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# The effect of flooding on the exchange of the volatile C<sub>2</sub>-compounds ethanol, acetaldehyde and acetic acid between leaves of Amazonian floodplain tree species and the atmosphere

S. Rottenberger<sup>1</sup>, B. Kleiss<sup>2</sup>, U. Kuhn<sup>1</sup>, A. Wolf<sup>1</sup>, M. T. F. Piedade<sup>3</sup>, W. Junk<sup>4</sup>, and J. Kesselmeier<sup>1,\*</sup>

<sup>1</sup>Max Planck Inst. for Chemistry, Biogeochemistry Dept., P.O. Box 3060, 55020 Mainz, Germany

<sup>2</sup>Max Planck Inst. for Chemistry, Air Chemistry Dept., P.O. Box 3060, 55020 Mainz, Germany

<sup>3</sup>Inst. Nacional de Pesquisas da Amazônia, Caixa Postal 478, 69011-970, Manaus-Am, Brazil

<sup>4</sup>Max Planck Inst. for Limnology, Tropical Ecology Workgroup, P.O. Box 165, 24302 Plön, Germany

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Correspondence to: J. Kesselmeier (jks@mpch-mainz.mpg.de)

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## Abstract

The effect of root inundation on the leaf emissions of ethanol, acetaldehyde and acetic acid 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 significant emissions of any of the compounds. A slight deposition of acetaldehyde and acetic acid was mainly 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 occurred only by 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 confirmed 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. Emission rates substantially varied among tree species, with maxima differing by up to two orders of magnitude ( $3\text{--}200\text{ nmol m}^{-2}\text{ min}^{-1}$  for ethanol and  $5\text{--}500\text{ nmol m}^{-2}\text{ min}^{-1}$  for acetaldehyde). Acetic acid emissions reached  $12\text{ nmol m}^{-2}\text{ min}^{-1}$ . 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

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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. 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.

## 1 Introduction

Covering more than 300 000 km<sup>2</sup>, 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<sup>2</sup> (Sippel et al., 1998; Hamilton et al., 2002) and plays an important role in the atmospheric budgets of CO<sub>2</sub>, 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 pose multiple constraints on the trees that inhabit these areas by causing drastic changes in soil chemistry and O<sub>2</sub> availability to plant roots, because of the 10 000 times slower transfer of dissolved O<sub>2</sub> in the water filled pore space of the soil (reviewed in Armstrong et al., 1994; Ernst, 1990; Kozłowski, 1997). At low oxygen levels plant roots switch from their aerobic metabolism to fermentation for generating energy. Several studies on European 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

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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, and to avoid an accumulation of highly phytotoxic ethanol and acetaldehyde. 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<sub>2</sub>-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 peroxyacetylnitrate (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 con-

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ventional 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 data were related to results from earlier studies focusing on morphological and metabolic root adaptations of the investigated tree species, as 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 for 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 with stem heights reaching 10–12 m. *Tabernaemontana juruana* (Markgr. Schumann ex J. F. Macbride) (Apocynaceae) is a late-successional, shade tolerant understory species. *Pouteria glomerata* (M. 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 stem height of 25 m. All species are subjected to a similar water regime.

Experiments were carried out with 2–3 years 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 daily watered.

The flooding experiments were performed under semi-controlled greenhouse conditions. Plants were illuminated with  $150 \mu\text{mol m}^{-2} \text{s}^{-1}$  PAR supplied by Philips

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IP 23 lamps (12h-light period) and a humidifier ensured a high relative humidity. Combined with natural sunlight entering the greenhouse, a maximum irradiation of  $350 \mu\text{mol m}^{-2} \text{s}^{-1}$  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 18–36°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) and 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 ( $40 \text{ L min}^{-1}$ ) cleaned from ozone by scrubbers (MnO<sub>2</sub>-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 and Sauer, 1997; Neeb et al., 1997). Each of the three sample cuvettes was equipped with PAR (LI-190 SA, LI-COR, Inc. USA), humidity and temperature sensors (YA-100-F, Rotronic, Switzerland) and teflonized fine wire thermocouples (0.005", Chromel/Constantan, Omega, USA). An infrared dual-channel gas analyzer was operated in differential mode (LI-6262, LI-COR, Inc., USA) for continuous monitoring of CO<sub>2</sub>/H<sub>2</sub>O exchange. Oxygenated VOCs were measured at the outlets of the cuvettes with trapping devices 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 numer-

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ous 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 which are measured 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. For ethanol however, only 10–20% is not expected to fragment upon protonation and is detected at mass 47 (R. Holzinger, personal communication). The protonation of ethanol is followed by the ejection of an H<sub>2</sub>O molecule, yielding a fragment on mass 29, which is obviously not detectable. Hence, ethanol concentrations were largely 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. Protonated acetaldehyde was detected at mass 45, without an 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  $3.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  was used for the reaction of H<sub>3</sub>O<sup>+</sup> and acetaldehyde. For ethanol, a reaction rate of  $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  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 0.7 ppb for acetaldehyde and ethanol, respectively.

