However, taking an average of these two heights (44 and 51 m), the same profile shape as in the wet season is evident, with higher values above the canopy as compared

to inside the canopy. The general trend of the profiles suggests that the forest canopy is an effective sink due to deposition inside the canopy and/or photochemical production of organic acids in the air layers above the canopy. However, it is not possible to discern between the influence of the atmospheric production and the canopy exchange based on these ambient air measurements alone.

[17] Figure 5 shows the correlations between formic acid and acetic acid at different heights. For a better comparison of the two seasons, the two uppermost heights measured above the canopy (44 and 51 m) in the dry season were merged to one averaged level comparable to the measurement height of 46 m in the wet season. In the dry season (Figure 5, right column) the ratio has highest values above the canopy, showing a relative predominance of acetic acid. The height dependence of the concentration ratio is less pronounced in the wet season. Although the lowest ratio is also found inside the canopy at near ground level (0.15), the ratio in the intermediate canopy height is higher than the ratio above the canopy.

3.3. Branch Enclosure Measurements

[18] The direct exchange of the organic acids between the vegetation and the atmosphere was investigated by using a

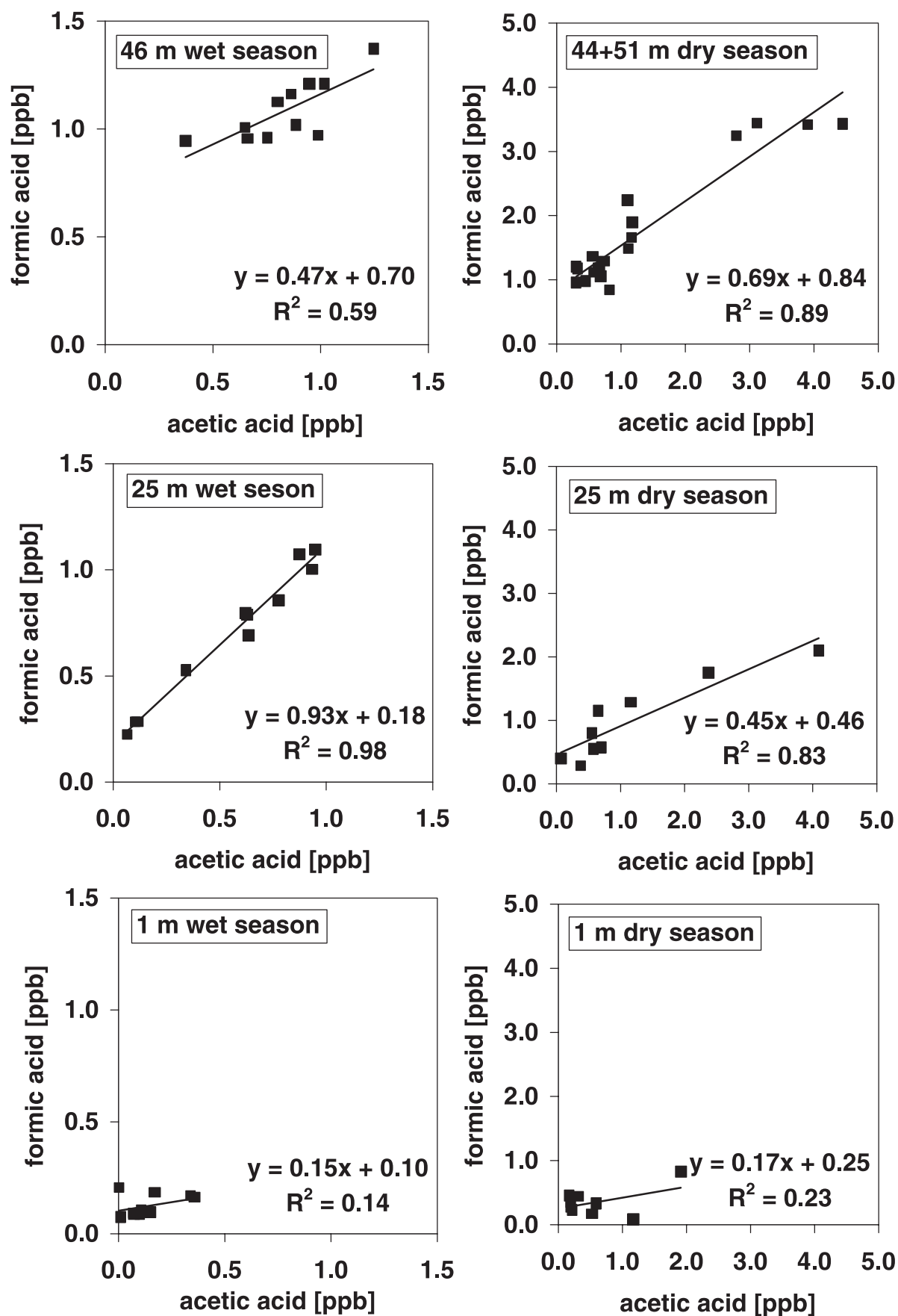


Figure 5. Correlation between HCOOH and CH₃COOH at different heights in and above the primary forest in the wet season (left panels) and the dry season (right panels).

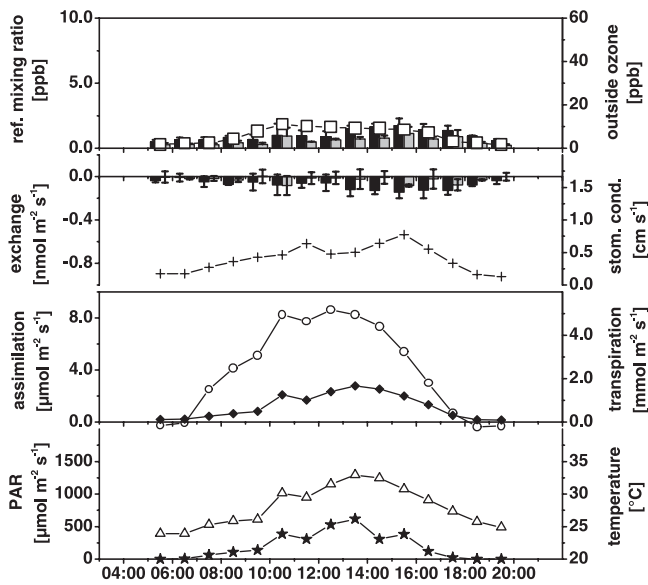


Figure 6. *Apeiba tibourbou* in the wet season, investigated on 03–05 May 1999: formic acid (black columns) and acetic acid (gray columns) exchange rates, reference mixing ratios (ozone: open squares), plus physiological (assimilation: open circles, transpiration: solid diamonds) and climatological (temperature: open triangles, PAR: solid stars) data (3 days, $n = 3-5$; mean $\pm 1\sigma$).

