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Institut II: Troposphäre

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# Untersuchungen der Emissionen von Monoterpenen aus Waldkiefern

## Kurzzusammenfassung

Pflanzen produzieren und emittieren eine Vielzahl flüchtiger organischer Verbindungen (VOC) wie Isopren und die Monoterpene ($C_{10}H_{16}$). Im Rahmen dieser Arbeit wurden Emissionsraten von Monoterpenen aus Waldkiefern (*Pinus sylvestris*), einer in Mitteleuropa weit verbreiteten Baumart, unter Freilandbedingungen untersucht. Die Studien konzentrierten sich auf die Untersuchung der tageszeitlichen und der jahreszeitlichen Variation der Emissionen, sowie auf die Variation der Emissionen aus verschiedenen Zweigen derselben Pflanze und aus verschiedenen individuellen Pflanzen. Darüber hinaus wurde die Übertragbarkeit der Ergebnisse aus Laborstudien (Arbeiten der Arbeitsgruppe Dr. J. Wildt) auf Freilandbedingungen untersucht.

Generell wurde kein unterschiedliches Emissionsverhalten der Kiefern zwischen Laborstudien und Freilandexperimenten gefunden. Sowohl unter Labor- als auch unter Freilandbedingungen wurde ein Anstieg der Emissionsraten mit der Nadeltemperatur von etwa 5-16 % pro Kelvin beobachtet. Die Variation dieses Parameters war unabhängig von der Art des Monoterpens, von der Jahreszeit und von der untersuchten Pflanze. Eine Abhängigkeit der Emissionsraten von der photosynthetisch aktiven Strahlung (PAR) konnte nur unter Laborbedingungen festgestellt werden (Anstieg von 20-30 % bei konstanter Temperatur, Sättigung der Lichtabhängigkeit bereits bei etwa 15 % der Sonneneinstrahlung unter Freilandbedingungen). Unter Freilandbedingungen wurde keine Lichtabhängigkeit der Emissionen nachgewiesen.

Die saisonale Variation des Emissionsmusters an Monoterpenen, sowie die Zweig-zu-Zweig Variabilität waren gering. Verschiedene Waldkiefern emittierten hingegen ein völlig unterschiedliches Spektrum an Monoterpenen. Die temperaturnormierten Standardemissions-raten waren sehr variabel. Die Summe der Standardemissionsraten der Monoterpene variierte zwischen 0.06 und 0.65 $\mu g\ g(dw)^{-1}\ h^{-1}$ für jungen Kiefern und zwischen 0.24 and 3.7 $\mu g\ g(dw)^{-1}\ h^{-1}$ für die erwachsene Kiefer. Streß war eine mögliche Erklärung als Ursache für diese Variation, aber die Auswirkungen von Streß konnten nicht quantitativ beschrieben werden. Basierend auf den Ergebnissen wurde ein Monoterpenfluß für den Bestand des Hartheimer Waldes von 54 bis 941 $ng\ m^{-2}\ s^{-1}$ (für T = 30°C) berechnet.

Zukünftige Labormessungen sollten sich insbesondere auf Streßeffekte und deren Auswirkung auf VOC Emissionen konzentrieren. Für eine Verbesserung der Hochrechnungen auf Bestandsflüsse muß der Einfluß von Streß auf VOC Emissionsraten quantifiziert und durch eine Erweiterung der bestehenden Modelle berechnet werden können.

# Investigations of the Emissions of Monoterpenes from Scots Pine


## Abstract

Plants produce and emit a large number of volatile organic compounds (VOC) such as isoprene and monoterpenes ($C_{10}H_{16}$). Monoterpene emission rates from Scots pine (*Pinus sylvestris*), a typical central European conifer, were measured under ambient conditions within the scope of this work. The studies focused on diurnal and seasonal cycles of monoterpene emissions, branch-to-branch and plant-to-plant variability of emission rates, and on the transferability of results from laboratory (studies of Dr. J. Wildt and coworkers) and outdoor measurements.

Generally, no significant differences between the results obtained under laboratory and ambient environmental conditions were found. Under both laboratory and ambient conditions, monoterpene emissions were found to increase with needle temperature at a rate of 5 % to 16 % per Kelvin and followed under otherwise unchanged conditions an Arrhenius type dependence on temperature. The temperature dependence of emissions was without a clear seasonal trend and without significant differences from plant-to-plant. Only in the laboratory a dependence of emission rates on photosynthetic active radiation (PAR) was found (increase of 20-30 % at a constant temperature, saturation in the light dependence at about 15 % of full sunlight). Under outdoor conditions, a PAR dependence was not detected.

Seasonal variations of a single branch and branch-to-branch variations in the spectrum of emitted monoterpenes were small, but different individual Scots pines emitted a completely different spectrum of monoterpenes. The temperature normalized standard emission rates were found to be highly variable. Values for the sum of monoterpenes ranged between 0.06 and 0.65 $\mu g\ g(dw)^{-1}\ h^{-1}$ (microgram monoterpenes per gram dry weight of needles and hour) for young pines and between 0.24 and 3.7 $\mu g\ g(dw)^{-1}\ h^{-1}$ for the adult pine. The variations of the standard emission rates from the same plant at different times of the year were on the same order of magnitude as the plant-to-plant variability. Stress to the plant was a possible explanation for these variations, but this effect could not be described quantitatively. Based on the results a monoterpene flux was calculated for a forest in Southern Germany (Hartheimer Wald, near Freiburg), ranging between 54-941 $ng\ m^{-2}\ s^{-1}$ at T = 30°C.

Future laboratory studies should focus on stress effects and their impact on VOC emissions. The effect of stress on VOC emission rates must be quantified and included in the existing models for better predictions of emission rates and fluxes.

## Zusammenfassung

Flüchtige organische Verbindungen (VOC) spielen eine zentrale Rolle in der Chemie der Atmosphäre. VOC gelangen durch biogene und anthropogene Emissionen in die Troposphäre. Entfernt werden sie vor allem durch Reaktionen mit Hydroxylradikalen (OH). In Verbindung mit erhöhten Konzentrationen an Stickoxiden tragen sie während des Abbauprozesses wesentlich zur photochemischen Ozonbildung bei. Nach aktuellen Abschätzungen beläuft sich der globale Eintrag an VOC in die Atmosphäre durch die Vegetation auf über 1000 Megatonnen Kohlenstoff pro Jahr und liegt damit etwa eine Größenordnung höher als der Eintrag durch anthropogene Quellen. Neben dem Isopren ($C_5H_8$) sind Monoterpene (isomere Verbindungen der Summenformel $C_{10}H_{16}$) Hauptemissionsprodukte biogenen Ursprungs.

Im Rahmen dieser Arbeit wurden Emissionsraten von Monoterpenen aus Waldkiefern (*Pinus sylvestris*), einer in Mitteleuropa weit verbreiteten Baumart, unter Freilandbedingungen untersucht. Die Studien konzentrierten sich auf die Untersuchung der tageszeitlichen und der jahreszeitlichen Variation der Emissionen, sowie auf die Variation der Emissionen aus verschiedenen Zweigen derselben Pflanze und aus verschiedenen individuellen Pflanzen. Darüber hinaus wurde die Übertragbarkeit der Ergebnisse aus Laborstudien (Arbeiten der Arbeitsgruppe Dr. J. Wildt) auf Freilandbedingungen untersucht. Die Ergebnisse der vorliegenden Arbeit werden in Emissionskatastern zur Berechnung des Flusses biogener VOC in die Atmosphäre verwendet.

Die Untersuchungen wurden mit einem mobilen, kontinuierlich von Luft durchströmten Pflanzeneinschlußsystem durchgeführt, das den Anforderungen zur Bestimmung von Emissionsraten biogener VOC unter Freilandbedingungen genügt (z.B. ähnliche Werte für Temperatur, photosynthetisch aktiver Strahlung, $CO_2$-Konzentration etc. in der Kammer wie außerhalb). Bereits vorhandene Komponenten, wie das Luftversorgungssystem, wurden verbessert und das Sammeln von Proben automatisiert. Die biogenen VOC wurden auf Adsorbentien angereichert und anschließend im Labor nach thermischer Desorption mittels Gaschromatographie analysiert. Als Detektoren wurden ein Massenspektrometer und ein Flammenionisationsdetektor verwendet. Die zur quantitativen Analyse notwendigen gasförmigen Kalibrationsmischungen biogener VOC wurden mit einer eigens gebauten Diffusionsanlage hergestellt. Die Qualität der Messungen wurde erfolgreich in einem Interkalibrationsvergleich mit drei anderen Arbeitsgruppen getestet. Für die meisten untersuchten Monoterpene war der relative

statistische Fehler der Bestimmung von Mischungsverhältnissen der Größenordnung einiger 100 ppt (parts per trillion, dt.: Teile pro Billion) kleiner als 14 %. Aus den Ergebnissen des Interkalibrationsexperimentes wurde der systematische Fehler der Messungen auf kleiner als 10 % geschätzt.

Mit dem mobilen Pflanzeneinschlußsystem wurden die Monoterpenemissionen von acht verschiedenen 3-4-jährigen Kiefern und von zwei Zweigen einer 40-jährigen Kiefer untersucht. Die Experimente mit der erwachsenen Kiefer wurden im Hartheimer Wald (nähe Freiburg) während vier Feldmeßkampagnen zwischen April und Oktober 1998 durchgeführt. Die Untersuchungen der Emissionen der jungen Kiefern, die aus demselben Wald stammten, fanden jeweils zwischen Frühling und Herbst 1998 und 1999 statt. Parallel zu den Untersuchungen unter Freilandbedingungen wurden mit den jungen Kiefern auch Laboruntersuchungen in der Arbeitsgruppe von Dr. Jürgen Wildt durchgeführt. Die Ergebnisse der Laborstudien unter kontrollierten Umweltbedingungen sind zur Interpretation der Daten aus Freilandbedingungen notwendig und sind daher in der vorliegenden Arbeit ebenfalls enthalten.

Generell wurde kein unterschiedliches Emissionsverhalten der Kiefern zwischen Laborstudien und Freilandexperimenten gefunden. Die im Labor verwendeten kontinuierlich gespülten Glasreaktoren sind somit zur Herstellung freilandähnlicher Meßbedingungen (bzgl. Temperatur, photosynthetisch aktiver Strahlung, $CO_2$-Konzentration etc.) geeignet. Die Möglichkeit, unter Laborbedingungen insbesondere Temperatur und Licht unabhängig voneinander auf diskrete Werte eingestellen zu können, erlaubt aus Laborexperimenten Emissionsalgorithmen zur Beschreibung der Emissionen in Abhängigkeit von oben genannten Parametern abzuleiten.

Die emissionsstärksten Monoterpene der Waldkiefer waren α-Pinen, 3-Caren, β-Pinen, β-Myrcen, Limonen, Sabinen, Camphen, Tricyclen, sowie das oxygenierte Monoterpen 1,8-Cineol ($C_{10}H_{18}O$). Andere ebenfalls identifizierte Monoterpene wurden nur in vergleichsweise kleinen Mengen emittiert und trugen zusammen weniger als 10 % zur Summe der Masse emittierter Monoterpene bei. Sowohl unter Labor- als auch unter Freilandbedingungen wurde ein starker Anstieg der Emissionsraten mit der Nadeltemperatur beobachtet. Zur Beschreibung der Temperaturabhängigkeit der Emissionen wurde ein Algorithmus nach der Modellvorstellung von *Tingey et al.* (1991) verwendet. Werte für den Parameter, der die Temperaturabhängigkeit der Emissionen beschreibt ($c_{TP}$ $R^{-1}$) lagen zwischen $4.0 \cdot 10^3$ K und $13.9 \cdot 10^3$ K. Umgerechnet auf den vereinfachten Emissionsalgorithmus nach *Guenther et al.* (1993) entspricht dies einem

Anstieg von etwa 5 bis 16 % pro Kelvin. Die Variationen dieses Parameters waren unabhängig von der Art des Monoterpens, von der Jahreszeit und vom untersuchten Individuum. Die im Rahmen der vorliegenden Arbeit beobachteten Werte für die Temperaturabhängigkeit liegen im Bereich der in der Literatur beschriebenen Werte (*Guenther et al.*, 1993: 9 % pro Kelvin als beste Schätzung für alle Pflanzenarten, *Rinne et al.*, 2000: 14.6 % pro Kelvin für Waldkiefer).

Eine Abhängigkeit der Emissionsraten von der photosynthetisch aktiven Strahlung (PAR) konnte nur unter Laborbedingungen festgestellt werden. Zur Beschreibung dieser Abhängigkeit der Emissionen wurde der Algorithmus nach *Schuh et al.* (1997) verwendet. Die Lichtabhängigkeit der Monoterpenemissionen ging bereits bei sehr niedrigen Strahlungswerten in eine Sättigung über (etwa 15 % der Sonneneinstrahlung unter Freilandbedingungen). Bei einer konstanten Temperatur lag der Anstieg der Monoterpenemissionsraten als Folge von PAR im Bereich zwischen 20-30 %. Damit war der unter Laborbedingungen festgestellte Einfluß des Lichtes auf die Emissionsraten kleiner als der Einfluß der Temperaturschwankungen während des Sammelzeitraums einer Probe unter Freilandbedingungen (zwischen $\pm 1$ und $\pm 4$ K während 60 Minuten). Unter Freilandbedingungen wurde keine Abhängigkeit der Emissionsraten von PAR festgestellt.

Überraschenderweise wurde festgestellt, daß verschiedene Individuen der Waldkiefer ein sehr unterschiedliches Muster an Monoterpenen emittierten. Die saisonalen Schwankungen des Emissionsmusters einer einzigen Kiefer waren deutlich kleiner als die Variationen von Pflanze zu Pflanze. Das Emissionsmuster von zwei Zweigen derselben Pflanze war im Rahmen der Meßfehler gleich. Es wurde festgestellt, daß sich das Emissionsmuster als Folge von Streß (z. B. erhöhte Temperaturen) ändert, daß diese streßinduzierten Änderungen allerdings klein sind gegen die Pflanze-zu-Pflanze Variation des Emissionsmusters. Obwohl die Datenbasis schmal ist, deuten diese Ergebnisse an, daß das Emissionsmuster bestenfalls als ‚Fingerabdruck' einer einzelnen Pflanze gesehen werden kann, keinesfalls aber als ‚Fingerabdruck' der ganzen Pflanzenart (in diesem Fall der Waldkiefer), wie vielfach in der Literatur beschrieben wird (z.B. *Schindler und Kotzias*, 1989; *Roussis et al.*, 1995).

Die bestehenden Modelle zur Beschreibung der Emissionsraten waren nicht geeignet, um alle Meßdaten zu erklären. Die temperaturnormierte, sogenannte Standardemissionsrate, $\Phi^S$, eines Monoterpens war sehr variabel. Die Summe der Standardemissionsraten aller Monoterpene lag für die jungen Kiefern zwischen 0.06 und 0.65 $\mu g\ g(dw)^{-1}\ h^{-1}$ (Mikrogramm Monoterpene pro Gramm Trockengewicht an Nadeln

und Stunde) und für die erwachsene Kiefer zwischen 0.24 und 3.7 µg $g(dw)^{-1}$ $h^{-1}$. Die Standardemissionsraten zeigten dabei keinen klaren jahreszeitlichen Verlauf. Die jahreszeitliche Variation der Standardemissionsraten lag mit einer Schwankung von etwa einer Größenordnung im Bereich der Pflanze-zu-Pflanze Variabilität der Emissionsraten. Dieses Ergebnis deutet an, daß die Absoluthöhe der Emissionen (bei gegebenen Temperatur- und Lichtverhältnissen) nicht vom Individuum selbst, sondern durch nicht im Algorithmus berücksichtigte, andere Umwelteinflüsse bedingt ist. Streßfaktoren sind eine mögliche Erklärung für diese Schwankungen in den Emissionsraten. Erhöhte Temperaturen (> 30 °C) wurden als ein möglicher Streßfaktor identifiziert, jedoch konnte der Einfluß nicht quantitativ beschrieben werden.

Basierend auf den Ergebnissen der Freilandexperimente an der erwachsenen Kiefer wurde ein Bestandsfluß an Monoterpenen aus der Fläche des Hartheimer Waldes berechnet. Bei einer Temperatur von 30 °C liegt der berechnete Fluß an Monoterpenen im Bereich zwischen 54 bis 941 ng $m^{-2}$ $s^{-1}$ (Nanogramm Monoterpene pro Quadratmeter Bodenfläche und Sekunde). Diese große Schwankungsbreite ist eine direkte Folge der Schwankungen der Standardemissionsraten, die bislang noch nicht verstanden sind.

Im Hinblick auf zukünftige Untersuchungen biogener Emissionen werden folgende Empfehlungen gegeben: Es erscheint ausreichend, die Emissionsraten jeweils nur an einem Zweig eines Baumes zu untersuchen, um ein Maß für die Emissionen dieser Pflanze zu erhalten. Im Gegensatz dazu ist es unumgänglich, die Emissionen mehrere Individuen einer Pflanzenart zu betrachten, um sich ein Bild über die Pflanze-zu-Pflanze Variationen der Emissionen zu machen. Darüber hinaus ist es zwingend erforderlich, die bestehenden Modelle zur Beschreibung der Emissionsraten als Funktion von Umweltparametern (wie z.B. Temperatur und Licht) zu verbessern. Insbesonders der Einfluß von Streß (z.B. erhöhte Temperaturen, Pathogenbefall, Insektenbefall) muß in zukünftigen Laborstudien genau betrachtet werden. Die Auswirkungen von Streß auf die Monoterpenemissionen müssen auf meßbare biologische Parameter zurückgeführt, quantifiziert und in die bestehenden Algorithmen implementiert werden. Ohne ein besseres Verständnis der Prozesse, die zur Emission von Monoterpenen aus Pflanzen führen, bleiben Hochrechnungen auf Bestandsflüsse mit einer großen Unsicherheit behaftet. Parallel zu den Pflanzeneinschlußuntersuchungen sollten direkte Messungen von Bestandsflüssen durchgeführt werden. Die Kombination beider Meßmethoden sollte eine solide Datenbasis schaffen, auf deren Grundlage Emissionskataster biogener VOC verbessert werden können.

# Table of contents

# 1 Introduction and objectives

Vegetation plays an important role in regulating the exchange of gases between the biosphere and atmosphere. Besides the influence on concentrations of carbon dioxide, oxygen and water vapor, plants also influence the mass balance of many trace gases in the atmosphere.

Plants produce and emit a large number of volatile organic compounds (VOCs), such as isoprene and monoterpenes. These compounds are highly reactive in the atmosphere. They react with OH radicals, the most important oxidizing agent for hydrocarbons, and thus influence its tropospheric concentration (e.g. *Chameides et al.*, 1988; *Thompson*, 1992). In combination with sufficient levels of nitrogen oxides the oxidation of VOCs leads to the production of ozone and other photooxidants (e.g. *Trainer et al.*, 1987; *Fehsenfeld et al.*, 1992).

According to recent estimates, 1150 Tg (Tg = $10^{12}$ g) of carbon are released annually as VOCs into the atmosphere by plants (*Guenther et al.*, 1995). On a global scale, biogenic VOC emissions are approximately one order of magnitude larger than the estimated emissions from anthropogenic sources (*Mueller*, 1992). Estimates of biogenic VOC emissions are based on models considering biomass distribution, plant-specific emission factors, algorithms describing these emissions as a function of temperature, light intensity and moisture. Due to the multitude of parameters, these estimates are highly uncertain.

Calculations of monoterpene emissions from coniferous plants are based on an algorithm that only considers the temperature dependence of emissions (*Tingey et al.*, 1991). Very little is known of seasonal trends, and branch-to-branch and plant-to-plant variability of monoterpene emissions. Stress to a plant, such as drought, heat, and mechanical forcing, for example, have been observed to influence monoterpene emissions as well, but these influences on the emissions have not been quantified. Plant-specific emission factors used as inputs for models are often associated with errors of unknown magnitude.

In this work, monoterpene emissions from Scots pine (*Pinus sylvestris*), a typical central European conifer, have been investigated. Measurements were conducted under ambient conditions on several young pines and on branches of an adult pine using a plant enclosure technique.

The main objective of this work was to:

- Test the applicability of the emission algorithm describing monoterpene emissions as a function of temperature and light intensity, which was derived from studies carried out under laboratory conditions.
- Investigate the seasonal cycle of monoterpene emissions.
- Estimate the branch-to-branch and plant-to-plant variability of monoterpene emissions.
- Compare emission rates from young and adult pines.

The experimental results were used to estimate monoterpene fluxes from the 'Hartheimer Wald', a forest in Southern Germany that consisted mainly of Scots pines, and which was the location where the studies with the adult pine were conducted.

The studies were conducted as part of a program called 'Troposphären-ForschungsSchwerpunkt' (TFS, engl.: Tropospheric Research Program), specifically as part of the sub-project for the determination of the source strengths of VOCs emitted from forest ecosystems in Germany.

This thesis is divided into five parts. After a summary of the current state of knowledge for biogenic VOCs (chapter 2), the analytical instrumentation developed and improved for these studies is evaluated (chapter 3). The description focuses on the applicability of the analytical instrumentation for making emission rate measurements. The performance of the instrumentation was successfully tested in an intercalibration experiment which also allowed the estimate of overall errors in the measurements.

The results of the emission rate measurements of Scots pines are then presented (chapter 4). This chapter is subdivided into results of laboratory and outdoor enclosure studies with young pine seedlings, and outdoor studies with branches of an adult pine. The laboratory studies were conducted by J. Wildt and coworkers. Results of these studies are shown here, because they are necessary for the interpretation of the results obtained under outdoor conditions.

In the discussion (chapter 5), the results of the three types of emission rate measurements are compared. First, results obtained measuring the same branch, but at different times of year are presented, then emission rates obtained from different branches of the same plant and emission rates from different individual plants are discussed.

Finally, monoterpene emission rates from different age plants are compared along with studies under laboratory and field conditions.

In the final chapter (chapter 6) the results are summarized and recommendations for future emission rate studies are made.

# 2 Current knowledge concerning biogenic volatile organic compounds

Biogenic volatile organic compounds (biogenic VOCs) is a collective term for organic atmospheric trace gases released from natural sources. Biogenic VOCs include a large variety of organic compounds, such as the terpenoids, i.e. the hemiterpene isoprene ($C_5H_8$, 2-methyl-1,3-butadiene), monoterpenes ($C_{10}H_{16}$, e.g. α-pinene), sesquiterpenes ($C_{15}H_{24}$, e.g. β-caryophyllene), and longer chain compounds made up of $C_5H_8$-units. Biogenic VOCs also include alkanes (e.g. methane), alkenes (e.g. ethene), carbonyls (e.g. acetone, hexenal), alcohols (e.g. 2-methyl-3-buten-2-ol), esters (e.g. methyl salicylate), ethers (e.g. 1,8-cineol), and acids (e.g. acetic acid). A comprehensive compilation of isoprene and monoterpene emissions from a large number of plant species has been given by *Kesselmeier and Staudt* (1999). In this chapter, the biological origin and role of biogenic VOCs, different approaches to measuring their emission rates, and their impact on atmospheric chemistry are described briefly, with a focus on the terpenoids.

## 2.1 Biology of terpenoids

Emission of VOCs from plants represents a substantial loss of photosynthetically fixed carbon. Usually, the loss of assimilated carbon due to VOC emission is on the order of several percent or less (e.g. *Fehsenfeld et al.*, 1992; *Harly et al.*, 1994; *Sharkey*, 1996; *Street et al.*, 1996). Some studies have reported losses as high as between 10 and 50 % (*Sharkey and Loreto*, 1993; *Staudt et al.*, 1997; *Staudt and Bertin*, 1998). These high losses of photosynthetically fixed carbon raise the question as to whether these compounds are simply lost due to leakage, or if the production and emission of such complex hydrocarbons serve an ecophysiological purpose. In the next sections, a brief overview is given of the following:

- why monoterpenes are produced by plants,
- how they are synthesized, and
- what algorithms are used to describe their emissions from plants as a function of parameters such as temperature and light intensity.

Definitions of the biological terms used in this section can be found in the appendix (chapter 8.2).

### *2.1.1 Ecophysiological function*

There is still much uncertainty regarding the ecophysiological function of terpenoids despite numerous studies on biogenic VOCs. However, there are many indications that terpenoids help to improve an individual plant´s chances of survival and also the survival of the whole plant species.

Some monoterpenes are reported to have an allelopathic function, i.e. limiting seed germination and growth of other species nearby (*Fischer*, 1991; *Tarayré et al.*, 1995). Some monoterpenes have antimicrobial and toxic properties and serve as defense products against fungal pathogens and herbivory insects (*Gershenzon and Croteau*, 1991; *Himejima et al.*, 1992; *Snyder*, 1992; *Langenheim*, 1994; *Priemé et al.*, 2000). Besides protection against insect attack, monoterpenes also protect plants from being eaten by herbivory mammals by their deterrent smell or taste (*Farentinos et al.*, 1981; *Bell and Harestad*, 1987; *Elliott and Loudon*, 1987).

There is evidence that monoterpenes act as signalling molecules in plant-insect interactions. Linalool, for example, is a typical component of flowering fragrances that attract pollinators (*Bergström*, 1991; *Knudsen and Tollsten*, 1993). Monoterpenes have also been reported to act as kairomones, attracting predator insects, that are natural enemies of the herbivory insects attacking the plant (e.g. *Dicke and Sabelis*, 1990; *Dicke et al.*, 1993; *Turlings et al.*, 1993; 1995; *Tabayashi et al.*, 1994). A complex interaction was found for the relationship between coniferous plants and bark beetles with monoterpenes acting as signal compounds (*Delorme and Lieutier*, 1990; *Gershenzon and Croteau*, 1991; *Raffa*, 1991). VOC release due to herbivory attack has been observed to be systemic, i.e. not only by the part of the plant under attack, but by the whole organism (*Turlings and Tumlinson*, 1992; *Röse et al.*, 1996; *Paré and Tumlinson*, 1997a, 1997b, 1998) and the amount of relased VOC was found to be dependent on the number of herbivores (*Dicke et al.*, 1993; *Dicke*, 1994).

Biogenic VOCs have also been identified to serve as signalling substances in plant to plant interactions. For example, the release of methyl salicylate by infected tobacco plants warns and activates other plants against the tobacco mosaic virus (*Shulaev et al.*, 1997).

Thus, there are numerous indications that storage and production of monoterpenes serves an ecophysiological purpose.

### 2.1.2 *Biosynthesis*

According to *Ruzicka et al.* (1953), all isoprenoids are produced from the same precursor, a $C_5$ substrate called isopentenyl pyrophosphate (IPP), or 'active isoprene'. The production of IPP can be explained by two different biochemical pathways, shown in Figure 2.1.

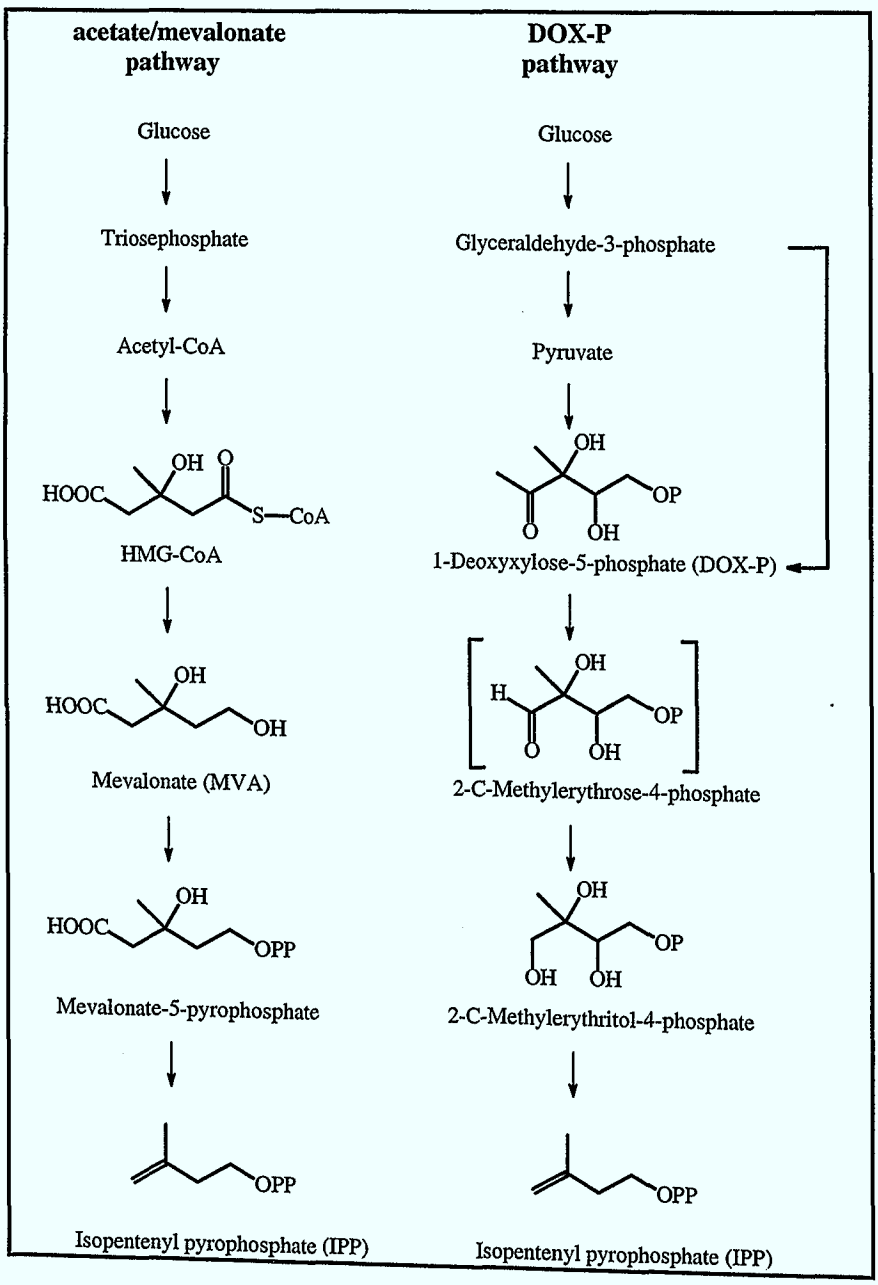


**Figure 2.1:** *Formation of isopentenyl-diphosphate (IPP) via the acetate/mevalonate and the DOX-P pathway after Lichtenthaler (1998). Abbreviations: P = phosphate, PP = pyrophosphate, CoA = coenzyme A.*

The left side of Figure 2.1 shows the so-called mevalonate pathway (*Goodwin*, 1965; *Spurgeon and Porter*, 1981; *Croteau*, 1987), which for decades was believed to be the only pathway for the production of IPP. In the past few years, a mevalonate independent pathway was found, termed DOX-P or *Rohmer* pathway (*Flesch and Rohmer*, 1988; *Rohmer et al.*, 1993, 1996; *Lichtenthaler*, 1998, 1999), shown on the right side. Both IPP forming processes start with glucose as the substrate and require phosphorylation by adenosine triphosphate (ATP) and reduction by nicotinamid adenine dinucleotide (NADH).

In the classical mevalonate pathway, three molecules of acetyl-Coenzyme A (acetyl-CoA) condense to form 3-hydroxy-3-methyl-glutaryl-CoA (HMG-CoA) (e.g. *Bach*, 1995). HMG-CoA is then enzymatically reduced to mevalonate. After phosphorylation with adenosine triphosphate (ATP) and subsequent dehydroxylation and decarboxylation, IPP is formed. In the novel *Rohmer* pathway, a $C_2$-unit derived from pyruvate is transferred to glyceraldehyde-3-phosphate to form 1-deoxyxylose-5-phosphate (DOX-P). IPP is then formed from this intermediate product. The two different pathways are spatially separated. IPP formation via the mevalonate pathway proceeds in the cytoplasm, whereas the DOX-P pathway occurs in the plastids (*Lichtenthaler*, 1998).

Figure 2.2 shows the subsequent pathways leading to the synthesis of isoprene, monoterpenes and sesquiterpenes. IPP is reversibly transformed into dimethylallyl pyrophosphate (DMAPP) by the enzyme isopentenyl pyrophosphate isomerase. By cleaving the pyrophosphate, isoprene is enzymatically formed from DMAPP (*Silver and Fall*, 1991; *Monson et al.*, 1992; *Kuzma and Fall*, 1993; *Schnitzler et al.*, 1996).

The common precursor of all monoterpenes is geranyl pyrophosphate (GPP), which is formed by addition of one unit of IPP to DMAPP (*Endo and Suga*, 1992). GPP is the substrate for a group of enyzmes called monoterpene synthases and cyclases, which synthesize all different monoterpenes via linalyl pyrophosphate and the $\alpha$-terpenyl cation (*Croteau et al.*, 1988; *Gershenzon and Croteau*, 1993). The monoterpene synthesizing enzymes were found to be highly specific, usually leading to only one or two products (*Croteau*, 1987; *Gershenzon*, 1994; *Bohlmann et al.*, 1997).

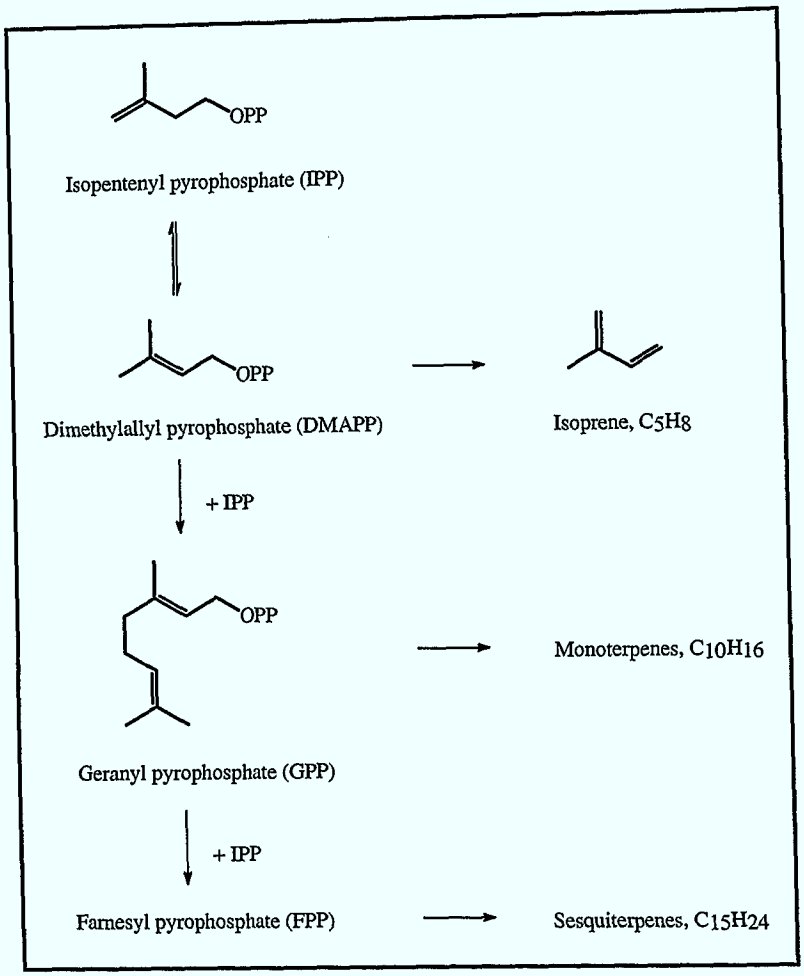


**Figure 2.2:** *Schematic pathways for the production of isoprene, monoterpenes and sesquiterpenes in plants.*

The addition of a second unit of IPP to GPP leads to the formation of farnesyl pyrophosphate (FPP), the substrate for the formation of all sesquiterpenes. According to current knowledge, sesquiterpenes are produced within the cytosol, whereas monoterpene production takes place within plastids (*Carde et al.*, 1980; *Gleizes et al.*, 1983; *McGarvey and Croteau*, 1995; *Bohlmann et al.*, 1997; *Lichtenthaler*, 1999).

Adding additional units of IPP to FPP leads to precursors to the formation of diterpenes ($C_{20}$), triterpenes ($C_{30}$), and tetraterpenes ($C_{40}$), and finally to the production of polyterpenes $(C_5H_8)_n$, found in rubber latex, and guttapercha (*Lichtenthaler*, 1999).

Only isoprene (boiling point: 34 °C), monoterpenes (e.g. α-pinene, boiling point: 155-156 °C), and sesquiterpenes (e.g. β-caryophyllene, boiling point: 262-264 °C) are volatile enough to be released into the atmosphere and thus be of importance to atmospheric chemistry. Whereas isoprene is emitted immediately after its production, monoterpenes can be stored within the plant, usually in special organs such as the resin ducts of conifer needles (*Lerdau*, 1991; *Tingey et al.*, 1991).

### *2.1.3 Description of emission algorithms*

A generally accepted algorithm to describe monoterpene emissions was established by *Tingey et al.* (1991). They explain the emissions of monoterpenes from coniferous plants as a result of diffusion out of the resin ducts (or 'pools') mentioned above. Monoterpene emissions are usually reported to be only temperature dependent, with emissions increasing with needle temperature (e.g. *Tingey et al.*, 1980; *Lamb et al.*, 1985; *Juuti et al.*, 1990). The emission rate of a VOC as a result of the diffusion out of pools, $\Phi_{VOC}^{P}$, can be described by the following equation:

$$\Phi_{VOC}^{P} = \Phi_{VOC}^{P,S} \cdot \exp\left[\frac{c_{TP}}{R} \cdot \left(\frac{T - T_S}{T \cdot T_S}\right)\right] \qquad \text{(E2.1)}$$

where $\Phi_{VOC}^{P}$ = VOC emission rate from pool [ng g(dw)$^{-1}$ h$^{-1}$]

$\Phi_{VOC}^{P,S}$ = VOC emission rate from pool [ng g(dw)$^{-1}$ h$^{-1}$] at standard temperature $T_S$

$c_{TP}$ = empirical parameter describing the temperature dependence [J mol$^{-1}$]

R = gas constant [J K$^{-1}$ mol$^{-1}$]

T = temperature [K]

$T_S$ = standard temperature [298 K]

The emission rate of a VOC from a plant is expressed in units of mass of the emitted VOC per dry weight (dw) of the investigated plant and per hour.

The most frequently used algorithm to describe the temperature dependence of monoterpene emissions is the following approximation to equation E2.1 proposed by *Guenther et al.* (1993)

$$\Phi_{VOC}^{P} = \Phi_{VOC}^{P,S} \cdot \exp[\beta \cdot (T - T_S)] \qquad \text{(E2.2)}$$

where $\Phi_{VOC}^{P}$ = VOC emission rate from pool [ng g(dw)$^{-1}$ h$^{-1}$]

$\Phi_{VOC}^{P,S}$ = VOC emission rate from pool [ng g(dw)$^{-1}$ h$^{-1}$] at standard conditions

T = temperature [K]

$T_S$ = standard temperature [298 or 303 K]

$\beta$ = empirical coefficient [K$^{-1}$]

This more simple algorithm (E2.2) makes the assumption that $c_{TP}$, which to a first approximation is the enthalpy of vaporization for the considered monoterpene, does not depend on temperature within the range of physiological relevant temperatures ($\beta = c_{TP} R^{-1} (T_S^{-1})^2$ for $T \approx T_S$). Both algorithms describe emissions as a product of a temperature dependent term and a so-called standard emission rate, i.e. the emission rate normalized to a specific temperature (e.g. 25 °C or 30 °C). Since this 'standard emission rate' is only normalized to temperature, it may not be constant if emissions are also dependent on other parameters (e.g. PAR, stress to the plant). Thus, only the temperature dependence of monoterpene emissions are described and a potential dependence on photosynthetic active radiation (PAR) is neglected.

There are some studies reporting a PAR dependence for monoterpene emissions from conifers contradicting the simple model described above. *Simon et al.* (1994) found a PAR dependence for monoterpene emissions for Maritime pine (*Pinus pinaster*) and *Janson* (1993) and *Shao et al.* (2000) for Scots pine (*Pinus sylvestris*). In $^{13}C$-labeling experiments *Shao et al.* (2000) observed labeling of four monoterpenes (α-pinene, camphene, 3-carene and β-pinene) emitted by Scots pine (*Pinus sylvestris*) within hours, indicating a direct link between monoterpene biosynthesis and emission. They described the emissions using the algorithm of *Schuh et al.* (1997), in which two independent pathways for the emissions are assumed. One is the diffusion from storage pools and the second is emissions in parallel with monoterpene biosynthesis, resulting in the following emission algorithm:

$$\Phi_{VOC} = \Phi_{VOC}^{P} + \Phi_{VOC}^{B} \qquad \text{(E2.3)}$$

where $\Phi_{VOC}$ = VOC emission rate [ng g(dw)$^{-1}$ h$^{-1}$]

$\Phi_{VOC}^{P}$ = emission rate from pool [ng g(dw)$^{-1}$ h$^{-1}$]

$\Phi_{VOC}^{B}$ = emission rate in parallel with VOC biosynthesis [ng g(dw)$^{-1}$ h$^{-1}$]

The algorithm describing emissions from pools, $\Phi_{VOC}^{P}$, is identical to the algorithm based on the model by *Tingey et al.* (1991) (E2.1). The algorithm describing emissions in parallel with VOC biosynthesis, $\Phi_{VOC}^{B}$, is based on the isoprene emission model of *Guenther et al.* (1993) and has been modified by taking the square of the term describing the dependence on PAR:

$$\Phi_{VOC}^{B} = \Phi_{VOC}^{B,S} \cdot c_L \cdot \left( \frac{\alpha \cdot L}{\sqrt{1+\alpha^2 \cdot L^2}} \right)^2 \cdot \frac{\exp\left[ \frac{c_{T1}}{R} \cdot \left( \frac{T - T_S}{T \cdot T_S} \right) \right]}{1+\exp\left[ \frac{c_{T2}}{R} \cdot \left( \frac{T - T_M}{T \cdot T_S} \right) \right]} \qquad \text{(E2.4)}$$

where $\Phi_{VOC}^{B}$ = emission rate in parallel with VOC biosynthesis [ng g(dw)$^{-1}$ h$^{-1}$]

$\Phi_{VOC}^{B,S}$ = emission rate in parallel with VOC biosynthesis [ng g(dw)$^{-1}$ h$^{-1}$] at standard light intensity ($L_S$ = 1000 μE m$^{-2}$ s$^{-1}$) and temperature ($T_S$ = 298 K)

$c_L$ = is an empirical factor used to force $c_L \cdot \left(\alpha \cdot L / \sqrt{1+\alpha^2 \cdot L^2}\right)^2$ to be 1 at standard light intensity ($L = L_S$ = 1000 μE m$^{-2}$ s$^{-1}$) [dimensionless]

α = empirical parameter that describes the emission rate as a function of light intensity, L [μE$^{-1}$ m$^2$ s]

L = photosynthetic active radiation [μE m-2 s-1], identical to PAR

$c_{T1}$ = empirical parameter [J mol$^{-1}$]

$c_{T2}$ = empirical parameter [J mol$^{-1}$]

R = gas constant [J K$^{-1}$ mol$^{-1}$]

T = temperature [K]

$T_S$ = standard temperature [298 K]

$T_M$ = temperature of maximum enzyme activity [K]

The emission algorithm of *Guenther et al.* (1993) (i.e. equation E2.4 without taking the term describing the PAR dependence to the square) was derived to describe the dependence of isoprene emissions on both light intensity and temperature. The temperature dependence term makes use of an equation which has been used to simulate the temperature response of enzymatic activity. The term describing the light dependence is similar to equations that have been used to model the light dependence of photosynthesis. *Schuh et al.* (1997) reported that in several cases the relative increase of VOC emission rates from sunflower was higher than the relative increase of light intensity. This observation was considered by squaring the light dependence term. To account for the origin of equation E2.4, it is shown here in its original form without further simplifications. The algorithm is explained in detail in *Guenther et al.* (1993) and *Schuh et al.* (1997).

Despite the fast labeling of small amounts of emitted 3-carene and β-pinene, *Shao et al.* (2000) did not find a detectable PAR dependence for the emissions of these compounds. Only the emissions of α-pinene and camphene were found to depend on PAR. PAR saturation of the emissions occurred at very low radiation levels ($L < 200$ μE $m^{-2}$ $s^{-1}$), less than 15 % of full sunlight, and the increase in the emissions due to PAR was only about 20 to 30 %.

Only little is known about the seasonal variability of standard emission rates of monoterpenes. *Janson* (1993) reported the seasonal variation of the standard emission rate of monoterpenes from Scots pine (*Pinus sylvestris*) as a factor of 6 between May and August, measured at four sites in Sweden. In October, he found standard emission rates a factor of 20 higher than the lowest value obtained at end of May for which he did not give an explanation.

Also, for branch-to-branch variability of standard emission rates only limited data are available. Results reported in the literature contradict one another. *Street et al.* (1997) found no statistically significant differences in isoprene emissions from two different branches of a Eucalyptus tree (*Eucalyptus globulus*). On the other hand, *Guenther et al.* (1991) reported leaf-to-leaf variations in the emission rates from the same plant species (Eucalyptus, *Eucalyptus globulus*) of 62 % for isoprene emissions and of nearly 80 % for monoterpene emissions. The effects of stress were given as a possible explanation for these variations.

*Lichtenthaler* (1996) gave an overview of the general stress concept in plants. According to this, stress is "any unfavorable condition or substance that affects or blocks a plant's metabolism, growth or development". Many natural (e.g. heat, drought, insect attack) and anthropogenic (e.g. ozone smog, acid rain) factors may serve as stress to plants. For a few of these stresses, the impact on monoterpene emissions has been investigated in the past. Table 2.1 summarizes the effects of different stresses and their impact on monoterpene emissions reported in the literature.

**Table 2.1:** *Different stress effects and their impact on monoterpene emissions as reported in the literature.*

| Stress | Plant species | Effect | Reference |
|---|---|---|---|
| Elevated ozone concentrations | Scots pine (*Pinus sylvestris*) | none | *Kainulainen et al.* (1998) |
| | Norway spruce (*Picea abies*) | none | *Lindskog and Potter* (1995) |
| Drought | Holm oak (*Quercus ilex*) | decrease | *Bertin and Staudt* (1996) |
| Heat stress (T > 30 °C) | Scots pine (*Pinus sylvestris*) | increase | *J. Wildt*, unpublished data |
| Mechanical stress | Monterey pine (*Pinus radiata*) | increase | *Juuti et al.* (1990) |
| Pathogen attack | Scots pine (*Pinus sylvestris*) | increase | *J. Wildt*, unpublished data |
| Herbivory attack | Corn (*Zea mays*) | increase | *Turlings and Tumlinson* (1992) |
| | Norway spruce (*Picea abies*) | increase | *Priemé et al.* (2000) |

Monoterpene emission rates are often observed to increase by more than one order of magnitude due to stress effects. Although the importance of stress on monoterpene emissions has been recognized, these effects have not been considered in any published algorithm and have not been described quantitatively.

## 2.2 Approaches to measuring biogenic VOC emissions

There are various approaches to measuring biogenic VOC emissions from live plants on different scales. On a biological scale, measurements are conducted at single leaves, at branches, and on entire small plants. With regard to atmospheric chemistry, landscape fluxes are of greater interest than emissions from just single plants. These fluxes can be measured directly, but such studies are very complicated, expensive, and require extensive resources with regard to instrumentation. In addition, the air sampled above a vegetative canopy does not necessarily represent the original emissions. Biogenic VOCs are very reactive (see next section), and their concentrations may already have changed between their emission and collection. To estimate 'net emissions', measurement techniques are required that are capable of separating emission process from atmospheric chemistry. The enclosure technique uses this approach. Net fluxes are calculated by scaling up the emissions from single branches or plants to entire landscapes. Following is a survey of different enclosure and flux measurement techniques.

*Monson and Fall* (1989) and *Guenther et al.* (1991) used small leaf cuvettes to investigate VOC emissions from single leaves in the laboratory. *Schuh et al.* (1997) conducted their laboratory studies in continuously stirred tank reactors (CSTR) of up to 1500 l in volume enclosing entire small plants. In all these studies, the cuvettes or enclosure chambers were continuously flushed with air. VOC emission rates were obtained from measurements of differences in VOC concentrations between the chamber inlet and outlet. Environmental conditions (e.g. leaf temperature, light intensity, relative humidity) could be adjusted independently, which allowed measurements suitable for deriving emission algorithms such as the ones described previously.

In outdoor conditions, the dynamic chambers described by *Kesselmeier et al.* (1996) and *Komenda et al.* (2000) (30-40 cm in diameter, 50-60 cm in length), for example, were used to measure emissions from branches of large plants, or from entire small plants. *Edwards et al.* (1994) and *Pier* (1995) used large open-top chambers (4.6 m in diameter, 8.5 m in height) to enclose entire adult trees. The environmental conditions inside outdoor enclosure chambers are usually controlled by the ambient conditions.

A typical approach to measuring landscape fluxes of biogenic VOCs is the flux-gradient technique, in which samples are collected at different heights above a forest canopy. In combination with meteorological data (e.g. vertical wind velocity), VOC fluxes can be calculated. Such studies can either be tower-based (e.g. *Schade et al.*, 1999; *Rinne et al.*, 2000) or the sampling system can be attached to a tethered ballon which allows sampling at heights up to 1000 m (e.g. *Helmig et al.*, 1998; *Greenberg et al.*, 1999).

Another approach to estimating landscape fluxes are eddy covariance measurements such as described by *Guenther and Hills* (1998). These measurements are conducted at one height and are accompanied by sonic anemometer measurements that allow the assignment of VOC concentrations to upward and downward air masses. The use of this technique is restricted by the availability of fast response gas analyzers (> 1 Hz). For isoprene, such a fast sensor is available, based on the chemiluminescence reaction of isoprene and ozone. For monoterpenes, such a sensor does not exist. This problem is circumvented by the so-called relaxed eddy accumulation (REA) technique. Air is sampled into two reservoirs, depending on the direction of the vertical wind velocity at a rate proportional to the vertical air velocity, and analyzed subsequently (e.g. *Baker et al.*, 1999; *Gallagher et al.*, 2000).

All estimates of global emissions of biogenic VOCs are based on these types of measurements.

## 2.3 Atmospheric role of biogenic VOCs

The importance of biogenic VOCs to the atmosphere was recognized as early as 1955 by *Went* (1955, 1960a, 1960b) who also made the first global estimation of VOC emissions. Table 2.2 summarizes global estimates of biogenic VOC emissions cited in the literature. The numbers given here are based on models that often consider biomass type and distribution, plant-specific emission factors, algorithms describing emissions as a function of temperature, light intensity and moisture, and on climatic data.

**Table 2.2:** *Global estimates of biogenic VOC emissions, in Tg C $yr^{-1}$, from Kesselmeier and Staudt (1999). OVOC are 'other VOCs', ORVOC are 'other reactive VOCs'. The classification is made dependent on the atmospheric lifetime of a VOC (lifetime longer or shorter than 1 day).*

| Literature | Isoprene | Monoterpenes | OVOC | ORVOC | Total |
|---|---|---|---|---|---|
| *Went* (1960b) | | | | | 175 |
| *Rasmussen and Went* (1965) | | | | | 432 |
| *Zimmerman* (1979) | 350 | 480 | | | |
| *Rasmussen and Khalil* (1988) | 452 | | | | |
| *Warneck* (1988) | | | | | > 800 |
| *Dignon and Logan* (1990) | 450 | | | | |
| *Taylor et al.* (1990) | 175 | 143 | | | |
| *Turner et al.* (1991) | 285 | | | | |
| *Mueller* (1992) | 250 | 147 | | | 491 |
| *Fehsenfeld* et al. (1992) | 420 | 128 | 279 | | 827 |
| *Guenther et al.* (1995) | 503 | 127 | 260 | 260 | 1150 |

The most recent estimate of biogenic VOC emissions was given by *Guenther et al.* (1995) with an annual flux of 1150 Tg carbon per year. Thus, estimated biogenic VOC emissions are approximately one order of magnitude larger than the estimated global VOC emissions from anthropogenic sources (*Mueller*, 1992). More than 80 % of biogenic VOC emissions occur in tropical regions (*Lerdau et al.*, 1997). According to the most recent estimate, isoprene ($C_5H_8$) makes the largest contribution (44 %) to the total flux of biogenic VOCs to the atmosphere. Monoterpenes ($C_{10}H_{16}$) contribute 11 % to the sum of biogenic VOC emissions. All other compounds are classified dependent on their atmospheric lifetimes (i.e. the decay of a compound to $e^{-1}$ of its initial concentration) into 'other VOCs' (OVOC, lifetime > 1 day, e.g. methanol) or 'other reactive VOCs' (ORVOC, lifetime < 1 day, e.g. 2-methyl-3-buten-2-ol).

Once released into the atmosphere, many biogenic VOCs are highly reactive. During the day, they rapidly react with OH radicals and with $NO_3$ radicals at night. The alkenes may also react with ozone. Table 2.3 summarizes the lifetimes of selected biogenic VOCs calculated with typical tropospheric concentrations of OH, $NO_3$ and $O_3$. The atmospheric lifetime of isoprene is on the order of hours, monoterpenes react even faster, resulting in lifetimes between a few minutes and several hours.

**Table 2.3:** *Calculated tropospheric lifetimes for selected biogenic VOCs with respect to gas-phase reaction with OH radicals, $NO_3$ radicals and $O_3$, from Atkinson and Arey (1998).*

| | Lifetime* for reaction with | | |
|---|---|---|---|
| **Biogenic VOC** | **OH** | **$NO_3$** | **$O_3$** |
| isoprene | 1.4 h | 1.6 h | 1.3 days |
| α-pinene | 2.6 h | 11 min | 4.6 h |
| 3-carene | 1.6 h | 7 min | 11 h |
| β-pinene | 1.8 h | 25 min | 1.1 days |
| sabinene | 1.2 h | 7 min | 4.6 h |
| β-myrcene | 40 min | 6 min | 50 min |
| camphene | 2.6 h | 1.7 h | 18 days |
| limonene | 50 min | 5 min | 2.0 h |
| β-phellandrene | 50 min | 8 min | 8 h |
| 1,8-cineol | 1.0 day | 1.5 yr | > 4.5 yr |
| β-caryophyllene | 40 min | 4 min | 2 min |
| longifolene | 3.0 h | 1.6 h | > 33 days |
| 2-methyl-3-buten-2-ol | 2.1 h | 8 days | 1.7 days |
| methanol | 12 days | ~ 1 yr | > 4.5 yr |

*Time for decay of compound to 1/e of its initial concentration, assuming concentrations of OH, 12 h daytime average of 2.0 $10^6$ $cm^{-3}$, $NO_3$, 12 h nighttime average of 5 $10^8$ $cm^{-3}$, and $O_3$, 24 h average of 7 $10^{11}$ $cm^{-3}$.

An excellent overview of the atmospheric chemistry of biogenic organic compounds has been published by *Atkinson and Arey* (1998). Although the kinetics of the gas-phase reactions of biogenic VOCs with OH, $NO_3$ and $O_3$ seems to be fairly well understood, the reaction mechanisms are less well-known and often the reaction products formed by these reactions have yet to be identified.

As an example, Figure 2.3 shows the reaction sequence of α-pinene starting with the reaction with OH, taken from *Atkinson and Arey* (1998).

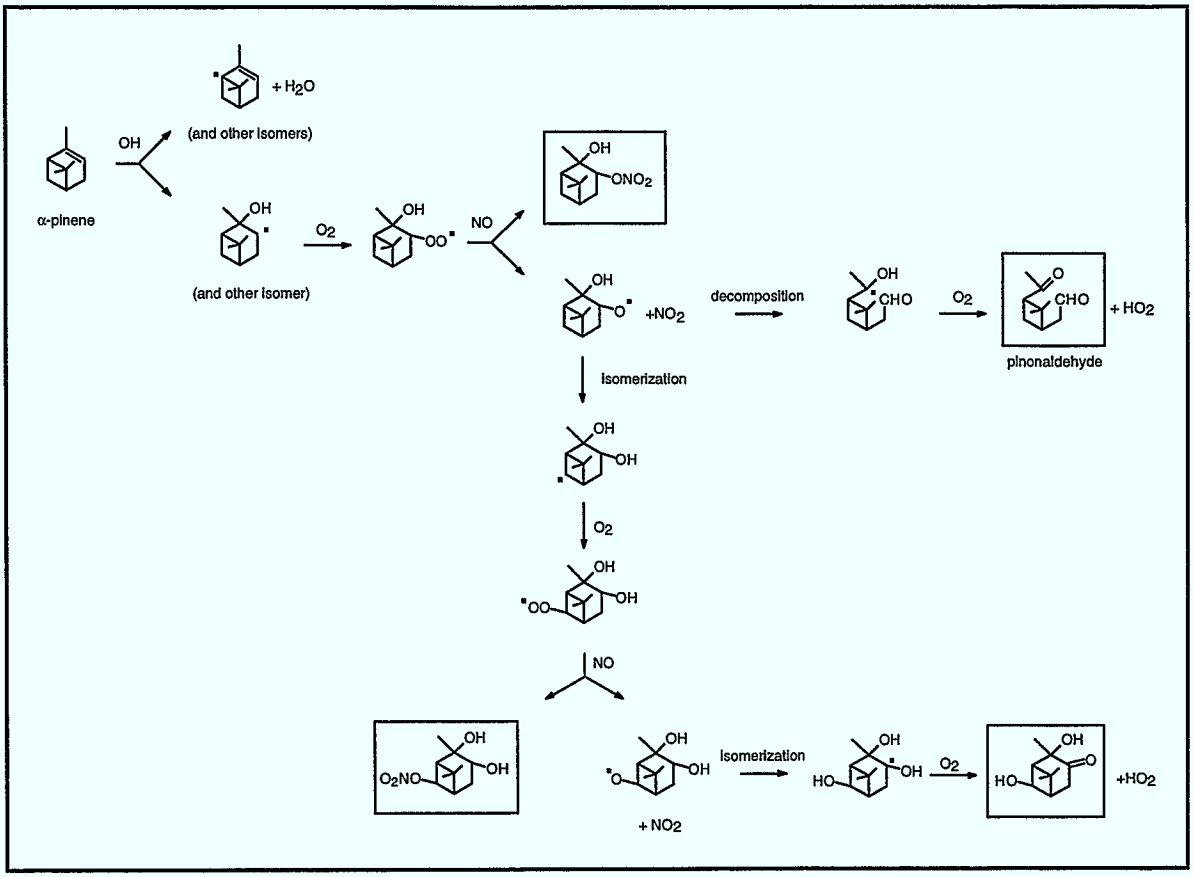


**Figure 2.3:** *Reaction sequence of α-pinene, initiated by reaction with OH, identified products shown in boxes, after Atkinson and Arey (1998).*

Subsequent to the addition of OH to the carbon-carbon double bond, the alkyl radical reacts with oxygen to form an alkylperoxy radical. This can react with NO either to form an organic nitrate or an alkoxy radical. By the latter reaction NO is converted into $NO_2$. In the atmosphere, this alkoxy radical can decompose by C-C bond dissociation and react with oxygen to form pinonaldehyde as a stable product, or it undergoes isomerization to another alkyl radical. Eventually, an organic nitrate or a stable product is formed by reaction with oxygen from this alkyl radical. The reaction with oxygen leads to the production of an $HO_2$ radical. Organic nitrates may be photolyzed and form $NO_2$ and an alkoxy radical which undergoes similar reactions as described above. As a net result of these first degradation reactions of α-pinene, OH is converted into $HO_2$ and NO into $NO_2$.

Due to their emissions in large quantities and their high reactivity, biogenic VOCs have a significant influence on tropospheric chemistry. They react with the OH radical, the most important oxidizing agent in the troposphere, and thus influence its concentration and distribution (e.g. *Chameides et al.*, 1988; *Thompson*, 1992).

In combination with sufficient levels of nitrogen oxides, VOCs lead to the production of ozone (e.g. *Trainer et al.*, 1987; *Fehsenfeld et al.*, 1992). As can be seen in Figure 2.3, the degradation of a VOC, in this case α-pinene, is accompanied by the conversion of NO to $NO_2$. At wavelengths less than 420 nm, $NO_2$ is photolyzed in the atmosphere and reconverted into NO. The oxygen atom formed in this reaction rapidly reacts with an oxygen molecule and forms ozone (Figure 2.4).

$$NO_2 \xrightarrow{h\nu\ (\lambda<420\ nm)} NO + O(^3P)$$

$$O(^3P) + O_2 \xrightarrow{M} O_3$$

**Figure 2.4:** *Production of ozone after photolysis of $NO_2$ and subsequent reaction of $O(^3P)$ with oxygen.*

Besides their ability to lead to the formation of ozone, biogenic alkenes may also react with ozone. Figure 2.5 gives the general mechanism of the reaction sequence, taken from a recent review article on the atmospheric chemistry of VOCs and $NO_x$ (*Atkinson*, 2000).

