*Biogeochemistry* **48:** 199–216, 2000.


# Influence of environmental factors on the emissions of gaseous formic and acetic acids from orange (*Citrus sinensis* L.) foliage

MICHAEL STAUDT*, ANNETTE WOLF & JÜRGEN KESSELMEIER
*Max Planck Institute for Chemistry, Biogeochemistry Department, PO Box 3060, 55020 Mainz, Germany (*Present address: CEFE-CNRS, 1919, route de Mende, F-34293 Montpellier Cedex 5, France; e-mail: staudt@cefe.cnrs-mop.fr)*

Received 17 February 1999; accepted 23 February 1999

**Key words:** acetic acid, biogenic VOC emission, *Citrus*, formic acid, organic acids, orange

**Abstract.** Gaseous acids can be emitted as well as taken up by plant foliage, but little is known about the influence of environmental factors on the exchange process. In a laboratory study we investigated the short-term effects of temperature and light on the exchange of acetic and formic acids between orange foliage and the atmosphere. The results were compared with diurnal exchange cycles obtained with the same species under field conditions. In the field, the exchange of volatile acids showed pronounced diurnal variations with maximum emissions of about 0.15 nmol $m^{-2}$ projected leaf area $s^{-1}$ for acetic acid and 0.3 nmol $m^{-2}$ $s^{-1}$ for formic acid during noon and afternoon and with acid deposition of up to 0.1 nmol $m^{-2}$ $s^{-1}$ for both acids during early morning and night. Under laboratory conditions no significant acid deposition (<0.01 nmol $m^{-2}$ $s^{-1}$) could be observed, and emission rates were lower than in the field and ranged around 0.035 nmol $m^{-2}$ $s^{-1}$ (SD = 0.013) for acetic acid and about 0.08 nmol $m^{-2}$ $s^{-1}$ for formic acid (SD = 0.033) at 30 °C and 1000 $\mu$mol $m^{-2}$ $s^{-1}$ PAR. A clear positive response of acid release to light could be observed. Emissions were very low in darkness and strongly increased with light up to 1000 $\mu$mol $m^{-2}$ $s^{-1}$ PAR. The emission response to light occurred within our hour and was also observed with other acids emitting plant species investigated. Response of emission to temperature was more variable, though, on the whole, the effect was also positive. Finally, we observed a diurnal rhythm in acid release which was not related to other measured climatic or physiological parameters. We conclude that in the short-term the exchange of volatile acids between leaves and air under natural conditions is stimulated by light and, somewhat, by temperature, while a leaf-internal process promotes acid release in the morning and higher acid concentrations in ambient air promote acid deposition.

## Introduction

The occurrence of organic acids in the atmosphere, biosphere, soils, and hydrosphere is well documented (Graedel & Weschler 1981; Keene & Galloway 1988). Rain water pH in remote areas is significantly influenced

by atmospheric organic acids, mainly formic and acetic acids (Andreae et al. 1987, 1988; Kawamura & Kaplan 1986; Likens & Galloway 1983; Lunde et al. 1977; Norton et al. 1983). In contrast, in anthropogenically dominated regions sulfuric and nitric acids influence the rain water pH in more polluted areas. Organic acids even significantly contribute to the acidity in industrial regions (Andreae et al. 1988; Keene et al. 1983; Keene & Galloway 1984; Kesselmeier et al. 1998a). A large data set for near-surface measurements over the European continent has been compiled by Puxbaum and co-workers (Puxbaum et al. 1988; Winiwarter et al. 1988).

Potential sources of organic acids are still under investigation. Biogenic emissions from vegetation, directly or indirectly (oxidation of precursors), are a dominant source of tropospheric organic acids (Andreae et al. 1987, 1988; Berresheim et al. 1988; Chameides & Davis 1983; Helas et al. 1988; Jacob 1988; Jacob & Wofsy 1988; Hartmann et al. 1989; Keene & Galloway 1986; Kesselmeier & Staudt 1999; Madronich et al. 1990). Talbot et al. (1995), however, assumed decomposition of isoprene or other nonmethane hydrocarbons not to be a dominant source of these acids in the midlatitude continental atmosphere. There is growing evidence that formic acid as well as acetic acid are directly emitted by vegetation (Bode 1994; Bode et al. 1996; Kesselmeier et al. 1991, 1997, 1998a; Schäfer et al. 1992, 1995; Talbot et al. 1990). These studies revealed that the exchange of those acids exhibit day-night cycles, similar to those of $CO_2$ and $H_2O$ gas exchanges, and demonstrated that the net release of acids is positively influenced by light and temperature, as reported for other biogenic VOCs (e.g. Guenther et al. 1993; Kesselmeier et al. 1998b; Kesselmeier & Staudt 1999; Staudt & Bertin 1998). However, light and temperature strongly covary over day-night cycles, so that the influence of individual factors is not yet known. In the present study we investigated the emissions of formic and acetic acids from young orange trees (*Citrus sinensis* var. Nave Late), a species widely cultivated in Mediterranean regions. In particular we examined the short-term influences of temperature and light on acid exchange under controlled laboratory conditions, and we compared the results with diurnal exchange cycles measured under natural field conditions. Furthermore, we studied some other plant species for a direct comparison.

## Experimental

Laboratory experiments were conducted from beginning November to middle December 1997, and field measurements from 7–20 June 1997. The principal plant species under investigation was *Citrus sinensis* L. var. Navel Late originating from Burriana (north of Valencia, Spain). Field measurements were made on the canopy top of an approximately 15-year-old tree in an

orange orchard at Burriana, and laboratory measurements on an approximately 7-year-old potted orange tree. All investigations were performed on the green foliage of the species without fruits and flowers. In the laboratory, some additional tests were performed on foliage of three other plant species, such as 5–6-year-old seedlings of *Pinus pinea* L. (Stone pine) and *Quercus ilex* L. (Holm oak), and the crassulaceae *Aeonium glutinosum* (Ait.) W.&B. (Viscid houseleek). All seedlings were planted in 7-l plastic pots with commercially available plant soil, regularly watered, and occasionally fertilized (Guano, Compo, Germany) during the growing season. From spring to fall, plants were grown outside in front of a south-exposed wall of the institute building. During the experiments seedlings were kept indoors at a cool and sunny place.

