Supplement to

The Chemical and Microphysical Properties of Secondary Organic Aerosols from Holm Oak Emissions

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In accompanying studies we investigated the dependence of biogenic volatile organic compound (BVOC) emissions from Mediterranean plant species on temperature and light intensity (Photosynthtic Photon Flux Density, PPFD). The chambers used in these experiments are described in detail by e.g. Schuh et al. (1997), Beauchamp et al., (2005), Schimang et al., (2006). Two different chambers were used. A 1150L chamber was used for investigating emissions from a tree stand. A 164 L and was used to investigate emissions from individual plants. Maximum obtainable PPFD ad mid canopy height of the plants was 480 ± 50 µmol m^{-2} s^{-1} in the large chamber and 800 ± 50 µmol m^{-2} s^{-1} in the small chamber. Plants used were Holm Oak (*Quercus ilex* L.), Palestine Oak (*Quercus calliprinos* L.), and Aleppo Pine (*Pinus halepensis* L.).

Stability of emissions and separation of monoterpene groups

The examined plants are monoterpene emitters. Holm Oak is the strongest and Aleppo Pine is the weakest emitter. Emissions of isoprene, sesquiterpenes, green leaf aldehydes, or BVOC originating from the phenylpropanoid pathway were either below the detection limit or extremely low. Therefore this study focused on monoterpene emissions. In a first step we tested the overall stability of the emission

rates by holding the plants at a constant chamber temperature and a diurnal cycle with 14 h illumination, 1 h twilight (lamps stepwise turned off), 8 h darkness, and 1 h twilight (lamps stepwise turned on). Figure S1 shows an example from an experiment with a set of Mediterranean plants (1 Holm Oak, 1 Palestine Oak and 2 Aleppo Pines). The emissions were mostly stable as long as the temperatures did not exceed 35 °C.

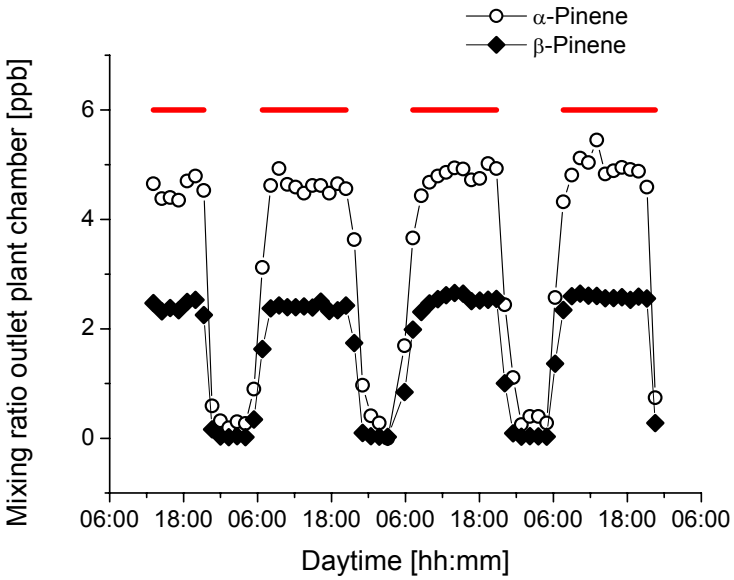

Figure S1: temporal BVOC concentrations at the outlet of the plant chamber. Chamber temperature 20 °C, PPFD = 480 / 0 µmol m^{-2} s^{-1} day/night. Red bars indicate periods of full illumination.

The emission rates of many monoterpenes were quite stable (from here on termed Group 1 monoterpenes, compare to Staudt and Bertin, 1998 who named this group cyclic monoterpenes). The emission rates of the acyclic ocimenes were less stable. Measuring the emissions of these Group 1 monoterpenes for an individual plant at a given temperature and a given PPFD with a time interval of 8 to 10 days showed that emission rates varied by less than 33 %. The strongest Group 1 monoterpene

emissions from each plant showed variations of less than 10 % in all cases when the plants were not exposed to hard stress situations (Examples given in Table S1).

Table S1: Emission rates measured for an individual *Quercus calliprinos*. Time interval between measurements = 8 days. T = 24 °C and PPFD = 800 µmol m^{-2} s^{-1} on both days. Emission rates (Φ) are given in units of 10^{-12} mol m^{-2} s^{-1}. $\Phi(t=1)$ is the mean of the emission rates measured during the first day and $\Phi(t=2)$ is the mean of the emission rates measured on the second measurement day. σ is the standard deviation of Φ during the respective measurement days (n=8 each) $\Delta\Phi$ is the difference of the emission rates measured on the first and second day, respectively. + indicates increase, - indicates a decrease from the first to the second measurement day.