For each cuvette, acetaldehyde and ethanol were measured once every min with a sampling (integration) time of 1 s over a 10-min period. An automatic valve system

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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 correct 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<sub>18</sub> glass cartridges in accordance with Zhou and Mopper (1990) and analysed by HPLC as described in detail elsewhere (Kesselmeier et al., 1997). Sampling air was sucked through the cartridges at a flow rate of 300 mL min<sup>-1</sup> 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<sup>-1</sup>, 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 acetic acid and acetaldehyde measurements using conventional techniques, a total of 5–8 samples per day were taken simultaneously for both, sample and reference cuvettes.

### 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

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cuvette ( $Q$ , in  $\text{L min}^{-1}$ ) and the enclosed leaf surface ( $A$ , in  $\text{m}^{-2}$ ) according to Eq. (1).

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

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

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

$E'_{\text{Csample}}$  and  $E'_{\text{Cref}}$  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 measurements by conventional techniques due to sampling and analytical errors were 7.1% and 10%, respectively. For acetaldehyde exchange rates, the variability of blank cartridges was included in the error calculation ( $\pm 0.6$  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 from the short integration time of 1 s. The variability in the signal observed during zero air measurements were  $\pm 0.74$  ppb and  $\pm 0.34$  ppb for ethanol and acetaldehyde, respectively.

## 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

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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)

## 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<sub>2</sub>-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 the second experiment, *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. O<sub>2</sub> 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 to anoxic soil conditions, corresponding to O<sub>2</sub> 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<sup>2</sup> and 23.4 g m<sup>-2</sup> for *S. martiana*, 0.39 m<sup>2</sup> and 58.2 g m<sup>-2</sup> for *L. corymbulosa* (1), 0.22 m<sup>2</sup> and 49.1 g m<sup>-2</sup> for

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*T. juruana*,  $0.54 \text{ m}^2$  and  $60.6 \text{ g m}^{-2}$  for *P. glomerata*, and  $0.29 \text{ m}^2$  and  $99.5 \text{ g m}^{-2}$  for *L. corymbulosa* Eq. (2).

### 3 Results

#### 3.1 Exchange of ethanol and acetaldehyde under non-flooded conditions

5 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. corymbulosa* and *P. glomerata*. Analysis of this 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* ( $0.24 \text{ cm s}^{-1}$ ) was more than twice that of *L. corymbulosa* ( $0.08 \text{ cm s}^{-1}$ ), following the interspecies differences in stomatal conductance for  $\text{CH}_3\text{CHO}$  ( $0.05$  vs  $0.03 \text{ cm s}^{-1}$ ). In both species, deposition velocity exceeded values of stomatal conductance normalized for  $\text{CH}_3\text{CHO}$ , indicating that deposition to the leaf cuticles also occurred in addition to stomatal uptake.

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## 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. Whilst 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, never exceeding  $5 \text{ nmol m}^{-2} \text{ min}^{-1}$ , and with the less 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  $304 \pm 7$  and  $525 \pm 18 \text{ nmol m}^{-2} \text{ min}^{-1}$  for the two specimens, respectively, as observed on the third day of the flooding period. Measured ethanol emissions were considerably lower, showing peak values of  $92 \pm 9$  and  $134.8 \pm 8 \text{ nmol m}^{-2} \text{ min}^{-1}$ . Induced ethanol and acetaldehyde emissions of *P. glomerata* were substantially lower, reaching maximum values of  $58 \pm 10$  and  $36 \pm 3 \text{ nmol m}^{-2} \text{ min}^{-1}$ , respectively.