Acid, $CO_2$, and $H_2O$ gas exchanges were determined by mounting the distal end of a branch in a dynamic plant enclosure system (Kesselmeier et al. 1996, 1997, 1998a). Each chamber consisted of a cylindrical Teflon bag sustained by a frame and was equipped with a Teflon fan placed at the top. In the laboratory we used a 5-l chamber flushed with pressurized, purified, and humidified air containing known concentrations of volatile acids (0.1 to 1.5 ppb). The field chamber had a volume of approximately 70 liters and was flushed with ambient air soaked from the branch insertion port at the chamber bottom. Acid concentrations in ambient air typically ranged between 0.3 and 5 ppb. Air residence times in chambers were around 1 min in lab and 2.5 min in field. Photosynthetically active radiation (PAR) was measured by quantum sensors (SB 190, Li-COR, U.S.A.) positioned outside on the chamber frame. Leaf temperature was measured on two leaves inside the chamber, one at the top and the other at the bottom, by attaching microthermocouples (Type TT-E-36, Newport Electronics, U.K.) at the abaxial leaf epidermis. Air temperatures were measured close to the leaf temperature sensors using the same type of thermocouples. Under well-ventilated conditions, leaf-to-air temperature differences were always small ($<0.5$ °C), but a 2–3 °C temperature gradient between the top and the bottom of the chamber appeared under strong illumination. For all calculations, we used the mean temperature of all air and leaf sensors. Mixing ratios of $CO_2$ and $H_2O$ were measured by an infrared dual-channel gas analyzer (Li-COR 6262, U.S.A.), and relative humidity by a thermo-hygrometer (Rotronics YA-100F, Walz, Germany). All data were recorded as 5-min averages by a data logger (Campbell, CSI Ltd, model 21X, U.K.). Transpiration, photosynthesis (net $CO_2$ assimilation), and stomatal conductance for water vapor were calculated according to von Caemmerer and Farqhuar (1981). In the laboratory an adjustable light source (Kobold DLF 1200 with Osram HMI 1200 W, Wolfratshausen, Germany) was installed above the chamber, providing a light intensity of up to 2000 $\mu$mol

photons $m^{-2}$ $s^{-1}$ PAR at chamber level. Chamber temperature was manually controlled by external heating or cooling of the chamber with commercial fan heaters. Outside, the measurement chamber and plant were maintained at room temperature and illuminated with 1000 $\mu$mol $m^{-2}$ $s^{-1}$ PAR from 800h to 1700h.

Volatile acids were trapped cryogenically at $-70$ °C and analyzed by ion-exchange chromatography on a Shimadzu HIC-6A ion chromatograph equipped with a Dionex IonPac AS 11.4 mm column, an electrochemical Dionex micomembrane suppressor, and a conductivity detector (Hofmann et al. 1997). Exchange rates of volatile acids were calculated from the concentration difference between the air entering and leaving the chamber, multiplied by chamber flow rate and divided by the projected leaf area. With foliage enclosed in the chambers, the mixing ratios ranged between 0.1 and 3.0 ppb in the laboratory and between 0.2 and 4.4 ppb in the field. Adsorption of gaseous acid and contamination by chamber material was regularly monitored on empty chambers. No adsorption occurred, but a slight contamination was observed, which tended to decrease during the experiment and was not influenced by light and temperature treatments. All emission rates were corrected for chamber contamination measured in the absence of foliage.

Projected leaf area and leaf dry weight were determined at the end of the experiments. Leaf area was measured by a calibrated scanner system (ScanJET IICX with DeskSCAN II, both HP, USA, and SIZE 1.10R, M. Müller, Germany), and dry weights by a microbalance (PM400, Mettler-Toledo, Germany) after drying for seven days in a ventilated oven at 95 °C. In the laboratory, all investigated foliage consisted of fully developed leaves of the current year. In the field, about half of the enclosed orange foliage consisted of old mature leaves, while the other half were young expanding or maturing leaves. Maturity was defined as the point when leaves reached full size and became dark green and more sclerophyllous. After two weeks of the experiment, almost all young leaves were fully developed and mature. Leaf area and biomass increase of enclosed foliage were assessed by measuring the leaf growth on nearby foliage. For further recalculations the following mean specific leaf weights (g leaf dry weight/$m^2$ leaf area) can be used: 109 (*Citrus sinensis*, laboratory), 140 (*Citrus sinensis*, field), 214 (*Pinus pinea*), 133 (*Quercus ilex*) and 131 (*Aeonium glutinosum*).

## Results

### *Laboratory experiments*

#### *General*

The enclosed foliage was physiologically active throughout all experiments. Under light conditions, photosynthesis, transpiration and stomatal conductance changed continuously at approximately hourly (more or less regular) cycles. The cycles probably resulted from the oscillation of stomatal aperture, reported for many plants, including *Citrus* species (Cowan 1972). Under saturating light, photosynthesis ranged between 2 and 6 $\mu$mol $m^{-2}$ $s^{-1}$ and transpiration between 0.4 and 1.2 mmol $m^{-2}$ $s^{-1}$. Photosynthesis saturated in the range of 600 to 1100 $\mu$mol $m^{-2}$ $s^{-1}$ PAR.

Exchange rates of volatile acids between foliage and atmosphere were repeatedly determined under the same standard temperature and light conditions (30 °C and 1000 $\mu$mol $m^{-2}$ $s^{-1}$). For the same branch, exchange rates varied considerably from one day to the next as well as during the day. This variability, which was only partly due to variable background concentrations, was higher for formic than for acetic acid, though in many cases both acids behaved identically. The average emission rates at 30 °C and 1000 $\mu$mol $m^{-2}$ $s^{-1}$ PAR ($n$ = 37) were about 0.035 nmol $m^{-2}$ projected leaf area $s^{-1}$ (SD = 0.013) for acetic acid and about 0.08 nmol $m^{-2}$ $s^{-1}$ for formic acid (SD = 0.033). For none of the light and temperature conditions used, did we observe any significant net acid deposition (negative emission rates).

#### *Influence of temperature and light on acid exchange*

In eight experiments we tested the influence of temperature and light on the exchange of volatile acids. In four experiments, temperature was stepwise increased or decreased between 15 and 40 °C with 5 °C increments, at constant light (1000 $\mu$mol $m^{-2}$ $s^{-1}$ PAR). In four further experiments, light varied between 0 and 1600 $\mu$mol $m^{-2}$ $s^{-1}$PAR at 30 °C. Single experiments lasted between 6.5 and 9.5 hours, depending on sampling time (45–55 min) and equilibration time (10–45 min). Figure 1 shows time series of emission, temperature, and PAR for each experiment. Emission response to increasing or decreasing temperature was variable (Figure 1, left panels). In two experiments (triangles and lozenges), the diurnal course of emissions seemed to be independent of the increase of temperature. In the two other experiments (squares and dots), emissions increased or decreased with increasing or decreasing temperature, following a sigmoid response curve.