Monoterpene	$\Phi(t=1)$ [mol m^{-2} s^{-1}] * 10^{12}	σ [%]	Φ (t=2) [mol m^{-2} s^{-1}] * 10^{12}	σ [%]	$\Delta\Phi$ [%]
α-Thujene	8.3	6.7	8.3	4.2	+ 0.6
α-Pinene	240	5.2	260	2.5	+ 5.3
Sabinene	30	3.1	22	3.7	- 27.4
β-Pinene	97	4.7	93	2.9	- 4.3
Myrcene	8.9	11.6	11	8.4	+24.0
α-Phellandrene	4.4	7.9	5.4	5.3	+21.3
α-Terpinene	16	8.1	16	6.5	+ 0.4
Limonene	51	6.0	67	0.2	+ 31.6
β-Phellandrene	11	6.5	13	4.3	+16.3
γ-Terpinene	31	8.8	39	4.9	+ 26.3

Emissions of ocimenes were substantially less stable. On a time scale of several days ocimene emissions varied even under constant temperature and PPFD. In most cases these emissions were very low when starting the measurements (*Quercus ilex,* see table S2) and when high temperatures (≈ 35 °C) were reached for the first time,

ocimene emissions increased by far. In case of Palestine Oak (*Quercus calliprinos*, see Table S2) ocimene emissions were even not observed until the plants were exposed to a high temperature.

Once abundant these emissions varied on a short time scale and these changes were somehow coupled to changes of PPFD or changes of temperature. During darkness these emissions were negligibly low and they increased with increasing PPFD. However, after the light was switched on, the emissions increased slowly and it took several hours until they reached a steady state (Figure S2). During the first hours under illumination the emissions changed by more than an order of magnitude although temperature and PPFD were held constant. Hence, besides temperature and PPFD there must be other quantities affecting ocimene emissions. A description of the temperature and PPFD dependence of ocimene emissions by algorithms that consider temperature and PPFD as variables only was therefore impossible.

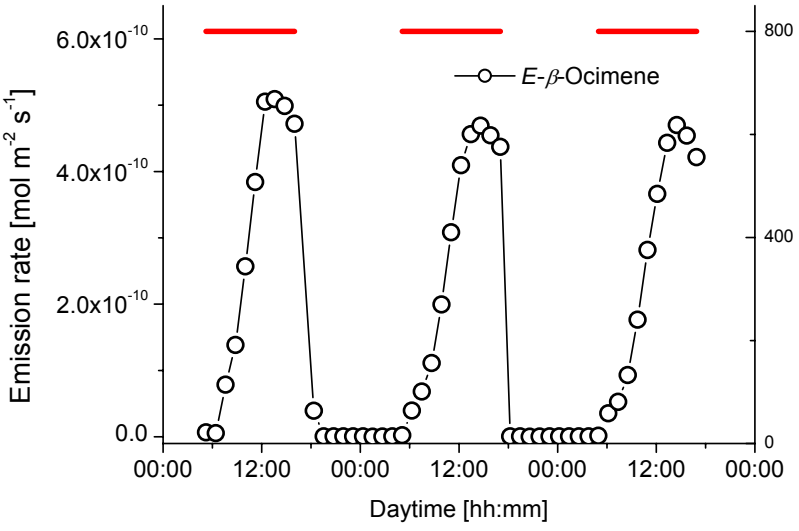

Figure S2: diurnal variation of *E*-β-ocimene emissions from an individual Palestine Oak. Periods of illumination are indicated by the red bars. Temperature: 29 / 25 °C during illumination from 6:00 to 18:00 h / darkness.

The behaviour found for the ocimene emission was general for all investigated plants. Another feature that was found to be general for all species investigated here was a good relationship between the emission rates of the strongest emissions within the single groups. Plotting the emission of a Group 1 monoterpene versus that of another one yielded in high correlations independent of the temperature and light regime applied during such an experiment (example see Fig. S3a). Relating the rates measured for the strongest emissions to each other led to coefficients of determination $R^2 > 0.8$ in all cases. The same observation was made when relating emission rates of ocimenes to each other (Fig. S3b). Emission rates of Group 1 monoterpenes and ocimenes were not related to each other.