dynamic enclosure system flushed with ambient air. Exchange rates were monitored in both seasons for the species *Hymenaea* and *Apeiba*, while the species *Sorocea* was monitored only in the dry season. The enclosure measurements were carried out over the period of several days each, allowing for an adaptation time of at least 1 day before the respective exchange measurements. The data, averaged for one hour intervals over 2–3 day measuring periods, are shown for the wet and the dry season, respectively, in Figures 6 and 7 for *Apeiba*, in Figures 8 and 9 for *Hymenaea* and in Figure 10 for *Sorocea*. The observed net assimilation and transpiration rates indicated a typical diel pattern of plant physiology as a function of the respective light intensity and temperature. The daytime peak assimilation values of sunlit leaves of *Hymenaea* and *Apeiba* at the canopy top ranged between 6 and 10 $\mu\text{mol m}^{-2} \text{s}^{-1}$ in both seasons. Although light and temperature were considerably enhanced during the dry season compared to the wet season, the range of CO_2 assimilation did not increase significantly if related to the leaf area surface (as compared to Table 1), i.e., surplus radiation in the dry season did not yield an additional CO_2 gain of the plants. Although the stomatal conductance was slightly reduced for *Apeiba* in the dry season, the transpiration rate was higher due to the increase in leaf temperature and the thereby amplified water vapor deficit. That resulted in a weaker water use efficiency for this species. *Hymenaea* reduced the stomatal conductance in the dry season to an extent that similar transpiration rates were preserved, a strategy of plants to maintain the same water use efficiency and avoid water stress. Considerably lower values for photosynthesis, transpiration and stomatal conductance were found for the species *Sorocea* growing in the understory (Figure 10), where it

was not exposed to direct sunlight. For *Sorocea*, although transpiration showed the normal diel pattern regulated by temperature and light, the CO_2 exchange was mainly restricted by the resultant stomatal resistance and thus followed very well the diel pattern of the stomata with peak values in the morning (Figure 10). However, the total daily carbon gain for this species was found to be significantly lower as compared to the other tree species investigated (Table 1).

[19] The organic acid exchange measurements mainly exhibited the uptake of formic acid and acetic acid for all plant species in both seasons investigated (Figures 6, 7, 8, 9, and 10), although diel, seasonal and interspecies variations were observed. For comparison, the plant's organic acid exchange data and the respective mixing ratios in Figures 6, 7, 8, 9, and 10 are plotted on the same scales (except for *Sorocea*, Figure 10). Both the diel and seasonal differences in the prevailing organic acid mixing ratios resulted in a corresponding change of the plant's uptake performance. Increased mixing ratios were directly linked to increased uptake rates. Interestingly the tree species *Sorocea* grown in the understory exhibited the highest uptake rates (the scale in Figure 10 is enlarged as compared to all other figures), even though the stomatal conductance was significantly lower than that of the other trees species. However, these high uptake rates can be rationalized by the extremely high reference mixing ratios, i.e., the mixing ratios supplied to the cuvette system during that specific period.

3.4. Deposition Velocities and Compensation Point Mixing Ratios

[20] A simple empirical model (adopted from Conrad [1994]) is applied to describe the dependence of the

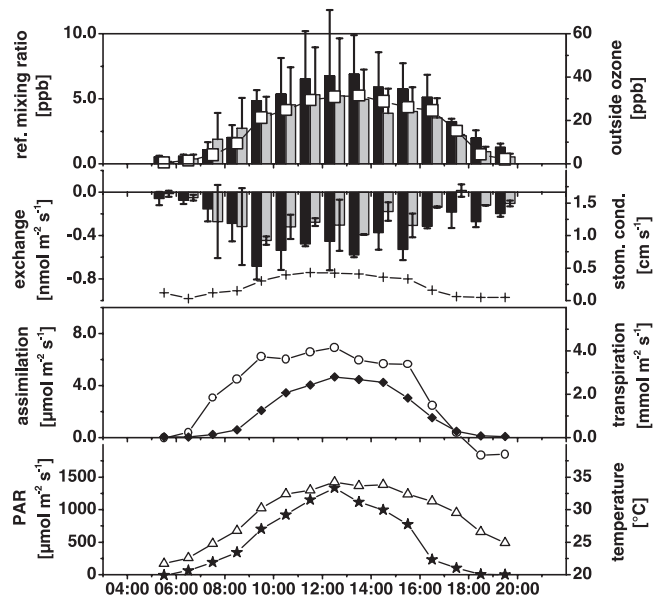


Figure 7. *Apeiba tibourbou* in the dry season, investigated on 18–19 October 1999: formic acid (black columns) and acetic acid (gray columns) exchange rates, reference mixing ratios (ozone: open squares), plus physiological (assimilation: open circles, transpiration: solid diamonds) and climatological (temperature: open triangles, PAR: solid stars) data (2 days, $n = 2-4$, mean $\pm 1\sigma$).

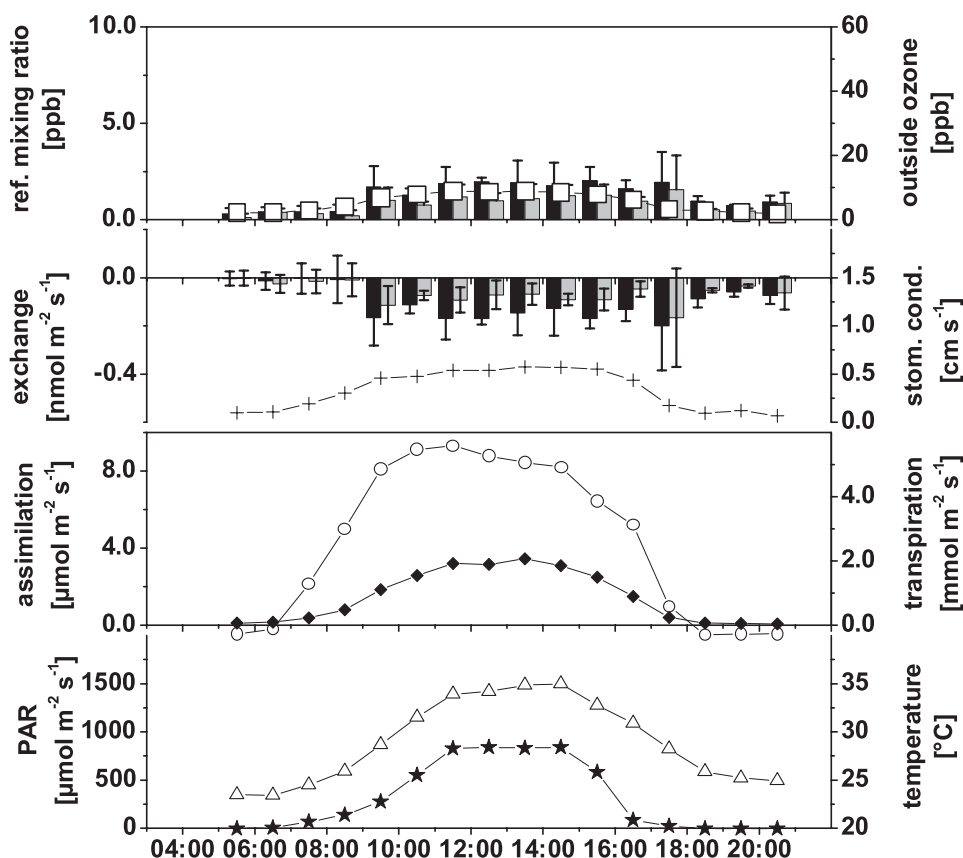


Figure 8. *Hymenaea courbaril* in the wet season, investigated on 08–10 May 1999: formic acid (black columns) and acetic acid (gray columns) exchange rates, reference mixing ratios (ozone: open circles), plus physiological (assimilation: open circles, transpiration: solid diamonds) and climatological (temperature: open triangles, PAR: solid stars) data (3 days, $n = 3-5$, mean $\pm 1\sigma$).

