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# Impact of drought on seasonal monoterpene emissions from *Quercus ilex* in southern France

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[1] We studied monoterpene emissions from the evergreen oak *Quercus ilex* exposed to different levels of summer drought to examine the seasonal variation of emissions in the Mediterranean area and to test the role of water limitations therein. Measurements were made in seven campaigns between June and January on intact leaves of mature trees growing in two adjacent sites, in one of which the natural water supply was reduced by a ground roof. In both sites, actual emission rates as well as light- and temperature-normalized emission rates (i.e., emission factor (EF)) significantly changed during the seasons: Mean EFs increased from June to July to a broad summer maximum between 5.2 and 9.4 nmol m<sup>-2</sup> leaf area s<sup>-1</sup> (12–21 μg g<sup>-1</sup> leaf dry mass h<sup>-1</sup>), dropped in October and November and reached a minimum of about 0.77 nmol m<sup>-2</sup> s<sup>-1</sup> (1.7 μg g<sup>-1</sup> h<sup>-1</sup>) in January. From June to July, mean EFs of the trees with reduced water supply were significantly lower than those of trees with normal water supply. The lowered EF in summer was paralleled by lower predawn water potentials, leaf transpiration, photosynthesis and stomatal conductance with respect to control trees. The results suggest that in natural *Q. ilex* habitats the seasonal evolution of EF follows a marked summer-winter cycle whose shape and intensity can be modified by summer drought. **INDEX TERMS:** 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; **KEYWORDS:** volatile organic compounds (VOC), biogenic emissions, monoterpenes, seasonal variation, water stress, emission modeling

## 1. Introduction

[2] Biogenic emissions of chemically reactive trace gases such as isoprene and monoterpenes drive important mechanisms of biosphere-atmosphere interactions [Fehsenfeld *et al.*, 1992]. The air-chemical breakdown of these compounds has substantial impact on the formation of tropospheric ozone and aerosols and enhances greenhouse effects, rain-water acidification and deposition of airborne nitrogen. At present, emissions are simulated on the basis of a species-dependent emission factor (EF) that is defined for standard light and temperature conditions (usually, 30°C and photosynthetically active radiation (PAR) of 1000 μmol m<sup>-2</sup> s<sup>-1</sup>) and then adjusted for short-term light and temperature influences [Geron *et al.*, 1997; Simpson *et al.*, 1999]. Because the correct assignment of EF to an emitting plant species is crucial for emission prediction, the extent of intra-specific variation has to be known. In recent years several studies investigated the seasonal variation of EF. Most of

them focused on isoprene emitting deciduous tree species [Monson *et al.*, 1994; Guenther, 1997; Pier and McDuffie, 1997; Schnitzler *et al.*, 1997; Fuentes and Wang, 1999; Geron *et al.*, 2000; Lehning *et al.*, 2001] while only a few concern monoterpene emitting evergreen species [Yokouchi *et al.*, 1984; Staudt *et al.*, 1997, 2000]. Generally the observed EF rapidly increased in spring, showed a broad maximum in summer and progressively declined in fall. In southern Europe, the vegetation of the Mediterranean basin is particularly rich in monoterpene producing evergreen oaks, *Quercus ilex* being the most important one. The emissions of this widespread tree species are as high as those from isoprene emitters and much higher than the monoterpene emissions from conifers [Kesselmeier and Staudt, 1999; Simpson *et al.*, 1999]. Yet the reported variations in the EF of *Q. ilex* do not show a consistent pattern with respect to seasonality: Bertin *et al.* [1997] noticed an increase of EF during leaf growth in May but could not detect significant differences in EF among successive measurements in June, August and October. Street *et al.* [1997] determined EFs from measurements made on *Q. ilex* during two periods in two sites. They found a much

higher EF in October than in May in a dune habitat site and almost the same EF during June and May in forest habitat. *Llusia and Peñuelas* [2000] reported highest EF in April, lowest in November, and intermediate levels in June and August for *Q. ilex* trees growing in northeast Spain. Finally, a recent study made on *Q. ilex* seedlings revealed a strong decline of EF during fall and winter [*Staudt et al.*, 2001].

[3] A potential factor introducing variation in the annual emission course of field grown *Q. ilex* trees is the impact of summer drought on emission. Terpenes released by *Q. ilex* leaves do not derive from a preformed storage pool but are synthesized prior emission from recently fixed carbon in a light and temperature driven process [*Staudt and Seufert*, 1995; *Kesselmeier et al.*, 1996; *Loreto et al.*, 1996]. Therefore, emissions from this species might be particularly sensitive to water limitation in summer that together with a high temperature regime limits photosynthetic carbon gain. Water limitations may affect the short-term emission variation of *Q. ilex* during hot summer days [*Bertin et al.*, 1997]. *Peñuelas and Llusia* [1999] observed that in summer field conditions the daily maximum in EF occurs early in the morning, which they attributed to water limitations. Drought experiments using potted plants showed that *Q. ilex* emissions are indeed inhibited under water shortage [*Bertin and Staudt*, 1996; *Llusia and Peñuelas*, 1998] as it has been demonstrated for other isoprene and monoterpene emitting trees species [*Sharkey and Loreto*, 1993; *Yani et al.*, 1993; *Fang et al.*, 1996]. These experiments, however, have been made on young potted plants in glasshouses and laboratories and hence did not allow one to conclude on the relevance of drought on emissions from mature trees growing under natural conditions. On the other hand, field studies are more difficult to carry out and to interpret, because of the heterogeneous plant material and variable environmental conditions in nature that affect emissions [*Kesselmeier and Staudt*, 1999] and may veil a potential influence of drought on emission. To overcome this problem we designed a field experiment to study drought effects within a single and homogenous population of mature *Q. ilex* trees. We monitored monoterpene emissions and plant physiological parameters in two adjacent sites, in one of which the tree's natural water input was artificially reduced. Our objectives were to (1) characterize the seasonal variation of EF under natural field conditions and (2) verify whether water limitations can modify this variation.