In some cases oxygenated monoterpenes as 1,8-cineole or linalool were observed. Emission rates of such oxygenated monoterpenes showed neither good relationships to those of the Group 1 monoterpenes nor to those of the ocimenes nor among each other. Emissions of the oxygenated monoterpenes were not dominant. These emissions are therefore not described in detail here.

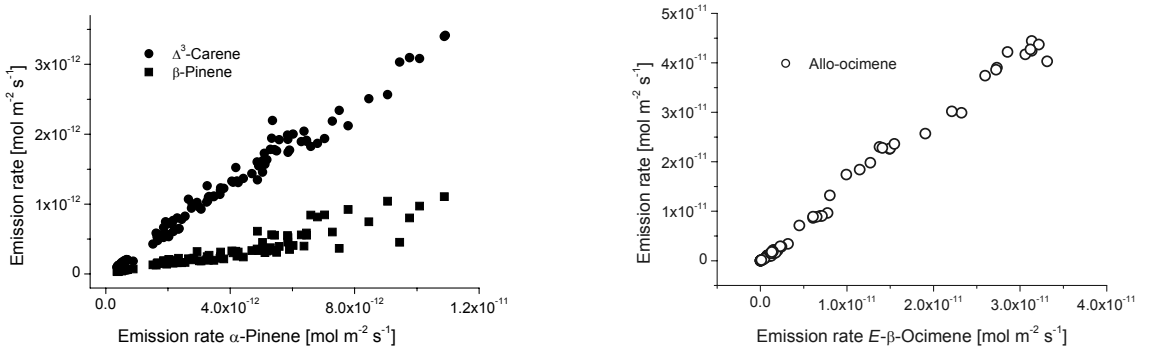

Figure S3: Correlation of monoterpene emissions rates a) emission rates of Δ^3-Carene and β-Pinene plotted versus emission rates of α-Pinene as examples for

Group 1 monoterpenes, plant species: Aleppo Pine, b) allo-ocimene emission rates plotted versus emission rates of *(E)-β*-ocimene emissions, plant species: Palestine Oak.

The good relationships were independent of the temperature- and PPFD regime applied to the plants and valid for all data points obtained for a given plant. This behaviour indicated that emissions of these compounds were based on a very similar emission mechanism. All Group 1 monoterpene emissions had the same temperature and PPFD dependencies allowing to describe these dependencies with the same values for the parameters. The only differences were the standard emission rates for the individual monoterpenes.

On the other hand the low correlations and the high scatter observed for plots of emission rates of an ocimene versus a Group 1 monoterpene indicated that the emissions of Group 1 monoterpenes and ocimenes varied differently with temperature and PPFD.

Methodology to describe temperature- and PPFD dependencies of monoterpene emissions

PPFD and temperature dependencies of BVOC emissions from individual plants were investigated using the small chamber. The experimental procedure is described in detail by Schuh et al. (1997). In short, for measuring the temperature dependence of BVOC emissions, PPFD was held constant (≈ 800 µmol m^{-2} s^{-1}) but temperature was varied stepwise from day to day. When steady state was reached 6 to 8 measurements were conducted. For measuring the PPFD dependence, PPFD was changed from day to day (exception Aleppo Pine). Leaf temperature was held

constant by increasing or decreasing the chamber temperature in response to changes in PPFD (≈ 0.5 °C per 100 µmol m^{-2} s^{-1} change of PPFD). Data were parameterized using either the algorithm given by Guenther et al. (1993) and Guenther (1997), (equation S1) or the algorithm of Schuh et al. (1997) (equation S2), both after slight modification.

$$\Phi_{VOC} = \Phi_{VOC}^{B,S} \cdot c_{L1} \cdot \frac{\alpha \cdot PPFD}{\sqrt{1+\alpha^2 \cdot PPFD^2}} \cdot \exp\left(\beta_2 \cdot \left(T - T_S\right)\right) \qquad \text{(eq. S1)}$$

$$\Phi_{VOC} = \Phi_{VOC}^{P,S} \cdot \exp\left(\beta_1 \cdot \left(T - T_S\right)\right) + \Phi_{VOC}^{B,S} \cdot c_{L1} \cdot \left(\frac{\alpha \cdot PPFD}{\sqrt{1+\alpha^2 \cdot PPFD^2}}\right)^2 \cdot \exp\left(\beta_2 \cdot \left(T - T_S\right)\right)$$

(eq. S2)

The descriptions of PPFD dependencies are identical to those given in Guenther et al. (1993) and Schuh et al. (1997). For plant species without special monoterpene storing organs it is assumed that, similar to isoprene, monoterpenes are emitted in parallel to their biosynthetic production. This production is PPFD dependent and this dependence is described by the two parameters C_{L1} and α. $\Phi_{VOC}^{B,S}$ is the standard emission rate i. e. the emission rate at standard temperature and standard light intensity. PPFD is the actual light intensity.