Emission response to increasing or decreasing light was less variable (Figure 1, right panels) for acetic acid emission which increased or decreased with increasing or decreasing light intensity. For formic acid, the emission

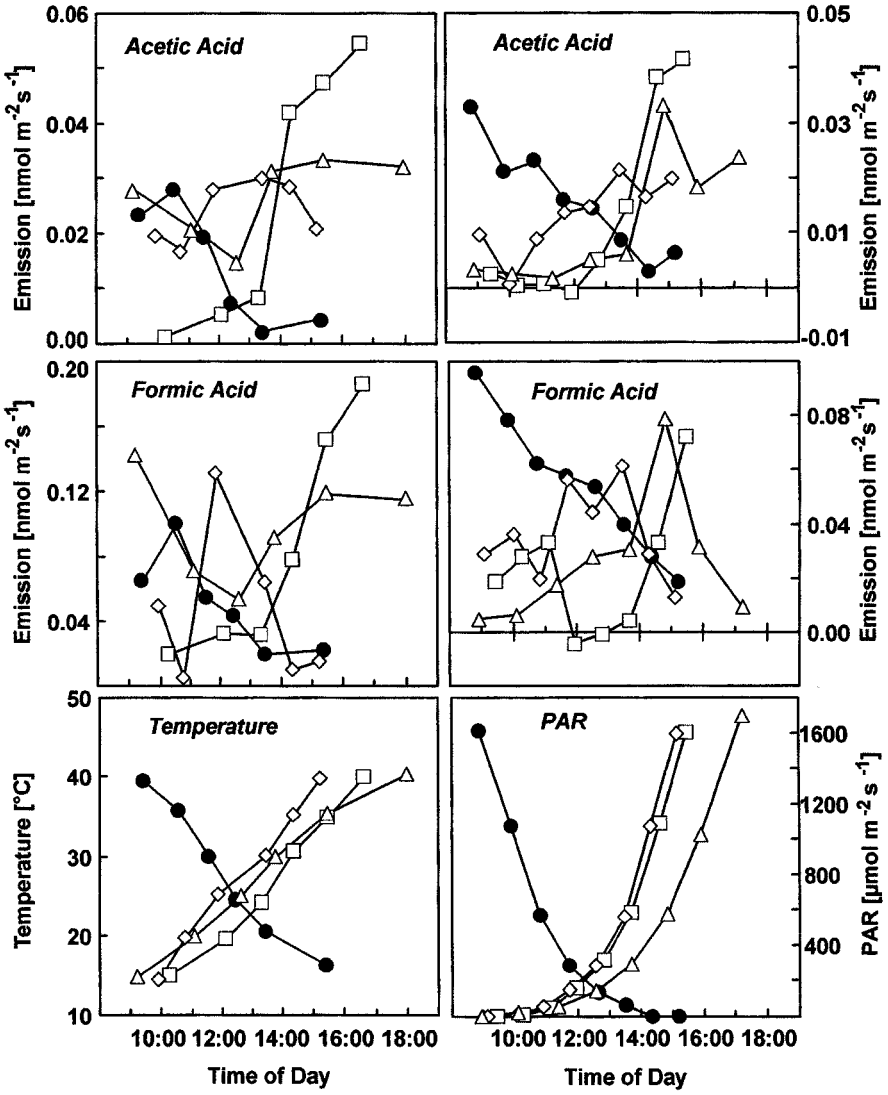


*Figure 1.* Time series of acid emissions from orange foliage in response to the variations of temperature (left panels) and light (right panels). In four experiments (denoted by different symbols) temperature was stepwise increased (open symbols) or decreased (closed symbols) between 15 and 40 °C at constant light ($1050 \pm 50$ $\mu$mol $m^{-2}$ $s^{-1}$ PAR; left panels). In four other experiments light was stepwise increased (open symbols) or decreased (closed symbols) between 0 and 1600 $\mu$mol $m^{-2}$ $s^{-1}$ PAR at constant temperature ($30 \pm 1$ °C; right panels).

time series followed the light course only at decreasing light intensity (black dots). With increasing light intensity, emissions were either relatively high in the morning (squares) or low in the evening (triangles and lozenges).

Figure 2 shows acid emissions, transpiration and photosynthesis at constant light and changing temperature (left panels) and at constant temperature and changing light (right panels). Each data set includes the results of the four experiments described above, plus other measurements made at the respective light or temperature level. The response of acid emissions to temperature was scattered, in particular for formic acid (Figure 2(A, C)). Nevertheless, higher temperature appears to stimulate acetic acid emission between 15 and 40 °C. By contrast, photosynthesis and transpiration as well as stomatal conductance (data not shown) were maximal at the lower temperatures and declined above 30 °C. Light, on the other hand, stimulated acid emission and $CO_2$ and $H_2O$ gas exchanges in a similar manner (Figure 2, right panels). Acid emissions were variable for a given light intensity, but the overall data distribution suggested a continuous increase with light up to 1000 $\mu$mol $m^{-2}$ $s^{-1}$ PAR. Beyond 1000 $\mu$mol $m^{-2}$ $s^{-1}$, acid release did not further increase but rather leveled off or even decreased. Because emissions strongly varied around 1000 $\mu$mol $m^{-2}$ $s^{-1}$, the behavior of the emission response to light could not be established from the data. However, for acetic acid most data at 1000 $\mu$mol $m^{-2}$ $s^{-1}$ PAR ranged between 0.02 and 0.04 nmol $m^{-2}$ $s^{-1}$, and only three data points were above 0.05 nmol $m^{-2}$ $s^{-1}$. Considering these points as outliers, the response to light could be roughly described by a saturation curve using an algorithm originally developed for the light dependence of isoprene emissions (Guenther et al. 1993; line drawn in Figure 2). The curve was fitted to acetic acid emission data by nonlinear regression analysis according to Marquardt (1963).

*Light-transition experiment and preliminary tests on other plant species*

As we observed a light dependency of volatile acid emissions by orange foliage, we investigated three further evergreen plant species (i.e., *Pinus pinea*, *Quercus ilex* and *Aeonium glutinosum*) in order to know whether the light dependence of acid exchange is a common phenomenon within terrestrial vegetation. Table 1 shows average exchange rates at approximately 30 °C under light and dark conditions for all four plant species studied. Under light conditions, all plants except *Pinus pinea* emitted acetic and formic acids at similar ratios (approximately 1:3). Highest emission rates were found for the crassulacee (*A. glutinosum*) and lowest for the pine (*P. pinea*). All emissions except those of pine were significantly stimulated by light. The emission rates of pine were also higher under light conditions but very variable and, hence, not significantly different from values measured in the dark.