## 2. Experimental

### 2.1. Site Description

[4] The study was conducted during the 1999 growing season (middle of June 1999 until middle of January 2000) at the experimental station of the CEFE-CNRS in southern France (43° 36'N, 3° 53'E). The station is located in the hollow of a valley containing a deep clay soil with good water availability. A weather station placed in the middle of the hollow monitors continuously air temperature (2 m above ground), soil temperature, air humidity and incoming global radiation. The climate is Mediterranean, with cool winters and hot dry summer, with a mean annual temperature of 14°C and a mean annual precipitation of 789 mm (1970–1999). The sum of precipitation during the experimental period was 618 mm, which is higher than the

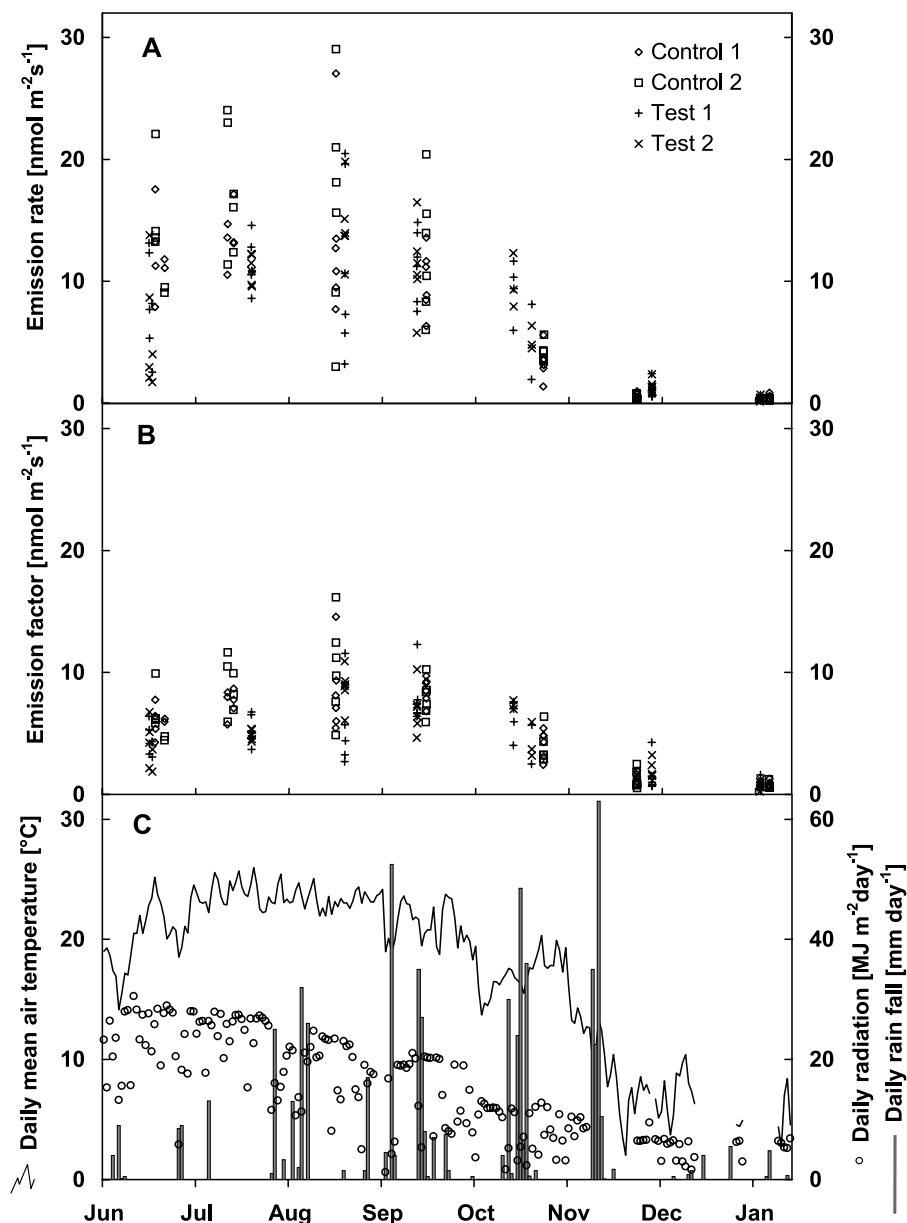
corresponding mean of 503 mm during the last 30 years (see also Figure 1c).

