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The effect of flooding on the exchange of the volatile C_2-compounds ethanol, acetaldehyde and acetic acid between leaves of Amazonian floodplain tree species and the atmosphere

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Abstract. The effect of root inundation on the leaf emissions of ethanol, acetaldehyde and acetic acid in relation to assimilation and transpiration was investigated with 2–3 years old tree seedlings of four Amazonian floodplain species by applying dynamic cuvette systems under greenhouse conditions. Emissions were monitored over a period of several days of inundation using a combination of Proton Transfer Reaction Mass Spectrometry (PTR-MS) and conventional techniques (HPLC, ion chromatography). Under non-flooded conditions, none of the species exhibited measurable emissions of any of the compounds, but rather low deposition of acetaldehyde and acetic acid was observed instead. Tree species specific variations in deposition velocities were largely due to variations in stomatal conductance. Flooding of the roots resulted in leaf emissions of ethanol and acetaldehyde by all species, while emissions of acetic acid were only observed from the species exhibiting the highest ethanol and acetaldehyde emission rates. All three compounds showed a similar diurnal emission profile, each displaying an emission burst in the morning, followed by a decline in the evening. This concurrent behavior supports the conclusion, that all three compounds emitted by the leaves are derived from ethanol produced in the roots by alcoholic fermentation, transported to the leaves with the transpiration stream and finally partly converted to acetaldehyde and acetic acid by enzymatic processes. Co-emissions and peaking in the early morning suggest that root ethanol, after transportation with the transpiration stream to the leaves and enzymatic oxidation to acetaldehyde and acetate, is the metabolic precursor for all compounds emitted, though we can not totally exclude other production pathways. Emission rates substantially varied among tree species, with maxima differing by up to two orders of magnitude (25–1700 nmol m^{-2} min^{-1} for ethanol and 5–500 nmol m^{-2} min^{-1} for acetaldehyde). Acetic acid emissions reached 12 nmol m^{-2} min^{-1}. The observed differences in emission rates between the tree species are discussed with respect to their root adaptive strategies to tolerate long term flooding, providing an indirect line of evidence that the root ethanol production is a major factor determining the foliar emissions. Species which develop morphological root structures allowing for enhanced root aeration produced less ethanol and showed much lower emissions compared to species which lack gas transporting systems, and respond to flooding with substantially enhanced fermentation rates and a non-trivial loss of carbon to the atmosphere. The pronounced differences in the relative emissions of ethanol to acetaldehyde and acetic acid between the tree species indicate that not only the ethanol production in the roots but also the metabolic conversion in the leaf is an important factor determining the release of these compounds to the atmosphere.

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1 Introduction

Covering more than 300 000 km^2, the Central Amazon floodplains represent one of the largest inundation areas in the world (Junk, 1997). The area of seasonally inundated floodplain forests is estimated to cover more than 97 000 km^2 (Sippel et al., 1998; Hamilton et al., 2002) and plays an

important role in the atmospheric budgets of CO_2, nutrients, trace gases, water and energy on multiple scales (Richey et al., 2002; Grace and Malhi, 2002). Seasonal fluctuations in water levels of the Amazon River subject trees to continuous flooding periods of up to 210 days per year with an average flood amplitude of about 10 m (Junk, 1989). Inundation poses multiple constraints on the trees that inhabit these areas by causing drastic changes in soil chemistry and O_2 availability to plant roots, because of the 10 000 times slower transfer of dissolved O_2 in the water filled pore space of the soil (reviewed in (Armstrong et al., 1994; Ernst, 1990; Kozlowski, 1997). At low oxygen levels plant roots switch from their aerobic metabolism to fermentation for generating energy. Several studies on temperate tree species have shown that leaves emit ethanol and acetaldehyde as a physiological response to anaerobic conditions in the roots (MacDonald et al., 1989; Kreuzwieser et al., 1999; Holzinger et al., 2000). Switching to alcoholic fermentation involves the production of ethanol from pyruvate in a two-step process under action of the enzymes pyruvate decarboxylase (PDC) and alcohol dehydrogenase (ADH). A major portion of ethanol produced in flooded roots is transported with the transpiration stream to the leaves, where it can be re-metabolized by stepwise oxidation to acetaldehyde and acetate, mediated by the leaf enzymes ADH and aldehyde dehydrogenase (ALDH) (Kreuzwieser et al., 2001). Acetate, activated as acetyl-CoA can be channeled into many anabolic and catabolic processes of the general aerobic metabolism (MacDonald and Kimmerer, 1993; for review see Bode et al., 1997; Kesselmeier and Staudt, 1999). This mechanism allows the plant to recapture carbon and energy invested into ethanol. While the toxicity of ethanol is not clearly demonstrated, its oxidation product acetaldehyde is regarded as highly phytotoxic, however (Perata and Alpi, 1991), and accumulation of ethanol and acetaldehyde should therefore be avoided. A fraction of these compounds is obviously lost into the atmosphere representing a "leak" between metabolic production and consumption of these compounds (Kreuzwieser et al., 2001). In the atmosphere all three C_2-compounds are of high importance for tropospheric chemistry. Acetaldehyde, and ethanol, a precursor to atmospheric acetaldehyde, influence the oxidant balance of the atmosphere by generating free radicals and are involved in the production of Peroxyacetlynitrate (PAN), an important "reservoir" for nitrogen oxides in the atmosphere (Carlier et al., 1986; Chebbi and Carlier, 1996; Thompson, 1992; Singh et al., 1995, 2004). Acetic acid can significantly contribute to the acidity of the atmosphere, especially in remote areas (Keene et al., 1983; Andreae et al., 1988; Talbot et al., 1990).

To date, only a limited number of studies of the flooding-induced release of compounds such as ethanol and acetaldehyde have been reported, and these have focused nearly exclusively on tree species from temperate zones. Flooding events in these regions are invariably less frequent and less intense than in tropical regions and occur mainly during winter when plants are in a dormant and leafless state. Considering the vast area of forest that is inundated, and the duration of flooding, the Amazonian floodplain forests potentially represent one of the most important vegetative sources of atmospheric ethanol, acetaldehyde and acetic acid, which may have an impact on both regional as well as global atmospheric chemistry and climate (Parolin et al., 2004).

The present study reports on the effect of flooding on the exchange of the metabolically-related compounds, ethanol, acetaldehyde and acetic acid, between four different Amazonian floodplain tree species and the atmosphere. The exchange process was investigated during a greenhouse experiment, using an enclosure technique. A combination of Proton Transfer Reaction Mass Spectrometry (PTR-MS) and conventional trapping techniques was used to simultaneously monitor the exchange of these oxygenated compounds over a period of several days of flooding. To evaluate the influence of adaptive strategies on leaf emissions, the observed exchange rates were related to results from earlier studies on the same tree species, focusing on morphological and metabolic root adaptations obtained by microscopic and biochemical techniques (De Simone et al., 2002 a,b; De Simone, 2002). By combining and concurrently interpreting the results of both sets of measurements, this study contributes to an integrative understanding of plant-atmosphere exchange processes, underlying the complexity of the plant internal and environmental factors involved in response to flooding.

2 Material and methods

2.1 Plant material and experimental conditions

Four different evergreen tree species representative of the Central Amazonian white-water floodplain forests (Várzea) were chosen for this study. *Salix martiana* (Leyb.) (Salicaceae) is a fast growing, light demanding pioneer species reaching 10–12 m in height. *Tabernaemontana juruana* ((Markgr.) Schumann ex J. F. Macbride) (Apocynaceae) is a late-successional, shade tolerant understory species. *Pouteria glomerata* ((Miguel) Radlkoffer) (Sapotaceae) is like *T. juruana* a widespread tree species in the várzea. *Laetia corymbulosa* (Spruce ex Bent.) (Flacourtiaceae) is widely distributed and one of the most abundant species reaching a height of 25 m. All species experience similar water regimes in their natural habitats.

Experiments were carried out with 2–3 year old seedlings, grown from seeds collected in Central Amazonia and cultivated in a climate-controlled greenhouse. One month prior to commencing the experiments, the plants were transferred into 10 L plastic pots filled with commercially-available potting soil and were watered daily.