The description of the temperature dependence differs slightly from that given in the original publications of Guenther and Schuh. It was simplified in two ways. First, we used the meanwhile common description by using a temperature coefficient (β_2) and the difference of actual leaf temperature (T) and standard temperature (T_S) (see also Folkers et al., 2008). Second, we neglected the decrease of BVOC emissions at

temperatures above the maximum enzyme activity. In the experiment described here we look at temperatures below 35 °C only. This allows the approximation by an exponential increase of monoterpene emissions with temperature.

One difference between both algorithms is the shape of the functions used to describe the PPFD dependence. Whereas the description according to Guenther et al. is an approximation to Michaelis Menten kinetics, the description according to equation S2 is that of a sigmoid function.

Another difference is the additional term in Equation S2 describing emissions from pools. These emissions are supposed to be independent of PPFD but dependent on temperature. Emissions from pools might exhibit temperature dependencies different from emissions in parallel to monoterpene biosynthesis. Thus they are described by an additional temperature coefficient (β_1). $\Phi_{VOC}^{P,S}$ represents the standard emission rate for these pool emissions. Details with respect to the reasons for introducing this term are given in Schuh et al. (1997) and in Shao et al. (2001).

Standard conditions chosen here for the descriptions were: standard temperature T_S = 24 °C, standard light intensity, $PPFD_S$ = 800 µmol m^{-2} s^{-1} for Holm Oak and Palestine Oak. Due to a failure of the set up the maximum obtainable PPFD was 600 µmol m^{-2} s^{-1} during the experiments with Aleppo Pine. Therefore chosen standard emissions for Aleppo Pine were T_S = 24 °C and PPFD = 600 µmol m^{-2} s^{-1}. Table S2 shows emission rates measured at these standard conditions.

Table S2: Emission rates of monoterpenes (given in nmol m^{-2} s^{-1}) and relative abundance of monoterpene emissions. Groups of emissions are treated separately, i.e. sum of Group 1 monoterpenes is set to 100% and the sum of ocimene emissions is set to 100 %. The fraction of Group1 monoterpene emissions over ocimene emissions is given for a temperature of 24 °C and PPFD = 800 µmol m^{-2} s^{-1} (for Aleppo Pine 600 µmol m^{-2} s^{-1}) for plants that were not exposed to temperatures far above 30 °C for the last 3 weeks before the respective measurements.

*: emission rates below 0.01 nmol m^{-2} s^{-1}, neglected for Holm Oak and Palestine Oak. ** for Aleppo Pine emission rates below 0.0001 nmol m^{-2} s^{-1} were neglected.

	Quercus ilex		*Quercus calliprinos*		*Pinus helepensis*	
Group 1 Monoterpene	Φ	Rel. abund. [%]	Φ	Rel. abund. [%]	Φ	Rel. abund. [%]
α-Pinene	1.6	27.5	0.24	28.5	0.003	43.8
Myrcene	0.57	11.5	0.09	2.6	0.0002	3.1
β-Pinene	0.86	15.4	0.1	13.6	0.0003	4.2
α–Terpinene	0.07	1.5	0.02	5.2	0.0002	2.8
Δ^3-Carene					0.0008	13.0
p-Cymene	0.03	0.5	0.04	9.5	**	
Limonene	2.7	31.1	0.05	10.6	0.0005	2.2
γ–Terpinene	0.1	2.1	0.03	9.3	0.0003	4.5
Ocimenes						
Z-Ocimene	0.72	54	*		**	
E-*β*–Ocimene	0.02	16	*		0.19	> 99
Allo-Ocimene	0.4	30	*		**	
Ratio Group 1/Ocimenes		4.7		> 100		0.33

Temperature dependence of monoterpene emissions

Temperature dependencies were determined at constant PPFD from the slopes of plots of the logarithms of emission rates normalized to the respective standard emission rates versus temperature (Figure S4). Results for temperature dependencies are given here only for temperatures up to 34 °C.