exchange rate of organic acids on the ambient air mixing ratios: the net flux of the plant tissue is interpreted as the result of simultaneously operating production and consumption processes. The consumption rate is assumed to be a function of trace gas mixing ratio, whereas the production rate is not. This implies the existence of a so-called compensation point, i.e., an ambient mixing ratio where the consumption and production balance each other and the net flux is zero. Ambient mixing ratios below the compensation point concentration result in net emission; a mixing ratio above it results in net deposition. The production rate, the deposition velocity, and the compensation point concentration are determined by the linear regression of observed fluxes versus mixing ratio, and are found as the ordinate intercept, the slope and the abscissa intercept of the regression line, respectively. According to *Winner and Greitner* [1989], the concentrations prevailing in the branch cuvette represent the actual relevant atmospheric conditions for the incubated samples. In general we agree with the aforementioned authors. But in spite of a reasonably high flush rate of about 40 L min^{-1} , the mixing ratios of the organic acids inside our branch cuvette were regularly less than one-fifth the mixing ratio in the reference cuvette (i.e., the mixing ratio entering the branch cuvette) due to the plant's uptake activity. Apparently, the uptake rate was then restricted by an insufficient supply of organic acids by the

flush air. We have to assume that the actual uptake rates would have been higher, if near ambient conditions could have been sustained in the branch enclosure by means of a higher enclosure flush rate. The mixing ratios were often decreased close to the potential compensation point mixing ratio (see below). Due to these low and rather stable mixing ratios in the branch cuvette, a correlation between the branch cuvette mixing ratio and the apparent uptake rate was not applicable and did not show a significant correlation. Alternatively, Figure 11 shows the significant correlation between the reference mixing ratios and the acid uptake rates of the two plant species *Apeiba* and *Hymenaea* for both seasons investigated. Following the line of interpretation presented above, the calculated deposition velocity, based on the concentrations of the reference cuvette mixing ratio, which were considerably higher than the mixing ratios inside the branch cuvette, rather represents a lower bound estimate. In order to characterize better the background conditions, only the wet season data were used for the regression analysis (Figure 11, closed symbols). Even though revealing the same tendency, the dependence of the uptake rate on the ambient mixing ratio was not as evident in the dry season (Figure 11, open symbols). Subsequent tests of the applied ozone scrubbers revealed that its efficiency was not 100%. In the dry season, with relatively high ozone mixing ratios of up to 60 ppb, small

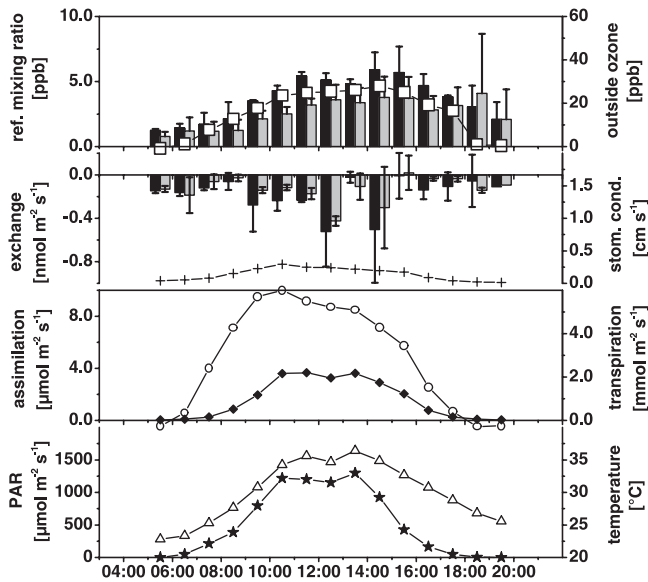


Figure 9. *Hymenaea courbaril* in the dry season, investigated on 22–23 October 1999: formic acid (black columns) and acetic acid (gray columns) exchange rates, reference mixing ratios (ozone: open squares), plus physiological (assimilation: open circles, transpiration: solid diamonds) and climatological (temperature: open triangles, PAR: solid stars) data (2 days, $n = 2-4$, mean $\pm 1\sigma$).

amounts of ozone may have entered the cuvettes. Secondary production of organic acids from chemical conversion (ozonolysis) of primarily emitted precursor compounds inside the cuvette might then have masked the (net-)deposition of organic acids [Neeb *et al.*, 1997a]. As a consequence the (net-)exchange values scattered with the tendency toward lower uptake rates. However, the dry season data show the same tendency as in the wet season, when ambient ozone mixing ratios were below 20 ppb and ozone was depleted totally inside the cuvette by the ozone scrubber. The calculated deposition velocities (related to a single sided leaf area surface), the compensation point concentrations, and the production rates under purified air conditions for the two tree species investigated in the wet season, *Apeiba* and *Hymenaea*, are listed in Table 2.

4. Discussion

4.1. Branch Level Exchange

[21] All direct exchange measurements on the branch level were accompanied by an assessment of the respective physiological and micrometeorological parameters. Our daytime CO_2 assimilation values of sunlit leaves of *Hymenaea* and *Apeiba*, between 6 and $10 \mu\text{mol m}^{-2} \text{s}^{-1}$ in both seasons, agree well with means like $6.5 \mu\text{mol m}^{-2} \text{s}^{-1}$ found in Costa Rica [Stephens and Waggoner, 1970], $9.4 \mu\text{mol m}^{-2} \text{s}^{-1}$ in Australia [Percy, 1987], $12 \mu\text{mol m}^{-2} \text{s}^{-1}$ in Brazil [McWilliams *et al.*, 1996] and ranges of $8-14 \mu\text{mol m}^{-2} \text{s}^{-1}$ found in Cameroon [Koch *et al.*, 1994] and $12.6-18.9 \mu\text{mol m}^{-2} \text{s}^{-1}$ in Malaysia [Koyama, 1981] for various other tropical tree species. CO_2 assimilation rates seem to correspond more to the respective environment

rather than to the particular tree species. Species that occupy a particular ecological niche might behave in a similar fashion, like a functional group [Körner, 1993]. The observed seasonal variations in the assimilation and transpiration of *Hymenaea* and *Apeiba* were only moderate, which is in close accordance with the studies of McWilliams *et al.* [1996] and Roberts *et al.* [1990] who reported that the gas exchange is not affected by the seasonal changes in rainfall and soil moisture content in Amazonia. However, the latter authors report strong vertical gradients, which supports the considerably lower values for photosynthesis, transpiration and stomatal conductance found for the species *Sorocea* growing in the understory (Figure 10), where it was not exposed to direct sunlight. Light intensities at the ground level of many rain forests can be less than 1% of that reaching the top of the canopy. As shade leaves are in general morphophysiologicaly adapted to these conditions, they have a low light compensation point.