The flooding experiments were performed under semi-controlled greenhouse conditions. Plants were illuminated with 150 μmol m^{-2} s^{-1} PAR supplied by Philips IP 23 lamps

(12 h-light period) and a humidifier ensured a high relative humidity. Combined with natural sunlight entering the greenhouse, a maximum irradiation of 350 μmol m^{-2} s^{-1} was achieved. The influence of natural PAR led to diurnal variations and day-to-day fluctuations in ambient air temperature and relative humidity with daytime average values ranging 28–36°C and 52–61%, respectively. Average night temperature and humidity ranged 22–23°C and 74–78%.

2.2 Branch enclosures

The gas exchange measurements were performed applying an open, dynamic (flow-through) cuvette system as described in detail by (Kesselmeier et al., 1996; Rottenberger et al., 2004). In the present study four identical cuvettes of ~75 L volume were operated: three sample cuvettes and one empty reference cuvette. All cuvettes were flushed with ambient air (40 L min^{-1}) cleaned from ozone by scrubbers (MnO_2-coated copper mesh, Ansyco, Germany) to prevent a secondary production of short-chain aldehydes through gas phase oxidation of primarily emitted reactive hydrocarbons within the cuvettes (Neeb et al., 1997a, b). Each of the three sample cuvettes was equipped with PAR (LI-190 SA, LI-COR, Inc. USA), and humidity/temperature sensors (YA-100-F, Rotronic, Switzerland) and teflonized fine wire thermocouples to measure leaf temperatures (0.005″, Chromel/Constantan, Omega, USA). An infrared dual-channel gas analyzer operated in differential mode (LI-6262, LI-COR, Inc., USA) for continuous monitoring of the CO_2/H_2O exchange. Oxygenated VOCs were measured at the outlets of the cuvettes with conventional solid phase extraction cartridges as well as a PTR-MS.

2.3 Sampling and analysis of oxygenated VOCs (OVOC)

2.3.1 Real time measurements of ethanol and acetaldehyde using PTR-MS

Proton Transfer Reaction Mass Spectrometry (PTR-MS; Ionicon, Austria) was employed to measure ethanol and acetaldehyde allowing real-time monitoring of numerous VOCs at high temporal resolution. The use of this method in the current study was considered especially important because ethanol and acetaldehyde were expected to be co-emitted in response to root flooding (Kreuzwieser et al., 1999) and to undergo rapid temporal changes in emission strength (Holzinger et al., 2000). The PTR-MS instrument has been described in detail elsewhere (Lindinger et al., 1998). The basic principle is protonation of VOC species that are measured online with a quadrupole mass spectrometer. In many cases, the protonated VOCs do not fragment, so that they are detected at their protonated mass, which is the molecular weight +1. Under standard conditions, only 10–20% of ethanol is expected not to fragment upon protonation, and is detected at mass 47 (R. Holzinger, personal communication). The remaining fraction of protonated ethanol molecules lose a H_2O fragment, yielding $C_2H_5^+$, which should be detected at mass 29. However, since $C_2H_5^+$ has a lower proton affinity than water, the collision of H_2O and $C_2H_5^+$ leads to reformation of H_3O^+ and the fragments cannot be detected. Thus, ethanol concentrations solely based on mass 47 are highly underestimated. Another contributor to *mass* 47 is protonated formic acid, but direct organic acid measurements performed by ion chromatography confirmed that the contribution by formic acid was negligible. Therefore, ethanol mixing ratios measured by PTR-MS were corrected by a factor of 6.667, assuming mass 47 to being representative for 15% (10–20%, see above) of the total. Protonated acetaldehyde was detected at *mass* 45, without consideration of any interference with other atmospheric gases postulated for this mass.

The instrumental accuracy, which is largely determined by the uncertainties of the reported protonation reaction rate constants, is estimated to be better than ±30% (Lindinger et al., 1998). In this work, an experimentally determined rate constant of 3.6×10^{-9} cm^3 s^{-1} was used for the reaction of H_3O^+ and acetaldehyde. For ethanol, a reaction rate of 2×10^{-9} cm^3 s^{-1} was used. The precision of the PTR-MS is predominantly determined by the background signal (noise), which is the signal detected at the relevant mass in air being scrubbed of organics by passing through an activated charcoal filter. The detection limit for ethanol and acetaldehyde was defined as the minimum mixing ratio that can be detected with a signal-to-noise ratio (S/N) of 3. For a 1 s integration time, this resulted in theoretical detection limits around 0.4 ppb and 4.7 ppb for acetaldehyde and ethanol, respectively.

Acetaldehyde and ethanol were measured within each cuvette once every min with a sampling (integration) time of 1 s over a 10-min period. An automatic valve system switched sequentially between the four different cuvettes. Every 40 min, the reference cuvette air was passed through a catalytic (charcoal) converter for 10 min to determine the system background signal. The interpolated background signal was subtracted from the cuvette air measurements. In order to determine the actual concentration difference between the reference and the sample cuvette, reference cuvette concentrations were interpolated to account for the sequential measurements.

2.3.2 Measurements of organic acids and aldehydes using conventional techniques

Aldehydes were trapped on 2,4-dinitrophenylhydrazine (DNPH)-coated C_{18} glass cartridges in accordance with Zhou and Mopper (1990) and analyzed by HPLC as described in detail elsewhere (Kesselmeier et al., 1997). The sampling efficiency for aldehydes, tested by parallel sampling of ambient air or air from a permeation device, was found to be 99% for HCHO and 94–96% for CH_3CHO (Schäfer, 1997). Calibration was performed

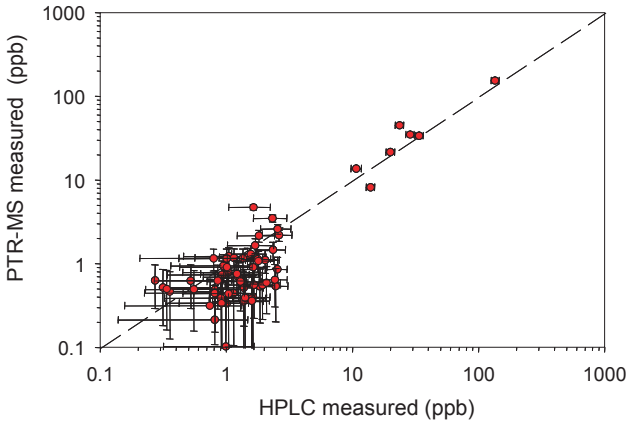

Fig. 1. Comparison between PTR-MS and HPLC acetaldehyde data obtained during branch cuvette measurements in the second flooding experiment. Only simultaneously sampled data were considered. HPLC data represent concentration measurements integrated over a 40 min sampling period. Instantaneously measured PTR-MS data were interpolated to obtain comparable 40 min average values. The dashed line gives the 1:1 relationship. For HPLC data, absolute errors were estimated by error propagation including the analytical and the blank cartridge error. For PTR-MS, the error is the instrumental noise at 1s integration time.

by injecting known concentrations (200–2600 nmol L^{-1}) of commercially-available HCHO- and CH_3CHO-DNPH standards (Supelco, Sigma-Aldrich Chemie, Germany). Sampling air was sucked through the cartridges at a flow rate of 300 mL min^{-1} for a period of 40 min (sample volume 12 L) on non-flooded days. During the flooding period sampling time and flow rate were reduced to 20 min and 200 mL min^{-1}, respectively. To ensure efficient trapping of high acetaldehyde concentrations, cartridges were impregnated with double and triple amounts of DNPH for measurements during the flooding period.

Organic acids were cryogenically co-trapped with atmospheric water vapor, according to Hofmann et al. (1997). The samples were analyzed by ion chromatography either immediately or after storage at −18°C (Hofmann et al., 1997; Gabriel et al., 1999).

For the conventional measurements of acetic acid and acetaldehyde, samples were taken simultaneously at the reference and the three sample cuvettes 5–8 times per day.