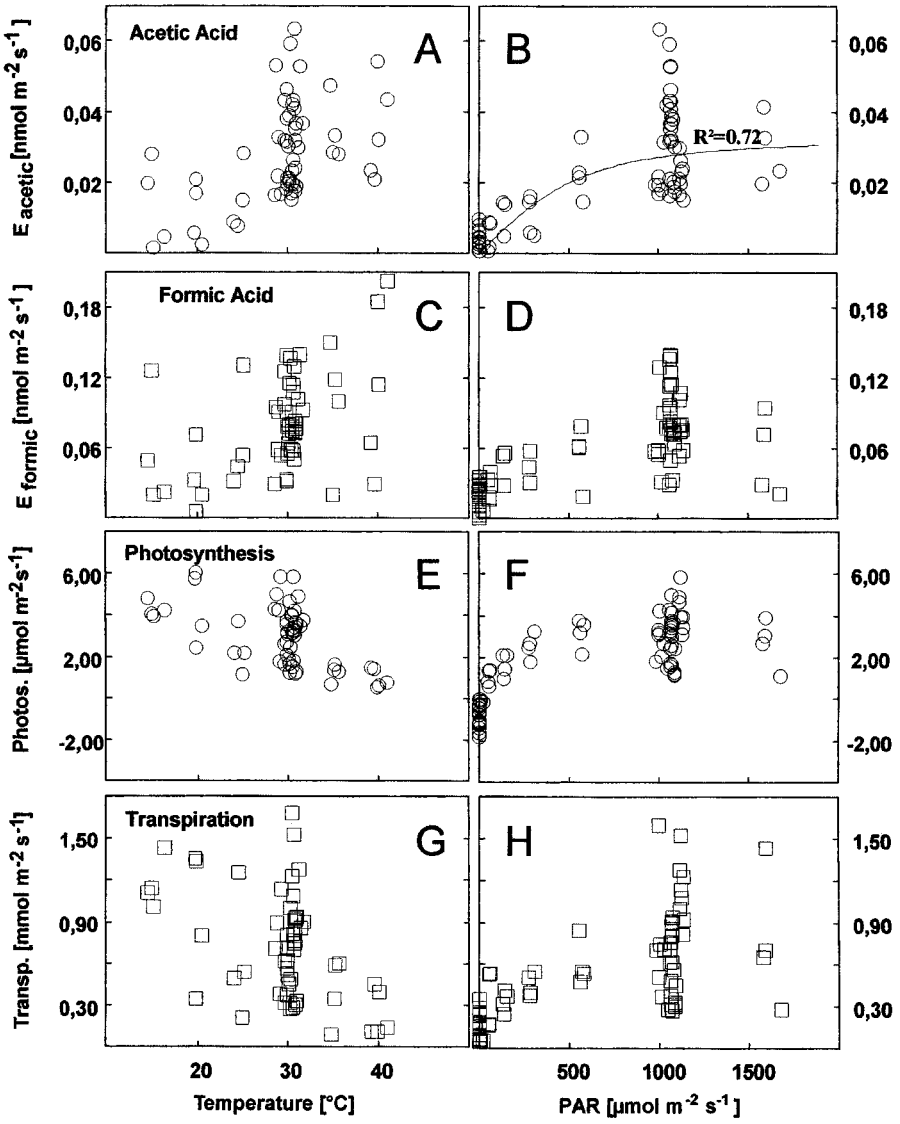


*Figure 2.* Dependency on temperature (left panels) and light (right panels) of emissions of acetic acid (A, B) and formic acid (C, D), photosynthesis (E, F) and transpiration (G, H) from orange foliage. Constant light was 1050±50 $\mu$mol m$^{-2}$ s$^{-1}$ PAR and constant temperature was 30±1 °C respectively. The line in the upper right panel stimulates the light response curve of acetic acid emissions using the equation $E = C_{L1} \times C_{L2} \times \mathrm{PAR}/\sqrt{1 + C_{L1}^2 \times \mathrm{PAR}^2}$ (Guenther et al. 1993). $C_{L1}$ (0.319) and $C_{L2}$ (0.00159) are empirical parameters estimated by best-fit regression excluding the three data points above 0.5 nmol m$^{-2}$ s$^{-1}$ ($n$ = 74, $R^2$ = 0.72).

*Table 1.* Mean acid exchange rates ± standard deviations ($n$ = 3) from 4 evergreen species under light and dark conditions (1050 and 0 $\mu$mol $m^{-2}$ $s^{-1}$ PAR). Asterisks following exchange rates in the dark indicate significant differences from values in the light (bilateral $t$-test according to Sachs 1988). Significance levels: *** $P < 0.001$; ** $0.001 < P < 0.010$; * $0.010 < P < 0.050$; not significant $P > 0.050$.

| | Light | | | Dark | | |
|---|---|---|---|---|---|---|
| | Temp. °C | $E_{acetic}$ nmol $m^{-2}$ $s^{-1}$ | $E_{formic}$ nmol $m^{-2}$ $s^{-1}$ | Temp. °C | $E_{acetic}$ nmol $m^{-2}$ $s^{-1}$ | $E_{formic}$ nmol $m^{-2}$ $s^{-1}$ |
| *Citrus sinensis* | 29.5 | 0.036 ± 0.006 | 0.104 ± 0.019 | 29.9 | $-0.004^{**}$ ± 0.006 | $0.004^{***}$ ± 0.005 |
| *Quercus ilex* | 30.9 | 0.030 ± 0.008 | 0.105 ± 0.013 | 31.0 | $-0.017^{***}$ ± 0.003 | $0.013^{***}$ ± 0.002 |
| *Pinus pinea* | 30.6 | 0.010 ± 0.019 | 0.078 ± 0.082 | 29.1 | $-0.006^{n.s.}$ ± 0.013 | $0.018^{n.s.}$ ± 0.039 |
| *Aeonium glutinosum* | 30.9 | 0.059 ± 0.013 | 0.142 ± 0.023 | 30.0 | $0.002^{**}$ ± 0.012 | $0.012^{**}$ ± 0.005 |

A light-transition experiment was performed to test whether the time needed for emissions to stabilize lasts longer than the measuring frequency applied in our experiments. If the light induction proceeds slowly, the observed variability in the emission responses (Figure 1) could result from the differences of the rapid illumination changes during single experiments (length of sampling plus the equilibration time ranged between 55 and 80 min). Figure 3 shows acid exchange rates during a light-to-dark and dark-to-light transition on two consecutive days. On each day, light was switched on or off after the third measurement immediately before the fourth measurement started. On both days, measurements started at 1000h and ended at 1700h with a measurement frequency of 60 min. For the light-to-dark transition, emission already decreased under constant light and immediately dropped further when light was switched off. For the dark-to-light transition, emissions immediately recovered after light was switched on. These results suggest that the response of acid release to light proceeds faster than one hour. It is therefore unlikely that the observed variability in the emission responses (Figure 1) was due to differences in the rapidity of light changes. The experiment was repeated with *Quercus ilex*, yielding the same result (data not shown).

