Emissions of Volatile Organic Compounds from Sunflower and Beech: Dependence on Temperature and Light Intensity

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Abstract. Emissions of volatile organic compounds (VOCs) from sunflower (*Helianthus annuus* L. cv. giganteus) were measured in a continuously stirred tank reactor. The compounds predominantly emitted from sunflower were: isoprene, the monoterpenes α-pinene, β-pinene, sabinene, 3-carene and limonene, an oxygenated terpene, not positively identified so far and the sesquiterpene β-caryophyllene. Emission rates ranged from 0.8×10^{-16} to 4.3×10^{-15} mol cm^{-2} s^{-1} at a temperature of 25 °C and at a light intensity of 820 μE m^{-2} s^{-1}. A dependence of the emission rates on temperature as well as on light intensity was observed. The emission rates of α-pinene, sabinene and thujene from beech (*Fagus sylvatica* L.) were also affected by temperature as well as by light intensity. Our results suggest that an emission algorithm for all compounds emitted from sunflower and beech has to consider temperature and light intensity simultaneously. The observations strongly indicate that the emissions of VOCs from sunflower and beech are in part closely coupled to the rate of biosynthesis and in part originate from diffusion out of pools. The emission rates can be described by an algorithm that combines the model given by Tingey and coworkers with the algorithm given by Guenther and coworkers after slight modification.

Key words: emission algorithm, isoprene, monoterpene, sesquiterpene, sunflower, beech.

1. Introduction

Numerous field experiments as well as laboratory studies have been conducted in order to quantify the source strength of vegetation for volatile organic compounds (VOC). However, the amount of VOCs emitted from vegetation is still uncertain because not all factors affecting the emission rates of VOCs by higher plants are identified so far (e.g., Fehsenfeld *et al.*, 1992).

Investigations of factors that control the VOC emissions were mainly conducted with respect to temperature and light intensity. From many measurements it has been concluded that the monoterpene emissions are dependent on temperature but

independent of light intensity (e.g., Tingey *et al.*, 1980; Goldan *et al.*, 1995). The model described in Tingey *et al.* (1991) can be used to explain the experimental results that were obtained with respect to the temperature dependence of monoterpene emissions from conifers. In this model it is assumed that the emissions are mainly controlled by physical processes. Terpenes stored in pools diffuse through the epidermis cells into the extra cellular airspace and thereafter to the substomatal cavities. The flux from the pools to the air is determined by the vapor pressure gradient of the terpenes between the pools and the atmosphere. To a first approximation this gradient is equivalent to the vapor pressure of the individual terpenes within the pools because the vapor pressures of terpenes in the atmosphere are orders of magnitude lower compared to those in the pools. Tingey *et al.* (1991) introduced a correction term considering the temperature dependence of the diffusive resistance for the VOC flux inside the plant. However, the exponential increase of vapor pressure with temperature is believed to be the dominant factor for the exponential increase of the emission rates with temperature. Since vapor pressure of VOCs in the pools is not influenced by light intensity, a dependence of the emission rates on light flux cannot be explained by this model.

It is well known that the emission of isoprene is dependent on light intensity (e.g., Tingey *et al.*, 1979). Only small pools exist for isoprene inside the plants (Sharkey *et al.*, 1991). Hence, the isoprene emissions are related to the rate of isoprene biosynthesis with only marginal time delay. Since the rate of isoprene biosynthesis is dependent on light intensity, the dependence of its emission rates on light intensity can be explained. Guenther *et al.* (1991, 1993) developed an emission algorithm for isoprene which describes both, the dependence of isoprene emissions on light intensity and on temperature.

We found that light intensity affects terpene emissions from sunflower and those of sabinene and thujene from beech. As mentioned before, this behavior is not explainable with the model of Tingey *et al.* (1991). Furthermore, we observed monoterpene emissions during darkness that cannot be described by the algorithm of Guenther *et al.* (1991, 1993). Therefore, another approach for an emission algorithm is employed to describe the VOC release from sunflower and beech by combining the algorithm of Guenther *et al.* (1993) with that based on the model of Tingey *et al.* (1991).

2. Experimental

The experiments with sunflower were performed in a continuously stirred tank reactor (CSTR) described in Neubert *et al.* (1993) and Wildt *et al.* (1997). The upper part of the CSTR contained stem and leaves of the plants. The lower part of the system containing the plant's roots and the nutrient solution, was separated from the upper part by a PTFE sheet with a hole at the midpoint as a feedthrough for the plant's stem.

Ambient air was purified from ozone, NO, and NO_2 by charcoal and $KMnO_4$ (Purafil) and then passed over a palladium catalyst at 250 °C to reduce the concentrations of hydrocarbons in the air entering the chamber. The air flow through the chamber which had a volume of 164 L was adjustable between 10 and 50 L min^{-1}. Consequently, the residence time of the air in the CSTR ranged from 3 to 16 min. Fourteen discharge lamps (6 lamps Osram HQI-R 250 W/NDL and 8 lamps Osram HQI T 1000 W) were used as light sources. At full illumination the light flux was 1090 μE m^{-2} s^{-1} at the midplane of the chamber. The concentrations of O_3, NO, NO_2, CO_2, H_2O and those of the VOCs were measured at chamber inlet and at chamber outlet.

For the measurements of VOC concentrations two GC systems were employed. One system consisted of a gas chromatograph/flame ionization detector system (GC/FID, Airmotec HC 1010, column: DB-5, 9 m × 0.25 mm i.d., film thickness: 1 μm, C_5–C_{10}–VOCs, time resolution 30 min). Samples were taken with adsorption tubes containing carbotrap/carbosieve SIII (Supelco Bellefonte, 48 mg carbotrap and 40 mg carbosieve, respectively). Three liters of air were passed through the tubes and after thermal desorption the VOCs were injected onto the column.

The second technique to measure VOC concentrations used a gas chromatography/mass spectrometer system (GC/MS, Fisons MD 800, GC: Carlo Erba CE 8060, column: DB-5, 30 m × 0.25 mm i.d., filmthickness: 0.33 μm, C_{10}–C_{15}–VOCs, time resolution determined by sampling frequency: about 3 h). The samples were taken on charcoal adsorption tubes (Paxton Scientific Glass, length 5 cm, diameter 0.4 cm, filled with 5 mg charcoal). 50 to 120 L of air were sampled. The VOCs adsorbed on the charcoal were extracted with 100 μL of a benzene/acetonitrile mixture (80/20 (V/V), respectively) and 1 μL of the extract was injected into the GC/MS system (split/splitless injector, 125 °C). The GC/MS system was used for identification as well as for quantitative determinations of emission rates.

Calibration of the GC/MS instrument was based on liquid standards. Self made liquid standards with known concentrations of the single substances in benzene/acetonitrile were injected into the GC/MS system and the areas of the signals obtained for the total ion current as well as for the base peaks were used for calibration.

The GC/FID system was calibrated using a permeation source. Mono- and sesquiterpenes were stored as pure substances (Aldrich, Fluka, purity 93 to 96%) in small glass tubes covered with Teflon membranes. The glass tubes were positioned in a temperature controlled glass vessel (25 ± 0.5 °C, volume 2 L). Nitrogen (1 L min^{-1}) was passed through the glass vessel and the VOCs permeating through the Teflon membranes were diluted by the nitrogen flux to concentrations below 1 ppm. A small fraction of this nitrogen flux (70 mL min^{-1}) was diluted in a second step again with pure nitrogen (2–5 L min^{-1}) resulting in VOC concentrations between 1 and 20 ppb.

The concentrations of the VOCs from the calibration device were calculated from the mass loss rate of the liquid VOCs in the glass tubes and from the flow

rates of nitrogen. The mass loss rates of the liquid VOCs were determined by weighing each of the tubes regularly every two to three days.

The permeation source was checked by comparison with liquid standards. Samples taken from the permeation source on charcoal tubes were extracted with benzene/acetonitrile and the extracts were injected into the GC/MS system. After calibration of the GC/MS system with liquid standards, the concentrations of the VOCs emitted from the calibration source were measured. These concentrations were compared to those calculated from the mass loss of the liquids in the permeation source. The concentrations calculated in both ways led to the same results within an error of less than 30% except for β-caryophyllene and α-humulene. Using the concentration data from the permeation source the response for these two substances was lower by about 50% compared to the data from liquid standards which indicates losses of the sesquiterpenes in the permeation source.

The detection limit ranged between 0.02 and 0.05 ng for the GC/FID system and 0.01 ng for the GC/MS system (3σ). The reproducibility of the concentration measurements was 15%. For the GC/MS system this was tested by several injections of extracts from a given mixture. For the GC/FID system this was tested with the permeation source. Figure 1 shows the peak areas obtained from measurements with the GC/FID system for α-pinene and sabinene as measured over a time period of several days. The reproducibility of both, the GC/FID system and the calibration source was within 15% for all substances.

Identification was based on the mass spectra and on the retention times. Substances were assumed to be identified when the mass spectra of the substances emitted from the plants corresponded to those of injected substances and when the retention times for the injected substances and the compounds emitted by the plants were identical within 3 sec.

The identification procedure for the substances measured with the GC/FID system was as follows: Substances which were emitted from sunflower and identified with the help of the GC/MS system were introduced as single compounds into the calibration source. Identification of the peaks in sample chromatograms was based on the retention times of the individual compounds.