2.4 Calculation of exchange rates and error estimation

Exchange rates were calculated from the concentration differences between the branch and the reference cuvette ($\Delta c = c_{\text{sample}} - c_{\text{ref}}$,), taking into account the airflow through the cuvette (Q, in L min^{-1}) and the enclosed leaf surface (A, in m^{-2}) according to Eq. (1):

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

Total errors associated with the exchange rates were assessed by conventional Gaussian error propagation according to Doerffel (1984) (Eq. 2).

$$E_{\text{exchange}} = \sqrt{\frac{(E'_{\text{Csample}})^2 + (E'_{\text{Cref}})^2}{(\Delta c)^2} + E_Q + E_A} \tag{2}$$

E'_{Csample} and E'_{Cref} are the absolute errors for the concentration measurements in the sample cuvette and the reference cuvette, respectively. The error for the cuvette flow E_Q and leaf area E_A were 5% and 0.2%, respectively. Relative errors associated with acetaldehyde and acetic acid concentration measurements by conventional techniques due to sampling and analytical errors were 7% and 10%, respectively. For acetaldehyde exchange rates, the variability of blank cartridges was included in the error calculation (±0.6 ppb, n=37). Blank concentrations for acetic acid, obtained from rinsing cleaned traps with Milli-Q-water, were negligible.

Estimations of errors associated with exchange rates determined from PTR-MS measurements were performed for selected measurements days. The error associated with of the PTR-MS exchange rates was mainly attributable to the high variability of the zero air (charcoal-filtered) measurements resulting form the short integration time of 1 s. The variability in the signal observed during zero air measurements were ±0.74 ppb and ±0.34 ppb for ethanol and acetaldehyde, respectively.

Stomatal conductance was derived from the relation of the observed transpiration rate to the vapor pressure deficit between the stomatal cavity (derived from the observed leaf surface temperature, assuming 100% relative humidity) and within the cuvette (measured rh within the branch cuvette). The stomatal conductances for VOC were estimated by accounting for the different molecular diffusion coefficients as compared to water vapor (factor 0.63 for acetaldehyde and 0.50 for acetic acid).

2.5 Validation of acetaldehyde measurements

For validation purposes, PTR-MS and HPLC acetaldehyde measurements were performed simultaneously. Figure 1 shows the comparison between branch cuvette data obtained by the two techniques during simultaneous sampling periods. To compensate for the shorter sampling period of the PTR-MS the 10 min PTR-MS measurements were interpolated and averaged to obtain comparable 40 min average values. The comparison of the acetaldehyde data obtained from both techniques showed a quite good agreement in the high concentration range, while in the concentration range of 0–3 ppb, the agreement was rather poor, presumably caused by the high blank variabilities of both methods (variability of the PTR-MS background signal and blank DNPH cartridges).

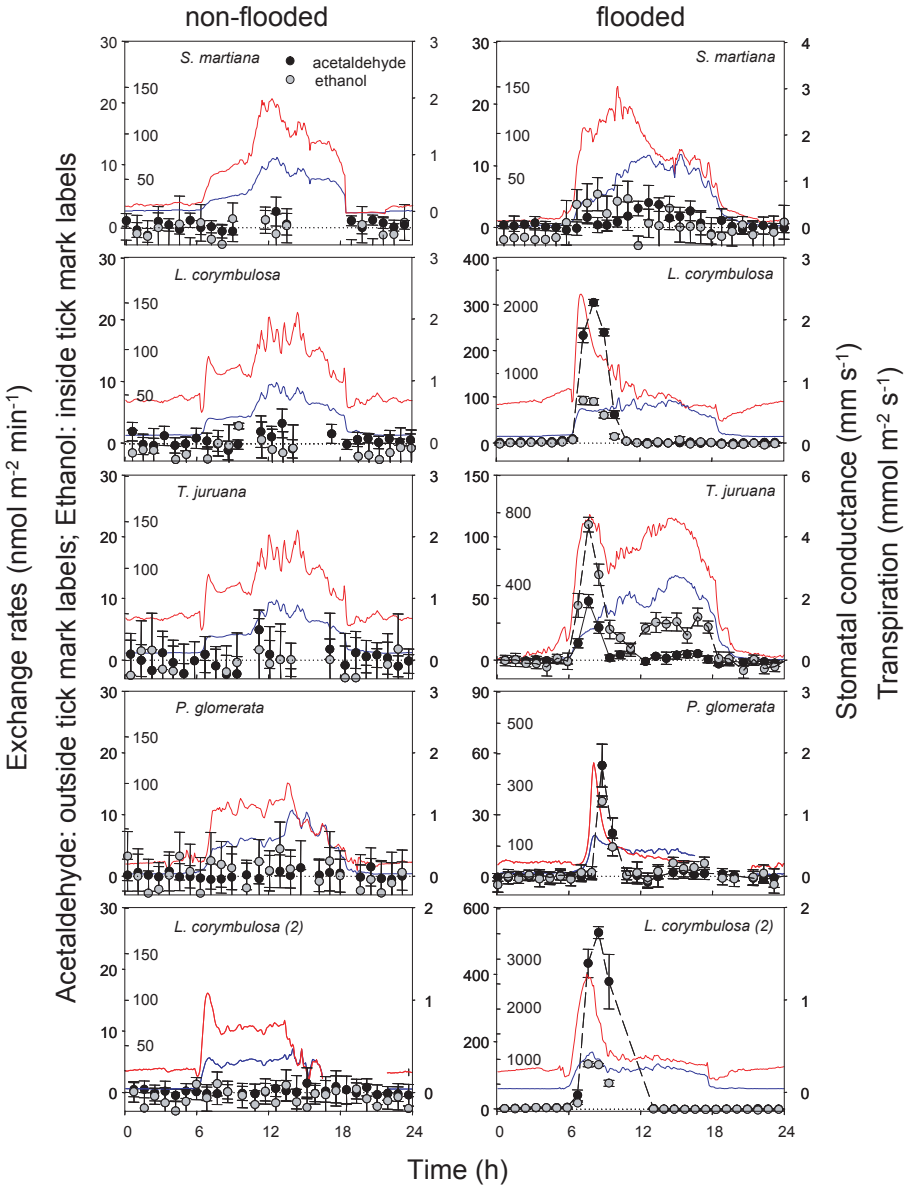

Fig. 2. Effect of flooding on the exchange of ethanol (grey circles) and acetaldehyde (black circles) for the four Amazonian floodplain tree species investigated within the two flooding experiments. Shown are diurnal courses of exchange rates, together with stomatal conductance (red lines) and transpiration (blue lines) measured before flooding (left panels) and during flooding (right panels). For flooded conditions, days on which maximum emissions were observed are presented (day 3 for both specimens of *L. corymbulosa*, day 6 or all other species). Data are 10-min means ±SD of 1 min PTR-MS measurements. Note the different scales used for emission rates during flooding.

2.6 Experimental procedure

Three trees were investigated simultaneously in each of the two flooding experiments. The cuvettes enclosed all branches of the young tree seedlings. Measurements started under normal watered conditions for a period of 1–2 days (aerobic control). Subsequently, the root system was flooded with N_2-flushed deoxygenated tap water, to a water level of 5 cm above the soil surface inducing hypoxic conditions. Measurements were continued for several days under flooding. In the first experiment, *S. martiana*, *L. corymbulosa* and *T. juruana* were investigated over a 6-day flooding period. In Experiment 2, *P. glomerata* and a second specimen of *L. corymbulosa* were studied over a 9-day flooding period. Measurements on *T. juruana* were continued to study the long term effect of flooding over a 24-day period. Evaporative water loss was compensated for by adding deoxygenated water daily. Oxygen content of the flooding solution was measured sporadically by taking liquid samples with a syringe at flooded soil depths of 4, 10, and 20 cm.

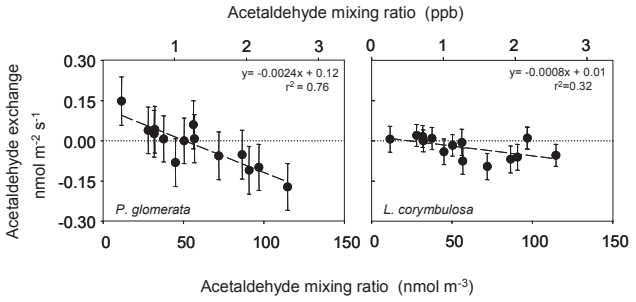

Fig. 3. Dependency of acetaldehyde exchange rates on atmospheric mixing ratios of *L. corymbulosa* and *P. glomerata* under non-flooded conditions as determined by the DNPH technique. Error bars are absolute errors estimated by error propagation. Results of the regression analysis are indicated.