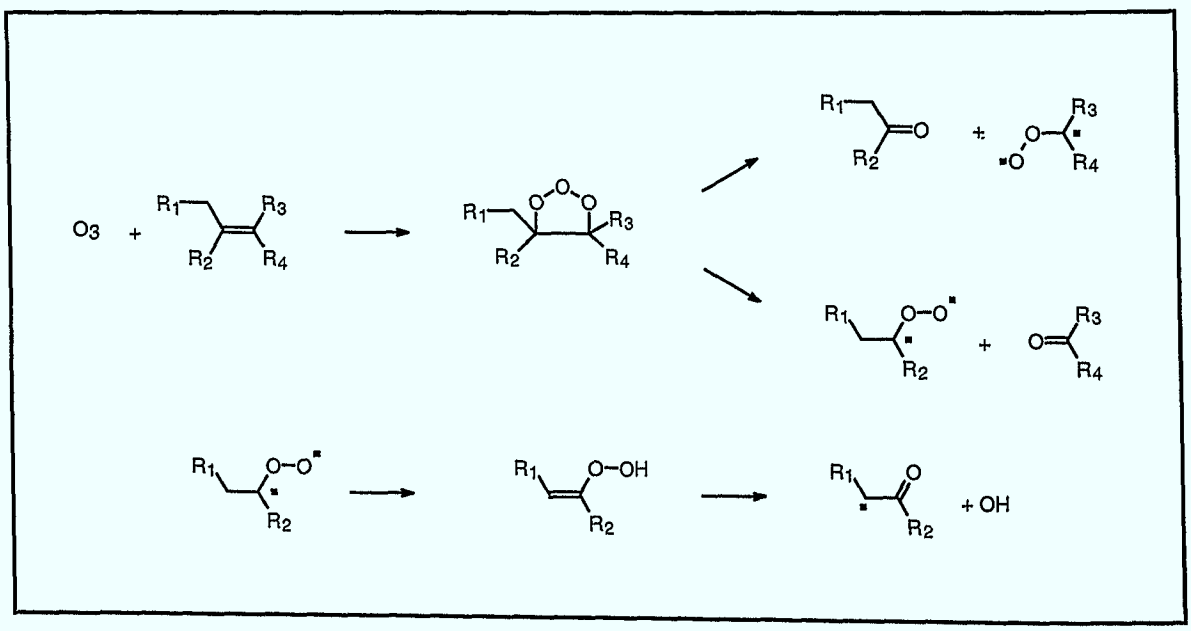


**Figure 2.5:** *OH Formation initiated by reaction of ozone with an alkene.*

In the primary reaction, ozone is added to the carbon-carbon double bond to form a primary ozonide which decomposes into a carbonyl and a biradical. The fate of the initially formed biradical is not well understood, but one reaction sequence ultimately leads to the production of an OH radical. Thus, the ozone oxidation of biogenic alkenes is a potential source of OH and $HO_2$ radicals during the night and early morning (e.g. *Makar et al.*, 1999).

Furthermore, oxidation products of biogenic VOCs, such as pinonaldehyde (see Figure 2.3), may condense on existing particles or lead to the formation of secondary organic aerosols (SOA), which influence the radiative balance of the atmosphere (*Hoffmann et al.*, 1997; *Brasseur et al.*, 1999; *Koch et al.*, 2000).

Due to the multitude of influences on atmospheric chemistry, it is essential to have an accurate quantitative knowledge of the source strength of biogenic VOCs.

# 3 Experimental Section

This chapter deals with the sampling, analysis, and calibration of biogenic VOCs and the determination of emission rates for individual plants. The sampling technique is described in detail with regard to its suitability for emission rate measurements and compared to approaches used in other studies. The improvements in the development of complex calibration mixtures of biogenic VOCs, and the performance of the calibration system, which was successfully tested in an intercalibration experiment, are presented. The normalization of measured mixing ratios to plant physiological variables is explained. The importance of the different plant species sampled in this work with respect to growing range and frequency is presented.

## 3.1 Enclosure system

The primary requirements for a plant/branch enclosure system are to maintain ambient conditions inside the enclosure and to operate at conditions which are suitable for emission rate measurements. The main parameters influencing biogenic VOC emissions from plants are temperature, photosynthetically active radiation (PAR, e.g. *Tingey et al.*, 1980; *Guenther et al.*, 1993; *Schuh et al.*, 1997) and stress (e.g. *Juuti et al.*, 1990; *Prieme et al.*, 2000). The effects of carbon dioxide concentration (*Sharkey et al.*, 1991) and relative humidity (*Schade et al.*, 1999) have also been discussed in the literature. Since these parameters are known, and are presumed to have an influence on VOC emissions from plants, it is essential that they are continuously monitored and kept at ambient levels.

Figure 3.1 shows a schematic drawing of the system used for sampling biogenic VOC emissions during the outdoor studies. It was based on the system described in detail by *Parusel* (1996). Air temperature, relative humidity, and photosynthetic active radiation were measured inside the enclosure using an HTR-1 probe (PP Systems). Carbon dioxide concentrations were measured with an environmental gas monitor (PP Systems, EGM-2). The enclosure chamber consisted of FEP foil which was mounted in a cylindrical aluminium frame (500 mm length, 300 mm diameter) and had a volume of approx. 30 l. The FEP foil (50 µm thickness) had 90-95 % light transmission at photosynthetic relevant wavelengths between 400-700 nm. Thus, radiation intensity inside the enclosure was only slightly less than outside.

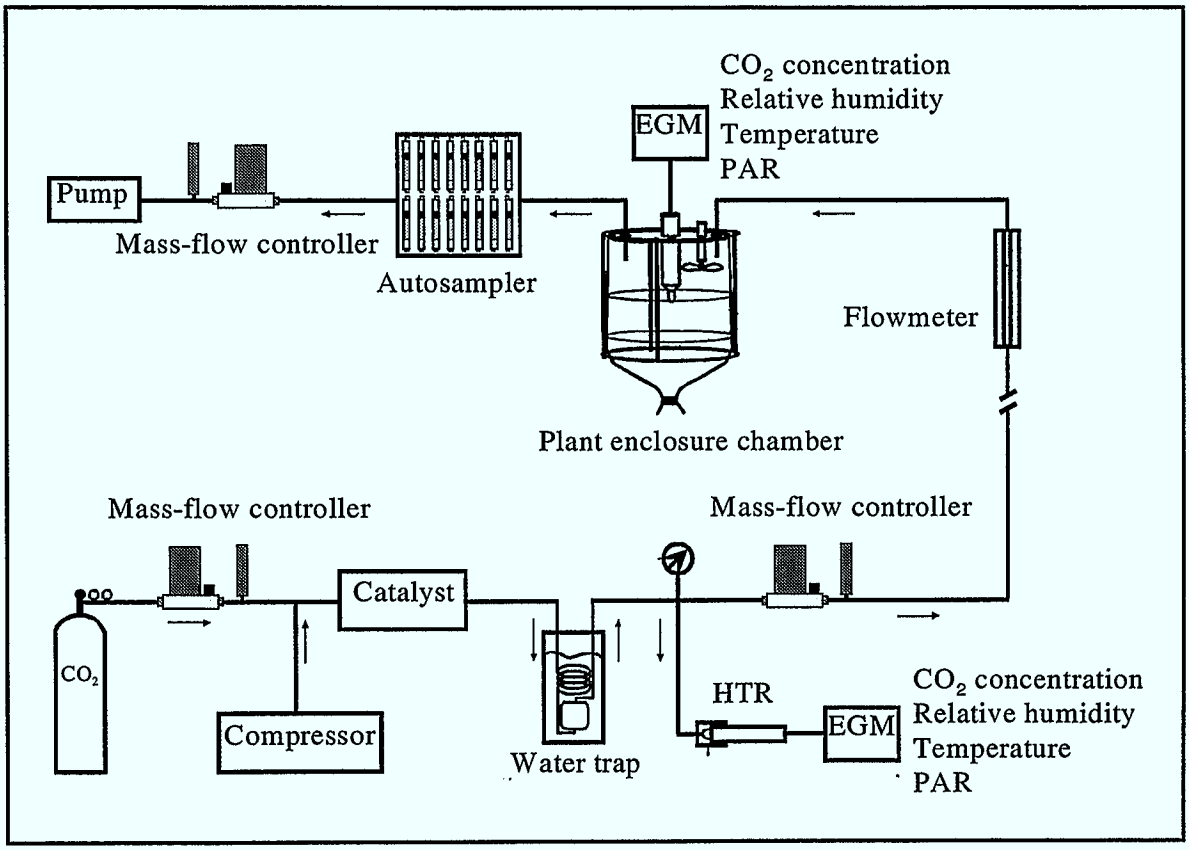


**Figure 3.1:** *Schematic drawing of the system used for sampling of biogenic VOCs. HTR: Probe for measuring relative humidity, temperature and PAR. EGM: Environmental gas monitorfor measuring the concentration of carbon dioxide.*

On one side, the enclosure was closed with a PTFE plate, its other side could be closed around the stem of a plant. This was done by carefully tying up the foil with a string. Mounting a plant inside an enclosure system can stress a plant resulting in increased VOC emission rates. *Juuti et al.* (1990) reported an increase in monoterpene emissions by more than one order of magnitude from *Pinus radiata* after rough handling. After the initial handling procedure the emission rates decreased to normal values in 1 hour. To eliminate a bias in the obtained emission data due to this stress effect, the measurements of VOC mixing ratios always began at least 12 hours after mounting the branch inside the enclosure.

In general, there are two different enclosure systems described in the literature: static enclosures (i.e. wihout exchange of the air inside the enclosure, e.g. *Zimmerman et al.*, 1978) and flow-through enclosures (i.e. an enclosure continuously flushed with air, e.g. *Winer et al.*, 1992, *MacDonald and Fall*, 1993, *König et al.*, 1995). Static enclosure systems have the problem of radiative overheating and of a constant increase in relative humidity due to transpiration of the plant. Without air movement temperatures measured

inside the enclosure increased up to 8.5 K higher than outside ambient temperatures. With a constant air flow of several liters per minute through the enclosure, the temperature differences were reduced to ±3 K. To regulate the relative humidity, and especially to avoid water condensation inside the enclosure, the inlet air flow was dried by trapping water in a stainless steel loop cooled to 273 K.

The enclosure system used within the scope of this work was a flow-through enclosure. In order to continuously flush the enclosure with air, a mobile air supply system was built. The air flow through the enclosure was kept constant by a mass-flow controller (Brooks, 5850TR) at a flow rate of several liters per minute. In contrast to other studies in which ambient air was used to flush the system (e.g. *Janson*, 1993; *Fuentes et al.*, 1995; *Street et al.*, 1997) the emission rate measurements described here were simplified by using clean, VOC free air. This avoided the problem of detecting small differences between high background concentrations that occur when using ambient air that contains VOCs also emitted by the enclosed plant. Ambient air was purified by a $Pd/Al_2O_3$-catalyst at 723 K to reduce VOC concentrations to values on the order of several parts per trillion (less than 10 parts per trillion for monoterpenes) at the chamber inlet. The advantage of catalytic VOC destruction over adsortive techniques using charcoal (e.g. *Bertin et al.*, 1997) is that problems such as breakthrough and adsorbents blow out does not occur.

Besides VOCs in the inlet air stream, outgassing from the foil and memory effects are also a potential problem. Outgassing of VOCs from the FEP foil was tested by flushing the enclosure with air from the air supply system. No significant differences in the VOC concentrations measured at the inlet and outlet were observed. Memory effects due to adsorption on the enclosure walls were studied by continuously flushing the enclosure with a standard gas mixture containing monoterpenes with mixing ratios on the order of 0.1 to 3.7 parts per billion (ppb). After flushing the enclosure with clean air from the air supply system for one hour, monoterpene mixing ratios ranged between 1 and 10 parts per trillion (ppt), 4 % or less than the standard mixing ratios flushed through the enclosure just one hour previous. Table 3.1 summarizes the results of the blank measurements. The mixing ratios shown here represent baseline VOC mixing ratios for the zero air supply and enclosure system. Mixing ratios measured during plant enclosure experiments were usually on the order of several hundred ppt to a few ppb. Therefore, contamination of the system due to ineffective destruction of VOCs in the air supply system and outgasing from the foil could be neglected.

**Table 3.1** *Baseline VOC mixing ratios in ppt of the air supply and enclosure system. Mean value and standard deviation (1σ) of 15 measurements are shown.*

| Compound | Mixing ratio [ppt] |
|---|---|
| benzene | 57 ± 21 |
| hexanal | 2 ± 2 |
| n-hexane | 5 ± 5 |
| toluene | 9 ± 6 |
| n-heptane | 5 ± 4 |
| iso-octane | 3 ± 2 |
| α-pinene | 5 ± 4 |
| camphene | 3 ± 2 |
| β-pinene | 3 ± 3 |
| β-myrcene | 2 ± 1 |
| 3-carene | 10 ± 7 |
| limonene | 2 ± 2 |
| ocimene | 2 ± 2 |
| terpinolene | 3 ± 4 |
| 1,8-cineol | 1 ± 2 |
| citronellal | 2 ± 3 |
| n-undecane | 10 ± 7 |
| dodecane | 11 ± 6 |
| tetradecane | 13 ± 8 |
| longicyclene | 1 ± 1 |
| β-caryophyllene | 2 ± 1 |

Besides VOC concentrations, the ozone concentration of the inlet air is of interest as well. Ozone can stress the plant and under ozone fumigation plants have been observed to emit VOCs differently than without ozone exposure (*Heiden et al.*, 1999a). In addition to the physiological effects, ozone is also of interest with regard to the analytical system. Ozone is known to lead to interferences during sampling and storage of biogenic VOCs on cartridges by causing artifact formation and reduction of observed hydrocarbons (*Helmig*, 1997 and references therein). The air supply system previously described was able to destroy ozone before it entered the enclosure system. As described by *Koppmann et al.* (1995) ozone was lost within seconds on heated stainless steel surfaces such as the catalyst and the lines used in the air supply system.

Carbon dioxide concentrations were measured at the chamber inlet and inside the enclosure using an environmental gas monitor (PP Systems, EGM-2). $CO_2$ was added from a cylinder to maintain ambient concentrations of $CO_2$ inside the enclosure that were reduced due to photosynthetic activity. Low $CO_2$ concentrations had to be avoided in order to prevent the plant from suffering from a lack of carbon dioxide, but $CO_2$

concentrations that are too high might also influence VOC emissions (*Sharkey et al.*, 1991). During the enclosure measurements, the carbon dioxide concentration was kept between 300-500 ppm.

Since only a small fraction of the air passing through the enclosure was actually collected, it was essential that the air sample was characteristic of the average air composition inside the enclosure. Therefore, mixing the air inside the enclosure and maintaining steady-state conditions during sampling was of great importance. A Teflon coated fan that provided air mixing was installed on the Teflon plate of the enclosure chamber. The rotation speed of the fan could be varied by adjusting the voltage of the power supply (1-24 V DC). Air movement inside the enclosure was measured at different rotation frequencies of the fan using an anemometer. Even at the fan´s lowest power, sufficient air movement was measured at all locations inside the chamber (*Parusel*, 1996).

In order to test the mixing of the air inside the enclosure, it was continuously flushed with $CO_2$ free air at a flow rate of 7 l $min^{-1}$. At the beginning of the experiment, $CO_2$ was added from a cylinder at a flow rate of 7 ml $min^{-1}$. The carbon dioxide concentration was continuously monitored. The average residence time was measured to be 4.6 minutes which was consistent with the calculated expected value of 4.3 minutes (enclosure volume = 30 l, flow rate = 7 l $min^{-1}$). A value of 95 % of the calculated steady state concentration was reached after approx. 15 minutes (*Parusel*, 1996). Thus, fluctuations of emission rates on a timescale faster than 15 minutes could not be detected.

## 3.2 Sampling

Samples were collected by pumping air from the outlet air stream through an adsorption tube at a flow rate of 100 ml $min^{-1}$. A sampling system was used which allowed the collection of up to 16 individual air samples. Given the typical sampling time of 60 minutes, the system ran automatically for up to 16 hours. The flow rates and sampling times could be programmed and were monitored using a data logger (a.b.i. data, VL 100).

VOCs were sampled on glass tubes containing solid adsorbents. The tubes had a length of 180 mm and an outer diameter of 6 mm. Prior to their first use, the tubes were cleaned with methanol inside a Soxhlet extactor for 24 hours and subsequently dried in a vacuum chamber at 363 K. A combination of two different adsorbents were used: Tenax

TA (60/80 mesh, Macheray & Nagel) and Carbotrap (20/40 mesh, Supelco). Before using the Tenax TA, it was purified with methanol inside a Soxhlet extractor and subsequently dried. 100 mg of Tenax TA and 50 mg of Carbotrap were packed into each glass tube and fixed with silanized glass wool. The adsorption tubes were conditioned for 24 hours at 450 K by flushing them continuously with nitrogen (99.999 % purity) at several ml $min^{-1}$. Both ends of the adsorption tubes were closed with Swagelok fittings.

The breakthrough volumes of several VOCs on these adsorption tubes were determined. Since the breakthrough volume is a function of the adsorbent temperature, sampling flow rate, and VOC mixing ratio, conditions were chosen that were typical for the enclosure measurements described later. The adsorption tube was kept at a temperature of 298 K and the sampling flow rate was kept constant at 100 ml $min^{-1}$. Between 1 and 18 l of air with VOC mixing ratios between 20 ppt and 7 ppb were sampled (equivalent to a sampling time of 10 minutes to 3 hours). Figure 3.2 shows the peak areas of α-pinene and hexane as a function of the sampling volume (signal of flame ionization detector).

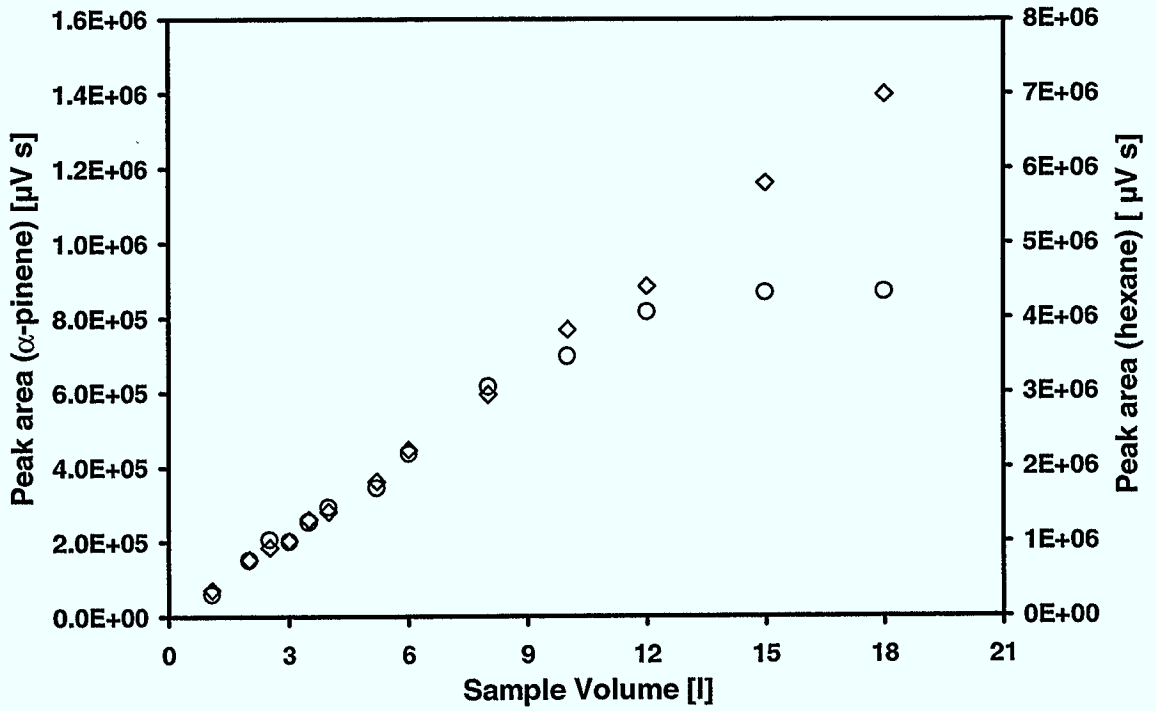


**Figure 3.2:** *Peak area of the FID signal for α-pinene (diamonds, left axis) and hexane (circles, right axis) as function of the sample volume.*

The breakthrough volume is defined as the sample volume corresponding to the end of the linear domain. Breakthrough was not observed for any of the monoterpenes and sesquiterpenes for sampling volumes of up to 18 l. Among the tested VOCs (listed in Table 8.1, Appendix), the smallest breakthrough volume was observed for hexane with a value of approx. 8 l which is still larger than the typical sampling volume of 6 l used for the enclosure measurements described here.

The sensitivity to water vapor was checked by sampling VOC standard mixtures at 298 K with different water contents. Within a range of 5 % to 95 % relative humidity no significant change in the sensitivity was observed (*Wedel*, 1997).

## 3.3 Analysis

Figure 3.3 shows a schematic drawing of the gas chromatograph (Fisons Instruments, GC 8000) equipped with a quadrupole mass spectrometer (Fisons Instruments, MD 800) in parallel with a flame ionization detector (Fisons Instruments, FID 80). Details of this system were given by *Wedel et al.* (1998).

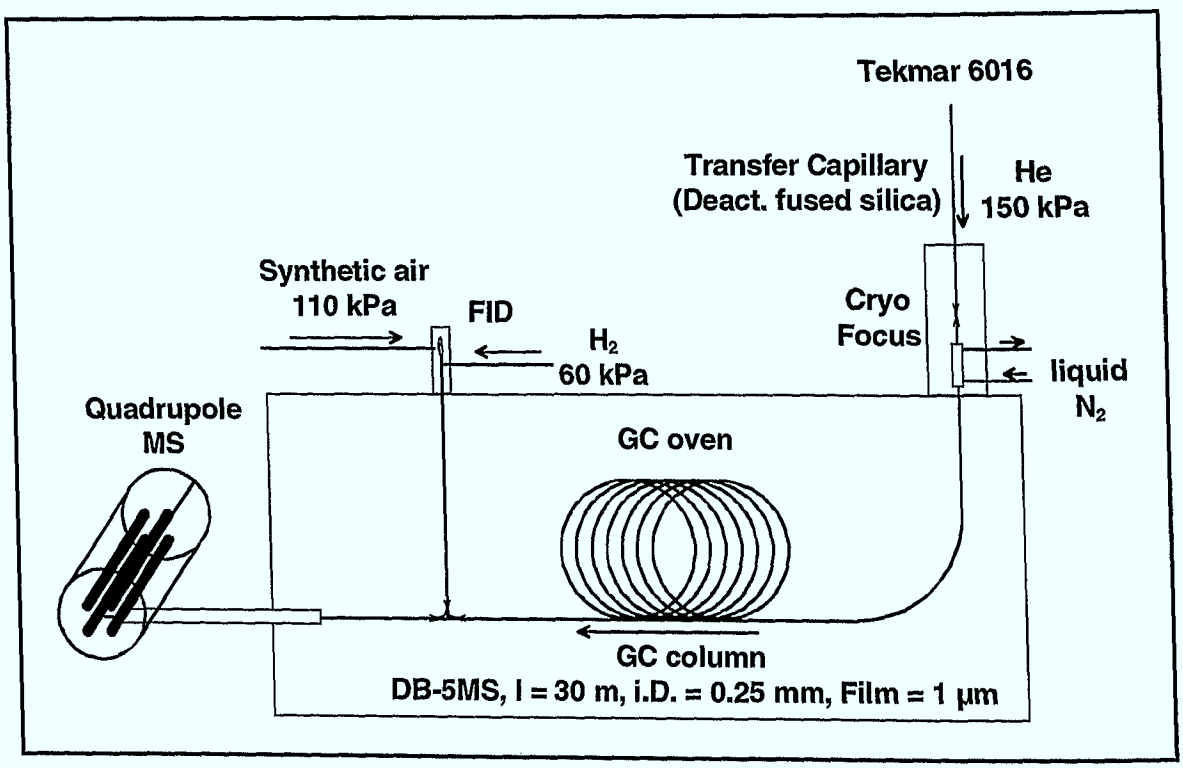


**Figure 3.3:** *Schematic drawing of the GC-FID/MS system.*

The adsorption tubes were placed inside an automated thermal desorption device (Tekmar, Aerotrap 6016) and purged at room temperature for one minute with 45 ml $min^{-1}$ of helium (99.9999 % purity) to reduce the water content. The VOCs were then thermally desorbed by flushing the heated tubes (533 K) for 10 minutes. Helium of 99.9999 % purity was used as the transfer and carrier gas. The desorbed VOCs were cryogenically trapped at 123 K in a stainless-steel column (6" length, 1/8" i.d.) packed with glass beads. The trap was heated to 493 K, and the VOCs were transferred to the gas chromatograph via a heated (473 K) deactivated fused-silica column, and cryogenically preconcentrated a second time at 123 K inside a cryo focus device (Fisons Instruments, Cryo 820) to reduce peak broadening on the analytical column. When the sample transfer was complete, the cryo focus device was heated to 473 K and the sample was injected onto a chromatographic column (DB-5MS, 30 m length, 0.25 mm i.D.). The initial temperature of the GC oven was held at 298 K for 3 min and then ramped to 398 K at 4 K $min^{-1}$ and then to 523 K at of 10 K $min^{-1}$. The final temperature was held for 10 min. The flow-rate of the carrier gas was 2.1 ml $min^{-1}$. At the end of the chromatographic column the flow was split, directing 50 % of the flow to the quadrupole MS and 50 % to the FID.

## 3.4 Calibration

Figure 3.4 shows a schematic drawing of the diffusion system used for the preparation of standard gas mixtures. It was based on the system described by *Gautrois and Koppmann* (1999), developed for the preparation of gas mixtures of halogenated hydrocarbons, and was modified for use with biogenic VOCs. The modifications concerned the material used for the diffusion vials and gas lines. If possible, metal surfaces were avoided and the material was replaced by glass or Teflon.

The system consisted of two diffusion chambers with a volume of approx. 2 l which were mounted inside insulated transport boxes. The temperature inside the diffusion devices was kept constant at 298 K by continuously flushing the double walled glass chambers with water from an external thermostat (Julabo, F20-HC). Up to eighteen diffusion vials, each containing several ml of a pure hydrocarbon could be placed inside each diffusion chamber. The diffusion vials were made of glass with glass capillaries on top that had different lengths (10 to 50 mm) and internal diameters (1 to 3 mm).

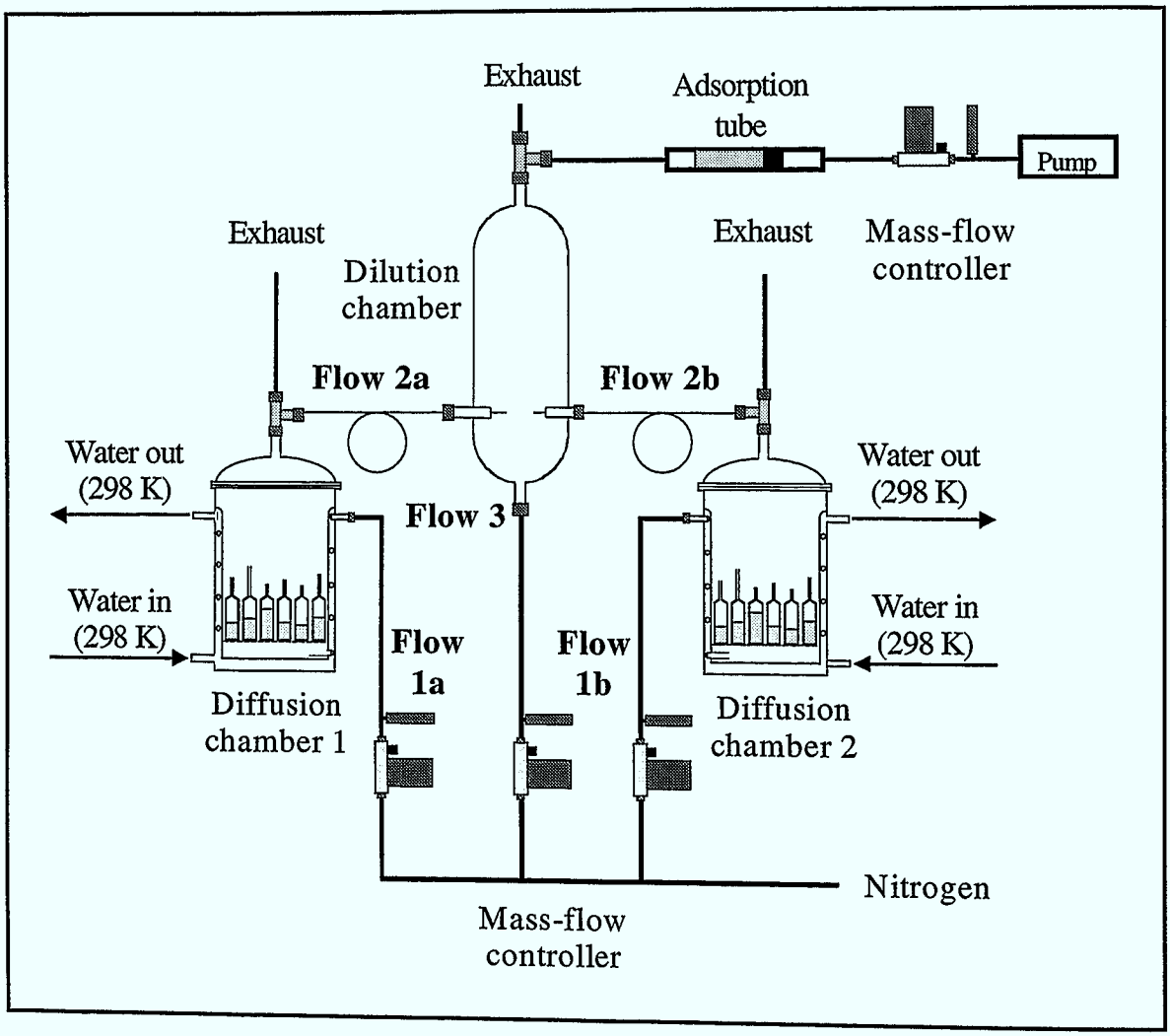


**Figure 3.4:** *Flow diagram of the diffusion system.*

Nitrogen (99.999 % purity) was flushed through the diffusion chambers from bottom to top. By using mass-flow controllers (Brooks, 5850TR), the flow rates were kept constant at 4.1±0.1 l $min^{-1}$ (Flow 1a) and 4.3±0.1 l $min^{-1}$ (Flow 1b), resulting in a residence time for the nitrogen inside the diffusion chambers of approx. 30 seconds. Passing the diffusion vials, the pure nitrogen was enriched with the VOCs inside the chambers resulting in mixing ratios on the order of 0.5 to 750 ppb of individual VOCs at the chamber outlets. Fractions of the flows exiting the diffusion chambers (Flow 2a = 15.7±0.3 ml $min^{-1}$; Flow 2b = 8.5±0.2 ml $min^{-1}$) were transferred to a dilution chamber through deactivated fused-silica columns. These fused-silica columns also served as flow restrictors which assured constant pressure inside the diffusion chambers. The pressure inside the diffusion chambers was set to approx. 200 mbar above ambient. Changes in this excess pressure would result in variable diffusion rates and had to be avoided. The dilution chamber was made of glass and had a volume of approx. 500 ml. Nitrogen (99.999 % purity) was used

for the dilution. The dilution flow (Flow 3) could be adjusted by a mass-flow controller (Brooks, 5850TR) to between 100 and 500 ml $min^{-1}$. The design of the dilution chamber was also critical with regard to the corresponding pressure inside. The previous design used by *Wedel* (1997) had inlet and outlet connections of equal inner diameter (4 mm). Increasing the dilution flow rate led to an increase in the pressure inside the dilution chamber of more than 15 mbar (Figure 3.5, filled circles, left axis). The impact of this increase on the capillary flow was calculated using Hagen-Poisseuille's law and is shown in Figure 3.5 (open squares, right axis). The capillary flow may vary by more than 40 % within the range of the dilution flow rate. For the updated dilution chamber that had a wider outlet (8 mm inner diameter) than the inlet connection, the pressure increase was less than 1 mbar and the impact on the capillary flow was negligible.

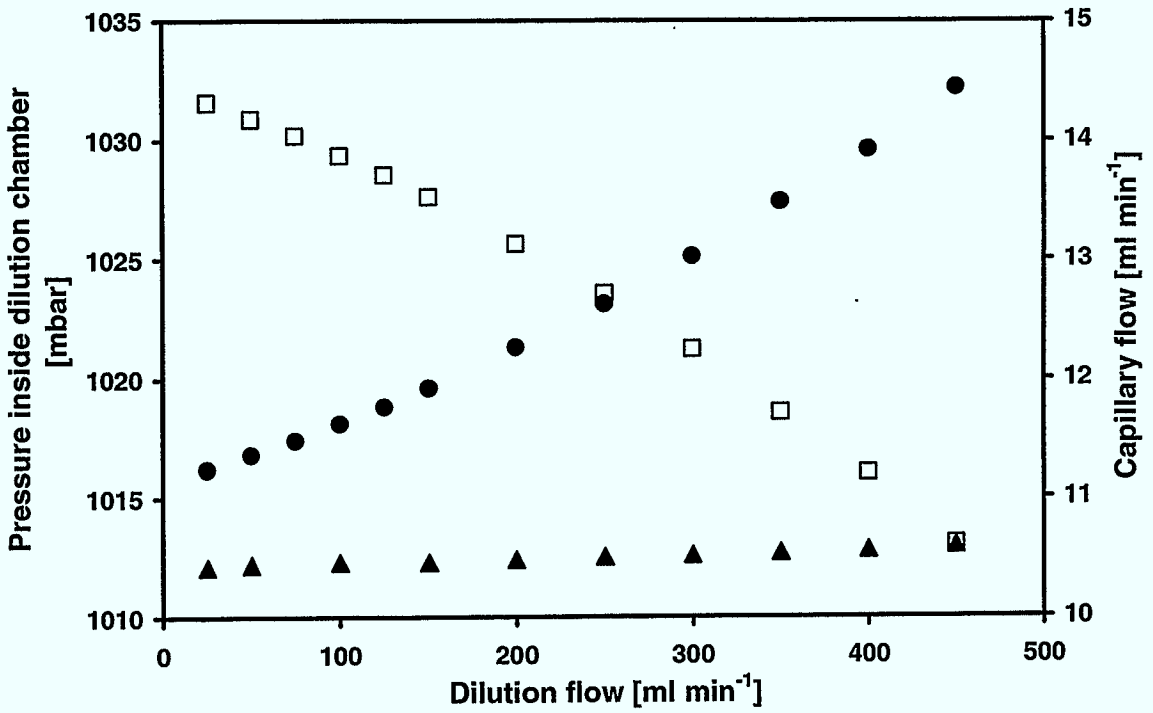


**Figure 3.5:** *Pressure measured inside the dilution chamber (filled circles, previous design with similar inlet and outlet; filled triangles, updated design with wider outlet, both left axis) and calculated capillary flow for conditions with previous dilution chamber (open squares, right axis).*

The different hydrocarbons used for preparing the standard gas mixtures are listed in Table 8.1 (Appendix). In total, 35 different VOCs were tested, among them 11 monoterpenes, 4 sesquiterpenes and several oxygenated compounds. The diffusion rates of

the VOCs were determined by monitoring the mass loss of the liquid compound in the glass vials on a microbalance over time (Sartorius Research, R 160 P).

The temporal stability of the diffusion rates were monitored by weighing the diffusion vials at regular intervals of one to several weeks over a period of 17 months. To minimize the effect of enhanced diffusion rates for short weighing intervals as reported by *Gautrois and Koppmann* (1999), the minimum weighing interval was one week at the beginning of the experiments. Table 3.2 lists the number of weighings, the mean diffusion rates and their variabilities for all investigated compounds.

**Table 3.2:** *Mean und standard deviation (1σ s.d.) of diffusion rates in ng min$^{-1}$. The first two figures are significant.*

| Compound | Number of weighings n | Mean mass loss rate [ng min$^{-1}$] | 1σ s.d. [%] |
|---|---|---|---|
| benzene* | 15 | 9972 | 4.0 |
| | 8 | 4848 | 0.8 |
| hexanal | 15 | 1339 | 5.6 |
| cis-3-hexen-1-ol | 11 | 484 | 17.3 |
| n-hexane | 6 | 7436 | 4.0 |
| toluene | 21 | 3638 | 3.4 |
| n-heptane | 7 | 5765 | 3.3 |
| methyl salicylate | 11 | 18 | 44.4 |
| 6-methyl-5-hepten-2-one | 11 | 401 | 25.7 |
| iso-octane | 5 | 7770 | 3.8 |
| nonanal | 8 | 292 | 14.1 |
| (-)-myrtenal | 3 | 25 | 7.1 |
| (-)-α-pinene | 23 | 584 | 3.4 |
| camphene | 20 | 3123 | 7.6 |
| (-)-β-pinene | 23 | 397 | 3.1 |
| β-myrcene | 15 | 227 | 5.8 |
| (-)-α-phellandrene | 10 | 138 | 20.4 |
| (+)-3-carene | 23 | 250 | 4.1 |
| α-terpinene | 10 | 177 | 33.6 |
| (+)-limonene | 23 | 200 | 6.2 |
| ocimene | 3 | 147 | 0.2 |
| γ-terpinene | 18 | 423 | 35.5 |
| terpinolene | 9 | 117 | 5.0 |
| 1,8-cineole | 22 | 215 | 7.2 |
| (±)-linalool | 9 | 28 | 20.4 |
| (-)-citronellal | 3 | 34 | 2.5 |
| n-undecane | 18 | 405 | 3.0 |
| (-)-bornyl acetate | 11 | 18 | 50.6 |
| dodecane | 14 | 120 | 6.3 |
| geranyl acetone | 9 | 13 | 42.4 |
| tetradecane | 14 | 14 | 30.1 |
| (+)-longicyclene | 23 | 54 | 10.6 |
| (-)-β-caryophyllene | 23 | 36 | 22.0 |
| (-)-α-cedrene | 8 | 30 | 22.6 |
| (+)-longifolene | 3 | 48 | 11.8 |

** The design of the diffusion vial of benzene was changed during the experiments to reduce the diffusion rate.*

The maximum number of weighings was 23 (for α-pinene, β-pinene, 3-carene, limonene, longicyclene, and β-caryophyllene). Other VOCs were placed into the diffusion chamber later and fewer data are available. The standard deviation of the diffusion rates ranged between 0.2 % and 50.6 %. With the exception of (-)-α-phellandrene, α-terpinene and γ-terpinene, the standard deviation of the monoterpene diffusion rates were between

0.2 % and 7.6 %. For the sesquiterpenes, which had smaller diffusion rates, standard deviations between 10.6 % and 22.6 % were observed. Generally, the reproducibility was significantly higher for compounds with higher diffusion rates. Figure 3.6 shows the relative standard deviation as a function of the mean mass loss rate for all compounds listed in Table 3.2.

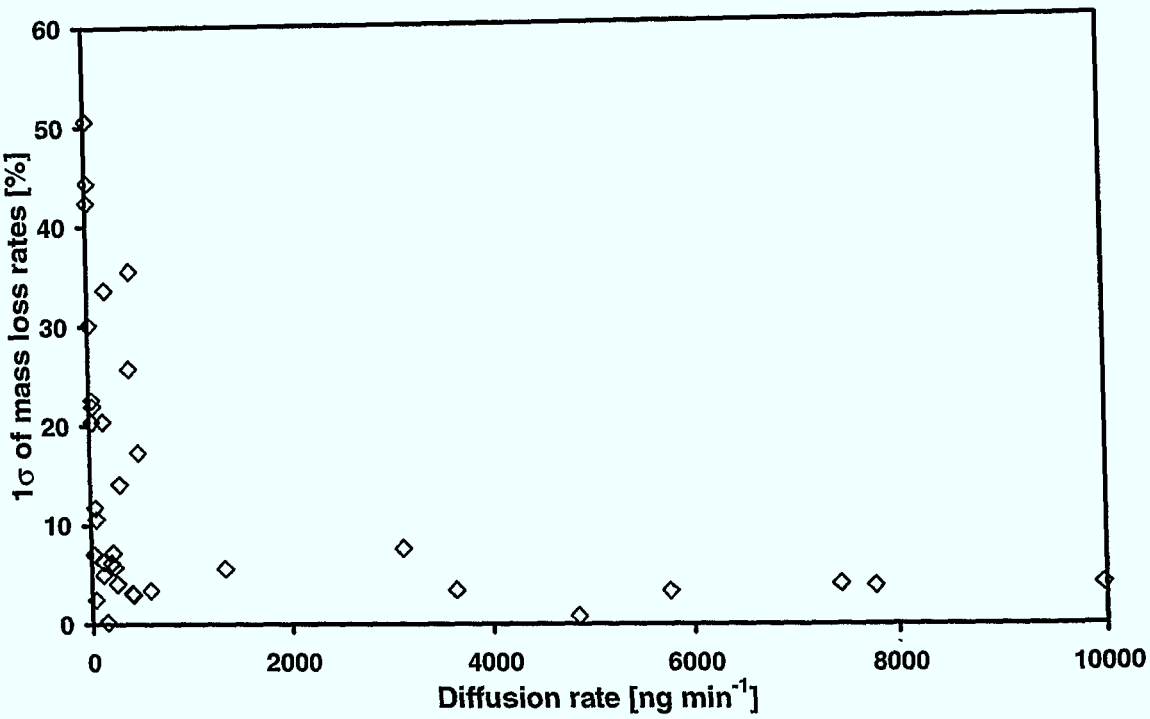


**Figure 3.6:** *Relative standard deviation of mass loss rate as function of mass loss rate for all compounds listed in Table 3.2.*

For compounds with mean mass loss rates higher than 500 ng $min^{-1}$ the reproducibility was always better than 10 %. Compounds with lower mass loss rates showed standard deviations of up to 50 %. The reason for this was short time intervals between weighings. Figure 3.7 shows the deviation of individual mass loss rates from the mean value versus the time interval between two weighings for α-pinene (mean diffusion rate: 584 ng $min^{-1}$) and β-caryophyllene (mean diffusion rate: 36 ng $min^{-1}$) as examples. For α-pinene, the relative deviation from the mean value was always within a range of ±10 % even for the shortest weighing interval of one week. For β-caryophyllene, the scatter was much higher for short weighing intervals and individual mass loss rates differ from the mean value by up to +40 % and –50 %. For weighing intervals longer than

approximately 5 weeks, the observed deviations were also within a range of ±10 %. In response to the results, the weighing intervals of the diffusion vials were increased during the course of the experiments. Compounds that were placed into the diffusion source later during the experiments and were always weighed at longer intervals showed more stable diffusion rates even if their diffusion rates were relatively small.

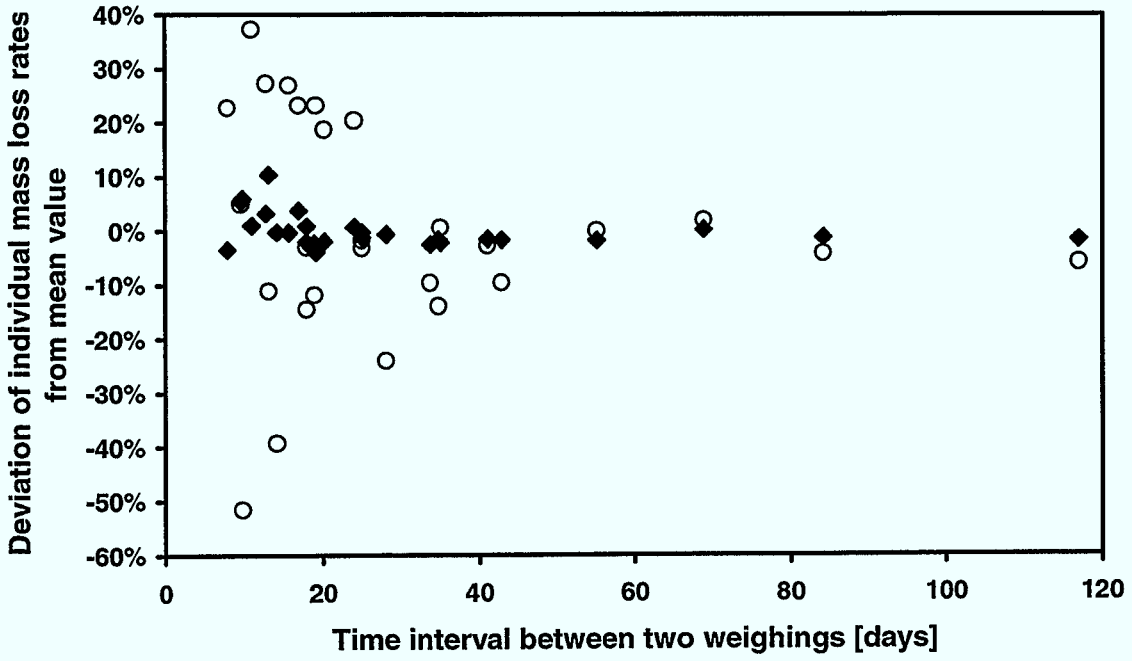


**Figure 3.7:** *Relative deviation of individual mass loss rates from mean mass loss rate as a function of weihging interval (filled diamonds, α-pinene; open circles, β-caryophyllene).*

Besides the problems connected with the reproducibility of mass loss rates of compounds with small diffusion rates, the applicability of the described diffusion source to produce a standard gas mixture of biogenic VOCs had another limitation. The diffusion rates of (-)-α-phellandrene, α-terpinene and γ-terpinene showed a long term trend of decreasing mass loss. Other monoterpenes did not show such a trend (examples shown in Figure 3.8).

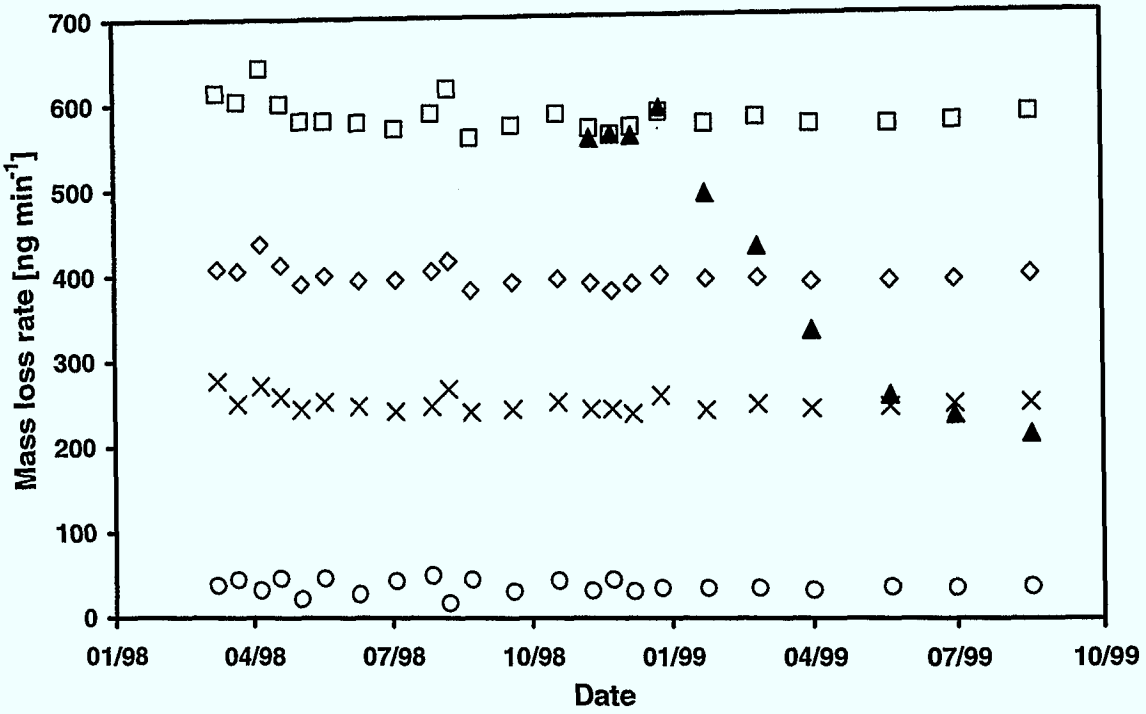


**Figure 3.8:** *Mass loss rate as a function of time (open squares, α-pinene; crosses, 3-carene; open circles, trans-caryophyllene; filled triangles, γ-terpinene).*

Detailed GC/MS analysis showed that these three compounds were converted into p-cymene following the conversions shown in Figure 3.9. With the diffusion source described here, it was thus not possible to produce standard gas mixtures containing α-phellandrene, α-terpinene and γ-terpinene. Other groups reported similar problems connected with diffusion standards for these compounds (C. Plass-Dülmer, private communication).

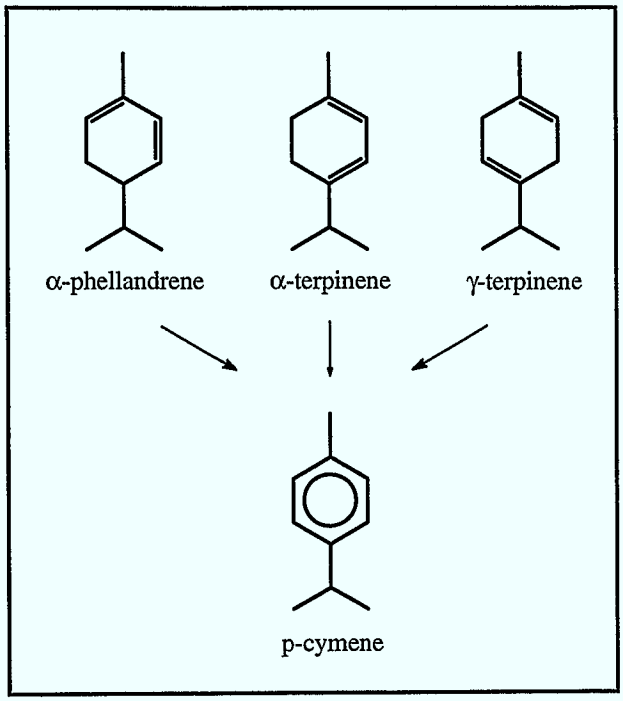


**Figure 3.9:** *Conversion of three monoterpenes into p-cymene in the diffusion source.*

It was possible to produce VOC mixtures with a known composition with the diffusion source. Mixing ratios were adjusted by varying the dilution flow only (Figure 3.4, Flow 3). The flows through the diffusion chambers and the fused-silica tubing were always kept constant. The dilution factor was calculated using equation E3.1a. The corresponding statistical error (equation E3.1b) was calculated by Gaussian addition of the errors of the different flows.

$$\lambda = \frac{j_2}{j_1 \cdot j_3} \tag{E3.1a}$$

$$\frac{\Delta\lambda}{\lambda} = \sqrt{\left(\frac{\Delta j_1}{j_1}\right)^2 + \left(\frac{\Delta j_2}{j_2}\right)^2 + \left(\frac{\Delta j_3}{j_3}\right)^2} \tag{E3.1b}$$

where $\lambda$ = dilution factor [min ml$^{-1}$]

$j_1$ = flow through diffusion chamber [ml min$^{-1}$]

$j_2$ = flow through fused-silica tubing [ml min$^{-1}$]

$j_3$ = dilution flow [ml min$^{-1}$]

$\Delta j_i$ = standard deviation of flow i [ml min$^{-1}$]

The relative standard deviation of each flow was measured to be 3 %. Thus, the statistical error in the dilution factor was 5 %.

The sample mass of a VOC preconcentrated on the adsorbents was calculated by multiplying the dilution factor with the sample volume and the diffusion rate of that specific compound:

$$m_i = V \cdot r_i \cdot \lambda \tag{E3.2a}$$

$$\frac{\Delta m_i}{m_i} = \sqrt{\left(\frac{\Delta V}{V}\right)^2 + \left(\frac{\Delta r_i}{r_i}\right)^2 + \left(\frac{\Delta \lambda}{\lambda}\right)^2} \tag{E3.2b}$$

where m = sample mass of compound i [ng]

V = sample volume [ml]

r = diffusion rate of compound i [ng $min^{-1}$]

$\lambda$ = dilution factor [min $ml^{-1}$]

$\Delta x_i$ = statistic error of $x_i$

The statistical error in the dilution flow ($\Delta\lambda/\lambda$) was calculated to be 5 %. The sample volume was calculated by multiplying the sampling flow rate and sampling time. Since sampling was automated, the error in the sampling time could be neglected. The standard deviation of the sampling flow was measured to be 3 % and thus the reproducibility of the sample volume ($\Delta V/V$) was also 3 %. The statistical error in the diffusion rate ($\Delta r_i/r_i$) was given by the standard deviation of the diffusion rates summarized in Table 3.2. The criteria for the stable diffusion rate of a compound was a reproducibility of better than 10 % over at least five weighings. The most stable diffusion rate was found for benzene with a standard deviation of 0.8 %. Thus, the statistical error of the sample mass was dependent on the compound within a range of 4-11 %.

The reproducibility and linearity of the system was tested by sampling different volumes at different concentrations of the standard mixtures. The FID response for the different VOCs was calculated from the slope of linear regressions of the peak area versus sample mass. As an example, Figure 3.10 shows the observed peak area of $\alpha$-pinene versus sample mass from measurements with different concentrations.

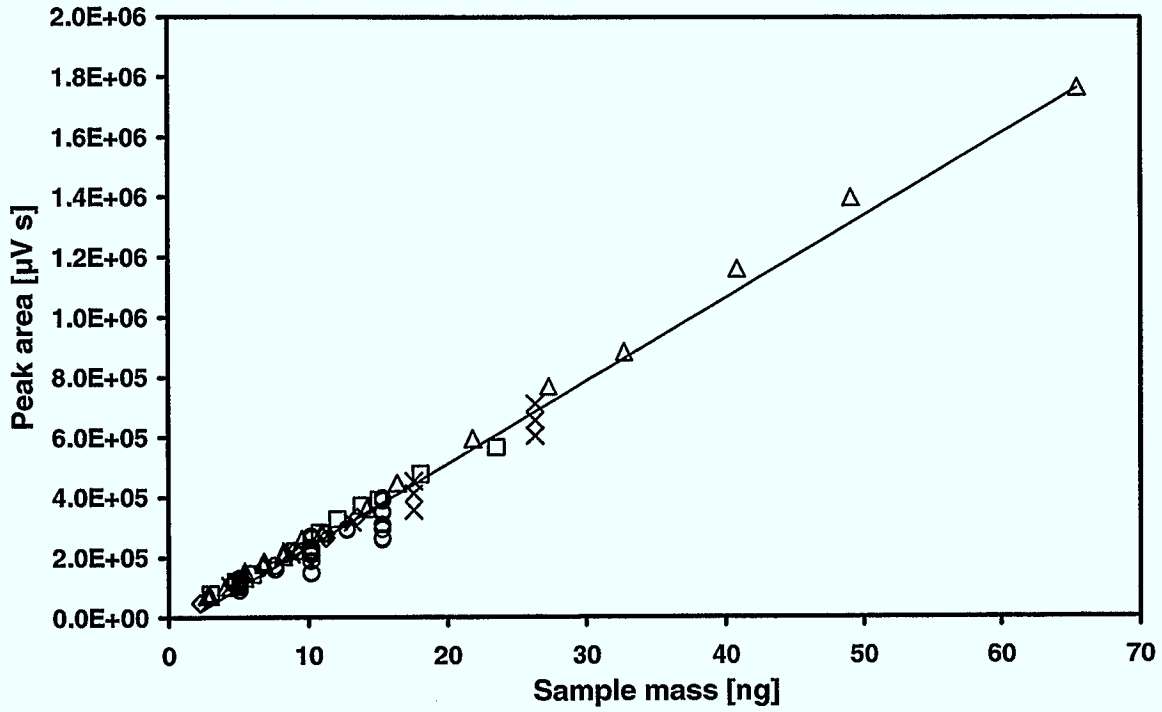


**Figure 3.10:** *Peak area (FID signal) of α-pinene versus sample mass for measurements with different mixing ratios (triangles, 490 ppt; diamonds, 808 ppt; circles, 916 ppt; squares, 1081 ppt; crosses, 1574 ppt;).*

As expected, it was found that the peak area was only dependent on the sampled mass of a VOC. Sampling twice the volume of a mixture containing only half the concentration resulted in the same peak area as long as the sampling volume was smaller than the breakthrough volume.

The individual reponse factor ($RF_i$) of each VOC was calculated by equation E3.3.

$$RF_i = F_i \cdot \frac{A_i}{m_i} \qquad \text{(E3.3)}$$

where $RF_i$ = individual response factor [µV s $ng^{-1}$]

F = correction factor of compound i [dimensionless]

$A_i$ = peak area of compound i [µV s]

$m_i$ = sampled mass of compound i [ng]

The error in $RF_i$ was calculated from the error of the linear regression of peak area versus sample mass. Comparing individual response factors of different VOCs is a useful tool to check the performance of the system. In theory, all VOCs consisting only of carbon and

hydrogen atoms should have the same relative FID response. An $RF_i$ of an individual VOC showing large deviations from the mean response factor indicates problems in the analysis of that compound. Moreover, the mean response factor is normally used to quantify VOCs that are not calibrated individually. Generally, the latter procedure is only used for VOCs containing only carbon and hydrogen. Oxygen containing hydrocarbons were observed to have a smaller FID response which is consistent with theory (*Sternberg et al.*, 1962; *Ackmann*, 1964; *Clementi et al.*, 1972; *Tong and Karasek*, 1984; *Scanlon and Willis*, 1985).

There is growing awareness of the importance of biogenic emissions of oxygenated VOCs such as the short chained organic acids, aldehydes, alcohols, and oxygenated terpenoids (e.g. *König et al.*, 1995; *Kesselmeier et al.*, 1997; *Baker et al.*, 1999). Therefore, accurate measurements of these compounds are necessary. Using correction factors for FID measurements of compounds that are not calibrated individually can prevent a substantial underestimation of the source strength of oxygenated VOCs. Applying a correction ($F_i$) to the mean response factor ($RF_m$) allows quantification of oxygen containing VOCs that are not calibrated individually. In the following, the procedure used to evaluate these corrections is described.

The correction factors reported in the literature were normally derived from measurements of binary mixtures, usually with n-heptane as the reference. Usually, incremental corrections for different functional groups were applied. Three different approaches are described in the literature: the concept of available carbon atoms (*Onkiehong*, 1960), relative molar responses (RMR) (*Ackmann*, 1964), and effective carbon numbers (ECN) (*Sternberg et al.*, 1962). *Onkiehong* (1960) gave the following approximation:

$$F_i = \frac{M_i}{z_i' \cdot 12g \cdot mol^{-1}} \qquad \text{(E3.4)}$$

where $F_i$ = correction factor of compound i [dimensionless]

$M_i$ = molecular weight of compound i [g $mol^{-1}$]

$z_i'$ = "number of available carbon atoms".

*Onkiehong* (1960) reported that the number of available carbon atoms in a compound is equal to its number of carbon atoms that have a C-H bond. One C-O bond reduces the

"availability" $z_i^*$ to 0.3-0.5, a C-O double bond makes that carbon atom "unavailable". The figure 12 $g \cdot mol^{-1}$ in the denominator is a consequence of the normalization with respect to carbon atoms.

*Ackmann* (1964) and *Sternberg et al.* (1962) applied the same functional dependencies by multiplying the ratio of molecular weights and the ratios of RMR or ECN values of the compound of interest and a reference compound:

$$F_i = \frac{M_i \cdot X_{reference}}{M_{reference} \cdot X_i} \qquad \text{(E3.5)}$$

where $F_i$ = correction factor of compound i [dimensionless]

M = molecular weight of compound i or reference [$g\ mol^{-1}$]

X = RMR (relative molar response) or X = ECN (effective carbon number) [both dimensionless].

The RMR and ECN value of a compound are given by the sum of the incremental contributions of its functional groups. The incremental contributions of different functional groups to the RMR and ECN value are given in Table 3.3 and Table 3.4.