[22] The organic acid exchange measurements mainly exhibited uptake of formic acid and acetic acid for all plant species in all seasons investigated, although we observed diel, seasonal and interspecies variations. The primary triggering function of the uptake of organic acids by the plants was the respective reference mixing ratios supplied to the plant; even though other physicochemical and physiological parameters, most prominently stomatal conductance, may have contributed to the overall pattern. It is therefore meaningful to discuss the quantitative uptake by the tree leaves in terms of deposition velocity (or resistance). Up to

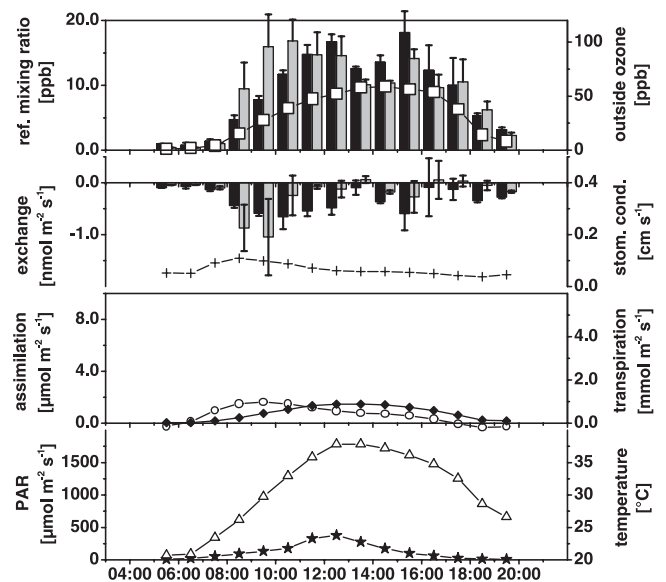


Figure 10. *Sorocea guilleminiana* in the dry season, investigated on 10–11 October 1999: formic acid (black columns) and acetic acid (gray columns) exchange rates, reference mixing ratios (ozone: open squares), plus physiological (assimilation: open circles, transpiration: solid diamonds) and climatological (temperature: open triangles, PAR: solid stars) data (3 days, mean $\pm 1\sigma$). Note: The scales for mixing ratios of the organic acids and ozone and the acid exchange rates are enlarged by a factor of 2, whereas the scale of the stomatal conductance is divided by a factor of 4 compared to Figures 6 and 9.

Table 1. Daily Carbon Balance of the Three Tree Species Investigated in Both Seasons Including the Recycling of Organic Carbon by Organic Acid Deposition^a

| Tree species, date (season) | Carbon gain by CO ₂ exchange, μg C g ⁻¹ dw | Carbon gain by acid deposition, μg C g ⁻¹ dw | Fraction, % C _{acid} /C _{CO2} |
|--------------------------------|------------------------------------------------------------------------|---------------------------------------------------------------|----------------------------------------------------|
| <i>Apeiba tibourbou</i> | | | |
| 03 May 1999 (wet season) | 30,898 | 1.5 | 0.005 |
| 04 May 1999 (wet season) | 26,877 | 0.9 | 0.003 |
| 05 May 1999 (wet season) | 29,052 | 0.5 | 0.002 |
| 18 October 1999 (dry season) | 22,144 | 5.0 | 0.022 |
| 19 October 1999 (dry season) | 25,552 | 5.1 | 0.020 |
| <i>Hymenaea courbaril</i> | | | |
| 08 May 1999 (wet season) | 22,267 | 2.10 | 0.010 |
| 09 May 1999 (wet season) | 24,919 | 0.97 | 0.004 |
| 10 May 1999 (wet season) | 25,845 | 0.88 | 0.003 |
| 22 October 1999 (dry season) | 38,291 | 3.43 | 0.009 |
| 23 October 1999 (dry season) | 35,648 | 3.23 | 0.009 |
| <i>Sorocea guilleminiana</i> | | | |
| 10 October 1999 (dry season) | 3233 | 5.34 | 0.165 |
| 11 October 1999 (dry season) | 3490 | 4.67 | 0.134 |

^aData are given per day (0000–2400 h) in μg carbon and are related on leaf dry weight (μg C g⁻¹ dw).

the present, few efforts had been made to determine the deposition velocities of organic acids and direct measurements are very scarce. Several authors have assumed a deposition velocity of 1 cm s⁻¹, related to canopy surface [Talbot *et al.*, 1988; Jacob and Wofsy, 1988; Grosjean, 1989; Pierson and Brachaczek, 1990]. Wesely [1989] estimated the same value in a Regional Acid Deposition Model (RADM). Helas *et al.* [1992] calculated a deposition velocity of 1.3 cm s⁻¹ for both acids by applying a box model in and above the rain forest of the northern Congo. Estimated dry deposition velocities by Hartmann *et al.* [1991] ranged between 0.5 and 1.0 cm s⁻¹. Sanhueza *et al.* [1996a] calculated a deposition velocity of 0.7–0.8 cm s⁻¹ for the dry season and 0.8–1.0 cm s⁻¹ for the wet season for both acids in Venezuela. Multiplying our calculated deposition velocities on a leaf area level of 0.17–0.23 cm s⁻¹ for the wet season (Table 2) with the actual leaf area index of the presently investigated primary forest site of about 5.5 [Andreae *et al.*, 2002], our lower bound estimate (see chapter 3.4) fits perfectly well into this scenario.