To estimate the hydrocarbon emission rates from beech under varying environmental conditions, outdoor plant enclosure chambers with volumes of 320 L were used (Kahl *et al.*, 1997). The chambers allow the simulation of typical ambient conditions. PFA and special glass-materials were used because they minimise wall-losses of the emitted substances. Furthermore, these materials transmit a wide spectral range of solar radiation, especially the UV and photosynthetic active range (PAR). A purified ambient air supply was used to give one air change per 10 minutes. A specially designed ventilator reduced the boundary layer resistance at the surface of the plants and resulted in a constant wind speed of about 1 m s^{-1}. Temperature and humidity were controlled and reported by sensors positioned inside the chamber. In addition, the CO_2-, NO_x- and O_3-concentrations were recorded at the inlet and outlet of each chamber. The light intensity inside the chamber could

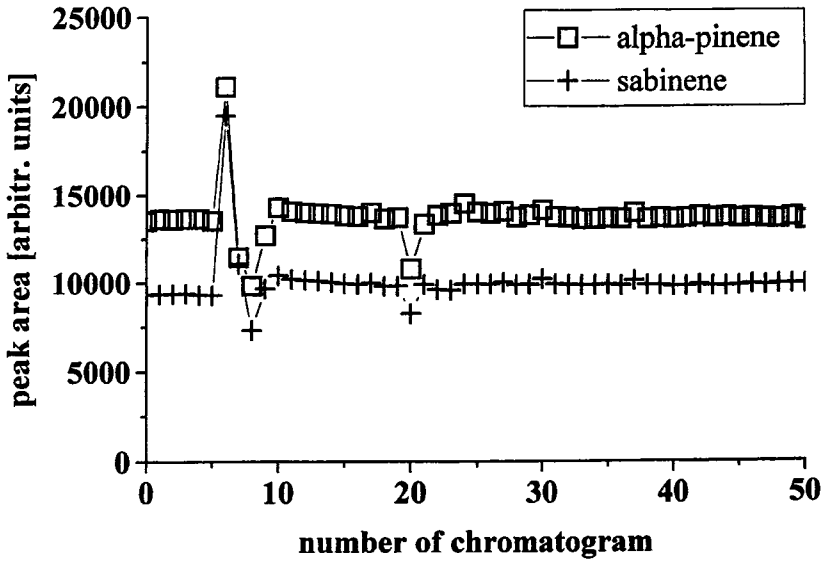

Figure 1. Peak areas for α-pinene and sabinene from chromatograms taken at the permeation source over a time period of about 3 days. Data were obtained by GC/FID analysis, samples were taken with an individual adsorption tube. Time resolution 90 minutes. Numbers of chromatograms are chronological. The deviations in the chromatograms number 6, 8 and 20 are caused by disturbances of the source by manual operations, e.g. control of gas flow.

be adjusted by sequentially shielding the incoming sunlight with an array of thin plastic plates and was measured with a PAR-sensor (Li-COR). The monoterpenes released by beech were preconcentrated on Tenax TA/Carbopack B filled sampling tubes and quantified by a thermodesorption/GC/MS-system using a gas-phase calibration source similar to the system described above. A more detailed description of the analytical method used for the studies on VOC emission from beech can be found in Hoffmann (1995).

3. Method

Experiments were conducted with sunflower plants (*Helianthus annuus* L. cv. giganteus, 11 plants) and with beech (*Fagus sylvatica* L., 3 plants together).

For sunflower the germination of the seeds took place in moist quartz sand at a temperature of 28 °C and at a relative humidity of 85%. After two to three weeks the plants were placed into a hydroponic system with 100 liters of aerated nutrient solution. The concentration of NO_3^-, pO_2 as well as pH were controlled and kept constant. Nitrate concentration was 0.75 mM, pO_2 was 70% and pH was 6.0 ± 0.3. During the experiments in the CSTR the plants were nourished identically.

Rates of net photosynthesis, Φ_{CO_2}, rates of transpiration, Φ_{H_2O}, and stomatal conductivities to water vapor, $g^s_{H_2O}$, were calculated from the measured CO_2 or H_2O concentrations, respectively using the formulas given by von Caemmerer and Farquhar (1981).

The calculations to determine the VOC emission rates consider the following processes:

$$\mathrm{VOC_{plant}} \xrightarrow{\Phi_{VOC}} \mathrm{VOC_{air}} \quad \text{Emission of a certain VOC from the plant} \quad \text{(R1)}$$

$$\mathrm{VOC_{air}} \xrightarrow{v^w \cdot A^w} \mathrm{VOC_{wall}} \quad \text{Loss of VOC on the chamber walls} \quad \text{(R2)}$$

$$\mathrm{VOC_{air}} + \mathrm{OH} \xrightarrow{k} \mathrm{Products} \quad \text{Loss of VOC by gas phase reactions} \quad \text{(R3)}$$

In Reaction (R1), Φ_{VOC} represents the flux density of the VOC under consideration. Wall losses are described by $v^w_{VOC} \cdot A^w$, where v^w_{VOC} is the deposition velocity of a certain VOC to the walls of the chamber and A^w is the wall area of the CSTR. Gas phase reactions of individual VOCs with hydroxyl radicals are described by the rate constant k. However, assuming a gas kinetic rate constant of 10^{-10} cm^3 s^{-1} and hydroxyl radical concentrations of 10^6 cm^{-3} the losses described by Reaction (R3) would lead to losses lower than 10% of the VOC concentrations. Therefore, Reaction (R3) was neglected and the mass balance for the VOCs in the chamber is given by Equation (1):

$$V \cdot \frac{\mathrm{d[VOC]}}{\mathrm{d}t} = -F \cdot ([\mathrm{VOC}] - [\mathrm{VOC}]_{in}) + \Phi_{VOC} \cdot A^L - v^w_{VOC} \cdot A^w \cdot [\mathrm{VOC}] \quad (1)$$

[VOC] and $[\mathrm{VOC}]_{in}$ are the concentrations of the individual VOCs at chamber outlet and at chamber inlet, respectively and F is the air flow through the chamber. V is the volume of the chamber and A^L represents the leaf area of the plant (one sided).

Steady-state conditions for Φ_{VOC} were assumed when [VOC] was constant from one measurement to another within the error limits of the measurements. Since the time resolution was half an hour, variations on time scales lower than half an hour cannot be considered and the flux densities given here are averages for the time scale given by the time resolution of the measurements. For steady state conditions rearrangement of Equation (1) leads to Equation (2).

$$\Phi_{VOC} = \frac{F}{A^L} \cdot ([\mathrm{VOC}] - [\mathrm{VOC}]_{in}) + v^w_{VOC} \cdot \frac{A^w}{A^L} \cdot [\mathrm{VOC}]\,. \quad (2)$$

$v^w_{VOC} \cdot A^w$ was determined without a plant in the chamber but under otherwise identical conditions. Terpenes emitted from a permeation source were introduced into the air entering the chamber resulting in concentrations between 0.2 and 5 ppb for single compounds. $v^w_{VOC} \cdot A^w$ was calculated according to Equation (3) using

the data from concentration measurements at chamber inlet and chamber outlet, respectively

$$v^{w}_{\mathrm{VOC}} \cdot A^{w} = F \cdot \frac{([\mathrm{VOC}]_{\mathrm{in}} - [\mathrm{VOC}])}{[\mathrm{VOC}]} \,. \tag{3}$$

No losses of the VOCs on the walls of the chamber were found within the uncertainty caused by the reproducibility of the concentration measurements. In no case the VOC concentrations at chamber outlet were below 80% of those measured at chamber inlet. Thus, wall losses were neglected and therefore, the values for the emission rates given here may be up to 20% too low.

The air at chamber inlet was analyzed at least once a day. The chromatograms obtained from the air at chamber inlet did not differ significantly from those of blanks. Obviously, the efficiency of the palladium catalyst was good enough to reduce the concentrations of VOCs with C numbers $\geq$5 at chamber inlet to vlaues below the detection limit. Therefore, the concentrations of VOCs at chamber inlet were set to zero and the emission rates for the individual VOCs were calculated according to Equation (4):

$$\Phi_{\mathrm{VOC}} = \frac{F}{A^{L}} \cdot [\mathrm{VOC}] \,. \tag{4}$$

The error in the absolute values of Φ_{VOC} is estimated from the results of the different calibration procedures to about 30% for the monoterpenes. The calculations of the β-caryophyllene and α-humulene concentrations are based on liquid injection only. It cannot be excluded that the absolute uncertainties in the determination of the emission rates of these two compounds may be higher than 30%. However, the good agreement between the calibrations for other compounds gives us confidence that there is no major calibration error also for β-caryophyllene and α-humulene.

Most of the data were obtained with the GC/FID system. At the retention times where β-pinene and 3-carene eluted, peaks were observed in chromatograms of blanks. The areas of these peaks varied with time. Therefore, the emission rates for β-pinene and 3-carene are highly uncertain. For tricyclene and γ-terpinene the emission rates from sunflower were too low to obtain reliable data with respect to the modulation of these rates as a function of temperature and light flux. Quantitative data for β-pinene, 3-carene, tricyclene and γ-terpinene were not taken into consideration for the interpretation of our data and are not presented here.

One compound emitted from sunflower is unidentified yet. For this compound it is assumed that wall losses are also negligible. The error in the determination of the absolute values for the emission rates of this compound cannot be estimated. However, the conclusions concerning the dependence of the emission rates on temperature and light intensity are based on relative data. Therefore, the errors in the determination of the absolute values are of minor importance. For the interpretation of our data with respect to the dependence of the emission rates on temperature or light intensity, the reproducibility of the measurements (10 to 15%) is the main error source that has to be considered.