*Influence of other factors than temperature and light*

To understand the variability of emission from orange foliage, emission data obtained under the same temperature and light conditions of 30 °C and 1000 $\mu$mol $m^{-2}$ $s^{-1}$ PAR were pooled and analyzed for correlation to other factors and variables such as relative air humidity, net photosynthesis, transpiration, stomatal conductance as well as hour and date of measurement (data not shown). No correlation to either $CO_2$ and $H_2O$ gas exchanges or air humidity could be observed. Instead, a negative correlation between the emission rates of both acids and the time of day at which the acids were collected was indicated (see also first three measurements under light conditions in Figure 2). This was further confirmed by continuously monitoring emissions at constant light and temperature from 1000h to 1600h (Table 2). Emission rates were highest at the time of the first measurement in the morning and then progressively declined (Table 2). $CO_2$ and $H_2O$ gas exchanges did not show a similar trend.

*Field measurements*

In the field, the exchange of acids between orange foliage of mature trees and air were monitored over several days. Figure 4 displays acid, $CO_2$, and $H_2O$ exchanges as well as climate data of two days. $CO_2$ and $H_2O$ gas exchanges showed typical diurnal profiles with values of the same order as

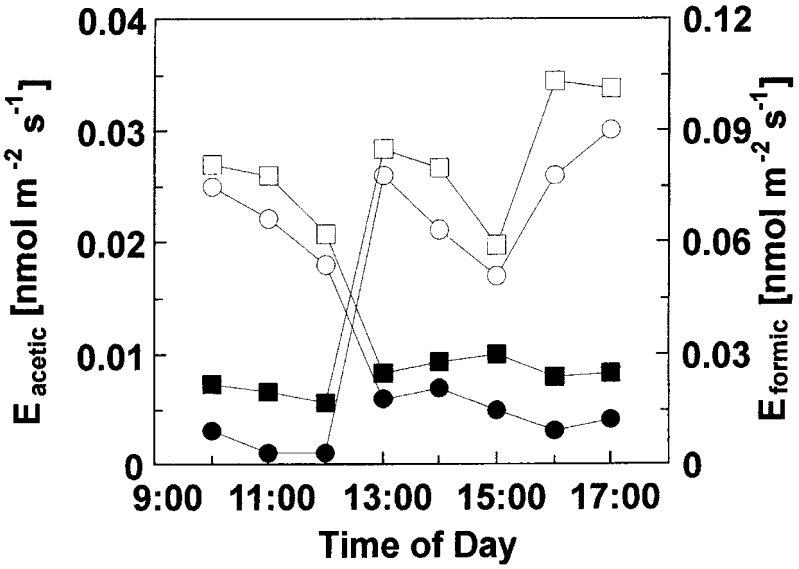


*Figure 3.* Emission of acetic (circles) and formic (squares) acids measured on two successive days during light-to-dark and dark-to-light transitions. Open symbols indicate emissions during the light periods (PAR = 1130 $\mu$mol $m^{-2}$ $s^{-1}$) and closed symbols represent dark emissions (PAR = 0). Temperature was constant ($30 \pm 0.5$) during the whole experiment. Under light conditions, average photosynthesis and transpiration rates were $3.5 \pm 0.4$ $\mu$mol $m^{-2}$ $s^{-1}$ and $1.0 \pm 0.2$ mmol $m^{-2}$ $s^{-1}$, respectively on the first day, and $5.0 \pm 0.8$ $\mu$mol $m^{-2}$ $s^{-1}$ and $1.2 \pm 0.2$ mmol $m^{-2}$ $s^{-1}$ respectively on the second day. During dark periods, photosynthesis and transpiration rates were $-1.3 \pm 0.3$ $\mu$mol $m^{-2}$ $s^{-1}$ and $0.2 \pm 0.1$ mmol $m^{-2}$ $s^{-1}$, respectively.

*Table 2.* Diurnal development of acid emissions ($E_{acetic}$, $E_{formic}$), net photosynthesis (A), transpiration (Tr) and stomatal conductance ($gH_2O$) from orange foliage under constant temperature ($30.4 \pm 0.5$ °C) and light ($1075 \pm 2$ $\mu$mol $m^{-2}$ $s^{-1}$ PAR). Relative air humidity was $39 \pm 3$%. Sampling time for acids was 50 min for each measurement. Other values are averaged over the sampling period.

| Local time | $E_{acetic}$ nmol $m^{-2}$ $s^{-1}$ | $E_{formic}$ nmol $m^{-2}$ $s^{-1}$ | A $\mu$mol $m^{-2}$ $s^{-1}$ | Tr mmol $m^{-2}$ $s^{-1}$ | $gH_2O$ mmol $m^{-2}$ $s^{-1}$ |
|---|---|---|---|---|---|
| 1000 | 0.063 | 0.140 | 2.9 | 0.44 | 30 |
| 1100 | 0.047 | 0.092 | 3.1 | 0.45 | 31 |
| 1200 | 0.053 | 0.095 | 4.1 | 0.43 | 42 |
| 1300 | 0.035 | 0.083 | 3.1 | 0.42 | 34 |
| 1400 | 0.032 | 0.073 | 2.5 | 0.45 | 35 |
| 1500 | 0.037 | 0.076 | 2.7 | 0.46 | 34 |
| 1600 | 0.040 | 0.050 | 2.4 | 0.46 | 29 |

those measured in the lab. The acid exchanges also exhibited a pronounced diurnal profile with net acid deposition during morning and night and with maximum emission rates during noon and afternoon. On the first day, a sole maximum of acid emission was observed around 1300h co-occurring with the maximum of temperature and light. On the second day, two emission peaks were found, one around 1100h and one around 1600h. Typically, from 600h to 800h, under a still stable thermal stratification, high acid concentrations of up to 5 ppb were observed in ambient air, likely caused by anthropogenic sources, such as biomass burning by farmers in the surrounding area. As a consequence, the acid emissions calculated on background concentrations were low or negative (net deposition). Around 900h, air turbulence developed, causing ambient concentrations to drop, leading to an emission. Maximum emissions were about 0.15 nmol $m^{-2}$ $s^{-1}$ for acetic acid and 0.3 nmol $m^{-2}$ $s^{-1}$ for formic acid, and the maximum deposition was about 0.1 nmol $m^{-2}$ $s^{-1}$ for both acids. Peak emission rates were about four times higher than those found in the lab.