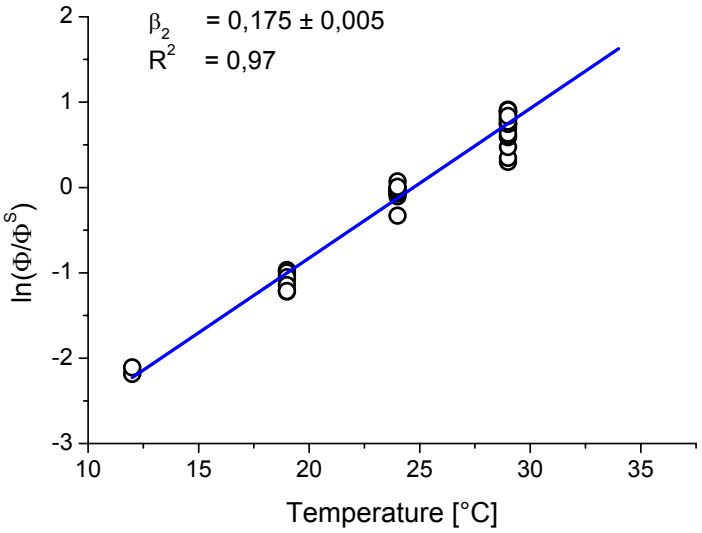

Figure S4: logarithm of the emission rate of α-thujene normalized to its standard emission rate versus temperature. *Quercus calliprinos* L., α-thujene as an example for Group 1 monoterpenes. Linear regression analysis yields a temperature dependence of about 17.5 % per degree for Group 1 monoterpene emissions from Q. *calliprinos*.

For ocimene emissions such plots showed a strong scatter. Changing the temperature on a daily basis caused a change of the emission rates superimposed by the diurnal rhythm as shown in Fig. S2. Due to this behaviour we could not describe the temperature dependence of the ocimene emissions directly. However, to obtain an idea how ocimene emissions were affected by temperature we used

cumulative emissions (emission rates integrated over the respective time periods of full illumination and steady state temperature ≈ 10.5 h per day, Fig. S5).

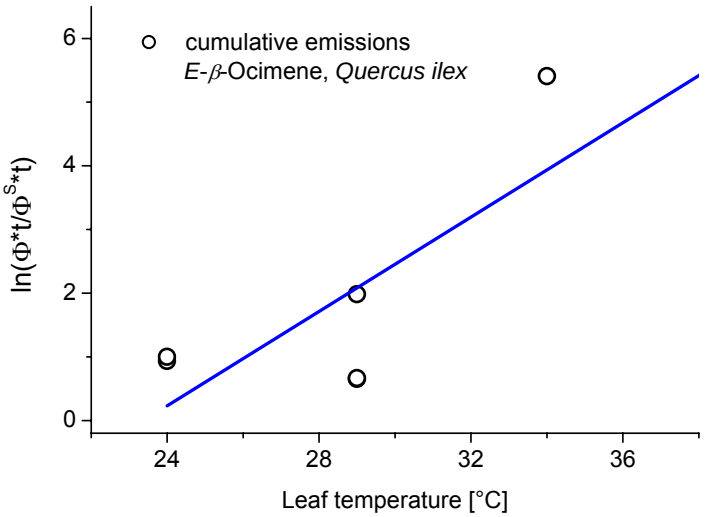

Figure S5: plot of the logarithm of cumulative *E*-β-ocimene emissions normalized to the cumulative emissions obtained at standard conditions versus leaf temperature. Holm Oak, emissions were added over the time periods of illumination after the chamber temperatures had obtained steady state (t = 10.5 h). Linear regression yields a temperature dependence of about 31 % per degree.

Table S3 summarises the temperature dependencies measured in our pilot studies. These temperature coefficients are only valid for plants that have not experienced temperatures far above 30 °C for several weeks before the measurements.

Table S3: Temperature dependencies of monoterpene emissions for temperatures below 34 °C. Measurements were made at a PPFD of 800 µmol m^{-2} s^{-1} for Holm Oak and Palestine Oak and at a PPFD of 600 µmol m^{-2} s^{-1} for Aleppo Pine. Temperature dependencies for Group 1 monoterpenes were obtained as usual, temperature dependencies for the ocimenes were obtained using cumulative emissions.