In contrast to the other tree species *T. juruana* emitted predominately ethanol. While maximal ethanol emission rates of  $110 \pm 6 \text{ nmol m}^{-2} \text{ min}^{-1}$  were similar to those of *L. corymbulosa*, acetaldehyde emission were an order of magnitude lower, reaching  $48 \pm 5 \text{ nmol m}^{-2} \text{ min}^{-1}$  at maximum. Also the emission pattern of *T. juruana* was different to that of the other species. Following the emission burst in the morning, *T. juruana* continued to emit ethanol and acetaldehyde in the afternoon hours, albeit at low rates (maximal  $35 \pm 7$  and  $6.3 \pm 3.9 \text{ nmol m}^{-2} \text{ min}^{-1}$ , 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, stomata of *P. glomerata* and *L. corymbulosa* regularly closed in the afternoon, while stomatal conductance of *T. juruana* was not negatively affected by flooding until day

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6, and stomata remained open throughout the entire day. Although this demonstrates the role of stomata in emission regulation, in none of the species diurnal emission variability was directly correlated with variations in stomatal conductance.

### 3.3 Temporal pattern of induced ethanol and acetaldehyde emissions

5 For all 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. Figures 4a and b show the species specific differences in the temporal profiles of daytime integrals of ethanol and acetaldehyde emissions, as well as that of physiological activities. Varying temperature  
10 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 constantly 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.

20 All other species investigated responded to the decreasing O<sub>2</sub> 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.

25 *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

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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.

5 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 und flooded conditions. Towards 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.

15 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  $9.5$  and  $15.4 \text{ nmol m}^{-2} \text{ min}^{-1}$  were substantially lower as compared to the three days before ( $33.9 \pm 2.9$  and  $48.8 \pm 13.9 \text{ nmol m}^{-2} \text{ min}^{-1}$ , 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

25 Although an ethanol recovery by metabolic oxidation processes in the leaf should principally lead to a final product like acetic acid, a significant emission of acetic acid occurred only in *L. corymbulosa*, whereas *S. martiana* and *T. juruana* predominantly showed a 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

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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  $11.8 \text{ nmol m}^{-2} \text{ min}^{-1}$  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 a deposition of acetic acid before and during 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 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 ( $0.1 \text{ cm s}^{-1}$ ) and *T. juruana* the highest values ( $0.21 \text{ cm s}^{-1}$ ), 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 cuticular deposition was negligible and that the uptake is largely under stomatal control.

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## 4 Discussion

### 4.1 OVOC exchange behavior as influenced by flooding

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 and 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). 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 acetic acid uptake was completely under stomatal control, for acetaldehyde an additional deposition to leaf surfaces had to be taken into account to explain the observed deposition velocities. Consistent with previous studies on the uptake of acetaldehyde (Rottenberger et al., 2004) the present results support the view that leaf surfaces can represent an additional non-stomatal sink for acetaldehyde. 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 hydrophobic cuticle.

In all investigated tree species flooding of the root system induced leaf emissions of

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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 they 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/or 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 sol-

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5 ability (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

10 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., 2002 a, b; De Simone, 2002). Based on these studies we found evidence that those tree species with developed anatomical structures allowing for an improved O<sub>2</sub> 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 potential oxidation products.

20 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<sub>2</sub> 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

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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. 2002 a, 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. corymbulosa* responded with highest ethanol and acetaldehyde emissions 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

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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 that 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. The adaptation mechanisms to long term flooding, resulting in reduced leaf emissions, imply all factors that influence the alcoholic fermentation rate. 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 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 overseen 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 using root ADH activity as a

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proxy. 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 did not determine leaf enzyme activities but 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 mixture 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). 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 ( $7.0 \text{ Pa m}^3 \text{ mol}^{-1}$ ) is much higher than that of ethanol ( $0.5 \text{ Pa m}^3 \text{ mol}^{-1}$ ) and acetic acid ( $0.01 \text{ Pa m}^3 \text{ mol}^{-1}$ ) (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 behav-

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5 iors 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 was higher for this species than for *L. corymbulosa*. These findings indicate that leaf enzyme activities may have a strong impact on the emission behavior. However, 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

20 The ecological importance of foliar ethanol metabolism might not only be avoidance of toxic levels of ethanol and acetaldehyde, but may also be a contribution to energy and carbon metabolism. <sup>14</sup>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. For *L. corymbulosa* with highest emissions and a low photosynthetic CO<sub>2</sub> gain, the C-loss accounted for about 1% even without taking into account the underestimation of ethanol by PTR-MS. This is in the same order of magnitude as the C-loss through isoprene and monoterpene emissions (Harley et al., 1999; Kesselmeier et al.,