3.1. VARIATIONS OF TEMPERATURE AND LIGHT INTENSITY

The temperatures given here are leaf temperatures which were measured with microthermistors. Measurements at different leaves of a sunflower showed temperature differences among the leaves. From such measurements the uncertainty of the mean leaf temperature, $\overline{T_L}$, is estimated to be about $\pm 1.5\,^{\circ}C$.

The temperature dependence of the emission rates was studied at constant light intensity. After concentration measurements at a given temperature, the temperature of the CSTR was changed in increments of about 5 degrees. Within less than two hours the leaf temperature was constant and 3 to 5 measurements of VOC concentrations were conducted at constant leaf temperature. This procedure was repeated several times. For the time of the measurements, the rate of transpiration as well as the rate of net photosynthesis were constant.

Light intensity was varied stepwise between 0 and 1090 $\mu E\ m^{-2}\ s^{-1}$ by switching lamps on or off. Because variations of light intensity caused changes of leaf temperature, the temperature of the CSTR was regulated until the leaf temperature was the same as before the change of light intensity. This regulation procedure took about 2 h. Again, the measurements were conducted at steady state conditions for the rate of transpiration and the rate of net photosynthesis.

4. Results

Figure 2a shows a typical chromatogram taken at chamber outlet with the GC/MS system and Figure 2b shows a chromatogram taken with the GC/FID system.

The mass spectrum of the unidentified compound emitted from sunflower is nearly identical to that shown by Arey *et al.* (1991) and suggests an oxygenated terpene ($C_{10}H_{14}O$). Arey *et al.* (1991) found an oxygenated hydrocarbon that was emitted from several plant species and tentatively identified this compound as 2-methyl-6-methylene-1,7-octadiene-3-one. 2-methyl-6-methylene-1,7-octadiene-3-one was not available. Therefore, a positive identification cannot be given here. However, our conclusions with respect to the mechanism of the emission of this compound are independent of such a positive identification. In the following we refer to this compound as 'BOVOC' (Biogenic Oxygenated Volatile Organic Compound).

At a light intensity of 820 $\mu E\ m^{-2}\ s^{-1}$ and a temperature of 25 to 26 °C, emission rates from sunflower range from 8×10^{-17} to 4.3×10^{-15} mol $cm^{-2}\ s^{-1}$. The VOC emission rates vary from plant to plant although the plants are studied under similar conditions. Table I shows the range of the emission rates found under the conditions given above, the averages of the emission rates and the standard deviations obtained for these averages. These averages are obtained with a statistical weight of 1 for individual plants in order to be independent of the number of measurements conducted for each plant.

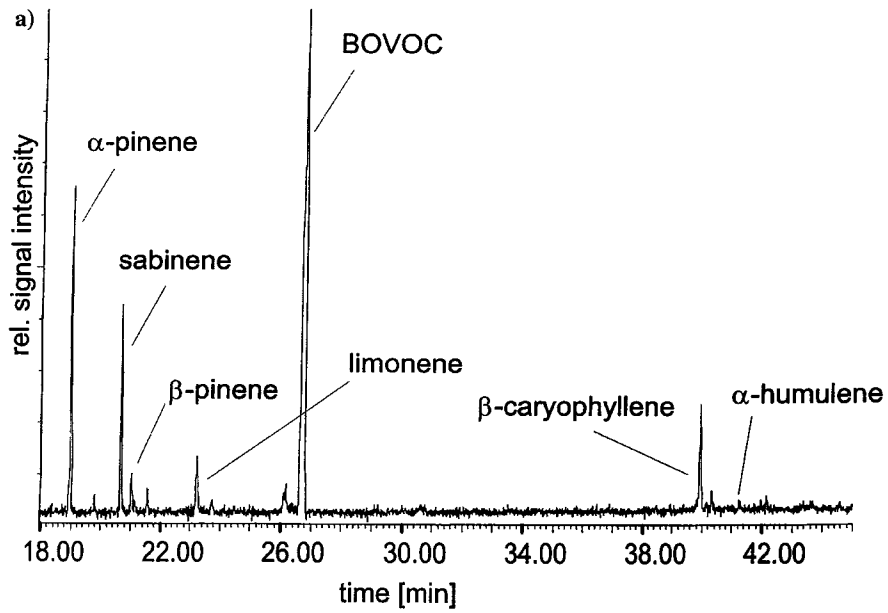

Figure 2a. Chromatogram (sum of the mass traces $m/z = 69$ and 93) of a sample from the air in the CSTR containing a sunflower measured with the GC/MS system. Sampling volume about 120 L.

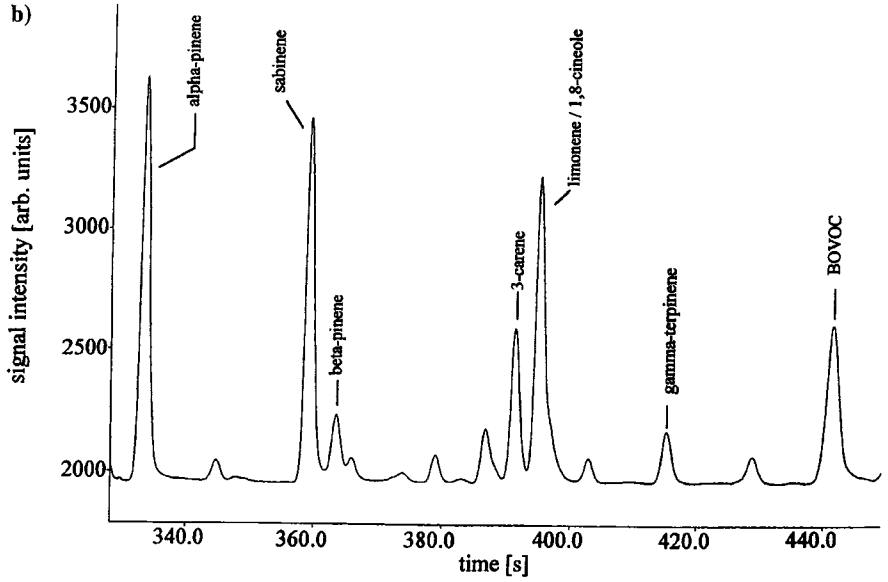

Figure 2b. Chromatogram of a sample from the CSTR measured with the GC/FID system. Sampling volume about 3 L.

Table I. Range of VOC emission rates from sunflower at a light intensity of 820 μE m^{-2} s^{-1} and leaf temperatures between 25 and 26 °C. Φ_{VOC} in units of mol cm^{-2} s^{-1} × 10^{16} and in units of ng $g(dw)^{-1}$ h^{-1}

Compound	Range mol cm^{-2} s^{-1} × 10^{16}	Mean mol cm^{-2} s^{-1} × 10^{16}	1σ	Range ng $g(dw)^{-1}$ h^{-1}	Mean ng $g(dw)^{-1}$ h^{-1}	1σ
Isoprene	2.7–13.3	6.2	4.3	18–88	30	28
α-pinene	3.6–20.0	7.3	6.8	47–264	96	90
Sabinene	2.6–17.1	7.3	5.5	34–226	96	73
Limonene	2.6–9.5	5.7	2.6	34–125	75	34
BOVOC	3.5–43.3	15.1	16.1	52–647	226	241
α-humulene	0.5–1.9	0.97	0.81	9.9–38	19	16
β-caryophyllene	4.7–15.3	9.6	4.6	93–303	190	91

Figure 3 shows the emission rates of α-pinene and BOVOC from an individual sunflower over a period of about three days. The emission rates measured for an individual plant are constant during daytime. Over a period of one day under conditions of constant temperature and constant light flux the emission rates of all VOCs vary less than 15 to 30%. Over a period of a week the variability is less than a factor of two for an individual plant studied at a given temperature and a given light intensity. However, a significant diurnal variation of Φ_{VOC} is obvious from Figure 3. During nighttime at temperatures of 22 to 23 °C the emission rates are much lower than under illumination (820 μE m^{-2} s^{-1}) and at temperatures of 25 to 26 °C.

The data for sunflower were obtained at the same vegetative stage of the plants. Measurements using beech were conducted in spring and in autumn. These measurements show that the emission rates are dependent on the vegetative stage of the plants. During springtime the emission rates can be up to a factor of 16 higher than in autumn.

Temperature increase from 20 to 30 °C at constant light intensity leads to changes of the VOC emission rates by more than one order of magnitude. Exponential relationships between Φ_{VOC} and temperature are found. Plots of $\ln \Phi_{VOC}$ versus the inverse temperature lead to linear relationships. Examples for the results obtained with respect to the temperature dependence of the emission rates from sunflower are listed in Table II.

In one series of measurements the mean leaf temperature was varied up to 34 °C. Figure 4 shows a plot of $\ln \Phi_{VOC}$ versus the inverse temperature from this experiment for α-pinene. No significant deviation from an exponential behavior is found for the emission rates of sabinene and limonene. But for isoprene, α-pinene and the BOVOC significantly lower emissions are observed than expected from an exponential increase at temperatures above 30 °C.