O_2 measurements were performed with O_2 electrodes (YSI 53, USA). O_2 concentrations measured at three different soil depths decreased progressively with the duration of flooding to minimum values ranging between 20 and 30% of saturation after 5 days of flooding, representing hypoxic rather than anoxic soil conditions, corresponding to O_2 conditions occurring naturally in the Amazon water.

The leaf area was measured by a calibrated scanner system (ScanJET IIXC, HP, USA) and calculated with the software SIZE 1.10 (Müller, Germany). Leaf dry weight was determined after drying in a ventilated oven at 90°C until constant mass. The total enclosed leaf areas and specific leaf weights were: 0.42 m^2 and 23.4 $g\,m^{-2}$ for *S. martiana*, 0.39 m^2 and 58.2 $g\,m^{-2}$ for *L. corymbulosa* (1), 0.22 m^2 and 49.1 $g\,m^{-2}$ for *T. juruana*, 0.54 m^2 and 60.6 $g\,m^{-2}$ for *P. glomerata*, and 0.29 m^2 and 99.5 $g\,m^{-2}$ for *L. corymbulosa* (2).

3 Results

3.1 Exchange of ethanol and acetaldehyde under non-flooded conditions

To characterize the effect of flooding on the exchange of the oxygenated VOCs, measurements over 1–2 days under normal conditions were compared to the exchange pattern after flooding. PTR-MS measurements did not show any measurable amount of ethanol or acetaldehyde, in case of all four plant species investigated (Fig. 2, left panels) suggesting a zero exchange of acetaldehyde throughout the day. However, due to the short integration time of 1 s the sensitivity of the PTR-MS may have been insufficient to resolve small concentration differences between the reference and the sample cuvette, when both ranged between 0–1 ppb. This open question was resolved by the use of the DNPH technique sampling on adsorber tubes. Contrasting PTR-MS data, these results clearly showed a deposition of acetaldehyde during the afternoon for *L. corymbulos*a and *P. glomerata*. We can not explain this difference between PTR-MS and DNPH-technique except assuming fluctuations of ambient acetaldehyde concentrations, sometimes between 0 and 3 ppb, causing a false difference signal by the sequential PTR-MS sampling protocol. As the cartridge sampling (DNPH analysis) was performed simultaneously at reference and sample cuvette, this technique is not significantly influenced by ambient air fluctuations. Analysis of the exchange behavior determined by DNPH technique showed a clear dependency of acetaldehyde exchange rates on the actual ambient air concentrations (Fig. 3). Increasing ambient air concentrations favored an uptake, low concentrations resulted in emissions. Compensation points of 0.6 and 1.2 ppb were calculated for *L. corymbulosa* and *P. glomerata*, respectively. The average deposition velocity determined for *P. glomerata* (0.24 $cm\,s^{-1}$) was more than twice that of *L. corymbulosa* (0.08 $cm\,s^{-1}$), following the interspecies differences in stomatal conductance for CH_3CHO (0.05 vs. 0.03 $cm\,s^{-1}$). In both species, deposition velocity exceeded values of stomatal conductance normalized for CH_3CHO, indicating that deposition to the leaf cuticles also occurred in addition to stomatal uptake.

3.2 Effect of flooding on ethanol and acetaldehyde exchange

Flooding of the root system induced emission of ethanol and acetaldehyde in all tree species (Fig. 2, right panel), which became easily detectable by PTR-MS. Significantly enhanced emissions were first observed after 24 h of flooding. A pronounced diurnal pattern in acetaldehyde and ethanol emissions was observed with zero exchange at night, a strong emission burst in the morning when stomata opened, followed by a decrease in the afternoon. While this was a general feature, emission rates and the ethanol-to-acetaldehyde emission ratios differed markedly among the species. *S. martiana* emitted both compounds at lowest rates and with the least pronounced diurnal pattern. *L. corymbulosa* showed the highest emission rates and was by far the strongest acetaldehyde emitter of the four species investigated. Maximum acetaldehyde emissions reached 304±7 and 525±18 $nmol\,m^{-2}\,min^{-1}$ for the two specimens, respectively, as observed on the third day of the flooding period. Measured ethanol emissions were considerably higher, showing peak values of 775 ±75 and 1140±68 $nmol\,m^{-2}\,min^{-1}$. Induced ethanol and acetaldehyde emissions of *P. glomerata* were substantially lower, reaching maximum values of 490±84 and 36±3 $nmol\,m^{-2}\,min^{-1}$, respectively.

In contrast to the other tree species *T. juruana* emitted predominantly ethanol. While maximal ethanol emission rates of 928±50 $nmol\,m^{-2}\,min^{-1}$ were similar to those of *L. corymbulosa*, acetaldehyde emissions were an order of magnitude lower, reaching 48±5 $nmol\,m^{-2}\,min^{-1}$ at maximum. Also the emission pattern of *T. juruana* was different than that of the other species. Following the emission burst in