[5] Measurements were made in a 15 m large and approx. 200 m long double row of 35-years old *Quercus ilex* trees planted in south–north direction at the western border of the hollow. In this row two plots in 30 m distance were equipped with a tower scaffold providing access to the top of the canopy at a height of 8 to 9 m. In each plot two opposite east–west facing *Q. ilex* trees were chosen to determine the seasonal development of foliar monoterpene emission and gas exchange, and predawn water potential. The water availability of the southern plot was artificially reduced by installing a roof approx. 30 cm above the soil surface that extended outside the tree crowns and surrounded by a 1.5 m deep trench to exclude any further root extension. This plot is hereafter referred to as test site and the other as control site.

### 2.2. Measurement of Emissions and Plant Physiological Parameters

[6] Measurements were started in June 1999 when leaves of the new flush were fully expanded and mature. The trees of the test site visibly developed less new leaves than the trees of the control site. Monoterpene emissions and CO<sub>2</sub>/H<sub>2</sub>O-gas exchanges (i.e., net-photosynthesis and transpiration) were determined in seven campaigns on six different terminal shoots per tree (12 per site) on the canopy top. Shoots were exclusively composed of current year leaves (1999) with sun-adapted morphology. In all campaigns the 12 replicates per site were obtained by measuring alternately on tree 1 and 2. For technical reasons, the two sites were measured one after the other and hence on different days. All measurements were conducted on sunny days between 10 a.m. and 17 p.m. During winter at hours when natural light intensity was low, leaves were artificially illuminated 30 to 60 min before measurement with 800 to 1000 μmol m<sup>-2</sup> s<sup>-1</sup> PAR. Each campaign was finished within one week except for that in October, during which poor weather conditions delayed the measurements in the control site (see also Figure 1). After each campaign, the leaves of the shoots were collected to determine leaf dry mass and projected leaf area. Leaf area was determined by a video leaf area meter (Delta-T Area Meter MK2, Delta-T Devices, Ltd, U.K.) and leaf dry mass by weighing on a micro balance (Mettler PM200) after drying 48 hours in a ventilated oven at 60°C. Predawn water potentials (Ψ<sub>pd</sub>) were determined once in each campaign by means of a Scholander pressure chamber. The measurements were made within 1 hour with three replicates per tree.

[7] Leaf emission and gas exchanges were measured by means of a gas-exchange system (CI-301 CO<sub>2</sub> Gas Analyzer, CID Inc., USA) connected via Teflon tubing to a translucent Plexiglas cuvette of 0.5 L Vol. The cuvette was flushed with ambient air at a constant flow rate of 0.5 L min<sup>-1</sup>. Leaf temperature and photosynthetically active radiation (PAR) were measured by an infrared temperature sensor inserted in the cuvette bottom and a quantum sensor laterally inserted at the cuvette top. For the measurement the leaves of an intact shoot twig were clamped inside a cuvette and arranged so that the temperature sensor was shaded by a leaf. Monoterpene sampling started after two cycles of photosynthesis measurement and lasted between 5 and 8



**Figure 1.** Seasonal development of monoterpene emissions from *Quercus ilex* (Figures 1a and 1b), and climate parameters (Figure 1c) during the 1999 growing season at the experimental station of the CEFÉ-CNRS in Montpellier (France). (a) Actual emission rates (sum of 5 main compounds). (b) Emission factors. (c) Daily mean of air temperature (solid line) and daily sum of global radiation (dots) and rainfall (columns). Emission measurements were made in seven campaigns on four trees growing in two adjacent sites, one with natural water supply (control trees 1 and 2) and one with artificially reduced water supply (test trees 1 and 2). In each campaign, monoterpene emissions were determined during daytime hours on six different terminal shoots per tree by means of a gas exchange chamber system. The emission factors in Figure 1b are emission rates normalized to standard light and temperature conditions of  $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$  PAR and  $30^\circ\text{C}$  according to *Staudt and Bertin* [1998] using the light and leaf temperature values recorded by the chamber system. PAR values ranged between  $700$  and  $2000 \mu\text{mol m}^{-2} \text{s}^{-1}$  during emission measurements, and leaf temperature ranged between  $15$  and  $41^\circ\text{C}$ . The climate data shown in Figure 1c were monitored by a weather station close to the sites.

min. Leaf temperature, PAR and gas exchange data were recorded every minute.