	Q. ilex	*Q. calliprinos*	*P. halepensis*
Group 1 monoterpenes	0.2 ± 0.017	0.175 ± 0.005	0.13 ± 0.004
Ocimenes	0.31 ± 0.15	0.23 ± 0.04	0.15 ± 0.01

All descriptions of temperature- and PPFD dependencies by phenomenological algorithms presuppose that BVOC emissions are independent of time. This was not the case for the ocimene emissions (Fig. S2). Measurements using snapshots taken at different temperatures may therefore lead results very different from those listed in Table S3. However, the use of cumulative emissions is to our opinion the most best reliable way to find a guess on the impact of temperature on these emissions.

PPFD dependence of monoterpene emissions

Emissions of Group 1 monoterpenes from Holm Oak and Palestine Oak were negligibly low in darkness and increased strongly with increasing PPFD. Figure S5 shows an example for a measurement of PPFD dependencies together with a fit to the algorithm of Guenther et al. (1993) and to the algorithm of Schuh et al. (1997), respectively at the example of a Group 1 monoterpene emission from *Quercus ilex*.

As darkness emissions were negligible, $\Phi_{VOC}^{P,S}$ in Equation 2 was set to zero. Furthermore, no clear indications of PPFD saturation were observed for both oak species. This led to high uncertainties of the data fitted for the coupled parameters C_{L1} and α. However, both algorithms described the PPFD dependencies quite well.

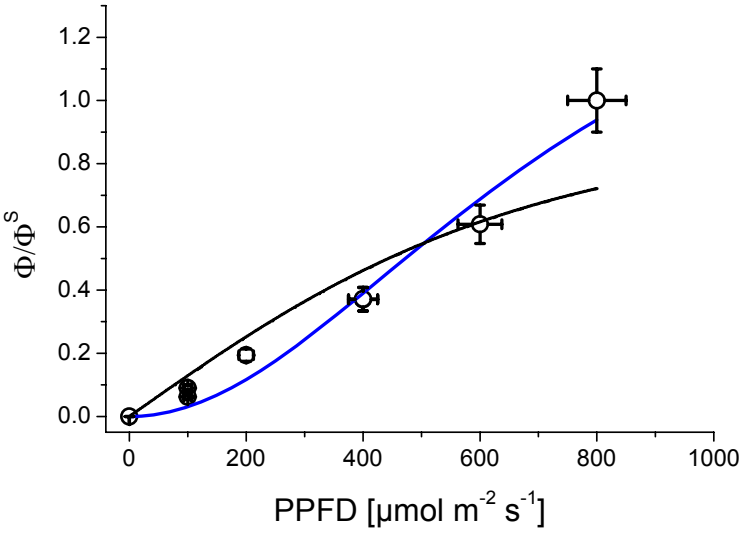

Figure S6: Emission rate of a Group 1 monoterpene normalized to its standard emission rate plotted versus PPFD. The lines show the result of least square fits to the data points. Black line: equation S1, blue line: equation S2 with $\Phi_{VOC}^{P,S}$ being set to zero. Example: α-Thujene emission from *Quercus ilex*. Data points indicate the mean of at least 6 measurements at steady state conditions during one day each.

Table S4 summarizes the values obtained from fits of the emission rates normalized to emission rates measured at standard temperature according to Equations 1 and 2, respectively.

Table S4: PPFD dependencies of monoterpene emissions Measurements were made at PPFD between 0 and 800 µmol m^{-2} s^{-1} for Holm Oak and Palestine Oak. The high uncertainties of parameter values were due to the nearly linear increase of the emissions with increase of PPFD.

	algorithm	Holm Oak	Palestine Oak
α	S 97	0.0013 ± 0.0002	0.002 ± 0.00012
C_{L1}	S 97	1.81 ± 0.53	1.05 ± 0.04
α	G 93	0.0004 ± 0.0008	0.00091 ± 0.00023
C_{L1}	G 93	2.9 ± 5.9	1.73 ± 0.33

No significant PPFD dependence was found for the Group 1 monoterpene emissions from Aleppo Pine. Aleppo Pine emitted these compounds also during darkness which is explainable by a diffusion of these monoterpenes from resin ducts where they are stored in such coniferous species. For the Group 1 monoterpenes the emissions in parallel to biosynthesis (Φ_{VOC}^{B}) were low. Φ_{VOC}^{P} was the dominant term and a description of a PPFD dependence (second term of Equation S2) was unnecessary.