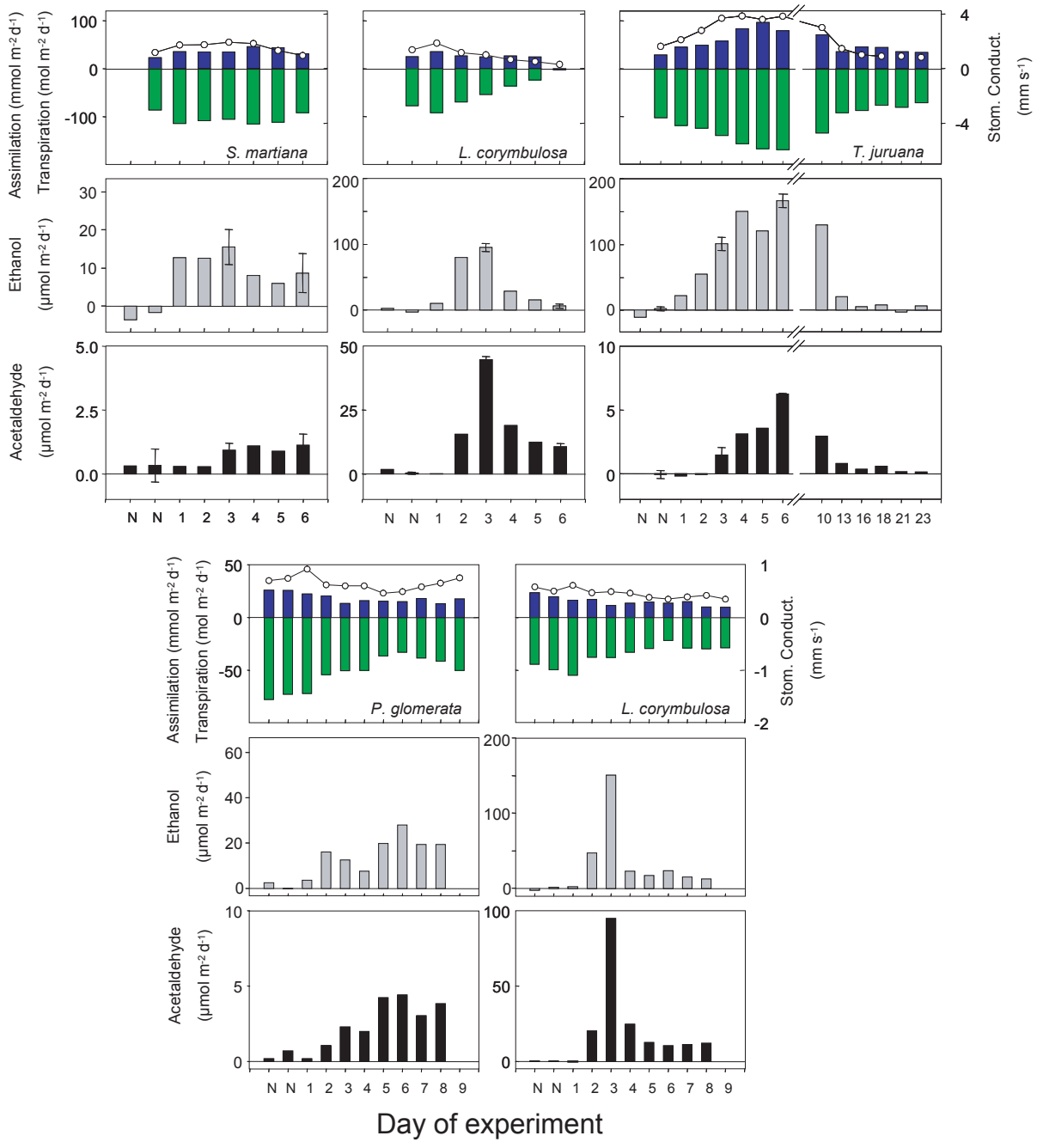

Fig. 4. Temporal emission pattern of acetaldehyde and ethanol for the four Amazonian floodplain species in response to several days of continuous flooding in relation to physiological activities. The panels show daytime integrals of assimilation (green bars; given as negative values) and transpiration (blue bars), together with average stomatal conductance (circles). Daytime integrals of ethanol and acetaldehyde emissions are given in grey or black bars, respectively. The upper part of the figure shows data as obtained with *S. martiana* and *L. corymbulosa* and *T. juruana* investigated in Experiment 1. The lower part of the figure shows data as obtained with *L. corymbulosa* and *P. glomerata* investigated in Experiment 2. Values observed on days prior to flooding are indicated (N). Assimilation and transpiration daytime integrals were obtained by totalizing the continuously measured CO_2 and H_2O exchange data. CO_2 integrals were obtained by totalizing the continuously measured data over the 12-h light ($n > 140$). Ethanol and acetaldehyde integrals were derived from PTR-MS measurements recorded every 50 min for each plant species. Note the different scales used for ethanol and acetaldehyde, as well as for the different plant species.

the morning, *T. juruana* continued to emit ethanol and acetaldehyde in the afternoon hours, albeit at low rates (maximal 295±60 and 6.3±3.9 nmol m^{-2} min^{-1}, respectively), while afternoon-emission of *L. corymbulosa* and *P. glomerata* were negligible (Fig. 2). This different emission behavior was associated with differences in stomatal behavior. Under flooding stress, stomatal conductance of *P. glomerata* and *L. corymbulosa* regularly decreased substantially in the afternoon, while for *T. juruana* stomata were not negatively affected by flooding until day 6, and remained open throughout the entire day. Although this demonstrates the role of stomata in emission regulation, in none of the species the diurnal emission variability was directly correlated with variations in stomatal conductance.

3.3 Temporal pattern of induced ethanol and acetaldehyde emissions

For all tree species the shape of the diurnal emission pattern described above was maintained throughout the entire flooding period. However, the absolute amounts released varied with the duration of the flooding period. Figure 4a and b shows the species specific differences in the temporal profiles of daytime integrals of ethanol and acetaldehyde emissions, as well as the respective physiological activities. Varying temperature and light conditions over the course of the flooding periods contributed to a certain extent to the emission responses. However, comparing the emission behavior of simultaneously measured tree species it became evident that each of the investigated tree species responded differently to the experimental conditions.

Emission rates of *S. martiana* were not significantly affected by the duration of flooding and remained consistently low over the whole 6-day period. Similarly, physiological activities did not vary greatly throughout the flooding period. *S. martiana* was the only species developing adventitious roots near the water surface in response to flooding. Initials began to emerge after 2 days of flooding and continued to grow extensively throughout the period of flooding.

All other species investigated responded to the decreasing O_2 availability in the soil during the flooding treatment with a progressive increase in emissions during the first days of the flooding period. With prolonged flooding, emissions stabilized or began to decline after 3–7 days.

L. corymbulosa showed the most pronounced day-to-day variability in ethanol and acetaldehyde emissions. In both specimens, emissions increased to extremely high values within the first three days of the flooding period, then declined sharply on day 4 and continued at a significantly lower level (Fig. 4a, b). For *L. corymbulosa* the decline in emission rates was associated with a progressive and pronounced reduction in leaf physiological activities, indicating a poor acclimation to the unfavorable conditions. In the first specimen investigated leaves showed a strong turgor loss on day 6, followed by partial leaf abscission, suggesting that the decrease in emissions was the result of severe deteriorations of the whole plant.

For *T. juruana* subjected to a flooding period of 24 days, both emissions and physiological activities constantly increased over the first 6-days of flooding. Over the next 6 days emissions declined and then remained close to zero. Among the species investigated *T. juruana* achieved the highest assimilation and transpiration rates under both, normal water and flooded conditions. Toward the end of the flooding period, physiological activity was reduced. Nevertheless, values of assimilation, transpiration and stomatal conductance remained at fairly constant levels, while emissions decreased, suggesting that the reduction in emissions reflected an acclimatization response rather than an injury induced decline.

The ethanol and acetaldehyde emissions of *P. glomerata* investigated in Experiment 2, increased during the first 5 days of flooding and then remained rather constant over the following 3 days (Fig. 4b). On day 9 PTR-MS measurements indicated a reduction in the emission activity. A daytime emission integral could not be calculated because PTR-MS measurements were terminated during midday, but morning peak ethanol and acetaldehyde emission rates of 80 and 15 nmol m^{-2} min^{-1} were substantially lower as compared to the three days before (285±25 and 48.8±13.9 nmol m^{-2} min^{-1}, respectively). Together with the observed trend for a recovery in physiological activities this suggests an acclimatization process to the flooding situation.

3.4 Acetic acid emissions under flooding conditions

Although in principal ethanol recovery by metabolic oxidation processes in the leaf might ultimately generate acetic acid, a significant emission of acetic acid occurred only in *L. corymbulosa*, whereas *S. martiana* and *T. juruana* predominantly showed deposition of acetic acid (Fig. 5). Acetic acid was co-emitted with ethanol and acetaldehyde, as indicated by the similar diurnal emission profiles of the three compounds, each displaying a pronounced morning peak followed by an afternoon decrease. Compared to ethanol and acetaldehyde, emission rates for acetic acid were substantially lower, reaching a maximum of 11.8 nmol m^{-2} min^{-1} on day 3 of the flooding period. As found for ethanol and acetaldehyde, acetic acid emissions decreased steadily with the duration of flooding (data not shown).

S. martiana and *T. juruana* predominantly showed deposition of acetic acid prior as well as during the flooding (Fig. 6), with exchange rates varying as a function of ambient air concentrations. Low emissions were restricted to the morning hours when ambient air concentrations were lowest and increasing deposition was observed with increasing ambient concentrations (Fig. 5). The relationship between exchange rates and ambient air concentrations was quantitatively similar under non-flooded and flooded conditions for both species (Fig. 6), demonstrating that the acetic acid

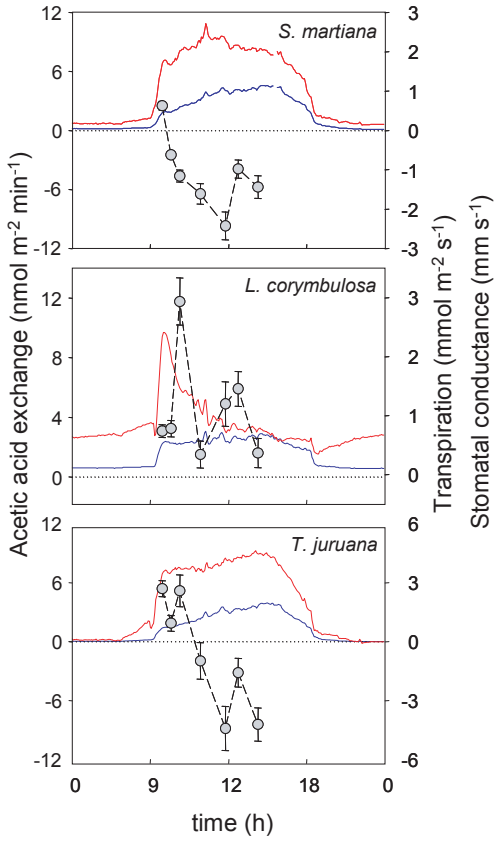

Fig. 5. Diurnal acetic acid (grey circles) exchange pattern, transpiration (blue line), and stomatal conductance (red line) of three simultaneously investigated Amazonian floodplain tree species on day 3 of flooding. Organic acid exchange was determined by cryotrapping and subsequent IC analysis. Error bars are absolute errors estimated by error propagation.