[8] Monoterpenes were collected by diverting a fraction of the air exiting the cuvette through a sampling line connected to an adsorption tube containing  $200 \text{ mg}$  of

Tenax TA (20–35 mesh, Chrompack). Sampling was done at a controlled flow rate of  $100 \text{ ml min}^{-1}$  from either  $0.5 \text{ L}$  air samples (summer) or  $0.8 \text{ L}$  air samples (winter). Adsorption tubes were stored at  $4^\circ\text{C}$  until they were analyzed (usually the day after). The sampling line was

fitted with a micro ozone scrubber (eight layers of MnO<sub>2</sub>-coated copper nets of 4 mm diameter) to avoid discrimination of ozone sensitive monoterpene species [Calogirou *et al.*, 1996]. Between two measurements, the chamber was flushed with ambient air for at least 20 min to remove terpene residuals from air lines and chamber walls. Monoterpene concentrations in the empty chamber (background) were measured at least three times per day. The emission rate was calculated as the difference between the air concentration in the chamber enclosing a shoot and the concentration measured in the empty chamber (mean of the day) multiplied by air flow and divided by enclosed leaf area (nmol m<sup>-2</sup> s<sup>-1</sup>) or leaf dry weight (μg g<sup>-1</sup> h<sup>-1</sup>). Leaf gas exchange was calculated according to von Caemmerer and Farquhar [1981].

### 2.3. Gas Chromatography

[9] The samples were analyzed in a Chrompack gas chromatograph (CP9003) equipped with a fused silica capillary column (CP-Sil 8 CB, 25 m × 0.32 mm, 1.2 μm d.f., Chrompack), a flame ionization detector and a custom made thermal desorption and cold trap injection unit. Sampled VOCs were desorbed from the Tenax tube by rising the temperature from 50 to 250°C within 10 min, flushed on a cold trap kept at a temperature of -100 ± 5°C, and thermally injected on the analytical column by flash-heating the cold trap to 220°C for 3 min. Separation occurred with the following oven program: 4 min at 65°C, 2.5°C min<sup>-1</sup> to 80°C, 2°C min<sup>-1</sup> to 100°C, 10°C min<sup>-1</sup> to 220°C. Carrier gas was Helium with a constant flow rate of 1.2 ml min<sup>-1</sup>. Monoterpenes were identified by comparison of their retention times with authentic monoterpene standards (Fluka Chemie AG, Buchs Switzerland), and by contrasting with previous studies, during which the same analytical set-up was used and peaks were identified by mass-spectrometry [Bertin *et al.*, 1997; Kesselmeier *et al.*, 1997]. Calibration was done by evaporating aliquots of freshly prepared monoterpene solutions (MeOH) on the sample tubes with approx. 300 ml N<sub>2</sub> (quality C) at flow-rates around 30 ml min<sup>-1</sup>.

### 2.4. Calculation of Emission Factors

[10] EF was calculated by normalizing the emission rates measured under various ambient conditions to standard light and temperature conditions of 1000 μmol m<sup>-2</sup> s<sup>-1</sup> PAR and 30°C. The normalization was made with the light and temperature relationship described by Staudt and Bertin [1998], which is the isoprene algorithm of Guenther *et al.* [1993] adjusted to monoterpene emissions from *Q. ilex* leaves:

$$E_{(\text{PAR},T)} = \text{EF} \times \left[ \frac{C_1 \alpha \text{PAR}}{\sqrt{1 + \alpha^2 \text{PAR}^2}} \times \frac{\exp(C_2(T - T_s)/(RTT_s))}{1 + \exp(C_3(T - T_m)/(RTT_s))} \right]$$

$E_{(\text{PAR},T)}$  is the emission rate at a given temperature  $T$  (K) and PAR, EF is the emission factor,  $T_s$  is the standard temperature (303 K),  $R$  is the gas constant (8.134 J K<sup>-1</sup> mol<sup>-1</sup>) and  $\alpha$ ,  $C_1$ ,  $C_2$ ,  $C_3$  and  $T_m$  are empirical parameters with the following values for *Q. ilex* emissions:  $\alpha = 0.0041$ ,  $C_1 = 1.040$ ,  $C_2 = 87620$  J mol<sup>-1</sup>,  $C_3 = 188200$  J mol<sup>-1</sup>,  $T_m = 317$  K.

[11] During enclosure the leaf temperature progressively increased by 1 to 4°C. For light and temperature normalization we used the temperature and PAR values at the beginning of the measurement (but see below), because response time of emissions to light and temperature changes is long with respect to the enclosure time [Staudt and Seufert, 1995]. Throughout the seven campaigns, leaf temperatures during emission measurements ranged between 15 and 41°C and PAR-values between 700 and 2000 μmol m<sup>-2</sup> s<sup>-1</sup>.

### 2.5. Statistics

[12] Bilateral student tests were applied to evaluate the effects of the factors tree and site (drought treatment) on emission factors and on other measured variables such as photosynthesis and transpiration. The factor tree was tested separately for each campaign and each site on the six replicate measurements per tree. The factor site was tested separately for each campaign using the mean values of each tree ( $n = 2$  per site and campaign).

[13] Analysis of variance (one-way ANOVA, SigmaStat 2.0 Jandel Scientific Software) was applied to determine the effect of measuring campaign (season) on emission factors in each site using the mean values of each tree. F-tests were used to determine the statistical significance ( $P < 0.05$ ) and Student tests for the multiple pairwise comparison of the seven measuring campaigns.