4.2. Potential Uptake Mechanisms and Metabolism of Organic Acids

[23] With our measurement methodology we are not able to discern between leaf (cuticle) surface dry deposition and direct uptake by the leaf's stomata. For a quantitative description of the uptake behavior the concepts of resistance analogy can be applied. The total resistance against trace gas deposition (r_{tot} , the inverse of deposition velocity) is usually broken down into a network of particular resistances (r_a , r_b , and r_c), representing turbulent, quasilaminar, and (leaf-) surface related processes of the deposition pathway [see, e.g., Monteith, 1975; Galbally and Roy, 1980; Hicks *et al.*, 1987]. Our well mixed cuvette systems simulate highly turbulent conditions. Thus, the aerodynamic resistance (r_a) and the diffusion through the quasilaminar sublayer close to the surface (r_b) are negligible and deposition is limited by the residual resistance (r_c) [Ludwig, 1994; Gut *et al.*, 2002a]. The latter can be assigned to processes at the surface and inside the plants, e.g., stomatal and mesophyll molecular

diffusion or the transition from the gas phase to the liquid and solid phase [see Hicks *et al.*, 1987]. The calculated stomatal resistance of *Apeiba* and *Hymenaea* for water vapor (i.e., the inverse of the stomatal conductance in Figures 6, 7, 8, and 9) was as low as 2 s cm⁻¹. Taking into account the different diffusion coefficients for formic acid (0.15 cm² s⁻¹) and acetic acid (0.13 cm² s⁻¹), as compared to water vapor (0.26 cm² s⁻¹), results in analog stomatal resistances of about 3.5 s cm⁻¹ for formic acid and 4 s cm⁻¹ for acetic acid. Comparison with our observed mean uptake resistance of about 4.5 s cm⁻¹ (i.e., the inverse of the deposition velocity in Table 2) for both acids reveals that foliar uptake of the acids could have been predominantly through the stomata. Nevertheless cuticular surface deposition may additionally contribute, especially if taking into account that the calculated deposition velocities should be regarded as a lower limit approximation (see chapter 3.4). Even though the leaf cuticle is supposed to be an excellent barrier for lipophobic compounds like the organic acids, the surface properties of the cuticles are subject to environmental influences such as cloud shading, high humidity, dew, fog or guttation (excretion of liquids by leaves) and the dry deposition of the organic acids might be strongly enhanced especially over wet surfaces as reported for other water-soluble species like sulfur dioxide and ammonia [Erismann *et al.*, 1994; Duyzer *et al.*, 1994]. However, both formic acid and acetic acid are also present inside leaves [Nicholas, 1973] and have been found in a plant's internal apoplastic solution, where the plant's liquid phase is directly linked to the gas phase of the substomatal caves [Gabriel and Kesselmeier, 1999; Gabriel *et al.*, 1999]. The latter authors calculated the potential stomatal exchange behavior of the leaf surface according to Henry's law. As the short-chain monocarboxylic acids form ions (dissociate) upon dissolution in water, they must be protonated before release and the gas liquid equilibrium is expressed in terms of K_H^* , the pseudo Henry's law constant, which takes dissociation and pH into account. The exchange rate of dissolved acids between leaf cells and the apoplast and the subsequent volatilization to the air is thus strongly influenced by the

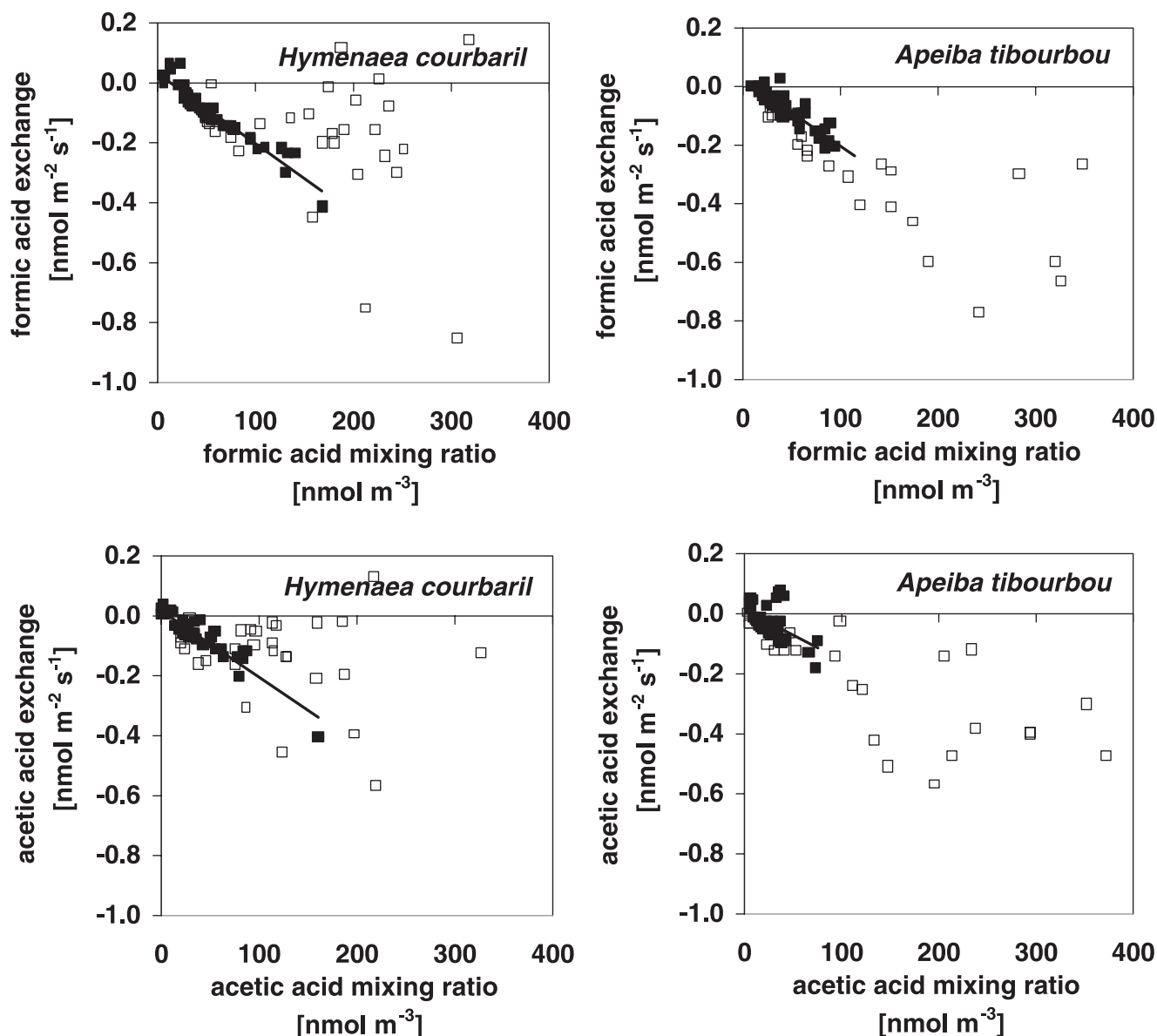


Figure 11. Correlation between the organic acid uptake by different tree species and the respective reference mixing ratios. For regression analysis only the wet season data were used (solid symbols) because of potential technical problems during the dry season (see text). The conversion factor from nmol m⁻³ to ppb is 0.0225 (i.e., 400 nmol m⁻³ ~ 9 ppb).