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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<sub>2</sub> 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  $4\,000\text{ nmol m}^{-2}\text{ min}^{-1}$  of acetaldehyde and ethanol, respectively) were much larger than those observed for the flooding tolerant Amazonian trees species in the present study ( $3\text{--}200\text{ nmol}$  and  $5\text{--}500\text{ nmol m}^{-2}\text{ min}^{-1}$  of acetaldehyde and ethanol, respectively) and much larger than flooding tolerant and intolerant European tree species ( $\sim 100\text{--}1\,000\text{ nmol m}^{-2}\text{ min}^{-1}$  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

The results obtained in course of the greenhouse experiments on individual Amazonian floodplain tree species during inundation provide evidence that floodplain forests

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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.

5 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 plants 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. Confirmation and characterization of such an emission behavior of flood plain forests may significantly contribute to our understanding of floodplain forests and their impact on atmospheric chemistry processes.

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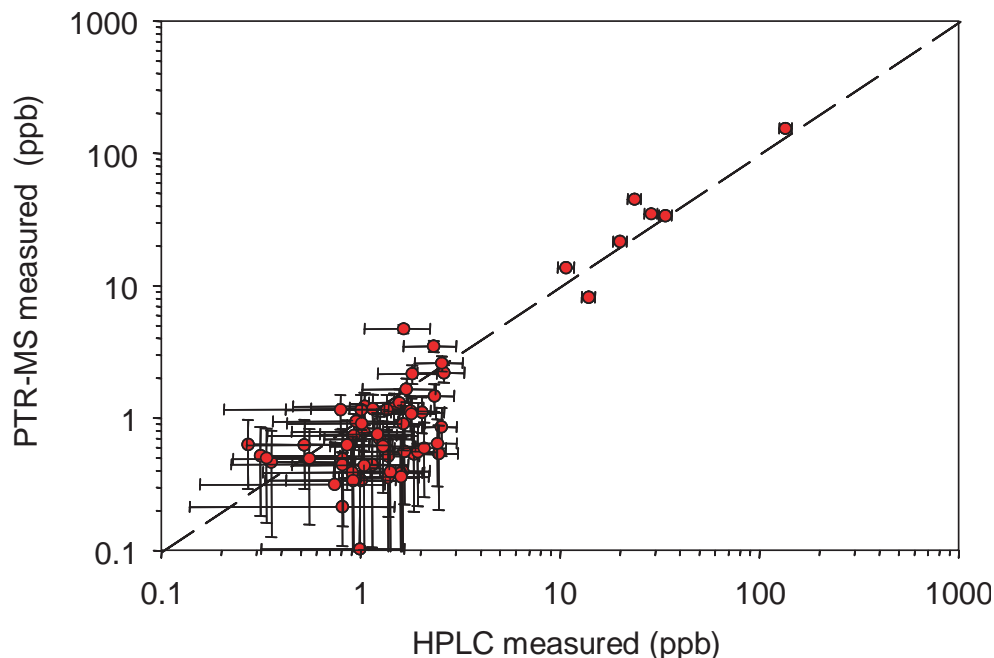
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**Fig. 1.** Comparison between PTR-MS and HPLC acetaldehyde data obtained during branch cuvette measurements in the second flooding experiment. Only simultaneously sampled data were considered. HPLC data represent concentration measurements integrated 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 1 s integration time.