## 3. Results

### 3.1. Between-Tree and Within-Tree Variation of Emissions

[14] All four trees emitted the same five principal monoterpenes throughout the experimental period:  $\alpha$ -pinene (35–45%),  $\beta$ -pinene (20–35%), sabinene (5–25%), myrcene (5–15%) and limonene (2–7%). In addition, traces of  $\alpha$ -thujene, camphene, p-cymene, cis- and trans- $\beta$ -ocimene,  $\gamma$ -terpinene and linalool were detected in the emissions. For a given tree, the percentage composition was similar in all leaves and almost stable from campaign to campaign. Ocimene emissions, however, were found only in the campaigns from June to August while the emissions of other trace compounds were detected in all seasons. In the following all emission rates refer to the sum of the five major compounds.

[15] The whole data set of emission rates and derived emission factors (EF) measured on four trees during seven campaigns are displayed on Figure 1 together with climate data monitored by the nearby weather station during the same period. In both sites actual emission rates (Figure 1a) as well as emission factors (Figure 1b) strongly scattered within individual campaigns, but without significant differences between the two tree replicates. However, in the August campaign, significant differences between predawn water potentials and/or CO<sub>2</sub> and H<sub>2</sub>O gas exchanges of the two trees were observed at both sites. These differences were coherent with the general trend of emission data in that the tree having the lower physiological activity also emitted less monoterpenes, but differences in emissions were not significant due to the data scattering within each tree. Globally over the diverse seven campaigns, in the absence of significant tree effects at sites, the high emission variability was mainly associated with the actual within-tree variation.

[16] The normalization of actual emission rates to EF reduced this variability by a relatively small amount (Figures 1a and 1b). The average of the variation coefficients (CV) of the seven campaigns for non-normalized and normalized emission rates (EF) were 41 and 37% in the test site and 37 and 29% in the control site. The variability of EF observed within the campaigns may be related to uncertainty in the emission normalization. A potential error in the normalization could result from the use of inappropriate parameter values, although the applied parameters have been developed specifically for *Q. ilex* emissions over a wide range of PAR and temperature conditions [Staudt and Bertin, 1998]. To check the sensibility of EF variability to parameter values, additional normalization were run using global parameters suggested by Guenther et al. [1993] as well as parameter values obtained from a current growth chamber study, in which *Q. ilex* plants were acclimatized to different light and temperature regimes (M. Staudt, unpublished results, 2001). Overall the use of other parameters had little influence on EF variability. CVs were similar and results remained the same with respect to seasonal variation and differences between trees and sites.

[17] Another source of potential error can be the variable leaf shading, leaf inclination and cuvette heating during enclosure leading to uncertainties of PAR and leaf temperature values used for the emission normalization. This potential error should be less important for PAR than for leaf temperature values, because nearly all measurements were made in the range of light saturation. To test this, emissions were normalized using the mean leaf temperature during enclosure, as well as the mean temperature between leaf and ambient air temperatures recorded by the nearby weather station during the same hour. In both cases EF variation within the campaigns slightly increased (mean CVs of 31 to 39%) suggesting that the leaf temperature at the beginning of the enclosure was the most appropriate value for normalization. Together there was no consistent way to associate the variation of EF within the campaigns to uncertainties in the normalization procedure.

### 3.2. Seasonal Variation of Emission

[18] The amount of terpenes released by *Q. ilex* leaves largely varied over the seasons (Figure 1a). During summer mean emission rates per campaign ranged between  $7 \text{ nmol m}^{-2} \text{ s}^{-1}$  and  $15.5 \text{ nmol m}^{-2} \text{ s}^{-1}$  ( $17\text{--}38 \mu\text{g g}^{-1} \text{ h}^{-1}$ ) with peak emission rates in July and August reaching values of up to  $29 \text{ nmol m}^{-2} \text{ s}^{-1}$  ( $80 \mu\text{g g}^{-1} \text{ h}^{-1}$ ). Emissions dropped strongly from October onwards and the annual mean minimum observed at the beginning of January amounted to  $0.4 \text{ nmol m}^{-2} \text{ s}^{-1}$  ( $0.9 \mu\text{g g}^{-1} \text{ h}^{-1}$ ) only. The lowest emission rates recorded in January were about  $0.15 \text{ nmol m}^{-2} \text{ s}^{-1}$  ( $0.4 \mu\text{g g}^{-1} \text{ h}^{-1}$ ). On average, emission rates in the January campaign were 30 to 40 fold lower than in the July and August campaigns. This difference was somewhat higher when emissions were expressed on a leaf dry weight basis, because leaf dry mass per area increased from summer to winter by approx. 10 % (from  $201 \text{ g m}^{-2}$  to  $225.5 \text{ g m}^{-2}$ ). Normalization of emissions to standard conditions (i.e., EF) reduced the summer to winter difference in emissions to a factor of around 10 (Figure 1b). Mean EF during summer ranged between  $4.2$  and  $7.5 \text{ nmol m}^{-2} \text{ s}^{-1}$  ( $10\text{--}18 \mu\text{g g}^{-1}$