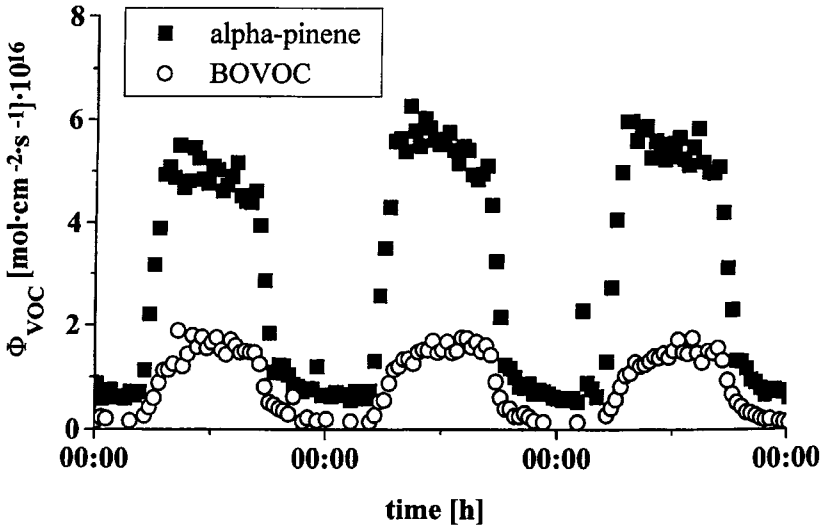

Figure 3. Emission rates of α-pinene and BOVOC from sunflower over a time period of about 3 days. Temperature: 25–26 °C/22–23 °C (day/night), respectively. Light intensity: 820 μE m^{-2} s^{-1}. Data obtained from GC/FID analysis.

Table II. Temperature dependence of VOC emission rates from a sunflower. The numerical values of the slopes of $\ln(\Phi_{VOC})$ versus $1/T$ are given in units of K × 10^{-3}, S = slope. Light flux: 1090 μE m^{-2} s^{-1}, r^2 = correlation coefficient, number of measurements 12

Compound	S[K] × 10^{-3}	r^2
Isoprene	8.7 ± 1.1	0.86
α-pinene	15.1 ± 0.8	0.97
Sabinene	11.3 ± 0.9	0.94
Limonene	11.2 ± 0.7	0.97
BOVOC	13.7 ± 1.5	0.86

Experiments with variations of light intensity at constant leaf temperature show that Φ_{VOC} is dependent on light flux. Figure 5a shows a plot of the emission rates of α-pinene, BOVOC, and β-caryophyllene versus light intensity for a mean leaf temperature of 23 ± 1.5 °C, Figure 5b those of α-pinene and sabinene from beech at a temperature of 25 ± 2 °C. The data shown in Figure 5b were measured in spring.

Light intensity affects the emission rates of different substances in a different manner. The emissions of sabinene from beech are nearly zero during darkness and increase rapidly with increasing light intensity. Emission of α-pinene is sig-

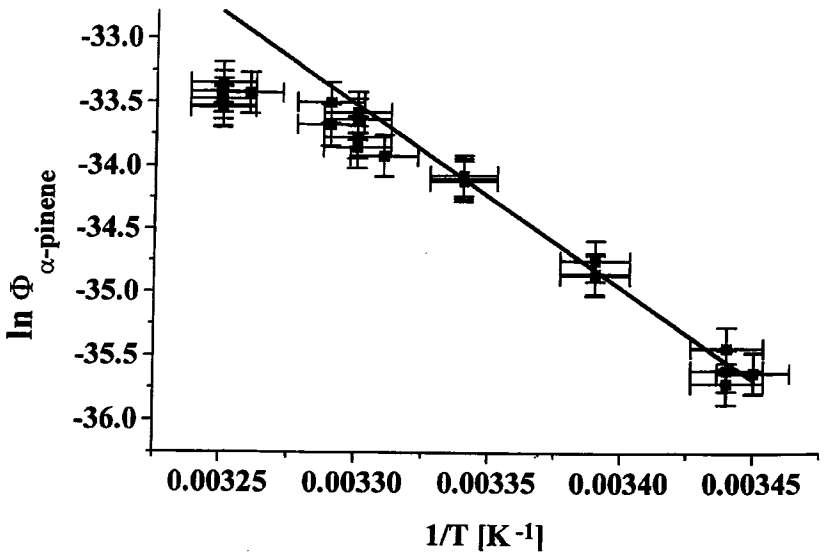

Figure 4. Plot of $\ln(\Phi_{\alpha\text{-pinene}})$ versus inverse temperature. The natural logarithm was taken for the absolute value of $\Phi_{\alpha\text{-pinene}}$ in [mol cm^{-2} s^{-1}]. Temperature was varied from 17 to 34 °C at a constant light flux of 1090 μE m^{-2} s^{-1}. The line results from a linear fit to the data points obtained at temperatures below 30 °C.

nificantly above zero during darkness and the dependence of its emission rate on light intensity is much lower than for sabinene.

For sunflower the emissions of isoprene and BOVOC during darkness are low, if detectable at all. For the other VOCs they are significantly above zero. Saturation effects such as observed for the sabinene emissions from beech are not significant for the VOCs emitted from sunflower. Moreover, the relative increase of Φ_{VOC} in most cases is much higher than the relative increase of light flux. Only for the isoprene emissions from sunflower indications of a beginning light saturation are found.

To compare our results with literature data, the dependence of the emission rates on light intensity, $\partial\Phi_{VOC}/\partial$PAR, is analyzed by linear regression. Examples for the values obtained in this way are given in Table III.

A series of experiments was conducted with a single sunflower, where temperature as well as light intensity were changed independently from each other. Light intensity was varied at constant leaf temperature. This was repeated for different mean leaf temperatures. The averages of the flux densities obtained from a minimum of three measurements at a given temperature and light intensity as well as the standard deviations of these averages are listed in Table IV.

The values for the slopes of $\partial \ln \Phi_{VOC}/\partial(1/T)$ are shown in Table V. The slopes differ for different light intensities. With few exceptions they increase with increas-

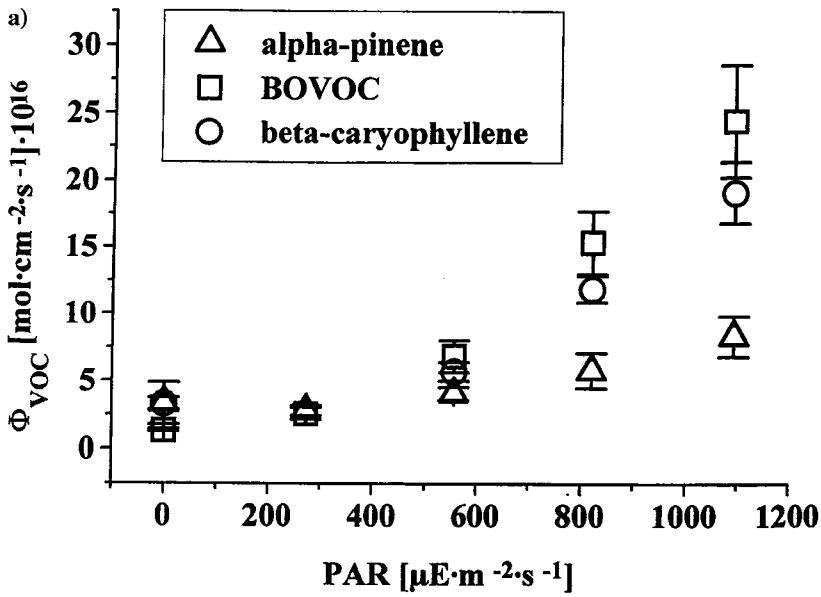

Figure 5a. Emission rates of α-pinene, BOVOC and β-caryophyllene from sunflower at a constant temperature of 23 °C as a function of light flux. Data points represent means of single measurements at the same temperature and constant light intensity. The error bars represent the standard deviation (1σ).

Table III. Results of linear regression analysis for $\partial\Phi_{VOC}/\partial PAR$ for a sunflower. $\overline{T_L} = 30\,°C$. Values for slopes (S) in units of mol_{VOC}/Einstein $\times 10^9$ (yield) and in units of ng g(dw)$^{-1}$ h^{-1}/μE m^{-2} s^{-1}, respectively. Values for intercepts (A) at light intensity zero in units of mol cm^{-2} s^{-1} $\times 10^{16}$ and in units of ng g(dw)$^{-1}$ h^{-1}, respectively. $N = 13$, r^2 = correlation coefficient

Compound	S	A	S	A	r^2
	$\frac{mol_{VOC} \times 10^9}{Einstein}$	mol cm^{-2} s^{-1} $\times 10^{16}$	$\frac{ng\ g(dw)^{-1}\ h^{-1}}{\mu E\ m^{-2}\ s^{-1}}$	ng g(dw)$^{-1}$ h^{-1}	
α-pinene	26.4 ± 2.6	2.8 ± 1.9	0.35 ± 0.034	37 ± 25	0.91
Sabinene	27.5 ± 3.9	8.9 ± 3.0	0.36 ± 0.05	117 ± 40	0.82
Limonene	10.7 ± 1.4	4.07 ± 1.1	0.14 ± 0.018	54 ± 14	0.83
BOVOC	27.6 ± 3.2	0.5 ± 2.5	0.41 ± 0.05	7.5 ± 37	0.87

ing photon flux. With regard to the temperature dependence of $\partial\Phi_{VOC}/\partial PAR$ we find that $\partial\Phi_{VOC}/\partial PAR$ increases with increasing temperature. $\partial\Phi_{VOC}/\partial PAR$ as obtained at three different temperatures is shown in Figure 6 for BOVOC.