When measuring the PPFD dependencies of BVOC emissions with Palestine Oak, the plant did not emit ocimenes and during such measurements with Holm Oak these emissions were too low to obtain reliable data. We observed a large scatter making any further conclusions impossible. However, after high temperatures were reached ocimene emissions were stronger and easily measurable. As obvious from Figure S2 ocimene emissions dropped nearly instantaneous when the light was turned off in the evening. To obtain information how PPFD impacts these emissions we made the following experiment. After ocimene emissions reached a steady state, PPFD was changed by switching off lamps stepwise when the adsorption of the sample on the GC-MS System was finished (time intervals about 70min.). Figure S7 shows the result of this experiment.

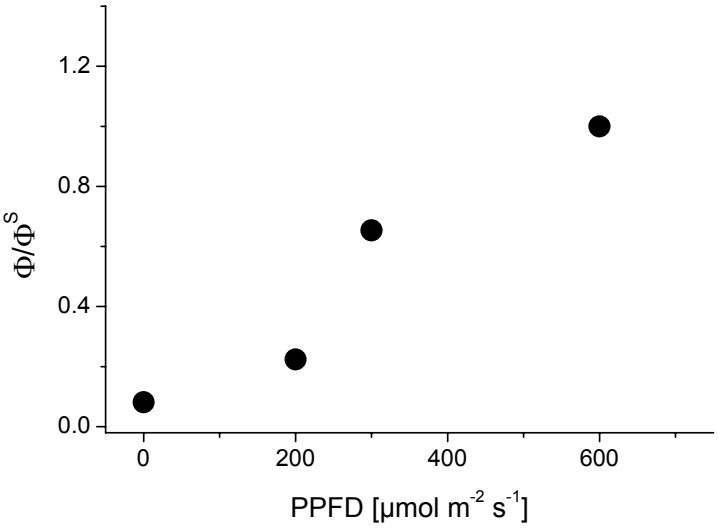

Figure S7: Emission rate of *(E)*-*β*-ocimene from Aleppo Pine normalized to its emission rate at PPFD = 600 µmol m^{-2} s^{-1} rate plotted versus PPFD. T = 24 °C.

As can be seen from Figure S7 also ocimene emissions were strongly dependent on PPFD, however, we refrained from a description. Such a description would presuppose that the PPFD dependence were independent of time and independent of decreasing or increasing PPFD.

Summary

The results shown here clearly indicate that a part of the monoterpene emissions from Holm Oak, Palestine Oak and Aleppo Pine can be parameterized using phenomenological algorithms. For ocimene emissions this is not possible. Ocimene emissions showed a high variability although temperature and PPFD were constant and it was impossible to apply the usual phenomenological algorithms. Nevertheless, ocimene emissions were strongly dependent on both, temperature and light intensity.

This has been observed before and in particular the extreme dependence of ocimene emissions on temperature is extensively described in Staudt and Bertin (1998).

However, some basic information can be obtained regarding the generalization of the behaviour observed for the Holm Oak used for the measurements with respect to SOA formation.

1) Identical to the findings described by Staudt and Bertin (1998) we observed that ocimene emissions may have exceedingly high temperature dependencies. Caused by the lower temperature dependence of Group 1 monoterpene emissions a change of temperature will lead to a changed emission pattern. At higher temperatures emissions of ocimenes are favoured, and vice versa. This was observed for all species investigated here and also for the *Quercus ilex* plant used to determine microphysical properties of secondary organic aerosols. The behaviour of the latter may therefore be seen as quite typical for one of the broad spread Mediterranean species investigated here.

2) Temperature coefficients determined for the Group 1 monoterpene emissions are also very high. Compared to the temperature coefficient recommended for Boreal species (e.g. 9 % per degree, Guenther et al., 1993, Guenther, 1997, 13 % per degree, Shao et al., 2001) they are up to a factor of 2 higher (Table S3). Hence, temperature increases should have stronger impacts on monoterpene emissions in the Mediterranean region than in the Boreal regions. This effect is enhanced by the strong increases of ocimene emissions with temperature.

As shown by Mentel et al. (2009), the incremental yield of SOA formation from monoterpenes is to a good approximation independent of the detailed emission pattern. Thus, at otherwise unchanged conditions, the stronger increases of

monoterpene emissions from Mediterranean species would be followed by stronger SOA formation compared to the increases in regions with Boreal forests.

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