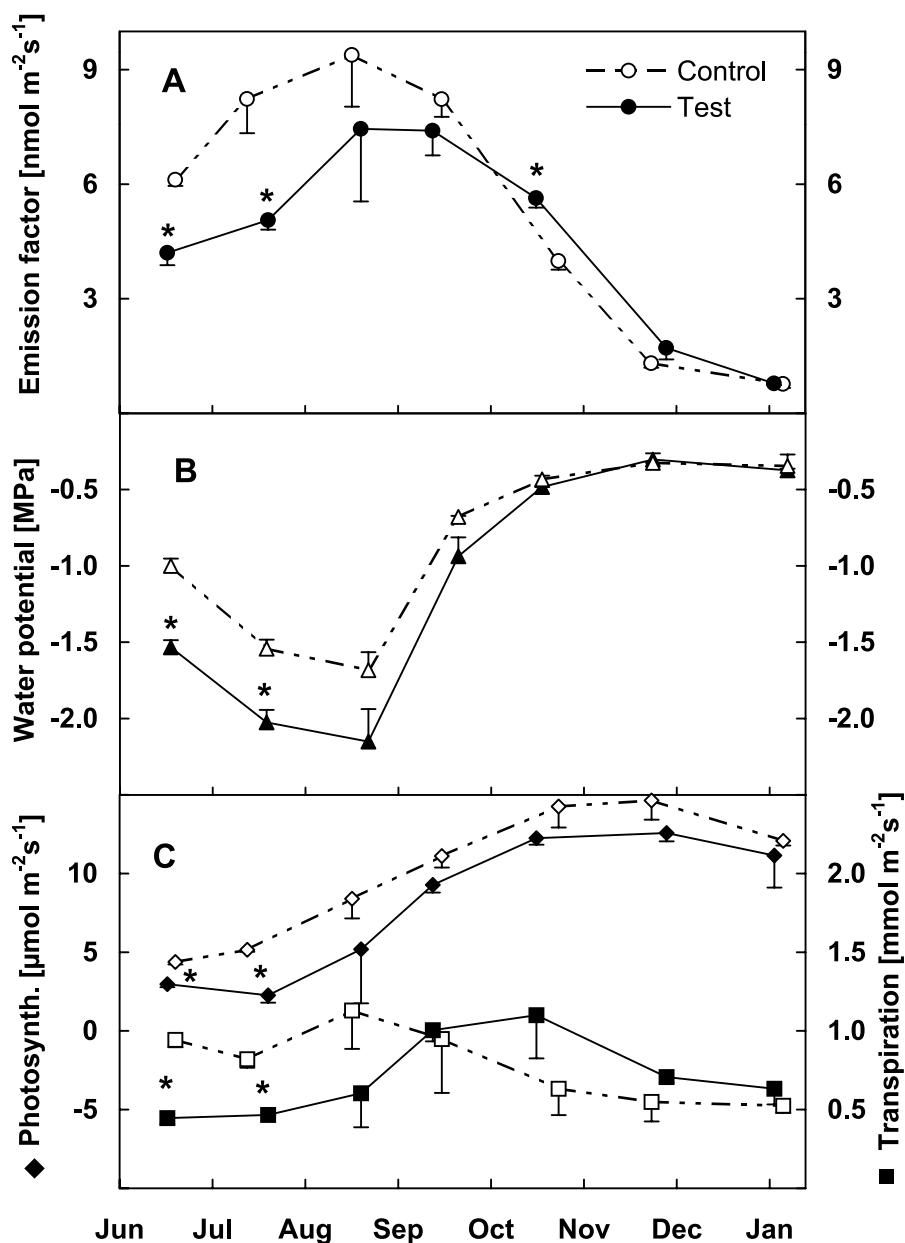
$\text{h}^{-1}$ ) in the test site and between  $6.1$  and  $9.4 \text{ nmol m}^{-2} \text{ s}^{-1}$  ( $15\text{--}21 \mu\text{g g}^{-1} \text{ h}^{-1}$ ) in the control site. Minimal EF in January averaged  $0.77 \text{ nmol m}^{-2} \text{ s}^{-1}$  ( $1.7 \mu\text{g g}^{-1} \text{ h}^{-1}$ ) in both sites. ANOVA detected a statistically significant effect of seasons on EF in both sites ( $P < 0.001$ ). There was, however, no significant difference between the mean EFs of the July, August and September campaigns in the control site, and between the mean EFs of the June to October campaigns in the test site. EF significantly decreased from September to October in the control site and from October to November in both sites. This suggests that for the control trees the foliar capacity to produce monoterpenes increased after leaf development to a summer plateau and then progressively declined during the fall and winter period, whereas that of the test trees remained more or less stable after leaf maturation at the end of spring until the middle of fall.