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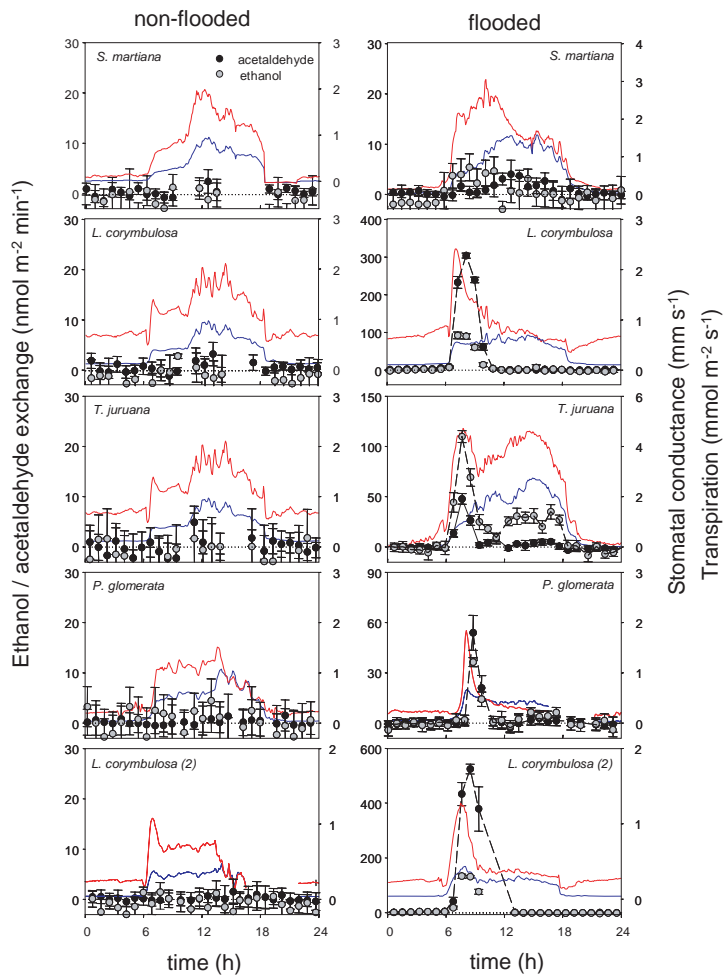


Fig. 2.

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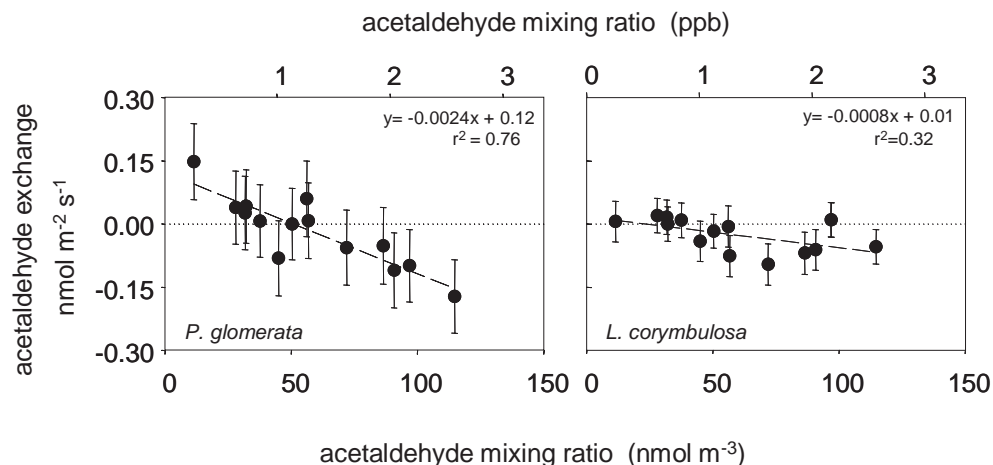
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**Fig. 2.** Effect of flooding on the exchange of ethanol (grey circles) and acetaldehyde (black circles) for the four Amazonian floodplain tree species investigated within the two flooding experiments. Shown are diurnal courses of exchange rates, 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  $\pm$  SD of 1 min PTR-MS measurements. Note the different scales used for emission rates during flooding.



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

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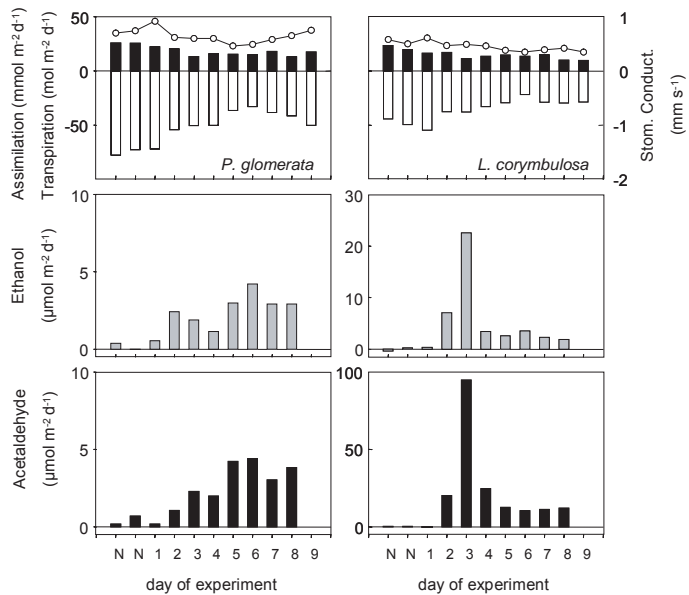
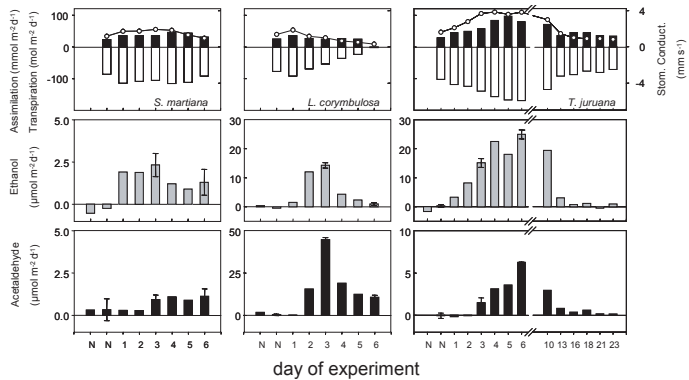