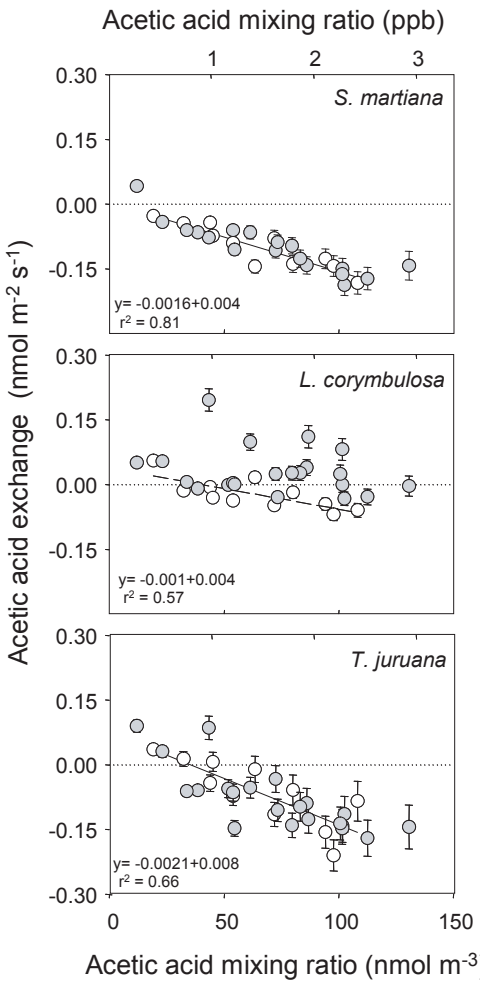

Fig. 6. Scatter plot of acetic acid exchange rates versus atmospheric mixing ratios for three Amazonian floodplain tree species simultaneously investigated during Experiment 1. Shown are all 6 days data obtained under non-flooded (open circles) and flooded (grey circles) conditions. Results of the regression analysis are indicated. Error bars are absolute errors estimated by error propagation.

exchange behavior was not affected by flooding. Prior to flooding, *L. corymbulosa* exhibited a fairly similar exchange pattern, with exchange rates strongly depending on the actual ambient air concentrations (Fig. 6, open circles). The deposition velocities of acetic acid (slope of the regression), varied strongly among the species with non-flooded *L. corymbulosa* showing in average the lowest (0.1 cm s^{-1}) and *T. juruana* the highest values (0.21 cm s^{-1}), consistent with the observed interspecies variations in stomatal conductance. A quantitative analysis of the acetic acid deposition behavior for each individual tree species revealed that average values for deposition velocities behaved very similarly as compared to average values of stomatal conductance (data not shown), suggesting that in contrast to acetaldehyde the cuticular deposition of the more polar compound acetic acid was negligible and that the uptake is largely under stomatal control.

4 Discussion

4.1 OVOC exchange behavior as influenced by flooding

The adaptation potential of tree species to flooding conditions in the Amazonian floodplain areas is impressive (cf. Parolin et al., 2004; Haase and Rätsch, 2009). Morphological and physiological adaptations enable plants not only to survive these long term flood pulses, but also to maintain a substantial physiological activity. The consequences of this sort of environmental stress on reactive trace gas exchange between the tree's crown and the atmosphere is unexplored. The present study was conducted to examine the effect of root flooding on the foliar exchange of ethanol, acetaldehyde, and acetic acid of four flood tolerant floodplain species that are exposed to regular flooding periods in their natural

habitat, in order to contribute to an evaluation of the potential role of floodplain forests in the Amazon region to the atmospheric budgets of these compounds.

Under normally watered, aerobic soil conditions, none of the investigated tree species was a significant source for ethanol, acetaldehyde, or acetic acid. Moreover, measurements by conventional techniques showed predominantly a deposition of acetaldehyde and acetic acid at rates which were linearly correlated to the ambient air concentrations. The compensation points were in the range of 0.1 to 1.1 ppb, suggesting that under natural ambient air conditions Amazonian floodplain forests may represent a sink for these oxygenated compounds during the non-flooded terrestrial phase, similar to vegetation from the adjacent *terra firme* forests (Rottenberger et al., 2004; Kuhn et al., 2002) or European forests (Kesselmeier 2001). Contrasting these low compensation points, Jardin et al. (2008) observed very high compensation points for poplar (>12 ppb) and Holm oak (>22 ppb) in the light and suggested that solar radiation and/or temperature may have a large impact on acetaldehyde exchange patterns, due to a stimulation of acetaldehyde production in leaves. Such high compensation points were not observed before (Kesselmeier, 2001; Rottenberger et al., 2004; Karl et al., 2005) and, excluding apparent production by oxidation of emitted precursors (Neeb et al., 1997a, b), can only be understood in view of a very substantial increase of acetaldehyde production in leaves, which was despite a substantial delivery of ethanol from root anoxia, not observed in our flooding experiments.

The analysis of the deposition behavior demonstrated clear stomatal controls over acetaldehyde and acetic acid fluxes. Nonetheless, some differences in the uptake mechanisms for the two compounds became evident. While the calculated stomatal conductance was ample to explain the total amount of the observed uptake of acetic acid, for acetaldehyde a supplementary non-stomatal deposition to leaf surfaces has to be assumed to explain the observed deposition velocities. Stomatal uptake accounted for only 20% and 38% of the total acetaldehyde deposition of *P. glomerata* and *L. corymbulosa*, respectively. The differences in the uptake of acetic acid and acetaldehyde might arise from the higher water solubility of acetic acid, allowing a very efficient uptake in the liquid phase of the leaf and restricting the diffusion through the cuticle, due to its hydrophobic character. The calculation of stomatal conductance is based on the assumption that the uptake of water-soluble gases is primarily by way of their solution into the aqueous phase being committed within the stomatal cavities of the leaves (Wesely and Hicks, 2000; Niinemets and Reichstein, 2003). Deposition rates exceeding this upper bound estimate for the potential uptake of water-soluble gases were attributed to be non-stomatal, and hence (quasi by default) to surface deposition. However, we are not able to differentiate between the different impacts of pure physicochemical deposition onto the hydrophobic cuticle (that would favor the less soluble acetaldehyde uptake), or onto humid leaf surface components (rather favoring the more soluble acetic acid), and/or the involvement of active uptake by surface biological consumers. The assumption of non-stomatal uptake of acetaldehyde is consistent with previous studies of Rottenberger et al. (2004) within the natural habitat of the Amazon tropical rainforest, whereas Jardin et al. (2008) did not find an indication of acetaldehyde deposition to leaf surfaces of the temperate species poplar and Holm oak. Unfortunately our present data set does not provide enough nighttime measurements to examine the influence of cuticular resistances when stomata are almost closed. However, Dindorf (2000) provided experimental evidence that (passive) cuticular uptake can play a substantial role in the exchange process. In the course of her work in our laboratory, she induced stomatal closure of *Quercus ilex* leaves by treatment with plant hormones, and showed that acetaldehyde uptake remained high when fumigating with mixing ratios of 15–25 ppb acetaldehyde.