Variation of light intensity or of temperature results in changes of stomatal conductivity, the rate of transpiration and the rate of net photosynthesis. Figure 7 shows an example for a plot of $\Phi_{\alpha\text{-pinene}}$ versus stomatal conductivity, $g^s_{H_2O}$, from an experiment where the light intensity is varied. It is obvious from Figure 7

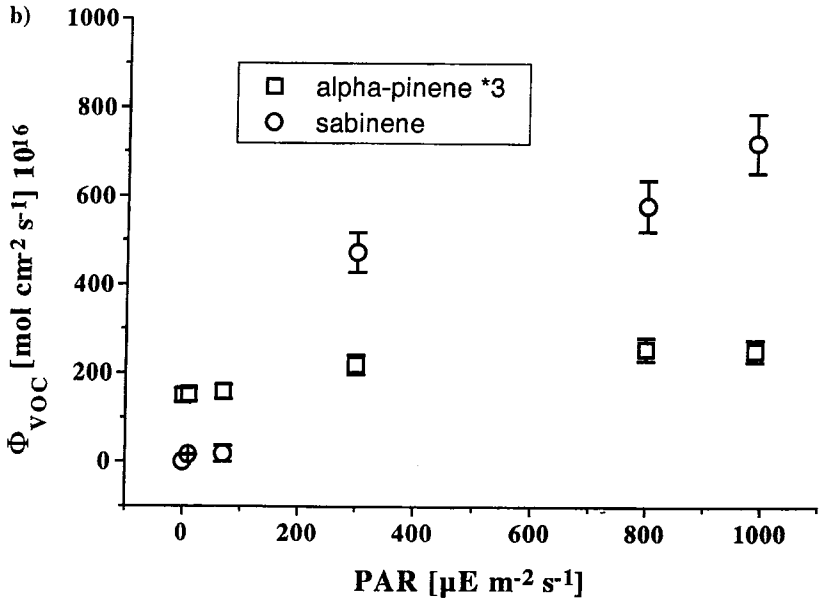

Figure 5b. Emission rates of α-pinene and sabinene from beech at constant temperature of 25 °C as a function of light flux. Emission rates of α-pinene are multiplied by 3.

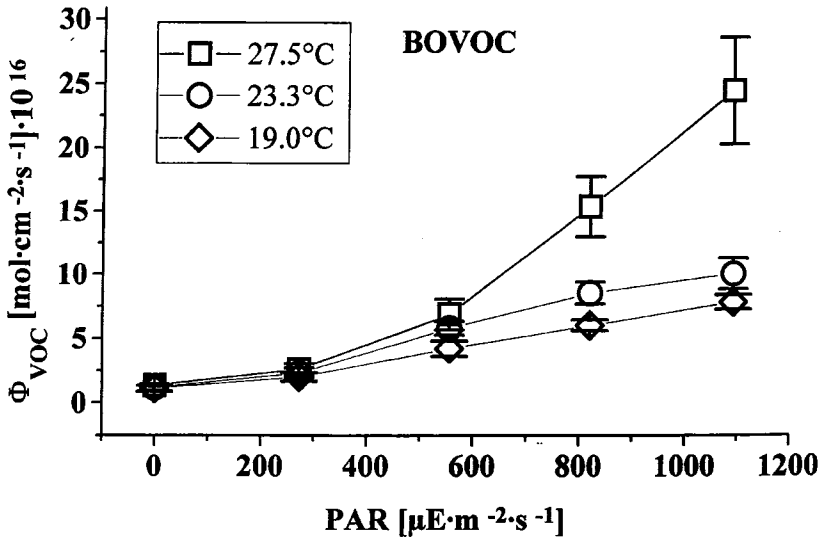

Figure 6. Emission rates of BOVOC from sunflower at constant temperatures of 19, 23.3 and 27.5 °C, respectively, as a function of light flux.

Table IV. Emission rates from an individual sunflower as a function of light intensity and temperature. Φ_{VOC} in units of mol cm^{-2} s^{-1} $\times$ 10^{16} PAR in units of μE m^{-2} s^{-1}, $\overline{T_L}$ in °C

PAR	$\overline{T_L}$	Isoprene	σ	α-pinene	σ	Sabinene	σ	Limonene	σ	BOVOC	σ
1090	27.5	3.79	0.77	8.37	1.5	11.5	1.87	3.93	0.52	24.5	4.16
820	27.6	3.38	0.49	5.83	2.4	9.73	0.98	3.51	0.38	15.4	2.36
550	27.6	2.41	0.3	4.10	2.2	7.38	1.26	2.42	0.52	6.86	1.19
270	27.6	1.0	0.29	2.83	2.2	3.96	0.43	1.61	0.22	2.61	0.43
0	27.7	–	–	3.34	1.6	5.33	0.56	1.91	0.24	1.34	0.10
1090	22.9	1.66	0.22	3.49	0.31	4.73	1.23	3.14	0.33	10.1	1.22
820	23.2	1.46	0.09	3.38	0.15	3.90	0.18	2.56	0.58	8.54	0.86
550	23.3	1.27	0.15	2.77	0.15	3.70	0.73	2.58	0.35	5.79	0.54
270	23.3	0.66	0.23	2.24	0.24	2.97	0.98	2.15	0.38	2.31	0.37
0	23.6	–	–	2.23	0.25	2.48	0.57	1.81	0.19	1.15	0.18
1090	19.1	1.22	0.21	2.99	0.26	4.08	0.92	2.75	0.28	7.83	0.58
820	19.1	0.85	0.04	2.53	0.24	3.13	0.17	2.51	0.33	6.04	0.42
550	19.0	0.66	0.23	1.99	0.22	2.66	0.21	2.15	0.26	4.20	0.60
270	18.9	0.39	0.1	1.91	0.18	2.68	0.36	1.88	0.21	2.00	0.33
0	19.5	–	–	1.83	0.13	2.27	0.24	1.77	0.20	1.09	0.22

Table V. Values from linear regression analysis of $\ln(\Phi_{VOC})$ versus $1/T$. The numerical values of the slopes are given in units of $K \times 10^{-3}$. Data obtained from an individual sunflower studied at different light intensities. PAR is in units of $\mu E\ m^{-2}\ s^{-1}$, N: number of measurements, r^2 = correlation coefficient

PAR; N compound	0; 35 [K] $\times 10^{-3}$	r^2	270; 17 [K] $\times 10^{-3}$	r^2	550; 16 [K] $\times 10^{-3}$	r^2	820; 12 [K] $\times 10^{-3}$	r^2	1090; 12 [K] $\times 10^{-3}$	r^2
Isoprene	–	–	4.8 ± 0.7	0.73	9.6 ± 1.4	0.78	9.7 ± 0.5	0.98	8.5 ± 0.9	0.86
α-pinene	5.1 ± 0.3	0.91	3.3 ± 0.4	0.8	5.7 ± 0.4	0.95	6.9 ± 0.7	0.9	8.7 ± 1.0	0.83
Sabinene	8.9 ± 1.2	0.62	4.0 ± 1.1	0.44	10.6 ± 1.06	0.89	11.9 ± 1.2	0.91	11.8 ± 1.9	0.69
Limonene	1.4 ± 3.3	0.37	0.05 ± 0.7	<0.01	1.4 ± 0.7	0.23	3.3 ± 0.6	0.72	3.4 ± 0.5	0.72
BOVOC	2.5 ± 0.7	0.26	2.7 ± 0.9	0.35	5.5 ± 0.9	0.78	9.7 ± 0.8	0.94	11.6 ± 1.2	0.86

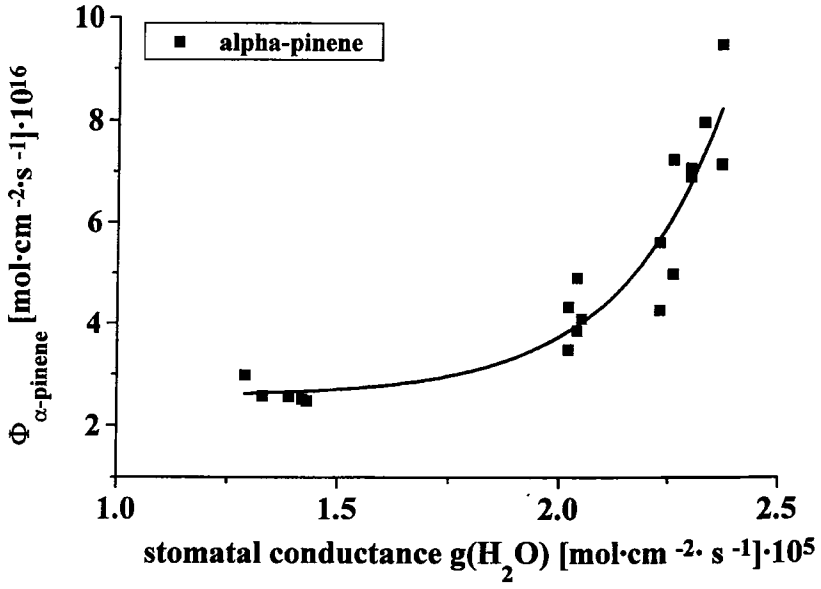

Figure 7. Emission rates of α-pinene as a function of stomatal conductivity to water vapor. Stomatal conductivity was varied by changes of light intensity.

that no linear correlation exists between $g^s_{H_2O}$ and $\Phi_{\alpha\text{-pinene}}$. Also in cases where temperature is varied, no linear correlation is observed between Φ_{VOC} and $g^s_{H_2O}$. In all cases the relative increase of the emission rates is much higher than the relative increase of stomatal conductivity. Therefore, a simple direct stomatal control of Φ_{VOC} is ruled out.