### 3.3. Effect of Enhanced Water Limitation During Summer

[19] Figure 2 shows the seasonal evolution of the mean EFs at each site in comparison with mean predawn water potentials, mean photosynthesis and transpiration rates. Predawn water potentials ( $\Psi_{\text{pd}}$ , Figure 2b) indicated water limitations from June to August with values ranging between  $-1.0$  to  $-2.0$  MPa. After heavy rainfalls at the end of August and at the beginning of September (compare Figure 1)  $\Psi_{\text{pd}}$  subsequently recovered and remained stable from October to January. In the campaigns from June to August  $\Psi_{\text{pd}}$  values were approx.  $0.5$  MPa lower in the test site than in the control site. The differences in  $\Psi_{\text{pd}}$  between test and control site were statistically significant in the June and July campaigns and were accompanied by significantly reduced EFs (Figure 2a), photosynthesis and transpiration rates (Figure 2c) as well as stomatal conductance (not shown) in the test site. In August emission and gas exchanges of test trees were also largely reduced compared to control trees, but differences were not significant due to the larger tree-to-tree variability occurring during this month in both sites (see above). When this potential tree effect was ignored in the statistical analysis by pooling the data of the six shoot replicates of each tree to a total sample size of 12 per site, differences in EF and gas exchanges between the two sites were significant also in August.

[20] There was no other significant difference between the physiological activities of test and control trees except for the October campaign, during which measurements proceeded over a longer period than usual (compare Figure 1). The mean EF of the control trees measured at the end of October was significantly lower than that of the test trees measured 4 and 10 days before (Figure 2a). This difference in EF was not associated with differences in other measuring variables.

[21] Figure 3 summarizes the between-site differences of some measuring variables and displays their relations to differences in EF (dEF). Good correlation to dEF can be seen for the difference in transpiration ( $R^2 = 0.807$ , Figure 3b), predawn water potential ( $R^2 = 0.794$ , Figure 3c) as well as stomatal conductance ( $R^2 = 0.619$ , data not shown), whereas correlation to differences in photosynthesis ( $R^2 = 0.213$ , Figure 3a) and leaf temperature ( $R^2 = 0.152$ , Figure 3d) were low. These results suggested that differences in EF



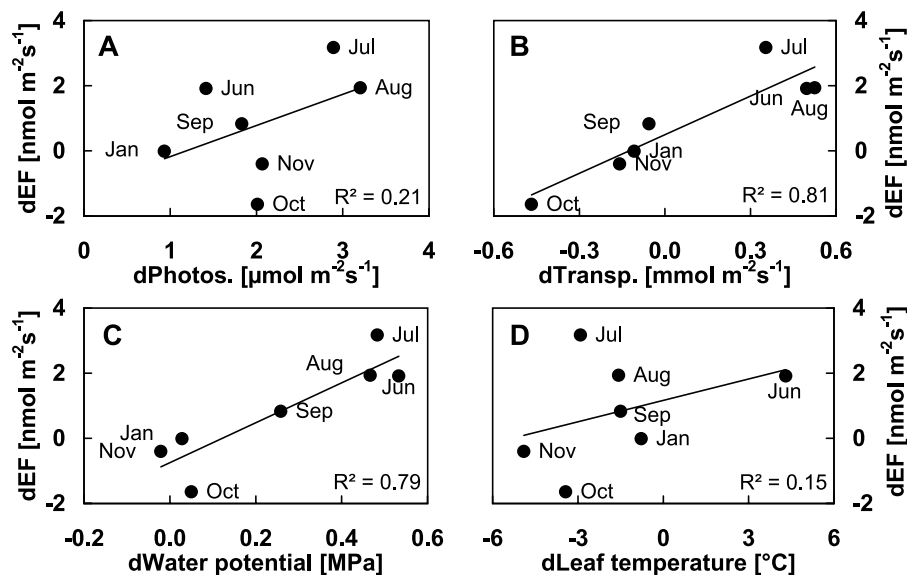
**Figure 2.** Seasonal development of the mean emission factors (a), predawn water potentials (b) and photosynthesis (diamonds) and transpiration (squares) (c) of *Q. ilex* trees growing in two sites with natural (open symbols, dashed lines) and reduced water supply (closed symbols, solid lines). Data are the means of two trees per site (each tree value is the mean of six replicates measured on different current-year flushes). Error bars denote standard deviations ( $n = 2$ ), and asterisks denote significant differences between control and test site (t-test,  $P < 0.05$ ,  $n = 2$ ).

between the two sites were mainly related to the different water availability of the trees.

#### 4. Discussion

[22] In both sites EF dropped from summer to winter by one order of magnitude emphasizing that in the natural course of the seasons the capacity of evergreen trees to produce volatiles is strongly inhibited during winter. Decreases in the monoterpene EF during fall and winter seasons have been previously observed on the same and other evergreen tree species [Yokouchi *et al.*, 1984; Janson,

1993; Llusà and Peñuelas, 2000; Staudt *et al.*, 2000, 2001; Kesselmeier *et al.*, 2002] and are concordant with a recent study on seasonal fluctuations of the enzymatic activity of monoterpene synthases in leaf extracts of *Q. ilex* [Fischbach *et al.*, 2002]. At present the seasonal drop in EF during fall/winter is not taken into account in inventories estimating the annual amount of this type of emissions. Because in the past most of the field studies were conducted during the warm seasons when emissions are high, current emission inventories have to rely on EF values that risk overestimating emissions on an annual scale. For instance the EF of  $20 \mu\text{g g}^{-1} \text{h}^{-1}$  assigned to *Q. ilex* forests in a recent European