In all investigated tree species flooding of the root system induced leaf emissions of ethanol and acetaldehyde, demonstrating that the roots of each of the plant species responded to hypoxic soil conditions by ethanolic fermentation supporting the view of a metabolic oxidation of root-derived ethanol in the leaves (Kreuzwieser et al., 1999). Moreover, we demonstrate for the first time flooding induced emissions of acetic acid, adding this compound to the intermediates to be discussed within the oxidative pathway in leaves. Consistently with flooding experiments on European tree species (Holzinger et al., 2000), we observed a typical diurnal pattern with zero exchange at night, an emission burst in the morning, and a decline the afternoon. We interpret this emission pattern to result from continued root ethanol production and its accumulation at night when stomata are closed and the root-to-leaves transport is restricted due to the lack of transpiration. This night phase is followed by the release of ethanol and its oxidation products as soon as stomata open in the morning and the light induced transpiration stream serves as a carrier of accumulated ethanol to the leaves, where it can be metabolized. The strong decline in emissions and the rather low emission rates during the afternoon are considered to result from daytime variations in ethanol delivery to the leaves: Following the morning burst with its depletion of the night time pool of root ethanol, the amount of ethanol delivered to the leaves becomes dependent on the current in-situ ethanol production rate in the roots and emissions decline. This suggests a strong influence of synthesis rate of ethanol and its oxidation products on emission dynamics. Nonetheless, the results clearly showed that stomatal opening is a prerequisite for the release of all three compounds to the atmosphere. Emissions were generally restricted to daytime hours and only species with stomata open throughout the entire day showed emissions all day long. In contrast tree species with a depression in stomatal conductance during the afternoon showed decreased and negligible emissions. These effects can be understood by the dominating

role of stomatal control of the release of all three compounds by affecting transpiration and thus delivery of ethanol from roots to leaves as well as the final control over the release into the atmosphere, which is in close accordance with the modeling work of Niinemets and Reichstein (2003), who demonstrated the close relation between stomatal emission control and water solubility (Henry's law constants) of volatiles. However, there are additional parameters significantly influencing emission rates and fluctuations, such as ethanol production in the roots, storage capacity as well as enzymatic oxidation activities in the leaves. This is indicating that emissions may be controlled by stomata only to a certain degree and that for some compounds several simultaneous processes may superimpose stomatal control.

4.2 Influence of root morphological and metabolic adaptations on OVOC emission behavior

The diurnal emission pattern described above was common to all species investigated, but emission rates substantially differed between species. Although ethanol concentrations in the roots were not measured in the present study, the major differences in the emission strength between the species could indirectly be related to differences in the root ethanol production, resulting from species specific morphological and metabolic adaptations of the roots. Root adaptive strategies of the investigated tree species were obtained from microscopic and biochemical investigations (De Simone et al., 2002a, b; De Simone, 2002). Based on these studies we found evidence that those tree species with developed anatomical structures allowing for an improved O_2 availability in the roots showed lowest emissions. Conversely, species with an insufficient oxygen supply need to switch over to fermentation, resulting in subsequent transport of ethanol to the leaves and emission of ethanol and its oxidation products.

The oxygen content was measured sporadically and we observed a drop of O_2 levels from near saturation to 40–50% at 4–10 cm depth and to 20–30% at 20 cm depth within the first 5 days. However, we assume that not the variation in the relative amount of solved O_2 in the water column plays the pivotal role in provision of oxygen to the roots, but rather the generally low solubility of O_2 in water, being at least three orders of magnitude lower than in air. For plants not specially adapted to these conditions this will already result in anoxic stress. As demonstrated by a comparison of different tree species (De Simone et al., 2002b; Haase and Rätsch, 2009) plants from Amazonian floodplain areas are able to adapt by internal transport of air and oxygen down to the roots. There was nearly no oxygen deficiency detected in case of *Salix martiana*, whereas the oxygen concentration was low in case of *Tabernaemontana juruana* and not detectable in case of *Laetia corymbulosa*. These data fit perfectly with the assumed production rates and observed emission rates, respectively, of products of the anoxic metabolism. Within this context we would like to point out a difference between potted trees and trees in their natural floodplain habitat, where plants are flooded by high water columns, sometime up to the crown. But in most of these floodplain areas a constant flow of water is maintained, indicating the steady exchange of water with more or less constant oxygen content. This leads to the conclusion that it is the generally limited oxygen concentration in water, rather than a further decrease in oxygen content which drives adaptation.

The low emission rates of *S. martiana* can be attributed to the development of adventitious roots close to the water surface and the formation of large airspaces in the root cortex (aerenchyma) facilitating longitudinal O_2 transport from aerated to submerged parts of the plant. The improved root aeration provided by these formations is reflected by extremely low root alcohol dehydrogenase (ADH) activities, indicating that the energy required is predominantly generated via aerobic metabolism (De Simone, 2002). Consequently, only low amounts of ethanol are produced and delivered to the leaves, explaining the low emission of *S. martiana*. In addition, ethanol diffusion from the roots to the flooded soil might have contributed to low ethanol concentrations in the transpiration stream, since the root exodermis of *S. martiana* is only weakly suberized (De Simone et al., 2002a, b; De Simone, 2002). The capacity to maintain aerobic root metabolism during flooding helps the plant to maintain an adequate energy status for nutrient and water uptake (Jackson and Armstrong, 1999) and enabled this species to preserve a relatively undisturbed level of assimilation and transpiration activity over the 6-day period of inundation.

L. corymbulos a responded with the second highest ethanol and highest acetaldehyde emission rates to flooding and was the only species showing flooding induced acetic acid emissions. Roots of *L. corymbulosa* are characterized by the complete lack of air spaces thus limiting internal aeration. Consequently, root metabolism was found to be fully dependent on fermentation processes. Flooding induced an acceleration of alcoholic fermentation with a 10 fold increase in ADH activity (De Simone, 2002). This suggests the intensive production of ethanol and explains the observed high leaf emissions of ethanol and its oxidation products. The strong reduction in physiological activities suggests that the energy yield through fermentation processes did not meet the energy requirements for water and nutrient uptake. The concomitant decrease in emissions could have been the consequence of a progressive damage of the root system in response to energy deprivation, linked to a pronounced limitation in carbohydrate availability for glycolysis and alcoholic fermentation since assimilation was substantially affected. Under greenhouse conditions *L. corymbulosa* showed a rather flooding intolerant behavior, and it remains an open question which exact conditions and mechanisms allow this species to successfully colonize its natural habitat.

Classifying the investigated tree species according to their emission strength, *P. glomerata* and *T. juruana* took an intermediate position. Their emissions were lower than that

of *L. corymbulosa* but larger than those of *S. martiana*. Investigation on the root characteristics of both tree species showed a combination of metabolic and morphological adaptations (De Simone, 2002). Roots of both species exhibit enlarged non-aerenchymatous intercellular spaces facilitating the transport of gases in longitudinal direction and a heavily suberized root hypodermis, functioning as an effective barrier against oxygen loss from the roots to the soil. Although this gas transporting system enables the plant to maintain an aerobic internal microenvironment, it was insufficient to generate the required energy through aerobic metabolism as indicated by enhanced ADH activities of *T. juruana* (De Simone, 2002). The higher ADH activity as compared to *S. martiana* and the presence of a suberin layer, which is assumed to restrict the diffusion of ethanol to the soil, is expected to result in higher root ethanol concentrations and in the observed higher emissions. The root ADH activities of *T. juruana* were found to be very similar to those of *L. corymbulosa* (De Simone, 2002) although emission rates were lower in *T. juruana*. It is important to notice that the root biomass of the investigated trees could have been different, thereby directly influencing the absolute amount of ethanol produced. Another important factor that may influence emissions is the metabolisation of root-derived ethanol in the leaves (see following section). No data on the root metabolism of *P. glomerata* are available, but its root anatomy suggests a strategy to withstand flooding similar to that of *T. juruana*. In both species emissions declined towards the end of the flooding period while leaf physiological activities stabilized, pointing towards acclimation processes rather than to flooding induced irreparable injuries. Reduced leaf emission as an adaptation mechanism to long term flooding has to be discussed in view of a complex mixture of factors influencing alcoholic fermentation rates. Such adjustments may have been a result of reduced energy demands of the roots and the induction of alternative metabolic pathways diverting pyruvate to e.g. alanine, malate and succinate, as reported for other tropical tree species (De Simone, 2002; Joly, 1991; Schlüter et al., 1993). In the case of *T. juruana*, the flooding induced proliferation of hypertrophied lenticels at the stem, which can serve as an inlet for oxygen and enhance root aeration (Haase et al., 2003), could have contributed to a reduced ethanol production. Simultaneous release of ethanol could have occurred through this route and may have been overlooked because the lower part of the stem was not enclosed by the cuvette.

Overall we found a good agreement between the emission behavior of each individual tree species and the potential ethanol production rate comparing to root ADH activity as a measure. However, this can only be taken as a rough rule of thumb. For an exact quantitative analysis ethanol concentrations should be measured since the level of pyruvate decarboxylase activity (PDC), the enzyme catalyzing pyruvate to acetaldehyde, might be the limiting step in alcoholic fermentation and affecting ethanol synthesis (Ismond et al., 2003) rather than ADH.