A simple direct stomatal control of Φ_{VOC} by the rate of net photosynthesis is ruled out, too, although in many cases a linear correlation is found between Φ_{VOC} and Φ_{CO_2}. The slopes of plots of Φ_{VOC} versus Φ_{CO_2} may be considered as a yield for the emission of VOC with respect to the uptake of CO_2. These yields are different for different plants. Moreover, for the single sunflower studied with respect to both, changes of temperature as well as changes of light intensity, the slopes obtained from the experiments at variable light intensities but constant temperatures are different for different temperatures. These results are shown in Table VI where the values for $\Delta\Phi_{VOC}/\Delta\Phi_{CO_2}$ are given in units of mol(C) emitted per mol(C) taken up as CO_2.

5. Discussion

Table VII shows some examples for ranges of VOC emission rates measured under ambient conditions. The VOC emission rates measured here for sunflower are comparable to those measured for other annual species and the emission rates measured

Table VI. VOC yield relative to CO_2 uptake ($mol(C)_{VOC}/mol(C)_{CO_2}$) for an individual sunflower at different temperatures

Compound	$\overline{T_L} = 19\,°C$		$\overline{T_L} = 23.5\,°C$		$\overline{T_L} = 27.5\,°C$	
	Yield $\times 10^6$	r^2	Yield $\times 10^6$	r^2	Yield $\times 10^6$	r^2
Isoprene	0.5 ± 0.05	0.8	0.5 ± 0.05	0.78	1.4 ± 0.4	0.4
α-pinene	1.2 ± 0.2	0.72	1.2 ± 0.2	0.73	5.2 ± 0.5	0.84
Sabinene	1.3 ± 0.3	0.48	1.8 ± 0.5	0.46	7.2 ± 0.6	0.87
Limonene	1.2 ± 0.2	0.76	0.9 ± 0.2	0.52	2.3 ± 0.3	0.78
BOVOC	6.4 ± 0.5	0.93	7.4 ± 0.6	0.89	19.7 ± 1.6	0.89

here for beech are comparable to those listed for other tree species. The similarity of our data obtained from measurements in laboratory experiments to those measured under ambient conditions implies that the results of our measurements are basically comparable to those of field studies.

The main goal of our experiments was to characterize the effects of the two fundamental factors temperature and light intensity that determine the emission of VOCs. We used sunflower as a model plant to develop an algorithm that describes the effects of these factors on the emission rates and we used beech to confirm the applicability of this algorithm for another plant species.

The comparison of Φ_{VOC} with stomatal conductivity or the rate of net photosynthesis shows that neither Φ_{CO_2} nor stomatal conductivity is generally usable as a normalization factor to describe the VOC emissions from sunflower or beech.

Several algorithms for VOC emissions are given in literature. However, except for isoprene, it is impossible to describe the emission rates from sunflower and beech with one of these algorithms alone. Only the isoprene emissions are well described by the algorithm given in Guenther *et al.* (1993). Following this algorithm, emissions during nighttime do not occur. Nevertheless, we find significant mono- and sesquiterpene emissions also during darkness.

In the absence of light, when the rate of terpene biosynthesis is low (Gleizes *et al.*, 1980), the emissions may result from the diffusion of mono- and sesquiterpenes out of storage pools in the plant. As mentioned before, this behavior is described by the model given in Tingey *et al.* (1991). But the dependence of the emission rates on light intensity clearly indicates that an algorithm considering only temperature as an independent variable is inadequate to describe the VOC emissions from sunflower and beech.

Similar to the findings of Kesselmeier *et al.* (1996) for the monoterpene emissions from *Quercus ilex*, we assume that there are two mechanisms that lead to VOC emissions from sunflower and beech. These are: diffusion out of pools, basically a temperature dependent process, and emissions related with the process of photosynthesis, a temperature and insolation dependent process. Consequently, we

Table VII. Examples for ranges of VOC emission rates

Compound	Plant species	Emission rate [ng g(dw)$^{-1}$ h^{-1}]	Reference
α-pinene	Pine	450	Tingey *et al.* (1980)
α-pinene	Pine, gum tree, cypress, water hickory	2300–12000	Khalil and Rasmussen (1992)
α-pinene	Rape, beech, birch, oak	5–16	König *et al.* (1995)
Σ monoterpenes	Lemon, orange, alfalfa, whitethorn, pistachio tomato (diff. species)	100–67000	Winer *et al.* (1992)
Σ monoterpenes	Holm oak, oak, pine	400–33700	Street *et al.* (1994)
Σ monoterpenes	Pine	700 ± 300	Janson (1992)
	Spruce	400 ± 600	
Σ sesquiterpenes	Cherry, cotton, grape, olive, peach, safflower, tomato	100–800	Winer *et al.* (1992)
Σ sesquiterpenes	Cypress, gum tree	50–300	Khalil and Rasmussen (1992)
Isoprene	Herbs, cropland	1000–20000	Street *et al.* (1994)
Limonene	Pine	20	Tingey *et al.* (1980)
Limonene	Pine, gum tree, water hickory	2900–12100	Khalil and Rasmussen (1992)
Sabinene	Rape, beech, birch	22–40	König *et al.* (1995)
Sabinene	Water hickory	10600	Khalil and Rasmussen (1992)
Σ monoterpenes	Rape, rye, beech, birch, oak, grass	53–190	König *et al.* (1995)
Σ monoterpenes	Pine, fir, larch	500–20000	Isidorov *et al.* (1985)
Σ monoterpenes	Lemon, cotton, orange, walnut, oak, whitethorn, pistachio	400–12000	Arey *et al.* (1991)
Σ monoterpenes	Holm oak	20000–40000	Staudt and Seufert (1995)
Σ monoterpenes	Pine	10–900	Lerdau *et al.* (1994)

use an approach that combines the model given in Tingey *et al.* (1991) and the algorithm given in Guenther *et al.* (1993).

We assume that the VOC emissions during darkness are mainly determined by diffusion out of pools. The emissions resulting from diffusion out of pools, Φ^{P}_{VOC}, only depend on temperature. The temperature dependence of the emission rates can be described by Equation (5):

$$\Phi^{P}_{\mathrm{VOC}} = \Phi^{P,S}_{\mathrm{VOC}} \exp\left[\frac{c_{TP}}{R} \cdot \left(\frac{T - T_S}{T \cdot T_S}\right)\right] . \tag{5}$$

Here $\Phi^{P,S}_{\mathrm{VOC}}$ is the emission from pools at a standard temperature, T_S. T is the leaf temperature and R the gas constant, c_{TP} is an empirical constant that, to a

first approximation, is similar to the enthalpy of vaporization for the VOC under consideration.

The contribution of the emissions that are closely coupled to biosynthesis and enzyme activity is denominated here as Φ^B_{VOC}. We assume that these emissions and those originating from diffusion out of pools are independent from each other, that is

$$\Phi_{\mathrm{VOC}} = \Phi^P_{\mathrm{VOC}} + \Phi^B_{\mathrm{VOC}} \,. \tag{6}$$

To describe the dependence of Φ^B_{VOC} on temperature and light intensity we use the algorithm given in Guenther *et al.* (1993). Therein the dependence of the isoprene emission rates on light intensity is given by

$$\Phi_{\mathrm{isoprene}} = \Phi^S_{\mathrm{isoprene}} \cdot c_L \cdot \frac{\alpha \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}} \,. \tag{7}$$

$\Phi^S_{\mathrm{isoprene}}$ is the emission rate of isoprene at standard light intensity and standard temperature (usually 1000 μE m^{-2} s^{-1}, 30 °C), c_L is a factor used to force $c_L \cdot (\alpha \cdot L)/(\sqrt{1 + \alpha^2 \cdot L^2})$ to be 1 at standard conditions and α describes the emission rate of isoprene as a function of light intensity, L (L is identical to PAR).

We find that in several cases the relative increase of Φ^B_{VOC} is higher than the relative increase of light intensity (see Figure 5a, β-caryophyllene and BOVOC). This behavior cannot be described by the function: $(\alpha \cdot L)/(\sqrt{1 + \alpha^2 \cdot L^2})$. The first derivative of this function in L monotonously declines to zero which is used to describe the light saturation of the isoprene emissions. The shape for Φ^B_{VOC} as a function of light intensity is better described by

$$\Phi^B_{\mathrm{VOC}} = \Phi^{B,S}_{\mathrm{VOC}} \cdot c_L \cdot \left(\frac{\alpha \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}} \right)^2 , \tag{8}$$

where $\Phi^{B,S}_{\mathrm{VOC}}$ is Φ^B_{VOC} at standard conditions.

Combining Equation (5) and the algorithm given in Guenther *et al.* (1993) with the modification given in Equation (8) it follows:

$$\begin{aligned} \Phi_{\mathrm{VOC}} = \; & \Phi^{P,S}_{\mathrm{VOC}} \exp\left[\frac{c_{TP}}{R} \cdot \left(\frac{T - T_S}{T \cdot T_S} \right) \right] + \Phi^{B,S}_{\mathrm{VOC}} \cdot c_L \cdot \left(\frac{\alpha \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}} \right)^2 \times \\ & \times \frac{\exp\left[\frac{c_{T1}}{R} \cdot \left(\frac{T - T_S}{T \cdot T_S} \right) \right]}{1 + \exp\left[\frac{c_{T2}}{R} \cdot \left(\frac{T - T_M}{T \cdot T_S} \right) \right]} \,. \end{aligned} \tag{9}$$

In Equation (9), c_{T1}, c_{T2} and T_M are empirical parameters to describe the dependence of Φ^B_{VOC} on temperature. The notation used here as well as the values for standard conditions are identical to those used in Guenther *et al.* (1993).