**Table 3.3:** *Contribution to relative molar response of different functional groups (Ackmann, 1964).*

| Functional group | Incremental RMR value |
|---|---|
| -CH2-OH | 55 |
| >CH-OH | 35 |
| -C(O)-CH3 | 100 |
| >C=O | 0 |
| -CH2-C(O)H | 135 |
| -C(O)H | 0 |
| -C(O)-C(O)- | 90 |
| -C(O)-CH2-C(O)- | 170 |
| -O-CH2- | 0 |
| -O-CH3 | 0 |
| >C=CH2 | 178 |
| primary –OH | -45 |
| secundary -OH | -65 |
| terminal CO | -100 |
| middle CO | -65 |
| ether –O | -100 |
| lack of 2H | -22 |

**Table 3.4:** *Contribution to effective carbon number of different functional groups (Sternberg et al., 1962).*

| Atom | Type | Incremental ECN value |
|---|---|---|
| C | Aliphatic | 1.0 |
| C | Aromatic | 1.0 |
| C | Olefinic | 0.95 |
| C | Acetylenic | 1.30 |
| C | Carbonyl | 0.0 |
| C | Nitrile | 0.3 |
| O | Ether | -1.0 |
| O | Primary Alcohol | -0.6 |
| O | Secondary Alcohol | -0.75 |
| O | Tertiary alcohol, esters | -0.25 |

To make measurements using different reference compounds comparable, equation E3.5 was simplified. Usually, an aliphatic hydrocarbon was taken as the reference compound. For an aliphatic hydrocarbon the ECN value is equal to the number of carbon atoms. Assuming that the reference compound consists of $CH_2$-groups only (which is a reasonable simplification for large hydrocarbons such as heptane), a value of $1 / (14\ g\ mol^{-1})$ is approximated for the ratio of effective carbon number and molecular weight. Thus, the following equation to calculate the correction factor was used:

$$F_i = \frac{M_i}{14g \cdot mol^{-1} \cdot ECN_i} \qquad \text{(E3.6)}$$

where $F_i$ = correction factor of compound i [dimensionless]

$M_i$ = molecular weight of compound i [g $mol^{-1}$]

$ECN_i$ = effective carbon number of compound i [dimensionless].

In order to test which equation was most suitable, measured FID responses reported in the literature were compared to calculated values (Table 3.5).

**Table 3.5:** *Comparison of measured and calculated correction factors using different incremental systems and formulas.*

| Compound | Measured | | Calculated | | |
|---|---|---|---|---|---|
| | *Dietz*, 1967 | *Sternberg et al.*, 1962 | E3.4, RMR-increments | E3.5, $z_i$'-increments | E3.6, ECN-increments |
| ethene | 0.98 | 1.04 | 1.05 | 1.17 | 1.05 |
| ethyne | 0.93 | 0.72 | 1.11 | 1.08 | 0.71 |
| ethane | 1.03 | 1.08 | 1.00 | 1.25 | 1.07 |
| propane | 1.02 | 1.05 | 1.00 | 1.22 | 1.05 |
| acetone | 2.04 | 2.01 | 1.82 | 2.42 | 2.07 |
| i-pentane | 0.95 | 1.10 | 1.00 | 1.20 | 1.03 |
| n-pentane | 0.96 | 1.04 | 1.00 | 1.20 | 1.03 |
| 2,2-dimethylbutane | 0.96 | 1.00 | 1.00 | 1.43 | 1.02 |
| 2-methylpropanal | | 1.82 | 1.66 | 3.00 | 1.71 |
| butanal | 1.61 | | 1.66 | 2.00 | 1.71 |
| butanone | 1.64 | 1.63 | 1.56 | 2.00 | 1.71 |
| n-hexane | 0.97 | 1.03 | 1.00 | 1.19 | 1.02 |
| methylcyclopentane | | 1.04 | 1.01 | 1.17 | 1.00 |
| benzene | 0.89 | 0.94 | 1.06 | 1.08 | 0.93 |
| cyclohexene | | 1.04 | 1.03 | 1.14 | 0.99 |
| n-heptane | 1.00 | | 1.00 | 1.19 | 1.02 |
| toluene | 0.93 | 0.93 | 1.05 | 1.10 | 0.94 |
| n-octane | 1.03 | 1.03 | 1.00 | 1.19 | 1.02 |
| ethylbenzene | 0.97 | | 1.04 | 1.10 | 0.95 |
| heptanal | 1.30 | | 1.33 | 1.58 | 1.36 |
| n-nonane | 1.02 | | 1.00 | 1.19 | 1.02 |

Although there are only limited data of measured correction factors available, Table 3.5 shows that the calculated correction factors using the simplified equation E3.6 and the incremental system of effective carbon numbers were in better agreement to the measured values than the other incremental systems. The differences to the measured values were always less than 10 %.

To test whether this procedure could be applied to the measurements described here as well, uncorrected and corrected response factors were compared.

**Table 3.6:** *Number of measurements (n), correlation coefficient for linear regression of peak area versus sample mass ($R^2$), correction factor and uncorrected and corrected individual response factors ($RF_i$).*

| Compound | n | Correlation coefficient, $R^2$ | $RF_i$ (uncorrected) [$10^3$ µV s $ng^{-1}$] | Correction factor | $RF_i$ (corrected) [$10^3$ µV s $ng^{-1}$] |
|---|---|---|---|---|---|
| benzene | 64 | 0.91 | 21.1 ± 0.8 | 0.93 | 19.6 ± 0.8 |
| n-hexane | 37 | 0.93 | 21.0 ± 0.9 | 1.02 | 21.5 ± 0.9 |
| toluene | 73 | 0.94 | 23.4 ± 0.7 | 0.94 | 22.0 ± 0.7 |
| n-heptane | 46 | 0.86 | 24.1 ± 1.5 | 1.02 | 24.6 ± 1.5 |
| iso-octane | 34 | 0.86 | 21.1 ± 1.5 | 1.02 | 21.4 ± 1.5 |
| (-)-α-pinene | 81 | 0.98 | 27.6 ± 0.5 | 0.98 | 27.1 ± 0.5 |
| camphene | 80 | 0.96 | 22.3 ± 1.3 | 0.98 | 21.9 ± 1.3 |
| (-)-β-pinene | 81 | 0.97 | 23.3 ± 0.4 | 0.98 | 22.9 ± 0.4 |
| β-myrcene | 81 | 0.97 | 22.8 ± 0.5 | 1.00 | 22.8 ± 0.5 |
| (+)-3-carene | 81 | 0.98 | 25.8 ± 0.4 | 0.98 | 25.4 ± 0.4 |
| (+)-limonene | 80 | 0.91 | 27.4 ± 1.0 | 0.99 | 27.2 ± 1.0 |
| terpinolene | 57 | 0.74 | 21.6 ± 1.7 | 0.99 | 21.0 ± 1.7 |
| n-undecane | 73 | 0.78 | 22.1 ± 1.4 | 1.01 | 22.4 ± 1.4 |
| dodecane | 81 | 0.93 | 22.5 ± 0.7 | 1.01 | 22.7 ± 0.7 |
| tetradecane | 64 | 0.82 | 23.0 ± 1.4 | 1.01 | 23.2 ± 1.4 |
| (+)-longicyclene | 81 | 0.99 | 26.2 ± 0.5 | 0.97 | 25.5 ± 0.5 |
| hexanal | 81 | 0.98 | 15.2 ± 0.4 | 1.43 | 21.7 ± 0.4 |
| 1,8-cineol | 81 | 0.96 | 19.5 ± 0.4 | 1.22 | 23.8 ± 0.4 |
| (-)-citronellal | 32 | 0.90 | 17.3 ± 1.1 | 1.24 | 21.4 ± 1.1 |
| Mean value of all compounds | | | 22.5 | | 23.1 |
| Relative standard deviation | | | 14 % | | 9 % |

Table 3.6 lists the individual response factors which were corrected by applying factors calculated using equation E3.6 for compounds with stable diffusion rates (standard deviation less than 10 % and at least 5 weighings). The corrected individual response factors ranged between $19.6 \cdot 10^3$ µV s $ng^{-1}$ and $27.2 \cdot 10^3$ µV s $ng^{-1}$. The mean response factor based on 23 individual response factors was calculated to be $23.1 \cdot 10^3$ µV s $ng^{-1}$ with a standard deviation of 9 %. Without applying correction factors to the measured responses, the mean response factor had a higher standard deviation (14 %). From Table 3.6 it is evident that for VOCs consisting only of carbon and hydrogen, the correction factors had values between 0.93 and 1.02. Within the accuracy of the measurements these corrections could be neglected. On the other hand, oxygen containing VOCs had much higher correction factors. For the three oxygen containing VOCs which had stable diffusion rates (hexanal, 1,8-cineol, and citronellal), correction factors could be applied successfully. Without correction their responses differed by up to 32 % from the mean value; after correction by only 7 %.

The concentrations of sampled VOCs and their corresponding statistical error were calculated using the following equations:

$$c_i = \frac{F_i \cdot A_i}{V \cdot RF_m} \tag{E3.7a}$$

$$\frac{\Delta c_i}{c_i} = \sqrt{\left(\frac{\Delta V}{V}\right)^2 + \left(\frac{\Delta RF_m}{RF_m}\right)^2 + \left(\frac{\Delta A_i}{A_i}\right)^2} \tag{E3.7b}$$

where $c_i$ = concentration of compound i [ng $l^{-1}$]

$F_i$ = FID correction factor of compound i [dimensionless]

$A_i$ = peak area of compound i [μV s]

V = sample volume [l]

$RF_m$ = mean response factor [μV s $ng^{-1}$]

$\Delta x_i$ = statistical error of quantity $x_i$

The concentrations given in units of mass per volume could easily be converted into mixing ratios using the following equation:

$$[i] = \frac{c_i \cdot N_A}{N \cdot M_i} \tag{E3.8}$$

where [i] = mixing ratio of compound i [ppb]

$c_i$ = concentration of compound i [ng $l^{-1}$]

$N_A$ = Avogadro´s number [6.022 $10^{23}$ $mol^{-1}$]

N = number density [2.4651 $10^{19}$ $ml^{-1}$] for T = 298 K and p = 1013 mbar

M = molecular weight [g $mol^{-1}$]

The relative standard deviation of sample volumes (ΔV/V) was measured to be 3 % and for statistical error in the mean response factors ($\Delta RF_m/RF_m$) the relative standard deviation of the corrected individual reponse factors was used (9 %, see Table 3.6). Since samples collected on solid adsorbents and thereafter thermally desorbed can only be measured once, the standard deviation of the peak area ($\Delta A_i/A_i$) was not directly accessible. To estimate this statistical error, samples of a standard VOC mixture were taken on 10

different adsorption tubes. As a standard gas mixture, air from the permeation source used for the intercalibration experiment (see chapter 3.5) was used. The results obtained are summarized in Table 3.7.

**Table 3.7:** *Reproducibility of 10 samples collected from the permeation source used for the intercalibration experiment. Given is the mean value of the measured mixing ratio and the relative reproducibility of the peak area.*

| Compound | Measured mixing ratio [ppt] | Reproducibility of peak area [%] |
|---|---|---|
| benzene | 941 | 7 |
| toluene | 458 | 5 |
| α-pinene | 382 | 9 |
| camphene | 244 | 9 |
| β-pinene | 230 | 10 |
| 3-carene | 174 | 6 |
| sabinene | 109 | 31 |
| limonene | 108 | 7 |
| 6-methyl-5-hepten-2-one | 45 | 32 |
| n-undecane | 41 | 26 |
| bornyl acetate | 15 | 24 |
| longicyclene | 8 | 8 |
| β-caryophyllene | 3 | 22 |

The reproducibility of the measurements were between 5-32 %. In general, compounds with higher mixing ratios produced more reproducible results. Since the emission rate measurements focused on monoterpenes, the reproducibility of the other compounds are not discussed in detail. The standard deviations of the peak areas of the monoterpenes were within a range of 6-10 %. The only exception was sabinene (31 %) which could not be measured with the same high reproducibility. The problems connected with the measurements of that specific monoterpene are described in the following chapter. Taking an upper limit of 10 % as a value for the reproducibility of the peak areas of monoterpenes (β-pinene, Table 3.7), the overall statistical error ($\Delta c_i/c_i$, equation E3.7b) was calculated to be 14 %.

### 3.5 Intercalibration experiment

An intercalibration experiment was performed to estimate the accuracy of the VOC mixing ratio determinations described above. The experiment was part of the quality assurance within the Troposphärenforschungsschwerpunkt (TFS, Tropospheric Research Project). Four groups of sub-project LT2C participated (Institut für Chemie der Belasteten Atmosphäre, Forschungszentrum Jülich; Institut für Atmosphärische Chemie, Forschungszentrum Jülich; Institut für Spektrochemie und Angewandte Spektroskopie, ISAS, Dortmund; Fraunhofer Institut für Atmosphärische Umweltforschung, IFU, Garmisch-Partenkirchen). For the intercalibration experiment, a permeation source similar to the system described by *Schuh et al.* (1997) was set up to produce a complex mixture of VOCs with mixing ratios in the range of some ppt to several hundred ppt. Among the VOCs, several monoterpenes, sesquiterpenes, and oxygenated VOCs were included. The VOC mixing ratios were unknown to the participants of the experiment. All groups took samples at the same time over a time period of two days, each using their own instrumentation. While the GC-MS system, which was used for the laboratory studies described in this work, was performing an on-line analysis, 10 samples were collected simultaneously on the glass tubes described above and analyzed later with the GC-MS/FID system which was used for the analysis of all outdoor samples. Also, the group from the ISAS was collecting samples on solid adsorbents which were analyzed later, whereas the IFU was using an online GC-FID system. Each group determined the VOC mixing ratios and the corresponding errors independently, using their own calibration gas mixtures and calibration techniques.

The results of all participating groups are summarized in Table 3.8 in anonymous form, except for the two systems (outdoor enclosure system and laboratory system) for which results of emission rate measurements are presented in chapter 4. In addition, the calculated mixing ratio is included in Table 3.8, obtained by multiplying the permeation rate of a VOC with the dilution factor.

**Table 3.8:** *Results of intercalibration experiment. Given here are mixing ratios in ppt. The mixing ratio of the permeation source is a calculated value, derived from the permeation rate and the dilution factor.*

| | **Permeation source** [ppt] | **Outdoor enclosure system** [ppt] | **Laboratory system** [ppt] | **Lab I** [ppt] | **Lab II** [ppt] |
|---|---|---|---|---|---|
| aromatics: | | | | | |
| benzene | 759 | 941 ± 112 | - | 482 ± 104 | 711 ± 28 |
| toluene | 469 | 458 ± 50 | 447 ± 89 | 660 ± 119 | 291 ± 12 |
| monoterpenes: | | | | | |
| α-pinene | 385 | 382 ± 49 | 334 ± 67 | 256 ± 51 | 678 ± 27 |
| camphene | 308 | 244 ± 32 | 201 ± 40 | 159 ± 29 | 501 ± 20 |
| β-pinene | 236 | 230 ± 31 | 239 ± 48 | 145 ± 24 | - |
| 3-carene | 190 | 174 ± 19 | 193 ± 39 | 137 ± 21 | 342 ± 14 |
| sabinene | 225 | 109 ± 35 | 215 ± 43 | 130 ± 19 | - |
| limonene | 110 | 108 ± 13 | 104 ± 21 | 77 ± 11 | 298 ± 12 |
| others: | | | | | |
| 6-methyl-5-hepten-2-one | 109 | 45 ± 15 | 86 ± 17 | - | - |
| n-undecane | 44 | 41 ± 11 | 55 ± 11 | 17 ± 11 | - |
| bornyl acetate | 24 | 15 ± 4 | - | 4 ± 0.5 | - |
| longicyclene | 17 | 8 ± 1 | 23 ± 5 | 5 ± 0.6 | - |
| caryophyllene | 14 | 3 ± 1 | 20 ± 4 | 2 ± 0.2 | - |
| methyl salicylate | 34 | - | 34 ± 7 | - | - |

Since this work deals with monoterpene emissions exclusively, the following discussion focuses on these compounds. Three groups quantified the mixing ratios of the complete set of six monoterpenes (i.e. α-pinene, camphene, β-pinene, 3-carene, sabinene, and limonene). The fourth group (Lab II) only quantified the mixing ratios of four of the six compounds. The mixing ratios of β-pinene and sabinene could not be quantified.

Figure 3.11 shows the percent deviation of monoterpene mixing ratios of the measurements of each participating group from the value calculated for the permeation source.

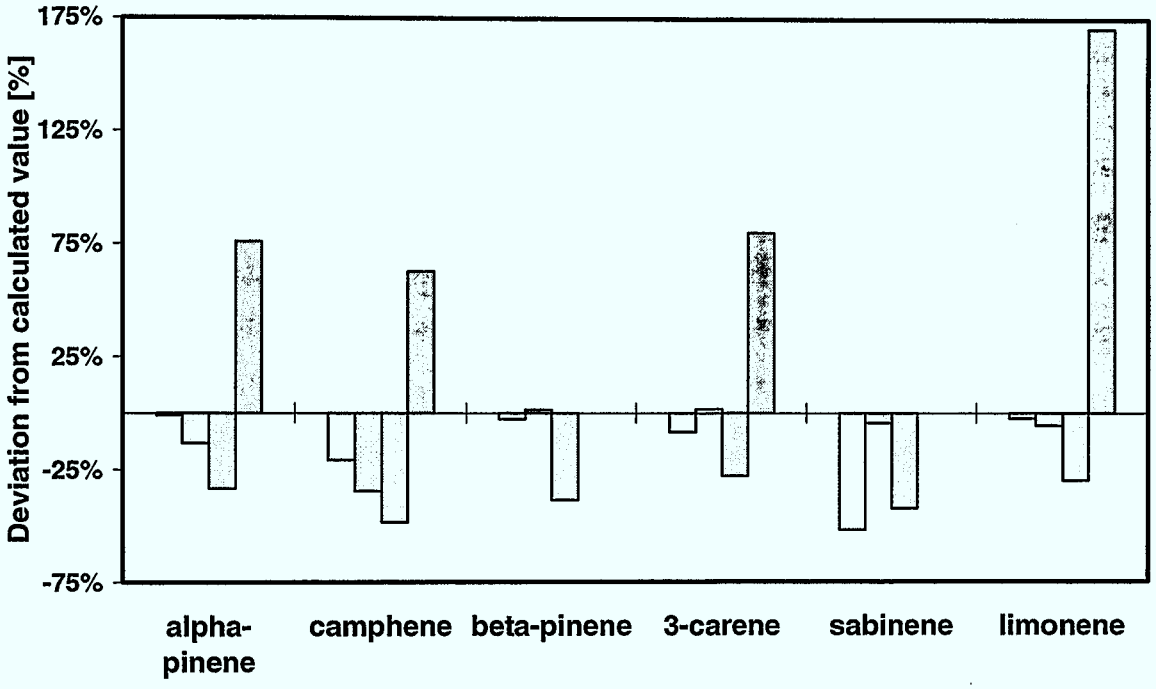


**Figure 3.11:** *Percent deviation of monoterpene mixing ratios measured by the different groups from the value calculated for the permeation source. Bars from left to right: white: outdoor enclosure system, light grey: laboratory system, grey: Lab I, and dark grey: Lab II.*

The data displayed in Figure 3.11 show that the measurements tended to underestimate the calculated values. Only the results obtained by Lab II overestimated the calculated monoterpene mixing ratios. For the four of the six monoterpenes that could be quantified by this group, the measured mixing ratios were between 63 and 171 % higher than calculated. Lab I, on the other hand, underestimated all mixing ratios by at least 28 %. The largest deviation from the calculated mixing ratio was observed for camphene, which was underestimated by 48 %. The results shown in Table 3.8 and Figure 3.11 reveal that the two systems used within the scope of this work (i.e. the outdoor enclosure system and the laboratory system) produced more reliable results than the systems of the other two working groups. Within measurement error, the mixing ratios of α-pinene, β-pinene, 3-carene, and limonene measured with both systems were equal to the values calculated from the permeation rates. The measured mixing ratios of camphene were similar for both systems, but these values were approximately 20-30 % lower than the calculated mixing ratio. Sabinene was the only monoterpene which could not be measured with the same high accurarcy with the outdoor system and was underestimated by approximately 50 %. Detailed GC-MS analysis of this compound revealed that it was depleted in the analytical system previously described and decomposed into more than 6 different compounds. The

low reproducibility of the sabinene measurements described above (Table 3.7) indicated that these losses were irreproducible and could not be easily accounted for.

The overall result of the intercalibration experiment shows that the system described here was capable of measuring monoterpene mixing ratios on the order of several hundred ppt with a systematical error of $\leq$ 10 % for α-pinene, β-pinene, 3-carene, limonene and $\leq$ 30 % for camphene, which were expected to be the major emission products from Scots pines

### 3.6 Calculation of VOC emission rates

Emission rates of VOCs from plants are usually expressed in units of mass or moles of the emitted VOC per time and normalized to a physiological parameter such as dry weight or surface area of the investigated plant. In this study, the measured concentrations of individual VOCs were converted into emission rates normalized to the dry weight of the needles of the enclosed plant using the following equation:

$$\Phi = \frac{j_{Air}}{m_N} \cdot (c_{out} - c_{in}) \qquad \text{(E3.8)}$$

where $\Phi$ = emission rate [µg g(dry weight)$^{-1}$ h$^{-1}$]

$j_{Air}$ = air flow through the chamber [l h$^{-1}$]

$m_N$ = dry weight of the needles [g(dry weight)]

c = VOC concentrations at chamber outlet and inlet, respectively [µg l$^{-1}$]

Monoterpene concentrations at the chamber outlet, $c_{out}$, were usually on the order of several hundred parts per trillion to several parts per billion. Concentrations at the chamber inlet, $c_{in}$, were reduced to concentrations below 10 ppt (see Table 3.1) by the air supply system. The low concentrations of $c_{in}$ were within the error in the measurements for $c_{out}$ and thus, this term could be neglected in equation E3.8.

The problems connected with normalization to physiological and ecological parameters for measurements with conifers were described in detail by *Peterer and Körner* (1990). The emission rates in this study were normalized with respect to the dry weight of

the needles which were estimated as follows. In total, five different branches of adult Scots pines were investigated to estimate the average number of needles growing per length of branch, the average needle weight, and the average needle surface.

The average dry needle weight was measured by drying the needles in an oven for 48 hours at 80°C under vacuum. To estimate the average projected needle surface, a photocopy of about 100 needles was made and scanned by a computer. The amount of black pixels was counted by a computer program. The results are summarized in Table 3.9.

**Table 3.9:** *Physiological parameters of 5 different branches.*

| | **Total number of needles** | **Length of branch [cm]** | **Needles per length of branch [$cm^{-1}$]** | **Total weight (dry matter) [g]** | **Mass per needle [g]** | **Surface of a needle [$cm^2$]** |
|---|---|---|---|---|---|---|
| Branch 1 | 1678 | 114.5 | 14.7 | 29.34 | 0.0175 | 0.83 |
| Branch 2 | 1338 | 94.5 | 14.2 | 16.20 | 0.0121 | 0.54 |
| Branch 3 | 1771 | 115 | 15.4 | 30.55 | 0.0172 | |
| Branch 4 | 2458 | 158 | 15.6 | 40.49 | 0.0165 | 0.61 |
| Branch 5 | 4229 | 283 | 14.9 | 67.69 | 0.0160 | 0.61 |
| Mean value | | | 15 | | 0.016 | 0.65 |
| 1σ | | | 4 % | | 14 % | 20 % |

The total needle area was then calculated by multiplying the projected needle surface with a conversion factor accounting for the three dimensional structure of a needle. For Scots pine (*Pinus Sylvestris*) this conversion factor is 2.56 (*Peterer and Körner*, 1990). The total dry weight of the needles of an enclosed branch was estimated by multiplying the total length of the branch with the average number of needles per length (15 needles per cm) and the average needle weight (0.016 g per needle). This had the advantage that it was not necessary to harvest the enclosed branch immediately after the measurements.

In the literature, a normalization to needle area was described. To convert between the emission rate per surface area to the emission rate per gram dry weight, the following equation was used for emission rates from Scots pine:

$$\Phi(dw) = \Phi(A) \cdot 0.65 \cdot 2.56 \frac{cm^2}{needle} \cdot 3600 \frac{s}{h} \cdot \frac{1}{0.016} \frac{needle}{g(dry\ weight)} \cdot 10^6 \frac{\mu g}{g} \cdot M$$
$$= \Phi(A) \cdot 3.75 \cdot 10^{11} \frac{cm^2 \cdot s \cdot \mu g}{g(dry\ weight) \cdot h \cdot g} \cdot M \qquad \text{(E3.9)}$$

where $\Phi(dw)$ = emission rate normalized to dry weight [µg g(dry weight)$^{-1}$ h$^{-1}$]

$\Phi(A)$ = emission rate normalized to total needle surface area [mol cm$^{-2}$ s$^{-1}$]

M = molecular weight of the VOC [g mol$^{-1}$]

# 4 Results

In this chapter measurements of monoterpene emission rates from Scots pines (*Pinus sylvestris*) are presented. First, a summary describing the plant material and the conducted studies is given. Then, results of laboratory studies are shown with respect to the dependence of monoterpene emissions on temperature and light intensity. This is followed by a brief description of the emission algorithm. The influence of stress effects on the temporal stability of emission rates is described. The results obtained with the outdoor enclosure system are subdivided into measurements on young pine seedlings and measurements on branches of an adult pine. In addition to the dependence of monoterpene emissions on the parameters mentioned above, branch-to-branch, plant-to-plant and seasonal variabilities of monoterpene emissions are also discussed.

## 4.1 Summary describing plant material and studies conducted

Results from three different types of studies are presented and compared in this work. These are:

- Laboratory studies with young pines (conducted by J. Wildt et al.).
- Outdoor enclosure measurements with young pines
- Outdoor enclosure measurements with branches of an adult pine.

From 1996 to 1998 15 different 3 to 4 year old Pine seedlings were taken from the Hartheimer Wald (near Freiburg, Southern Germany, 47°56'N, 7°37E'). The young pines were dug out with the soil surrounding the roots and placed in pots. Before and between the individual experiments the plants were stored outside in Juelich under ambient conditions.

The laboratory studies were conducted by J.Wildt and coworkers in the continuously stirred tank reactors (CSTR) described in detail in *Wildt et al.* (1997). VOC emissions from 4 different 3-4 year old Scots pines were studied. The objective of these studies was to derive an emission algorithm that describes VOC emissions as a function of temperature and light intensity and to test if other parameters also influence monoterpene

emissions from Scots pine. The plants were either placed individually or two at a time inside the glass tanks for several days to weeks. With the laboratory system it was possible to vary temperature and light intensity independent of each other. Diurnal cycles were simulated by switching lamps on and off. During some experiments, the temperature was also varied.

During the outdoor experiments, emission studies were performed placing a single plant inside the enclosure system for several consecutive days. The studies were conducted between June and August 1998 and between May and August 1999. Both temperature and solar radiation were dependent on ambient conditions. In total, VOC emissions from 8 different plants were investigated. Four of the plants were enclosed alternately in the laboratory and outdoor system. Two plants were placed inside the enclosure system at different times of the year. Table 4.1 summarizes the dry weight of the young pines as well as the date and temperature range of the experiments in both laboratory and outdoor studies. The main objectives of these studies were to:

- Test the applicability of the emission algorithm under outdoor conditions.
- Look for systematic differences in the response of a plant inside the continuously stirred tank reactors in the laboratory and inside the outdoor enclosure system.
- Estimate the plant-to-plant variability of VOC emissions from different individual plants of the same species and of the same origin.

**Table 4.1:** *Summary of the dry weight of the young pines and the date and temperature range of the experiments in both laboratory and outdoor studies.*

| Plant | Dry weight of needles [g] | Outdoor studies | | Laboratory studies | |
|---|---|---|---|---|---|
| | | Date | Temperature range [°C] | Date | Temperature range [°C] |
| No. 1 | 31.4 | June '98 | 10-45 | None | - |
| No. 2 | 38.7 | June '98 | 11-39 | None | - |
| No. 3 | 36.9 | August '98 | 10-40 | None | - |
| No. 4 | 36.9 | August '98 | 8-29 | None | - |
| No. 5 | 60.8 | May '99 | 8-33 | May/June '99 | 10-28 |
| | 60.8 | July '99 | 13-39 | | |
| No. 6 | 62.5 | June '99 | 10-43 | May '99, together with plant No. 7 | 11-26 |
| No. 7 | 69.6 | June '99 | 9-36 | May '99, together with plant No. 6 | 11-23 |
| No. 8 | 48.4 | May '99 | 6-40 | June '99 | 17-32 |
| | 48.4 | July '99 | 12-38 | July '99 | 25 |
| | 46.0 | August '99 | 14-40 | August '99 | 25 |

The outdoor enclosure measurements with an adult pine were conducted in a 40 year old pine plantation in the Hartheimer Wald, the same location as where the young pines originated. The forest included Scots pine (*Pinus sylvestris*) and Black pine (*Pinus nigra*) in a total area of 10 x 1.5 km². No other vegetation was present in significant amounts at this location. Longterm data for solar radiation, air temperature, precipitation, soil moisture, and other pertinent parameters (e.g. evapotranspiration, latent heat flux) were available at this field site. A detailed description can be found in *Jaeger* (1997). In 1998, the average height of the trees was 15 m. A 20 m high tower gave access to the forest canopy. Between April and October 1998 four field campaigns were conducted at this site. Between 40 to 57 samples were collected during each campaign to quantify VOC emission rates. Monoterpene emissions were measured at two branches of a Scots pine at canopy height. The first branch (A) was a sunlit branch at the canopy top with many new needles (63 % of dry weight) and some cones. The second branch (B) of the same tree was 1.8 times larger with fewer new needles (48 % of dry weight), located approx. 1.5 m below branch A in the shadow of the canopy. Between April and July the biomass of branch A more than doubled. From July to September, some needles on both branches became yellow and both branches lost approximately 10 % of their older needles. From September to October the branches again lost some old needles. Table 4.2 lists physiological parameters for the two branches. The projected needle surface and dry weight of the two branches were determined using the methods described in section 3.6.

**Table 4.2:** *Physiological parameters of branches A and B.*

| | Projected needle surface [cm²] | | Total dry weight of needles [g] | |
|---|---|---|---|---|
| | **Branch A** | **Branch B** | **Branch A** | **Branch B** |
| April '98 | 872 | - | 21 | - |
| July '98 | 1788 | 3149 | 44 | 77 |
| September '98 | 1553 | 2871 | 38 | 70 |
| October '98 | 1495 | 2570 | 37 | 63 |

The main objectives of the outdoor studies with the adult pines were to:

- Investigate the seasonal variability of emissions.
- Estimate the branch-to-branch variability of monoterpene emissions by enclosing two different branches of the same plant.
- Compare monoterpene emissions from an adult pine to those from young pine seedlings.

The results of the monoterpene emission rate measurements were used to estimate fluxes for the pine plantation where the studies were conducted.

## 4.2 Results of laboratory studies

Since the emission rates obtained from the outdoor enclosure studies with Scots pines can only be interpreted with the use of data from studies under controlled laboratory conditions, these results are shown first. The studies determining an emission algorithm for monoterpene emissions from Scots pines were conducted by J. Wildt and coworkers. Details can be found in *Shao et al.* (2000). They found that Scots pine emit monoterpenes, sesquiterpenes, acetone and small amounts of isoprene. Only emission rates of monoterpenes are described here. Emission rates are presented for α-pinene, 3-carene, β-pinene, β-myrcene, limonene, sabinene, camphene, tricyclene, and 1,8-cineol.

In the following, the emission rates of α-pinene are described in more detail. This compound was chosen as a typical monoterpene to show the functional dependencies of monoterpene emission rates on temperature and light intensity, because it was usually one of the major emission products and emissions of all other monoterpenes generally followed

the same dependencies on ambient parameters. The emission rates of all other monoterpenes were highly correlated to those of α-pinene. Figure 4.1 shows as an example, the emission rates of 3-carene, β-pinene and camphene versus those of α-pinene.

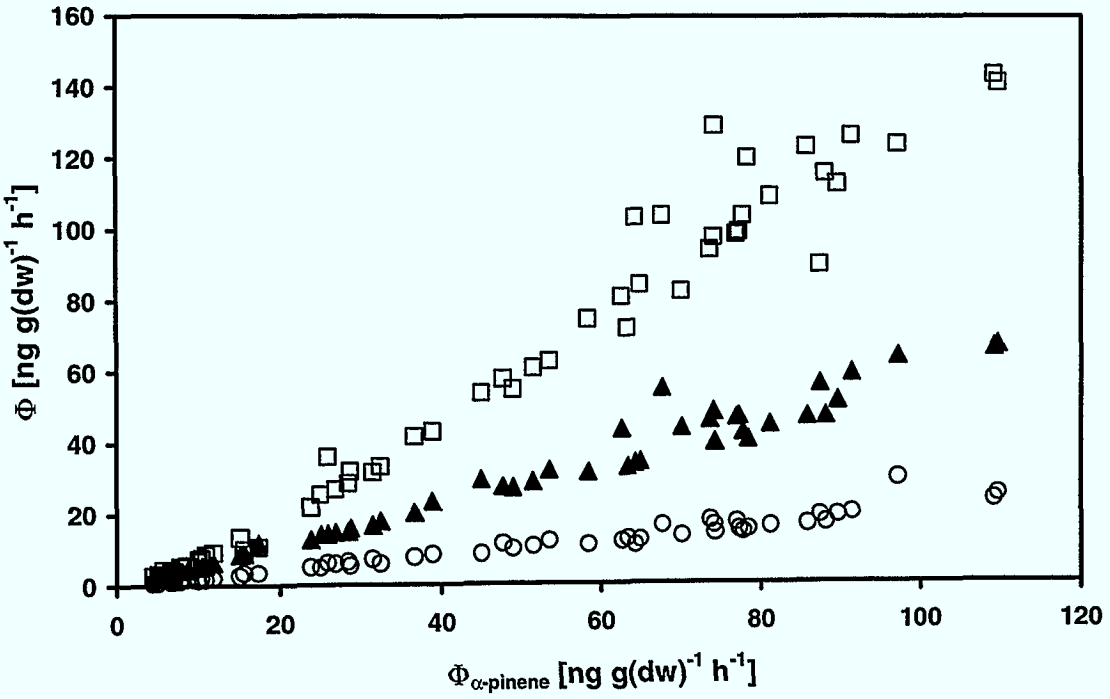


**Figure 4.1:** *Emission rates of three selected monoterpenes (open squares: 3-carene, filled triangles: camphene, open circles: β-pinene) versus the emission rate of α-pinene for same data set as shown in Figure 4.8.*

### 4.2.1 *Diurnal cycle of emissions*

Diurnal cycles of temperature and light intensity were simulated in continuously stirred tank reactors (CSTR). As an example, Figure 4.2 shows the simulated diurnal cycle of temperature and PAR, and the measured emission rates of α-pinene.

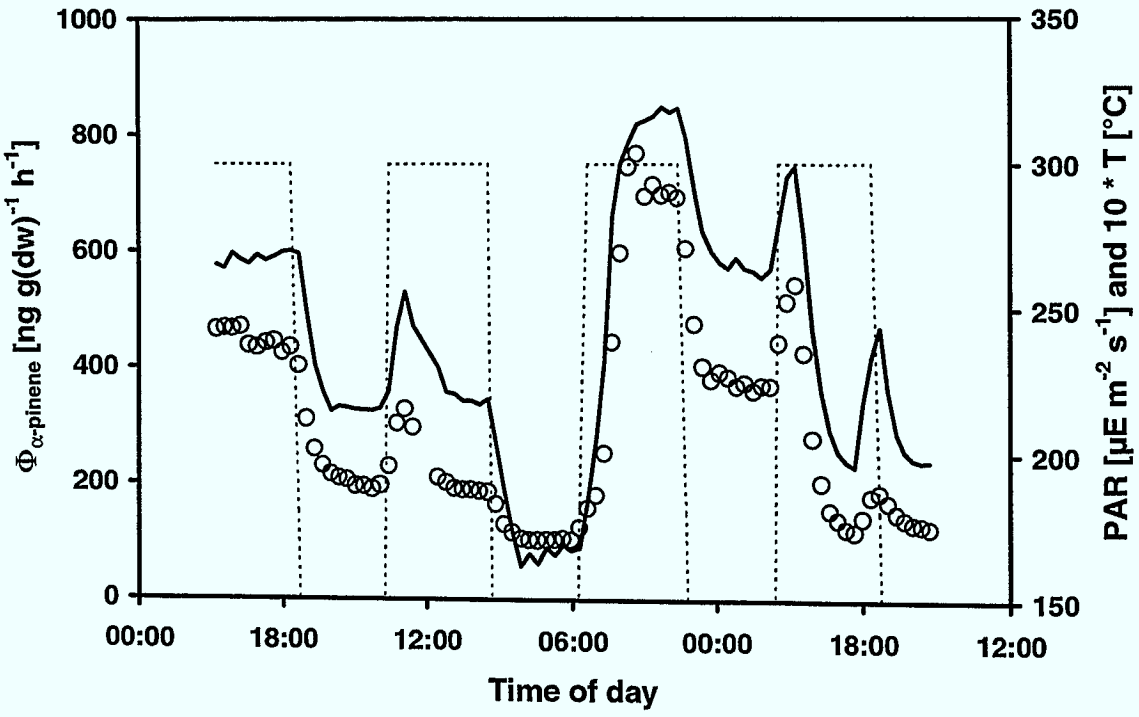


**Figure 4.2:** *Simulated diurnal cycle of the α-pinene emission rate (open circles, left axis). Dashed line: photosynthetic active radiation (right axis), solid line: temperature (right axis, numbers to be divided by 10).*

PAR was varied between 0 and 300 µE $m^{-2}$ $s^{-1}$ by switching lamps on and off, resulting in a rectangular shape for the variation in light intensity. The temperature was varied between 16 and 32 °C. As can be seen in Figure 4.2, the emission rate of α-pinene clearly follows changes in the needle temperature, which was measured with microthermistors.

### 4.2.2 *Temperature dependence of monoterpene emissons*

As expected from the literature data and the models describing monoterpene emissions from conifers (see chapter 2.1.3), monoterpene emission rates followed an Arrhenius type dependence on temperature. Figure 4.3 shows a logarithmic plot of the emission rate of α-pinene versus inverse temperature for the same data set as shown in Figure 4.2.

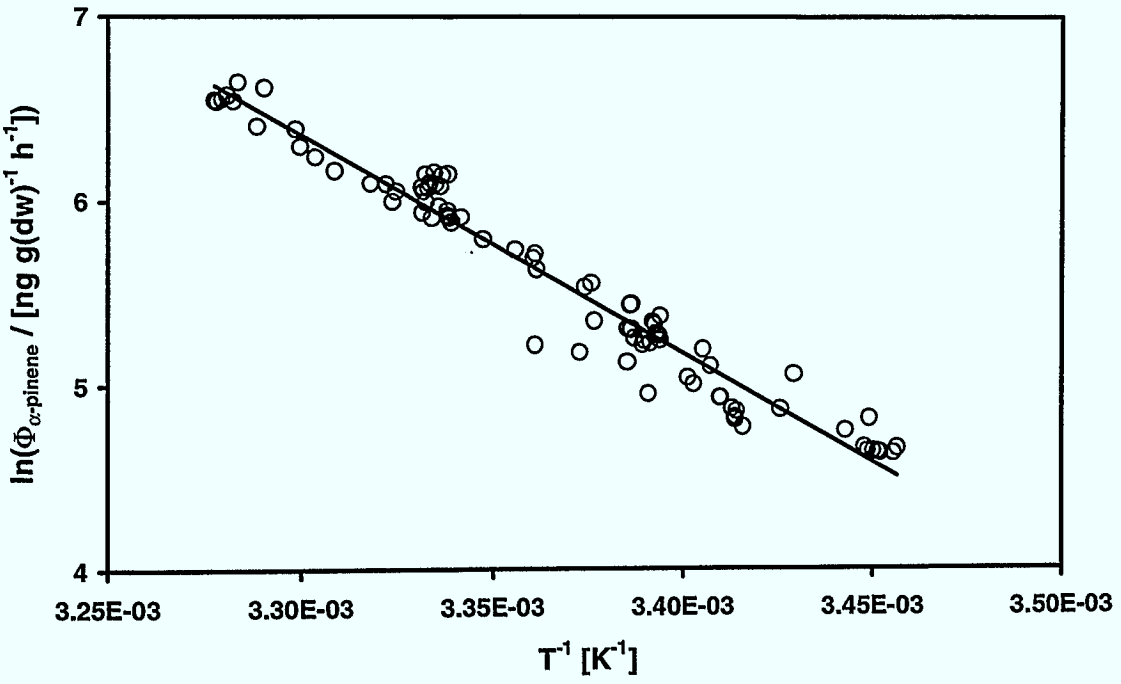


**Figure 4.3:** *Logarithmic plot of the emission rate of α-pinene versus inverse temperature for the same data set as shown in Figure 4.2. The line is a fit to the data using equation E2.1 (chapter 2.1.3). From this linear regression, values for* $c_{TP}\,R^{-1}$ *and* $\Phi^{S}$ *are derived.*

The line in this plot is a least-square fit to the data. In general, the emission rates for all other monoterpenes showed a similar dependence on temperature. Therefore no plots for the other monoterpenes are shown here.

### 4.2.3 *Light dependence of monoterpene emissions*

According to results reported by *Shao et al.* (2000), only the emission rates of α-pinene and camphene showed any PAR dependence. For other monoterpenes no detectable dependence on PAR was measured. Figure 4.4 shows the PAR dependence of α-pinene emissions.

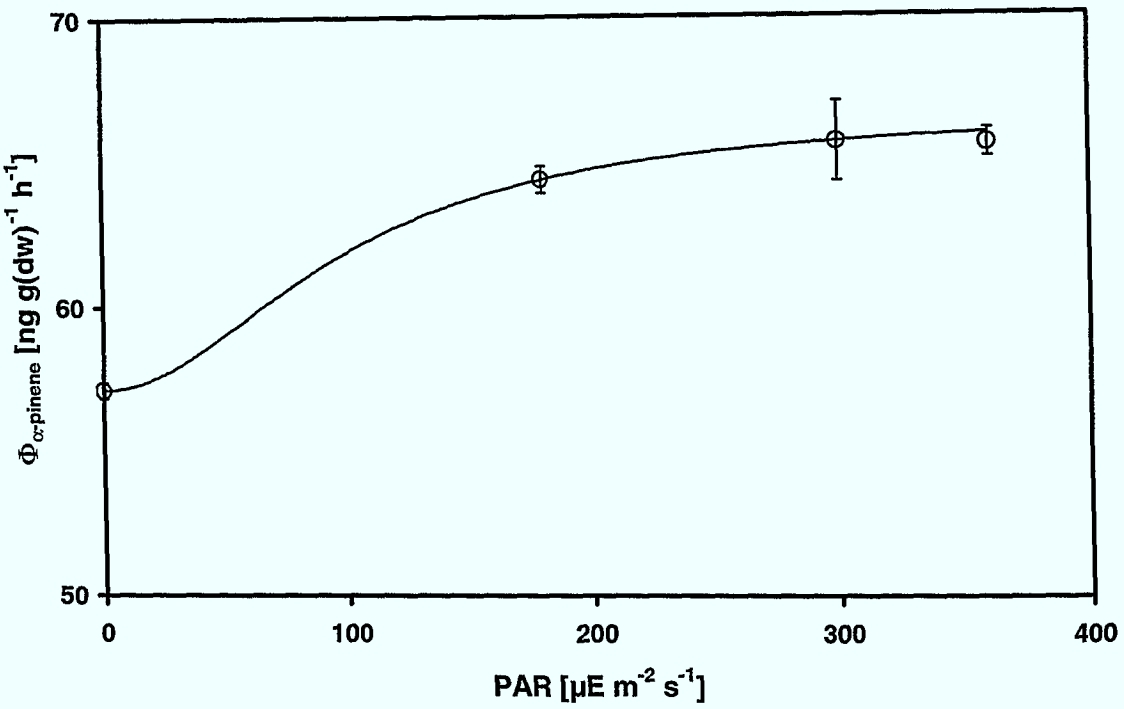


**Figure 4.4:** *Plot of emission rates of α-pinene measured at a constant temperature of 27°C versus PAR. Open circles are results from measurements, the solid line is a simulation of the PAR dependence according to equation E2.4 (chapter 2.1.3). Data taken from Shao et al. (2000).*

While temperature was kept constant at 27 °C, PAR was varied between 0 and 360 µE m$^{-2}$ s$^{-1}$. As can be seen, the emission rate of α-pinene increased by roughly 20 % under the influence of PAR. Equation E1.4 (chapter 2.1.3) was used to calculate the PAR dependence of emissions. A PAR saturation was found at very low radiation levels, corresponding to about 15 % of full sunlight under ambient conditions.

### 4.2.4 *Emission algorithm*

In order to describe the observed influence of temperature and PAR on monoterpene emissions from Scots pine, an emission algorithm was taken from the literature. The algorithm of *Tingey et al.* (1991) (equaion E2.1, section 2.1.3) neglects a PAR dependence and so the following algorithm given by *Schuh et al.* (1997) was found to be more suitable to describe the combined influence of temperature and PAR:

$$\Phi_{VOC} = \Phi_{VOC}^{P,S} \cdot \exp\left[\frac{c_{TP}}{R} \cdot \left(\frac{T - T_S}{T \cdot T_S}\right)\right] + \Phi_{VOC}^{B,S} \cdot c_L \cdot \left(\frac{\alpha \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}}\right)^2 \cdot \frac{\exp\left[\frac{c_{T1}}{R} \cdot \left(\frac{T - T_S}{T \cdot T_S}\right)\right]}{1 + \exp\left[\frac{c_{T2}}{R} \cdot \left(\frac{T - T_M}{T \cdot T_S}\right)\right]} \quad \text{(E4.1)}$$

where $\Phi_{VOC}^{P,S}$ = emission rate from the monoterpene pool [ng g(dw)$^{-1}$ h$^{-1}$] at standard temperature $T_S$

$c_{TP}$ = empirical parameter describing the temperature dependence [J mol$^{-1}$]

R = gas constant [J mol$^{-1}$ K$^{-1}$]

T = temperature [K]

$T_S$ = standard temperature [298 K]

$\Phi_{VOC}^{B,S}$ = emission rate parallel to VOC biosynthesis [ng g(dw)$^{-1}$ h$^{-1}$] at standard light intensity ($L_S$ = 1000 µE m$^{-2}$ s$^{-1}$) and standard temperature ($T_S$ = 298 K)

$c_L$ = normalization factor [dimensionless]

$\alpha$ = parameter that determines the PAR dependence [µE$^{-1}$ m$^2$ s]

L = photosynthetic active radiation [µE m$^{-2}$ s-1]

$C_{T1}$ = empirical parameter [J mol$^{-1}$]

$C_{T2}$ = empirical parameter [J mol$^{-1}$]

$T_M$ = temperature of maximum enzyme activity [K]

*Schuh et al.* (1997) derived this emission algorithm to desribe the temperature and PAR dependence of VOC emissions from sunflower (*Helianthus annuus*) and beech (*Fagus sylvatica*). A detailed description of this algorithm can be found there. In summary, monoterpene emissions occur via two independent pathways. The diffusion out of storage pools is described by the first term, which is temperature dependent. Emissions in parallel

with monoterpene biosynthesis are described by the second temperature and light intensity dependent term.

In $^{13}C$-labeling experiments the plants were exposed to $^{13}CO_2$. Using GC-MS measurements, how fast the $^{13}C$ was incorporated into the emitted monoterpenes was investigated. Labeling was observed for all emitted monoterpenes within a few hours, including those monoterpenes that did not show a detectable PAR dependence (e.g. 3-carene and β-pinene). This result could not be explained by the idea that monoterpenes were simply emitted by diffusion out of pools, and therefore the light dependent term in equation E4.1 was necessary to describe emissions of these monoterpenes.

Figure 4.5 shows a surface plot of the calculated emission rate of α-pinene as a function of temperature and PAR. Data were simulated using the algorithm described above (E4.1). Since no values for $c_{T2}$ and $T_M$ were available and since all measurements were conducted at $T < T_M$, the denominator of the second term describing the temperature dependence of the emissions in parallel to VOC biosynthesis was set to unity. The parameters were taken from *Shao et al.* (2000) who described the results of the laboratory studies with young Scots pine, i.e. $\Phi^{P,S}$ = 30 ng g(dw)$^{-1}$ h$^{-1}$; $\Phi^{B,S}$ = 5 ng g (dw)$^{-1}$ h$^{-1}$; $c_L$ = 1.3; $\alpha$ = 0.01; $c_{TP}\,R^{-1}$ = 10000 K; and $c_{T1}\,R^{-1}$ = 10000 K. It should be noted that values for $c_L$, $\alpha$, $c_{TP}\,R^{-1}$ and $c_{T1}\,R^{-1}$ are typical values and were relativly constant over several experiments. Values for $\Phi^{P,S}$ and $\Phi^{B,S}$, on the other hand, were not reproducible. Other factors such as stress have an influence on the amount of emissions (see section 4.2.6), but are not described by the algorithm. Therefore, results from one specific experiment were taken.

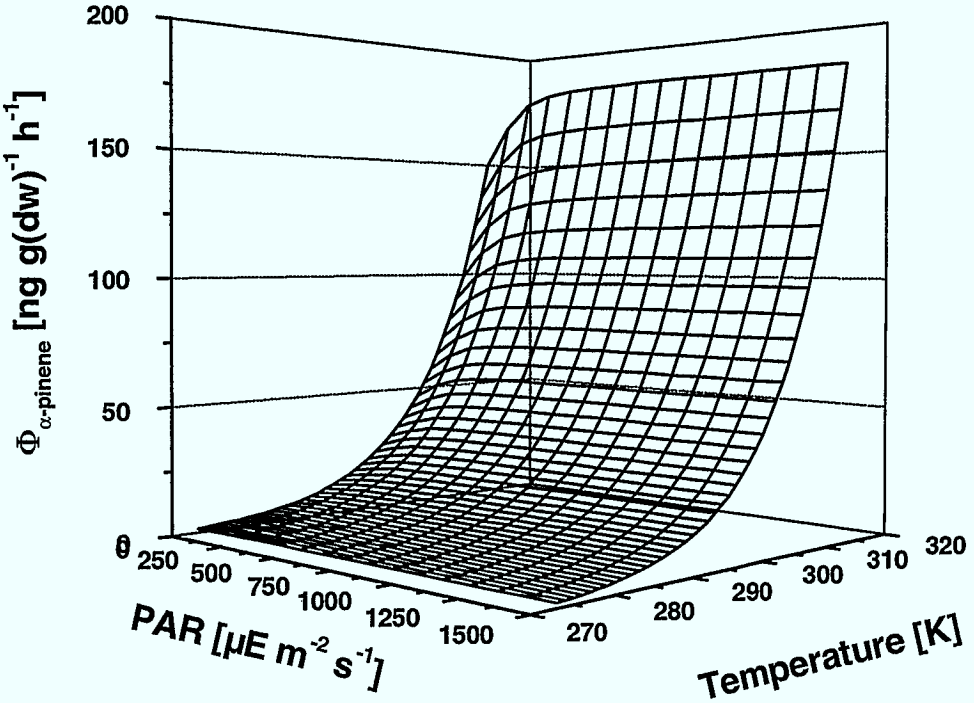


**Figure 4.5:** *Surface plot of the emission rate of α-pinene as a function of needle temperature and photosynthetic active radition, calculated using the complete algorithm by Schuh et al. (1997), and the following parameters:* $\Phi^{P,S} = 30$ *ng g(dw)*$^{-1}$ *h*$^{-1}$; $\Phi^{B,S} = 5$ *ng g (dw)*$^{-1}$ *h*$^{-1}$; $c_L = 1.3$; $\alpha = 0.003$; $c_{TP} R^{-1} = 10000$ *K;* $c_{TI} R^{-1} = 10000$ *K (taken from Shao et al., 2000).*

As can be seen, the emission rate increases with needle temperature. Emission rates are also dependent on PAR, but reach a saturation at low radiation levels. Varying PAR between 0 and 1500 µE m$^{-2}$ s$^{-1}$, which is about the full range observed under outdoor conditions, changes the emission rate of α-pinene by only about 20 %. For all measurements, the increase in α-pinene and camphene emission rates due to PAR was between 20 and 30 %. For β-pinene and 3-carene dependence on PAR was not detectable (*Shao et al.*, 2000). On the other hand, changes in the needle temperature by 1 K increased or decreased the emission rate by approximately 10 %. Thus, the laboratory results show that monoterpene emission rates are much more sensitive to changes in temperature than to changes in PAR.

Unfortunately, this algorithm (E4.1) was not suitable to describe the results obtained from the outdoor enclosure studies, which is explained in the following. Under typical outdoor conditions, both temperature and PAR were highly variable over the

sampling period of one hour. A typical value for the temperature variation during sampling was ±1 K, but could easily increase to variations of ±4 K under conditions of drastically changing solar radiation (see Figure 4.6).

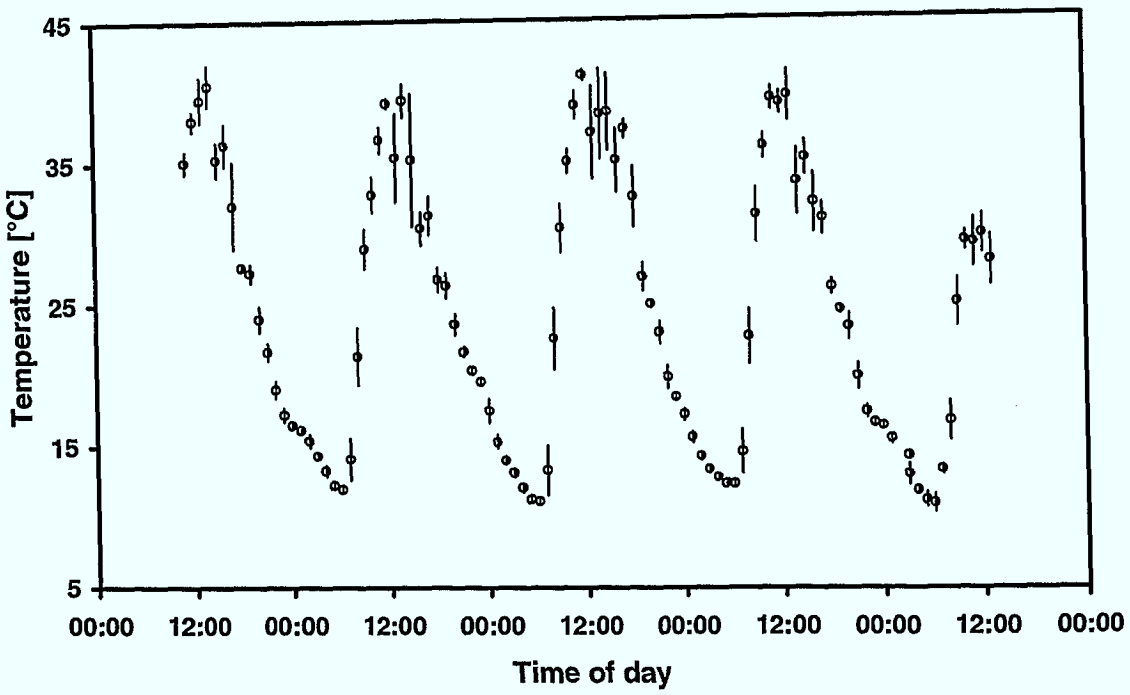


**Figure 4.6:** *Example of the diurnal temperature cycle during outdoor enclosure measurements (pine No. 6, June 1999). The open circles give 1 hour mean values, the bars indicate the 1σ variation of temperature during that hour.*

Thus, the variation in the emission rates due to the variations in temperature was larger than the expected influence of PAR, even over the full range. In addition, under outdoor conditions, temperature and solar radiation do not change independently, but are highly correlated. These conditions make the detection of a PAR dependence almost impossible.

In order to make emission rates obtained from laboratory and outdoor enclosure studies comparable and to eliminate systematic differences due to the use of different algorithms to describe the emission rates, values for $\Phi^S$ were derived using the algorithm from the model of *Tingey et al.* (1991), i.e. the first term of the algorithm shown above (E4.1, equal to E2.1), and which neglects the PAR dependence of emissions, both for laboratory and outdoor enclosure measurements. This simplification is justified, because

under stress-free conditions, temperature has the predominant influence on monoterpene emissions. As the first term of equation E4.1 shows, the emission rate can then be described as the product of a term describing the functional dependence of emissions on temperature, including $c_{TP}\,R^{-1}$, and of a temperature normalized standard emission rate, $\Phi^S$. Values for $c_{TP}\,R^{-1}$ and $\Phi^S$ were derived from fits of the natural logarithm of the obtained emission rate, $\ln\Phi$, versus inverse temperature as shown in Figure 4.3. The slope of the linear regession gave $c_{TP}\,R^{-1}$, and $\Phi^S$ was derived from both the slope and the intercept.

### *4.2.5 Standard emission rates of monoterpenes*

Table 4.3 summarizes the results of measurements with different individual plants. Plants No. 5 and 8 were placed separately inside the CSTR, plants No. 6 and 7 were placed inside at the same time. Plant No. 8 was investigated four times, and results are shown for each experiment separately. Some studies focussed on the standard emission rate only, and were conducted at the standard temperature of 298 K. Therefore, no data are shown for $c_{TP}\,R^{-1}$ and only the standard emission rates, $\Phi^S$, are compared.

**Table 4.3:** *Standard emission rates $\Phi^S$ in* [ng g(dry weight)$^{-1}$ h$^{-1}$] *from laboratory studies with individual pine seedlings and plant-to-plant range of emissions. b.l. = below detection limit. Also given is the period of time of the measurements.*

| | **No. 5 05/28-06/05** | **No. 6 + 7 05/19-05/28** | **No. 8 06/99** | **No. 8 07/13-07/14** | **No. 8 07/20-07/21** | **No. 8 08/17-08/24** | **Range** |
|---|---|---|---|---|---|---|---|
| α-pinene | 190 ± 97 | 16 ± 3.7 | 152 ± 18 | 29 ± 3.8 | 19 ± 1.4 | 89 ± 21 | 16-152 |
| 3-carene | 0.02±0.06 | 21 ± 13 | 326 ± 57 | 19 ± 5.7 | 11 ± 1.1 | 93 ± 25 | 0-326 |
| β-pinene | 15 ± 8.1 | 6.0 ± 1.6 | 98 ± 13 | 13 ± 2.1 | 8.2 ± 0.5 | 45 ± 14 | 6-45 |
| β-myrcene | b.l. | 5.2 ± 2.0 | 38 ± 11 | 9.2 ± 4.0 | 7.3 ± 1.6 | 29 ± 9.9 | 0-38 |
| limonene | 24 ± 17 | 0.6 ± 0.2 | 7.1 ± 1.2 | b.l. | b.l. | 4.5 ± 1.2 | 0-24 |
| sabinene | 2.6 ± 1.8 | b.l. | 22 ± 5.9 | 5.2 ± 1.2 | 3.6 ± 0.5 | 11 ± 3.7 | 0-22 |
| camphene | 7.6 ± 1.8 | 7.8 ± 1.7 | 18 ± 2.0 | 9.6 ± 1.7 | 6.2 ± 0.4 | 20 ± 4.6 | 6-20 |
| tricyclene | 0.8 ± 0.7 | 1.2 ± 0.3 | 3.7 ± 0.4 | b.l. | b.l. | b.l. | 0-4 |
| 1,8-cineole | 12 ± 12 | 6.9 ± 2.4 | 73 ± 88 | 41 ± 4.4 | 28 ± 4.8 | 53 ± 18 | 7-73 |
| sum | 252 | 64 | 737 | 126 | 83 | 343 | 64-737 |

The compounds listed in Table 4.3 are the monoterpenes predominantly emitted from Scots pines. Other monoterpenes were also identified, but their emission rates were relatively low. The combined contribution of the compounds not shown was less than 10 % to the sum of monoterpene emission rates shown in Table 4.3.

The standard emission rates varied both from plant to plant and also for the same plant measured at different times. For plant No. 8, the standard emission rate, $\Phi^S$, of $\alpha$-pinene varied between 19 and 152 ng $g(dw)^{-1}$ $h^{-1}$ for measurements conducted between June and July. For 3-carene, $\Phi^S$ varied by almost a factor of 30 (11-326 ng $g(dw)^{-1}$ $h^{-1}$), the sum of $\Phi^S$ for monoterpenes (including 1,8-cineol as an oxygenated monoterpene) varied by almost one order of magnitude between 83 and 737 ng $g(dw)^{-1}$ $h^{-1}$ for measurements taken under similar conditions on the same individual plant over a time period of two months.

The plant-to-plant variability of the sum of standard emission rates for monoterpenes was on the same order of magnitude as the temporal variability for a single plant (No. 8) and also varied by more than one order of magnitude between 64 and 737 ng $g(dw)^{-1}$ $h^{-1}$. Individual monoterpenes showed a much higher variability. For example, 3-carene was the most abundant monoterpene emitted from plant No. 8 in June, but negligible amounts were detected in the emissions from plant No. 5 (May and June).

Thus, not only the absolute amount of emissions, but also the composition of the emitted monoterpenes varied for unknown reasons. To take a closer look at the variation of the composition of emitted monoterpenes and to eliminate differences in the absolute amount of emissions, Table 4.4 gives the percent contribution of individual monoterpenes to the sum of monoterpenes for the same data as presented in Table 4.3.