4.3 The role of leaf metabolism on OVOC emission composition

We could derive some reasonable assumptions from the interpretation of the emitted compound composition. The investigated tree species differed not only in terms of emission rates but also in the ratio of the emitted ethanol, acetaldehyde, and acetic acid. Emissions of these compounds can be considered to reflect production and consumption processes, suggesting large interspecies differences in the metabolic oxidation of ethanol to acetaldehyde and acetic acid involving the leaf enzymes alcohol dehydrogenase (ADH) and aldehyde dehydrogenase (ALDH), respectively (Kreuzwieser et al., 1999; Kreuzwieser et al., 2001). Within this context we also do not exclude changes of the enzyme activities in the course of the studies. It should be noted that the fraction of each of the compounds involved in the metabolic oxidation chain does not directly relate to the activity of each of the leaf enzymes since all three compounds have different liquid-gas phase partitioning coefficients (Henry's Law constants). The Henry's law constant of acetaldehyde ($7.0\,\mathrm{Pa\,m^3\,mol^{-1}}$) is much higher than that of ethanol ($0.5\,\mathrm{Pa\,m^3\,mol^{-1}}$) and acetic acid ($0.01\,\mathrm{Pa\,m^3\,mol^{-1}}$) (Niinemets and Reichstein, 2003). Thus similar emission rates of the three compounds would correspond to significantly higher liquid phase leaf concentrations of acetic acid and ethanol. Another masking factor might be a direct release of ethanol from the apoplast without passing the leaf cell mesophyll. However, studies on Eastern cottonwood and poplar leaves showed that transported ethanol is metabolized by leaf tissues with negligible loss to the atmosphere (<5%) (MacDonald and Kimmerer, 1993; Kreuzwieser et al., 1999). Hence, a qualitative comparison of the ethanol-acetaldehyde-acetic acid emission ratios among the tree species investigated in the present study suggests differences in leaf enzyme activities. This is most evident from the emission behaviors of *L. corymbulosa* and *T. juruana*, which showed very similar ethanol emission rates, while acetaldehyde and the acetic acid emission rates were substantially different. *L. corymbulosa* was a high acetaldehyde emitter indicative of a high ADH activity. The co-emission of acetic acid demonstrates a substantial activity of ALDH with an acetic acid production too high to be fully metabolized by other anabolic and catabolic pathways. Acetaldehyde emissions of *T. juruana* were an order of magnitude lower compared to *L. corymbulosa* and acetic acid was deposited rather than emitted. At comparable ethanol emission rates this may reflect a lower ADH activity as compared to *L. corymbulosa* causing acetaldehyde amounts low enough to be easily converted by the subsequent metabolic consumptions. Under these conditions similar ethanol emission rates can only occur when the amount of root-derived ethanol delivered to the leaves was lower in *T. juruana*, especially when taking into account that stomatal conductance and transpiration were higher for this species than for *L. corymbulosa*. These findings indicate that leaf enzyme activities may have

a strong impact on the emission behavior. But as we did not investigate leaf enzyme activities, all discussions about the role of these activities are tentative. We would like to indicate potential differences in leaf metabolism to understand the variation of emission quality. There is more information needed to link enzymatic activities with emission rates, and our data provide good arguments to further invest time into such kind of research. The biochemical regulation of leaf emissions in plants subjected to root flooding is rarely investigated and requires more experimental work.

4.4 Emissions, carbon budget and flooding tolerance

The ecological importance of foliar ethanol metabolism might not only be avoidance of an accumulation of ethanol and acetaldehyde, but may also be a contribution to the energy and carbon metabolism. ^{14}C labeling experiments on poplar have shown that only a small fraction of ethanol supplied to the leaves is lost through acetaldehyde and ethanol emissions (Kreuzwieser et al., 1999). However, relating the amount of carbon released as ethanol and acetaldehyde emission to the total amount of assimilated carbon, flooding-induced emissions of ethanol and acetaldehyde represent a non-trivial C-loss for the plants. In case of Salix martiana the loss was negligible, but for L. corymbulosa with highest emissions and a low photosynthetic CO_2 gain, the C-loss accounted for about 0.5–0.8% for the first series of measurements and 2–3% for the second series. Emissions of ethanol and acetaldehyde by *T. juruana* and *P. glomerata* represented a loss below 0.5%. These data are in the same order of magnitude as the C-loss through isoprene and monoterpene emissions (Harley et al., 1999; Kesselmeier et al., 2002). Taking into account that *L. corymbulosa* is also an isoprene emitting species (unpublished data), the total C-loss through emissions of volatile organic compounds might be quite substantial.

Kreuzwieser et al. (2004) hypothesized from their observations on European tree species that an effective carbon recycling of root derived ethanol inside plant leaves can be regarded as an important mechanism of flooding tolerance. Within this context a high emission rate of acetaldehyde may indicate a high metabolic turnover of ethanol in the leaves and an increased flooding tolerance. Such a view might apply for species depending mainly on alcoholic fermentation to maintain root metabolism. However, according to the present study, tree species that are able to tolerate long-term flooding, by avoiding O_2 deficiency and fermentation, are expected to show rather low emissions and the carbon recycling mechanism becomes of minor importance. Moreover, *Q. ilex*, a typical Mediterranean tree species generally experiencing rather water limitations than flooding conditions, has been reported to exhibit extremely high ethanol and acetaldehyde emission rates when exposed to flooding (Holzinger et al., 2000). These rates ($\sim$15 000 and 4000 nmol m^{-2} min^{-1} of acetaldehyde and ethanol, respectively) were larger than those observed for the flooding tolerant Amazonian trees species in the present study (3–200 nmol and 42–4220 nmol m^{-2} min^{-1} of acetaldehyde and ethanol, respectively) and much larger than those for flooding tolerant and intolerant European tree species ($\sim$100–1000 nmol m^{-2} min^{-1} acetaldehyde) (Kreuzwieser et al., 2004). Hence, not the flooding tolerance itself, but different physiological mechanisms contributing to a flooding tolerance determine the emission rates of ethanol and its oxidation products and emissions rates alone can not be used as indicators a flooding tolerance.

5 Conclusions

Tree species were chosen along their morphological and physiological adaptation capability to floodplain conditions as reported previously (De Simone et al., 2002a, b; Haase and Rätsch, 2009), and consistent measurements over several days were performed for each individual. The VOC emission composition of the different tree species was found to be in close agreement with their respective morphological and physiological adaptation strategies in response to flooding. The results obtained in course of the greenhouse experiments on individual Amazonian floodplain tree species during inundation provide evidence that floodplain forests represent a potentially significant source of ethanol and acetaldehyde, and, to a lesser extent, acetic acid. The results indicate that much of the variations in the emission strength between tree species can be attributed to differences in the ethanol production in the roots as one of the root adaptive strategies to withstand flooding and anoxia. Differences in the relative proportions of the emissions of ethanol, acetaldehyde and acetic acid between the investigated tree species suggest a large variability in the metabolic activity of the leaf enzymes responsible for the re-oxidation of root derived ethanol. However, flooding induced emissions may be only intermittent since our data indicated a decline in emissions with time. The emissions of flooded trees are controlled by a complex interaction of multiple plant internal factors which makes it difficult to parameterize flooding induced emissions and to estimate their contribution to atmospheric concentrations. However, though the reported emission behavior fits well with other observations on each species' anatomy, morphology and physiology field measurements on adult tree species are urgently needed to verify the emission response to flooding under natural soil and microclimatic conditions. Studies on potted trees under artificial conditions in the laboratory or greenhouse represent only a very first step towards characterizing the significance of such emissions from seasonally flooded tropical forests for the atmosphere. Our conclusions have to be confirmed by field studies in the natural floodplain environment from the leaf level to ecosystem and regional scales. Studies along flooding gradients (inundation level and duration) based on primary emission

measurements as well as flux studies may also help to answer the question which strategy is more successful, avoidance of roots hypoxia or switching to fermentation. Confirmation and characterization of such an emission behavior of floodplain forests may significantly contribute to our understanding of their impact on atmospheric chemistry processes.

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