In the absence of light the second term of Equation (9) is zero. Thus, the determination of Φ^P_{VOC} and c_{TP} is straightforward. Φ^P_{VOC} and c_{TP} are determined

from the data obtained during darkness. The values obtained for c_{TP}/R are those listed in the first column of Table V.

Φ^B_{VOC} is calculated according to Equation (6) where the data for Φ_{VOC} and Φ^P_{VOC} are taken at the same temperature. The data obtained at 1090 μE m^{-2} s^{-1} are assumed to be identical to those at standard light intensity. Φ^B_{VOC} is then obtained as follows: Φ^B_{VOC} as determined from data obtained at different temperatures and at 1090 μE m^{-2} s^{-1} is fitted to the exponential function given in the numerator of Equation (9). Extrapolations to 30 °C lead to $\Phi^{B,S}_{\mathrm{VOC}}$.

The values calculated for Φ^B_{VOC} are normalized by division through $\Phi^{B,S}_{\mathrm{VOC}}$ and then fitted to the second term of Equation (9). Results of fits to the data obtained from the sunflower investigated with respect to variations of temperature as well as to variations of light intensity are listed in Table VIII together with those obtained from fits to sabinene emissios from beech.

The data listed in Table VIII are obtained after a simplification of Equation (9). The denominator in Equation (9) is set to be 1 because the data used for the fits were obtained at temperatures well below the temperature of maximum enzyme activity, T_M. T_M generally is well above 300 K. The high difference between T and T_M leads to low values for the exponent in the denominator of Equation (9) and thus, the denominator of Equation (9) is very close to unity. Consequently, the temperature dependence of Φ^B_{VOC} is described by a simple exponential curve in accordance to the experimental data obtained at temperatures below 30 °C.

There is one series of experiments that allows to estimate c_{T2} and T_M (data for α-pinene are shown in Figure 4). T_M is fitted to about 311 K and c_{T2}/R to about 3×10^4 K for α-pinene and the BOVOC. Not too much significance is attached to these fit parameters because a leaf temperature of 34 °C is not high enough to find reliable values. However, the experimental data obtained at temperatures below 30 °C are well described by Equation (9) neglecting the effects of temperature optima of enzyme activities.

Figure 8 shows the data points obtained for $\Phi^B_{\mathrm{limonene}}$ normalized to 30 °C together with the function given by Equation (8) using α and c_L as listed in Table VIII. It is obvious that all temperature normalized data points and their dependence on light intensity is described by Equation (8). Figure 9 shows the data points obtained for BOVOC normalized to 1090 μE m^{-2} s^{-1} using α and c_L from Table VIII. The function given by

$$\exp[\frac{c_{T1}}{R} \cdot (\frac{T - T_S}{T \cdot T_S})]$$

using c_{T1} as listed in Table VIII also describes these data points.

In summary, Equation (9) describes the emission rates measured for all compounds emitted from sunflower and beech. Furthermore, our experimental data set as a whole cannot be described even qualitatively with one of these parameters missing. The need to use all parameters included in Equation (9) for a general algorithm that describes the monoterpene emissions from sunflower is established from

Table VIII. Best fit values for sunflower and beech

	Sunflower					Beech
	Isoprene[a]	α-pinene	Sabinene	Limonene	BOVOC	Sabinene[b]
$\Phi^{P,S}$ [mol cm^{-2} s^{-1}] $\times 10^{16}$	0	3.8 ± 1.8	6.7 ± 0.7	2 ± 0.4	1.43 ± 0.1	0
c_{TP}/R [K] $\times 10^{3}$	–	5.1 ± 0.3	8.9 ± 1.2	1.4 ± 3.3	2.5 ± 0.7	–
$\Phi^{B,S}$ [mol cm^{-2} s^{-1}] $\times 10^{16}$	5.0 ± 1.0	7.4 ± 2.8	9.3 ± 3.2	2.4 ± 0.7	34.1 ± 4.2	93 ± 6.8
c_L	1.8 ± 0.1	7.5 ± 2.9	3.0 ± 0.9	10.5 ± 2.6	7.5 ± 2.9	1 ± 0.07
α [m^2 s/μE] $\times 10^{3}$	0.74 ± 0.21	0.36 ± 0.23	0.66 ± 0.41	0.33 ± 0.08	0.36 ± 0.23	12 ± 2.7
C_{T1}/R [K] $\times 10^{-3}$	14.3 ± 1.0	16.7 ± 5.0	17.0 ± 4.4	11.9 ± 2.8	16.7 ± 5.0	15.3 ± 2.3

[a] Data for isoprene fitted according to the algorithm of Guenther *et al.* (1993).
[b] Data measured in autumn.

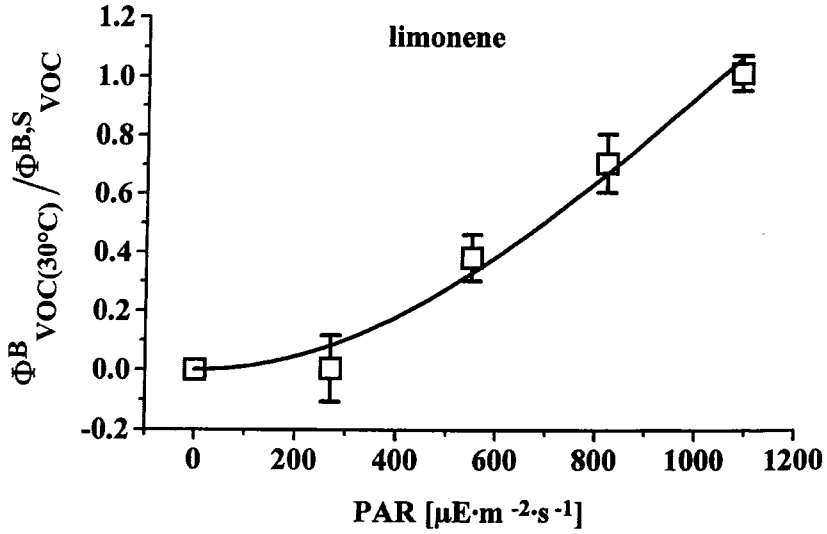

Figure 8. Plot of $\Phi^{B}_{\text{limonene}}/\Phi^{B,S}_{\text{limonene}}$ normalized to 30 °C versus light intensity. Data points represent the arithmetic means of the data measured at 19, 23.3, and 27.5 °C extrapolated to 30 °C. Error bars are the 1σ standard errors. The line is the simulation of: $c_L \cdot \left(\frac{\alpha \cdot L}{\sqrt{1+\alpha^2 \cdot L^2}}\right)^2$ using α and c_L as listed in Table VIII for limonene. In darkness Φ^{B}_{VOC} is zero.

measurements with different sunflower plants. The results obtained from beech confirm this conclusion.

The algorithm given by Equation (9) also includes the description of interdependent effects of temperature and light intensity. These interdependent effects are caused by the two different mechanisms that lead to the emissions. For example, from Table V it is obvious that $\partial \ln \Phi_{\text{VOC}}/\partial(1/T)$ increases with increasing light flux which is explained by the contributions of both, Φ^{P}_{VOC} and Φ^{B}_{VOC} to the total emission rate. The contribution of Φ^{B}_{VOC} increases with increasing light flux and thus, $\partial \ln \Phi_{\text{VOC}}/\partial(1/T)$ increases with increasing light flux.

Equation (9) represents a general form for an algorithm that describes the emission of monoterpenes from sunflower and beech. However, there are special cases where a description of the VOC emissions is possible with fewer parameters. One example was mentioned above. The denominator of Equation (9) is 1 for temperatures below 30 °C. Another example is the sabinene emission from beech where the emissions from pools are negligible. In such cases the first term of Equation (9) can be neglected. For plants where the emissions from pools by far exceed those coupled to enzyme activity, the second term of Equation (9) is negligible. Then, no significant dependence of the emission rates on light intensity will be detectable. Moreover, the temperature dependence of the emission rates in such cases is described by Equation (5).

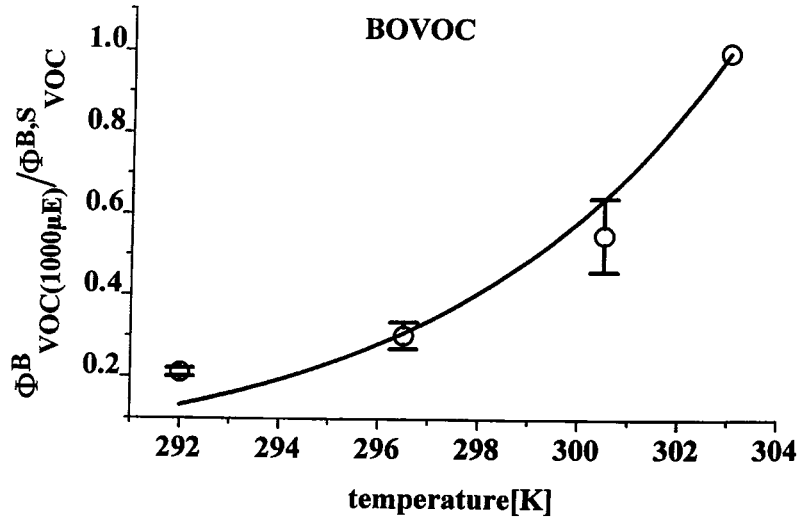

Figure 9. Plot of $\Phi^{B}_{\mathrm{BOVOC}}/\Phi^{B,S}_{\mathrm{BOVOC}}$ normalized to 1000 μE m^{-2} s^{-1} versus temperature. Data points represent the arithmetic means of the data measured 270, 550, 820 and 1090 μE m^{-2} s^{-1}. Error bars are the 1σ standard errors. The line is the simulation of: $\exp\left[\frac{c_{T1}}{R}\cdot\left(\frac{T-T_s}{T\cdot T_s}\right)\right]$ using c_{T1} as listed in Table VIII. At 30 °C and 1000 μE m^{-2} s^{-1}, Φ^{B}_{VOC} is identical to $\Phi^{B,S}_{\mathrm{VOC}}$.