**Table 4.4:** *Contribution of individual monoterpenes to the sum of monoterpenes in %, b.l. = below detection limit. Given also is the period of time of measurements.*

| | No. 5 05/28-06/05 | No. 6 and 7 05/19-05/28 | No. 8 06/99 | No. 8 07/13-07/14 | No. 8 07/20-07/21 | No. 8 08/17-08/24 |
|---|---|---|---|---|---|---|
| α-pinene | 75 | 25 | 21 | 23 | 23 | 26 |
| 3-carene | 0.01 | 32 | 44 | 15 | 13 | 27 |
| β-pinene | 5.8 | 9.4 | 13 | 10 | 9.8 | 13 |
| β-myrcene | b.l. | 8.1 | 5.1 | 7.3 | 8.7 | 8.4 |
| limonene | 9.6 | 0.9 | 1.0 | b.l. | b.l. | 1.3 |
| Sabinene | 1.0 | b.l. | 3.0 | 4.2 | 4.2 | 3.2 |
| camphene | 3.0 | 12 | 2.4 | 7.6 | 7.4 | 5.8 |
| tricyclene | 0.3 | 1.9 | 0.5 | b.l. | b.l. | b.l. |
| 1,8-cineole | 4.9 | 11 | 9.9 | 33 | 34 | 15 |

For plant No. 5, the spectrum of emitted monoterpenes was dominated by α-pinene which contributed 75 % to the total mass of emitted monoterpenes. The contribution of 3-carene was on the order of 0.01 % whereas this compound was the predominantly emitted monoterpene measured at plant No. 8 in June (44 %). The series of measurements conducted at plant No. 8 between June and August 1999 also revealed that the composition of emitted monoterpenes varied with time for the same plant.

### *4.2.6 Stress effects*

Under stress free conditions, $c_{TP}\,R^{-1}$ and $\Phi^S$ were found to be constant over time periods of several days (*Shao et al.*, 2000). For plants suffering from any kind of stress, the parameters showed variation with time. As an example of such behavior, Table 4.5 shows $c_{TP}\,R^{-1}$ and $\Phi^S$ of α-pinene emissions measured at a single plant over a time period of approximately one week. The complete data set of 169 measurements is separated into daily subsets of 12 to 23 measurements each.

**Table 4.5:** *Temporal variability of derived values for the temperature dependence of emissions, $c_{TP}\,R^{-1}$, and standard emission rate, $\Phi^S$, of α-pinene measured at the same plant between May 19th and May 27th. n is the number of measurements, $R^2$ is the correlation coefficient for ln$\Phi$ versus inverse temperature. The errors are with respect to the linear fits to the data using equation E2.1.*

| Date | n | Temperature range [°C] | $R^2$ | $c_{TP}\,R^{-1}$ [$10^3$ K] | $\Phi^S$ [ng g(dw)$^{-1}$ h$^{-1}$] |
|---|---|---|---|---|---|
| 05/19/99 | 15 | 16.4-21.2 | 0.76 | 13.4 ± 2.2 | 30 ± 4.6 |
| 05/20/99 | 23 | 10.8-20.1 | 0.85 | 12.9 ± 1.1 | 26 ± 3.9 |
| 05/21/99 | 20 | 11.1-26.1 | 0.98 | 11.7 ± 0.4 | 17 ± 2.0 |
| 05/22/99 | 23 | 21.5-25.7 | 0.87 | 13.1 ± 1.1 | 15 ± 1.6 |
| 05/22/99 | 16 | 21.6-25.8 | 0.98 | 14.4 ± 0.5 | 13 ± 0.5 |
| 05/23/99 | 12 | 16.7-21.4 | 0.80 | 14.1 ± 2.1 | 18 ± 2.5 |
| 05/25/99 | 22 | 16.7-20.5 | 0.91 | 17.7 ± 1.2 | 19 ± 1.9 |
| 05/26/99 | 23 | 18.0-21.8 | 0.65 | 15.0 ± 2.3 | 12 ± 1.9 |
| 05/27/99 | 15 | 18.4-21.6 | 0.23 | 14.5 ± 7.1 | 12 ± 3.5 |
| Mean value ± standard deviation | | | | 14 ± 1.7 | 18 ± 6.4 |

For each subset, ln$\Phi$ was found to be highly correlated with the inverse temperature, with correlation coefficients of up to 0.98 (the only exception were the measurements on May 27$^{th}$ with $R^2 = 0.23$). The value of $c_{TP}\,R^{-1}$ varied between $11.7 \cdot 10^3$ and $17.7 \cdot 10^3$ K over the eight days and the mean value of $14 \cdot 10^3$ K had a standard deviation of 12 %. The absolute amount of emissions, given by the standard emission rate, $\Phi^S$, varied by a factor of 2.5 between 12 to 30 ng g(dw)$^{-1}$ h$^{-1}$ without a significant temporal trend. The mean value (18 ng g(dw)$^{-1}$ h$^{-1}$) had a 1σ standard deviation of more than 35 %. The specific form of stress causing these variations was not identified.

## 4.3 Outdoor enclosure measurements with 3-4 year old pine seedlings

The young Scots pines investigated with the outdoor enclosure system emitted mainly the follwing monoterpenes: α-pinene, 3-carene, β-pinene, camphene, sabinene, β-myrcene, limonene and β-phellandrene. The first four monoterpenes were the major emission products contributing at least 75 % to the total mass of all emitted monoterpenes. γ-terpinene, terpinolene, 2-carene, α-terpinene, tricyclene and α-phellandrene were also found as emission products, but only in very small amounts. The combined contribution of these compounds to the sum of all monoterpenes was always less than 10 %. Results for

these compounds are not shown here. Figure 4.7 gives, as an example, the chromatogram of an outdoor enclosure measurement with a young pine (in this case plant No. 8).

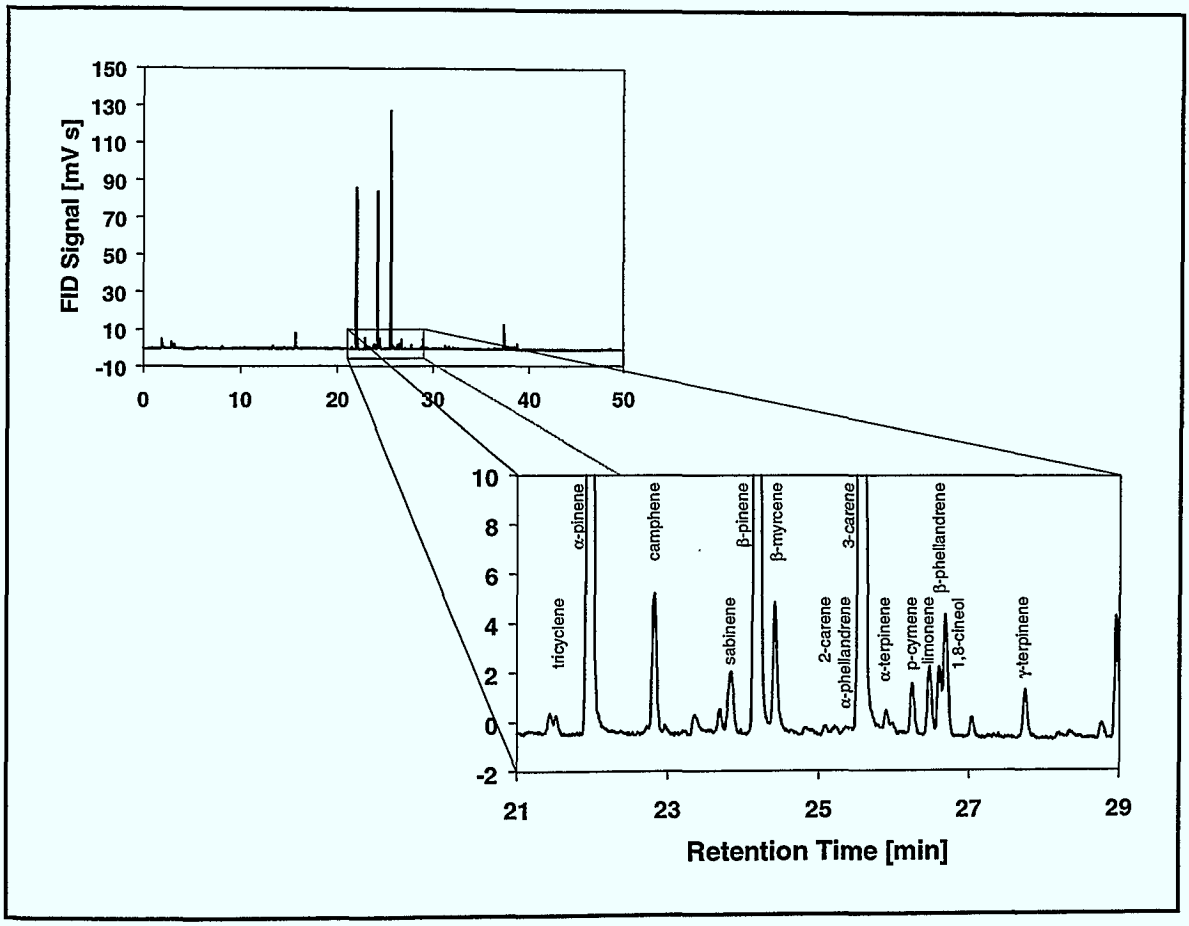


**Figure 4.7:** *Chromatogram of emission rate measurement with a young Scots pine (Pinus sylvestris). The enlarged window shows the part of the chromatogram where monoterpenes elute from the column. Identified monoterpenes are assigned to the peaks.*

The enlarged plot shows the time range where monoterpenes eluted from the chromatographic column. Identified monoterpenes were assigned to the corresponding peaks. Besides monoterpenes, sesquiterpenes and also toluene were emitted. Emission rates were always very low so data are not shown here. The results of the toluene emissions are described in detail by *Heiden et al.* (1999b). Since the sampling and analytical systems were not optimized for measurements of acetone and isoprene (especially with respect to the breakthrough volumes on the adsorption tubes), no conclusive data concerning emissions of these compounds can be given here.

### *4.3.1 Diurnal cycle of emissions*

Monoterpene emissions from Scots pines showed a pronounced diurnal cycle with maximum emission rates in the daytime and the lowest at night. Figure 4.8 shows the emission rate of α-pinene measured on four consecutive days in June 1999. This data set was chosen as a typical example for the diurnal cycle of monoterpene emissions.

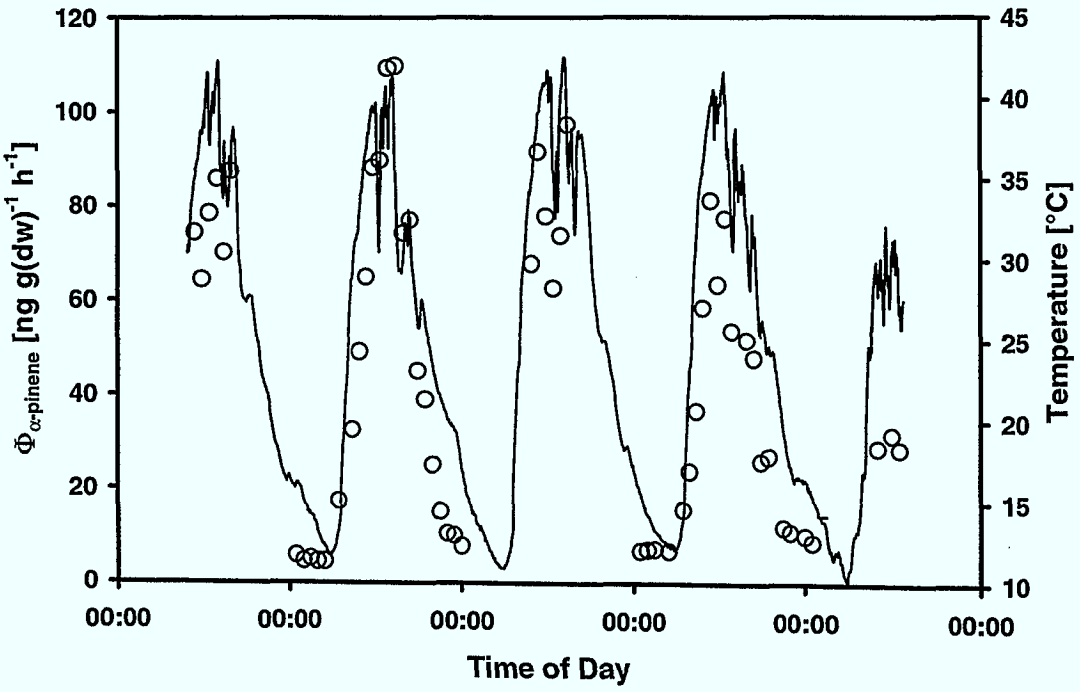


**Figure 4.8:** *Diurnal cycle of the emission rate of α-pinene (open circles, left axis) and temperature (solid line, right axis) measured at a young pine seedling for four consecutive days (pine No. 6, June 14-18 1999).*

Within a temperature range of 12 to 41 °C, the emission rates of α-pinene varied by more than a factor of 24 between 4.5 and 110 ng g(dw)$^{-1}$ h$^{-1}$. Clearly, the emission rates followed the same diurnal cycle as the temperature. The emission rates of all other monoterpenes are not shown in detail here, but generally showed the same diurnal pattern. The emission rates of all outdoor enclosure measurements are included in the Appendix (chapter 8.7).

### 4.3.2 *Temperature dependence of monoterpene emissions*

As expected from published data (e.g. *Tingey et al.*, 1980; *Lamb et al.*, 1985; *Juuti et al.*, 1990) and from the laboratory results, the emission rates of monoterpenes increased with temperature. The algorithm given by *Tingey et al.* (1991) (E2.1) was used to describe the temperature dependence of monoterpene emissions. The parameter describing the temperature dependence of emissions, $c_{TP}$ $R^{-1}$, and standard emission rates, $\Phi^S$, were obtained using the same procedure as for the results of the laboratory studies described in chapter 4.2. Figure 4.9 shows a logarithmic plot of the emission rate of α-pinene versus the inverse temperature and the obtained fit from the linear regression to the data.

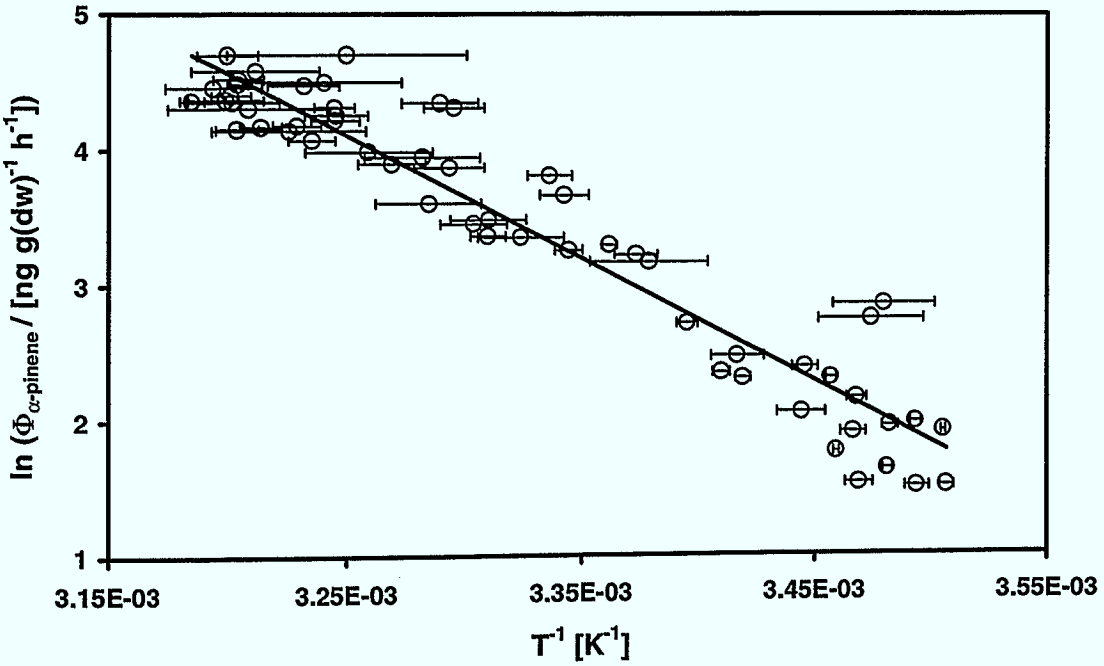


**Figure 4.9:** *Logarithmic plot of the emission rate of a-pinene versus inverse temperature for the same data set as shwon in Figure 4.8. The error bars represent the 1σ variation of temperature during the sampling period of one hour.*

Again, only the variation of temperature during the sampling period is shown in this plot. Errors in the measured emission rates are not shown since the errors were very small relative to the absolute emission rate measurements. The correlation coefficient of this fit

had a value of $R^2 = 0.91$. The derived values for the temperature dependence of α-pinene emissions was $c_{TP}\ R^{-1} = (9.1 \pm 0.4) \cdot 10^3$ K.

Table 4.6 summarizes the values for $c_{TP}\ R^{-1}$ for all outdoor enclosure measurements with young pines for the most abundant monoterpenes, obtained from fits to the data. Also given is the range of values for $c_{TP}\ R^{-1}$.

**Table 4.6:** *Values for the temperature dependence of emissions, $c_{TP}$ $R^{-1}$, in [$10^3$ K] from outdoor enclosure studies with 8 different pine seedlings and the plant-to-plant range of values (only for fits with correlation coefficients $R^2 \geq 0.4$). Errors are 1 $\sigma$ from fits to the data. Numbers in brackets give the correlation coefficients for fits of ln$\Phi$ versus inverse temperature, $R^2$. n.d. means not detected. Also shown are the dates of the measurements*

| | **No. 1 06/98** | **No. 2 06/98** | **No. 3 08/98** | **No. 4 08/98** | **No. 5 05/99** | **No. 5 07/99** |
|---|---|---|---|---|---|---|
| α-pinene | 11.3 ± 0.9 (0.73) | 8.6 ± 1.4 (0.53) | 5.8 ± 0.3 (0.91) | 6.5 ± 0.5 (0.85) | 11.9 ± 1.0 (0.96) | 6.0 ± 1.2 (0.52) |
| 3-carene | 13.4 ± 1.2 (0.70) | 10.2 ± 1.6 (0.55) | 7.0 ± 0.3 (0.92) | 9.5 ± 0.7 (0.87) | 7.3 ± 2.4 (0.14) | 0.8 ± 2.8 (0.00) |
| β-pinene | 9.5 ± 0.9 (0.69) | 7.8 ± 1.2 (0.56) | 5.6 ± 0.6 (0.70) | 0.5 ± 1.6 (0.01) | 13.9 ± 1.1 (0.72) | 7.3 ± 1.1 (0.65) |
| camphene | 10.5 ± 0.8 (0.76) | 9.0 ± 1.3 (0.58) | 5.6 ± 0.4 (0.86) | 3.8 ± 1.4 (0.21) | 12.8 ± 0.9 (0.76) | 7.1 ± 1.0 (0.68) |
| sabinene | 8.6 ± 1.0 (0.67) | 3.9 ± 1.8 (0.16) | 6.3 ± 1.4 (0.67) | -0.3 ± 6.0 (0.00) | 7.8 ± 1.5 (0.33) | 9.6 ± 2.0 (0.47) |
| β-myrcene | 11.3 ± 0.9 (0.75) | 6.3 ± 1.6 (0.34) | 9.5 ± 0.5 (0.90) | 4.4 ± 1.7 (0.22) | 9.9 ± 1.1 (0.55) | 5.4 ± 1.2 (0.46) |
| limonene | 7.3 ± 0.9 (0.54) | 7.2 ± 1.7 (0.39) | 8.8 ± 0.4 (0.94) | 1.1 ± 2.6 (0.02) | 12.7 ± 0.8 (0.79) | 5.0 ± 1.3 (0.39) |
| β-phellandrene | 8.7 ± 1.7 (0.37) | 1.9 ± 2.4 (0.03) | 7.5 ± 1.0 (0.65) | -9.1 ± 22.2 (0.08) | 12.2 ± 0.9 (0.74) | 7.0 ± 1.1 (0.62) |
| 1,8-cineol | 16.6 ± 1.1 (0.84) | 14.8 ± 2.4 (0.61) | 7.1 ± 0.7 (0.83) | n.d. | 17.6 ± 1.8 (0.62) | 16.2 ± 1.8 (0.77) |

| | **No. 6 06/99** | **No. 7 06/99** | **No. 8 05/99** | **No. 8 07/99** | **No. 8 08/99** | **range** |
|---|---|---|---|---|---|---|
| α-pinene | 9.1 ± 0.4 (0.91) | 7.1 ± 0.6 (0.74) | 7.9 ± 0.9 (0.58) | 9.4 ± 0.5 (0.93) | 11.2 ± 0.8 (0.88) | 6.0-11.9 |
| 3-carene | 11.9 ± 0.4 (0.93) | 8.9 ± 0.5 (0.86) | 9.0 ± 1.2 (0.72) | 11.3 ± 0.5 (0.95) | 13.8 ± 0.9 (0.91) | 7.3-13.8 |
| β-pinene | 9.7 ± 0.5 (0.88) | 5.9 ± 0.8 (0.56) | 8.0 ± 1.0 (0.56) | 9.7 ± 0.5 (0.94) | 11.7 ± 0.9 (0.88) | 5.6-13.9 |
| camphene | 9.4 ± 0.5 (0.89) | 7.5 ± 0.6 (0.76) | 10.1 ± 0.7 (0.74) | 7.8 ± 0.8 (0.78) | 10.2 ± 1.0 (0.82) | 5.6-12.8 |
| sabinene | 13.3 ± 0.7 (0.88) | 10.7 ± 0.8 (0.80) | 10.1 ± 1.1 (0.58) | 6.6 ± 0.8 (0.72) | 9.6 ± 1.7 (0.57) | 6.3-13.3 |
| β-myrcene | 12.2 ± 0.6 (0.88) | 7.1 ± 1.0 (0.50) | 7.0 ± 1.0 (0.47) | 6.6 ± 1.0 (0.64) | 10.3 ± 1.2 (0.75) | 5.4-11.3 |
| limonene | 9.4 ± 0.5 (0.87) | 5.7 ± 0.9 (0.46) | 11.3 ± 1.1 (0.61) | 7.3 ± 0.6 (0.85) | 10.3 ± 1.5 (0.65) | 5.0-12.7 |
| β-phellandrene | 11.1 ± 0.4 (0.94) | 7.8 ± 0.6 (0.78) | 11.0 ± 1.3 (0.54) | 7.6 ± 0.7 (0.82) | 11.9 ± 1.8 (0.65) | 7.0-12.2 |
| 1,8-cineol | 20.6 ± 1.1 (0.86) | 16.5 ± 0.8 (0.91) | 17.8 ± 0.5 (0.95) | 13.8 ± 1.5 (0.77) | 30.1 ± 2.6 (0.84) | 7.1-30.1 |

It should be noted, that for some measurements the emission rates had only a low correlation with temperature, and for unknown reasons. The range of $c_{TP}\ R^{-1}$, given in the last column, only includes values for fits with correlation coefficients of $R^2 \geq 0.4$. The plant-to-plant variability of values for $c_{TP}\ R^{-1}$ was very similar for all monoterpenes. On average, $c_{TP}\ R^{-1}$ varied by approximately a factor of 2 between $6.0 \cdot 10^3$ K and $12.7 \cdot 10^3$ K. The range of $c_{TP}\ R^{-1}$ for measurements conducted with the same plant, but at different times of year (only plants No. 5 and 8), was on the same order of magnitude as the plant-to-plant variability, i.e. a variation of a factor of 2. Measurements conducted between May and August at plant No. 8 showed variations but no clear seasonal trend in $c_{TP}\ R^{-1}$.

For 1,8-cineol the range of $c_{TP}\ R^{-1}$ was significantly larger than for the monoterpenes with values between $7.1 \cdot 10^3$ K and $30.1 \cdot 10^3$ K. With the exception of the measurements at plant No.3, the temperature dependence of the 1,8-cineol emission rate was always higher than those of the monoterpene emission rates.

### *4.3.3 Standard emission rates of monoterpenes*

From the same fits used to derive $c_{TP}\ R^{-1}$ the standard emission rates, $\Phi^S$, were also calculated. Table 4.7 summarizes values for $\Phi^S$ for the most abundant monoterpenes from all outdoor enclosure measurements with young pines.

The sum of the standard emission rates of all monoterpenes (including 1,8-cineol) varied by more than one order of magnitude between 59 and 648 ng $g(dw)^{-1}\ h^{-1}$ for measurements with different plants. The plant-to-plant variability of the emission rates of individual monoterpenes was even larger. The largest variation was observed for 3-carene, which was the most abundant monoterpene emitted from pine No. 8 with a standard emission rate of 313 ng $g(dw)^{-1}\ h^{-1}$, but was almost absent in the emissions from plant No. 5 with a standard emission rate less than 1 ng $g(dw)^{-1}\ h^{-1}$.

**Table 4.7:** *Standard emission rates, $\Phi^S$, in* [ng g(dw)$^{-1}$ h$^{-1}$] *from outdoor enclosure studies with 8 different pine seedlings and plant-to-plant range of emissions. Errors are 1 σ errors from fits to the data. Also shown is the date of the measurements.*

| | **No. 1 06/98** | **No. 2 06/98** | **No. 3 08/98** | **No. 4 08/98** | **No. 5 05/99** | **No. 5 07/99** |
|---|---|---|---|---|---|---|
| α-pinene | 35 ± 3.8 | 66 ± 14 | 283 ± 19 | 46 ± 5.1 | 330 ± 37 | 165 ± 41 |
| 3-carene | 58 ± 7.0 | 84 ± 18 | 50 ± 3.2 | 36 ± 3.9 | 0.6 ± 0.3 | 0.3 ± 2.3 |
| β-pinene | 10 ± 1.3 | 27 ± 5.5 | 13 ± 1.9 | 5.0 ± 18 | 32 ± 3.4 | 8.6 ± 1.7 |
| camphene | 19 ± 2.0 | 12 ± 2.3 | 22 ± 2.0 | 8.3 ± 4.2 | 13 ± 1.3 | 18 ± 3.3 |
| sabinene | 11 ± 1.7 | 12 ± 7.2 | 7.2 ± 2.1 | 5.1 ± 192 | 2.7 ± 0.7 | 1.4 ± 0.4 |
| β-myrcene | 8.1 ± 0.9 | 9.2 ± 3.1 | 20 ± 1.5 | 7.1 ± 3.7 | 9.5 ± 1.5 | 5.2 ± 1.5 |
| limonene | 4.4 ± 0.7 | 4.6 ± 1.5 | 12 ± 0.7 | 4.0 ± 12 | 54 ± 4.7 | 17 ± 5.6 |
| β-phellandrene | 5.7 ± 1.5 | 3.3 ± 5.2 | 3.8 ± 0.7 | 2.9 ± 10 | 15 ± 1.5 | 2.4 ± 0.5 |
| 1,8-cineol | 9.1 ± 0.9 | 10 ± 2.3 | 2.7 ± 0.4 | n.d. | 2.7 ± 0.4 | 1.5 ± 0.2 |
| Sum | 160 | 228 | 414 | 117 | 459 | 219 |

| | **No. 6 06/99** | **No. 7 06/99** | **No. 8 05/99** | **No. 8 07/99** | **No. 8 08/999** | **range** |
|---|---|---|---|---|---|---|
| α-pinene | 23 ± 1.3 | 15 ± 1.7 | 134 ± 21 | 35 ± 2.7 | 46 ± 4.6 | 15-330 |
| 3-carene | 22 ± 1.1 | 22 ± 1.7 | 313* | 50 ± 3.2 | 54 ± 4.7 | 0.3-313 |
| β-pinene | 4.5 ± 0.3 | 6.4 ± 1.1 | 104 ± 17 | 18 ± 1.2 | 23 ± 2.3 | 5-104 |
| camphene | 13 ± 0.9 | 8.4 ± 1.0 | 13.4 ± 1.4 | 6.5 ± 1.0 | 10 ± 1.4 | 7-22 |
| sabinene | 2.8 ± 0.2 | 2.5 ± 0.3 | 31 ± 4.3 | 4.7 ± 0.8 | 5.1 ± 1.2 | 1-31 |
| β-myrcene | 2.5 ± 0.2 | 1.9 ± 0.4 | 23 ± 4.3 | 3.2 ± 0.7 | 5.6 ± 0.9 | 2-23 |
| limonene | 1.0 ± 0.07 | 1.2 ± 0.3 | 12 ± 1.6 | 1.7 ± 0.2 | 1.7 ± 0.4 | 1-17 |
| β-phellandrene | 0.7 ± 0.04 | 0.5 ± 0.07 | 14 ± 2.2 | 1.0 ± 0.1 | 1.4 ± 0.3 | 1-15 |
| 1,8-cineol | 2.5 ± 0.2 | 1.6 ± 0.1 | 4.5 ± 0.2 | 1.9 ± 0.3 | 3.3 ± 0.4 | 2-10 |
| Sum | 72 | 59 | 648* | 122 | 150 | 59-648 |

* *only lower limit, because the peak of 3-carene was often out of the linear range.*

For measurements conducted at the same plant at different times, variations of the sum of $\Phi^S$ were quite high. For plant No. 5 this variation was about a factor of 2 (219-459 ng g(dw)$^{-1}$ h$^{-1}$), for plant No. 8 variations of a factor of 4 (122-648 ng g(dw)$^{-1}$ h$^{-1}$) were found.

### *4.3.4 Emission patterns*

In order to look for changes and variations in the composition of emitted monoterpenes, Table 4.8 summarizes the percent contribution of individual monoterpenes to the sum of emitted monoterpenes (including 1,8-cineol).

**Table 4.8:** *Contribution of individual monoterpenes to the sum of monoterpenes (shown here) in %. Also shown are the dates of the measurements.*

| | **No. 1 06/98** | **No. 2 06/98** | **No. 3 08/98** | **No. 4 08/98** | **No. 5 05/99** | **No. 5 07/99** |
|---|---|---|---|---|---|---|
| α-pinene | 22 | 29 | 68 | 39 | 72 | 75 |
| 3-carene | 36 | 37 | 12 | 31 | 0.1 | 0.1 |
| β-pinene | 6.4 | 12 | 3.2 | 4.3 | 6.9 | 3.9 |
| camphene | 12 | 5.0 | 5.3 | 7.1 | 2.9 | 8.1 |
| Sabinene | 6.9 | 5.3 | 1.7 | 4.4 | 0.6 | 0.7 |
| β-myrcene | 5.1 | 4.0 | 4.8 | 6.0 | 2.1 | 2.4 |
| Limonene | 2.7 | 2.0 | 2.8 | 3.4 | 12 | 7.7 |
| β-phellandrene | 3.5 | 1.4 | 0.9 | 2.5 | 3.2 | 1.1 |
| 1,8-cineol | 5.6 | 4.5 | 0.7 | 1.8 | 0.6 | 0.7 |

| | **No. 6 06/99** | **No. 7 06/99** | **No. 8 05/99** | **No. 8 07/99** | **No. 8 08/999** | **range** |
|---|---|---|---|---|---|---|
| α-pinene | 32 | 25 | 21 | 29 | 31 | 21-75 |
| 3-carene | 30 | 37 | 48 | 41 | 36 | 0.1-48 |
| β-pinene | 6.2 | 11 | 16 | 15 | 15 | 3.2-16 |
| camphene | 18 | 14 | 2.1 | 5.3 | 6.9 | 2.9-18 |
| Sabinene | 3.9 | 4.3 | 4.7 | 3.9 | 3.4 | 0.6-5.3 |
| β-myrcene | 3.4 | 3.3 | 3.6 | 2.7 | 3.7 | 2.1-6.0 |
| Limonene | 1.4 | 1.9 | 1.8 | 1.4 | 1.1 | 1.1-12 |
| β-phellandrene | 1.0 | 0.9 | 2.1 | 0.8 | 0.9 | 0.8-3.5 |
| 1,8-cineol | 3.5 | 2.8 | 0.7 | 1.6 | 2.2 | 0.6-5.6 |

The variability of emitted monoterpenes from the investigated young Scots pines was high. The plant-to-plant variability of the contribution of a single monoterpene to the sum of monoterpenes was also quite large. For example, the contribution of α-pinene varied between 21 and 75 %. The most variability was found for 3-carene, which was the most abundant monoterpene in the emissions from plant No. 8 with a contribution to the sum of monoterpenes of up to 48 %, but contributed less than 1 % to the sum of monoterpenes emitted by plant No. 5.

The variability in the composition of monoterpene emissions for measurements conducted at the same plant at different times was much smaller than the plant-to-plant variability. Plant No. 5 was measured twice and both times α-pinene dominated the emission spectrum with contributions between 72 and 75 %. 3-carene was only found in marginal amounts in both sets of measurements. In addition, the spectrum of plant No. 8, for which three sets of measurements are available, showed a much smaller temporal variation than the plant-to-plant variability.

### 4.3.5 *Dependence on light intensity*

To ascertain if other parameters besides temperature influenced the diurnal cycle of emissions as well, the temporal behaviour of the temperature normalized standard emission rate, $\Phi^S$, was analyzed. Figure 4.10 shows the diurnal variation for $\Phi^S$ of α-pinene and the diurnal cycle of PAR.

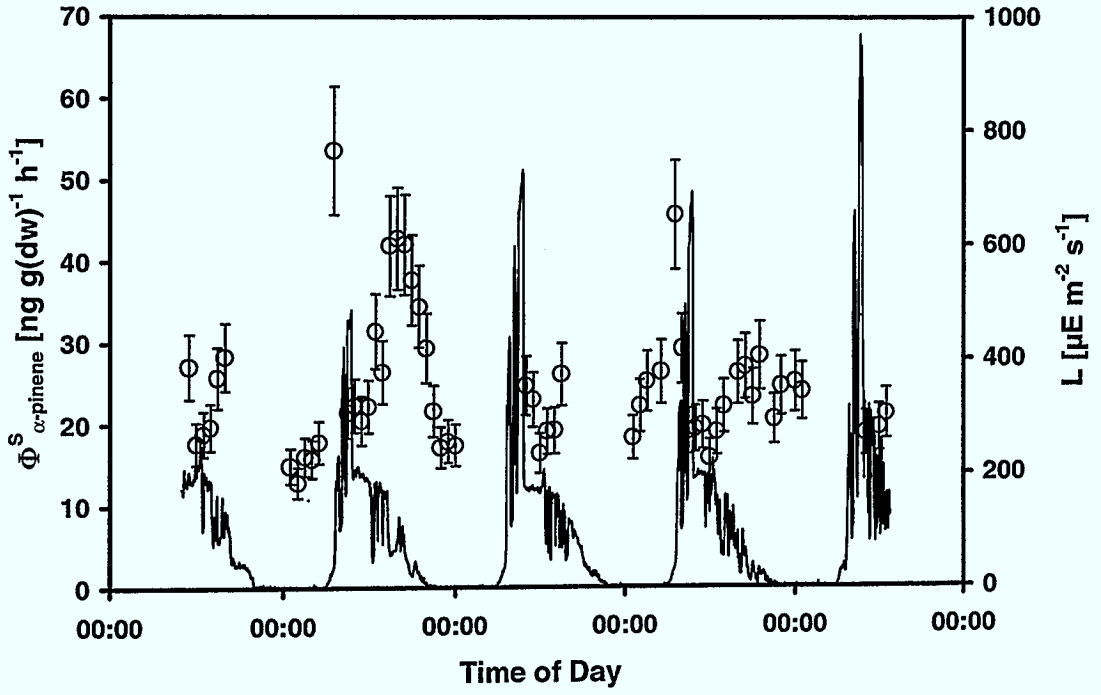


**Figure 4.10:** *Diurnal variation of temperature normalized standard emission rates, $\Phi^S$, of α-pinene (open circles, left scale) calculated from the same data set as shown in Figure 4.8 and Figure 4.9 and solar radiation inside the enclosure (solid line, right scale).*

The standard emission rate varied by a factor of 4 between 13 and 54 ng $g(dw)^{-1}$ $h^{-1}$, much less than the variation before normalization to temperature (factor 24, see Figure 4.8). The error bars in this plot give the statistical error of the calculated standard emission rate (14.6 %). No significant correlation between the standard emission rates and solar radiation was found.

### *4.3.6 Stress factors*

The laboratory results showed that stress to the plants influenced the amount of monoterpene emissions and led to variations in the standard emission rate of a single monoterpene of up to 2.5 over a time period of one week. Under outdoor conditions, such stress situations were also observed. Figure 4.11 to Figure 4.13 display the effect of temperature-induced stress on the emission rates of α-pinene. Figure 4.11 shows the diurnal variation of the emission rate of α-pinene on a day when the plant suffered from stress. A logarithmic plot of the emission rate is shown here. The emission rates clearly followed the same pattern as the temperature (open circles) before the stress effect. One hour after the temperature reached a maximum value of 30 °C, the emission rates increased (filled triangles). The logarithmic plots of the emission rates versus the inverse temperature (Figure 4.12) reveal that the dependence of the emissions on temperature had not changed. The two separate fits to the data obtained before and after temperature-induced stress had the same slope, but were shifted in parallel. The derived value for $c_{TP}\,R^{-1}$ was $(12.8\pm0.4)\cdot10^3$ K before and $(11.9\pm0.7)\cdot10^3$ K after the effect ($1\sigma$ error). Figure 4.13 displays the temporal behaviour of the standard emission rate of α-pinene, $\Phi^S$. Before temperature stress, $\Phi^S$ had a mean value of 168 ng $g(dw)^{-1}$ $h^{-1}$ with a relative standard deviation of 10 % (14 measurements). After temperature stress, $\Phi^S$ increased by more than a factor of 3 to 542 ng $g(dw)^{-1}$ $h^{-1}$ (9 % relative standard deviation, 11 measurements). Temperature-induced stress was observed twice, for the measurements at plant No. 5 in May (Figure 4.11 to Figure 4.13) and for plant No. 8 in May 1999.

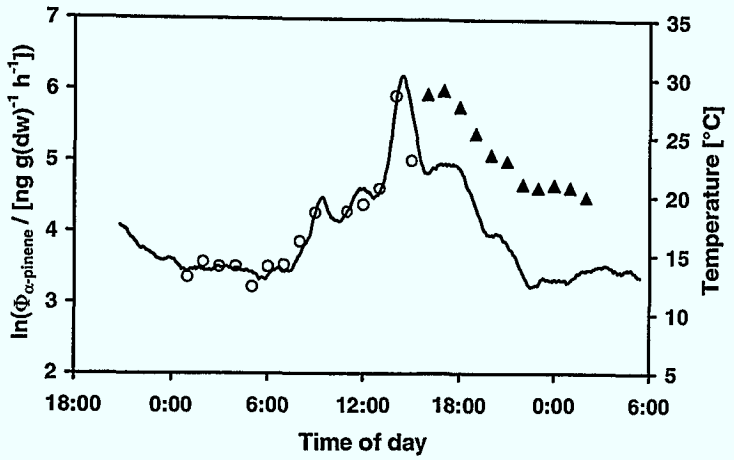


**Figure 4.11:** *Diurnal cycle of the emission rate of α-pinene (left axis, logarithmic plot) during a temperature stress episode (open circles: before, filled triangles: after temperature stress). Solid line: temperature (right axis).*

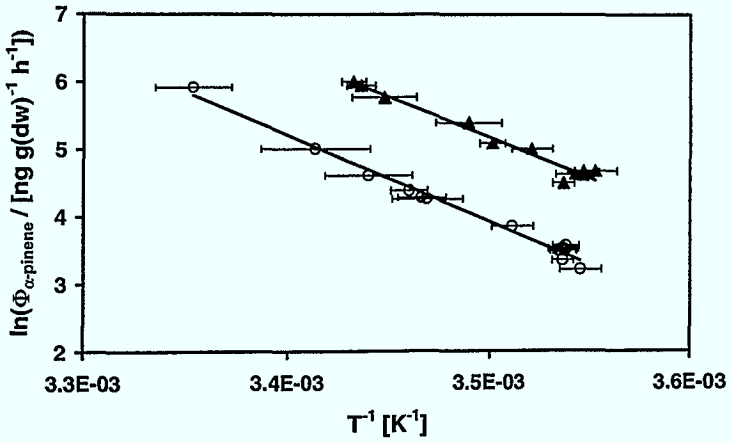


**Figure 4.12:** *Logarithmic plot of the emission rate of α-pinene before (open circles) and after (filled triangles) temperature stress versus inverse temperature. The error bars give the 1 σ variance of temperature during the sampling period of one hour. Lines are fits to the data.*

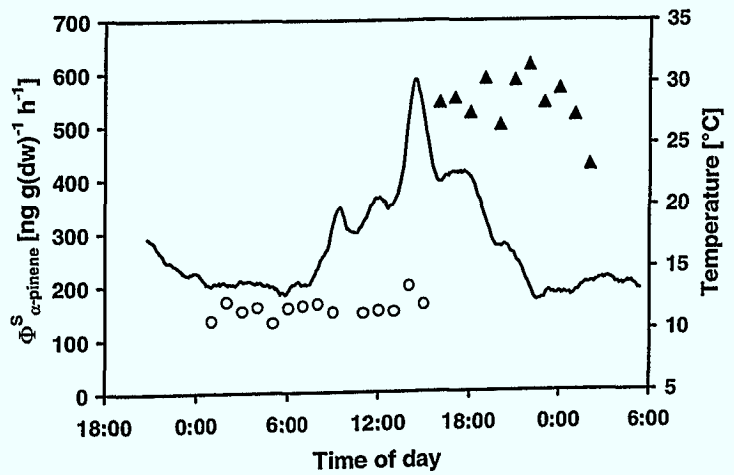


**Figure 4.13:** *Temporal behaviour of temperature normalized standard emisson rate, $\Phi^S$, of α-pinene (left axis) during temperature stress episode (open circles: before, filled triangles: after temperature stress). Solid line: Temperature (right axis).*

## 4.4 Outdoor enclosure studies with an adult pine

The following VOCs were identified as emission products from 40 year old Scots pine and measured during all four field campaigns: α-pinene, camphene, sabinene, β-pinene, β-myrcene, 3-carene, p-cymene, limonene, β-phellandrene, 1,8-cineol, and γ-terpinene. Other monoterpenes such as tricyclene, 2-carene, α-terpinene, and terpinolene which were also identified as emission products, but only observed in relatively small amounts and in a few samples, are not shown here. Besides monoterpenes, two sesquiterpenes (longicyclene and β-caryophyllene) and also toluene were identified as emission products. The problems connected with the analysis of sabinene, p-cymene and γ-terpinene are described in detail in chapter 3.5. Sabinene was partially depleted in the analytical instrumentation, and γ-terpinene was partially converted into p-cymene. Thus, the emission rates of sabinene and γ-terpinene presented here are only lower limits and those of p-cymene are upper limits.

### *4.4.1 Diurnal cycles*

Similar to the results obtained from the studies of young pines, the emission rates in all for the investigated monoterpenes showed a pronounced diurnal variation with maximum emission rates during the daytime and lowest emission rates at night. This was the case during all four field campaigns. Again, α-pinene is taken as a proxi for monoterpenes. Figure 4.14 a-d show the detailed diurnal cycles of the emission rates measured at branch A (see Table 4.2) in April, July, September and October (top to bottom). Data from all of the emission rate studies are included in the Appendix (8.7)

Although the range of temperatures observed was very similar during all four campaigns (between 5 and 30 °C), it is evident from these plots that the range of the α-pinene emission rates was different for each campaign. The seasonal cycle of monoterpene emission is described in detail in the following chapter.

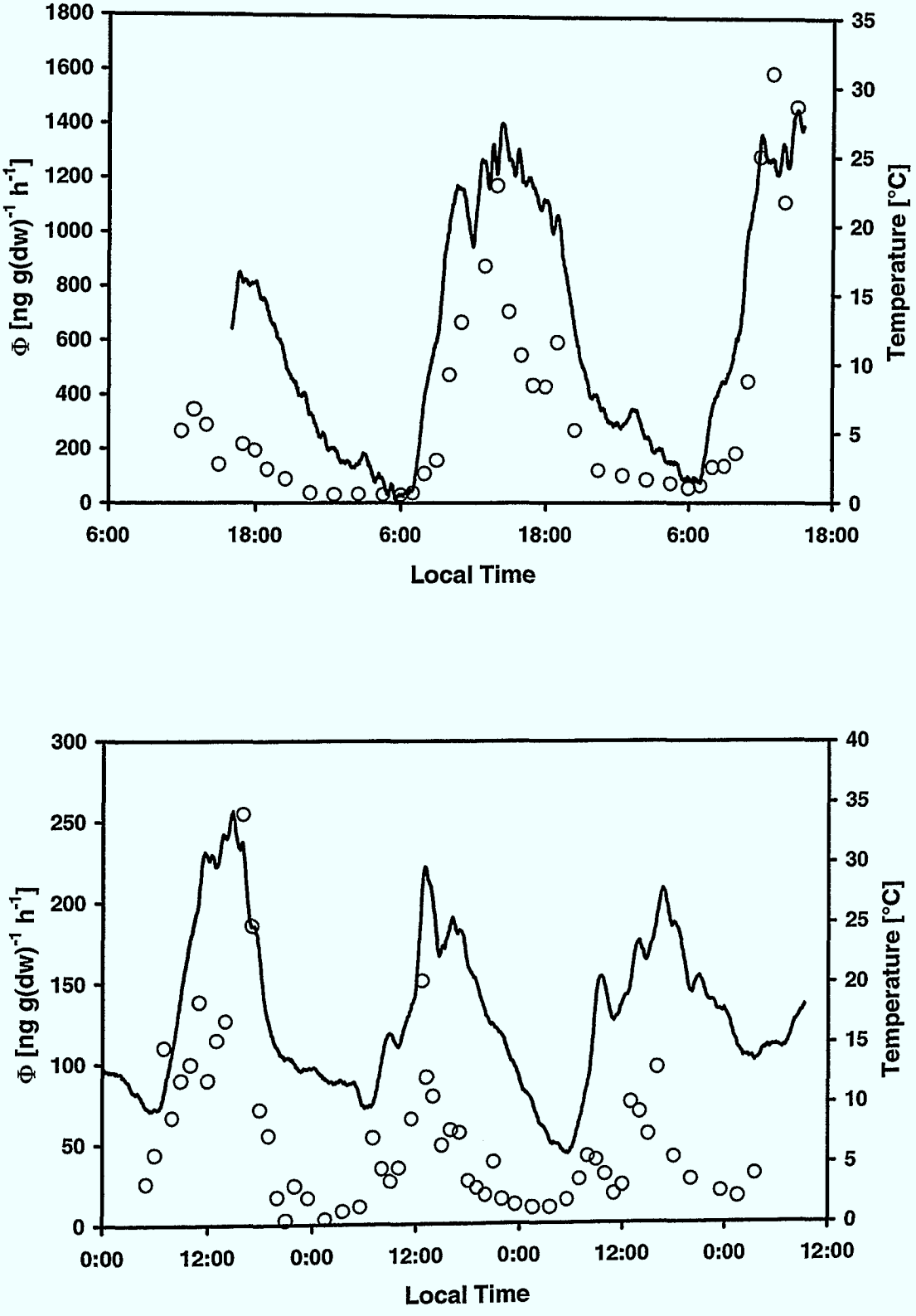


**Figure 4.14 a-b:** *Diurnal cycles of emission rates of a-pinene (circles, left axis) and temperature (solid line, right axis) measured at branch A at different times of year. Upper plot: April 28-30, lower plot: July 7-10.*

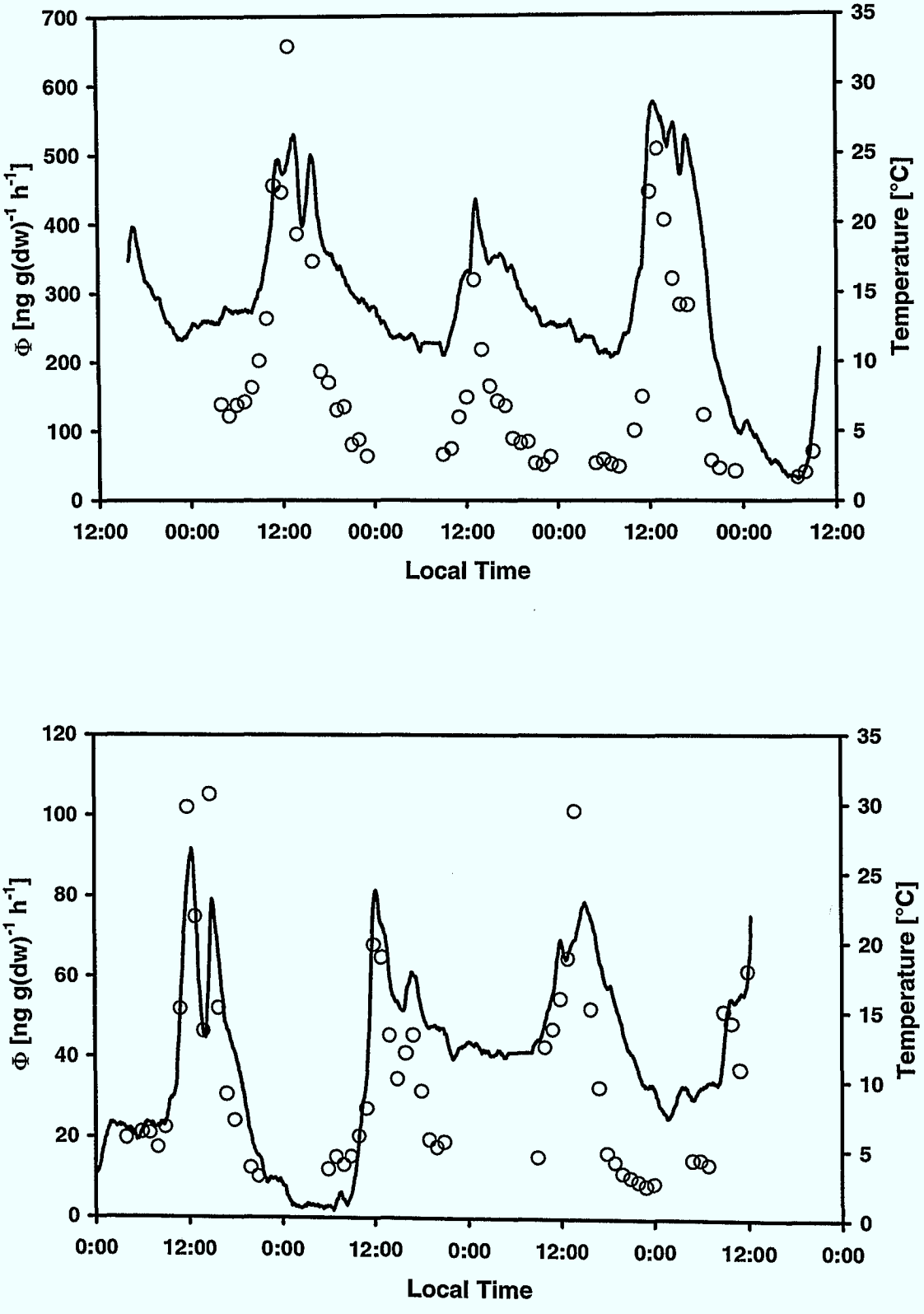


**Figure 4.14 c-d:** *Diurnal cycles of emission rates of a-pinene (circles, left axis) and temperature (solid line, right axis) measured at branch A at different times of year. Upper plot: September 16-19, lower plot: October 20-23.*

### *4.4.2 Seasonal cycle of emissions*

In general, the emission rates of monoterpenes from adult pines showed the same Arrhenius type dependence on temperature as young pine seedlings. Therefore, details for each set of measurements are not shown here. In contrast to studies with the young pines, measurements were conducted at the same branch of an adult pine at different times of year, from spring to fall. Figure 4.15 shows, as an example, a logarithmic plot of the emission rates of α-pinene versus the inverse temperature for measurements at branch A at different times of year (April to October).

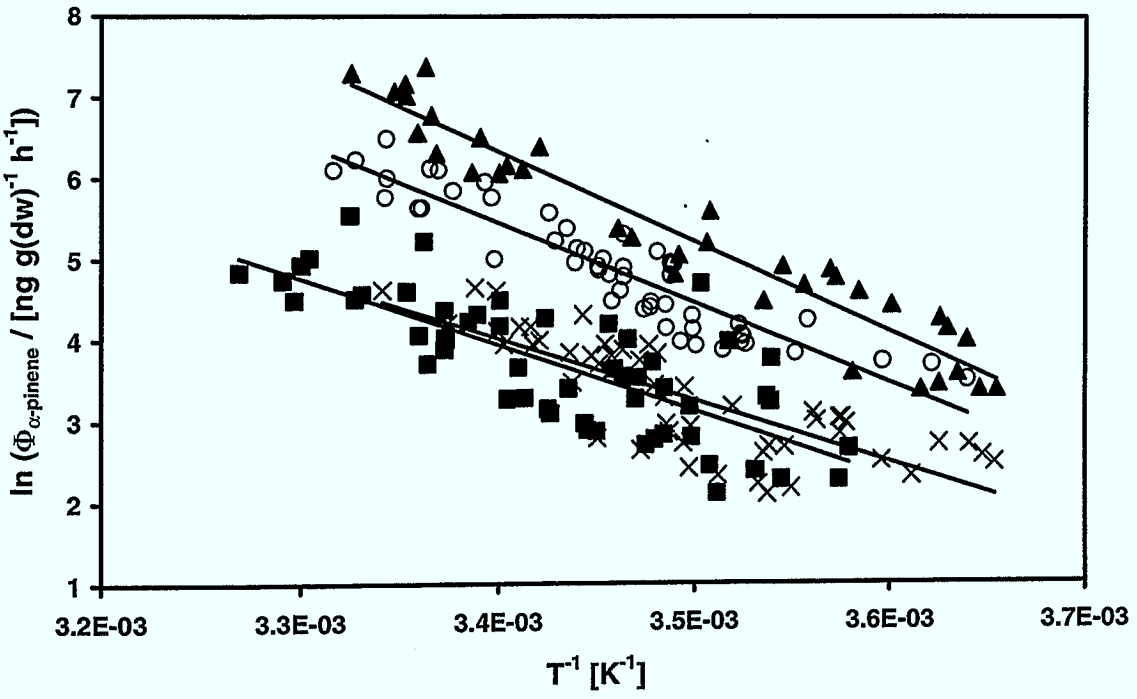


**Figure 4.15:** *Logarithmic plot of the emission rates of α-pinene versus inverse temperature measrued at branch A at different times of year. Solid triangles: April 28-30, filled squares: July 7-10, open circles: September 16-19, crosses: October 20-23. Lines: Regression lines after least square fit to each data set.*

The lines in this plot are least-square fits to the data obtained during each campaign. Both the slopes and the intercepts of the four fits varied by a factor of 1.5. The data obtained in July and October matched very well, but for the other two campaigns the fits seemed to be shifted to higher emission rates.

Table 4.9 summarizes the results for $c_{TP}\ R^{-1}$, obtained from fits to the data, for all monoterpenes measured at branch A between April and October 1998. Also shown is the

seasonal range of values for $c_{TP}\ R^{-1}$. For the three most abundant monoterpenes (3-carene, α-pinene and β-pinene) the seasonal variation of the obtained data for $c_{TP}\ R^{-1}$ is shown in Figure 4.16. The error bars in this plot are 1σ of the values obtained from the fits to each data set.

**Table 4.9:** *Temperature dependence of monoterpene emissions from branch A at different times of year. Data for $c_{TP}\ R^{-1}$ ± standard deviation in $10^3$ K obtained from linear regression of ln Φ versus $T^{-1}$.*

| | April 28-30 | July 7-11 | September 16-19 | October 20-23 | Range |
|---|---|---|---|---|---|
| 3-carene | 13.6 ± 0.5 | 9.1 ± 1.4 | 11.6 ± 0.7 | 12.1 ± 1.5 | 9.1-13.6 |
| α-pinene | 11.1 ± 0.5 | 8.1 ± 0.9 | 9.9 ± 0.6 | 7.6 ± 0.8 | 7.6-11.1 |
| β-pinene | 12.0 ± 0.7 | 8.3 ± 1.2 | 11.3 ± 0.6 | 7.9 ± 1.0 | 7.9-12.0 |
| camphene | 9.4 ± 0.5 | 6.1 ± 1.2 | 8.9 ± 0.6 | 5.5 ± 0.7 | 5.5-9.4 |
| β-myrcene | 9.0 ± 0.9 | 8.7 ± 1.6 | 11.1 ± 1.3 | 7.8 ± 1.0 | 7.8-11.1 |
| sabinene | 8.0 ± 0.5 | 5.5 ± 1.1 | 10.1 ± 0.9 | 4.0 ± 1.1 | 4.0-10.1 |
| limonene | 5.8 ± 0.5 | 5.4 ± 1.4 | 9.9 ± 0.8 | 6.7 ± 1.0 | 5.4-9.9 |
| β-phellandrene | 10.7 ± 0.6 | 4.5 ± 1.1 | 11.3 ± 0.7 | 9.4 ± 1.2 | 4.5-11.3 |
| γ-terpinene | 7.7 ± 0.8 | 7.0 ± 2.3 | 10.7 ± 1.0 | 5.9 ± 0.7 | 5.9-10.7 |
| p-cymene | 8.7 ± 0.7 | 6.0 ± 1.4 | 9.6 ± 0.8 | 6.3 ± 0.8 | 6.0-9.6 |
| 1,8-cineole | 15.8 ± 0.6 | 14.3 ± 1.7 | 18.7 ± 1.5 | 8.5 ± 1.3 | 8.5-18.7 |

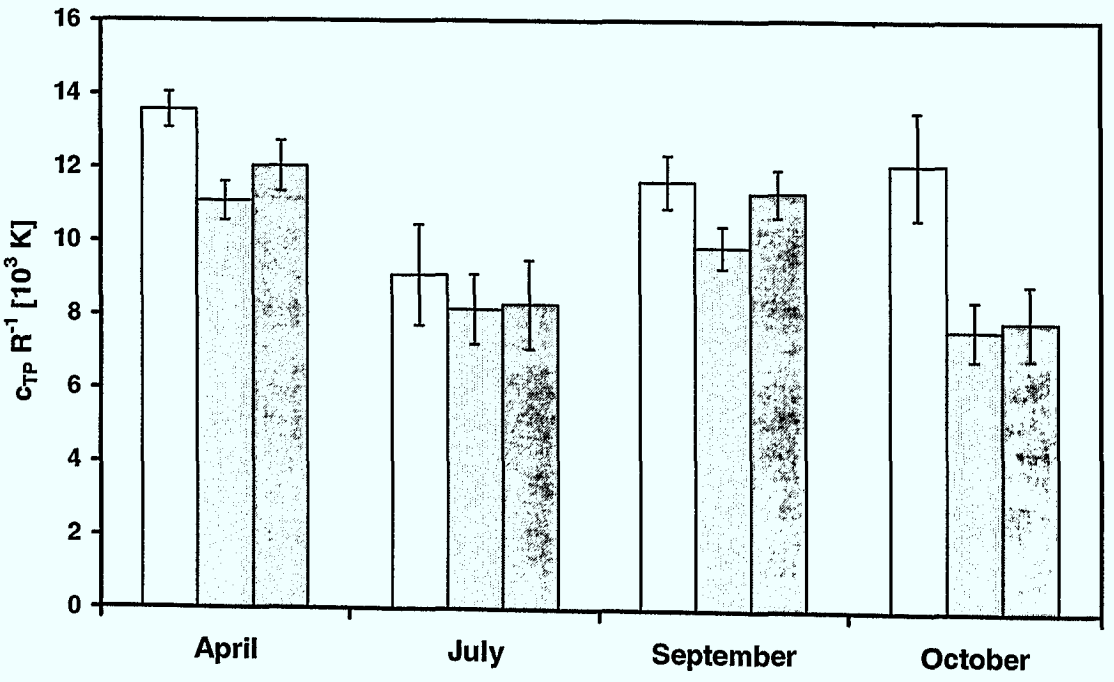


**Figure 4.16:** *Values for the parameters describing the temperature dependence of emissions $c_{TP}\ R^{-1}$ for the three most abundant monoterpenes (white: 3-carene, grey: α-pinene, dark grey: β-pinene) measured at branch A at different times of year. The error bars are the 1σ-errors of the linear regression.*

The range of the parameter describing the functional dependence of monoterpene emissions on temperature was very similar for all monoterpenes. On average, the values varied by roughly a factor of 2 between $6.4 \cdot 10^3$ and $10.9 \cdot 10^3$ K. No seasonal trend was observed in the values of $c_{TP}\, R^{-1}$.

Data for the standard emission rates of monoterpenes were obtained from the same fits. Table 4.10 summarizes the results of $\Phi^S$ for the measurements at branch A at different times of the year. For the three most abundant monoterpenes, the seasonal changes in the standard emission rates are also shown in Figure 4.17.

