







increase of the above specified decomposition products accounted completely for the observed sabinene decrease, the total sum of the measured monoterpene compounds was not affected by this decomposition. To specify the composition of monoterpene compounds that are emitted from European beech, a correction factor was applied to the relevant compounds taking a cartridge storage time of more than 7 days into account. In contrast, previous experiments performed for the GC-FID cartridges did not indicate a similar decomposition of sabinene on the respective VOC samples. However, during the present study some of the potential decomposition products were not investigated by the GC-FID analysis and assuming a similar decomposition process as observed for the GC-MS cartridges may therefore lead to an underestimation of the total sum of monoterpenes measured by GC-FID of up to 20%.

#### 2.1.4. Emission Algorithms

[15] The emission of monoterpenes from European beech was simulated by two different light and temperature dependent algorithms. The first algorithm applied (in the following referred to as G97) was developed for isoprene emission by *Guenther et al.* [1993, 1995] and *Guenther* [1997]. In previous studies, isoprene emission has been shown to be triggered by light as a result of the close link between its emission and production from photosynthetic precursor compounds. However, several authors demonstrated that the latter algorithm may also be used to calculate the emission of monoterpenes that are released directly upon their production [e.g., see *Kesselmeier et al.*, 1996; *BEMA-Project*, 1997; *Ciccioli et al.*, 1997; *Kuhn et al.*, 2002b; *Kuhn et al.*, 2004].

[16] The G97 algorithm assumes a hyperbolic increase of VOC emissions to light intensity, leading to a saturation effect. With respect to leaf temperature the algorithm assumes enzymatic processes leading to a temperature optimum of the VOC emission at temperatures of 39°C. Within the algorithm, the light dependent term of the G97 function (in the following referred to as  $C_L$ ) is specified by Formula 1. The temperature dependent term (in the following referred to as  $C_T$ ) is specified by Formula 2. To calculate the actual VOC emission, both factors ( $C_L$  and  $C_T$ ) are linked by multiplication with a standard emission factor (in the following referred to as SEF) that describes the basal VOC emission at standard light and standard temperature conditions (1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , 30°C, see Formula 3).

(1) Light dependent term of the G97 function:

$$C_L = \frac{\alpha \cdot C_{L1} \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}}$$

(2) Temperature dependent term of the G97 function:

$$C_T = \frac{\exp\left(\frac{C_{T1} \cdot (T - T_S)}{R \cdot T_S \cdot T}\right)}{C_{T3} + \exp\left(\frac{C_{T2} \cdot (T - T_M)}{R \cdot T_S \cdot T}\right)}$$

(3) Calculation of the actual VOC emission by the G97 function:

$$\text{VOC emission} = \text{SEF} \cdot C_L \cdot C_T$$

( $\alpha = 0.0027$ ,  $C_{L1} = 1.066$ ,  $C_L$  = light dependent term of the G97 function,  $C_T$  = temperature dependent term of the G97 function,  $C_{T1} = 95,000 \text{ J mol}^{-1}$ ,  $C_{T2} = 230,000 \text{ J mol}^{-1}$ ,  $C_{T3} = 0.961$ ,  $L$  = actual light intensity ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ),  $R$  = universal gas constant ( $8.314 \text{ J K}^{-1} \text{mol}^{-1}$ ), SEF = standard emission factor,  $T$  = leaf temperature ( $^{\circ}\text{K}$ ),  $T_M = 314^{\circ}\text{K}$ ,  $T_S = 303^{\circ}\text{K}$ ).

[17] The second algorithm (in the following referred to as S97) that was applied to the present data set was developed to describe the emission of monoterpenes from sunflower and European beech as a function of light and temperature by *Schuh et al.* [1997]. In comparison to the G97 function the S97 algorithm assumes also a saturation effect of VOC emission at high light intensities. However, in contrast to the G97 simulation which assumes a hyperbolic increase of VOC emission, the S97 algorithm assumes an allosteric enzyme regulation leading to a sigmoid increase of VOC emission at lower light intensities. This light dependent term (in the following referred to as  $C_{L(S)}$ ) of the S97 algorithm is described by Formula 4. The temperature dependent term, describing the instantaneous emission of monoterpenes, is identical to the G97 function (see  $C_T$ , Formula 2). In addition to the instantaneous emission of monoterpenes, the original S97 function assumes also a release of VOCs from unspecific storage pools (Formula not shown). However, in the present study a release of monoterpenes from unspecific storage pools was not detectable. Therefore the storage pool term of the S97 algorithm was neglected, as recommended for sabinene emission from European beech by *Schuh et al.* [1997]. To calculate the actual VOC emission by the S97 function, the respective terms were linked by multiplication with a standard emission factor (in the following referred to as  $\Phi_{LT}$ ) as described by Formula 5, yielding a modified form of the original S97 algorithm that neglects a monoterpene release from storage pools.

(4) Light dependent term of the S97 function:

$$C_{L(S)} = C_{L1} \cdot \left( \frac{\alpha \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}} \right)^2$$

(5) Calculation of the actual VOC emission by the S97 function:

$$\text{VOC emission} = \Phi_{LT} \cdot C_{L(S)} \cdot C_T$$

( $\alpha = 0.0027$ ,  $C_{L1} = 1.066$ ,  $C_{L(S)}$  = light dependent term of the S97 function,  $C_T$  = temperature dependent term of the G97 function,  $L$  = actual light intensity ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ),  $\Phi_{LT}$  = standard emission factor).

[18] As shown by Formulas 3 and 5, both standard emission factors (SEF or  $\Phi_{LT}$ ) can be calculated from the slope of linear regression of the measured VOC emission to the product of the light and temperature dependent terms of the respective algorithm (note that standard conditions correspond to 1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$  and 30°C for both algorithms). Since both algorithms assume a cessation of VOC emission in the dark, a linear regression without bias ( $y = 0$ ) was used for the calculation of both emission factors.























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