A large amount of data is given in literature with respect to the temperature dependence of monoterpene emissions. Contrary, not many quantitative data are published concerning the dependence of mono- and sesquiterpene emissions on light intensity. From the diurnal variation of the monoterpene emission rates from *Pinus densiflora*, Yokouchi and Ambe (1984) concluded that these emissions were not determined by temperature alone. Street *et al.* (1994) found a linear relationship between the myrcene emission from *Picea sitchensis* and light intensity. Dependent on the numerical value of α, the deviations of Equation (8) from a linear function can be small and in such cases a linear approximation to Equation (8) is possible. We can compare the data from Street *et al.* (1994) to those from our linear approximation as listed in Table III.

Street *et al.* (1994) plotted Φ_{myrcene} normalized to 20 °C versus light intensity which resulted in: $\Phi_{\mathrm{myrcene}} = 49.37 + 0.38 \times \mathrm{PAR}$ (emission rates in units of ng g(dw)$^{-1}$ h^{-1}, PAR is in units of μE m^{-2} s^{-1}). This value is comparable to the results listed for sunflower (Table III). Furthermore, from the significant myrcene emissions during darkness it may be assumed that the myrcene emissions from *Picea sitchensis* occur also from pools.

Staudt and Seufert (1995) observed that the α-pinene, β-pinene and sabinene emissions from *Quercus ilex* are dependent on light intensity. To describe the dependence of these emissions on light intensity and on temperature, Bertin *et al.*

(1997) used the algorithm of Guenther *et al.* (1993). They found that the emissions are described well with this algorithm.

This finding is different to our observations. The light intensity dependence of the monoterpene emissions from sunflower is not even qualitatively described by Equation (7). Contrary, the dependence of the monoterpene emissions from *Quercus ilex* on light intensity can be described by Equation (8). This is done using data given in Bertin *et al.* (1997). Such fits lead to a value of 0.0029 for α. c_L remains nearly unchanged.

In summary, descriptions according to Equation (8) include descriptions according to Equation (7). Hence, the monoterpene emissions from *Quercus ilex* can also be described by Equation (9). The algorithm of Guenther *et al.* (1993) is as a special case of Equation (9).

Janson (1993) measured the VOC emissions from *Scots pine*. He found that the emission rates were dependent on light flux and fitted the data for Φ^B_{VOC} (therein denominated as daytime minus nighttime emissions) as a function of PAR. He also reported seasonal variations of the shapes of plots of Φ^B_{VOC} versus PAR and used three functions to describe these dependencies at different vegetative stages. Good fits were obtained using an exponential dependence for the data obtained in May, a linear dependence and a logarithmic dependence for the data obtained in July.

As mentioned before, Equation (8) can describe different shapes of Φ^B_{VOC} as a function of light intensity. These also include an approximately exponential function, a linear function or in cases of light saturation an approximately logarithmic function. Indeed, the data given in literature for the dependence of the monoterpene emission rates on light intensity are described by Equation (8). Nevertheless, our motivation to describe the dependence of the monoterpene emission rates on light intensity according to Equation (8) and not according to Equation (7) is not only based on a phenomenological description of the observations.

The algorithm for the description of isoprene emission as given by Guenther *et al.* (1991, 1993) was based on the fact that isoprene emissions are closely coupled to enzyme activity. The direct precursor of isoprene is $\gamma\gamma$-dimethylallyl-pyrophosphate, DMAPP (e.g., McGarvey and Croteau, 1995). The turnover from DMAPP to isoprene occurs on time scales of minutes (Delwiche and Sharkey, 1993; Sharkey *et al.*, 1991). At low light intensities it may be assumed that the rate limiting step for the isoprene emission is the production of DMAPP in the plant and the isoprene emission is limited by substrate availability. At high light intensities saturation effects are observed which is described by Michaelis Menten kinetics. This behavior is approximated by Equation (7).

If the substrate availability activates the enzyme activity, the loss of substrate as a function of substrate concentration is given by a sigmoidal curve (e.g., Mohr and Schopfer, 1985). Such a curve is better approximated by Equation (8).

Geranyl-pyrophosphate, GPP, is the substrate from which the individual monoterpenes are formed by different enzymes. As long as the conversion of GPP to the monoterpenes is only limited by GPP availability the emission rates as a function

of light flux can be described by Equation (7). If the enzymes are activated by the availability of GPP, Equation (8) has to be used. Monoterpene emissions from sunflower are described by Equation (8), which indicates that the increase of GPP availability in the plants activates the enzymes that produce monoterpenes.

The enzyme activity may depend on the vegetative stage of the plants. Moreover, enzymes may change from predominantly inactive forms to permanently activated forms. Thus, it is plausible that the shape of the function that describes the dependence of the emission rates on light flux can be different for different vegetative stages of the plant.

To avoid the need to use different algorithms for different monoterpenes which, moreover, may be different for different vegetative stages of individual plants, we suggest to use Equation (8) for the following reasons: Equation (7) cannot even qualitatively describe the shape of $\partial\Phi_{\mathrm{VOC}}/\partial\mathrm{PAR}$ as observed for some compounds but Equation (8) does. Moreover, Equation (8) can describe shapes of the form described by Equation (7) with only small deviations at low light intensities.

Equation (9) describes the monoterpene emissions from sunflower and beech as a function of temperature and light intensity within the uncertainties of the measurements. However, for a determination of all fit parameters in Equation (9) the combined effects of temperature and light intensity have to be measured. If the temperature dependence of Φ_{VOC} is measured only at one constant light intensity, Equation (9) is underdetermined. The individual contributions of Φ^{P}_{VOC} and Φ^{B}_{VOC} cannot be derived.

Only minor problems occur when the dependence of Φ_{VOC} on light intensity is studied at one temperature. Φ^{P}_{VOC} is obtained from the data points measured in darkness, Φ^{B}_{VOC} can be calculated according to Equation (6) and the absolute values of Φ^{B}_{VOC} can be fitted to Equation (8). No values for c_L and $\Phi^{B,S}_{\mathrm{VOC}}$ can be determined but α can be fitted. Such fits were conducted for different sunflower plants studied at the same vegetative stage. The values obtained for α are the same within the experimental errors and the uncertainties of the fits.

Table IX shows the values for α fitted for the β-caryophyllene emissions from sunflower together with the values fitted for the emissions from beech in spring. These data were obtained from experiments at constant temperature and therefore, data for c_{TP}/R, c_L and c_{T1}/R are not obtained. However, from the results listed for β-caryophyllene we conclude that also the sesquiterpene emissions from sunflower are caused by the two different mechanisms mentioned above. This indicates that also sesquiterpene emissions from sunflower can be described by Equation (9). Comparing the data for the sabinene emission from beech listed in Tables VIII and IX it is obvious that α as well as the absolute emission rates depend on the vegetative stage of beech.

For different sunflower plants studied at the same light intensity, the same temperature, and at the same vegetative stage the absolute emission rates differ (see Table I). Since similar numerical values are found for the fit parameters obtainable from the given experiments, we conclude that only different values of $\Phi^{P,S}_{\mathrm{VOC}}$ or

Table IX. Best fit values from experiments with variations of light intensity at constant temperature. Absolute values of Φ_{VOC} are used for the fits. Data for c_{TP}/R, c_L and c_{T1}/R are not obtainable from such experiments

	Sunflower, 23 °C	Beech, 25 °C, data measured in spring		
	β-caryophyllene	Thujene	α-pinene	Sabinene
Φ^P [mol cm^{-2} s^{-1}] $\times 10^{16}$	3.3 ± 1.1	0	50 ± 5	0
Φ^B [mol cm^{-2} s^{-1}] $\times 10^{16}$	16 ± 5	41 ± 4	34 ± 3	720 ± 70
α [m^2 s/μE] $\times 10^3$	0.07 ± 0.004	5.3 ± 1.8	3.4 ± 0.1	5.3 ± 2.8

$\Phi_{VOC}^{B,S}$ can explain this high variability. On the one hand different values of $\Phi_{VOC}^{P,S}$ or $\Phi_{VOC}^{B,S}$ may be caused by biological variability. On the other hand it is possible that other factors that are not controlled or varied during our measurements have a large influence on the VOC emission rates. Therefore, Equation (9) can only be used to describe the variations of the VOC emission rates with temperature and light intensity. $\Phi_{VOC}^{P,S}$ and $\Phi_{VOC}^{B,S}$ have to be used as fixed points that have to be determined for individual plants and the key question that remains to be answered is: Which factors control $\Phi_{VOC}^{P,S}$ and $\Phi_{VOC}^{B,S}$?

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