**Figure 3.** Scatterplots of the differences between the average emission factors of test and control sites (dEF, y-axis) measured during seven campaigns between June 1999 and January 2000 versus the differences in average photosynthesis (a), transpiration (b), predawn water potential (c) and leaf temperature (d).

emission inventory [Simpson *et al.*, 1999] is close to the summer maxima observed in our study in the control and test site (21 and 18  $\mu\text{g g}^{-1} \text{h}^{-1}$ ) but it is about twice their annual mean EF (8.7 and 7.7  $\mu\text{g g}^{-1} \text{h}^{-1}$ ). To integrate the seasonal course of EF in emission inventories, models have been proposed that link observed variations in EF with a time variable or a climate variable such as the sums of temperature [Guenther, 1997; Staudt *et al.*, 2000; Lehning *et al.*, 2001]. The present study on *Q. ilex* confirms the need to consider seasonal variations of EF in emission inventories but it also shows that drought can potentially limit the accuracy of model predictions. Mean EF of the more stressed trees in the test site hardly varied during summer until October, which is consistent with previous field measurements made on *Q. ilex* near Rome [Bertin *et al.*, 1997]. This was the result of a compensation between drought inhibition and summer enhancement of emissions as indicated by the more pronounced summer peak of emissions from the trees in the adjacent control site. Compared to the control trees, the emissions from test trees were reduced during summer by about 25% due to the stronger water limitations in this site. It cannot be excluded, however, that the emissions of the trees in the control site were also affected by water limitations, because their predawn water potentials decreased in July to a level at which stress responses can be expected [Rambal, 1992]. Hence the overall reduction of emission related to drought in the test site might have been higher than 25%.

[23] Current emission models do not include variables that can preview drought driven reductions in emission. In the present work we retained  $\Psi_{\text{pd}}$  as the most adequate state variable to characterize the time course of water limitations. From a simulation model perspective, the easiest variable is the soil water storage cumulated over the root zone or a derived variable such as the relative water content, because it can be assessed from common climate data (potential

evaporation and rain). However, in the case of deep-rooted tree species it is very difficult to measure across the whole soil profile and to calculate all the water that is stored and available for plants [Rambal, 1984]. The availability of soil water is more related to the soil water potential ( $\Psi$ ) than to soil water content, because it depends on the energy status of the water (see Cochard *et al.* [2002] for a substantial account). Soil  $\Psi$  has been linked to soil water content by so-called retention curves, whose parameters strongly depend on soil texture [Campbell, 1985]. The prediction of such parameters by pedotransfer functions is of limited accuracy, in particular in fine-textured clay soil [Kern, 1995]. Leaf  $\Psi_{\text{pd}}$  is often used as substitute for soil  $\Psi$ , which is based on the expectation that plant  $\Psi_{\text{pd}}$  is in equilibrium with the “wettest” soil  $\Psi$  accessed by roots. This equilibrium offers great advantage in conditions under which an inverted vertical distribution of water occurs. For instance, after a rain event during a hot and dry summer the whole soil storage is only slightly modified, while the topsoil moisture is close to field capacity causing significant changes in both plant water potential and stomatal opening. Thus, even if some imbalance between soil  $\Psi$  and plant  $\Psi_{\text{pd}}$  may be observed [Donovan *et al.*, 2001],  $\Psi_{\text{pd}}$  offers the best tool to describe soil and plant water limitations in field conditions. It has been successfully used to predict stomatal closure and photosynthesis of *Q. ilex* leaves in water-limited environments [Acherar and Rambal, 1992; Sala and Tenhunen, 1996; Teixeira Filho *et al.*, 1998; Infante *et al.*, 1999].

[24] To conclude, our findings imply that for a given plant canopy the intensity of summer drought varying from one year to another will alter the source strength of *Q. ilex* emissions with respect to what is expected from light and temperature conditions alone. This view was recently confirmed by Loreto *et al.* [2001], who observed year-to-year variation in the EFs of *Q. ilex* trees growing in open-top chambers, which they attributed to year-to-year variation in



summer drought. Such drought-driven limitations in emissions during hot summers may be particularly important for the formation of photochemical pollutants in the Mediterranean area, a region that is recognized as one of the major sources of tropospheric ozone in Europe [e.g., Millan *et al.*, 1997]. It may be even more relevant under a future climate, which is supposed to become more arid in the Mediterranean [Rambal and Hoff, 1998]. Higher temperatures with regionally changed precipitation patterns will likely increase drought events resulting in lower canopy foliar biomass and altered species composition of Mediterranean oak forests [Sala and Tenhunen, 1996; Joffre *et al.*, 1999]. Future work should investigate whether geographic differences in the water budget of *Q. ilex* habitats have a similar impact on emissions. To date, it is unknown whether *Q. ilex* populations, native in dryer areas, emit less terpene than their relatives in more humid areas, or whether edaphic related adaptations exist that compensate the inhibitory effect of drought on emissions and on tree growth.

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