pH and the ion product of the sum of diverse other ions and polar groups present in the apoplastic solution. According to estimates of Gabriel and Kesselmeier [1999], an emission is less plausible for formic acid than for acetic acid and a relatively low pH in the apoplastic solution has to be

assumed. Laboratory measurements of Gabriel [1999] showed an increase of the apoplastic concentrations after fumigation with 15 ppb acetic acid for 3 hours, but fumigation with formic acid as low as 1 ppb (thus close to the compensation point mixing ratio) did not significantly alter

Table 2. Deposition Velocity, Compensation Point Concentration, and Production Rate, Determined by Linear Regression of Observed Fluxes Versus the Reference Mixing Ratio for the Wet Season^a

| Plant species | Acid compound | Deposition velocity, m s ⁻¹ | Compensation point, nmol m ⁻³ /ppb | Production rate, nmol m ⁻² s ⁻¹ | R ² |
|---------------------------|---------------|----------------------------------------|-----------------------------------------------|-------------------------------------------------------|----------------|
| <i>Apeiba tibourbou</i> | formic acid | 0.0023 | 10.9/0.24 | 0.025 | 0.79 |
| | acetic acid | 0.0017 | 7.6/0.17 | 0.031 | 0.27 |
| <i>Hymenaea courbaril</i> | formic acid | 0.0023 | 13.5/0.30 | 0.031 | 0.92 |
| | acetic acid | 0.0022 | 7.3/0.16 | 0.016 | 0.85 |

^a Values represent the slope, the abscissa intercept, and the ordinate intercept of the regression lines in Figure 11.

the concentration in the apoplast. These results indicate the internal uptake of acids from the atmosphere via the plant's apoplast, whenever mixing ratios higher than the compensation point are prevailing. After uptake, the organic acids may be transferred from the apoplast into the symplast (internal cell volume) and participate in the plant's metabolism. Metabolism of the absorbed acids maintains the concentration gradient between the atmosphere and the plant's interior and acts as the driving force that allows their continuous stomatal uptake. The metabolic fate of the deposited acids inside the leaves may be complex and is not the subject of our investigations here. However, organic acids are ubiquitously prevalent inside plants and are produced and consumed by many metabolic pathways. Acetic acid plays a central role in anabolic as well as catabolic processes [see *Bode et al.*, 1997 and references therein]. It may be activated with coenzyme A, i.e., converted to acetyl-CoA by acetyl-CoA synthetase and in this way enter general metabolism pathways such as the TCA cycle or synthesis of fatty acids, carotenoids and, as a prominent example, terpenes [*Kesselmeier and Staudt*, 1999]. Formic acid on the other hand may be produced during photorespiration at high light intensities. After activation with the coenzyme tetrahydrofolic acid, it is involved in plant metabolism including the transfer of methyl and hydroxymethyl groups necessary for the synthesis of ethene, purines, pyrimidines, alkaloids and amino acids. To a certain extent plants may thus benefit by the uptake of organic acids as metabolic substrates, as long as the acid concentration does not exceed levels that lead to damage of the epicuticular wax layer or cause stomata to remain open, through which trees become more vulnerable to drought, as it was suggested for high NH_3^+ loading [*Erismann et al.*, 1997].

[24] Considering the metabolism of the plants, the uptake of atmospheric organic carbon in the form of acid deposition has to be taken into consideration when discussing VOC emission by vegetation in the global carbon budget. The emission of isoprene and monoterpenes represent a nontrivial organic carbon loss for the plant, normally in the range of 0.5–3% of the carbon gained by CO_2 exchange [e.g., *Kesselmeier et al.*, 1998, 2002b; *Harley et al.*, 1999]. On the other hand, the uptake of organic acids by the leaves may in part compensate for that, as shown in Table 1. Even though the seasonal variation of assimilation rates is higher when related on the leaf dry weight (as compared to Figures 6, and 10), the considerably higher uptake rates of organic acids force the fraction of recycled organic carbon to higher values in the dry season. For the species *Sorocea*, investigated only in the dry season and showing high organic acid uptake rates but comparably very low assimilation rates, the acid fraction of the carbon gain is as high as 0.16%. Compared to the organic carbon released by VOC emission these values are substantial. However, for the other tree species the fraction is only up to 0.02%.

4.3. Direct Biogenic Emission Versus Uptake

[25] In spite of our findings presented above, we do not exclude emission of organic acids under natural conditions. Especially during the wet season, when normal ambient air mixing ratios were very low, our applied pump system artificially increased the mixing ratios in the air

supply significantly as compared to the ambient conditions, thus increasing the deposition rates. Even though the calculated compensation point mixing ratio is as low as 0.24 and 0.3 ppb for formic acid for both tree species and 0.17 and 0.16 ppb for acetic acid (Table 2), emission may have occurred in periods when the ambient mixing ratio was below that limit. This may as well explain the comparatively high ratio of formic acid to acetic acid found in the crown region of the primary forest (25 m height) during the wet season compared to the dry season (Figure 5). As the compensation point for formic acid is higher than that of acetic acid, and the mixing ratios of formic acid were frequently close to this level in the wet season, a significantly lower uptake rate or even an emission may be assumed under these conditions, leading to the observed increase in the respective ratio. However, the general tendency of the vertical profiles showing consistent increase of mixing ratios with height (Figure 4), suggests that the formation of organic acids by photochemical conversion of precursor compounds in the air layers above the canopy is the principal source of carboxylic acids, and clearly exceeds a potential direct emission by the plants at that site. Similar profiles for formic acid and acetic acid were found by *Andreae et al.* [1988] during the wet season and by *Talbot et al.* [1990] during the dry season in central Amazon. *Helas et al.* [1992] also found higher mixing ratios in the boundary layer above the canopy than in both the canopy and in free troposphere, respectively, at a remote site in the Congo.

[26] At our primary forest site in Brazil the mixing ratios near the ground were consistently very low for both acids, indicative of the existence of an additional strong sink near ground. This is in good agreement with the work of *Sanhueza and Andreae* [1991], who found through soil enclosure measurements that the forest soil in Venezuela acted as a sink for both acids. However, in other environments of the world the biogenic compartments may react differently to different conditions prevailing. *Sanhueza and Andreae* [1991] could also demonstrate that dry savanna soils acted as a significant source for both acids instead of a sink. Similarly, the exchange of organic acids between vegetation and the atmosphere may be a function of the ecosystem it grows in. An enhanced production of organic acids inside the plant tissue due to physicochemical stress effects might apparently superimpose deposition in certain circumstances as observed for other VOCs. As a prominent example for such a physiological response, the synthesis (and emission) of ethene, a plant hormone, is also enhanced under environmental stresses like arid conditions and/or extreme temperatures or following high pollution episodes and other stress treatments [*Bucher*, 1981; *Kimmerer and Kozlowski*, 1982; *Yang and Hoffmann*, 1984; *Heiden et al.*, 1999]. Concurrent release of formic acid might take place, because formic acid is produced as a by-product of the synthesis of ethene. Furthermore, *Heiden et al.* [1999] also report an enhanced emission of various hydrocarbons after exposure to high ozone mixing ratios, as another stress inductor. This behavior may also help to explain observed emission of organic acids in the Mediterranean area by *Kesselmeier et al.* [1997a, 1997b, 2001], *Gabriel et al.* [1999], and *Staudt et al.* [2000], where water stress, high temperatures, and pollution episodes