## Discussion

To our knowledge, the work presented in this paper is the first attempt to study the short-term effects of temperature and light on acid exchange between foliage and air under controlled conditions. For orange foliage light exerts a positive influence on acid release and appears to be a factor controlling the day-night cycles of acid exchange in natural conditions. In the laboratory, acid emission rates were very low or even negative in darkness and strongly increased with increasing light up to 1000 $\mu$mol $m^{-2}$ $s^{-1}$ PAR (Figures 1, 2). The emission from orange foliage responded to light within an hour, as in other acid-emitting plant species (Tables 1, Figure 3). Temperature probably also contributes to diurnal emission cycles, but less clearly (Figures 1, 2). There was no obvious correlation between acid emissions and photosynthesis, transpiration, stomatal conductance, or relative humidity. The diurnal rhythm in acid release involved high emissions under light conditions in the morning and decreased emissions afterwards, independent of the measured climatic or physiological parameters (Table 2). This apparently endogenic diurnal rhythm was partly responsible for the observed variability in the emission responses to light and temperature (Figures 1, 2) and complicates interpretation of experimental results.

In nearly all experiments, both acetic acid and formic acid exhibited similar time series of emission, though a higher variability was observed for formic acid. This similarity suggests that the exchange of acids is mainly controlled by physicochemical processes rather than by biochemical ones,

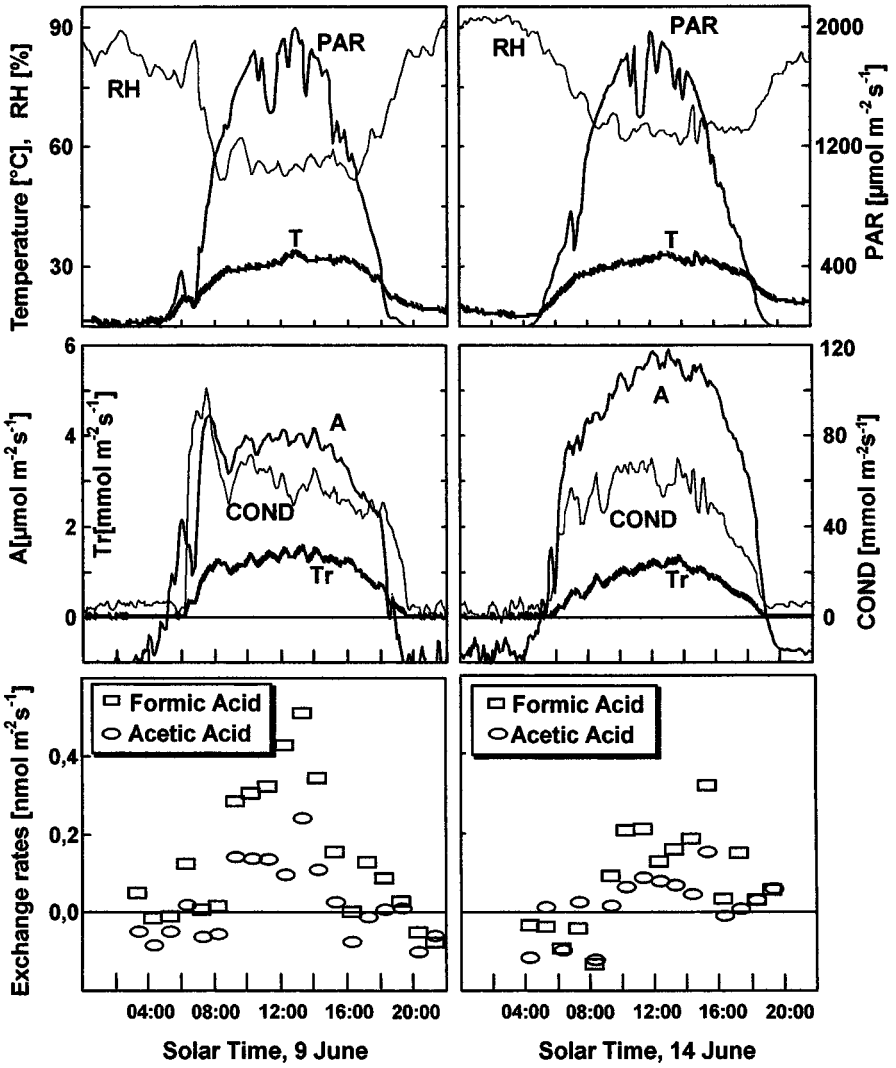


*Figure 4.* Diurnal cycles of photosynthetically active radiation PAR, temperature T, and relative humidity RH (upper panels); photosynthesis A, transpiration Tr, and stomatal conductance $gH_2O$, COND (middle panels); and exchange of formic and acetic acids (lower panels) between orange foliage and the atmosphere in the field on 9 June (left panels) and 14 June (right panels).

since these $C_1$ and $C_2$ compounds usually do not share the same metabolic pathways (Bode et al. 1997; Kesselmeier & Staudt 1999). Unlike many other VOCs emitted from vegetation, formic and acetic acids are readily soluble in water. Theoretically, the exchange rate of dissolved acids between leaf cells and the apoplast, and the subsequent volatilization to the air is strongly influenced by the concentrations of diverse ions and polar groups present in the apoplastic solution and matrix (Gabriel et al. 1997; Gabriel 1997). Gabriel et al. (1997, 1999) discuss an accumulation of formic and acetic acids in the apoplastic solution of fagaceae leaves during night and a depletion during day. The authors suggest the pH value of the apoplastic solution as one main controlling factor, increasing during night and decreasing during day. Such day-night cycles in the properties of the apoplastic solution could explain a light and temperature independent decrease of acid emissions during the morning as observed in the laboratory experiments.

Under field conditions acid exchange of volatile acids between orange foliage and air was strongly diurnal with highest emissions during noon and afternoon and zero or negative (deposition) emissions during early morning and in the night. In the laboratory, a deposition was not observed in light and only occasionally at very low rates in the dark. The more pronounced deposition in the field can be explained by the higher background concentrations in the ambient air of the orange orchard, especially in the morning between 600h and 800h. We thus conclude that, in addition to the factors outlined above, the net acid exchange between foliage and the atmosphere under field conditions is influenced by the prevailing concentrations of volatile acids in the tree canopy.