Fig. 4.

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**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 upper panels show daytime integrals of assimilation (open bars) and transpiration (hatched bars), together with average stomatal conductance (circles). The middle and bottom panels show daytime integrals of ethanol (grey bars) and acetaldehyde emissions (black panels). **(a)** *S. martiana* and *L. corymbulosa* and *T. juruana* investigated in experiment 1. **(b)** *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<sub>2</sub> and H<sub>2</sub>O exchange data. CO<sub>2</sub> 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.

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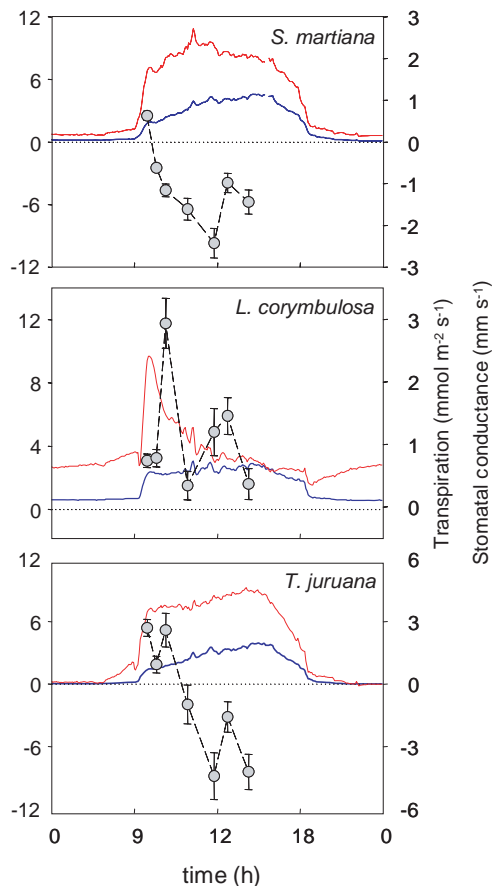
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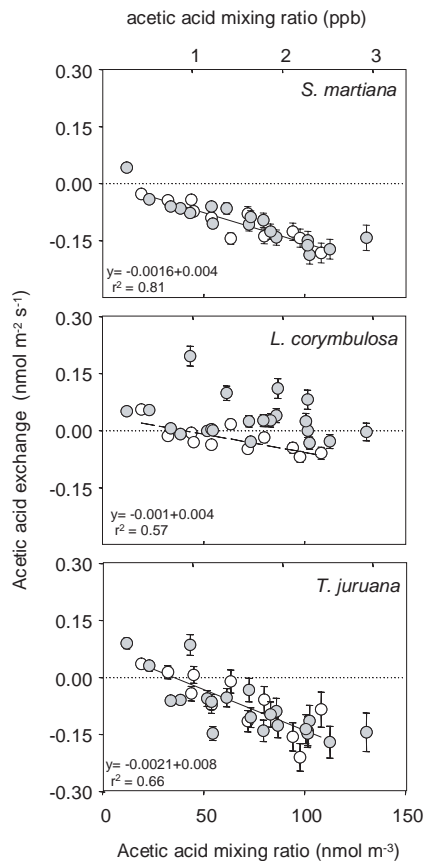


**Fig. 5.** Diurnal acetic acid (grey circles) exchange pattern, transpiration (blue line), and stomatal conductance (red line) of three simultaneously investigated Amazonian floodplain tree species on day 3 of flooding. Organic acid exchange was determined by cryo-trapping and subsequent IC analysis.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

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**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.

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