habitually occurred during measurement periods. To our knowledge the only group who have performed direct organic acid exchange measurements on tropical tree species to date were *Talbot et al.* [1990]. They applied a static chamber to investigate the acid exchange behavior during field investigations in the Amazon and reported significant emissions of organic acids. However, the application of a static enclosure (or even a dynamic enclosure with a too low flush rate) for measurements on photosynthetically active tissues can result in a severe CO₂ deficit in the enclosure, which causes a wide opening of the stomata and leads to nonphysiological behavior, that is not representative of normal conditions (“induced stress”). In other experiments carried out in the laboratory utilizing dynamic enclosures flushed with artificially purified or low-concentrated oxidant-free air, light-triggered emission of both acids were observed [*Kesselmeier et al.*, 1998; *Staudt et al.*, 2000]. Since this procedure generates an artificial gas concentration gradient between the enclosure air and the leaves, it enhances the diffusion of the organic acids from the plant into the enclosure and may lead to an overestimation of the natural emission strength. Furthermore, this procedure masks the potential of plants to act as a sink for organic acids and can thus not directly be transferred to natural conditions. The emission of organic acids under purified air, however, fits well with our finding of a compensation point concentration and the extrapolated production rates presented in Table 2.

4.4. Diel and Seasonal Variation of Ambient Mixing Ratios

[27] As the exchange of organic acids was found to be primarily a function of the ambient air mixing ratios, these must always be taken into account when discussing the role of vegetation in the budget of these compounds. Ambient mixing ratios have an important impact on the strength of deposition and thus determine the direction of the biogenic exchange. Formic acid and acetic acid are subject to distinct diel variations in all areas of the world. Especially in remote regions gas phase concentrations are lowest just before sunrise, increase steadily until the afternoon, and begin to decline in the late afternoon (for a review, see *Khare et al.* [1999]). This is in agreement with the results of this study. The observed diel course of formic acid and acetic acid mixing ratios (Figure 1) suggests a daytime source followed by removal from the atmosphere during the evening and nighttime. As discussed above, the dominant processes involved are assumed to be the chemical formation from precursor hydrocarbons during daytime and the deposition to the forest canopy. Provided a sink in the forest canopy, the nighttime minimum can be attributed to boundary layer dynamics. The observed depletion of the organic acids in the night is favored by the development of a nocturnal boundary layer (NBL) with stable meteorological conditions and the cessation of convective circulation. Together with frequently low wind speed, this leads to a limited NBL height, i.e., the layer that is interacting with the surface through turbulent mixing. Uptake of organic acids on plant and soil surfaces then governs the atmospheric burden in the decoupled NBL leading to the observed depletion. The rate constants of the chemical reaction with OH radicals are 3.2 and $6.0 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for HCOOH and

CH₃COOH, respectively [*Zetzsch and Stuhl*, 1982]. Assuming an average tropical OH concentration of 2×10^6 molecules cm⁻³, the chemical lifetimes of HCOOH and CH₃COOH are 18 and 10 days, respectively [*Sanhueza et al.*, 1996a]. Correspondingly, reentrainment of old boundary layer air can provide an additional source of the oxygenated species to the newly growing mixed layer in the morning hours. Substantial variations in OH radical and O₃ concentrations during the day can additionally result in a substantial variation in product (acid-) yields [*Altshuler*, 1991].

[28] Besides the pronounced diel cycle, strong seasonal differences in ambient organic acid mixing ratios were found. This strong seasonality had important impact on the deposition rates. Mixing ratios one order of magnitude higher in the dry season as compared to the wet season (Figure 1) were accompanied by an increase of the uptake rates in the same range (Figures 6 and 9). Similar differences in formic acid and acetic acid concentrations as reported in here were seen previously in the central Amazon by *Talbot et al.* [1990] who found average concentrations in the wet season of 0.51 ± 0.15 ppb and 0.41 ± 0.12 ppb for formic acid and acetic acid, respectively, while *Andreae et al.* [1988] report averages of 2.1 ± 0.8 ppb and 3.0 ± 0.8 ppb in the dry season. Less pronounced but similar trends were observed by *Talbot et al.* [1988] near the ground at a midlatitude temperate site in Virginia (0.69 ± 0.40 and 0.70 ± 0.37 ppb in the nongrowing season and 1.89 ± 1.23 and 1.31 ± 0.91 ppb in the growing season, respectively) and by *Sanhueza et al.* [1996a] in the Venezuela Savannah (0.79 and 0.54 ppb in the wet season and 1.6 and 1.4 ppb in the dry season, respectively). The various sources of organic acids may have different relative contributions during the dry and the wet season. In the dry season, especially in the tropics, the contribution of biomass burning activities are high and may be the main source. The direct emission of formic acid and acetic acid during the combustion of biomass has been reported by *Talbot et al.* [1988]. The high mixing ratios observed in the present study during the dry season (the scale of the dry season in Figure 1 is enlarged by a factor of 10) were maintained until dusk and decreased only slowly during the night. Because much higher ozone concentrations were observed during the dry season, this moderate decrease may in part be attributed to increased ozonolysis of reactive hydrocarbons that are also emitted in high amounts by biomass burning. Furthermore, in the dry season the deposition on wet surfaces is reduced due to less humid conditions. In general the mixing ratio of HCOOH correlates with ozone (Figure 1), isoprene, and formaldehyde [*Kesselmeier et al.*, 2002a], which is indicative of a significant chemical production by these precursor compounds [*Sanhueza et al.*, 1996a]. During the wet season, when biomass burning activity is low, indirect emission by the vegetation (i.e., conversion of biogenic hydrocarbons) is rather assumed to be the dominant daytime source. Due to their high water solubility, the lower troposphere is then continually depleted of organic acids by wet deposition, i.e., rainout.