**Table 4.10:** *Standard VOC emission rates, $\Phi^S$ in ng g(dw)$^{-1}$ h$^{-1}$, from branch A measured at different times of year. Data was obtained from the linear regression of ln $\Phi$ versus $T^{-1}$.*

| | **April 28-30** | **July 7-11** | **September 16-19** | **October 20-23** |
|---|---|---|---|---|
| 3-carene | 1725 ± 82 | 85 ± 17 | 412 ± 34 | 122 ± 20 |
| α-pinene | 917 ± 58 | 75 ± 12 | 361 ± 28 | 78 ± 11 |
| β-pinene | 832 ± 64 | 28 ± 6 | 173 ± 13 | 29 ± 5 |
| camphene | 63 ± 4 | 10 ± 3 | 37 ± 3 | 10 ± 2 |
| β-myrcene | 64 ± 8 | 15 ± 4 | 30 ± 5 | 7 ± 1 |
| Sabinene | 41 ± 3 | 14 ± 4 | 19 ± 2 | 5 ± 2 |
| limonene | 40 ± 5 | 5 ± 2 | 13 ± 1 | 4 ± 1 |
| β-phellandrene | 34 ± 3 | 3 ± 1 | 10 ± 1 | 3 ± 0.5 |
| γ-terpinene | 23 ± 3 | 4 ± 2 | 5 ± 1 | 2 ± 0.4 |
| p-cymene | 25 ± 3 | 5 ± 2 | 11 ± 1 | 4 ± 1 |
| 1,8-cineole | 68 ± 4 | 48 ± 8 | 27 ± 3 | 2 ± 0.4 |
| Sum of monoterpenes | 3739 ± 120 | 240 ± 22 | 1061 ± 47 | 260 ± 24 |
| Temperature range, °C | 0-29.5 | 5.0-35.3 | 1.0-29.5 | 0-28.7 |

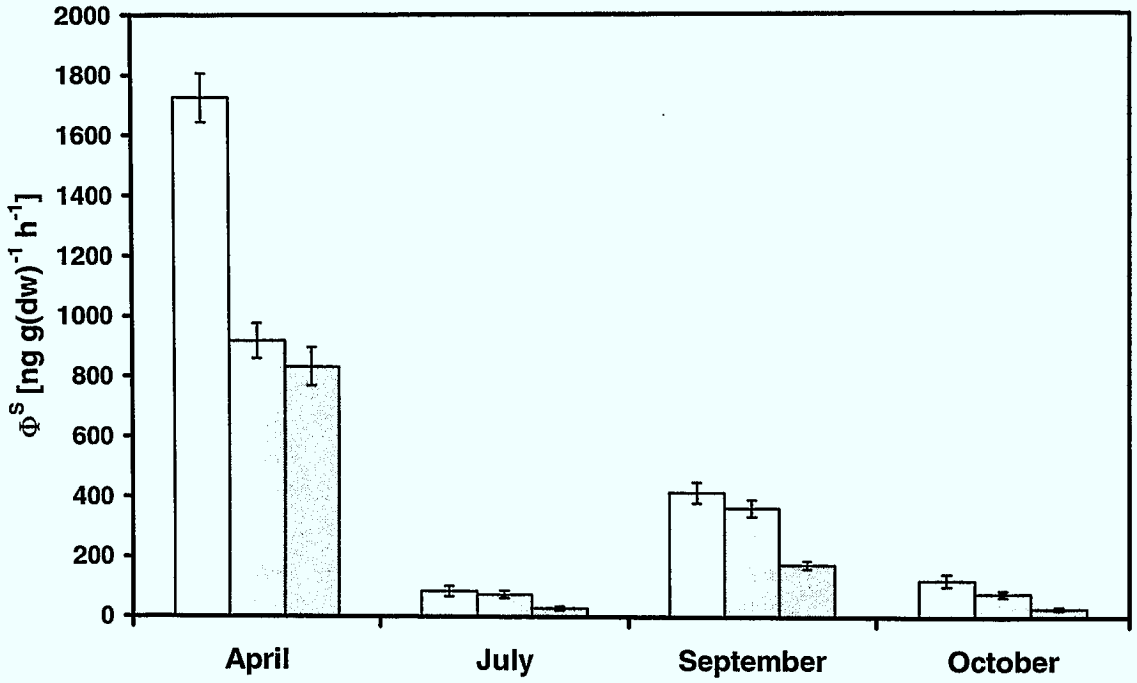


**Figure 4.17:** *Values for the temperature normalized standard emission rate $\Phi^S$ for the three most abundant monoterpenes (white: 3-carene, grey: α-pinene, dark grey: β-pinene) measured at branch A at different times of the year. The error bars are the 1σ-errors of the linear regression.*

The standard emission rates, $\Phi^S$, varied by up to a factor of 30 (β-pinene, dark grey bars in Figure 4.17). For all investigated monoterpenes, the highest standard emission rates were found in April and the lowest standard emission rates were found in July. The sum of standard emission rates of monoterpenes decreased by more than one order of magnitude from April (3739±120 ng g(dry weight)$^{-1}$ h$^{-1}$) to its lowest value in July (240±22 ng g(dry weight)$^{-1}$ h$^{-1}$) and then increased by a factor of 4 in September (1061±47 ng g(dry weight)$^{-1}$ h$^{-1}$). Within the detection limits, the sum of standard emission rates observed in October (260±24 ng g(dry weight)$^{-1}$ h$^{-1}$) was identical to the value observed in July. The standard emission rate of α-pinene varied by more than one order of magnitude between 75 and 917 ng g(dry weight)$^{-1}$ h$^{-1}$. The only compound that showed a pronounced seasonal trend wais 1,8-cineol. Emission rates were highest in April (68 ng g(dry weight)$^{-1}$ h$^{-1}$) and declined continuously until October (2 ng g(dry weight)$^{-1}$ h$^{-1}$).

Table 4.11 summarizes the percent contributions of individual monoterpenes to the sum of emitted monoterpenes measured at branch A between April and October. Also shown also is the mean value for the four field campaigns and the standard deviation.

**Table 4.11:** *Contribution of individual monoterpenes to the sum of monoterpenes in % and mean value ± standard deviation for measurements at branch A at different times of year.*

| | April 28-30 | July 7-11 | September 16-19 | October 20-23 | Mean |
|---|---|---|---|---|---|
| 3-carene | 46 | 35 | 39 | 47 | 42 ± 5.6 |
| α-pinene | 25 | 31 | 34 | 30 | 30 ± 4.0 |
| β-pinene | 22 | 12 | 16 | 11 | 15 ± 5.1 |
| camphene | 1.7 | 4.2 | 3.4 | 3.7 | 3.3 ± 1.1 |
| β-myrcene | 1.7 | 6.4 | 2.8 | 2.8 | 3.4 ± 2.1 |
| sabinene | 1.1 | 5.9 | 1.8 | 1.9 | 2.7 ± 2.2 |
| limonene | 1.1 | 2.3 | 1.2 | 1.5 | 1.5 ± 0.5 |
| β-phellandrene | 0.9 | 1.4 | 0.9 | 1.0 | 1.1 ± 0.2 |
| γ-terpinene | 0.6 | 1.6 | 0.5 | 0.8 | 0.9 ± 0.5 |

3-carene was always the monoterpene with the largest contribution to the sum of monoterpene emissions, followed by α-pinene and β-pinene. On average, 42 % of the emitted mass of monoterpenes were emitted as 3-carene, 30 % as α-pinene and 15 % as β-pinene. The average contribution of all the other monoterpenes was smaller than 5 % each. There was no clear trend in the composition of emissions. Changes in the composition of monoterpene emissions from the same branch at different times of year were small compared to the variations of the absolute amount of emissions.

### *4.4.3 Branch-to-branch variability of emissions*

The variability of monoterpene emissions from different branches of the same plant was tested by enclosing a second branch (branch B, see Table 4.2) in a separate enclosure chamber during the last three campaigns. Table 4.12 summarizes the values obtained for $\Phi^S$; the sum of the standard emission rates of monoterpenes are shown in Figure 4.18

**Table 4.12:** *Standard VOC emission rates, $\Phi^S$ in ng g(dw)$^{-1}$ h$^{-1}$, measured at two different branches of a mature Scots pine at different times of year. Data obtained from the linear regression of ln $\Phi$ versus inverse temperature.*

| | July 7-11 | | September 16-19 | | October 20-23 | |
|---|---|---|---|---|---|---|
| | Branch A | Branch B | Branch A | Branch B | Branch A | Branch B |
| 3-carene | 85 ± 17 | 124 ± 19 | 412 ± 35 | 223 ± 31 | 122 ± 20 | 119 ± 11 |
| α-pinene | 75 ± 12 | 85 ± 13 | 361 ± 28 | 190 ± 31 | 78 ± 11 | 77 ± 10 |
| β-pinene | 28 ± 6 | 36 ± 7 | 173 ± 13 | 97 ± 18 | 30 ± 5 | 31 ± 6 |
| Camphene | 10 ± 3 | 14 ± 2 | 37 ± 4 | 23 ± 6 | 10 ± 2 | 10 ± 3 |
| β-myrcene | 15 ± 4 | 13 ± 2 | 30 ± 5 | 24 ± 7 | 7 ± 1 | 9 ± 9 |
| sabinene | 14 ± 4 | 14 ± 3 | 19 ± 3 | 43 ± 32 | 5 ± 2 | 7 ± 4 |
| limonene | 6 ± 2 | 6 ± 1 | 13 ± 1 | 9 ± 4 | 4 ± 1 | 7 ± 1 |
| β-phellandrene | 3 ± 1 | 7 ± 3 | 10 ± 1 | 7 ± 2 | 3 ± 0.5 | 2 ± 1 |
| γ-terpinene | 4 ± 2 | 4 ± 1 | 5 ± 1 | 7 ± 5 | 2 ± 0.4 | 3 ± 2 |
| p-cymene | 5 ± 2 | 5 ± 1 | 11 ± 1 | 8 ± 3 | 4 ± 1 | 7 ± 2 |
| 1,8-cineole | 48 ± 8 | 43 ± 6 | 27 ± 3 | 16 ± 2 | 2 ± 0.4 | 2 ± 1 |
| Sum of monoterpenes | 240 ± 22 | 302 ± 25 | 1061 ± 47 | 624 ± 59 | 260 ± 24 | 266 ± 19 |

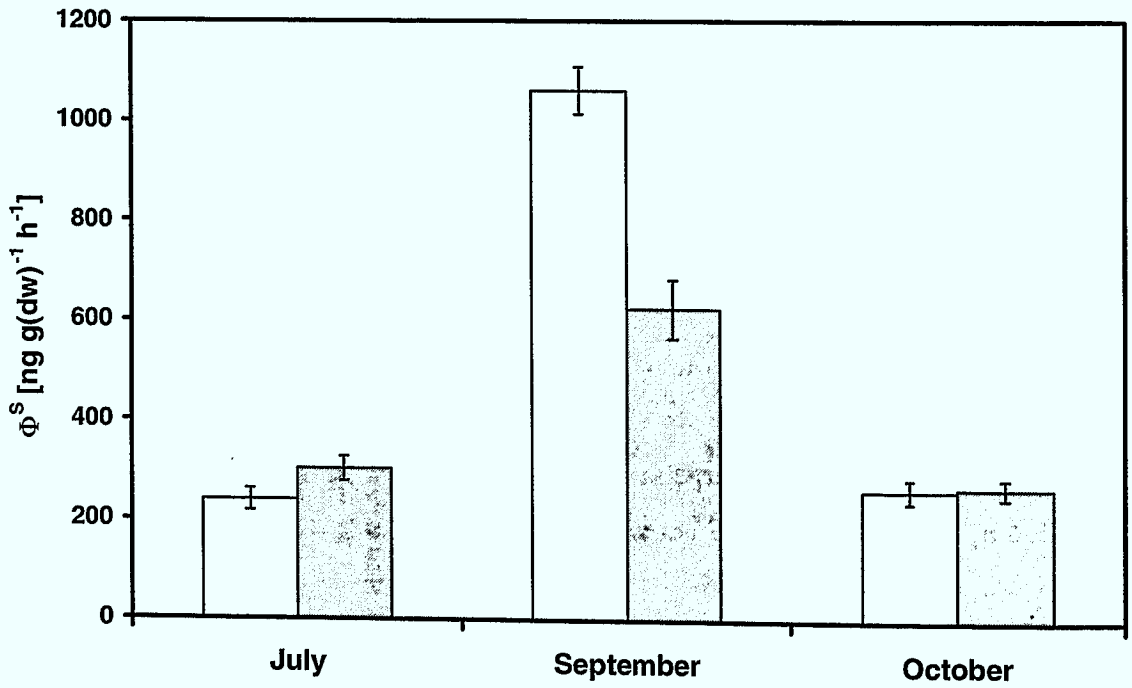


**Figure 4.18:** *Calculated standard emission rates for the sum of monoterpenes measured at two different branches of an adult pine (white bars: branch A, grey bars: branch B) at different times of year. The error bars are the 1σ-error after linear regression.*

In July and October the standard emission rates, $\Phi^S$, of all individual monoterpenes measured at the two branches were similar within one standard deviation. The only exceptions were the emission rates of 3-carene in July, when emissions from branch B

were significantly higher than those from branch A. In September, the standard emission rates calculated for the measurements at branch B were approximately a factor of 2 greater than those measured in July. An increase in the emissions between July and September was also observed for branch A. Here, the standard emission rate of the sum of monoterpens increased by a factor of 4. In September, emissions from branch A were almost twice as high as those from branch B.

Table 4.13 contains the percent contributions of individual monoterpenes to the sum of monoterpene emissions measured at branches A and B. The average contributions of measurements at different times of year and the corresponding standard deviation are shown here.

**Table 4.13:** *Contribution of individual monoterpenes to the sum of monoterpene emissions in % from two separate branches of the same pine tree. Given here are the average values of measurements at different times of year ± standard deviation.*

| | **Branch A** | **Branch B** |
|---|---|---|
| 3-carene | 42 ± 5.6 | 41 ± 4.6 |
| α-pinene | 30 ± 4.0 | 29 ± 1.1 |
| β-pinene | 15 ± 5.1 | 13 ± 2.3 |
| camphene | 3.3 ± 1.1 | 4.0 ± 0.4 |
| β-myrcene | 3.4 ± 2.1 | 3.9 ± 0.4 |
| sabinene | 2.7 ± 2.2 | 4.8 ± 2.1 |
| limonene | 1.5 ± 0.5 | 2.0 ± 0.6 |
| β-phellandrene | 1.1 ± 0.2 | 1.4 ± 0.8 |
| γ-terpinene | 0.9 ± 0.5 | 1.1 ± 0.2 |

The composition of monoterpene emissions from two different branches of the same tree was identical within one standard deviation of measurements at different times of the year.

# 5 Discussion

In this chapter, the results of the different emission rate measurements with Scots pines are discussed. The discussion focusses on the following questions:

- Are emission rate measurements conducted at the same branch of the same plant reproducible, and lead to similar results under similar conditions for temperature and light intensity, or is there a seasonal variation in the emission rates?
- Is there a variation in the emissions from different parts of the same plant and how large is this branch-to-branch variation?
- Is it necessary to investigate the emissions from more than one individual plant and how large is this plant-to-plant variability in emission rates?
- Is the age of the investigated plant relevant, or are emission rates from young and adult Scots pines similar?
- Are laboratory measurements a useful tool to predict emission rates, or do they lead to significantly different results compared to outdoor emission measurements?

The results are compared to those reported in the literature and used to estimate monoterpene fluxes from the Hartheimer Wald.

## 5.1 Seasonal variability of emission rates

The seasonal variability of emission rates was investigated by measuring the emissions from the same branch of the same adult pine between April and October 1998. The growth of the branch during the course of the year was taken into account for the normalization to the dry weight of needles. Since the seasonal cycles of monoterpenes and 1,8-cineol emissions differ, the emissions of these compounds are discussed separately.

### *5.1.1 Monoterpenes*

The standard emission rates of monoterpenes, $\Phi^S$, measured at branch A varied by more than one order of magnitude between April and October, but did not show any significant seasonal trend (Table 4.10, page 83). In general, the highest emission rates were measured in April. Standard emission rates of monoterpenes were about one order of magnitude lower in July, then increased in September by a factor of 4 and decreased in October to values comparable to those in July. Since the standard emission rates were already normalized to a specific temperature (in this case 25 °C) and since the temperature range was very similar during all four campaigns, temperature variations could not explain the observed differences.

Little is known about the seasonal variation of the standard emission rates of monoterpenes. *Janson* (1993) measured monoterpene emissions from Scots pine (*Pinus sylvestris*) at different times of year between May and October at four sites in Sweden. He found high standard emission rates in early May which decreased to the lowest measured values at end of May. In June and July standard emission rates were a factor of 3-4 higher than in the end of May and August. He speculated that emission rates of monoterpenes were enhanced during periods of active needle growth and monoterpene biosynthesis. Between April and July the biomass of branch A was more than doubled. Obviously, needle growth predominantly occurred in spring. Since in newly developed needles the monoterpene pools have to be filled, the assumption of Janson seems plausible. This is a possible explanation for the much higher emission rates in April compared to other times of year.

Nevertheless, this does not give an explanation for the increase in standard emission rates between July and September. Stress to plants is known to have a possible influence on monoterpene emissions. From July to September, some needles of the investigated branch became yellow, an observation that supports the idea that the plant suffered from stress. Although in this case the specific cause is unknown, the reasons can be speculated, which is done in the following.

*Kainulainen et al.* (1998) and *Lindskog and Potter* (1995) investigated the influence of elevated ozone concentrations and found no significant increase in monoterpene emissions after ozone fumigation of Scots pine (*Pinus sylestris*) and Norwegian spruce (*Picea abies*). Therefore, it is unlikely that high ozone concentrations can be used as an explanation.

*Bertin and Staudt* (1996) investigated water stress effects on monoterpene emissions from Holm oak (*Quercus ilex*) and reported a decrease in monoterpene emissions after a long period of drought. Although there was no rainfall during the campaigns, there was sufficient rain two weeks prior to each experiment (Figure 8.2 a-d, Appendix). Therefore, stress due to drought is also unlikely.

In studies with young Scots pine seedlings, elevated temperatures were observed as stress factors leading to an increase in monoterpene emissions (J. Wildt, private communication). The increase in emissions observed in these studies was of the same order of magnitude as the increase in the standard emission rates observed between July and September for the study described here. However, during the experiments in September, only temperatures below 30°C were observed and also in the four week period prior to the campaign temperatures did not exceed this value (Figure 8.3 a-d). Temperatures were lower on average than those measured during the field campaign in July when lower standard monoterpene emission rates were calculated. Therefore, it is unlikely that temperature stress can explain the elevated standard emission rates observed in September.

Under mechanical stress plants have been observed to emit higher amounts of monoterpenes (*Juuti et al.*, 1990; *Yatagai et al.*, 1995). *Juuti et al.* (1990) report an increase in monoterpene emission rates by factors of 10-50 during rough handling of Monterey pine (*Pinus radiata*) in their enclosure system. 1-2 hours after the 'contact stimulation', emission rates decreased to within the normal range. The mounting procedure was similar during each campaign and the branch was not treated differently in September. The sampling began at least 12 hours after mounting the branch inside the enclosure. Therefore, it can be assumed that the plant did not suffer from mechanical stress during the experiment.

Under pathogen (J. Wildt, unpublished data) and herbivory attack (*Turlings and Tumlinson*, 1992; *Priemé et al.*, 2000) plants have been observed to emit higher amounts of monoterpenes. Although no pathogens or herbivory were observed on the investigated branches, it can not be excluded that other parts of the tree were not affected. The plant-herbivory defense mechanism by release of monoterpenes has been observed to be systemic, i.e. not only by the part of the plant under attack, but by the whole organism (*Turlings and Tumlinson*, 1992; *Röse et al.*, 1996; *Paré and Tumlinson*, 1997a, 1997b, 1998). Since it cannot be excluded that branches other than the investigated were under

attack, a pathogen or herbivory attack is one possible explanation for the increase in the emission rates.

In summary, from the results discussed here it cannot be concluded that there exists a seasonal cycle of monoterpene emission rates from Scots pine. If one does exist, it is at least superimposed on top of stress effects that make the detection of a seasonal cycle difficult. In either case, the results show that similar environmental conditions do not necessarily lead to the same emission rates. The emission rates are also dependent on other parameters such as stress, and the 'history' of a plant also has an influence on the emissions.

### *5.1.2 1,8-Cineol*

The seasonal variation of 1,8-cineol emission was different than those of monoterpenes (Table 4.10, page 83). 1,8-cineol was the only investigated compound that showed a pronounced seasonal trend with maximum standard emission rates in spring which continuously declined to lower values through October. Unlike all the monoterpenes, the standard emission rates did not increase in September. Two possible explanations for this observation are given here: 1,8-cineol is either emitted from Scots pine by a different mechanism than the monoterpenes, or it is mostly produced in young needles and as the newly developed needles mature during the course of the year, the emission rates decrease.

The latter hypothesis was corroborated by a result reported by *Street et al.* (1997). They investigated VOC emissions from young and adult Eucalyptus trees (*Eucalyptus globulus*). They found only nondectectable or low 1,8-cineol emissions from the older vegetation (average value: 4 ng $g(dw)^{-1}$ $h^{-1}$), but it was the second highest emission from young trees (average value: 1671 ng $g(dw)^{-1}$ $h^{-1}$).

However, the available data set was insufficient to give a complete explanation for the observation.

## 5.2 Branch-to-branch variability of emissions

The branch-to-branch variability of monoterpene emissions was investigated by measuring the emission rates from two different branches of the same tree at the same time with two outdoor enclosure systems. The composition of monoterpene emissions, averaged over the course of the year was found to be similar for the selected branches (Table 4.13, page 87). Different branches of the same plant emitting an identical group of monoterpenes is a strong indication that the needle oil composition is also identical within the specific plant. Therefore, the pattern of emitted monoterpenes can be seen as a 'fingerprint' for an individual plant.

Surprisingly, during two of the three campaigns, the absolute amount of emissions was very similar (July: 240±22 and 302±25 $\mu g\ g(dw)^{-1}\ h^{-1}$, October: 260±24 and 266±19 $\mu g\ g(dw)^{-1}\ h^{-1}$ from branch A and B, respectively). Since these were the measurements with the lowest emission rates (see Table 4.12), it was speculated that these measurements were conducted under stress-free conditions. In September, on the other hand, emission rates were higher from both branches (1061±47 and 624±69 $\mu g\ g(dw)^{-1}\ h^{-1}$ from branch A and B, respectively), but the rate of increase in emissions was different for the two branches (branch A: a factor of 4, branch B: a factor of 2). The increase in the emission rates between July and September was probably a result of stress. Indeed, between July and September some needles on both branches turned yellow, a possible indicator of stress. The reason for the differences in the rates of increase can only be speculated. Maybe, the position or composition of the branches had an impact on this rate. Branch A was a sunlit branch located at the canopy top and had a larger contribution from newly developed needles to the total needle mass (63 % compared to 48 % for branch B). Branch B was located below branch A in the shadow of the canopy. Unfortunately, the amount of needles that turned yellow between summer and fall was not calculated. Differences in the amount of yellow needles were another possible explanation for the observed differences.

All in all, branch-to-branch variations of monoterpene emissions were much smaller both in composition and in amount than plant-to-plant variations that will be discussed below. The general result with regard to future outdoor enclosure measurements is that the emission rates of only one branch of a tree have to be investigated to get a measure of the emissions of that specific tree.

## 5.3 Plant-to-plant variability of emission rates

In order to estimate plant-to-plant variability in emission rates of monoterpenes, experiments were conducted under similar conditions with 8 different individual plants. These plants were of the same age and origin, and were treated equally during the measurements. In comparing the results of these emission rate measurements, the following features were the most striking:

- The standard emission rates, $\Phi^S$, of monoterpenes from different plants were highly variable, with variations of up to one order of magnitude (Table 4.7, page 73).
- The composition of emitted monoterpenes was highly variable from plant to plant (Table 4.8, page 74).
- The spectrum of emitted monoterpenes changed during stress situations, but this change was smaller than the plant-to-plant variation.

The literature gives no satisfactory explanations for these findings. In the following sections, possible explanations are given for these results that are in agreement with recent publications.

### *5.3.1 Composition of monoterpene emissions*

Probably the most interesting and unexpected result was the large plant-to-plant variation in the spectrum of emitted monoterpenes (Table 4.8, page 74). Especially surprising was the observation that one of the plants did not emit 3-carene in significant amounts (< 1 ng $g(dw)^{-1}$ $h^{-1}$, equal to 0.1 % of the total sum of monoterpene emissions), which was one of the major constituents in the emissions of the other plants. These observations were not only made with young Scots pines originating from the Hartheimer Wald, but also with adult plants at that location. Investigations of monoterpene emission rates from branches of two different adult pines showed that one of the pines emitted 3-carene and the other did not (C. Holzke, private communication, data to be published).

There are two possible explanations for the observed differences in the composition of the gas-phase emissions. Either the composition of the needle oil itself shows similar

differences from plant to plant, or the needle oil has an identical composition in each plant and differences in the gas-phase emissions are a result of differences in the emission process. The latter hypothesis seems to be unlikely, because differences in the emission process would require differences in plant to plant morphology. Unfortunately, the needle oil composition of the pines, with which the emission rate measurements have been conducted, has not been investigated to corroborate the first theory. Therefore, no conclusive answer can be given here and reasons for the observed differences can only be speculated.

As already pointed out, each monoterpene is synthesized by a specific enzyme (chapter 2.1.2). Differences in the monoterpene composition of the needle oil, and differences in gas-phase emissions might be attributed to differences in enzyme activity or enzyme composition. If in one plant the 3-carene synthesizing enzyme was inactive or absent, this plant could not emit 3-carene. Since the presence of enzymes is genetically controlled, the difference in monoterpene composition could be the result of genetic differences. Such a large intra-specific variability in monoterpene composition as observed during the experiments described here has not been reported in the literature. In general, each species of tree is believed to have its own distinctive leaf-oil composition (e.g. *Schindler and Kotzias*, 1989; *Roussis et al.*, 1995).

*Von Rudloff and Lapp* (1992) investigated the needle oil terpene composition of Ponderosa pine (*Pinus ponderosa*) from various sites in the U.S. They report that investigations of the leaf oil composition of three to five trees from the same location provided almost identical data. Even for trees from different sites, they found only small variations. Major components of the leaf oil were β-pinene, α-pinene and 3-carene with contributions between 54.6-61.7 %, 11.4-14.8 %, and 7.5-13.2 %, respectively.

So, either the intra-specific variation of the monoterpene composition of the needle oil is significantly higher for Scots pine (*Pinus sylvestris*) than reported in the literature for other pine species, or the differences in the gas-phase emissions are induced by other factors. The results presented here indicate that the monoterpene fingerprint is only specific for a single plant and not for the whole species.

It should be noted, that the composition of emitted monoterpenes can change, for example as a result of stress. Table 5.1 shows the standard emission rates before and after a stress episode (probably induced by high temperatures) and the corresponding rate of increase.

**Table 5.1:** *Temperature normalized standard emission rates, $\Phi^S$, observed before and after temperature-induced stress episode at pine No. 5 and rate of increase.*

| | $\Phi^S$, ng g(dw)$^{-1}$ h$^{-1}$ Before stress | $\Phi^S$, ng g(dw)$^{-1}$ h$^{-1}$ After stress | Rate of Increase |
|---|---|---|---|
| α-pinene | 168 ± 7.5 | 542 ± 43 | 3.2 ± 0.3 |
| limonene | 56 ± 3.9 | 108 ± 16 | 1.9 ± 0.3 |
| β-phellandrene | 19 ± 1.5 | 37 ± 8.2 | 2.0 ± 0.5 |
| β-pinene | 16 ± 1.2 | 79 ± 9.4 | 4.9 ± 0.7 |
| camphene | 8.8 ± 1.2 | 36 ± 7.7 | 4.1 ± 1.0 |
| β-myrcene | 6.9 ± 0.7 | 20 ± 3.0 | 2.8 ± 0.5 |
| 1,8-Cineol | 2.7 ± 0.8 | 1.8 ± 3.1 | 0.7 ± 1.2 |
| sabinene | 2.2 ± 0.4 | 1.7 ± 5.9 | 0.8 ± 2.7 |
| 3-carene | 0.4 ± 0.2 | 0.5 ± 1.9 | 1.3 ± 4.6 |
| Sum | 280 | 827 | Average: 2.9 |

As can be seen, the rate of increase was different for each monoterpene. Whereas the standard emission rate of β-pinene showed the highest increase in emission rate (factor of 4.9), 1,8-cineol, sabinene and 3-carene emission rates did not change significantly during the experiment.

Stress is a possible explanation for different rates of increases in emissions. Since each monoterpene is produced by a specific enzyme, a stress effect may have different impacts on the different enzymes. For example, the enzymes could be variably sensitive to high temperature. The different rates of increases in emissions can also be explained as a result of herbivory attack. *Turlings and Tumlinson* (1992) reported an increase in some terpenoid emissions after herbivory attack. *Supuka et al.* (1997) investigated the composition of terpenes in needles of Black Pine (*Pinus nigra* Arnold) grown in different environments. They reported differences in terpene composition of the needle oil as a result of air pollution, i.e. environmentally induced differences. It should be noted, that in the study presented here changes in the spectrum of emitted monoterpenes due to stress were small compared to the observed plant-to-plant variability of monoterpene spectra.

In summary, it can be said that the observed emission pattern of monoterpenes is most likely the result of two effects, a genetic and an environmentally induced effect. The overall monoterpene composition seems to be under genetic control, but environmental conditions (such as stress) could change this pattern. From the results shown here, it seems to be difficult to tell different pine species apart by the composition of their monoterpene emissions.

The results shown in Table 5.1 were also interesting from another point of view, because they were contradictory to the generally accepted model of monoterpene storage and emission from conifers given by *Tingey et al.* (1991). If monoterpenes are stored in the resin ducts of needles and are emitted exclusively by evaporation out of these resin ducts, these results cannot be explained by this model. The monoterpene pools are large compared to the amount of monoterpenes emitted during one year and if an evaporation process is the only source of emissions, the composition of emitted monoterpenes cannot change. On the other hand, the model behind the algorithm by *Schuh et al.* (1997) also implies a role of monoterpene biosynthesis in the emission process. From the results shown above, it can be speculated that stress induced additional biosynthesis of specific monoterpenes leading to an increase in standard emission rates and to a change in composition of the emission spectrum. Nevertheless, the latter algorithm was not capable of quantitatively describing changes in composition and amount of monoterpene emissions as a result of stress.

### *5.3.2 Amount of monoterpene emissions*

Of great interest is the large variability of standard emission rates of more than one order of magnitude, especially with regard to estimates of monoterpene fluxes to the atmosphere. These large variations are not yet understood and therefore cannot be described by any of the current algorithms. An important observation is that variations in monoterpene emission rates from the same plant measured at different times were on the same order of magnitude as from measurements with different individual plants. This strongly indicates that these variations are not under genetic control, but induced by environmental factors. From the results it was plausible that stress to the plant (as discussed above) was one of these environmental factors. Nevertheless, it was not possible to describe the effect of stress on monoterpene emission rates quantitatively.

## 5.4 Comparison of VOC emission rates from young and adult pines

In general, monoterpene emissions from young and adult Scots pines showed the same depedence on ambient parameters, i.e. an Arrhenius type dependence on temperature and a non-detectable influence from light under ambient conditions, confirming the results reported in the literature (e.g., *Tingey et al.*, 1980; *Lamb et al.*, 1985; *Juuti et al.*, 1990). Table 5.2 compares the observed plant-to-plant range of monoterpene emissions from plants of the same age with the seasonal range from the branch of an adult plant (branch A).

**Table 5.2:** *Temperature dependence, $c_{TP}\,R^{-1}$, in [$10^3$ K] and standard emission rate, $\Phi^S$ in [ng g(dw)$^{-1}$ h$^{-1}$], from young and adult Scots pine. For the young pines the range of measurements with 8 different individual pines is shown, for the adult pines the seasonal range of measurements at branch A between July and October is shown, the numbers in bracktes are values obtained from measurements in April.*

| | $c_{TP}\,R^{-1}$ [$10^3$ K] | | $\Phi^S$ [ng g(dw)$^{-1}$ h$^{-1}$] | |
|---|---|---|---|---|
| | **Young pines** | **Adult pine** | **Young pines** | **Adult pine** |
| α-pinene | 6.0-11.9 | 7.6-11.1 | 15-330 | 75-361 (917) |
| 3-carene | 7.3-13.8 | 9.1-13.6 | 0.3-313 | 85-412 (1725) |
| β-pinene | 5.6-13.9 | 7.9-12.0 | 5-104 | 28-173 (832) |
| sabinene | 6.3-13.3 | 4.0-10.1 | 1-31 | 5-14 (41) |
| β-myrcene | 5.4-11.3 | 7.8-11.1 | 2-23 | 7-30 (64) |
| camphene | 5.6-12.8 | 5.5-9.4 | 7-22 | 10-37 (63) |
| limonene | 5.0-12.7 | 5.4-9.9 | 1-17 | 4-13 (40) |
| β-phellandrene | 7.0-12.2 | 4.5-11.3 | 1-15 | 3-10 (34) |
| 1,8-cineol | 7.1-30.1 | 8.5-18.7 | 2-10 | 2-48 (68) |
| | | | 59-648 | 283-1077 (3784) |

The observed ranges of $c_{TP}\,R^{-1}$ were very similar for measurements with young and adult plants. No significant difference could be found. For monoterpenes the observed values for $c_{TP}\,R^{-1}$ were between $4.0 \cdot 10^3$ K and $13.9 \cdot 10^3$ K. Since most of the results reported in the literature did not make use of $c_{TP}\,R^{-1}$, but gave values for β using the simplified equation E2.2, values for $c_{TP}\,R^{-1}$ had to be converted into values for β by dividing by the standard temperature $T_S^2 = (298\text{ K})^2$. For T = 298 K the derived value of β was between 0.05 and 0.16 K$^{-1}$. *Guenther et al.* (1993) suggested a value of 0.09 K$^{-1}$ as a best estimate for all monoterpenes and plants which was within the range of the observations described here. In a more recent publication, *Rinne et al.* (2000) reported a value for β of 0.146 K$^{-1}$

for the temperature dependence of monoterpene emissions from *Pinus sylvestris*, which was also within the observed range, close to the upper limit.

It had to be taken into account that the first set of measurements conducted with the adult pine were conducted in April when comparing the ranges of standard emission rates. No measurements were performed with young pines at that time of the year. The standard emission rates obtained in April are given in brackets and the numbers given in the last column of Table 5.2 are the observed range of standard emission rates between July and October. Although the ranges of standard emission rates were very similar for young and adult pines, it has to be recognized that the range of $\Phi^S$ for measurements with young pines was at the lower end of the seasonal range of measurements with the adult plant, even if the measurements in April were not taken into account. The values for $\Phi^S$ obtained with the adult pine in April were significantly higher than the upper limit of the range of standard emission rates from young pines. For the sum of monoterpenes, the value was more than a factor of 5 higher than the upper limit of the range from young pines (3784 compared to 648 ng $g(dw)^{-1}$ $h^{-1}$). At this point, it could not be excluded that this difference was due to the fact that monoterpene emissions were increased at that time of year.

Table 5.3 compares the range of standard emission rates of monoterpenes observed within the scope of this study to results reported in the literature for Scots pine. Literature for this specific pine species is scarce and therefore only a small amount of data is available. It should be noted that standard emission rates from *Isidorov et al.* (1985) and *Staudt* (1997) were normalized to 30 °C, and those given by *Janson* (1993) to 20 °C. Since a 5 K difference in temperature has a substantial influence on the standard emission rate, the values given in the literature were converted into emission rates normalized to 25 °C. Equation E2.2 and a value of $\beta = 0.09\ K^{-1}$ was used for that conversion. The corresponding emission rates are given in brackets.

**Table 5.3:** *Comparison of standard emission rates of monoterpenes from Scots pine. Numbers in brackets were calculated for a temperature of 25 °C.*

| Emission rate [µg $g(dw)^{-1}$ $h^{-1}$] | Reference |
|---|---|
| 12.1[a] (7.7) | *Isidorov et al.*, 1985 |
| 0.8[b] (1.3) | *Janson*, 1993 |
| 6[a] (3.8) | *Staudt*, 1997 |
| 0.06-0.65[c] | This work, young pines |
| 0.24-3.7[c] | This work, adult pines |

[a] normalized to 30 °C; [b] normalized to 20 °C; [c] normalized to 25 °C.

The comparison of standard emission rates shows that for the young pines the observed range of emission rates was lower than the values reported in the literature. Only the standard emission rate of *Janson* (1993) was close to the upper limit of the observed range. Due to the much higher emission rates from branch A of the adult pine in April, the range of standard emission rates was closer to the values observed in other studies. Nevertheless, emission rates reported by *Staudt* (1997) and especially by *Isidorov et al.* (1985) were higher than the range of standard emission rates observed within this study. It cannot be excluded that stress to the plant or systematic differences in the normalization to needle weight were responsible for that difference.

In summary, there was no significant difference in the functional dependence of monoterpene emissions due to ambient parameters between young and adult Scots pines. Values for the parameter describing the temperature dependence of emissions matched well with those reported in the literature. The ranges of standard emission rates from young and adult pines overlapped, but emission rates from young pines were at the lower end of the range of standard emission rates from the adult plant. The temperature normalized emission rates were at the lower end of the range found in the literature.

## 5.5 Comparability of laboratory and outdoor emission studies

In order to ascertain the transferability of results from measurements conducted under controlled laboratory conditions to results obtained from outdoor enclosure studies, the general measurement techniques, i.e. the analytical and enclosure systems, have to be compared first. Emission rates from measurements with the same individual pines were also compared.

### *5.5.1 Comparability of measurement techniques*

The analytical aspect of the measurement systems were compared in the intercalibration experiment described in chapter 3.5. With the exception of sabinene, the mixing ratios of all monoterpenes, i.e. α-pinene, β-pinene, 3-carene, camphene and limonene, measured with both systems were identical within the detection limit (Table 3.8). The mixing ratio of sabinene measured with the outdoor system was approximately

50 % lower than measured with the laboratory system. Since the tested monoterpenes were the major emission products from Scots pine, a large bias in the absolute amount of emissions could be excluded for the individual compounds as well as for the sum of monoterpenes. For those individual monoterpenes, for which data are shown here, but which were not measured in the intercalibration experiment, i.e. β-myrcene, tricyclene, β-phellandrene and also 1,8-cineol, this assumption could not be made.

The enclosure systems used in the laboratory and in the field followed the same basic approach. The plant was placed inside a chamber which was continuously flushed with air. From the difference in concentrations of monoterpenes measured at chamber outlet and chamber inlet the emission rate was calculated. Both systems purified the air and monoterpene concentrations were reduced to concentrations below the detection limit at the chamber inlet. In both systems, ozone was catalytically destroyed at the chamber inlet.

One systematic difference between the systems was the concentration of nitrogen oxides. NO and $NO_2$ were removed from the inlet air stream by the adsorption dryer used in the laboratory. The air supply system of the outdoor enclosure system had no specific device to remove or measure $NO_x$. Concentrations of $NO_x$ inside the chamber were therefore unknown, but since ambient air was used to flush the chamber, $NO_x$ concentrations could not have exceeded ambient concentrations. In laboratory experiments, NO and $NO_2$ were added to the inlet air stream at mixing ratios of between 50 and 100 ppb to test their influence on monoterpene emissions. No changes in monoterpene emission rates from Scots pine were observed (J. Wildt, private communication).

Another difference between the systems was the light source. During the outdoor enclosure studies the sun provided irradiation of the plant during the day. The FEP foil used as a chamber material had 90-95 % light transmission at photosynthetic relevant wavelengths between 400-700 nm and more than 80 % light transmission at wavelengths of $\lambda > 270$ nm. In the laboratory, discharge lamps (Osram HQI 400 W/D) were used for illumination. Filters that reflect light at wavelengths between 750 and 1050 nm were placed between the lights and the plant chamber to avoid radiative overheating. The plant chamber itself consisted of glass which was not transparent for light at wavelengths $\lambda < 340$ nm. Thus, there were no significant differences in light at photosynthetic relevant wavelengths, but UV radiation, that is a potential stress to the plant, was absent inside the chamber. Effects of UV radiation on biogenic VOC emissions are unknown.

### *5.5.2 Comparison of standard emission rates*

Table 5.4 summarizes the results of the emission rate measurements conducted alternately under laboratory and outdoor enclosure conditions with the same individual pines. Shown here are values for the temperature normalized standard emission rates, $\Phi^S$. Emission rates were normalized to identical values for the needle dry weight. For plants that were investigated more than once, the range of observed standard emission rates is shown. Pines No. 6 and 7 were enclosed together at the same time during the laboratory studies. To make this result comparable to the outdoor measurements that were conducted with the pines individually, the average value of the individual measurements was calculated for the outdoor enclosure measurements and weighted by the dry weight of needles of the individual pines.

**Table 5.4:** *Standard emission rates $\Phi^S$ in [ng g(dw)$^{-1}$ h$^{-1}$] from laboratory and outdoor studies with the same individual pines. b.l. = below detection limit. For plants that had been measured once, the 1 $\sigma$ error is shown, for plants that have been studied more than once, the range of $\Phi^S$ observed is shown.*

| | No. 5 | | No. 6 + 7 | | No. 8 | |
|---|---|---|---|---|---|---|
| | **Laboratory** | **Outdoor** | **Laboratory** | **Outdoor*** | **Laboratory** | **Outdoor** |
| α-pinene | 190 ± 97 | 165-330 | 16 ± 3.7 | 19 ± 1.5 | 19-152 | 35-134 |
| 3-carene | 0.02±0.06 | 0.3-0.6 | 21 ± 13 | 22 ± 1.4 | 11-326 | 50-313** |
| β-pinene | 15 ± 8.1 | 8.6-32 | 6.0 ± 1.6 | 5.5 ± 0.7 | 8.2-98 | 18-104 |
| sabinene | 2.6 ± 1.8 | 1.4-2.7 | b.l. | 2.6 ± 0.3 | 3.6-22 | 4.7-31 |
| β-myrcene | b.l. | 5.2-9.5 | 5.2 ± 2.0 | 2.2 ± 0.3 | 7.3-38 | 3.2-23 |
| camphene | 7.6 ± 1.8 | 13-18 | 7.8 ± 1.7 | 11 ± 1.0 | 6.2-20 | 6.5-13 |
| limonene | 24 ± 17 | 17-54 | 0.6 ± 0.2 | 1.1 ± 0.2 | <7.1 | 1.7-12 |
| β-phellandrene | - | 2.4-15 | - | 0.6 ± 0.1 | - | 1.0-14 |
| 1,8-cineol | 12 ± 12 | 1.5-2.7 | 6.9 ± 2.4 | 2.0 ± 0.1 | 28-73 | 1.9-4.5 |
| tricyclene | 0.8 ± 0.7 | - | 1.2 ± 0.3 | - | <3.7 | - |
| Sum | 252 | 219-459 | 64 | 65 | 83-737 | 122-648** |

* *weighted average of measurements with individual pines.*
** *only lower limit, because peak of 3-carene was out of the linear range of the detector during stress.*
\- *not quantified.*

Before comparing the results of the measurements with pines No. 5 and 8 it must be noted that both plants suffered from stress, both during one of the laboratory experiments (plant No. 5 in May 1999, and plant No. 8 in May 1999) and outdoor experiments (plant No. 5 in May and June 1999, and plant No. 8 in June 1999). The only data sets obtained under stress-free conditions were the emission rates for pines No. 6 and 7.

For the measurements with these two pines, the sum of the standard emission rates of monoterpenes were lower than for the measurements with the other pines. Values obtained under laboratory and outdoor conditions were almost identical (64 and 65 ng g(dw)$^{1}$ h$^{-1}$, respectively). For α-pinene, 3-carene and β-pinene the emission rates were identical within the detection limits. Sabinene, camphene and limonene were found in slightly higher amounts under outdoor conditions, whereas β-myrcene and 1,8-cineol were more abundant under laboratory conditions. The emission rates of β-phellandrene and tricyclene could not be compared, because β-phellandrene was not quantified in the laboratory, and tricyclene was not quantified for the outdoor measurements. In either case, the emission rates were quite low (less than 3.5 % of the total sum of monoterpene emissions), and therefore the bias in the sum of the emission rates of monoterpenes due to their omission was very small.

Plant No. 5 was measured once in the laboratory and suffered from stress during the measurements. The standard emission rates indicated a temporal dependence. Therefore, the standard emission rates had larger error limits than usual for laboratory studies. The same pine was investigated twice in the field and also suffered from temperature-induced stress. The observed range of standard emission rates is given. Surprisingly, for most monoterpenes the value obtained under laboratory conditions was within the range observed under outdoor conditions. In addition, the sum of $\Phi^S$ was within the range observed with the outdoor enclosure system.

The emission rates from plant No. 8 were measured both in the laboratory and outdoors three times each and were both affected by stress during one set of measurements. Therefore, the range of standard emission rates observed with both systems is shown. Data from the outdoor enclosure studies were additionally biased by the fact that the upper limit of the range of the emission rates of 3-carene (and thus also of the sum of monoterpenes) represented only a lower limit. Under stress conditions 3-carene could not be quantified correctly, because the peak exceeded the linear range of the detector. Despite all these problems, the range of $\Phi^S$ for all individual monoterpenes and also for the sum of monoterpenes was very similar for laboratory and outdoor enclosure studies. The only exception was 1,8-cineol which was found in significantly higher amounts in the laboratory (28-73 ng g(dw)$^{-1}$ h$^{-1}$ compared to 1.9-4.5 ng g(dw)$^{-1}$ h$^{-1}$ under outdoor conditions). Since this is a compound for which the analytical devices were not compared, it is possible that differences in the analysis contributed to the measurement differences. Nevertheless, it is unlikely that the large difference in measured emission rates of

approximately one order of magnitude was due to analytical problems. A complete explanation for the difference cannot be given here.

In order to eliminate any difference in the absolute emission rates, the percent contributions of individual monoterpenes to the sum of monoterpenes are given in Table 5.5.

**Table 5.5:** *Contribution of individual monoterpenes to the sum of monoterpenes (shown here) in % from laboratory and outdoor enclosure studies.*

| | No. 5 | | No. 6 + 7 | | No. 8 | |
|---|---|---|---|---|---|---|
| | **Laboratory** | **Outdoor** | **Laboratory** | **Outdoor*** | **Laboratory** | **Outdoor** |
| α-pinene | 75 | 72-75 | 25 | 28 | 23-26 | 21-31 |
| 3-carene | 0.01 | 0.1 | 32 | 34 | 13-27 | 36-48 |
| β-pinene | 5.8 | 3.9-6.9 | 9.4 | 8.7 | 9.8-13 | 15-16 |
| sabinene | 1.0 | 0.6-0.7 | - | 4.1 | 3.2-4.2 | 3.4-4.7 |
| β-myrcene | - | 2.1-2.4 | 8.1 | 3.3 | 7.3-8.7 | 2.7-3.7 |
| camphene | 3.0 | 2.9-8.1 | 12 | 16 | 5.8-7.6 | 2.1-6.9 |
| limonene | 9.6 | 7.7-12 | 0.9 | 1.7 | <1.3 | 1.1-1.8 |
| β-phellandrene | - | 1.1-3.1 | - | 0.9 | - | 0.8-2.1 |
| 1,8-cineol | 4.9 | 0.6-0.7 | 11 | 3.1 | 15-34 | 0.7-2.2 |
| tricyclene | 0.3 | - | 1.9 | - | - | - |

* *weighted average of measurements with individual pines.*

As was expected from the emission rates, the spectrum of emitted monoterpenes observed in the laboratory and under outdoor enclosure conditions was very similar. A noteworthy point are the large differences in the emission spectra from different individual plants as already discussed above. The emissions from plant No. 5 are of particular interest, as this plant emitted 3-carene in significantly smaller amounts than all other plants, both in the laboratory and under ambient conditions.

## 5.6 Estimations of monoterpene fluxes from the Hartheimer Wald

Based on the results of the outdoor enclosure measurements with the adult pine, total monoterpene fluxes were calculated for the area of the Hartheimer Wald which consisted predominantely of Scots pines. This upscaling to a landscape flux considered the monoterpene emission rates, the temperature dependence of emissions, and the biomass density. The biomass density was taken into account by the leaf area index which gives the average leaf area (for deciduous trees) or projected needle area (for conifers) per land area. Other parameters, such as the potential deposition of monoterpenes on surfaces, the uptake of monoterpenes by plants, or the in-canopy oxidation of monoterpenes were not considered. Therefore, the values derived here do not represent net fluxes, but an upper limit of monoterpene fluxes.

As input parameters, values for the standard emission rate, $\Phi^S$, and the parameter describing the temperature dependence, $c_{TP}\ R^{-1}$, obtained from the measurements at branch A at different times of year were used. Since the values for $c_{TP}\ R^{-1}$ only showed minor variations with season (Table 4.9) the mean value of $c_{TP}\ R^{-1}$ was taken for each compound. For standard emission rates, which showed seasonal variations of more than one order of magnitude and no clear trend (Table 4.10), the lowest and highest values were taken to represent a range of monoterpene fluxes. These were calculated for monthly mean temperatures measured in the Hartheimer Wald (*H. Mayer*, unpublished data). Emission rates normalized to dry weight of the needles (ng g(dry weight)$^{-1}$ h$^{-1}$) were first converted into emission rates per projected needle surface using the physiological parameters given in Table 3.9 and then to the land area using a leaf area index of 2.07 for the Hartheimer Wald (*H. Mayer*, unpublished data). Figure 5.1 shows the calculated annual cycle of emission fluxes for the sum of monoterpenes. The monthly mean temperatures are plotted as circles (right scale) and the range of monoterpene emission fluxes is given by the bars (left scale). The simulated seasonal cycle followed the cycle of temperature and highest monoterpene fluxes were calculated for July, which was the month with the highest average temperature (19 °C).

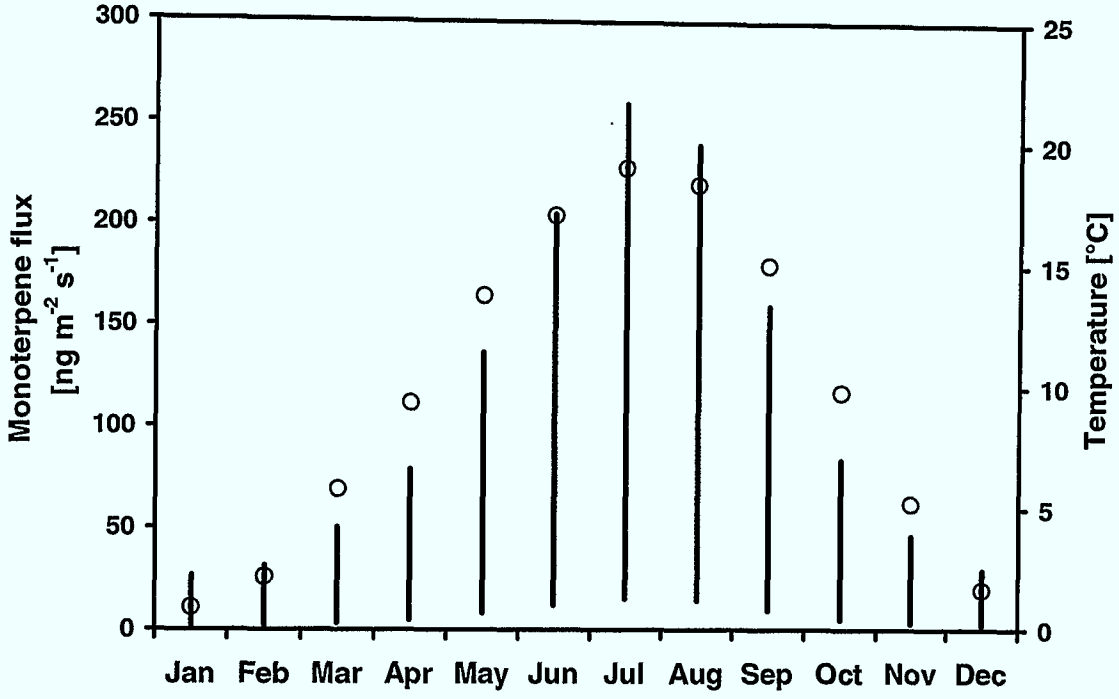


**Figure 5.1:** *Calculated flux of the sum of monoterpenes for the Hartheimer Wald. The bars represent the range between lowest and highest emission rates based on the observed range of standard emission rates measured at branch A at different time of year (left axis). Open circles show the monthly mean temperatures (right axis) given by Mayer [unpublished data].*

For July the range of the calculated monoterpene flux was between 16-260 ng $m^{-2}$ $s^{-1}$. *Rinne et al.* (2000) measured monoterpene emissions from a Scots pine (*Pinus sylvestris*) forest in Finland using a micrometeorological gradient method. Within a temperature range of 5-25 °C they reported monoterpene fluxes between a few ng $m^{-2}$ $s^{-1}$ and more than 100 ng $m^{-2}$ $s^{-1}$. From their observations they calculated a so-called emission flux potential for T = 30 °C of 268 ng $m^{-2}$ $s^{-1}$. The range of the calculated flux potential at T = 30 °C from the results described here was 54-941 ng $m^{-2}$ $s^{-1}$. Despite the large variation and uncertainties the estimated fluxes were thus in reasonable agreement with those reported by *Rinne et al.* (2000).

Nevertheless, the large range of the calculated flux potential was a direct result of high variations of the temperature normalized standard emission rates. As long as the parameters affecting the standard emission rate are not described quantitatively, extrapolations from enlosure studies with single plants to fluxes from forest lands remain highly uncertain.

# 6 Summary

Monoterpene emission rates from Scots pine (*Pinus sylvestris*) were measured within the scope of this work. The studies focussed on diurnal and seasonal cycles of monoterpene emissions, branch-to-branch and plant-to-plant variability of emission rates, and on the transferability of results from laboratory to outdoor measurements. The results will be used in emission inventories to calculate fluxes of biogenic volatile organic compounds to the atmosphere.

A sampling system was built that meets the requirements of outdoor enclosure measurements. Existing components, such as an air supply system, have been improved and the sampling has been automated. A diffusion source was built to produce standard gas mixtures of biogenic VOCs for the calibration of air samples. The performance of the system was tested successfully in an intercalibration experiment. For most of the investigated monoterpenes the statistical error of the determination of mixing ratios of several hundred parts per trillion (ppt) was less than 14 %. From the results of the intercalibration experiment the systematic error was estimated to be less than 10 % for most of the monoterpenes.

The outdoor enclosure systems were used to measure monoterpene emission rates from 8 individual 3-4 year old Scots pine seedlings and from two branches of a 40 year old Scots pine. The studies with the adult pine were conducted in the Hartheimer Wald (near Freiburg, Germany) during four field campaigns between April and October 1998. Emission rates from the young pines originating from this forest were investigated between 1998 and 1999. In addition to these outdoor experiments, laboratory studies have been conducted with the young pines by J. Wildt and coworkers. The results of the laboratory experiments under controlled environmental conditions were necessary for the interpretation of the experiment under ambient conditions.

Generally, no significant differences between the results obtained under laboratory and ambient environmental conditions were found. Thus, the continuously stirred tank reactors used as enclosure chambers in the laboratory were capable of providing ambient-like conditions and therefore have proven to be a useful tool for emission rate studies and the derivation of emission algorithms.

In both laboratory and ambient conditions, monoterpene emission rates were found to increase with needle temperature. The temperature dependence was modeled using the emission algorithm after the model established by *Tingey et al.* (1991). The parameter

describing the temperature dependence of emissions, $c_{TP}$ $R^{-1}$, ranged between $4.0 \cdot 10^3$ K and $13.9 \cdot 10^3$ K (i.e. $\beta$ between 0.05 and 0.16 $K^{-1}$) and was independent of the type of monoterpene. Variations of $c_{TP}$ $R^{-1}$ were random without a clear seasonal trend and without significant differences from plant-to-plant.

Only in the laboratory under controlled environmental conditions a dependence of the emissions on photosynthetic active radiation (PAR) was detected. The dependence of emission rates on PAR was desribed using the algorithm by *Schuh et al.* (1997). A saturation in the light dependence was found at very low PAR levels of about 15 % of full sunlight. The increase in the emission rates at a constant temperature due to PAR was only about 20-30 %. Thus, the increase in emission rates due to PAR was smaller than the variation of the emission rates due to fluctuations of temperature during the sampling period under outdoor conditions. In the experiments described here, a PAR dependence was not detected.

Surprisingly, different individual Scots pines emitted a completely different spectrum of monoterpenes. Seasonal variations in the emission spectrum from the same plant were much smaller than the plant-to-plant variability. The monoterpene emission spectra from two branches of the same tree were identical. Stress (e.g. high temperatures) was found to influence the spectrum of monoterpene emissions, but stress-induced changes in the emissions were observed to be smaller than the plant-to-plant variability of emissions. Although the data base is small, the results indicate, that the composition of emitted monoterpenes could be regarded as a fingerprint of an individual plant and not of a plant species as often reported in the literature.

Finally, the existing models describing monoterpene emissions were found to be insufficient to fully describe experimental results. The temperature normalized, so-called 'standard emission rate', was found to be highly variable. The sum of standard emission rates, $\Phi^S$, of all monoterpenes ranged between 0.06 and 0.65 $\mu g\ g(dw)^{-1}\ h^{-1}$ for young pines and between 0.24 and 3.7 $\mu g\ g(dw)^{-1}\ h^{-1}$ for the adult pine. There was no clear seasonal trend in the standard emission rates. The variation of the standard emission rates from the same plant measured at different times of the year was on the same order as the plant-to-plant variability (i.e. about one order of magnitude). This indicates that these variations were not due to differences between plants, but were induced by environmental factors. Stress to the plant was a possible explanation for these variations and high temperatures were identified as one possible stress factor, but this effect could not be described quantitatively.

Based on the results of the outdoor enclosure measurements with the adult pine, monoterpene fluxes from the Hartheimer Wald were calculated. The estimated monoterpene flux potential ranged between 54-941 ng $m^{-2}$ $s^{-1}$ at T = 30 °C. This large range was a result of the high variations of the temperature normalized standard emission rates that are not yet fully understood.

With regard to future emission rate studies, the following recommendations are made: It is sufficient to measure the emission rates on just one branch of a tree to get a measure of the emission rates of that specific tree. Nevertheless, it is absolutely necessary to investigate the emissions of more than one individual tree to estimate the plant-to-plant variability of emissions. The existing models desribing monoterpene emissions as a function of environmental parameters (such as temperature and PAR) need to be improved. Especially stress effects (e.g. high temperatures, pathogen attack, and insect attack) have to be investigated thoroughly in future laboratory studies. The effect of stress on monoterpene emissions must be quantified and included in the existing models for better predictions of emission rates. Without a better understanding of the processes leading to the emissions of monoterpenes, estimations of emission rates remain uncertain. In parallel to the enclosure studies at single plants, landscape fluxes of biogenic VOCs must be measured directly. In combination, these studies will provide a data base suitable to improve the current biogenic emission inventories.