Maximum volatile acid emission rates were significantly higher in the field than in the laboratory. Short-chain acids in air are potential products of the reaction of ozone or other oxidants with biogenic hydrocarbons like terpenes (Atkinson 1990 a, b; Atkinson et al. 1995; Carlier et al. 1986; Neeb et al. 1997). Within this context, it is of high interest that the main hydrocarbon $\beta$-caryophyllene emitted by orange foliage (BEMA Report 1997) is an extremely reactive sesquiterpene, whose average atmospheric lifetime of $<3$ min (Neeb et al. 1997) is close to the chamber air residence time of 2.5 min applied in our field experiment. In the laboratory experiments, air residence time was only 1 min, and ozone or other oxidants were absent. So part of the acid emission in field could have been formed inside the chamber by the ozonolysis of emitted reactive precursors, rather than by direct release. Another possibility is that in field the release of volatile acids from orange foliage was enhanced by phenology. At the beginning of the field measurements, half of the enclosed foliage was still growing. The specific metabolic activity during cell growth and cell expansion may involve high losses of $C_1$

and $C_2$ compounds, for example, during the synthesis of lipids or formation of cell wall pectin (Roughan 1995; Nemececk-Marshall et al. 1995). This could also explain why acid emissions were lower on 14 June than on 9 June (Figure 4), since growth was almost completed at the end of the experiment on 20 June.

## Acknowledgements

This work is a contribution to the project Biogenic Emission in the Mediterranean Area (BEMA) funded by the Commissions of the European Communities (ENV4-CT95-0014 BEMA II). We are grateful to S. Muth, G. Schebeske, and H. Hübenthal (all MPIC Mainz, Germany) for their valuable help and assistance during the experiments and to C. Strametz (MPIC Mainz, Germany) and N. Bertin (INRA Avignon, France) during preparation of the manuscript. M. Sanz (CEAM Valencia, Spain) and B. Müller (Botanical Garden, Univ. of Mainz, Germany) are gratefully acknowledged for providing plant material.

## References

Andreae MO, Talbot RW & Li S-M (1987) Atmospheric measurements of pyruvic and formic acid. J. Geophys. Res. 92: 6635–6641

Andreae MO, Talbot RW, Andreae TW & Harriss RC (1988) Formic and acetic acid over the central Amazon region, Brazil. 1. Dry season. J. Geophys. Res. 93: 1616–1624

Atkinson R (1990a) Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds. J. Physical Chem. Ref. Data, Monograph 1: 1–246

Atkinson R (1990b) Gas-phase tropospheric chemistry of organic compounds: A review. Atmos. Environ. 24A: 1–41

Atkinson R, Tuazon EC & Aschmann SM (1995) Products of the gas-phase reactions of $O_3$ with alkenes. Environ. Sci. Technol. 29: 1860–1866

BEMA Report: Report on the 3rd BEMA measuring campaign at Burriana (Valencia-Spain) July 12–23, 1995. European Commission Report EUR 17305 EN, Luxembourg

Berresheim H, Talbot RW, Andreae MO & Jacob DJ (1988) Sources and sinks of organic acids in the Amazonian wet season atmosphere. EOS 69: 319

Bode K (1994) Die Abgabe von organischen Säuren an die Atmosphäre durch Pflanzen verschiedener Entwicklungsstufen. Dissertation, Fachbereich Biologie, Universität Mainz

Bode K, Schebeske G, Weller D, Wolf A & Kesselmeier J (1996) Emission of short chained (C1/C2) organic acids and aldehydes in relation to physiological activities of Mediterranean tree and shrub species during the BEMA field campaigns in 1995. In: Biogenic Emissions in the Mediterranean Area, BEMA-Project. Report on the 2nd BEMA Measuring Campaign, Montpellier-France-June 1995 (pp 65–75). EUR 16449 EN, Brussels

Bode K, Helas G, Kesselmeier J (1997) Biogenic contribution to atmospheric organic acids. In: Helas G, Slanina J & Steinbrecher R (Eds) Biogenic Volatile Organic Carbon Compounds in the atmosphere (pp 157–170). SPB Academic Publishing, Amsterdam, The Netherlands

Carlier P, Hannachi H & Mouvier G (1986) The chemistry of carbonyl compounds in the atmosphere. A review. Atmos. Environ. 20: 2079–2099

Chameides WL & Davis DD (1983) Aqueous phase source of formic acid in clouds. Nature 304: 427–429

Cowan IR (1972) Oscillations in Stomatal conductance and plant functioning associated with stomatal conductance: Observations and a model. Planta 106: 185–219

Gabriel R (1997) Charakterisierung des pflanzlichen Apoplasten als Austauschfläche zwischen Pflanze und Atmosphäre am Beispiel von organischen Säuren. Dissertation, Fachbereich Biologie, Universität Frankfurt

Gabriel R, Schäfer L, Helas G & Kesselmeier J (1997) Relation between apoplastic concentration of organic acids and their diurnal exchange pattern between leaves of *Quercus ilex* (Holm oak) and the atmosphere. In: Borrell PM, Borrel P, Cvitas T, Kelly K & Seiler W (Eds) The Proceedings of EUROTRAC Symposium 1996 (pp 397–402). Computational Mechanics Publications, Southhampton

Gabriel R, Schäfer L, Gerlach C, Rausch T & Kesselmeier J (1999) Factors controlling the emissions of volatile organic acids from leaves of *Quercus iles* L. (Holm oak). Atmos. Environ. 33: 1347–1355

Graedel TE & Weschler CJ (1981) Chemistry within aqueous atmospheric aerosols and raindrops. Rev. Geophys. Space Phys. 19: 505–539

Guenther AB, Zimmerman P, Harley PC, Monson RK & Fall R (1993) Isoprene and monoterpene emission variability: Model evaluations and sensitivity analysis. J. Geophys. Res. 89: 12609–12617

Hartmann WR, Andreae MO & Helas G (1989) Measurements of organic acids over central Germany. Atmos. Environ. 23: 1531–1533

Helas G, Bingemer H & Andreae MO (1988) Organic acids over Equatorial Africa: Results from DECAFE 88. J. Geophys. Res. 97: 6187–6193

Hofmann U, Weller D, Ammann Ch, Jork E & Kesselmeier J (1997) Cryogenic trapping of atmospheric organic acids under laboratory and field conditions. Atmos. Environ. 31: 1275–1284

Jacob DJ (1988) The chemistry of OH in remote clouds and its role in the production of formic and peroxymonosulfate. J. Geophys. Res. 91: 9807–9826

Jacob DJ & Wofsy SC (1988) Photochemistry of biogenic emissions over the Amazon Forest. J. Geophys. Res. 93: 1477–1486

Kawamura K & Kaplan IR (1986) Biogenic and anthropogenic organic compounds in rain and snow samples collected in southern California. Atmos. Environ. 20: 115–124