4.5. Concentration Ratios

[29] In general the ratio between formic acid and acetic acid concentration can give further insight into the source/sink behavior of these species in the gas phase. Assuming

uptake of organic acids by the canopy, the progressive decrease of the ratio $\text{HCOOH}/\text{CH}_3\text{COOH}$ going from above the canopy to inside the canopy (Figure 5) can be rationalized with a proportionally stronger uptake affinity of the plant and/or soil surface toward HCOOH . The indication that formic acid is lost from the gas phase at a greater rate than acetic acid during daytime may also be indicated by the diel course of the formic acid to acetic acid ratio collected only above the secondary forest (Figure 3). Especially in the dry season, the ratio becomes lower during daytime, indicating a stronger depletion of formic acid close at the canopy top. However, in the mixed layer, the ratio is assumed to be more reflective of the relative production rates. A diel cycle of the respective ratio, with values above 1 during daytime and below 1 during night was also observed by *Talbot et al.* [1988] at a midlatitude temperate site during the growing season in Virginia and by *Hartmann et al.* [1991] in Venezuela. Furthermore, *Talbot et al.* [1988] found high concentrations of both acids in dew. The dissolution of the organic acids into the dew on the leaf surface during nighttime and the volatilization and concurrent release of the acids as the dew evaporates may contribute to the early morning peak in the ratio, assuming that this phenomenon is more important for formic acid ($\text{pK}^* = 3.77$) with a higher solubility than acetic acid ($\text{pK}^* = 4.76$) [*Hartmann et al.*, 1991]. The different pH dependent scavenging efficiencies for formic acid and acetic acid [*Andreae et al.*, 1988] may account for this difference. The increased predominance of acetic acid during daytime, on the other hand, is indicative of local anthropogenic biomass burning activity during the day, especially in the dry season. Biomass burning produces 2–10 times more acetic acid than formic acid [*Talbot et al.*, 1988; *Hartmann*, 1990] and the contribution of biomass burning products may have been steadily increased during the day. In general our observed formic acid/acetic acid ratios at the canopy top (Figure 3) are different from the value of *Andreae et al.* [1988] who found a ratio of 0.59 ± 0.06 at a site 25 km from Manaus, Brazil, in the dry season. These measurements, carried out at ground level in a forest clearing, may rather have reflected mixing ratios of in-canopy air, comparable to our measurements inside the primary forest (Figure 5).

5. Conclusion

[30] As part of the LBA-EUSTACH, the exchange of the short-chain volatile organic acids, formic acid and acetic acid, was investigated in the wet and the dry season 1999 in Rondônia, Brazil. The trend of the vertical concentration profiles in and above the canopy are indicative of an effective sink by uptake of the plant canopy and/or dry deposition to the ground. The strong uptake behavior of different plant species was explicitly demonstrated by direct exchange measurements. In general all tree species investigated by enclosure measurements in both seasons were found to act as a sink for organic acids, confirming the general trend of the vertical profiles. Uptake of formic acid seems to be rather favored above acetic acid as indicated by the formic acid/acetic acid ratios inside and above the canopy and by the deposition velocities calculated through the branch enclosure meas-

urements. The interspecies variation of the exchange of organic acids seems to be small, comparing the normalized fluxes (deposition velocities) found for *Hymenaea* and *Apeiba* in the wet season. Possibly the acid deposition rate may not be specific to any particular species but rather be a result of the environmental position it is in, as it was proposed for the CO_2 assimilation as well. Plant species that occupy a particular niche might behave in a similar fashion, like a functional group [*Körner*, 1993]. Even though other parameters like leaf temperature, light intensity and, most prominently, stomatal conductance also showed parallel diel and seasonal variations, the primary controlling function of the uptake of organic acids was found to be the atmospheric mixing ratios of organic acids supplied to the plants. However, the presence of organic acids in the plants apoplastic solution [*Gabriel and Kesselmeier*, 1999] and finding of a compensation point concentration points to the existence of a bidirectional flux of organic acids between vegetation and the atmosphere. When ambient air mixing ratios are higher than the compensation point, absorption of acids occurs, whereas emission occurs when ambient air mixing ratios are lower than the compensation point. Very low compensation point concentrations of 0.16–0.30 ppb for both acids found in our studies let assume that emission only will occur in clean air conditions of remote regions of the world, where mixing ratios are at least two orders of magnitude lower than in highly polluted areas [*Khare et al.*, 1999; *Chebbi and Carlier*, 1996]. However, environmental stress conditions (e.g., high temperature, frost, drought, flooding, high pollution episodes, ozone fumigation, wounding, etc.) may additionally trigger production and result in emission of these compounds. These dependencies have to be studied in more detail.

[31] Due to their very limited chemical transformation, the short-chain organic acids may be regarded as terminal products of the photooxidation of reactive volatile organic compounds in the planetary boundary layer. Calculations based on field measurements of ambient mixing ratios done by *Sanhueza et al.* [1996a] indicate that atmospheric organic acid loss by depositional processes is greater than by chemical loss mechanism. Organic carbon emitted by vegetation in form of isoprene or monoterpenes may this way be atmospherically recycled into vegetation by the uptake of organic acids. The plant's recovery of organic carbon by uptake of organic acids was found to not be substantial but was a significant fraction (Table 1). According to our results, indirect emission, i.e., release of precursor compounds like isoprene, and the subsequent atmospheric chemical conversion into organic acids represents the dominant input to the atmospheric burden for these oxygenated compounds, at least during the wet season. In the dry season biomass burning may dominate as both a primary and as a secondary source. This is in good agreement with results by *Skov et al.* [1997] and *Granby et al.* [1997], who found a good correlation of HCOOH and CH_3COOH with O_x (sum of O_3 and NO_2) in semirural as well as urban areas, stating that both acids are rather of photochemical origin than emitted directly. The implied changes in the relative composition of the atmospheric reactants (VOC, O_3 , OH, H_2O) may as well help to explain the observed diel and seasonal variation in the formic acid/acetic acid ratio. However,

according to an atmospheric model by *Jacob and Wofsy* [1988] and the derived one-dimensional model applied by *Talbot et al.* [1990] the chemical reactions considered were too slow to account for the observed high mixing ratios of organic acids in this area. Model calculations of *Madronich et al.* [1990] support photochemical production as the major contributor to the atmospheric mixing ratios observed in the Amazon, at least for acetic acid. But in general a satisfactory source attribution to explain atmospheric observations is lacking. Long-range transport of carboxylic acids, may also contribute considerably to the atmospheric burden. The atmosphere over the Amazon forest is particularly conducive to organic peroxy radical and peroxyacetyl radical reactions [*Talbot et al.*, 1990; *Madronich et al.*, 1990], for which reaction kinetics are still poorly known. High OH radical concentrations are expected for the tropical region [*Crutzen*, 1982], which react with high concentrations of isoprene [*Kesselmeier et al.*, 2002b] to produce peroxy radicals. Low NO concentrations [*Gut et al.*, 2002b] hinder the consumption of peroxy radicals by NO. There is an urgent need to improve the regional model approaches to further our understanding of the atmospheric chemistry in and above the forest canopy of the Amazon basin. The ongoing deforestation will considerably influence the atmospheric burden of carboxylic acids in the Amazon, not to mention all other VOCs. The loss of vegetation will lead to the loss of a very effective natural sink of organic acids, i.e., the leaf surface, capable of biologically filtering and consuming organic acids. However, the direct biogenic emission of precursor hydrocarbons would be reduced in contrast. Improved compilations on source and sink strength of VOCs might answer which effect will prevail.

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