# 7 Literature

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# 8 Appendix

## 8.1 List of abbreviations

| | |
|---|---|
| ATP | *adenosine triphosphate* |
| CSTR | *continuously stirred tank reactor* |
| DMAPP | *dimethylallyl pyrophosphate* |
| DOX-P | *1-deoxyxylulose-5-phosphate* |
| dw | *dry weight* |
| ECN | *effective carbon number* |
| FEP | *fluorinated ethylene polymer* |
| FID | *flame ionization detector* |
| FPP | *farnesyl pyrophosphate* |
| GC | *gas chromatograph* |
| GPP | *geranyl pyrophosphate* |
| IPP | *isopentenyl pyrophosphate* |
| MS | *mass spectrometer* |
| NADH | *nicotinamid adenine dinucleotide* |
| PAR | *photosynthetic active radiation* |
| ppb | *parts per billion (1 molecule in $10^9$ molecules of air)* |
| ppm | *parts per million (1 molecule in $10^6$ molecules of air)* |
| ppt | *parts per trillion (1 molecule in $10^{12}$ molecules of air)* |
| PTFE | *polytetrafluoroethylene* |
| RMR | *relative molar response* |
| VOC | *volatile organic compound* |

## 8.2 Biological glossary

| | |
|---|---|
| allelopathy (adj. allelopathic) | *The inhibition of growth of one plant species by another due to the release of chemical substances.* |
| antimicrobial | *An agent that inhibits the growth of and destroys bacteria.* |
| cytoplasm | *The cellular region within the plasma membrane, including the cytosol and the organelles but excluding the nucleus. Thus, cytoplasmic.* |
| cytosol | *The liquid medium of the cytoplasm.* |
| enzyme | *A protein molecule in a plant or animal that catalyzes specific metabolic reactions without itself being permanently altered or destroyed.* |
| herbivore (adj. herbivory) | *An organism that feeds on plants, especially an animal whose diet is exclusively plants.* |
| kairomone | *An interspecific chemical messenger, the adaptive benefit of which falls on the recipient rather than the emitter.* |
| pathogen | *Any virus, microorganism, or other substance that causes disease; an infecting agent.* |
| plastid | *Any of a number of membrane-bound organelles found in plant cells and performing a specific function for the cell, such as a photosynthetic chloroplast.* |
| predator | *An animal that kills other animals for food.* |
| resin duct | *A tubular intercellular duct surrounded by an epithelium, generally containing secondary plant products such as resins, gums, etc., secreted by the epithelial cells.* |

## 8.3 List of Figures

## 8.4 List of Tables

## 8.5 Molecular structure of monoterpenes

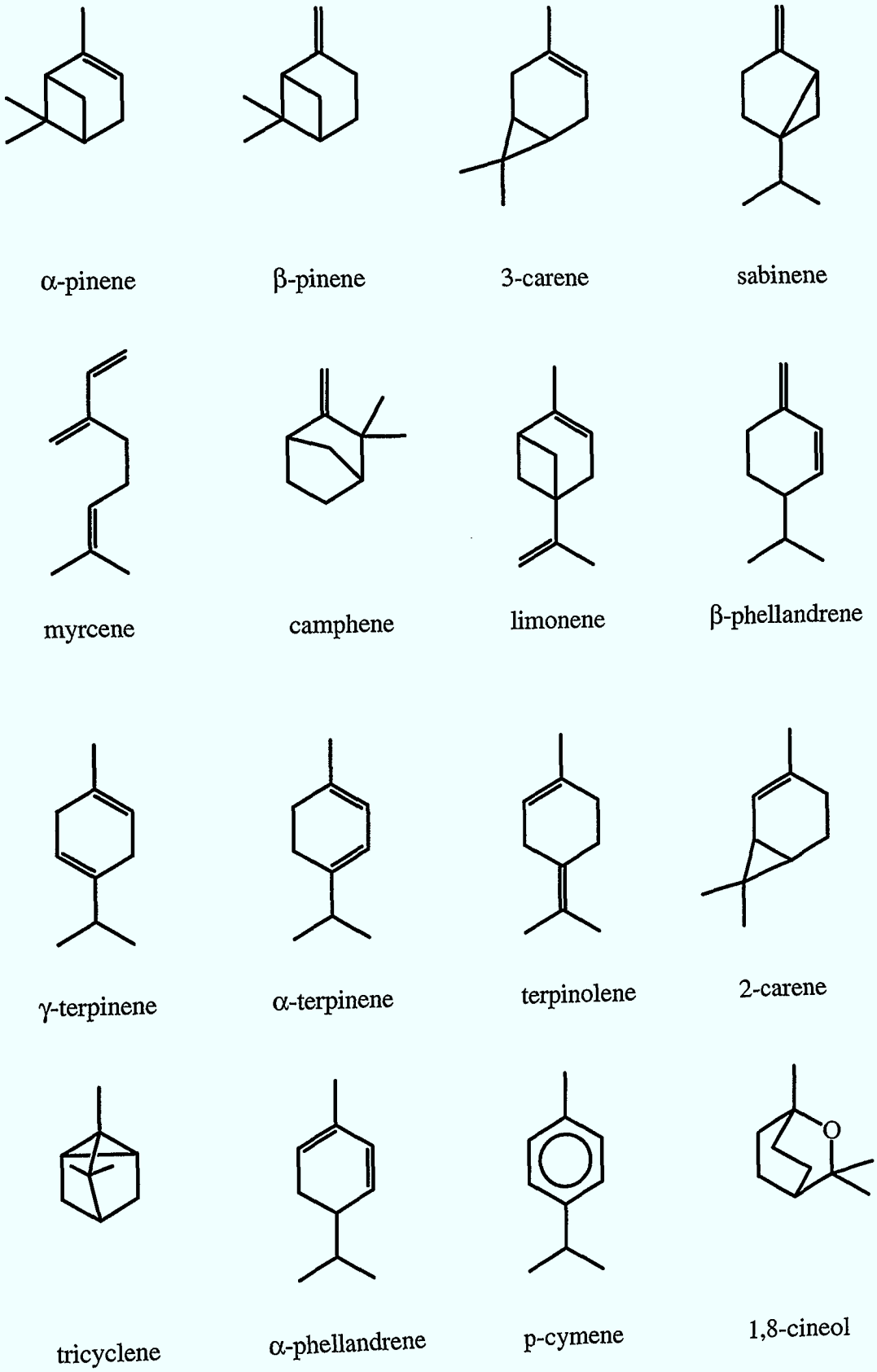



**Figure 8.1:** *Molecular structures of the most abundant monoterpenes (including p-cymene and 1,8-cineol), identified as emission products from Scots pine.*

## 8.6 Selected properties of hydrocarbons

**Table 8.1:** *Formula, molecular mass, supplier, purity, effective carbon number (ECN) and correction factor of the investigated compounds.*

| Compound | Formula | Molecular mass [g mol$^{-1}$] | Supplier | Purity of the compound (%) | ECN | Correction factor |
|---|---|---|---|---|---|---|
| benzene | $C_6H_6$ | 78.11 | Merck | > 99.8 | 6 | 0.93 |
| hexanal | $C_6H_{12}O$ | 100.16 | Fluka | > 98 | 5 | 1.43 |
| cis-3-hexen-1-ol | $C_6H_{12}O$ | 100.16 | Fluka | > 98 | 5.3 | 1.35 |
| n-hexane | $C_6H_{14}$ | 86.18 | Merck | > 97 | 6 | 1.02 |
| toluene | $C_7H_8$ | 92.14 | Merck | > 99.5 | 7 | 0.94 |
| n-heptane | $C_7H_{16}$ | 100.20 | Merck | > 99 | 7 | 1.02 |
| methyl salicylate | $C_8H_8O_3$ | 152.15 | Fluka | > 99 | 5.4 | 2.01 |
| 6-methyl-5-hepten-2-one | $C_8H_{14}O$ | 126.20 | Fluka | ~ 98 | 6.9 | 1.30 |
| iso-octane | $C_8H_{18}$ | 114.23 | Merck | > 99.5 | 8 | 1.02 |
| nonanal | $C_9H_{18}O$ | 142.24 | Fluka | ~ 97 | 8 | 1.27 |
| (-)-myrtenal | $C_{10}H_{14}O$ | 150.22 | Fluka | > 99 | 8.9 | 1.20 |
| (-)-α-pinene | $C_{10}H_{16}$ | 136.24 | Fluka | > 99 | 9.9 | 0.98 |
| camphene | $C_{10}H_{16}$ | 136.24 | EGA-Chemie | 95 | 9.9 | 0.98 |
| (-)-β-pinene | $C_{10}H_{16}$ | 136.24 | Fluka | > 99.5 | 9.9 | 0.98 |
| β-myrcene | $C_{10}H_{16}$ | 136.24 | Fluka | > 97 | 9.7 | 1.00 |
| (-)-α-phellandrene | $C_{10}H_{16}$ | 136.24 | Fluka | ~ 99 | 9.8 | 0.99 |
| (+)-3-carene | $C_{10}H_{16}$ | 136.24 | Fluka | > 99 | 9.9 | 0.98 |
| α-terpinene | $C_{10}H_{16}$ | 136.24 | Fluka | ~ 95 | 9.8 | 0.99 |
| (+)-limonene | $C_{10}H_{16}$ | 136.24 | Fluka | > 97 | 9.8 | 0.99 |
| ocimene | $C_{10}H_{16}$ | 136.24 | Fluka | ~ 97 | 9.7 | 1.00 |
| γ-terpinene | $C_{10}H_{16}$ | 136.24 | Aldrich | 98 | 9.8 | 0.99 |
| terpinolene | $C_{10}H_{16}$ | 136.24 | Fluka | 95 | 9.8 | 0.99 |
| 1,8-cineol | $C_{10}H_{18}O$ | 154.25 | Fluka | ~ 99 | 9 | 1.22 |
| (±)-linalool | $C_{10}H_{18}O$ | 154.25 | Fluka | ~ 97 | 9.55 | 1.15 |
| (-)-citronellal | $C_{10}H_{18}O$ | 154.25 | Fluka | > 98 | 8.9 | 1.24 |
| n-undecane | $C_{11}H_{24}$ | 156.31 | Merck | > 97 | 11 | 1.01 |
| (-)-bornyl acetate | $C_{12}H_{20}O_2$ | 196.29 | Fluka | > 99 | 10 | 1.40 |
| dodecane | $C_{12}H_{26}$ | 170.34 | Fluka | > 99 | 12 | 1.01 |
| geranyl acetone | $C_{13}H_{22}O$ | 194.32 | Fluka | > 98 | 11.8 | 1.17 |
| tetradecane | $C_{14}H_{30}$ | 198.39 | Fluka | > 99 | 14 | 1.01 |
| (+)-longicyclene | $C_{15}H_{24}$ | 204.36 | Fluka | ~ 97 | 15 | 0.97 |
| (-)-trans-caryophyllene | $C_{15}H_{24}$ | 204.36 | Fluka | ~ 99 | 14.8 | 0.98 |
| (-)-α-cedrene | $C_{15}H_{24}$ | 204.36 | Fluka | > 99 | 14.9 | 0.98 |
| (+)-longifolene | $C_{15}H_{24}$ | 204.36 | Fluka | > 99 | 15 | 0.97 |

## 8.7 Results of emission rate measurements

**Table 8.2:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at branch A in April 1998, n.q. = not quantified.*

| date, time | temperature | toluene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | 3-carene |
|---|---|---|---|---|---|---|---|---|
| 28.04.98 12:00 | | 16 | 266 | 12 | 20 | 240 | 21 | 536 |
| 28.04.98 13:00 | | 36 | 345 | 25 | 15 | 295 | 25 | 657 |
| 28.04.98 14:00 | | 9 | 289 | 22 | 17 | 222 | 27 | 540 |
| 28.04.98 15:00 | | 9 | 142 | 11 | 13 | 105 | 11 | 245 |
| 28.04.98 17:00 | 289 | 10 | 217 | 15 | 12 | 166 | 25 | 383 |
| 28.04.98 18:00 | 288 | 10 | 194 | 18 | 11 | 137 | 17 | 319 |
| 28.04.98 19:00 | 287 | 4 | 124 | 13 | 7 | 83 | 18 | 194 |
| 28.04.98 20:30 | 283 | 10 | 89 | 13 | 7 | 49 | 9 | 100 |
| 28.04.98 22:30 | 279 | 3 | 37 | 4 | 6 | 24 | 6 | 40 |
| 29.04.98 00:30 | 277 | 3 | 30 | 4 | 7 | 20 | 7 | 31 |
| 29.04.98 02:30 | 276 | 4 | 32 | 6 | 3 | 15 | 2 | 32 |
| 29.04.98 04:30 | 274 | 6 | 30 | 5 | 6 | 20 | 7 | 28 |
| 29.04.98 06:00 | 274 | 8 | 30 | 5 | n.q. | 23 | 14 | 28 |
| 29.04.98 07:00 | 275 | 7 | 36 | 9 | n.q. | 28 | 19 | 39 |
| 29.04.98 08:00 | 281 | 10 | 108 | 13 | 12 | 80 | 11 | 152 |
| 29.04.98 09:00 | 286 | 6 | 157 | 12 | 13 | 109 | 15 | 276 |
| 29.04.98 10:00 | 294 | 13 | 474 | 36 | 30 | 373 | 39 | 1211 |
| 29.04.98 11:00 | 295 | 21 | 668 | 89 | 34 | 522 | 56 | 1628 |
| 29.04.98 13:00 | 297 | 16 | 877 | 66 | 45 | 801 | 81 | 2050 |
| 29.04.98 14:00 | 299 | 15 | 1174 | 78 | 60 | 1071 | 86 | 2374 |
| 29.04.98 15:00 | 298 | 16 | 708 | 65 | 40 | 610 | 64 | 1321 |
| 29.04.98 16:00 | 297 | 10 | 547 | 46 | 30 | 472 | 44 | 961 |
| 29.04.98 17:00 | 295 | 9 | 436 | 41 | 26 | 373 | 37 | 697 |
| 29.04.98 18:00 | 294 | 11 | 431 | 38 | 19 | 403 | 34 | 644 |
| 29.04.98 19:00 | 292 | 10 | 594 | 28 | 22 | 586 | 32 | 670 |
| 29.04.98 20:30 | 285 | 7 | 269 | 13 | 9 | 250 | 14 | 271 |
| 29.04.98 22:30 | 280 | 13 | 120 | 9 | 8 | 91 | 40 | 105 |
| 30.04.98 00:30 | 279 | 5 | 100 | 7 | 7 | 77 | 6 | 90 |
| 30.04.98 02:30 | 278 | 4 | 85 | 6 | 5 | 66 | 4 | 76 |
| 30.04.98 04:30 | 276 | 4 | 72 | 5 | 4 | 53 | 3 | 66 |
| 30.04.98 06:00 | 275 | 5 | 55 | 5 | 6 | 46 | 10 | 48 |
| 30.04.98 07:00 | 276 | 10 | 64 | 4 | 5 | 56 | 3 | 58 |
| 30.04.98 08:00 | 280 | 10 | 132 | 11 | 8 | 95 | 6 | 129 |
| 30.04.98 09:00 | 282 | 5 | 137 | 13 | 10 | 114 | 9 | 164 |
| 30.04.98 10:00 | 285 | 7 | 183 | 12 | 21 | 169 | 10 | 251 |
| 30.04.98 11:00 | 293 | 12 | 451 | 27 | 27 | 435 | 39 | 951 |
| 30.04.98 12:00 | 298 | 18 | 1286 | 70 | 61 | 1265 | 91 | 2471 |
| 30.04.98 13:00 | 297 | 17 | 1595 | 89 | 56 | 1623 | 100 | 2182 |
| 30.04.98 14:00 | 298 | 20 | 1118 | 87 | 42 | 1062 | 75 | 1574 |
| 30.04.98 15:00 | 301 | 21 | 1472 | 97 | 57 | 1445 | 95 | 2250 |

**Table 8.2:** *(continued)*

| date, time | temperature | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | longicyclene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|
| 28.04.98 12:00 | | 6 | 24 | 17 | 9 | 8 | n.q. | n.q. |
| 28.04.98 13:00 | | 16 | 22 | 19 | 18 | 14 | 1 | 2 |
| 28.04.98 14:00 | | 9 | 18 | 14 | 18 | 9 | 2 | 3 |
| 28.04.98 15:00 | | 3 | 8 | 8 | 9 | 4 | 2 | 1 |
| 28.04.98 17:00 | 289 | 9 | 22 | 10 | 12 | 9 | 2 | 3 |
| 28.04.98 18:00 | 288 | 4 | 24 | 10 | 10 | 7 | 3 | 2 |
| 28.04.98 19:00 | 287 | 4 | 15 | 7 | 13 | 3 | n.q. | 2 |
| 28.04.98 20:30 | 283 | 5 | 8 | 3 | 3 | n.q. | n.q. | n.q. |
| 28.04.98 22:30 | 279 | 2 | 8 | 1 | n.q. | 2 | n.q. | n.q. |
| 29.04.98 00:30 | 277 | 4 | 6 | n.q. | n.q. | n.q. | n.q. | 1 |
| 29.04.98 02:30 | 276 | 1 | 5 | n.q. | 1 | n.q. | n.q. | n.q. |
| 29.04.98 04:30 | 274 | 2 | 5 | n.q. | n.q. | n.q. | n.q. | 1 |
| 29.04.98 06:00 | 274 | 3 | 18 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 29.04.98 07:00 | 275 | 3 | 10 | n.q. | n.q. | 3 | n.q. | n.q. |
| 29.04.98 08:00 | 281 | 5 | 13 | 4 | 5 | n.q. | n.q. | 1 |
| 29.04.98 09:00 | 286 | 8 | 19 | 10 | 12 | 6 | n.q. | 1 |
| 29.04.98 10:00 | 294 | 25 | 32 | 17 | 41 | 19 | 1 | 2 |
| 29.04.98 11:00 | 295 | 35 | 44 | 26 | 61 | 21 | 4 | n.q. |
| 29.04.98 13:00 | 297 | 33 | 42 | 37 | 68 | 28 | 2 | 4 |
| 29.04.98 14:00 | 299 | 31 | 49 | 45 | 78 | 29 | 2 | 4 |
| 29.04.98 15:00 | 298 | 23 | 34 | 30 | 57 | 20 | 2 | 4 |
| 29.04.98 16:00 | 297 | 18 | 34 | 25 | 46 | 21 | 1 | 4 |
| 29.04.98 17:00 | 295 | 16 | 21 | 20 | 29 | 15 | 1 | 4 |
| 29.04.98 18:00 | 294 | 11 | 25 | 21 | 23 | 11 | 2 | 5 |
| 29.04.98 19:00 | 292 | 11 | 25 | 20 | 13 | 9 | 1 | 5 |
| 29.04.98 20:30 | 285 | 7 | 11 | 8 | 7 | 12 | 3 | 4 |
| 29.04.98 22:30 | 280 | 7 | 10 | 6 | 2 | 9 | n.q. | 2 |
| 30.04.98 00:30 | 279 | 3 | 8 | 2 | 1 | 5 | 1 | 3 |
| 30.04.98 02:30 | 278 | 3 | 5 | 3 | 1 | 6 | 1 | 2 |
| 30.04.98 04:30 | 276 | 2 | 9 | 2 | 1 | 3 | n.q. | 1 |
| 30.04.98 06:00 | 275 | n.q. | 13 | n.q. | n.q. | n.q. | n.q. | 2 |
| 30.04.98 07:00 | 276 | 6 | 16 | 4 | 1 | n.q. | n.q. | 2 |
| 30.04.98 08:00 | 280 | 5 | 13 | 5 | 4 | 7 | 2 | 2 |
| 30.04.98 09:00 | 282 | 4 | 18 | 5 | 4 | n.q. | n.q. | 3 |
| 30.04.98 10:00 | 285 | 4 | 16 | 7 | 5 | 8 | n.q. | 2 |
| 30.04.98 11:00 | 293 | 17 | 24 | 14 | 29 | 13 | 1 | 3 |
| 30.04.98 12:00 | 298 | 37 | 49 | 39 | 93 | 35 | 2 | 4 |
| 30.04.98 13:00 | 297 | 31 | 55 | 47 | 93 | 32 | 2 | 5 |
| 30.04.98 14:00 | 298 | 29 | 59 | 38 | 68 | 26 | 1 | 5 |
| 30.04.98 15:00 | 301 | 32 | 47 | 44 | 84 | 36 | 2 | 5 |

**Table 8.3:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at branch A in July 1998, n.q. = not quantified.*

| date, time | temperature | toluene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | 3-carene |
|---|---|---|---|---|---|---|---|---|
| 07.07.98 05:00 | 283 | 2 | 26 | 4 | n.q. | 10 | 3 | 28 |
| 07.07.98 06:00 | 283 | 3 | 44 | 11 | n.q. | 19 | 4 | 41 |
| 07.07.98 07:00 | 285 | 6 | 110 | 21 | n.q. | 63 | 12 | 144 |
| 07.07.98 08:00 | 289 | 5 | 67 | 10 | n.q. | 33 | 7 | 133 |
| 07.07.98 09:00 | 294 | 6 | 90 | 11 | n.q. | 51 | 18 | 193 |
| 07.07.98 10:00 | 298 | 26 | 100 | 14 | n.q. | 52 | 24 | 178 |
| 07.07.98 11:00 | 303 | 5 | 138 | 19 | 30 | 60 | 26 | 236 |
| 07.07.98 12:00 | 303 | 4 | 90 | 16 | n.q. | 43 | 22 | 111 |
| 07.07.98 13:00 | 304 | 7 | 115 | 21 | 23 | 45 | 28 | 155 |
| 07.07.98 14:00 | 306 | 10 | 127 | 18 | 19 | 41 | 29 | 148 |
| 07.07.98 15:00 | 305 | 5 | n.q. | 2 | n.q. | n.q. | n.q. | 14 |
| 07.07.98 16:00 | 301 | 5 | 255 | 35 | 34 | 82 | 53 | 300 |
| 07.07.98 17:00 | 297 | 8 | 186 | 23 | n.q. | 104 | 45 | 286 |
| 07.07.98 18:00 | 292 | 4 | 72 | 10 | n.q. | 36 | 18 | 115 |
| 07.07.98 19:00 | 289 | 24 | 55 | 8 | n.q. | 24 | 55 | 62 |
| 07.07.98 20:00 | 287 | 2 | 17 | 2 | n.q. | 10 | 3 | 23 |
| 07.07.98 22:00 | 286 | 8 | 24 | 5 | 15 | n.q. | 23 | 22 |
| 07.07.98 23:30 | 286 | 1 | 16 | 3 | n.q. | 8 | 2 | 18 |
| 08.07.98 03:30 | 285 | 1 | 8 | n.q. | n.q. | 3 | 1 | 5 |
| 08.07.98 05:30 | 283 | 1 | 11 | 1 | 5 | 4 | 2 | 9 |
| 08.07.98 07:00 | 284 | 3 | 54 | 11 | 9 | 19 | 7 | 57 |
| 08.07.98 08:00 | 288 | 2 | 34 | 4 | 11 | 17 | 6 | 57 |
| 08.07.98 09:00 | 288 | 3 | 27 | 5 | 7 | 11 | 4 | 40 |
| 08.07.98 10:00 | 289 | 5 | 35 | 4 | 6 | 14 | 12 | 56 |
| 08.07.98 11:30 | 294 | 4 | 65 | 9 | n.q. | 20 | 8 | 95 |
| 08.07.98 12:45 | 303 | 5 | 151 | 20 | 23 | 49 | 24 | 240 |
| 08.07.98 13:15 | 301 | 5 | 91 | 16 | 15 | 31 | 21 | 116 |
| 08.07.98 14:00 | 297 | n.q. | 4 | 2 | 2 | 3 | 3 | 4 |
| 08.07.98 15:00 | 297 | 1 | 4 | 2 | 2 | 3 | 2 | 4 |
| 08.07.98 16:00 | 298 | 1 | 4 | 2 | 3 | 3 | 2 | 4 |
| 08.07.98 17:00 | 296 | 1 | 4 | 2 | 3 | 3 | 2 | 4 |
| 08.07.98 18:00 | 294 | 0 | 3 | 1 | 2 | 2 | 2 | 3 |
| 08.07.98 19:00 | 292 | 1 | 3 | 1 | n.q. | 2 | 1 | 3 |
| 08.07.98 20:00 | 290 | 1 | 3 | 1 | 2 | 2 | 1 | 3 |
| 08.07.98 21:00 | 289 | 2 | 4 | 3 | 3 | 3 | 4 | 4 |
| 08.07.98 22:00 | 288 | 1 | 3 | 1 | n.q. | 2 | 1 | n.q. |
| 08.07.98 23:30 | 285 | 1 | 2 | 0 | n.q. | 1 | 0 | 2 |
| 09.07.98 01:30 | 282 | 1 | 2 | n.q. | n.q. | 1 | 1 | 2 |
| 09.07.98 03:30 | 280 | 0 | 2 | 1 | n.q. | 1 | 0 | 2 |
| 09.07.98 05:30 | 279 | 0 | 3 | 1 | 1 | 1 | 0 | 2 |
| 09.07.98 07:00 | 283 | n.q. | 3 | 2 | n.q. | 2 | n.q. | 3 |
| 09.07.98 08:00 | 288 | 1 | 4 | 2 | n.q. | 3 | 2 | 4 |
| 09.07.98 09:00 | 293 | 2 | 4 | 2 | 2 | n.q. | n.q. | 4 |
| 09.07.98 10:00 | 291 | 1 | 3 | 2 | 2 | 2 | 1 | 3 |
| 09.07.98 11:00 | 290 | 2 | 3 | 1 | n.q. | 2 | 2 | 3 |
| 09.07.98 12:00 | 292 | 2 | 3 | 1 | 2 | 2 | 1 | 3 |
| 09.07.98 13:00 | 295 | 0 | 4 | 2 | 2 | 3 | 2 | 4 |
| 09.07.98 14:00 | 295 | 0 | 4 | 3 | 2 | 3 | 2 | 4 |
| 09.07.98 15:00 | 296 | 1 | 4 | 2 | n.q. | 3 | 2 | 4 |
| 09.07.98 16:00 | 300 | n.q. | 5 | 2 | 3 | 4 | 3 | 5 |
| 09.07.98 18:00 | 297 | 1 | 4 | 2 | 2 | 2 | 2 | 4 |
| 09.07.98 20:00 | 293 | 0 | 3 | 1 | n.q. | 2 | 1 | 3 |
| 09.07.98 23:30 | 290 | 1 | 3 | n.q. | 3 | 2 | 2 | 3 |
| 10.07.98 01:30 | 287 | 1 | 3 | 1 | n.q. | 2 | 2 | 2 |
| 10.07.98 03:30 | 287 | 2 | 3 | 1 | 1 | 2 | 3 | 3 |

**Table 8.3:** *(continued)*

| date, time | temperature | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | longicyclene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|
| 07.07.98 05:00 | 283 | 2 | 4 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 07.07.98 06:00 | 283 | 1 | 2 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 07.07.98 07:00 | 285 | 5 | 6 | 2 | 10 | n.q. | n.q. | n.q. |
| 07.07.98 08:00 | 289 | 6 | 7 | n.q. | 18 | 2 | n.q. | n.q. |
| 07.07.98 09:00 | 294 | 4 | 7 | 4 | 59 | 3 | n.q. | 1 |
| 07.07.98 10:00 | 298 | 7 | 9 | 5 | 94 | 4 | n.q. | n.q. |
| 07.07.98 11:00 | 303 | 8 | 9 | 4 | 114 | 5 | n.q. | 8 |
| 07.07.98 12:00 | 303 | 6 | 8 | 5 | 59 | 6 | n.q. | n.q. |
| 07.07.98 13:00 | 304 | 7 | 9 | 3 | 52 | 4 | n.q. | 5 |
| 07.07.98 14:00 | 306 | 5 | 6 | 3 | 46 | 3 | n.q. | 10 |
| 07.07.98 15:00 | 305 | n.q. | n.q. | n.q. | 861 | 29 | n.q. | n.q. |
| 07.07.98 16:00 | 301 | 7 | 11 | 5 | 67 | 5 | n.q. | 11 |
| 07.07.98 17:00 | 297 | 5 | 11 | 6 | 108 | 10 | n.q. | n.q. |
| 07.07.98 18:00 | 292 | 3 | 6 | n.q. | 43 | 3 | n.q. | 5 |
| 07.07.98 19:00 | 289 | n.q. | 12 | n.q. | 14 | n.q. | 1 | 10 |
| 07.07.98 20:00 | 287 | 2 | 2 | 2 | n.q. | n.q. | n.q. | 3 |
| 07.07.98 22:00 | 286 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 07.07.98 23:30 | 286 | 1 | 1 | n.q. | 2 | n.q. | n.q. | 5 |
| 08.07.98 03:30 | 285 | 0 | 0 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 08.07.98 05:30 | 283 | 1 | 1 | n.q. | n.q. | n.q. | n.q. | 0 |
| 08.07.98 07:00 | 284 | 5 | 6 | 2 | 9 | 2 | n.q. | 13 |
| 08.07.98 08:00 | 288 | 8 | 7 | 2 | 12 | n.q. | 1 | 7 |
| 08.07.98 09:00 | 288 | 3 | 3 | 1 | 8 | n.q. | n.q. | n.q. |
| 08.07.98 10:00 | 289 | 3 | 4 | n.q. | 13 | n.q. | n.q. | 2 |
| 08.07.98 11:30 | 294 | 17 | 10 | n.q. | 53 | 1 | 3 | 6 |
| 08.07.98 12:45 | 303 | 8 | 8 | n.q. | 102 | n.q. | n.q. | 49 |
| 08.07.98 13:15 | 301 | 7 | 7 | n.q. | 56 | 4 | n.q. | 16 |
| 08.07.98 14:00 | 297 | 2 | 2 | n.q. | 4 | n.q. | n.q. | n.q. |
| 08.07.98 15:00 | 297 | 1 | 2 | n.q. | 3 | n.q. | n.q. | 1 |
| 08.07.98 16:00 | 298 | 1 | 1 | n.q. | 4 | n.q. | n.q. | 1 |
| 08.07.98 17:00 | 296 | 1 | 1 | n.q. | 3 | 1 | n.q. | n.q. |
| 08.07.98 18:00 | 294 | 0 | 1 | n.q. | 2 | n.q. | n.q. | 1 |
| 08.07.98 19:00 | 292 | 1 | 0 | n.q. | 2 | n.q. | n.q. | 0 |
| 08.07.98 20:00 | 290 | 0 | 1 | n.q. | 1 | n.q. | 1 | 2 |
| 08.07.98 21:00 | 289 | 4 | 4 | n.q. | 3 | n.q. | 2 | 6 |
| 08.07.98 22:00 | 288 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 08.07.98 23:30 | 285 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 09.07.98 01:30 | 282 | n.q. | 1 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 09.07.98 03:30 | 280 | 0 | 0 | n.q. | 0 | n.q. | n.q. | n.q. |
| 09.07.98 05:30 | 279 | 0 | 0 | 0 | n.q. | n.q. | -1 | n.q. |
| 09.07.98 07:00 | 283 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 09.07.98 08:00 | 288 | 1 | 1 | n.q. | 3 | n.q. | n.q. | 1 |
| 09.07.98 09:00 | 293 | n.q. | n.q. | n.q. | 3 | n.q. | n.q. | n.q. |
| 09.07.98 10:00 | 291 | 1 | 0 | n.q. | 3 | 0 | n.q. | n.q. |
| 09.07.98 11:00 | 290 | n.q. | 1 | n.q. | 2 | n.q. | n.q. | n.q. |
| 09.07.98 12:00 | 292 | 1 | 1 | n.q. | 2 | n.q. | n.q. | 1 |
| 09.07.98 13:00 | 295 | 1 | 2 | n.q. | 4 | 1 | n.q. | 1 |
| 09.07.98 14:00 | 295 | 1 | 1 | 0 | 4 | n.q. | n.q. | n.q. |
| 09.07.98 15:00 | 296 | 1 | 1 | n.q. | 4 | 2 | 1 | 1 |
| 09.07.98 16:00 | 300 | 1 | 2 | n.q. | 4 | 2 | n.q. | n.q. |
| 09.07.98 18:00 | 297 | 1 | 1 | n.q. | 3 | 1 | n.q. | n.q. |
| 09.07.98 20:00 | 293 | 0 | n.q. | 1 | n.q. | 1 | n.q. | n.q. |
| 09.07.98 23:30 | 290 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 10.07.98 01:30 | 287 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 10.07.98 03:30 | 287 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | 0 |

**Table 8.4:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at branch A in September 1998, n.q. = not quantified.*

| date, time | temperature | toluene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | 3-carene |
|---|---|---|---|---|---|---|---|---|
| 16.09.98 04:00 | 287 | 5 | 139 | 18 | n.q. | 63 | 9 | 149 |
| 16.09.98 05:00 | 287 | 2 | 122 | 15 | n.q. | 50 | 7 | 141 |
| 16.09.98 06:00 | 287 | 1 | 137 | 14 | 11 | 55 | 8 | 151 |
| 16.09.98 07:00 | 287 | 1 | 142 | 14 | 10 | 57 | 5 | 159 |
| 16.09.98 08:00 | 287 | 3 | 163 | 20 | 3 | 69 | 10 | 192 |
| 16.09.98 09:00 | 289 | 2 | 202 | 22 | 13 | 88 | 7 | 235 |
| 16.09.98 10:00 | 292 | 1 | 263 | 33 | n.q. | 115 | 12 | 314 |
| 16.09.98 11:00 | 297 | n.q. | 455 | 40 | 22 | 218 | 20 | 524 |
| 16.09.98 12:00 | 297 | 3 | 445 | 56 | 19 | 219 | 36 | 556 |
| 16.09.98 13:00 | 299 | 4 | 656 | 71 | 29 | 321 | 53 | 731 |
| 16.09.98 14:00 | 295 | 7 | 385 | 44 | 8 | 198 | 29 | 391 |
| 16.09.98 16:00 | 296 | 3 | 345 | 36 | 21 | 158 | 16 | 348 |
| 16.09.98 17:00 | 292 | 2 | 186 | 23 | n.q. | 77 | 43 | 194 |
| 16.09.98 18:00 | 291 | 1 | 170 | 19 | 9 | 70 | 67 | 163 |
| 16.09.98 19:00 | 290 | 1 | 130 | 16 | n.q. | 56 | 67 | 135 |
| 16.09.98 20:00 | 289 | 1 | 135 | 17 | n.q. | 50 | 23 | 104 |
| 16.09.98 21:00 | 288 | 1 | 80 | 10 | 6 | 28 | 6 | 71 |
| 16.09.98 22:00 | 288 | 0 | 87 | 11 | 7 | 32 | 4 | 77 |
| 16.09.98 23:00 | 287 | 1 | 63 | 7 | 5 | 27 | 4 | 71 |
| 17.09.98 08:57 | 284 | 1 | 66 | 8 | 3 | 27 | 6 | 72 |
| 17.09.98 10:00 | 286 | 1 | 74 | 9 | 2 | 30 | 5 | 71 |
| 17.09.98 11:00 | 289 | 1 | 120 | 12 | n.q. | 53 | 12 | 126 |
| 17.09.98 12:00 | 290 | 5 | 149 | 15 | 6 | 65 | 13 | 163 |
| 17.09.98 13:00 | 294 | 5 | 318 | 29 | 12 | 147 | 21 | 335 |
| 17.09.98 14:00 | 291 | 4 | 217 | 22 | 8 | 92 | 15 | 215 |
| 17.09.98 15:00 | 290 | 4 | 164 | 16 | 5 | 67 | 18 | 157 |
| 17.09.98 16:00 | 291 | 9 | 143 | 13 | n.q. | 68 | 19 | 132 |
| 17.09.98 17:00 | 290 | 4 | 136 | 13 | 11 | 57 | 15 | 133 |
| 17.09.98 18:00 | 289 | 3 | 89 | 10 | n.q. | 36 | 4 | 80 |
| 17.09.98 19:00 | 288 | 5 | 82 | 9 | n.q. | 34 | 3 | 66 |
| 17.09.98 20:00 | 287 | 2 | 85 | 10 | 5 | 29 | 3 | 65 |
| 17.09.98 21:00 | 286 | 2 | 54 | 6 | 4 | 21 | 2 | 44 |
| 17.09.98 22:00 | 286 | 3 | 51 | 7 | 4 | 18 | 2 | 40 |
| 17.09.98 23:00 | 286 | 3 | 62 | 7 | 5 | 21 | 3 | 46 |
| 18.09.98 05:00 | 284 | 2 | 53 | 6 | 4 | 21 | 2 | 41 |
| 18.09.98 06:00 | 284 | 3 | 59 | 7 | 6 | 23 | 2 | 42 |
| 18.09.98 07:00 | 284 | 3 | 52 | 6 | 5 | 18 | 1 | 38 |
| 18.09.98 08:00 | 285 | 2 | 49 | 6 | n.q. | 21 | 5 | 36 |
| 18.09.98 10:00 | 289 | n.q. | 101 | 12 | n.q. | 39 | 5 | 99 |
| 18.09.98 11:00 | 294 | 1 | 150 | 15 | 8 | 62 | 13 | 159 |
| 18.09.98 12:00 | 302 | 14 | 445 | 44 | 41 | 236 | 45 | 539 |
| 18.09.98 13:00 | 301 | 2 | 506 | 52 | 28 | 258 | 42 | 526 |
| 18.09.98 14:00 | 299 | 3 | 404 | 39 | 21 | 196 | 34 | 430 |
| 18.09.98 15:00 | 299 | n.q. | 319 | 33 | 18 | 161 | 32. | 397 |
| 18.09.98 16:00 | 298 | 1 | 282 | 29 | 16 | 124 | 16 | 297 |
| 18.09.98 17:00 | 298 | 2 | 281 | 29 | 16 | 134 | 22 | 330 |
| 18.09.98 19:00 | 289 | n.q. | 123 | 14 | 5 | 47 | 12 | 107 |
| 18.09.98 20:00 | 284 | 1 | 57 | 6 | 2 | 19 | 10 | 44 |
| 18.09.98 21:00 | 282 | 2 | 47 | 6 | 3 | 15 | 8 | 33 |
| 18.09.98 23:00 | 278 | n.q. | 42 | 5 | n.q. | 13 | 5 | 24 |
| 19.09.98 07:00 | 275 | 5 | 33 | 4 | n.q. | 12 | 4 | 26 |
| 19.09.98 08:00 | 276 | 2 | 40 | 7 | n.q. | 14 | 1 | 30 |
| 19.09.98 09:00 | 281 | 4 | 70 | 9 | n.q. | 26 | 2 | 59 |

**Table 8.4:** *(continued)*

| date, time | temperature | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | longicyclene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|
| 16.09.98 04:00 | 287 | 5 | 5 | 3 | n.q. | 2 | n.q. | n.q. |
| 16.09.98 05:00 | 287 | 5 | 5 | 1 | n.q. | 2 | n.q. | n.q. |
| 16.09.98 06:00 | 287 | 5 | 5 | 3 | n.q. | 2 | n.q. | 2 |
| 16.09.98 07:00 | 287 | 5 | 4 | 2 | 0 | 1 | n.q. | n.q. |
| 16.09.98 08:00 | 287 | 6 | 6 | 4 | 2 | 1 | n.q. | 2 |
| 16.09.98 09:00 | 289 | 5 | 6 | 5 | 2 | 2 | n.q. | 1 |
| 16.09.98 10:00 | 292 | 10 | 12 | 8 | 6 | 2 | n.q. | n.q. |
| 16.09.98 11:00 | 297 | 11 | 13 | 13 | 26 | 5 | n.q. | 4 |
| 16.09.98 12:00 | 297 | 12 | 23 | 14 | 33 | 9 | n.q. | 28 |
| 16.09.98 13:00 | 299 | 18 | 27 | 18 | 55 | 11 | n.q. | 46 |
| 16.09.98 14:00 | 295 | 14 | 16 | 9 | 35 | 11 | 3 | 29 |
| 16.09.98 16:00 | 296 | 11 | 12 | 9 | 35 | 4 | n.q. | 6 |
| 16.09.98 17:00 | 292 | 6 | 8 | 5 | 7 | 2 | n.q. | 16 |
| 16.09.98 18:00 | 291 | 7 | 7 | 4 | 4 | 1 | n.q. | 31 |
| 16.09.98 19:00 | 290 | 6 | 7 | 3 | 2 | 1 | n.q. | 42 |
| 16.09.98 20:00 | 289 | 4 | 3 | 2 | 1 | 2 | n.q. | 2 |
| 16.09.98 21:00 | 288 | 3 | 4 | 2 | n.q. | n.q. | n.q. | 3 |
| 16.09.98 22:00 | 288 | 2 | 2 | 2 | n.q. | n.q. | n.q. | 5 |
| 16.09.98 23:00 | 287 | 3 | 3 | 2 | n.q. | 1 | n.q. | 11 |
| 17.09.98 08:57 | 284 | 1 | 3 | 2 | 1 | 1 | n.q. | 7 |
| 17.09.98 10:00 | 286 | 1 | 2 | 1 | 1 | 1 | n.q. | 2 |
| 17.09.98 11:00 | 289 | 3 | 4 | 3 | 3 | 1 | n.q. | 7 |
| 17.09.98 12:00 | 290 | 3 | 5 | 4 | 7 | 2 | n.q. | 6 |
| 17.09.98 13:00 | 294 | 6 | 10 | 8 | 23 | 4 | n.q. | 34 |
| 17.09.98 14:00 | 291 | 5 | 7 | 5 | 12 | 3 | n.q. | 22 |
| 17.09.98 15:00 | 290 | 4 | 5 | 4 | 5 | 2 | n.q. | 22 |
| 17.09.98 16:00 | 291 | 4 | 5 | 4 | 4 | 1 | n.q. | 18 |
| 17.09.98 17:00 | 290 | 4 | 5 | 4 | 4 | 1 | n.q. | 22 |
| 17.09.98 18:00 | 289 | 2 | 3 | 2 | 2 | n.q. | n.q. | 4 |
| 17.09.98 19:00 | 288 | 4 | 3 | 3 | 2 | n.q. | n.q. | n.q. |
| 17.09.98 20:00 | 287 | 2 | 3 | 2 | 1 | 1 | n.q. | 10 |
| 17.09.98 21:00 | 286 | 2 | 2 | 1 | n.q. | n.q. | n.q. | 5 |
| 17.09.98 22:00 | 286 | 2 | 2 | 1 | n.q. | n.q. | n.q. | 4 |
| 17.09.98 23:00 | 286 | 2 | 2 | 2 | n.q. | n.q. | n.q. | 5 |
| 18.09.98 05:00 | 284 | 1 | 1 | 1 | n.q. | n.q. | n.q. | 1 |
| 18.09.98 06:00 | 284 | 1 | 3 | 2 | n.q. | n.q. | n.q. | n.q. |
| 18.09.98 07:00 | 284 | 1 | 2 | 1 | 1 | n.q. | n.q. | n.q. |
| 18.09.98 08:00 | 285 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | 4 |
| 18.09.98 10:00 | 289 | 2 | 3 | 3 | 2 | n.q. | n.q. | 4 |
| 18.09.98 11:00 | 294 | 4 | 5 | 4 | 8 | 3 | n.q. | 6 |
| 18.09.98 12:00 | 302 | 14 | 17 | 13 | 57 | 6 | n.q. | 98 |
| 18.09.98 13:00 | 301 | 15 | 18 | 14 | 67 | 9 | n.q. | 69 |
| 18.09.98 14:00 | 299 | 13 | 17 | 11 | 51 | 8 | n.q. | 45 |
| 18.09.98 15:00 | 299 | 11 | 13 | 9 | 41 | 5 | n.q. | 42 |
| 18.09.98 16:00 | 298 | 10 | 9 | 8 | 25 | 4 | n.q. | 10 |
| 18.09.98 17:00 | 298 | 10 | 11 | 9 | 36 | 5 | 1 | 26 |
| 18.09.98 19:00 | 289 | 4 | 4 | 3 | 6 | 2 | n.q. | 17 |
| 18.09.98 20:00 | 284 | 2 | 1 | 1 | 1 | 1 | 0 | 5 |
| 18.09.98 21:00 | 282 | 2 | 1 | 1 | n.q. | n.q. | n.q. | 5 |
| 18.09.98 23:00 | 278 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | 1 |
| 19.09.98 07:00 | 275 | 2 | 2 | 1 | 0 | 1 | n.q. | 2 |
| 19.09.98 08:00 | 276 | 1 | 2 | 1 | 1 | n.q. | n.q. | n.q. |
| 19.09.98 09:00 | 281 | 2 | 2 | 1 | 2 | n.q. | n.q. | 1 |

**Table 8.5:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at branch A in October 1998, n.q. = not quantified.*

| date, time | temperature | toluene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | 3-carene |
|---|---|---|---|---|---|---|---|---|
| 20.10.98 04:00 | 280 | 1 | 20 | 4 | 3 | 7 | 2 | 17 |
| 20.10.98 06:00 | 280 | 2 | 21 | 4 | 2 | 8 | 1 | 19 |
| 20.10.98 07:00 | 280 | 1 | 21 | 4 | 2 | 8 | 2 | 19 |
| 20.10.98 08:00 | 280 | 2 | 17 | 3 | 2 | 7 | 1 | 16 |
| 20.10.98 09:00 | 281 | 1 | 22 | 4 | 4 | 9 | 2 | 22 |
| 20.10.98 11:00 | 293 | 2 | 52 | 8 | 7 | 21 | 4 | 64 |
| 20.10.98 12:00 | 299 | 2 | 102 | 13 | 8 | 41 | 9 | 150 |
| 20.10.98 13:00 | 290 | 1 | 75 | 9 | 5 | 35 | 7 | 108 |
| 20.10.98 14:00 | 287 | 2 | 46 | 6 | 3 | 20 | 4 | 61 |
| 20.10.98 15:00 | 295 | 2 | 105 | 12 | 7 | 42 | 8 | 143 |
| 20.10.98 16:00 | 290 | 2 | 52 | 8 | 7 | 23 | 5 | 65 |
| 20.10.98 17:00 | 286 | 1 | 31 | 5 | 4 | 12 | 3 | 34 |
| 20.10.98 18:00 | 284 | 2 | 24 | 4 | 2 | 9 | 2 | 23 |
| 20.10.98 20:00 | 278 | 1 | 12 | 2 | 2 | 4 | 1 | 9 |
| 20.10.98 21:00 | 277 | 0 | 10 | 2 | 3 | 3 | 1 | 7 |
| 21.10.98 06:00 | 274 | 0 | 12 | 3 | 3 | 4 | 1 | 9 |
| 21.10.98 07:00 | 275 | 2 | 15 | 4 | 3 | 6 | 1 | 0 |
| 21.10.98 08:00 | 274 | 0 | 13 | 3 | 2 | 5 | 1 | 11 |
| 21.10.98 09:00 | 276 | 0 | 15 | 3 | 2 | 6 | 1 | 14 |
| 21.10.98 10:00 | 281 | 1 | 20 | 4 | 5 | 9 | 2 | 19 |
| 21.10.98 11:00 | 287 | 2 | 27 | 5 | 2 | 10 | 2 | 28 |
| 21.10.98 12:00 | 296 | 1 | 68 | 9 | 5 | 25 | 5 | 82 |
| 21.10.98 13:00 | 293 | 1 | 65 | 9 | 4 | 24 | 5 | 80 |
| 21.10.98 14:00 | 289 | 2 | 45 | 6 | 4 | 17 | 3 | 50 |
| 21.10.98 14:57 | 288 | 1 | 35 | 5 | 4 | 13 | 4 | 35 |
| 21.10.98 16:04 | 290 | 2 | 41 | 6 | 4 | 16 | 5 | 43 |
| 21.10.98 17:00 | 290 | 2 | 45 | 7 | 4 | 17 | 5 | 48 |
| 21.10.98 18:00 | 287 | 1 | 32 | 4 | 4 | 11 | 6 | 31 |
| 21.10.98 19:00 | 287 | 2 | 19 | 3 | 3 | 7 | 3 | 16 |
| 21.10.98 20:00 | 287 | 2 | 18 | 3 | 3 | 6 | 2 | 14 |
| 21.10.98 21:00 | 286 | 2 | 19 | 4 | 1 | 7 | 6 | 14 |
| 22.10.98 09:00 | 286 | 1 | 15 | 3 | 1 | 6 | 1 | 13 |
| 22.10.98 10:00 | 288 | 2 | 43 | 7 | 1 | 18 | 4 | 51 |
| 22.10.98 11:00 | 291 | 1 | 47 | 7 | 4 | 17 | 3 | 57 |
| 22.10.98 12:00 | 292 | 1 | 55 | 7 | 4 | 18 | 4 | 62 |
| 22.10.98 13:00 | 293 | 2 | 65 | 8 | 4 | 21 | 6 | 70 |
| 22.10.98 14:00 | 294 | 2 | 101 | 15 | 7 | 31 | 8 | 121 |
| 22.10.98 16:00 | 294 | 1 | 52 | 7 | 4 | 19 | 5 | 67 |
| 22.10.98 17:00 | 291 | 2 | 33 | 4 | n.q. | 12 | 5 | 30 |
| 22.10.98 18:00 | 290 | 2 | 16 | 2 | 1 | 5 | 1 | 11 |
| 22.10.98 19:00 | 288 | 2 | 14 | 3 | 3 | 7 | 1 | 9 |
| 22.10.98 20:00 | 286 | 1 | 11 | 2 | 1 | 4 | 3 | 7 |
| 22.10.98 21:00 | 285 | 1 | 10 | 2 | 1 | 3 | 3 | 7 |
| 22.10.98 22:00 | 283 | 1 | 9 | 2 | 1 | 3 | 1 | 7 |
| 22.10.98 23:00 | 283 | 1 | 8 | 2 | 1 | 2 | 1 | 3 |
| 23.10.98 00:00 | 282 | 0 | 9 | 2 | 1 | 2 | 0 | 3 |
| 23.10.98 05:00 | 282 | 2 | 15 | 3 | 3 | 5 | 2 | 6 |
| 23.10.98 06:00 | 283 | 0 | 15 | 3 | 1 | 4 | 0 | 6 |
| 23.10.98 07:00 | 283 | 1 | 14 | 3 | 1 | 4 | 1 | 5 |
| 23.10.98 09:00 | 288 | 3 | 52 | 10 | 9 | 24 | 8 | 44 |
| 23.10.98 10:00 | 289 | 1 | 49 | 9 | 2 | 18 | 3 | 60 |
| 23.10.98 11:00 | 289 | 2 | 37 | 6 | 3 | 14 | 3 | 44 |
| 23.10.98 12:00 | 294 | 2 | 62 | 9 | 4 | 24 | 3 | 71 |

**Table 8.5:** *(continued)*

| date, time | temperature | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | longicyclene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|
| 20.10.98 04:00 | 280 | 2 | 1 | 1 | 0 | 1 | 3 | 0 |
| 20.10.98 06:00 | 280 | 1 | 1 | 1 | 1 | 1 | 1 | 0 |
| 20.10.98 07:00 | 280 | 2 | 1 | 1 | 1 | 1 | 2 | 0 |
| 20.10.98 08:00 | 280 | 1 | 1 | 0 | 0 | 1 | 0 | 0 |
| 20.10.98 09:00 | 281 | 2 | 1 | 1 | 1 | 1 | 1 | 0 |
| 20.10.98 11:00 | 293 | 3 | 3 | 2 | 1 | 2 | 1 | 1 |
| 20.10.98 12:00 | 299 | 5 | 6 | 3 | 4 | 2 | 2 | 0 |
| 20.10.98 13:00 | 290 | 4 | 4 | 2 | 3 | 2 | 7 | 0 |
| 20.10.98 14:00 | 287 | 2 | 2 | 1 | 1 | 1 | 3 | 0 |
| 20.10.98 15:00 | 295 | 5 | 5 | 3 | 3 | 3 | 7 | 1 |
| 20.10.98 16:00 | 290 | 3 | 3 | 2 | 2 | 1 | 3 | 1 |
| 20.10.98 17:00 | 286 | 2 | 2 | 1 | 1 | 1 | 3 | 0 |
| 20.10.98 18:00 | 284 | 2 | 2 | 1 | 1 | 1 | 1 | 0 |
| 20.10.98 20:00 | 278 | 1 | 1 | 0 | 0 | 0 | 0 | 0 |
| 20.10.98 21:00 | 277 | 1 | 1 | 0 | 0 | 0 | 0 | 0 |
| 21.10.98 06:00 | 274 | 1 | 1 | 0 | 0 | 0 | 0 | 0 |
| 21.10.98 07:00 | 275 | 2 | 1 | 0 | 1 | 1 | 1 | 0 |
| 21.10.98 08:00 | 274 | 1 | 1 | 0 | 0 | 0 | 1 | 0 |
| 21.10.98 09:00 | 276 | 1 | 1 | 0 | 0 | 1 | 1 | 0 |
| 21.10.98 10:00 | 281 | 1 | 1 | 1 | 1 | 1 | n.q. | n.q. |
| 21.10.98 11:00 | 287 | 2 | 2 | 1 | 1 | 1 | 4 | 1 |
| 21.10.98 12:00 | 296 | 3 | 3 | 2 | 2 | 2 | 1 | 0 |
| 21.10.98 13:00 | 293 | 3 | 4 | 2 | 2 | 2 | 2 | 0 |
| 21.10.98 14:00 | 289 | 3 | 3 | 1 | 1 | 1 | 2 | 0 |
| 21.10.98 14:57 | 288 | 2 | 2 | 1 | 1 | 1 | 1 | 0 |
| 21.10.98 16:04 | 290 | 3 | 3 | 1 | 1 | 2 | 4 | 0 |
| 21.10.98 17:00 | 290 | 4 | 3 | 1 | 1 | 1 | 2 | 0 |
| 21.10.98 18:00 | 287 | 3 | 2 | 1 | 1 | 1 | 3 | 1 |
| 21.10.98 19:00 | 287 | 2 | 1 | 0 | 0 | 1 | 6 | 0 |
| 21.10.98 20:00 | 287 | 2 | 1 | 1 | 0 | 1 | 1 | 0 |
| 21.10.98 21:00 | 286 | 2 | 2 | 1 | 0 | 1 | 1 | 0 |
| 22.10.98 09:00 | 286 | 1 | 1 | 0 | 0 | 1 | 0 | 1 |
| 22.10.98 10:00 | 288 | 1 | 2 | 1 | 1 | 3 | 1 | 1 |
| 22.10.98 11:00 | 291 | 2 | 3 | 1 | 1 | 1 | 1 | 0 |
| 22.10.98 12:00 | 292 | 2 | 2 | 1 | 1 | 1 | 1 | 0 |
| 22.10.98 13:00 | 293 | 4 | 3 | 2 | 1 | 2 | 2 | 1 |
| 22.10.98 14:00 | 294 | 5 | 6 | 3 | 2 | 3 | 3 | 1 |
| 22.10.98 16:00 | 294 | 3 | 3 | 2 | 1 | 2 | 1 | 0 |
| 22.10.98 17:00 | 291 | 3 | 2 | 1 | 1 | 2 | 2 | 1 |
| 22.10.98 18:00 | 290 | 1 | 1 | 0 | 0 | 1 | 1 | 0 |
| 22.10.98 19:00 | 288 | 2 | 1 | 1 | 1 | 1 | 1 | 0 |
| 22.10.98 20:00 | 286 | 1 | 1 | 1 | 0 | 1 | 1 | 3 |
| 22.10.98 21:00 | 285 | 1 | 1 | 1 | 0 | 1 | 2 | 1 |
| 22.10.98 22:00 | 283 | 1 | 2 | 0 | 1 | 1 | 3 | 1 |
| 22.10.98 23:00 | 283 | 1 | 1 | 0 | 0 | 1 | 0 | 0 |
| 23.10.98 00:00 | 282 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| 23.10.98 05:00 | 282 | 1 | 1 | 0 | 0 | 0 | 1 | 0 |
| 23.10.98 06:00 | 283 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 23.10.98 07:00 | 283 | 1 | 0 | 0 | 0 | 1 | 1 | 1 |
| 23.10.98 09:00 | 288 | 3 | 1 | 2 | 2 | 1 | 1 | 0 |
| 23.10.98 10:00 | 289 | 3 | 3 | 1 | 1 | 1 | 1 | 0 |
| 23.10.98 11:00 | 289 | 3 | 1 | 2 | 1 | 1 | 1 | 0 |
| 23.10.98 12:00 | 294 | 3 | 3 | 1 | 1 | 2 | 1 | 0 |

**Table 8.6:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at branch B in July 1998, n.q. = not quantified..*

| date, time | temperature | toluene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | 3-carene |
|---|---|---|---|---|---|---|---|---|
| 07.07.98 05:00 | 282 | 98 | 40 | 8 | 13 | 22 | 9 | 46 |
| 07.07.98 06:00 | 282 | 261 | 52 | 10 | 8 | 20 | 6 | 56 |
| 07.07.98 07:00 | 284 | 5 | 68 | 15 | 7 | 37 | 5 | 113 |
| 07.07.98 08:00 | 289 | 8 | 67 | 11 | 14 | 38 | 12 | 158 |
| 07.07.98 09:00 | 295 | 11 | 107 | 20 | 19 | 52 | 17 | 272 |
| 07.07.98 10:00 | 299 | 17 | 149 | 35 | 28 | 69 | 26 | 376 |
| 07.07.98 11:00 | 303 | 19 | 171 | 28 | 7 | 81 | 43 | 329 |
| 07.07.98 12:00 | 302 | 17 | 160 | 22 | 30 | 64 | 21 | 222 |
| 07.07.98 13:00 | 304 | 18 | 132 | 28 | 27 | 45 | 29 | 191 |
| 07.07.98 14:00 | 306 | 20 | 199 | 29 | 32 | 70 | 32 | 273 |
| 07.07.98 15:00 | 307 | 20 | 228 | 26 | 31 | 88 | 31 | 363 |
| 07.07.98 16:00 | 304 | 35 | 205 | 29 | 48 | 103 | 46 | 305 |
| 07.07.98 17:00 | 301 | 9 | 263 | 44 | 41 | 111 | 33 | 395 |
| 07.07.98 18:00 | 293 | 6 | 88 | 14 | 12 | 38 | 5 | 113 |
| 07.07.98 19:00 | 288 | 321 | 42 | 7 | 13 | 35 | 9 | 68 |
| 07.07.98 20:00 | 287 | 6 | 31 | 4 | n.q. | 18 | 4 | 46 |
| 07.07.98 21:00 | 286 | 85 | 28 | n.q. | 6 | 14 | 4 | 37 |
| 07.07.98 22:00 | 285 | 76 | 25 | 4 | 9 | 18 | 10 | 32 |
| 07.07.98 23:30 | 285 | 79 | 30 | 4 | 4 | 14 | 3 | 37 |
| 08.07.98 01:30 | 284 | 70 | 28 | 3 | 3 | 13 | 3 | 32 |
| 08.07.98 07:00 | 283 | 61 | 81 | 13 | 10 | 27 | 5 | 111 |
| 08.07.98 08:00 | 288 | 5 | 5 | 8 | 6 | 26 | 7 | 88 |
| 08.07.98 09:00 | 288 | 65 | 27 | 7 | 6 | 13 | 2 | 51 |
| 08.07.98 10:00 | 288 | 3 | 41 | 6 | n.q. | 21 | 3 | 69 |
| 08.07.98 11:00 | 291 | 81 | 23 | 6 | 9 | 11 | 4 | 16 |
| 08.07.98 12:00 | 296 | 22 | 89 | 11 | 15 | 37 | n.q. | 166 |
| 08.07.98 13:00 | 301 | 11 | 133 | 23 | 28 | 51 | 17 | 194 |
| 08.07.98 14:00 | 297 | 6 | 56 | 12 | 8 | 21 | 10 | 86 |
| 08.07.98 15:00 | 297 | 164 | 88 | 18 | 17 | 42 | 12 | 127 |
| 08.07.98 16:00 | 299 | 6 | 85 | 10 | 13 | 32 | 10 | 105 |
| 08.07.98 17:00 | 298 | 5 | 54 | 7 | 16 | 22 | 9 | 68 |
| 08.07.98 18:00 | 294 | 125 | 40 | 5 | 17 | 17 | 6 | 40 |
| 08.07.98 19:00 | 292 | 5 | 38 | 7 | 17 | 25 | 9 | 44 |
| 08.07.98 20:00 | 290 | 84 | 22 | n.q. | 22 | 16 | 13 | 27 |
| 08.07.98 21:00 | 289 | 164 | 21 | 5 | n.q. | 23 | 17 | 27 |
| 08.07.98 22:00 | 287 | 68 | 20 | 2 | n.q. | 14 | 5 | 21 |
| 08.07.98 23:30 | 284 | 1 | 14 | 2 | n.q. | 5 | 2 | 15 |
| 09.07.98 01:30 | 281 | 37 | 20 | 2 | 3 | 6 | n.q. | 17 |
| 09.07.98 03:30 | 279 | 32 | 22 | 3 | 3 | 11 | 2 | 20 |
| 09.07.98 05:30 | 278 | 26 | 23 | 3 | 3 | 9 | 2 | 20 |
| 09.07.98 07:00 | 282 | 27 | 33 | 6 | 7 | 20 | 6 | 37 |
| 09.07.98 08:00 | 287 | 59 | 49 | 7 | 7 | 22 | 6 | 66 |
| 09.07.98 09:00 | 293 | 88 | 70 | 11 | 11 | 30 | 10 | 117 |
| 09.07.98 10:00 | 291 | 4 | 55 | 7 | 6 | 17 | 3 | 77 |
| 09.07.98 12:00 | 291 | 4 | 34 | 4 | 4 | 13 | 3 | 46 |
| 09.07.98 13:00 | 295 | 4 | 66 | 10 | 8 | 22 | 7 | 82 |
| 09.07.98 14:00 | 296 | 4 | 61 | 7 | 7 | 18 | 6 | 72 |
| 09.07.98 15:00 | 296 | 5 | 70 | 10 | 9 | 21 | 12 | 77 |
| 09.07.98 16:00 | 303 | 12 | 143 | 21 | 21 | 49 | 18 | 131 |
| 09.07.98 17:00 | 300 | 145 | 85 | 13 | 12 | 27 | 21 | 105 |
| 09.07.98 20:00 | 293 | 83 | 30 | 4 | 3 | 11 | 4 | 39 |
| 09.07.98 21:00 | 292 | 92 | 30 | 4 | 1 | 10 | 2 | 36 |
| 09.07.98 22:00 | 291 | 104 | 30 | 4 | 2 | 12 | 4 | 33 |
| 09.07.98 23:30 | 290 | 4 | 24 | 3 | 1 | 8 | 3 | 27 |
| 10.07.98 01:30 | 287 | 50 | 18 | 2 | 1 | 6 | 1 | 18 |
| 10.07.98 03:30 | 286 | 44 | 15 | 2 | 2 | 6 | 2 | 18 |