Keene WC Galloway JN & Holden JD (1983) Measurement of weak organic acidity in precipitation from remote areas of the world. J. Geophys. Res. 88: 5122–5130

Keene WC & Galloway JN (1984) Organic acidity in precipitation of North America. Atmos. Environ. 18: 2491–2497

Keene WC & Galloway JN (1986) Considerations concerning sources for formic and acetic acids in the troposphere. J. Geophys. Res. 91: 14466–14474

Keene WC & Galloway JN (1988) The biogeochemical cycling of formic and acetic acids through the troposphere: An overview of current understanding. Tellus 40B: 322–334

Kesselmeier J, Schäfer L, Bliefernicht M, Andreae MO & Helas G (1991) Exchange of organic acids between plants and atmosphere. EUROTRAC Annual Report 1990, Part 4 BIATEX (pp 214–219). Garmisch-Partenkirchen

Kesselmeier J, Schäfer L, Ciccioli P, Brancaleoni E, Cecinato A, Frattoni M, Foster P, Jacob V, Denis J, Fugit JL, Dutaur L & Torres L (1996) Emission of monoterpenes and isoprene from a Mediterranean oak species *Quercus ilex* L. measured within the BEMA (Biogenic Emissions in the Mediterranean Area) project. Atmos. Environ. 30: 1841–1850

Kesselmeier J, Bode K, Hofmann U, Müller H, Schäfer L, Wolf A, Ciccioli P, Brancaleoni E, Cecinato A, Frattoni M, Foster P, Ferrari C, Jacob V, Fugit J-L, Dutaur L, Simon V & Torres L (1997) Emission of short chained organic acids, aldehydes and monoterpenes from *Quercus ilex* L. and *Pinus pinea* L. in relation to physiological activities, carbon budget and emission algorithms. Atmos. Environ. 31(SI): 119–134

Kesselmeier J, Bode K, Gerlach C & Jork E-M (1998a) Exchange of atmospheric formic and acetic acid with trees and crop plants under controlled chamber and purified air conditions. Atmos. Environ. 32: 1765–1775

Kesselmeier J, Bode K, Schäfer L, Schebeske G, Wolf A, Brancaleoni E, Cecinato A, Ciccioli P, Frattoni M, Dutaur L, Fugit J-L, Simon V & Torres L (1998b) Simultaneous field measurements of terpene and isoprene emissions from two dominant Mediterranean oak species in relation to a North American species. Atmos. Environ. 32: 1947–1953

Kesselmeier J. & Staudt M. (1999) Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology. J. Atmos. Chem., in press

Likens GE & Galloway JN (1983) The composition and deposition of organic carbon in precipitation. Tellus 35B: 16–24

Lunde G, Gether J, Gjos N & Stobet-Lande MB (1977) Organic micropollutants in precipitation in Norway. Atmos. Environ. 11: 1007–1014

Madronich S, Chatfield RB, Calvert JG, Moortgat GK, Veyret B & Lesclaux R (1990) A photochemical origin of acetic acid in the troposhere. Geophys. Res. Lett. 17: 2361–2364

Marquardt DW (1963) An algorithm for least squares estimation of nonlinear parameters. J. Soc. Indus. Appl. Math. 11: 431–453

Neeb P, Bode K, Beck J, Schäfer L, Kesselmeier J & Moortgat GK (1997) Influence of gas-phase oxidation on estimated emission rates of biogenic hydrocarbons. In: Proceedings of the 7th European Symposium on Physico-Chemical Behaviour of Atmospheric Pollutants: The oxidizing Capacity of the Troposphere (pp 295–299). Office for Official Publications of the European Communities, Luxembourg (EUR 17482) ISBN 92-828-0158-6

Nemececk-Marshall M, MacDonald RC, Franzen JJ, Wojciechowski CL & Fall R (1995) Methanol emissions from leaves. Enzymatic detection of gas-phase methanol and relation of methanol fluxes to stomatal conductance and leaf development. Plant Physiol. 108: 1359–1368

Norton RB, Roberts JM & Huebert BJ (1983) Tropospheric oxalate. Geophys. Res. Lett. 10: 517–520

Puxbaum H, Rosenberg C, Gregori M, Lanzerstorfer C, Ober E & Winiwarter W (1988) Atmospheric concentrations of formic and acetic acid in eastern and northern Austria. Atmos. Environ. 22: 2841–2850

Roughan PG (1995) Acetate concentration in leaves are sufficient to drive in vivo fatty acid synthesis at maximum rates. Plant Sci. 107: 49–55

Sachs L (1988) Statistische Methoden: Planung und Auswertung. 6. Auflage (p 298). Springer-Verlag, Berlin

Schäfer L, Kesselmeier J & Helas G (1992) Formic and acetic acid emission from conifers measured with a “cuvette” technique. In: Beilke S, Slanina J & Angeletti G (Eds) Field Measurements and Interpretation of Species Related to Photooxidants and Acid Deposition, CEC Air Pollution Research 39 (pp 319–323). E Guyot SA, Brussels

Schäfer L, Gabriel R, Müller H, Wolf A & Kesselmeier J (1995) Emission of short chained organic acids and aldehydes in relation to physiological activities and apoplastic ion concentration in Mediterranean tree species during the B.E.M.A. field campaign in May 1994. In: Biogenic Emissions in the Mediterranean Area, BEMA-Project. Report on the 1st BEMA Measuring Campaign at Castelporziano, Rome (Italy), May 1994 (pp 233–247). EUR 16293 EN, Brussels

Staudt M & Bertin N (1998) Light and temperature dependence of the emission of cyclic and acyclic monoterpenes from Holm oak (*Quercus ilex* L.) leaves. Plant, Cell & Environment 21: 385–395

Talbot RW, Andreae MO, Berresheim H, Jacob DJ & Beecher KM (1990) Sources and sinks of formic, acetic and pyruvic acids over Central Amazonia. 2. Wet season. J. Geophys. Res. 95: 16799–16811

Talbot RW, Mosher BW, Heikes BG, Jacob DJ, Munger JW, Daube BC, Keene WC, Maben JR & Artz RS (1995) Carboxylic acids in the rural continental atmosphere over the eastern United States during the Shenandoah Cloud and Photochemistry Experiment. J. Geophys. Res. 100: 9335–9343

Von Caemmerer S & Farquhar GD (1981) Some relationships between the biochemistry of photosynthesis and the gas exchange of leaves. Planta 153: 376–387

Winiwarter W, Puxbaum H, Fuzzi S, Facchini M, Orsi G, Beltz N, Enderle K & Jaeschke W (1988) Organic acid and liquid phase measurements in the Po valley. Fall-winter conditions in the presence of fog. Tellus 40B: 348–357