**Table 8.6:** *(continued)*

| date, time | temperature | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | longicyclene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|
| 07.07.98 05:00 | 282 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 07.07.98 06:00 | 282 | 2 | 4 | 1 | 1 | n.q. | n.q. | 2 |
| 07.07.98 07:00 | 284 | 4 | 5 | 3 | 9 | n.q. | n.q. | 3 |
| 07.07.98 08:00 | 289 | 4 | 6 | 4 | 19 | 2 | n.q. | 5 |
| 07.07.98 09:00 | 295 | 7 | 9 | 5 | 74 | 6 | n.q. | 6 |
| 07.07.98 10:00 | 299 | 10 | 16 | n.q. | n.q. | 7 | n.q. | 7 |
| 07.07.98 11:00 | 303 | 20 | 15 | 8 | 153 | 6 | 5 | 41 |
| 07.07.98 12:00 | 302 | 9 | 9 | n.q. | 120 | 6 | 2 | 7 |
| 07.07.98 13:00 | 304 | 11 | 13 | n.q. | 91 | 6 | n.q. | 15 |
| 07.07.98 14:00 | 306 | 8 | 10 | 6 | 89 | 4 | 2 | 17 |
| 07.07.98 15:00 | 307 | 11 | 10 | 7 | 65 | 5 | 1 | 10 |
| 07.07.98 16:00 | 304 | 10 | 14 | 6 | 75 | n.q. | n.q. | n.q. |
| 07.07.98 17:00 | 301 | 14 | 15 | 8 | 222 | 7 | n.q. | 6 |
| 07.07.98 18:00 | 293 | 4 | 5 | 4 | 60 | 4 | n.q. | n.q. |
| 07.07.98 19:00 | 288 | n.q. | 5 | 16 | n.q. | n.q. | n.q. | n.q. |
| 07.07.98 20:00 | 287 | 4 | 3 | 2 | 4 | 4 | n.q. | 2 |
| 07.07.98 21:00 | 286 | 2 | 3 | n.q. | 5 | n.q. | n.q. | 3 |
| 07.07.98 22:00 | 285 | n.q. | n.q. | n.q. | n.q. | n.q. | 2 | 8 |
| 07.07.98 23:30 | 285 | 1 | 1 | 1 | 2 | n.q. | n.q. | 5 |
| 08.07.98 01:30 | 284 | 1 | 2 | 1 | 1 | n.q. | n.q. | n.q. |
| 08.07.98 07:00 | 283 | 13 | 7 | 2 | 12 | 2 | n.q. | 7 |
| 08.07.98 08:00 | 288 | 3 | 4 | 17 | n.q. | 3 | n.q. | n.q. |
| 08.07.98 09:00 | 288 | 2 | 2 | 2 | 9 | 2 | n.q. | 5 |
| 08.07.98 10:00 | 288 | 1 | 3 | 17 | n.q. | 2 | n.q. | 4 |
| 08.07.98 11:00 | 291 | 5 | 3 | 9 | n.q. | 5 | 2 | 4 |
| 08.07.98 12:00 | 296 | n.q. | n.q. | 77 | n.q. | 4 | n.q. | n.q. |
| 08.07.98 13:00 | 301 | 5 | 7 | 4 | 118 | 5 | n.q. | 6 |
| 08.07.98 14:00 | 297 | 5 | 5 | n.q. | 46 | 3 | 1 | 3 |
| 08.07.98 15:00 | 297 | 3 | 6 | 3 | 43 | 3 | 3 | 5 |
| 08.07.98 16:00 | 299 | 3 | 6 | 3 | 50 | 5 | n.q. | 5 |
| 08.07.98 17:00 | 298 | 4 | 5 | n.q. | 36 | n.q. | 2 | 6 |
| 08.07.98 18:00 | 294 | 2 | 5 | n.q. | 14 | n.q. | n.q. | 2 |
| 08.07.98 19:00 | 292 | 4 | 4 | n.q. | 6 | n.q. | n.q. | 4 |
| 08.07.98 20:00 | 290 | 3 | 4 | n.q. | 4 | 2 | n.q. | 5 |
| 08.07.98 21:00 | 289 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 08.07.98 22:00 | 287 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | 2 |
| 08.07.98 23:30 | 284 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 09.07.98 01:30 | 281 | 1 | 1 | n.q. | 2 | n.q. | n.q. | n.q. |
| 09.07.98 03:30 | 279 | 1 | 2 | 1 | 2 | n.q. | n.q. | n.q. |
| 09.07.98 05:30 | 278 | n.q. | 2 | 0 | 2 | n.q. | n.q. | n.q. |
| 09.07.98 07:00 | 282 | n.q. | n.q. | n.q. | 6 | n.q. | n.q. | 3 |
| 09.07.98 08:00 | 287 | 2 | 2 | n.q. | 14 | n.q. | n.q. | 3 |
| 09.07.98 09:00 | 293 | 3 | 4 | n.q. | 51 | n.q. | n.q. | 4 |
| 09.07.98 10:00 | 291 | 3 | 5 | n.q. | 42 | n.q. | n.q. | 5 |
| 09.07.98 12:00 | 291 | 1 | 2 | n.q. | 10 | n.q. | n.q. | n.q. |
| 09.07.98 13:00 | 295 | 2 | 2 | n.q. | 48 | 2 | 3 | n.q. |
| 09.07.98 14:00 | 296 | 3 | 3 | n.q. | 68 | n.q. | n.q. | n.q. |
| 09.07.98 15:00 | 296 | 3 | 3 | n.q. | 56 | 2 | n.q. | 3 |
| 09.07.98 16:00 | 303 | 7 | 8 | n.q. | 73 | 6 | 1 | 5 |
| 09.07.98 17:00 | 300 | 4 | 4 | n.q. | 45 | 3 | n.q. | 10 |
| 09.07.98 20:00 | 293 | 3 | 3 | 5 | n.q. | n.q. | n.q. | 3 |
| 09.07.98 21:00 | 292 | n.q. | 1 | 1 | 3 | n.q. | n.q. | n.q. |
| 09.07.98 22:00 | 291 | n.q. | n.q. | n.q. | 3 | 1 | n.q. | n.q. |
| 09.07.98 23:30 | 290 | n.q. | 1 | n.q. | 2 | n.q. | n.q. | n.q. |
| 10.07.98 01:30 | 287 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 10.07.98 03:30 | 286 | n.q. | n.q. | n.q. | n.q. | n.q. | 1 | n.q. |

**Table 8.7:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at branch B in September 1998, n.q. = not quantified.*

| date, time | temperature | toluene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | 3-carene |
|---|---|---|---|---|---|---|---|---|
| 16.09.98 04:00 | 286 | 14 | 88 | 8 | n.q. | 35 | 7 | 82 |
| 16.09.98 05:00 | 286 | 21 | 127 | 14 | 5 | 48 | 5 | 125 |
| 16.09.98 06:00 | 286 | 15 | 103 | 16 | 8 | 45 | 9 | 127 |
| 16.09.98 07:00 | 286 | 11 | 38 | n.q. | 15 | 17 | n.q. | 53 |
| 16.09.98 08:00 | 287 | 12 | 141 | 16 | 14 | 57 | 12 | 155 |
| 16.09.98 09:00 | 288 | 24 | 153 | 21 | n.q. | 66 | 15 | 172 |
| 16.09.98 10:00 | 291 | 18 | 198 | 22 | n.q. | 74 | 11 | 212 |
| 16.09.98 11:00 | 296 | n.q. | 220 | 18 | 8 | 68 | 7 | 174 |
| 16.09.98 12:00 | 296 | 114 | 296 | 95 | n.q. | 169 | 129 | 370 |
| 16.09.98 13:00 | 299 | 118 | 359 | 56 | n.q. | 275 | 90 | 414 |
| 16.09.98 14:00 | 295 | 13 | 162 | 17 | 14 | 66 | 8 | 175 |
| 16.09.98 15:00 | 295 | 128 | 177 | 37 | n.q. | 243 | 177 | 198 |
| 16.09.98 16:00 | 296 | 122 | 169 | 22 | n.q. | 199 | 129 | 184 |
| 16.09.98 17:00 | 291 | 112 | 121 | 28 | n.q. | 93 | 37 | 128 |
| 16.09.98 18:00 | 290 | 5 | 33 | 5 | n.q. | 13 | 3 | 31 |
| 16.09.98 19:00 | 289 | 18 | 95 | 11 | n.q. | 43 | 7 | 89 |
| 16.09.98 20:00 | 288 | 28 | 97 | 15 | 7 | 50 | 9 | 85 |
| 16.09.98 21:00 | 288 | 37 | 90 | 13 | n.q. | 73 | 19 | 87 |
| 16.09.98 22:00 | 287 | 29 | 81 | 12 | 43 | 71 | n.q. | 77 |
| 16.09.98 23:00 | 287 | 10 | 99 | 16 | n.q. | 38 | 13 | 92 |
| 18.09.98 09:00 | 285 | 5 | 86 | 8 | 5 | 30 | 5 | 106 |
| 18.09.98 10:00 | 288 | 4 | 99 | 9 | 4 | 38 | 5 | 133 |
| 18.09.98 11:00 | 294 | 7 | 136 | 12 | 6 | 54 | 7 | 188 |
| 18.09.98 12:00 | 303 | 16 | 280 | 26 | 16 | 131 | 21 | 388 |
| 18.09.98 13:00 | 303 | 14 | 302 | 30 | 17 | 129 | 23 | 357 |
| 18.09.98 14:00 | 301 | 9 | 233 | 25 | 12 | 91 | 18 | 282 |
| 18.09.98 15:00 | 301 | 8 | 217 | 22 | 11 | 82 | 15 | 235 |
| 18.09.98 16:00 | 298 | 8 | 146 | 15 | 6 | 55 | 9 | 155 |
| 18.09.98 17:00 | 299 | 7 | 143 | 15 | 8 | 62 | 20 | 175 |
| 18.09.98 18:00 | 299 | 9 | 158 | 17 | 10 | 72 | 20 | 197 |
| 18.09.98 19:00 | 290 | 4 | 97 | 11 | 7 | 41 | 14 | 108 |
| 18.09.98 20:00 | 283 | 3 | 67 | 7 | 3 | 21 | 2 | 54 |
| 18.09.98 21:00 | 281 | 4 | 54 | 6 | 2 | 26 | 19 | 42 |
| 19.09.98 06:00 | 274 | 1 | 32 | 5 | n.q. | 11 | 1 | 24 |
| 19.09.98 07:00 | 274 | 2 | 35 | 4 | n.q. | 10 | n.q. | 24 |
| 19.09.98 08:00 | 275 | 9 | 104 | 13 | n.q. | 29 | 2 | 79 |
| 19.09.98 09:00 | 280 | 3 | 63 | 9 | 4 | 23 | 3 | 60 |

**Table 8.7:** *(continued)*

| date, time | temperature | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | longicyclene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|
| 16.09.98 04:00 | 286 | 4 | 5 | 2 | 1 | n.q. | n.q. | n.q. |
| 16.09.98 05:00 | 286 | 7 | 8 | 4 | 6 | 6 | n.q. | n.q. |
| 16.09.98 06:00 | 286 | 5 | 6 | 3 | 4 | 2 | n.q. | n.q. |
| 16.09.98 07:00 | 286 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | 3 |
| 16.09.98 08:00 | 287 | 4 | 9 | 5 | 2 | n.q. | n.q. | n.q. |
| 16.09.98 09:00 | 288 | 4 | 7 | 3 | 2 | n.q. | n.q. | n.q. |
| 16.09.98 10:00 | 291 | 7 | 7 | 4 | 4 | 6 | n.q. | n.q. |
| 16.09.98 11:00 | 296 | 2 | 6 | 5 | n.q. | 3 | n.q. | n.q. |
| 16.09.98 12:00 | 296 | 67 | 90 | 7 | 22 | 5 | 6 | 4 |
| 16.09.98 13:00 | 299 | 18 | 16 | 14 | 33 | 84 | 24 | 6 |
| 16.09.98 14:00 | 295 | 6 | 6 | 4 | 15 | 3 | n.q. | n.q. |
| 16.09.98 15:00 | 295 | 15 | 16 | 45 | 11 | 87 | 29 | n.q. |
| 16.09.98 16:00 | 296 | 7 | 7 | 29 | 11 | 58 | 4 | n.q. |
| 16.09.98 17:00 | 291 | 5 | n.q. | 12 | n.q. | 22 | n.q. | n.q. |
| 16.09.98 18:00 | 290 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 16.09.98 19:00 | 289 | 3 | 5 | 3 | 2 | 2 | n.q. | 3 |
| 16.09.98 20:00 | 288 | 5 | 11 | n.q. | n.q. | 4 | n.q. | 3 |
| 16.09.98 21:00 | 288 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 16.09.98 22:00 | 287 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 16.09.98 23:00 | 287 | 3 | 8 | 5 | n.q. | 2 | n.q. | 13 |
| 18.09.98 09:00 | 285 | 2 | 3 | 2 | 1 | n.q. | n.q. | 1 |
| 18.09.98 10:00 | 288 | 2 | 4 | 3 | 2 | 2 | n.q. | 1 |
| 18.09.98 11:00 | 294 | 4 | 5 | 4 | 6 | 3 | n.q. | 2 |
| 18.09.98 12:00 | 303 | 10 | 11 | 9 | 36 | 2 | 1 | 6 |
| 18.09.98 13:00 | 303 | 11 | 12 | 9 | 42 | 7 | n.q. | 14 |
| 18.09.98 14:00 | 301 | 9 | 9 | 7 | 30 | 5 | n.q. | 15 |
| 18.09.98 15:00 | 301 | 7 | 7 | 6 | 23 | 6 | n.q. | 12 |
| 18.09.98 16:00 | 298 | 4 | 6 | 4 | 11 | 4 | 1 | 5 |
| 18.09.98 17:00 | 299 | 5 | 5 | 4 | 13 | 3 | n.q. | 7 |
| 18.09.98 18:00 | 299 | 7 | 7 | 5 | 22 | 3 | 1 | 3 |
| 18.09.98 19:00 | 290 | 3 | 3 | 2 | 8 | 2 | n.q. | n.q. |
| 18.09.98 20:00 | 283 | 3 | 2 | 1 | 1 | 2 | 1 | n.q. |
| 18.09.98 21:00 | 281 | n.q. | 2 | n.q. | n.q. | n.q. | 1 | n.q. |
| 19.09.98 06:00 | 274 | n.q. | n.q. | n.q. | n.q. | n.q. | 2 | 7 |
| 19.09.98 07:00 | 274 | n.q. | n.q. | n.q. | n.q. | n.q. | 1 | n.q. |
| 19.09.98 08:00 | 275 | 1 | 3 | 2 | 1 | 1 | n.q. | n.q. |
| 19.09.98 09:00 | 280 | 1 | 2 | 2 | 2 | n.q. | n.q. | 3 |

**Table 8.8:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at branch B in October 1998, n.q. = not quantified.*

| date, time | temperature | toluene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | 3-carene |
|---|---|---|---|---|---|---|---|---|
| 20.10.98 05:00 | 277 | 6 | 31 | 4 | 6 | 8 | 3 | 23 |
| 20.10.98 06:00 | 278 | 5 | 25 | 4 | 5 | 8 | 3 | 19 |
| 20.10.98 07:00 | 279 | 8 | 26 | 4 | 3 | 9 | 5 | 21 |
| 20.10.98 08:00 | 279 | 26 | 30 | 7 | 3 | 12 | 15 | 20 |
| 20.10.98 10:00 | 282 | 6 | 29 | 5 | 6 | 10 | 3 | 26 |
| 20.10.98 12:00 | 294 | 15 | 61 | 8 | 5 | 27 | 9 | 88 |
| 20.10.98 13:00 | 288 | 9 | 45 | 6 | 13 | 23 | 10 | 62 |
| 20.10.98 14:00 | 285 | 7 | 34 | 5 | 10 | 17 | 8 | 45 |
| 20.10.98 15:00 | 292 | 8 | 54 | 6 | 6 | 22 | 5 | 69 |
| 20.10.98 16:00 | 288 | 16 | 83 | 12 | 20 | 26 | 16 | 105 |
| 20.10.98 17:00 | 285 | 6 | 29 | 4 | 5 | 11 | 4 | 30 |
| 20.10.98 18:00 | 283 | 5 | 21 | 3 | 2 | 6 | 3 | 20 |
| 20.10.98 19:00 | 280 | 4 | 16 | 2 | 5 | 6 | 4 | 14 |
| 20.10.98 21:00 | 276 | 15 | 14 | 3 | 2 | 4 | 6 | 10 |
| 21.10.98 06:00 | 273 | 23 | 57 | 13 | n.q. | 8 | 25 | 50 |
| 21.10.98 07:00 | 273 | 8 | 13 | 3 | 5 | 8 | 8 | 10 |
| 21.10.98 08:00 | 273 | 40 | 17 | 8 | 6 | 15 | 19 | 12 |
| 21.10.98 09:00 | 274 | 17 | 12 | 4 | 4 | 6 | 10 | 9 |
| 21.10.98 10:00 | 279 | 11 | 13 | 4 | 2 | 7 | 8 | 13 |
| 21.10.98 11:00 | 285 | 4 | 20 | 4 | 4 | 8 | 9 | 21 |
| 21.10.98 12:00 | 293 | 7 | 27 | 6 | 5 | n.q. | 11 | 32 |
| 21.10.98 13:00 | 291 | 32 | 54 | 9 | 4 | 23 | 9 | 63 |
| 21.10.98 14:00 | 288 | 22 | 41 | 8 | 7 | 20 | 16 | 48 |
| 21.10.98 15:04 | 287 | 23 | 35 | 7 | 3 | 14 | 15 | 35 |
| 21.10.98 16:04 | 289 | 30 | 28 | 6 | 3 | 13 | 12 | 27 |
| 21.10.98 17:00 | 288 | 25 | 36 | 12 | 17 | 19 | 14 | 55 |
| 21.10.98 18:00 | 286 | 30 | 41 | 7 | 4 | 18 | 11 | 53 |
| 21.10.98 19:00 | 286 | 12 | 20 | 3 | 4 | 8 | 5 | 24 |
| 21.10.98 20:00 | 286 | 10 | 24 | 3 | 4 | 8 | 4 | 26 |
| 21.10.98 21:00 | 285 | 8 | 23 | 4 | 3 | 7 | 3 | 25 |
| 22.10.98 09:00 | 285 | 7 | 22 | 4 | 2 | 8 | 3 | 25 |
| 22.10.98 10:00 | 287 | 11 | 22 | 4 | 3 | 8 | 5 | 22 |
| 22.10.98 12:00 | 291 | 26 | 21 | 7 | 5 | 7 | 10 | 21 |
| 22.10.98 14:00 | 293 | 76 | 59 | 16 | 11 | 30 | 32 | 55 |
| 22.10.98 15:00 | 294 | 22 | 52 | 7 | 6 | n.q. | 21 | 64 |
| 22.10.98 16:00 | 293 | 21 | 63 | 9 | 7 | 26 | 6 | 81 |
| 22.10.98 17:00 | 290 | 20 | 70 | 8 | 7 | 30 | 7 | 98 |
| 22.10.98 18:00 | 289 | 24 | 69 | 10 | 7 | 28 | 13 | 88 |
| 22.10.98 19:00 | 287 | 17 | 54 | 8 | 5 | 22 | 9 | 64 |
| 22.10.98 20:00 | 285 | 11 | 43 | 6 | 4 | 16 | 6 | 51 |
| 22.10.98 23:00 | 281 | 9 | 39 | 5 | 7 | 15 | 5 | 43 |
| 23.10.98 00:00 | 280 | 7 | 31 | 4 | 3 | 12 | 3 | 34 |
| 23.10.98 05:00 | 281 | 9 | 23 | 4 | 4 | 9 | 3 | 21 |
| 23.10.98 06:00 | 281 | 24 | 30 | 8 | 3 | 13 | 13 | 30 |
| 23.10.98 07:00 | 282 | 30 | 101 | 15 | 10 | 37 | 6 | 101 |
| 23.10.98 08:00 | 282 | 9 | 24 | 4 | 3 | 8 | 3 | 22 |
| 23.10.98 09:00 | 286 | 10 | 29 | 5 | 3 | 11 | 4 | 31 |
| 23.10.98 10:00 | 288 | 24 | 28 | 5 | 4 | 10 | 4 | 25 |

**Table 8.8:** *(continued)*

| date, time | temperature | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | longicyclene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|
| 20.10.98 05:00 | 277 | 2 | 1 | 1 | 1 | 1 | 0 | 1 |
| 20.10.98 06:00 | 278 | 2 | 1 | 0 | n.q. | 1 | 0 | 1 |
| 20.10.98 07:00 | 279 | 2 | 0 | 1 | 0 | 2 | 1 | 1 |
| 20.10.98 08:00 | 279 | 4 | 1 | 2 | n.q. | 3 | 1 | 1 |
| 20.10.98 10:00 | 282 | 0 | 1 | 1 | 1 | 1 | 1 | 2 |
| 20.10.98 12:00 | 294 | 6 | 5 | 2 | 3 | 3 | 2 | 1 |
| 20.10.98 13:00 | 288 | 5 | 4 | 1 | 2 | 3 | 2 | 2 |
| 20.10.98 14:00 | 285 | 3 | 2 | 1 | 1 | 1 | 1 | 1 |
| 20.10.98 15:00 | 292 | 3 | 4 | 2 | 1 | 2 | 2 | 1 |
| 20.10.98 16:00 | 288 | 11 | 8 | n.q. | 9 | 5 | 3 | 2 |
| 20.10.98 17:00 | 285 | 2 | 2 | 1 | 1 | 2 | 2 | 1 |
| 20.10.98 18:00 | 283 | 1 | 1 | 0 | 0 | 1 | 0 | 0 |
| 20.10.98 19:00 | 280 | 2 | 1 | 1 | 0 | 1 | 0 | 0 |
| 20.10.98 21:00 | 276 | 1 | 2 | 1 | n.q. | 2 | 0 | 1 |
| 21.10.98 06:00 | 273 | 5 | 5 | 2 | 2 | 4 | 2 | 2 |
| 21.10.98 07:00 | 273 | 1 | 2 | 0 | 0 | 2 | 1 | 1 |
| 21.10.98 08:00 | 273 | 3 | 1 | 3 | 3 | 5 | 1 | 3 |
| 21.10.98 09:00 | 274 | 2 | 2 | n.q. | n.q. | 3 | 1 | 2 |
| 21.10.98 10:00 | 279 | 1 | 1 | 1 | 1 | 2 | 0 | 1 |
| 21.10.98 11:00 | 285 | 3 | 2 | 1 | 1 | 1 | 6 | 1 |
| 21.10.98 12:00 | 293 | 1 | 3 | 1 | 1 | 1 | 4 | 1 |
| 21.10.98 13:00 | 291 | 4 | 4 | 1 | 2 | 2 | 3 | 1 |
| 21.10.98 14:00 | 288 | 7 | 5 | 2 | 3 | 3 | 6 | 1 |
| 21.10.98 15:04 | 287 | 3 | 3 | 1 | 1 | 2 | 6 | 1 |
| 21.10.98 16:04 | 289 | 3 | 3 | 1 | 1 | 3 | 1 | 1 |
| 21.10.98 17:00 | 288 | 9 | 5 | 1 | 1 | 4 | 2 | 2 |
| 21.10.98 18:00 | 286 | 3 | 3 | 1 | 1 | 2 | 1 | 1 |
| 21.10.98 19:00 | 286 | 2 | 2 | 1 | 1 | 2 | 1 | 1 |
| 21.10.98 20:00 | 286 | 2 | 2 | 1 | n.q. | 1 | 2 | 0 |
| 21.10.98 21:00 | 285 | 2 | 2 | 1 | n.q. | 1 | 3 | 0 |
| 22.10.98 09:00 | 285 | 2 | 2 | 1 | n.q. | 1 | 3 | 1 |
| 22.10.98 10:00 | 287 | 2 | 2 | 1 | 0 | 1 | 2 | 0 |
| 22.10.98 12:00 | 291 | 8 | 5 | 2 | 2 | 3 | 9 | 1 |
| 22.10.98 14:00 | 293 | 10 | 9 | 5 | 5 | 10 | 5 | 2 |
| 22.10.98 15:00 | 294 | 4 | 4 | 2 | 2 | 4 | 1 | 0 |
| 22.10.98 16:00 | 293 | 4 | 4 | 2 | 2 | 5 | 1 | 0 |
| 22.10.98 17:00 | 290 | 4 | 4 | 2 | 2 | 3 | 2 | 1 |
| 22.10.98 18:00 | 289 | 6 | 4 | 3 | 2 | 5 | 8 | 3 |
| 22.10.98 19:00 | 287 | 6 | 4 | 2 | 2 | 2 | 19 | 2 |
| 22.10.98 20:00 | 285 | 5 | 3 | 2 | 1 | 2 | 4 | 1 |
| 22.10.98 23:00 | 281 | 3 | 2 | 1 | 0 | 1 | 2 | 1 |
| 23.10.98 00:00 | 280 | 2 | 1 | 1 | n.q. | 1 | 1 | 0 |
| 23.10.98 05:00 | 281 | 2 | 1 | 1 | 0 | 1 | 0 | 1 |
| 23.10.98 06:00 | 281 | 3 | 4 | 1 | 0 | 2 | 1 | 0 |
| 23.10.98 07:00 | 282 | 6 | 5 | 3 | 1 | 2 | 1 | 0 |
| 23.10.98 08:00 | 282 | 2 | 1 | 1 | 1 | 1 | 1 | 0 |
| 23.10.98 09:00 | 286 | 3 | 2 | 1 | 1 | 1 | 8 | 1 |
| 23.10.98 10:00 | 288 | 3 | 2 | 1 | 1 | 2 | 3 | 2 |

**Table 8.9:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at pine No.1 in June 1998, n.q. = not quantified.*

| date, time | temperature | toluene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | 2-carene | 3-carene |
|---|---|---|---|---|---|---|---|---|---|
| 04.06.98 14:30 | 303 | 7 | 23 | 15 | n.q. | 7 | 6 | 5 | 36 |
| 04.06.98 15:30 | 302 | 5 | 12 | 5 | n.q. | 2 | 12 | 8 | 17 |
| 04.06.98 16:30 | 303 | 6 | 48 | 27 | 24 | 20 | 13 | 5 | 85 |
| 04.06.98 17:30 | 303 | 7 | 42 | 24 | n.q. | 18 | 12 | 3 | 64 |
| 04.06.98 18:30 | 297 | 6 | 31 | 18 | 6 | 12 | 5 | 4 | 43 |
| 04.06.98 19:30 | 293 | 5 | 15 | 11 | n.q. | 8 | 5 | 2 | 18 |
| 04.06.98 20:30 | 292 | 6 | 9 | 6 | n.q. | 16 | 7 | 1 | 9 |
| 04.06.98 21:30 | 289 | 4 | 11 | 7 | 3 | 2 | 3 | 4 | 14 |
| 04.06.98 22:30 | 287 | 4 | 9 | 6 | n.q. | 3 | 2 | 1 | 10 |
| 05.06.98 00:00 | 286 | 4 | 7 | 5 | n.q. | 4 | 3 | 2 | 7 |
| 05.06.98 02:30 | 285 | 2 | 6 | 4 | n.q. | 4 | 3 | 1 | 4 |
| 05.06.98 05:00 | 284 | 1 | 5 | 4 | n.q. | 2 | 2 | n.q. | 4 |
| 05.06.98 07:00 | 288 | 3 | 12 | 7 | n.q. | 4 | 1 | 1 | 12 |
| 05.06.98 09:30 | 300 | 7 | 39 | 19 | n.q. | 9 | 8 | 5 | 70 |
| 05.06.98 10:30 | 301 | 96 | 19 | 14 | 15 | 9 | 4 | 7 | 23 |
| 05.06.98 11:30 | 299 | 9 | 30 | 18 | n.q. | 10 | 7 | 2 | 43 |
| 05.06.98 12:30 | 299 | 10 | 43 | 24 | 16 | 13 | 4 | 7 | 63 |
| 05.06.98 13:30 | 303 | 10 | 58 | 35 | n.q. | 15 | 6 | 2 | 91 |
| 05.06.98 14:30 | 300 | 6 | 34 | 20 | 9 | 10 | 4 | 6 | 38 |
| 05.06.98 15:30 | 300 | 4 | 8 | 6 | n.q. | 12 | 6 | 2 | 12 |
| 05.06.98 16:30 | 303 | 8 | 45 | 29 | 25 | 21 | 14 | 3 | 73 |
| 05.06.98 17:30 | 303 | 8 | 38 | 24 | 12 | 14 | 9 | 4 | 59 |
| 05.06.98 19:30 | 297 | 9 | 29 | 31 | 5 | 6 | 3 | 2 | 32 |
| 05.06.98 20:30 | 295 | 6 | 16 | 11 | 10 | 8 | 4 | 4 | 19 |
| 05.06.98 21:30 | 293 | 6 | 11 | 9 | 10 | 6 | 2 | 3 | 18 |
| 05.06.98 22:30 | 292 | 5 | 23 | 8 | 9 | 3 | 3 | 2 | 51 |
| 19.06.98 11:00 | 296 | 3 | 30 | 13 | 6 | 5 | 3 | 2 | 64 |
| 19.06.98 12:00 | 300 | 5 | 54 | 28 | 20 | 17 | 16 | 7 | 166 |
| 19.06.98 13:00 | 300 | 6 | 13 | 8 | n.q. | 3 | 4 | n.q. | 52 |
| 19.06.98 14:00 | 302 | 16 | 81 | 34 | 23 | 29 | 20 | 17 | 210 |
| 19.06.98 15:00 | 302 | 8 | 96 | 48 | 23 | 21 | 20 | 5 | 246 |
| 19.06.98 16:00 | 306 | 11 | 136 | 67 | n.q. | 28 | 33 | 11 | 370 |
| 19.06.98 17:00 | 306 | 13 | 131 | 78 | 21 | 24 | 23 | 4 | 290 |
| 19.06.98 18:00 | 304 | 9 | 109 | 54 | 18 | 23 | 18 | 11 | 227 |
| 19.06.98 19:00 | 298 | 5 | 52 | 25 | 6 | 11 | 8 | 5 | 93 |
| 19.06.98 20:00 | 296 | 5 | 45 | 20 | 10 | 8 | 8 | 4 | 161 |
| 19.06.98 21:00 | 294 | 9 | 64 | 24 | 10 | 11 | 9 | 8 | 160 |
| 19.06.98 22:00 | 291 | 7 | 38 | 15 | 8 | 5 | 6 | 3 | 79 |
| 19.06.98 23:00 | 290 | 8 | 28 | 14 | 9 | 7 | 4 | 6 | 67 |
| 20.06.98 10:00 | 307 | 28 | 53 | 30 | 14 | 13 | 11 | 16 | 113 |
| 20.06.98 11:00 | 309 | 14 | 193 | 93 | 100 | 49 | 61 | 16 | 411 |
| 20.06.98 12:00 | 310 | 19 | 248 | 121 | 68 | 66 | 67 | 13 | 514 |
| 20.06.98 13:00 | 310 | 31 | 306 | 149 | 14 | 83 | 94 | 27 | 604 |
| 20.06.98 14:00 | 311 | 13 | 187 | 97 | 50 | 54 | 68 | 13 | 456 |
| 20.06.98 15:00 | 311 | 28 | 200 | 125 | 33 | 33 | 59 | 5 | 391 |
| 20.06.98 16:00 | 312 | 25 | 291 | 148 | 72 | 74 | 86 | 8 | 730 |
| 20.06.98 17:00 | 311 | 15 | 248 | 129 | 37 | 56 | 68 | 6 | 605 |
| 21.06.98 11:00 | 312 | n.q. | 4 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 21.06.98 12:00 | 313 | 11 | 162 | 71 | 21 | 37 | 46 | 6 | 367 |
| 21.06.98 13:00 | 315 | 20 | 253 | 123 | 32 | 39 | 61 | 3 | 456 |
| 22.06.98 10:00 | 293 | 25 | 425 | 175 | 50 | 89 | 77 | 15 | 848 |
| 22.06.98 11:00 | 298 | 5 | 45 | 17 | 4 | 8 | 10 | 7 | 89 |
| 22.06.98 12:00 | 303 | 6 | 58 | 30 | 7 | 13 | 14 | 5 | 149 |
| 22.06.98 13:00 | 300 | 31 | 44 | 22 | 25 | 11 | 7 | 10 | 93 |
| 22.06.98 14:00 | 303 | 9 | 78 | 35 | 19 | 18 | 15 | 6 | 137 |
| 22.06.98 15:00 | 301 | 8 | 84 | 41 | 16 | 21 | 19 | 9 | 170 |
| 22.06.98 16:00 | 301 | 7 | 52 | 25 | 10 | 12 | 12 | 7 | 103 |

**Table 8.9:** *(continued)*

| date, time | temperature | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | longicyclene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|
| 04.06.98 14:30 | 303 | 3 | 3 | n.q. | 16 | 4 | 3 | 4 |
| 04.06.98 15:30 | 302 | 1 | 2 | 5 | n.q. | n.q. | 5 | 6 |
| 04.06.98 16:30 | 303 | 6 | 5 | 3 | 35 | 4 | 5 | 32 |
| 04.06.98 17:30 | 303 | 4 | 3 | 3 | 20 | 2 | 4 | 20 |
| 04.06.98 18:30 | 297 | 4 | 6 | 2 | 11 | n.q. | 4 | 25 |
| 04.06.98 19:30 | 293 | 2 | 2 | n.q. | 5 | n.q. | 4 | n.q. |
| 04.06.98 20:30 | 292 | n.q. | 3 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 04.06.98 21:30 | 289 | n.q. | 6 | n.q. | n.q. | n.q. | 4 | n.q. |
| 04.06.98 22:30 | 287 | n.q. | 2 | n.q. | n.q. | n.q. | 9 | 4 |
| 05.06.98 00:00 | 286 | 2 | 2 | n.q. | n.q. | n.q. | 2 | 2 |
| 05.06.98 02:30 | 285 | 1 | 1 | n.q. | n.q. | n.q. | 2 | 1 |
| 05.06.98 05:00 | 284 | n.q. | 1 | n.q. | n.q. | n.q. | 1 | 2 |
| 05.06.98 07:00 | 288 | 1 | 1 | 1 | 2 | n.q. | 2 | 2 |
| 05.06.98 09:30 | 300 | 5 | 4 | 3 | 24 | 3 | n.q. | 5 |
| 05.06.98 10:30 | 301 | 3 | 2 | 12 | n.q. | 2 | 16 | 5 |
| 05.06.98 11:30 | 299 | 3 | 4 | 16 | n.q. | 2 | 3 | 9 |
| 05.06.98 12:30 | 299 | 5 | 7 | 2 | 22 | 3 | 4 | n.q. |
| 05.06.98 13:30 | 303 | 7 | 3 | 4 | 44 | 6 | n.q. | n.q. |
| 05.06.98 14:30 | 300 | 4 | 2 | 2 | 15 | 6 | 4 | 4 |
| 05.06.98 15:30 | 300 | 3 | 4 | 6 | n.q. | 5 | n.q. | n.q. |
| 05.06.98 16:30 | 303 | 5 | 4 | 3 | 33 | 2 | 4 | 3 |
| 05.06.98 17:30 | 303 | 6 | 7 | 3 | 23 | 2 | 5 | n.q. |
| 05.06.98 19:30 | 297 | 6 | 7 | 1 | 3 | n.q. | 5 | n.q. |
| 05.06.98 20:30 | 295 | 3 | 4 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 05.06.98 21:30 | 293 | 2 | 5 | n.q. | n.q. | 2 | 3 | n.q. |
| 05.06.98 22:30 | 292 | 2 | 4 | 7 | 2 | n.q. | n.q. | 9 |
| 19.06.98 11:00 | 296 | 5 | 4 | 4 | 5 | 3 | n.q. | 4 |
| 19.06.98 12:00 | 300 | 9 | 6 | 15 | 22 | 7 | n.q. | 16 |
| 19.06.98 13:00 | 300 | 7 | 1 | 4 | 5 | n.q. | n.q. | n.q. |
| 19.06.98 14:00 | 302 | 10 | 9 | 15 | 26 | 9 | n.q. | 37 |
| 19.06.98 15:00 | 302 | 9 | 8 | 17 | 23 | 10 | n.q. | 26 |
| 19.06.98 16:00 | 306 | 16 | 8 | 24 | 39 | 16 | n.q. | 41 |
| 19.06.98 17:00 | 306 | 19 | 10 | 17 | 34 | 12 | n.q. | 22 |
| 19.06.98 18:00 | 304 | 12 | 11 | 14 | 29 | 13 | n.q. | 32 |
| 19.06.98 19:00 | 298 | 5 | 3 | 7 | 4 | 4 | 3 | 20 |
| 19.06.98 20:00 | 296 | 5 | 4 | 17 | n.q. | 5 | n.q. | 8 |
| 19.06.98 21:00 | 294 | 3 | 4 | 11 | n.q. | n.q. | 3 | 8 |
| 19.06.98 22:00 | 291 | 4 | 9 | 7 | 2 | 2 | n.q. | 8 |
| 19.06.98 23:00 | 290 | 6 | 5 | 4 | n.q. | 1 | n.q. | 5 |
| 20.06.98 10:00 | 307 | 10 | 6 | 7 | 25 | 8 | n.q. | 1 |
| 20.06.98 11:00 | 309 | 24 | 15 | 24 | 106 | 22 | 4 | 190 |
| 20.06.98 12:00 | 310 | 28 | 17 | 27 | 132 | 25 | 2 | 92 |
| 20.06.98 13:00 | 310 | 43 | 25 | 32 | 148 | 29 | 4 | 277 |
| 20.06.98 14:00 | 311 | 25 | 15 | 24 | 119 | 20 | n.q. | 88 |
| 20.06.98 15:00 | 311 | 43 | 18 | 100 | 25 | 8 | 4 | 79 |
| 20.06.98 16:00 | 312 | 34 | 19 | 41 | 140 | 20 | n.q. | 104 |
| 20.06.98 17:00 | 311 | 28 | 18 | 32 | 111 | 17 | n.q. | 183 |
| 21.06.98 11:00 | 312 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 21.06.98 12:00 | 313 | 17 | 14 | 20 | 99 | 16 | 4 | 197 |
| 21.06.98 13:00 | 315 | 114 | 36 | 6 | 85 | 6 | n.q. | n.q. |
| 22.06.98 10:00 | 293 | 45 | 27 | 34 | 156 | 22 | 5 | 182 |
| 22.06.98 11:00 | 298 | 3 | 4 | 6 | 3 | 5 | 4 | 10 |
| 22.06.98 12:00 | 303 | 4 | 6 | 17 | 8 | 6 | n.q. | 15 |
| 22.06.98 13:00 | 300 | 4 | 4 | 4 | 20 | 4 | n.q. | 4 |
| 22.06.98 14:00 | 303 | 4 | 3 | 6 | 22 | 3 | n.q. | 6 |
| 22.06.98 15:00 | 301 | 4 | 6 | 7 | 33 | 4 | n.q. | 35 |
| 22.06.98 16:00 | 301 | 3 | 4 | 20 | 4 | 5 | n.q. | 14 |

**Table 8.10:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at pine No.2 in June 1998, n.q. = not quantified..*

| date, time | temperature | toluene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | 2-carene | 3-carene |
|---|---|---|---|---|---|---|---|---|---|
| 24.06.98 15:00 | 305 | 13 | 56 | 10 | n.q. | 41 | 15 | 3 | 82 |
| 24.06.98 16:00 | 308 | 6 | 87 | 14 | 12 | 43 | 9 | 5 | 153 |
| 24.06.98 17:00 | 307 | 5 | 80 | 13 | 10 | 42 | 10 | 3 | 136 |
| 24.06.98 18:00 | 304 | 7 | 175 | 35 | 19 | 63 | 19 | 4 | 251 |
| 24.06.98 19:00 | 297 | 7 | 70 | 16 | n.q. | 32 | 9 | 5 | 90 |
| 24.06.98 20:00 | 296 | 13 | 28 | 5 | 19 | 17 | 5 | 9 | 31 |
| 24.06.98 21:00 | 295 | 3 | 52 | 9 | 8 | 20 | 4 | 3 | 62 |
| 24.06.98 22:00 | 294 | n.q. | 11 | 3 | n.q. | 7 | n.q. | 2 | 13 |
| 24.06.98 23:00 | 293 | 5 | 36 | 6 | n.q. | 19 | 6 | 5 | 40 |
| 25.06.98 00:00 | 293 | 3 | 50 | 9 | n.q. | 18 | 3 | 3 | 54 |
| 25.06.98 09:00 | 309 | 13 | 239 | 55 | 34 | 92 | 33 | 7 | 484 |
| 25.06.98 10:00 | 308 | 5 | 89 | 21 | 19 | 40 | 16 | 6 | 167 |
| 25.06.98 11:00 | 309 | 11 | 221 | 67 | 24 | 54 | 28 | 3 | 412 |
| 25.06.98 12:00 | 306 | 11 | 287 | 48 | 20 | 84 | 25 | 4 | 361 |
| 25.06.98 13:00 | 301 | 7 | 140 | 23 | 14 | 51 | 12 | 7 | 168 |
| 25.06.98 14:00 | 300 | 5 | 82 | 13 | 10 | 30 | 13 | 3 | 119 |
| 25.06.98 15:00 | 296 | 5 | 75 | 15 | n.q. | 28 | 8 | 5 | 95 |
| 25.06.98 16:00 | 295 | 10 | 72 | 13 | 36 | 32 | 9 | 11 | 90 |
| 25.06.98 18:00 | 296 | 4 | 84 | 12 | 12 | 27 | 9 | 3 | 99 |
| 25.06.98 20:00 | 302 | 4 | 39 | 7 | 7 | 16 | 3 | 3 | 50 |
| 26.06.98 08:00 | 302 | 3 | 59 | 10 | 6 | 15 | 5 | 2 | 26 |
| 26.06.98 09:00 | 302 | 5 | 119 | 16 | 18 | 47 | 10 | 6 | 178 |
| 26.06.98 10:00 | 302 | 6 | 114 | 18 | 14 | 46 | 14 | 9 | 151 |
| 26.06.98 12:00 | 303 | 7 | 137 | 23 | 15 | 43 | 16 | 4 | 185 |
| 26.06.98 13:00 | 303 | 7 | 129 | 20 | 12 | 43 | 10 | 5 | 171 |
| 26.06.98 14:00 | 298 | 7 | 120 | 19 | 17 | 53 | 26 | n.q. | 172 |
| 29.06.98 15:00 | 299 | 6 | 101 | 14 | 10 | 37 | 15 | 5 | 133 |
| 29.06.98 16:00 | 303 | 6 | 166 | 21 | 26 | 65 | 23 | 8 | 246 |
| 29.06.98 17:00 | 301 | 6 | 124 | 19 | n.q. | 42 | 15 | n.q. | 178 |
| 29.06.98 18:00 | 298 | 3 | 71 | 11 | 8 | 30 | 9 | n.q. | 96 |
| 29.06.98 19:00 | 295 | 3 | 67 | 12 | 32 | 38 | 16 | 8 | 97 |
| 29.06.98 20:00 | 294 | 3 | 40 | 8 | 4 | 19 | 5 | 4 | 60 |
| 29.06.98 21:00 | 292 | 3 | 47 | 7 | 8 | 19 | 11 | 6 | 60 |
| 29.06.98 22:00 | 290 | 3 | 17 | 3 | 6 | 12 | 5 | n.q. | 20 |
| 30.06.98 00:00 | 289 | n.q. | 26 | 4 | n.q. | 6 | n.q. | 2 | 29 |

**Table 8.10:** *(continued)*

| date, time | temperature | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | longicyclene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|
| 24.06.98 15:00 | 305 | 3 | 2 | n.q. | 17 | 3 | n.q. | 7 |
| 24.06.98 16:00 | 308 | 5 | 6 | 2 | 18 | 4 | n.q. | 1 |
| 24.06.98 17:00 | 307 | 4 | 4 | 2 | 16 | 2 | n.q. | 13 |
| 24.06.98 18:00 | 304 | 10 | 9 | 3 | 36 | 4 | n.q. | 26 |
| 24.06.98 19:00 | 297 | 4 | 5 | 1 | 7 | 2 | n.q. | 10 |
| 24.06.98 20:00 | 296 | n.q. | 3 | n.q. | 3 | n.q. | n.q. | n.q. |
| 24.06.98 21:00 | 295 | 4 | 2 | 3 | n.q. | n.q. | n.q. | 6 |
| 24.06.98 22:00 | 294 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 24.06.98 23:00 | 293 | 3 | 4 | n.q. | 5 | n.q. | n.q. | 9 |
| 25.06.98 00:00 | 293 | 2 | 3 | 1 | 3 | 2 | n.q. | 3 |
| 25.06.98 09:00 | 309 | 20 | 24 | 8 | 88 | 9 | n.q. | 34 |
| 25.06.98 10:00 | 308 | 7 | 8 | 3 | 32 | 7 | 2 | 33 |
| 25.06.98 11:00 | 309 | 22 | 29 | 7 | 57 | 7 | 3 | 36 |
| 25.06.98 12:00 | 306 | 13 | 12 | 5 | 52 | 6 | 1 | 27 |
| 25.06.98 13:00 | 301 | 6 | 7 | n.q. | 20 | 6 | n.q. | 10 |
| 25.06.98 14:00 | 300 | 5 | 5 | 2 | 21 | 4 | n.q. | 15 |
| 25.06.98 15:00 | 296 | 5 | 3 | 2 | 8 | 2 | n.q. | 6 |
| 25.06.98 16:00 | 295 | 3 | 8 | 13 | n.q. | n.q. | n.q. | 8 |
| 25.06.98 18:00 | 296 | 4 | 3 | 2 | 10 | 2 | n.q. | 5 |
| 25.06.98 20:00 | 302 | 3 | 4 | n.q. | 6 | n.q. | n.q. | n.q. |
| 26.06.98 08:00 | 302 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 26.06.98 09:00 | 302 | 11 | 6 | 3 | 39 | 6 | n.q. | n.q. |
| 26.06.98 10:00 | 302 | 5 | n.q. | n.q. | 35 | n.q. | n.q. | n.q. |
| 26.06.98 12:00 | 303 | 6 | 7 | 4 | 33 | 6 | n.q. | n.q. |
| 26.06.98 13:00 | 303 | 11 | 11 | 6 | 28 | n.q. | n.q. | n.q. |
| 26.06.98 14:00 | 298 | 11 | 12 | 4 | 30 | 6 | n.q. | n.q. |
| 29.06.98 15:00 | 299 | 5 | 5 | 3 | 20 | 4 | n.q. | 15 |
| 29.06.98 16:00 | 303 | 9 | 8 | 5 | 47 | 5 | n.q. | 44 |
| 29.06.98 17:00 | 301 | 7 | 7 | 4 | 33 | 5 | n.q. | 23 |
| 29.06.98 18:00 | 298 | 2 | 3 | 14 | n.q. | 3 | n.q. | n.q. |
| 29.06.98 19:00 | 295 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | 14 |
| 29.06.98 20:00 | 294 | n.q. | 2 | 4 | n.q. | 3 | n.q. | 13 |
| 29.06.98 21:00 | 292 | 4 | 4 | 4 | 2 | 1 | n.q. | 13 |
| 29.06.98 22:00 | 290 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 30.06.98 00:00 | 289 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |

**Table 8.11:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at pine No.3 in August 1998, n.q. = not quantified..*

| date, time | temperature | toluene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | 2-carene | 3-carene |
|---|---|---|---|---|---|---|---|---|---|
| 18.08.98 15:00 | 306 | 82 | 484 | 38 | n.q. | 25 | 72 | 23 | 125 |
| 18.08.98 16:00 | 308 | 7 | 678 | 46 | 13 | 23 | 82 | 9 | 151 |
| 18.08.98 17:00 | 307 | 26 | 602 | 57 | n.q. | 29 | 93 | 20 | 144 |
| 18.08.98 18:00 | 296 | 14 | 321 | 27 | n.q. | 21 | 28 | 50 | 56 |
| 18.08.98 19:00 | 295 | 9 | 266 | 29 | n.q. | 10 | 15 | 6 | 43 |
| 18.08.98 20:00 | 294 | 20 | 238 | 15 | n.q. | 16 | 20 | 13 | 38 |
| 18.08.98 21:00 | 292 | 25 | 206 | 12 | n.q. | 18 | 14 | 10 | 34 |
| 18.08.98 22:00 | 290 | 4 | 125 | 12 | n.q. | 7 | 10 | 3 | 19 |
| 18.08.98 23:00 | 291 | 6 | 176 | 13 | n.q. | 7 | 8 | 4 | 27 |
| 19.08.98 09:02 | 294 | 13 | 228 | 18 | n.q. | 23 | 14 | 32 | 39 |
| 19.08.98 10:00 | 304 | 6 | 356 | 27 | n.q. | 15 | 33 | 7 | 70 |
| 19.08.98 11:00 | 306 | 5 | 511 | 35 | 16 | 26 | 55 | 14 | 106 |
| 19.08.98 12:00 | 307 | 10 | 465 | 33 | 15 | 18 | 40 | 13 | 97 |
| 19.08.98 13:00 | 310 | 40 | 579 | 39 | 24 | 28 | 69 | 28 | 131 |
| 19.08.98 14:00 | 310 | 15 | 546 | 49 | n.q. | 26 | 54 | 13 | 111 |
| 19.08.98 15:00 | 311 | 5 | 645 | 46 | 29 | 34 | 71 | 13 | 130 |
| 19.08.98 16:00 | 310 | 4 | 659 | 45 | 16 | 29 | 70 | 17 | 128 |
| 19.08.98 18:00 | 303 | 5 | 441 | 36 | n.q. | 19 | 38 | 8 | 76 |
| 19.08.98 19:00 | 296 | 10 | 287 | 22 | 8 | 13 | 19 | 7 | 48 |
| 19.08.98 20:00 | 294 | 3 | 267 | 24 | n.q. | 7 | 11 | 3 | 44 |
| 19.08.98 21:00 | 290 | 4 | 164 | 11 | n.q. | 6 | 8 | 5 | 27 |
| 19.08.98 22:00 | 288 | 3 | 134 | 10 | 4 | 6 | 7 | 7 | 23 |
| 19.08.98 23:00 | 287 | 4 | 154 | 11 | n.q. | 6 | 6 | 2 | 24 |
| 20.08.98 09:03 | 295 | 4 | 205 | 15 | n.q. | 7 | 10 | 1 | 33 |
| 20.08.98 10:00 | 304 | 6 | 351 | 25 | n.q. | 14 | 29 | 3 | 65 |
| 20.08.98 11:00 | 308 | 16 | 522 | 36 | n.q. | 30 | 56 | 9 | 107 |
| 20.08.98 12:00 | 310 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 20.08.98 13:00 | 307 | 10 | 303 | 21 | 8 | 16 | 32 | 6 | 59 |
| 20.08.98 15:00 | 310 | 5 | 611 | 43 | 16 | 26 | 59 | 7 | 115 |
| 20.08.98 16:00 | 310 | 9 | 490 | 52 | n.q. | 20 | 55 | 4 | 104 |
| 20.08.98 17:00 | 309 | 13 | 565 | 42 | 9 | 20 | 50 | 8 | 102 |
| 20.08.98 18:00 | 303 | 11 | 452 | 32 | 7 | 18 | 32 | 11 | 77 |
| 20.08.98 19:00 | 298 | 9 | 295 | 24 | n.q. | 18 | 16 | 17 | 47 |
| 20.08.98 20:00 | 295 | 3 | 260 | 19 | n.q. | 10 | 13 | 7 | 40 |
| 20.08.98 21:00 | 292 | 5 | 166 | 13 | n.q. | 7 | 10 | 6 | 25 |
| 21.08.98 06:00 | 290 | 9 | 164 | 12 | n.q. | 5 | 8 | 5 | 28 |
| 21.08.98 07:00 | 290 | 12 | 146 | 12 | n.q. | 5 | 3 | 2 | 21 |
| 21.08.98 08:00 | 290 | 27 | 133 | 15 | n.q. | 14 | 10 | 29 | 23 |

**Table 8.11:** *(continued)*

| date, time | temperature | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | longicyclene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|
| 18.08.98 15:00 | 306 | 21 | 35 | 22 | 7 | n.q. | n.q. | 9 |
| 18.08.98 16:00 | 308 | 9 | 42 | 15 | n.q. | 3 | n.q. | 25 |
| 18.08.98 17:00 | 307 | 9 | 47 | 13 | n.q. | 2 | n.q. | 16 |
| 18.08.98 18:00 | 296 | 5 | 11 | 9 | n.q. | n.q. | n.q. | 9 |
| 18.08.98 19:00 | 295 | 3 | 10 | 2 | n.q. | 3 | n.q. | 3 |
| 18.08.98 20:00 | 294 | 4 | 7 | 3 | n.q. | n.q. | n.q. | n.q. |
| 18.08.98 21:00 | 292 | 6 | 8 | 7 | n.q. | n.q. | n.q. | n.q. |
| 18.08.98 22:00 | 290 | 2 | 5 | 2 | n.q. | n.q. | n.q. | n.q. |
| 18.08.98 23:00 | 291 | 3 | 5 | 1 | n.q. | n.q. | n.q. | n.q. |
| 19.08.98 09:02 | 294 | 4 | 10 | 5 | 2 | n.q. | n.q. | n.q. |
| 19.08.98 10:00 | 304 | 2 | 19 | 5 | 3 | 4 | n.q. | 1 |
| 19.08.98 11:00 | 306 | 5 | 27 | 7 | 3 | 3 | 1 | 8 |
| 19.08.98 12:00 | 307 | 4 | 24 | 6 | 4 | 4 | n.q. | 6 |
| 19.08.98 13:00 | 310 | 11 | 38 | 15 | 7 | 4 | 3 | 17 |
| 19.08.98 14:00 | 310 | 6 | 36 | 9 | 7 | 5 | n.q. | 11 |
| 19.08.98 15:00 | 311 | 6 | 36 | 10 | 7 | 3 | 3 | 33 |
| 19.08.98 16:00 | 310 | 8 | 39 | 10 | 5 | 5 | 3 | 42 |
| 19.08.98 18:00 | 303 | 5 | 21 | 4 | 4 | 5 | n.q. | 10 |
| 19.08.98 19:00 | 296 | 3 | 10 | 4 | 2 | n.q. | 1 | 6 |
| 19.08.98 20:00 | 294 | 4 | 9 | 2 | 2 | n.q. | n.q. | 2 |
| 19.08.98 21:00 | 290 | 2 | 6 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 19.08.98 22:00 | 288 | 2 | 4 | 2 | 2 | n.q. | n.q. | n.q. |
| 19.08.98 23:00 | 287 | 1 | 4 | 1 | n.q. | n.q. | n.q. | n.q. |
| 20.08.98 09:03 | 295 | 1 | 7 | 2 | 1 | n.q. | n.q. | n.q. |
| 20.08.98 10:00 | 304 | 3 | 15 | 4 | 4 | 3 | n.q. | 1 |
| 20.08.98 11:00 | 308 | 6 | 28 | 8 | 9 | 8 | n.q. | 5 |
| 20.08.98 12:00 | 310 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 20.08.98 13:00 | 307 | 4 | 16 | 4 | 5 | 3 | n.q. | 5 |
| 20.08.98 15:00 | 310 | 6 | 33 | 8 | 8 | 5 | n.q. | 27 |
| 20.08.98 16:00 | 310 | 9 | 41 | 8 | 9 | 5 | n.q. | 15 |
| 20.08.98 17:00 | 309 | 6 | 28 | 7 | 9 | 3 | n.q. | 15 |
| 20.08.98 18:00 | 303 | 5 | 17 | 4 | 5 | 3 | n.q. | 2 |
| 20.08.98 19:00 | 298 | 3 | 10 | 6 | n.q. | n.q. | n.q. | n.q. |
| 20.08.98 20:00 | 295 | 4 | 8 | 3 | 3 | n.q. | n.q. | 2 |
| 20.08.98 21:00 | 292 | 3 | 5 | 1 | 1 | n.q. | n.q. | n.q. |
| 21.08.98 06:00 | 290 | n.q. | 4 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 21.08.98 07:00 | 290 | 4 | 5 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 21.08.98 08:00 | 290 | 2 | 6 | n.q. | n.q. | n.q. | n.q. | n.q. |

**Table 8.12:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at pine No.4 in August 1998, n.q. = not quantified..*

| date, time | temperature | toluene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | 2-carene | 3-carene |
|---|---|---|---|---|---|---|---|---|---|
| 26.08.98 12:00 | 294 | 4 | 38 | 6 | 4 | 3 | 5 | 3 | 25 |
| 26.08.98 13:00 | 298 | 5 | 39 | 7 | 8 | 4 | 5 | 5 | 36 |
| 26.08.98 14:00 | 299 | 7 | 56 | 14 | 12 | 8 | 16 | 11 | 40 |
| 26.08.98 15:00 | 295 | 7 | 43 | 10 | n.q. | 5 | 8 | 10 | 27 |
| 26.08.98 16:00 | 291 | 8 | 29 | 6 | n.q. | 4 | 3 | 4 | 15 |
| 26.08.98 17:00 | 291 | 3 | 30 | 7 | n.q. | 6 | 5 | 5 | 17 |
| 26.08.98 18:00 | 290 | n.q. | 26 | 6 | n.q. | n.q. | n.q. | 5 | 12 |
| 26.08.98 19:00 | 287 | 3 | 22 | 6 | n.q. | n.q. | n.q. | 4 | 10 |
| 26.08.98 20:00 | 286 | 3 | 22 | 5 | n.q. | n.q. | n.q. | 9 | 13 |
| 26.08.98 21:00 | 286 | 3 | 19 | 4 | n.q. | 4 | 1 | 3 | 10 |
| 27.08.98 06:00 | 283 | n.q. | 11 | 3 | n.q. | 6 | 4 | 5 | 5 |
| 27.08.98 07:00 | 284 | n.q. | 14 | 4 | n.q. | 5 | 5 | 5 | 7 |
| 27.08.98 08:00 | 285 | 6 | 23 | 14 | 15 | 6 | 7 | 20 | 15 |
| 27.08.98 09:00 | 288 | n.q. | 23 | 5 | 3 | 4 | 3 | 5 | 15 |
| 27.08.98 10:00 | 295 | 3 | 31 | 7 | 2 | 9 | 5 | 12 | 30 |
| 27.08.98 11:00 | 293 | n.q. | 34 | 8 | n.q. | 3 | 6 | 4 | 25 |
| 27.08.98 12:00 | 292 | 3 | 32 | 7 | n.q. | 10 | 9 | 15 | 25 |
| 27.08.98 13:00 | 297 | 5 | 44 | 10 | n.q. | 9 | 10 | 9 | 37 |
| 27.08.98 14:00 | 298 | 4 | 49 | 10 | n.q. | 4 | 8 | 13 | 35 |
| 27.08.98 20:00 | 286 | 3 | 20 | 5 | n.q. | 5 | 5 | 9 | 8 |
| 27.08.98 21:00 | 285 | n.q. | 17 | 5 | n.q. | n.q. | 2 | 3 | 8 |
| 28.08.98 06:00 | 285 | 5 | 18 | 5 | n.q. | n.q. | 6 | 10 | 9 |
| 28.08.98 07:00 | 285 | 10 | 16 | 4 | n.q. | 9 | 5 | 16 | 9 |
| 28.08.98 09:00 | 288 | 18 | 14 | 5 | n.q. | 3 | 4 | 2 | 7 |
| 28.08.98 10:00 | 292 | 3 | 30 | 7 | n.q. | 3 | 3 | 7 | 18 |
| 28.08.98 11:00 | 293 | 2 | 22 | 5 | n.q. | 3 | 3 | 5 | 15 |
| 28.08.98 12:00 | 292 | 4 | 28 | 7 | 4 | 4 | 5 | 6 | 17 |
| 28.08.98 13:00 | 293 | 16 | n.q. | 1 | n.q. | n.q. | 6 | 58 | n.q. |

**Table 8.12:** *(continued)*

| date, time | temperature | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | longicyclene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|
| 26.08.98 12:00 | 294 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 26.08.98 13:00 | 298 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 26.08.98 14:00 | 299 | 3 | 5 | 3 | 2 | n.q. | n.q. | n.q. |
| 26.08.98 15:00 | 295 | 2 | 3 | 3 | n.q. | n.q. | n.q. | n.q. |
| 26.08.98 16:00 | 291 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 26.08.98 17:00 | 291 | 3 | 4 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 26.08.98 18:00 | 290 | 3 | 7 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 26.08.98 19:00 | 287 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 26.08.98 20:00 | 286 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 26.08.98 21:00 | 286 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 27.08.98 06:00 | 283 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 27.08.98 07:00 | 284 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 27.08.98 08:00 | 285 | 8 | 5 | n.q. | 6 | n.q. | n.q. | n.q. |
| 27.08.98 09:00 | 288 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 27.08.98 10:00 | 295 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 27.08.98 11:00 | 293 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 27.08.98 12:00 | 292 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 27.08.98 13:00 | 297 | n.q. | 6 | 7 | n.q. | n.q. | n.q. | n.q. |
| 27.08.98 14:00 | 298 | 2 | 4 | 2 | n.q. | n.q. | n.q. | n.q. |
| 27.08.98 20:00 | 286 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 27.08.98 21:00 | 285 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 28.08.98 06:00 | 285 | n.q. | 3 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 28.08.98 07:00 | 285 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 28.08.98 09:00 | 288 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 28.08.98 10:00 | 292 | n.q. | 1 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 28.08.98 11:00 | 293 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 28.08.98 12:00 | 292 | n.q. | 3 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 28.08.98 13:00 | 293 | n.q. | n.q. | n.q. | n.q. | 16 | n.q. | n.q. |

**Table 8.13:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at pine No.5 in May 1999, n.q. = not quantified..*

| date, time | temperature | toluene | tricyclene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | α-phellandrene |
|---|---|---|---|---|---|---|---|---|---|
| 18.05.99 01:00 | 287 | 1 | 0 | 29 | 2 | 0 | 2 | 2 | 0 |
| 18.05.99 02:00 | 287 | 1 | 0 | 35 | 2 | 1 | 3 | 2 | 0 |
| 18.05.99 03:00 | 287 | 1 | 0 | 33 | 2 | n.q. | 4 | 2 | 0 |
| 18.05.99 04:00 | 287 | 0 | 0 | 33 | 2 | 1 | 3 | 2 | 0 |
| 18.05.99 05:00 | 286 | 1 | 0 | 25 | 1 | n.q. | 2 | 2 | 0 |
| 18.05.99 06:00 | 287 | 3 | 1 | 33 | 3 | n.q. | 4 | 2 | 0 |
| 18.05.99 07:00 | 287 | 1 | 0 | 34 | 2 | 0 | 3 | 2 | 0 |
| 18.05.99 08:00 | 289 | 1 | 0 | 47 | 2 | 1 | 5 | 2 | 0 |
| 18.05.99 09:00 | 293 | 1 | 1 | 71 | 3 | 1 | 7 | 3 | 0 |
| 18.05.99 11:00 | 293 | 1 | 1 | 72 | 4 | 1 | 7 | 3 | 0 |
| 18.05.99 12:00 | 293 | 1 | 1 | 80 | 4 | 1 | 7 | 4 | 0 |
| 18.05.99 13:00 | 295 | 4 | 1 | 100 | 5 | 2 | 10 | 5 | 0 |
| 18.05.99 14:00 | 303 | 3 | 3 | 369 | 20 | 6 | 37 | 14 | 1 |
| 18.05.99 15:00 | 297 | 4 | 2 | 149 | 10 | 2 | 14 | 6 | 0 |
| 18.05.99 16:00 | 295 | 2 | 3 | 379 | 17 | 1 | 52 | 13 | 0 |
| 18.05.99 17:00 | 296 | n.q. | 3 | 402 | 18 | 3 | 68 | 19 | 1 |
| 18.05.99 18:00 | 294 | 1 | 5 | 319 | 39 | 1 | 33 | 9 | 0 |
| 18.05.99 19:00 | 291 | 11 | 2 | 218 | 9 | 2 | 21 | 7 | 1 |
| 18.05.99 20:00 | 290 | 1 | 1 | 161 | 3 | 1 | 11 | 3 | 0 |
| 18.05.99 21:00 | 288 | 1 | 1 | 148 | 4 | n.q. | 10 | 4 | n.q. |
| 18.05.99 22:00 | 285 | 5 | 1 | 107 | 3 | 1 | 8 | 3 | 0 |
| 18.05.99 23:00 | 286 | 2 | 0 | 101 | 3 | n.q. | 10 | 3 | 0 |
| 19.05.99 00:00 | 286 | 1 | 0 | 106 | 3 | 3 | 8 | 3 | 0 |
| 19.05.99 01:00 | 286 | 8 | 1 | 102 | 4 | 1 | 8 | 3 | 1 |
| 19.05.99 02:00 | 287 | 13 | 3 | 89 | 5 | 2 | 8 | 3 | 1 |
| 19.05.99 10:00 | 304 | 2 | 9 | 691 | 50 | 6 | 173 | 50 | 2 |
| 19.05.99 11:00 | 298 | 1 | 3 | 392 | 17 | 2 | 57 | 16 | 0 |
| 19.05.99 12:00 | 300 | 2 | 5 | 481 | 26 | 3 | 89 | 27 | 1 |
| 19.05.99 13:00 | 299 | 6 | 0 | 4 | n.q. | 10 | n.q. | 3 | 7 |
| 19.05.99 14:00 | 299 | 1 | 4 | n.q. | 22 | 3 | 82 | 25 | 1 |
| 19.05.99 15:00 | 299 | 3 | 5 | 641 | 37 | 4 | 58 | 20 | 1 |
| 19.05.99 16:00 | 299 | n.q. | 2 | 331 | 13 | 2 | 41 | 13 | 0 |
| 19.05.99 17:00 | 296 | 4 | 2 | 260 | 9 | 2 | 25 | 8 | 0 |
| 19.05.99 18:00 | 294 | 17 | 2 | 329 | 9 | n.q. | 22 | 8 | 1 |
| 19.05.99 20:00 | 290 | 13 | 6 | 168 | 7 | 2 | 13 | 6 | 1 |
| 19.05.99 21:00 | 288 | 1 | 1 | 143 | 3 | 0 | 8 | 3 | 0 |
| 19.05.99 22:00 | 288 | 1 | 0 | 150 | 3 | 1 | 9 | 4 | 0 |
| 20.05.99 01:00 | 287 | 2 | 0 | 89 | 3 | 6 | 7 | 6 | 1 |
| 20.05.99 09:15 | 292 | 2 | 0 | 1 | n.q. | 4 | n.q. | 1 | 1 |
| 20.05.99 09:45 | 292 | 1 | 1 | 225 | 4 | 1 | 13 | 5 | n.q. |
| 20.05.99 10:15 | 295 | 1 | 1 | 321 | 6 | 2 | 19 | 6 | 0 |
| 20.05.99 11:15 | 294 | 1 | 1 | 306 | 6 | 2 | 18 | 6 | 0 |
| 20.05.99 11:45 | 293 | 2 | 1 | 304 | 7 | 1 | 18 | 6 | n.q. |
| 20.05.99 12:15 | 292 | 3 | 1 | 236 | 5 | 1 | 14 | 6 | n.q. |
| 20.05.99 12:45 | 291 | 3 | 1 | 183 | 3 | 0 | 11 | 6 | n.q. |
| 20.05.99 13:15 | 292 | 2 | 1 | 215 | 5 | n.q. | 14 | 7 | 0 |
| 20.05.99 13:45 | 296 | 1 | 1 | 319 | 7 | 1 | 19 | 6 | n.q. |
| 20.05.99 14:15 | 295 | 2 | 1 | 288 | 7 | 2 | 17 | 7 | 0 |
| 20.05.99 14:45 | 294 | 2 | 1 | 192 | 5 | 1 | 12 | 3 | n.q. |
| 20.05.99 15:15 | 293 | 1 | 1 | 172 | 5 | 3 | 11 | 4 | n.q. |
| 20.05.99 15:45 | 291 | 2 | 1 | 139 | 4 | 2 | 9 | 4 | 0 |
| 20.05.99 16:15 | 291 | 2 | 1 | 156 | 4 | 1 | 10 | 4 | 0 |
| 20.05.99 16:45 | 290 | 1 | 0 | 113 | 3 | 1 | 7 | 3 | 0 |
| 20.05.99 17:15 | 290 | 1 | 0 | 108 | 3 | 9 | 8 | 4 | 0 |
| 20.05.99 23:00 | 284 | 1 | 0 | 42 | 2 | 0 | 3 | 2 | 0 |
| 21.05.99 01:00 | 284 | 1 | 0 | 35 | 1 | 0 | 2 | 1 | n.q. |
| 21.05.99 02:00 | 285 | 1 | 0 | 35 | 1 | 2 | 1 | 3 | n.q. |
| 21.05.99 03:00 | 285 | 2 | 0 | 40 | 2 | n.q. | 4 | 1 | 0 |
| 21.05.99 04:00 | 286 | 6 | 1 | 60 | 3 | 1 | 5 | 5 | 0 |
| 21.05.99 05:00 | 287 | 0 | 0 | 57 | 2 | 1 | 4 | 1 | n.q. |
| 21.05.99 06:00 | 286 | 5 | 1 | 72 | 2 | 2 | 6 | 4 | 0 |
| 21.05.99 07:45 | 287 | 6 | 1 | 66 | 4 | 2 | 6 | 5 | 0 |
| 21.05.99 09:15 | 288 | 1 | 0 | 86 | 3 | 2 | 6 | 2 | n.q. |
| 21.05.99 09:45 | 289 | 4 | 0 | 94 | 3 | n.q. | 8 | 4 | 1 |
| 21.05.99 10:15 | 290 | 6 | 1 | 98 | 4 | 1 | 8 | 1 | 0 |
| 21.05.99 10:45 | 292 | 27 | 5 | 161 | 10 | 7 | 17 | 22 | 2 |
| 21.05.99 11:15 | 297 | 1 | 1 | 296 | 7 | 3 | 19 | 4 | 0 |
| 21.05.99 12:15 | 303 | 2 | 4 | 440 | 29 | 5 | 30 | 7 | 1 |
| 21.05.99 12:45 | 305 | 3 | 2 | 353 | 12 | 3 | 24 | 6 | 1 |
| 21.05.99 13:15 | 305 | 1 | 0 | 1 | n.q. | 11 | 3 | n.q. | 1 |

**Table 8.13:** *(continued)*

| date, time | temperature | 3-carene | α-terpinene | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | terpinolene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|---|---|
| 18.05.99 01:00 | 287 | 0 | 0 | 1 | 15 | 2 | 0 | 0 | 1 | 2 |
| 18.05.99 02:00 | 287 | 0 | 0 | 1 | 17 | 3 | 0 | 0 | 0 | 2 |
| 18.05.99 03:00 | 287 | n.q. | 0 | 0 | 16 | 3 | 0 | 0 | 2 | 2 |
| 18.05.99 04:00 | 287 | 0 | n.q. | 0 | 15 | 0 | 3 | 0 | 1 | 2 |
| 18.05.99 05:00 | 286 | 0 | 0 | 0 | 11 | 2 | 0 | n.q. | n.q. | 2 |
| 18.05.99 06:00 | 287 | 0 | 0 | 1 | 15 | 3 | 0 | 0 | 2 | 2 |
| 18.05.99 07:00 | 287 | 0 | 0 | 0 | 14 | 3 | 0 | 0 | 1 | 2 |
| 18.05.99 08:00 | 289 | 0 | 0 | 1 | 20 | 6 | 0 | 0 | 1 | 2 |
| 18.05.99 09:00 | 293 | 0 | 0 | 1 | 30 | 8 | 1 | 0 | 0 | 3 |
| 18.05.99 11:00 | 293 | 0 | 0 | 1 | 28 | 8 | 1 | 0 | 1 | 4 |
| 18.05.99 12:00 | 293 | 0 | 0 | 1 | 30 | 9 | 1 | 1 | 6 | 6 |
| 18.05.99 13:00 | 295 | 1 | 0 | 1 | 38 | 13 | 2 | 1 | 2 | 8 |
| 18.05.99 14:00 | 303 | 1 | 0 | 2 | 115 | 39 | 6 | 2 | 4 | 28 |
| 18.05.99 15:00 | 297 | 1 | 1 | 1 | 43 | 14 | 3 | 1 | 3 | 17 |
| 18.05.99 16:00 | 295 | 0 | 0 | 1 | 65 | 23 | 1 | 1 | 2 | 9 |
| 18.05.99 17:00 | 296 | 1 | 1 | 3 | 80 | 30 | 3 | 2 | 5 | 14 |
| 18.05.99 18:00 | 294 | 0 | n.q. | 5 | 59 | 15 | 1 | 1 | 2 | 10 |
| 18.05.99 19:00 | 291 | 3 | 1 | 3 | 28 | 10 | n.q. | 1 | 3 | 8 |
| 18.05.99 20:00 | 290 | 0 | 0 | 0 | 15 | 5 | 0 | 0 | 1 | 4 |
| 18.05.99 21:00 | 288 | n.q. | n.q. | n.q. | 8 | n.q. | n.q. | n.q. | n.q. | 3 |
| 18.05.99 22:00 | 285 | 1 | 0 | 1 | 11 | 4 | 1 | 1 | 2 | 3 |
| 18.05.99 23:00 | 286 | 1 | 1 | 1 | 11 | 4 | n.q. | 1 | 6 | 3 |
| 19.05.99 00:00 | 286 | 1 | 0 | 0 | 12 | 4 | 0 | 1 | 11 | 3 |
| 19.05.99 01:00 | 286 | 1 | 0 | 1 | 12 | 4 | 1 | 1 | 2 | 3 |
| 19.05.99 02:00 | 287 | 2 | 2 | 3 | 11 | 1 | 5 | 1 | 4 | 5 |
| 19.05.99 10:00 | 304 | 1 | 0 | 3 | 204 | 7 | 85 | 1 | 4 | 47 |
| 19.05.99 11:00 | 298 | 0 | 0 | 1 | 88 | 27 | 3 | 1 | 2 | 20 |
| 19.05.99 12:00 | 300 | 1 | 0 | 2 | 132 | 39 | 6 | 1 | 2 | 27 |
| 19.05.99 13:00 | 299 | 9 | 1 | 1 | n.q. | 0 | 0 | 29 | 1 | 2 |
| 19.05.99 14:00 | 299 | 1 | 0 | 2 | 116 | 35 | 4 | 1 | 4 | 23 |
| 19.05.99 15:00 | 299 | 1 | 0 | 4 | 102 | 29 | 4 | 2 | 5 | 18 |
| 19.05.99 16:00 | 299 | 1 | 0 | 1 | 65 | 19 | 3 | 1 | 2 | 16 |
| 19.05.99 17:00 | 296 | 0 | 0 | 1 | 41 | 12 | 1 | 1 | 6 | 10 |
| 19.05.99 18:00 | 294 | 1 | 1 | 2 | 33 | 10 | 2 | 1 | 4 | 10 |
| 19.05.99 20:00 | 290 | 1 | 1 | 3 | 22 | 7 | 2 | n.q. | 3 | 8 |
| 19.05.99 21:00 | 288 | 0 | 0 | 0 | 15 | 5 | 0 | 1 | 0 | 3 |
| 19.05.99 22:00 | 288 | 0 | 0 | 1 | 16 | 5 | 0 | 0 | 1 | 3 |
| 20.05.99 01:00 | 287 | n.q. | 1 | 2 | 11 | 4 | n.q. | 1 | 5 | 3 |
| 20.05.99 09:15 | 292 | 7 | n.q. | n.q. | n.q. | n.q. | 0 | 6 | 1 | n.q. |
| 20.05.99 09:45 | 292 | 0 | 0 | 0 | 20 | 6 | 1 | 1 | 1 | 4 |
| 20.05.99 10:15 | 295 | 0 | 0 | 0 | 28 | 9 | 1 | 1 | 4 | 5 |
| 20.05.99 11:15 | 294 | 0 | 0 | 1 | 26 | 8 | 1 | 1 | 2 | 4 |
| 20.05.99 11:45 | 293 | n.q. | 0 | 1 | 28 | 9 | 1 | 1 | 3 | 6 |
| 20.05.99 12:15 | 292 | n.q. | 0 | 1 | 24 | 7 | 1 | 1 | 2 | n.q. |
| 20.05.99 12:45 | 291 | n.q. | 0 | 0 | 20 | 5 | 0 | 1 | 4 | 4 |
| 20.05.99 13:15 | 292 | 0 | 0 | 0 | 23 | 6 | 0 | 1 | 3 | 5 |
| 20.05.99 13:45 | 296 | 0 | 0 | 1 | 29 | 9 | 1 | 1 | 2 | 8 |
| 20.05.99 14:15 | 295 | 0 | 0 | 1 | 29 | 8 | 1 | 1 | 2 | 7 |
| 20.05.99 14:45 | 294 | n.q. | 0 | 1 | 19 | 6 | 1 | 1 | 2 | 5 |
| 20.05.99 15:15 | 293 | n.q. | 0 | 0 | 18 | 5 | 1 | 1 | 3 | 6 |
| 20.05.99 15:45 | 291 | n.q. | 2 | 2 | 17 | 6 | 1 | n.q. | 3 | 5 |
| 20.05.99 16:15 | 291 | 0 | 0 | 1 | 16 | 5 | 0 | 1 | 2 | 4 |
| 20.05.99 16:45 | 290 | 0 | 0 | 0 | 13 | 4 | 0 | 1 | 2 | 3 |
| 20.05.99 17:15 | 290 | 0 | 0 | 1 | 11 | 4 | n.q. | 1 | 1 | 3 |
| 20.05.99 23:00 | 284 | 0 | 0 | 0 | 6 | 1 | 0 | 0 | 1 | 1 |
| 21.05.99 01:00 | 284 | n.q. | 0 | 0 | 4 | 1 | 0 | 0 | 1 | 1 |
| 21.05.99 02:00 | 285 | 0 | 0 | 0 | 4 | 1 | 0 | 0 | 0 | 0 |
| 21.05.99 03:00 | 285 | 1 | 0 | 1 | 5 | 2 | 0 | 1 | 14 | 1 |
| 21.05.99 04:00 | 286 | 1 | 0 | 1 | 7 | 3 | 1 | 1 | 2 | 2 |
| 21.05.99 05:00 | 287 | 0 | 0 | 0 | 6 | 2 | 0 | 0 | 4 | 1 |
| 21.05.99 06:00 | 286 | 0 | 0 | 1 | 7 | 2 | n.q. | 2 | 3 | 2 |
| 21.05.99 07:45 | 287 | 1 | 0 | 1 | 7 | 2 | 0 | 1 | 2 | 1 |
| 21.05.99 09:15 | 288 | n.q. | 0 | 0 | 9 | 3 | 0 | 1 | 3 | 2 |
| 21.05.99 09:45 | 289 | 0 | 1 | 1 | 8 | 3 | 0 | 1 | 4 | 1 |
| 21.05.99 10:15 | 290 | 1 | 0 | 1 | 10 | 4 | 1 | 1 | 3 | 2 |
| 21.05.99 10:45 | 292 | 5 | 2 | 4 | 16 | 7 | 3 | 6 | 108 | 3 |
| 21.05.99 11:15 | 297 | 0 | 0 | 1 | 26 | 9 | 3 | 1 | 12 | 7 |
| 21.05.99 12:15 | 303 | 1 | 0 | 4 | 53 | 14 | 5 | 2 | 3 | 18 |
| 21.05.99 12:45 | 305 | 0 | 0 | 2 | 37 | 11 | 5 | 1 | 1 | 16 |
| 21.05.99 13:15 | 305 | 5 | 0 | 0 | n.q. | 0 | n.q. | n.q. | 0 | n.q. |

**Table 8.14:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at pine No.5 in July 1999, n.q. = not quantified..*

| date, time | temperature | toluene | tricyclene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | α-phellandrene |
|---|---|---|---|---|---|---|---|---|---|
| 06.07.99 01:00 | 288 | 3 | 1 | 117 | 7 | 1 | 5 | 5 | n.q. |
| 06.07.99 02:00 | 288 | 2 | 1 | 101 | 6 | 1 | 4 | 4 | n.q. |
| 06.07.99 03:00 | 287 | 1 | 1 | 88 | 6 | 0 | 3 | 3 | n.q. |
| 06.07.99 04:00 | 287 | 5 | 1 | 111 | 9 | 0 | 4 | 4 | n.q. |
| 06.07.99 05:00 | 287 | 1 | 0 | 41 | 3 | 0 | 1 | 1 | 0 |
| 06.07.99 06:00 | 287 | 2 | 2 | 119 | 9 | 0 | 4 | 4 | 0 |
| 06.07.99 07:00 | 289 | 4 | 2 | 127 | 10 | 0 | 5 | 4 | n.q. |
| 06.07.99 08:00 | 290 | 4 | 2 | 127 | 11 | 1 | 6 | 4 | n.q. |
| 06.07.99 09:00 | 291 | 2 | 2 | 122 | 11 | 1 | 5 | 3 | n.q. |
| 06.07.99 10:00 | 294 | 3 | 3 | 213 | 20 | 1 | 9 | 6 | n.q. |
| 06.07.99 11:00 | 295 | 3 | 3 | 173 | 19 | 1 | 8 | 5 | n.q. |
| 06.07.99 13:00 | 294 | 4 | 2 | 130 | 15 | 1 | 7 | 4 | n.q. |
| 06.07.99 14:00 | 295 | 2 | 1 | 84 | 9 | 1 | 4 | 2 | n.q. |
| 06.07.99 15:00 | 295 | 1 | 3 | 191 | 19 | 2 | 9 | 5 | n.q. |
| 06.07.99 16:00 | 296 | 1 | 3 | 179 | 19 | 1 | 8 | 5 | n.q. |
| 06.07.99 17:00 | 295 | 1 | 2 | 142 | 17 | 3 | 7 | 5 | n.q. |
| 06.07.99 18:00 | 294 | 1 | 2 | 131 | 17 | 1 | 7 | 5 | 0 |
| 06.07.99 20:00 | 293 | 1 | 1 | 71 | 9 | 1 | 4 | 2 | n.q. |
| 06.07.99 21:00 | 292 | 1 | 2 | 107 | 14 | 2 | 6 | 4 | n.q. |
| 06.07.99 22:00 | 291 | 1 | 1 | 21 | 3 | 0 | 1 | 1 | n.q. |
| 06.07.99 23:00 | 289 | 2 | 2 | 68 | 10 | 1 | 5 | 3 | n.q. |
| 07.07.99 00:00 | 289 | 3 | 2 | 78 | 11 | 1 | 5 | 3 | n.q. |
| 07.07.99 01:00 | 289 | 1 | 2 | 76 | 11 | 1 | 5 | 3 | n.q. |
| 07.07.99 11:00 | 305 | 3 | 6 | 340 | 32 | 3 | 19 | 8 | n.q. |
| 07.07.99 12:00 | 309 | 2 | 8 | 398 | 43 | 5 | 25 | 12 | 1 |
| 07.07.99 13:00 | 308 | 8 | 7 | 318 | 31 | 3 | 19 | 11 | n.q. |
| 07.07.99 14:00 | 308 | 1 | 4 | 225 | 30 | 3 | 13 | 8 | 0 |

**Table 8.14:** *(continued)*

| date, time | temperature | 3-carene | α-terpinene | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | terpinolene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|---|---|
| 06.07.99 01:00 | 288 | 1 | 0 | 1 | 16 | 2 | 0 | 1 | 3 | 1 |
| 06.07.99 02:00 | 288 | 0 | 0 | 0 | 13 | 1 | 0 | 0 | 1 | 1 |
| 06.07.99 03:00 | 287 | 0 | n.q. | 0 | 12 | 1 | 0 | 0 | 0 | 1 |
| 06.07.99 04:00 | 287 | 1 | 0 | 1 | 15 | 2 | 0 | 0 | 1 | 1 |
| 06.07.99 05:00 | 287 | 0 | n.q. | 0 | 5 | 1 | 0 | 0 | 2 | 0 |
| 06.07.99 06:00 | 287 | 0 | 0 | 1 | 15 | 2 | 0 | 1 | 1 | 1 |
| 06.07.99 07:00 | 289 | 1 | 0 | 1 | 15 | 2 | 1 | 0 | 4 | 1 |
| 06.07.99 08:00 | 290 | 1 | 0 | 1 | 14 | 1 | 1 | 1 | 1 | 1 |
| 06.07.99 09:00 | 291 | 0 | n.q. | 0 | 12 | 1 | 0 | n.q. | 1 | 2 |
| 06.07.99 10:00 | 294 | 0 | 0 | 1 | 21 | 2 | 2 | 0 | 2 | 2 |
| 06.07.99 11:00 | 295 | 1 | 0 | 1 | 18 | 2 | 2 | 0 | 2 | 1 |
| 06.07.99 13:00 | 294 | 1 | 0 | 1 | 14 | 2 | 1 | 0 | 1 | 2 |
| 06.07.99 14:00 | 295 | 0 | 0 | 0 | 8 | 1 | 1 | n.q. | 1 | 1 |
| 06.07.99 15:00 | 295 | 0 | 0 | 1 | 19 | 2 | 2 | 0 | 1 | 2 |
| 06.07.99 16:00 | 296 | 0 | 0 | 1 | 18 | 2 | 2 | 0 | 3 | 3 |
| 06.07.99 17:00 | 295 | n.q. | 0 | 1 | 15 | 2 | 1 | n.q. | n.q. | 1 |
| 06.07.99 18:00 | 294 | n.q. | 2 | 2 | 15 | 2 | 1 | 0 | 2 | 2 |
| 06.07.99 20:00 | 293 | n.q. | n.q. | 0 | 7 | 1 | 0 | n.q. | 1 | 1 |
| 06.07.99 21:00 | 292 | n.q. | 2 | 3 | 7 | n.q. | n.q. | n.q. | n.q. | n.q. |
| 06.07.99 22:00 | 291 | 0 | 0 | 0 | 2 | 0 | 0 | n.q. | 0 | 0 |
| 06.07.99 23:00 | 289 | 0 | 0 | 1 | 8 | 1 | 0 | n.q. | 2 | 1 |
| 07.07.99 00:00 | 289 | 1 | 0 | 0 | 8 | 1 | 0 | n.q. | 2 | 1 |
| 07.07.99 01:00 | 289 | 0 | 0 | 1 | 8 | 1 | 0 | 0 | 2 | 1 |
| 07.07.99 11:00 | 305 | 0 | 0 | 2 | 30 | 5 | 7 | n.q. | 12 | 13 |
| 07.07.99 12:00 | 309 | 0 | 0 | 2 | 41 | 8 | 10 | 1 | 8 | 18 |
| 07.07.99 13:00 | 308 | 1 | 1 | 1 | 29 | 5 | 8 | 1 | 3 | 13 |
| 07.07.99 14:00 | 308 | 0 | 0 | 1 | 25 | 4 | 6 | 1 | 1 | 12 |

**Table 8.15:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at pine No.6 in June 1999, n.q. = not quantified..*

| date, time | temperature | toluene | tricyclene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | α-phellandrene |
|---|---|---|---|---|---|---|---|---|---|
| 14.06.99 11:00 | 308 | 5 | 6 | 74 | 40 | 18 | 14 | 11 | 0 |
| 14.06.99 12:00 | 311 | 3 | 4 | 64 | 34 | 13 | 11 | 9 | 0 |
| 14.06.99 13:00 | 313 | 4 | 6 | 78 | 41 | 16 | 15 | 10 | 0 |
| 14.06.99 14:00 | 313 | n.q. | 7 | 86 | 47 | 14 | 16 | 8 | 0 |
| 14.06.99 15:00 | 308 | 4 | 5 | 70 | 44 | 12 | 13 | 7 | 0 |
| 14.06.99 16:00 | 309 | 7 | 7 | 87 | 56 | 21 | 19 | 9 | n.q. |
| 15.06.99 01:00 | 289 | 1 | 0 | 6 | 3 | 2 | 2 | 1 | 0 |
| 15.06.99 02:00 | 288 | 2 | 1 | 5 | 2 | 0 | 1 | 1 | n.q. |
| 15.06.99 03:00 | 287 | 1 | 0 | 5 | 3 | 0 | 1 | 1 | n.q. |
| 15.06.99 04:00 | 286 | 1 | 0 | 4 | 2 | 0 | 1 | 0 | n.q. |
| 15.06.99 05:00 | 285 | 1 | 0 | 5 | 2 | 0 | 1 | 1 | n.q. |
| 15.06.99 07:00 | 287 | 1 | 1 | 17 | 12 | 1 | 3 | 1 | 0 |
| 15.06.99 09:00 | 302 | 2 | 3 | 32 | 18 | 5 | 6 | 4 | 0 |
| 15.06.99 10:00 | 306 | 4 | 4 | 49 | 27 | 8 | 10 | 9 | 0 |
| 15.06.99 11:00 | 310 | 3 | 5 | 65 | 34 | 12 | 12 | 11 | 0 |
| 15.06.99 12:00 | 312 | 5 | 7 | 88 | 47 | 19 | 17 | 16 | 0 |
| 15.06.99 13:00 | 309 | 5 | 7 | 90 | 51 | 15 | 19 | 15 | 0 |
| 15.06.99 14:00 | 313 | 4 | 9 | 109 | 66 | 20 | 23 | 12 | 0 |
| 15.06.99 15:00 | 308 | 4 | 8 | 110 | 67 | 21 | 25 | 16 | n.q. |
| 15.06.99 16:00 | 303 | 2 | 6 | 74 | 48 | 11 | 16 | 13 | 0 |
| 15.06.99 17:00 | 304 | 2 | 6 | 77 | 47 | 12 | 17 | 13 | 0 |
| 15.06.99 18:00 | 300 | 2 | 3 | 45 | 29 | 6 | 8 | 7 | 0 |
| 15.06.99 19:00 | 299 | 1 | 3 | 39 | 23 | 6 | 8 | 6 | 0 |
| 15.06.99 20:00 | 296 | 2 | 2 | 25 | 14 | 3 | 5 | 3 | n.q. |
| 15.06.99 21:00 | 295 | 2 | 1 | 15 | 9 | 1 | 3 | 1 | 0 |
| 15.06.99 22:00 | 293 | 1 | 1 | 10 | 6 | 2 | 2 | 1 | n.q. |
| 15.06.99 23:00 | 292 | 1 | 1 | 10 | 5 | 1 | 1 | 0 | 0 |
| 16.06.99 00:00 | 290 | 1 | 1 | 8 | 4 | 1 | 1 | 1 | 0 |
| 16.06.99 10:00 | 308 | 21 | 9 | 68 | 55 | 22 | 16 | 14 | 0 |
| 16.06.99 11:00 | 312 | 12 | 10 | 91 | 59 | 29 | 20 | 17 | 1 |
| 16.06.99 12:00 | 314 | 3 | 7 | 78 | 43 | 11 | 14 | 9 | 0 |
| 16.06.99 13:00 | 310 | 2 | 6 | 63 | 43 | 10 | 12 | 9 | 1 |
| 16.06.99 14:00 | 312 | 5 | 6 | 74 | 46 | 15 | 18 | 9 | 0 |
| 16.06.99 15:00 | 311 | 11 | 8 | 97 | 64 | 40 | 29 | 49 | n.q. |
| 17.06.99 01:00 | 288 | 1 | 1 | 7 | 3 | 0 | 1 | 0 | 0 |
| 17.06.99 02:00 | 287 | 1 | 1 | 7 | 3 | 1 | 1 | 0 | n.q. |
| 17.06.99 03:00 | 286 | 2 | 1 | 7 | 4 | 8 | 3 | 12 | 0 |
| 17.06.99 05:00 | 285 | 2 | 1 | 7 | 5 | 0 | 1 | 3 | 0 |
| 17.06.99 07:00 | 288 | 1 | 1 | 16 | 9 | 2 | 3 | 1 | 0 |
| 17.06.99 08:00 | 296 | 1 | 2 | 24 | 13 | 3 | 5 | 2 | n.q. |
| 17.06.99 09:00 | 304 | 2 | 3 | 37 | 20 | 8 | 8 | 4 | 0 |
| 17.06.99 10:00 | 309 | 3 | 4 | 58 | 31 | 8 | 11 | 7 | 1 |
| 17.06.99 11:00 | 312 | 4 | 6 | 81 | 45 | 17 | 16 | 15 | 1 |
| 17.06.99 12:00 | 312 | 4 | 5 | 63 | 33 | 11 | 13 | 11 | 0 |
| 17.06.99 13:00 | 312 | 4 | 7 | 77 | 47 | 14 | 15 | 14 | 1 |
| 17.06.99 14:00 | 307 | 3 | 4 | 54 | 32 | 10 | 12 | 8 | 0 |
| 17.06.99 16:00 | 305 | 3 | 4 | 52 | 29 | 8 | 11 | 8 | 0 |
| 17.06.99 17:00 | 304 | 3 | 4 | 48 | 27 | 8 | 11 | 7 | 0 |
| 17.06.99 18:00 | 299 | 2 | 2 | 26 | 14 | 4 | 6 | 5 | 0 |
| 17.06.99 19:00 | 297 | 2 | 2 | 27 | 15 | 4 | 6 | 3 | n.q. |
| 17.06.99 21:00 | 293 | 2 | 1 | 12 | 6 | 1 | 2 | 1 | n.q. |
| 17.06.99 22:00 | 290 | 1 | 1 | 11 | 6 | 1 | 2 | 1 | n.q. |
| 18.06.99 00:00 | 289 | 1 | 1 | 10 | 5 | 1 | 1 | 0 | n.q. |
| 18.06.99 01:00 | 288 | 1 | 1 | 9 | 4 | 2 | 2 | 0 | n.q. |
| 18.06.99 10:00 | 302 | 2 | 2 | 29 | 16 | 5 | 5 | 4 | 0 |
| 18.06.99 12:00 | 303 | 3 | 2 | 32 | 17 | 7 | 7 | 5 | 0 |
| 18.06.99 13:00 | 301 | 2 | 2 | 29 | 15 | 6 | 6 | 5 | 0 |

**Table 8.15:** *(continued)*

| date, time | temperature | 3-carene | α-terpinene | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | terpinolene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|---|---|
| 14.06.99 11:00 | 308 | 129 | 1 | 4 | 4 | 4 | 58 | 2 | 4 | 1 |
| 14.06.99 12:00 | 311 | 103 | 0 | 4 | 3 | 3 | 42 | 2 | 3 | 2 |
| 14.06.99 13:00 | 313 | 120 | 1 | 5 | 3 | 3 | 28 | 2 | 4 | 5 |
| 14.06.99 14:00 | 313 | 123 | 0 | 4 | 3 | 3 | 20 | 2 | 2 | 5 |
| 14.06.99 15:00 | 308 | 82 | 0 | 3 | n.q. | n.q. | n.q. | n.q. | 3 | 1 |
| 14.06.99 16:00 | 309 | 90 | 1 | 4 | 2 | 2 | 30 | 2 | 3 | 1 |
| 15.06.99 01:00 | 289 | 4 | 0 | 1 | 0 | 0 | 0 | 0 | 4 | 0 |
| 15.06.99 02:00 | 288 | 3 | 0 | 0 | 0 | 0 | 0 | n.q. | 6 | 0 |
| 15.06.99 03:00 | 287 | 3 | n.q. | 0 | 0 | 0 | 0 | n.q. | 1 | 0 |
| 15.06.99 04:00 | 286 | 3 | 0 | 0 | 0 | n.q. | 0 | 0 | 1 | n.q. |
| 15.06.99 05:00 | 285 | 3 | n.q. | 0 | 0 | 0 | 0 | n.q. | 2 | n.q. |
| 15.06.99 07:00 | 287 | 11 | 0 | 0 | 0 | 0 | 3 | n.q. | 0 | n.q. |
| 15.06.99 09:00 | 302 | 33 | 0 | 1 | 1 | 1 | 12 | 1 | 2 | 1 |
| 15.06.99 10:00 | 306 | 55 | 0 | 2 | 2 | 1 | 23 | 1 | 3 | 2 |
| 15.06.99 11:00 | 310 | 84 | 0 | 2 | 2 | 2 | 32 | 1 | 1 | 2 |
| 15.06.99 12:00 | 312 | 116 | 1 | 4 | 3 | 3 | 41 | 3 | 4 | 4 |
| 15.06.99 13:00 | 309 | 113 | 1 | 3 | 4 | 3 | 44 | 2 | 2 | 6 |
| 15.06.99 14:00 | 313 | 143 | 1 | 4 | 4 | 3 | 47 | 3 | 4 | 1 |
| 15.06.99 15:00 | 308 | 141 | 0 | 3 | 3 | 4 | 38 | 3 | 1 | 1 |
| 15.06.99 16:00 | 303 | 97 | 0 | 3 | 4 | 3 | 30 | 2 | 1 | 4 |
| 15.06.99 17:00 | 304 | 98 | 0 | 2 | 3 | 3 | 29 | 2 | 2 | 7 |
| 15.06.99 18:00 | 300 | 54 | 0 | 2 | 2 | 1 | 14 | 1 | 3 | 5 |
| 15.06.99 19:00 | 299 | 43 | 0 | 1 | 2 | 1 | 7 | 1 | 3 | 3 |
| 15.06.99 20:00 | 296 | 25 | 0 | 1 | 2 | 1 | 2 | 1 | 2 | 2 |
| 15.06.99 21:00 | 295 | 13 | 0 | 1 | 1 | 0 | 1 | 1 | 9 | 1 |
| 15.06.99 22:00 | 293 | 8 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 1 |
| 15.06.99 23:00 | 292 | 7 | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 0 |
| 16.06.99 00:00 | 290 | 5 | n.q. | 1 | 0 | 0 | 0 | n.q. | 1 | n.q. |
| 16.06.99 10:00 | 308 | 104 | 6 | 22 | 7 | 3 | 32 | 2 | 6 | 5 |
| 16.06.99 11:00 | 312 | 126 | 5 | 13 | 7 | 5 | 42 | 2 | 13 | 2 |
| 16.06.99 12:00 | 314 | 104 | 1 | 4 | 3 | 3 | 25 | 2 | 2 | 1 |
| 16.06.99 13:00 | 310 | 81 | 1 | 3 | 4 | 2 | 19 | 2 | 1 | 2 |
| 16.06.99 14:00 | 312 | 94 | n.q. | 4 | 3 | 3 | 22 | n.q. | 4 | 1 |
| 16.06.99 15:00 | 311 | 124 | 1 | 6 | 4 | n.q. | 31 | 11 | 9 | 6 |
| 17.06.99 01:00 | 288 | 4 | 0 | 0 | 0 | 0 | 0 | n.q. | 1 | 0 |
| 17.06.99 02:00 | 287 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 17.06.99 03:00 | 286 | 4 | 1 | 1 | 1 | 0 | n.q. | n.q. | 26 | 0 |
| 17.06.99 05:00 | 285 | 4 | 0 | 1 | 0 | 0 | n.q. | n.q. | 1 | 0 |
| 17.06.99 07:00 | 288 | 10 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | n.q. |
| 17.06.99 08:00 | 296 | 22 | n.q. | 1 | 1 | 1 | 6 | 0 | 1 | 0 |
| 17.06.99 09:00 | 304 | 42 | 2 | 2 | 3 | 2 | 17 | 1 | 2 | 1 |
| 17.06.99 10:00 | 309 | 74 | 1 | 3 | 3 | 3 | 31 | 2 | 1 | 1 |
| 17.06.99 11:00 | 312 | 109 | 1 | 5 | 5 | 4 | 42 | 2 | 9 | 1 |
| 17.06.99 12:00 | 312 | 72 | 0 | 3 | 4 | 2 | 28 | 2 | 3 | 2 |
| 17.06.99 13:00 | 312 | 99 | 1 | 4 | 6 | 3 | 38 | 3 | 2 | 2 |
| 17.06.99 14:00 | 307 | 63 | 0 | 2 | 3 | 2 | 19 | 2 | 2 | 1 |
| 17.06.99 16:00 | 305 | 61 | 0 | 2 | 3 | 2 | 17 | 1 | 3 | 1 |
| 17.06.99 17:00 | 304 | 58 | 0 | 2 | 2 | 2 | 13 | 2 | 25 | n.q. |
| 17.06.99 18:00 | 299 | 36 | 0 | 1 | 1 | 1 | 5 | 1 | 1 | 1 |
| 17.06.99 19:00 | 297 | 27 | n.q. | 1 | 1 | 1 | 3 | 1 | 3 | 1 |
| 17.06.99 21:00 | 293 | 9 | 0 | 1 | 0 | 0 | 1 | 0 | 1 | n.q. |
| 17.06.99 22:00 | 290 | 8 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | n.q. |
| 18.06.99 00:00 | 289 | 7 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 18.06.99 01:00 | 288 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | n.q. |
| 18.06.99 10:00 | 302 | 32 | 0 | 1 | 1 | 1 | 19 | 1 | 1 | n.q. |
| 18.06.99 12:00 | 303 | 32 | 0 | 1 | 2 | 1 | 18 | 1 | 1 | n.q. |
| 18.06.99 13:00 | 301 | 29 | 0 | 1 | 1 | 1 | 16 | 1 | 3 | 0 |

**Table 8.16:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at pine No.7 in June 1999, n.q. = not quantified..*

| date, time | temperature | toluene | tricyclene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | α-phellandrene |
|---|---|---|---|---|---|---|---|---|---|
| 08.06.99 01:00 | 285 | 6 | 0 | 5 | 2 | 0 | 1 | 3 | 0 |
| 08.06.99 02:00 | 285 | 1 | 0 | 3 | 2 | 0 | 1 | 0 | n.q. |
| 08.06.99 03:00 | 284 | 1 | 0 | 3 | 1 | 0 | 1 | 1 | n.q. |
| 08.06.99 04:00 | 284 | 1 | 0 | 3 | 1 | 0 | 1 | 1 | n.q. |
| 08.06.99 05:00 | 284 | 2 | 0 | 4 | 2 | 0 | 1 | 1 | n.q. |
| 08.06.99 07:00 | 284 | 1 | 0 | 4 | 2 | 0 | 2 | 1 | n.q. |
| 08.06.99 09:00 | 299 | 2 | 1 | 13 | 8 | 6 | 6 | 2 | 0 |
| 08.06.99 10:00 | 301 | 2 | 1 | 15 | 8 | 4 | 7 | 3 | 0 |
| 08.06.99 11:00 | 302 | 3 | 2 | 21 | 12 | 4 | 8 | 3 | n.q. |
| 08.06.99 12:00 | 303 | 3 | 2 | 19 | 12 | 3 | 7 | 3 | n.q. |
| 08.06.99 13:00 | 298 | 3 | 1 | 13 | 7 | 2 | 5 | 2 | n.q. |
| 08.06.99 14:00 | 302 | 3 | 1 | 13 | 7 | 5 | 7 | 2 | n.q. |
| 08.06.99 15:00 | 300 | 3 | 1 | 14 | 8 | 7 | 3 | 7 | n.q. |
| 08.06.99 19:00 | 291 | 3 | 1 | 6 | 3 | 6 | 6 | 4 | n.q. |
| 08.06.99 20:00 | 289 | 1 | 0 | 4 | 2 | 2 | 3 | 1 | 0 |
| 08.06.99 21:00 | 287 | 1 | 0 | 4 | 2 | 0 | 2 | 0 | n.q. |
| 08.06.99 22:00 | 284 | 5 | 0 | 3 | 2 | 0 | 3 | 3 | n.q. |
| 09.06.99 08:00 | 289 | 2 | 1 | 7 | 4 | 1 | 2 | 2 | 0 |
| 09.06.99 15:00 | 308 | 3 | 3 | 31 | 17 | 9 | 11 | 8 | 0 |
| 09.06.99 16:00 | 304 | 3 | 2 | 28 | 14 | 6 | 12 | 6 | 0 |
| 09.06.99 17:00 | 299 | 3 | 1 | 14 | 9 | 2 | 7 | 3 | 0 |
| 09.06.99 18:00 | 297 | 3 | 1 | 12 | 7 | 2 | 6 | 2 | 0 |
| 09.06.99 19:00 | 293 | 2 | 1 | 10 | 5 | 2 | 4 | 1 | 0 |
| 09.06.99 20:00 | 291 | 3 | 1 | 7 | 4 | 1 | 4 | 1 | n.q. |
| 09.06.99 23:00 | 283 | 3 | 0 | 3 | 2 | 0 | 2 | 0 | 0 |
| 10.06.99 01:00 | 282 | 3 | 0 | 2 | 1 | 0 | 2 | 1 | n.q. |
| 10.06.99 10:00 | 301 | 3 | 1 | 14 | 8 | 3 | 6 | 2 | 0 |
| 10.06.99 11:00 | 303 | 2 | 1 | 18 | 10 | 3 | 6 | 2 | 0 |
| 10.06.99 12:00 | 301 | 2 | 1 | 12 | 7 | 2 | 6 | 3 | 0 |
| 10.06.99 13:00 | 303 | 6 | 2 | 20 | 12 | 3 | 9 | 2 | 0 |
| 10.06.99 14:00 | 304 | 4 | 2 | 23 | 14 | 4 | 8 | 2 | 0 |
| 10.06.99 15:00 | 303 | n.q. | 2 | 23 | 14 | 3 | 9 | 2 | 0 |
| 10.06.99 16:00 | 304 | 3 | 2 | 26 | 16 | 4 | 12 | 3 | n.q. |
| 10.06.99 17:00 | 303 | n.q. | 3 | 36 | 22 | 5 | 16 | 4 | 1 |
| 10.06.99 18:00 | 299 | 4 | 1 | 20 | 12 | 2 | 11 | 2 | n.q. |
| 10.06.99 19:00 | 296 | 1 | 2 | 18 | 11 | 2 | 9 | 2 | n.q. |
| 10.06.99 20:00 | 293 | 2 | 1 | 15 | 10 | 2 | 7 | 1 | n.q. |
| 10.06.99 21:00 | 289 | 2 | 1 | 14 | 8 | 1 | 7 | 1 | n.q. |
| 10.06.99 22:00 | 288 | n.q. | 1 | 12 | 7 | 1 | 7 | 0 | n.q. |
| 10.06.99 23:00 | 287 | 2 | 1 | 7 | 5 | 1 | 5 | 0 | n.q. |
| 11.06.99 00:00 | 286 | 1 | 1 | 10 | 5 | 1 | 5 | 0 | n.q. |
| 11.06.99 01:00 | 286 | 2 | 1 | 10 | 6 | 1 | 5 | 1 | n.q. |
| 11.06.99 02:00 | 286 | 2 | 1 | 10 | 5 | 1 | 5 | 0 | n.q. |
| 11.06.99 09:00 | 290 | 2 | 1 | 21 | 7 | 3 | 14 | 1 | 0 |
| 11.06.99 10:00 | 292 | 2 | 1 | 11 | 6 | 1 | 5 | 0 | n.q. |
| 11.06.99 11:00 | 292 | 1 | 1 | 11 | 6 | 1 | 5 | 1 | n.q. |
| 11.06.99 13:00 | 291 | 1 | 1 | 10 | 5 | 1 | 4 | 1 | n.q. |
| 11.06.99 14:00 | 291 | 1 | 1 | 10 | 6 | 1 | 4 | 1 | n.q. |
| 11.06.99 15:00 | 292 | 2 | 1 | 11 | 6 | 1 | 5 | 0 | 0 |

**Table 8.16:** *(continued)*

| date, time | temperature | 3-carene | α-terpinene | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | terpinolene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|---|---|
| 08.06.99 01:00 | 285 | 19 | 1 | 5 | 1 | n.q. | n.q. | 1 | 8 | 0 |
| 08.06.99 02:00 | 285 | 6 | 0 | 1 | 0 | 0 | 0 | 1 | 3 | 0 |
| 08.06.99 03:00 | 284 | 5 | 0 | 1 | 0 | 0 | 0 | 0 | 2 | 0 |
| 08.06.99 04:00 | 284 | 5 | 0 | 1 | 0 | 0 | 0 | 0 | 9 | 0 |
| 08.06.99 05:00 | 284 | 6 | 0 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| 08.06.99 07:00 | 284 | 6 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 0 |
| 08.06.99 09:00 | 299 | 24 | n.q. | 1 | 1 | n.q. | 2 | 1 | 8 | 1 |
| 08.06.99 10:00 | 301 | 26 | n.q. | 1 | 1 | 1 | 2 | 1 | 5 | 1 |
| 08.06.99 11:00 | 302 | 35 | n.q. | 2 | 2 | 1 | 3 | 1 | 4 | 3 |
| 08.06.99 12:00 | 303 | 32 | n.q. | 2 | 2 | 1 | 2 | 1 | 3 | 4 |
| 08.06.99 13:00 | 298 | 21 | 0 | 2 | 1 | 0 | 1 | 1 | 2 | 3 |
| 08.06.99 14:00 | 302 | 20 | n.q. | 2 | 1 | 0 | 2 | 1 | 4 | 2 |
| 08.06.99 15:00 | 300 | 22 | 0 | 1 | 1 | 0 | 2 | 1 | 3 | 2 |
| 08.06.99 19:00 | 291 | 8 | 0 | 1 | 0 | 0 | 1 | 1 | 2 | 2 |
| 08.06.99 20:00 | 289 | 6 | n.q. | 0 | 0 | 0 | 0 | n.q. | 1 | 1 |
| 08.06.99 21:00 | 287 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 08.06.99 22:00 | 284 | 4 | n.q. | 1 | 0 | 0 | 0 | 1 | 4 | 0 |
| 09.06.99 08:00 | 289 | 12 | 0 | 1 | 0 | 0 | 0 | 1 | 2 | 0 |
| 09.06.99 15:00 | 308 | 143 | 1 | 4 | 4 | 2 | 6 | 2 | 11 | 4 |
| 09.06.99 16:00 | 304 | 62 | 0 | 3 | 3 | 1 | 5 | 2 | 3 | 7 |
| 09.06.99 17:00 | 299 | 25 | 0 | 2 | 1 | 1 | 2 | 1 | 1 | 3 |
| 09.06.99 18:00 | 297 | 20 | 0 | 1 | 1 | 0 | 2 | 1 | 1 | 3 |
| 09.06.99 19:00 | 293 | 15 | 0 | 1 | 1 | 0 | 1 | 1 | 2 | 2 |
| 09.06.99 20:00 | 291 | 9 | 0 | 1 | 1 | 0 | 0 | 1 | 2 | 2 |
| 09.06.99 23:00 | 283 | 4 | 0 | 1 | 2 | 0 | 0 | 1 | 1 | n.q. |
| 10.06.99 01:00 | 282 | 2 | 0 | 1 | 0 | n.q. | n.q. | 0 | 2 | 0 |
| 10.06.99 10:00 | 301 | 20 | 0 | 1 | 2 | 1 | 3 | 1 | 4 | 1 |
| 10.06.99 11:00 | 303 | 26 | 0 | 2 | 2 | 1 | 5 | 1 | 2 | 2 |
| 10.06.99 12:00 | 301 | 24 | 0 | 1 | 1 | 1 | 4 | 2 | 1 | 3 |
| 10.06.99 13:00 | 303 | 27 | 0 | 2 | 1 | 1 | 4 | 2 | 30 | 1 |
| 10.06.99 14:00 | 304 | 30 | 0 | 3 | 3 | 1 | 5 | 2 | 2 | 1 |
| 10.06.99 15:00 | 303 | 28 | 0 | 2 | 1 | 1 | 4 | 1 | 2 | 1 |
| 10.06.99 16:00 | 304 | 37 | 0 | 2 | 1 | 1 | 4 | 1 | 2 | 1 |
| 10.06.99 17:00 | 303 | 51 | 0 | 3 | 2 | 1 | 8 | 1 | 3 | 2 |
| 10.06.99 18:00 | 299 | 24 | 0 | 1 | 1 | 1 | 2 | 1 | 1 | n.q. |
| 10.06.99 19:00 | 296 | 19 | 0 | 1 | 1 | 1 | 1 | 1 | 1 | 2 |
| 10.06.99 20:00 | 293 | 15 | 0 | 1 | 1 | 0 | 1 | 1 | 1 | 2 |
| 10.06.99 21:00 | 289 | 12 | 0 | 1 | 1 | 0 | 0 | 1 | 1 | 1 |
| 10.06.99 22:00 | 288 | 23 | 0 | 2 | 1 | 1 | 4 | 1 | 1 | 1 |
| 10.06.99 23:00 | 287 | 7 | 0 | 1 | 1 | 0 | 0 | 1 | 1 | n.q. |
| 11.06.99 00:00 | 286 | 7 | 0 | 0 | 1 | 0 | 0 | 0 | n.q. | n.q. |
| 11.06.99 01:00 | 286 | 8 | 0 | 1 | 1 | 0 | 0 | 1 | 1 | 0 |
| 11.06.99 02:00 | 286 | 7 | 0 | 1 | 2 | n.q. | 0 | 1 | 1 | n.q. |
| 11.06.99 09:00 | 290 | 75 | 1 | 5 | 2 | 2 | 1 | 1 | 2 | 1 |
| 11.06.99 10:00 | 292 | 11 | 0 | 1 | 0 | 0 | 1 | 1 | 2 | 0 |
| 11.06.99 11:00 | 292 | 11 | 0 | 1 | 0 | 0 | 1 | 0 | 1 | n.q. |
| 11.06.99 13:00 | 291 | 10 | n.q. | 1 | 0 | 0 | 1 | 1 | 1 | 0 |
| 11.06.99 14:00 | 291 | 10 | n.q. | 0 | 0 | 0 | 1 | 0 | 1 | 0 |
| 11.06.99 15:00 | 292 | 12 | 0 | 1 | 1 | 0 | 1 | 1 | 2 | n.q. |

**Table 8.17:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at pine No.8 in May 1999, n.q. = not quantified..*

| date, time | temperature | toluene | tricyclene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | α-phellandrene |
|---|---|---|---|---|---|---|---|---|---|
| 25.05.99 00:00 | 285 | 2 | 1 | 23 | 3 | 4 | 16 | 5 | 0 |
| 25.05.99 01:00 | 286 | 8 | 2 | 25 | 3 | 4 | 18 | 5 | 0 |
| 25.05.99 02:00 | 285 | 2 | 1 | 23 | 2 | 4 | 17 | 5 | 0 |
| 25.05.99 03:00 | 285 | 2 | 1 | 24 | 2 | 5 | 18 | 5 | 0 |
| 25.05.99 04:00 | 286 | 1 | 1 | 28 | 3 | 5 | 21 | 7 | 1 |
| 25.05.99 05:00 | 286 | 3 | 1 | 30 | 4 | 5 | 21 | 6 | 0 |
| 25.05.99 06:00 | 286 | 2 | 1 | 31 | 3 | 5 | 24 | 6 | 0 |
| 25.05.99 07:00 | 287 | 2 | 1 | 29 | 3 | 5 | 23 | 5 | 1 |
| 25.05.99 08:00 | 288 | 3 | 1 | 29 | 2 | 8 | 24 | 5 | 1 |
| 25.05.99 09:00 | 289 | 2 | 1 | 39 | 3 | 6 | 30 | 7 | 1 |
| 25.05.99 10:00 | 289 | 9 | 1 | 41 | 6 | 6 | 32 | 7 | 0 |
| 25.05.99 11:00 | 292 | 2 | 2 | 72 | 5 | 10 | 55 | 9 | 1 |
| 25.05.99 12:00 | 291 | 2 | 1 | 46 | 3 | 7 | 36 | 8 | 0 |
| 25.05.99 14:00 | 299 | 4 | 4 | 145 | 10 | 19 | 111 | 22 | 2 |
| 25.05.99 15:00 | 305 | 8 | 8 | n.q. | 35 | 29 | 145 | 35 | 4 |
| 25.05.99 16:00 | 301 | 7 | 5 | 164 | 14 | 17 | 108 | 21 | 2 |
| 25.05.99 18:00 | 296 | 4 | 3 | 74 | 16 | 9 | 43 | 12 | 1 |
| 25.05.99 19:00 | 294 | 3 | 2 | 57 | 6 | 6 | 34 | 8 | 1 |
| 25.05.99 20:00 | 292 | 8 | 2 | 44 | 5 | 7 | 32 | 9 | 0 |
| 25.05.99 21:00 | 290 | 6 | 1 | 35 | 5 | 10 | 25 | 14 | 2 |
| 25.05.99 23:00 | 285 | 1 | 0 | 17 | 2 | 3 | 11 | 4 | 0 |
| 26.05.99 00:00 | 284 | 1 | 0 | 17 | 2 | 3 | 11 | 3 | 0 |
| 26.05.99 01:00 | 283 | 3 | 1 | 15 | 2 | 3 | 11 | 2 | 0 |
| 26.05.99 09:15 | 301 | 4 | 3 | 150 | 9 | 21 | 118 | 13 | 1 |
| 26.05.99 09:45 | 303 | 7 | 5 | 211 | 18 | 30 | 161 | 24 | 2 |
| 26.05.99 10:15 | 305 | 6 | 6 | 261 | 15 | 37 | 225 | 27 | 3 |
| 26.05.99 11:15 | 306 | 9 | 6 | 250 | 23 | 37 | 189 | 31 | 3 |
| 26.05.99 11:45 | 306 | 9 | 6 | 228 | 22 | 33 | 158 | 31 | 2 |
| 26.05.99 12:15 | 306 | 8 | 5 | 195 | 15 | 27 | 143 | 24 | 3 |
| 26.05.99 13:15 | 308 | 9 | 6 | 220 | 22 | 33 | 156 | 29 | 2 |
| 26.05.99 13:45 | 308 | 12 | 4 | 201 | 15 | 33 | 152 | 25 | 1 |
| 26.05.99 14:15 | 309 | 9 | 5 | 212 | 15 | 32 | 158 | 33 | 3 |
| 26.05.99 14:45 | 309 | 9 | 5 | 220 | 15 | 31 | 165 | 35 | 3 |
| 26.05.99 15:15 | 309 | 7 | 4 | 189 | 13 | 26 | 143 | 28 | 2 |
| 26.05.99 15:45 | 309 | 10 | 9 | 405 | 22 | 46 | 288 | 55 | 4 |
| 26.05.99 16:15 | 308 | 9 | 7 | 298 | 20 | 38 | 250 | 43 | 4 |
| 26.05.99 16:45 | 307 | 10 | 7 | 336 | 20 | 43 | 315 | 51 | 3 |
| 26.05.99 17:15 | 305 | 10 | 9 | n.q. | 21 | 61 | n.q. | 70 | 6 |
| 26.05.99 18:00 | 299 | 7 | 5 | 244 | 13 | 36 | 231 | 23 | 2 |
| 26.05.99 20:00 | 293 | 3 | 3 | 111 | 6 | 16 | 93 | 17 | 2 |
| 26.05.99 21:00 | 290 | 4 | 2 | 100 | 7 | 17 | 86 | 14 | 1 |
| 26.05.99 22:00 | 287 | 3 | 1 | 59 | 6 | 13 | 49 | 7 | 1 |
| 26.05.99 23:00 | 285 | 2 | 1 | 51 | 3 | 9 | 45 | 7 | 1 |
| 27.05.99 01:00 | 284 | 2 | 1 | 41 | 3 | 7 | 34 | 6 | 1 |
| 27.05.99 09:15 | 303 | 13 | 18 | n.q. | 68 | 147 | n.q. | 51 | 6 |
| 27.05.99 10:15 | 307 | 18 | 104 | n.q. | 202 | 572 | n.q. | n.q. | 49 |
| 27.05.99 10:45 | 307 | 17 | 57 | n.q. | 159 | 425 | n.q. | n.q. | 8 |
| 27.05.99 11:15 | 308 | 20 | 72 | n.q. | 143 | 362 | n.q. | n.q. | 16 |
| 27.05.99 12:15 | 309 | 12 | 76 | n.q. | 127 | 438 | n.q. | n.q. | 12 |
| 27.05.99 12:45 | 310 | 21 | 98 | n.q. | 126 | 538 | n.q. | n.q. | 34 |
| 27.05.99 13:15 | 311 | 27 | 79 | n.q. | 114 | 442 | n.q. | n.q. | 13 |
| 27.05.99 13:45 | 311 | 20 | 74 | n.q. | 237 | 432 | n.q. | n.q. | 20 |
| 27.05.99 16:15 | 311 | 4 | 3 | 112 | 2 | 45 | 125 | 56 | 2 |
| 28.05.99 01:00 | 292 | 3 | 6 | n.q. | 10 | 40 | n.q. | 63 | 5 |
| 28.05.99 02:00 | 293 | 3 | 5 | 259 | 11 | 46 | 214 | 60 | 5 |
| 28.05.99 03:00 | 292 | 4 | 5 | 242 | 9 | 36 | 186 | 44 | 4 |
| 28.05.99 04:00 | 290 | 3 | 4 | 198 | 7 | 35 | 163 | 42 | 3 |
| 28.05.99 05:00 | 289 | 2 | 3 | 141 | 5 | 23 | 115 | 21 | 2 |
| 28.05.99 06:00 | 291 | 3 | 4 | n.q. | 8 | 41 | n.q. | 28 | 1 |
| 28.05.99 07:00 | 292 | 3 | 4 | n.q. | 8 | 40 | n.q. | 43 | 4 |
| 28.05.99 10:15 | 293 | 7 | 6 | 291 | 9 | 46 | 242 | 61 | 5 |
| 28.05.99 10:45 | 294 | 6 | 7 | 332 | 11 | 56 | 274 | 76 | 5 |
| 28.05.99 11:15 | 294 | 6 | 7 | 333 | 13 | 56 | 275 | 75 | 4 |
| 28.05.99 12:15 | 295 | 4 | 6 | 297 | 15 | 50 | 234 | 59 | 2 |
| 28.05.99 12:45 | 295 | 8 | 5 | 268 | 9 | 51 | 226 | 27 | 5 |
| 28.05.99 13:15 | 294 | 10 | 6 | 276 | 10 | 50 | 235 | 44 | 5 |
| 28.05.99 13:45 | 295 | 5 | 6 | 297 | 9 | 51 | 244 | 65 | 5 |

**Table 8.17:** *(continued)*

| date, time | temperature | 3-carene | α-terpinene | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | terpinolene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|---|---|
| 25.05.99 00:00 | 285 | 66 | 1 | 2 | 2 | 1 | 1 | 1 | 9 | 0 |
| 25.05.99 01:00 | 286 | 75 | 0 | 2 | 2 | 2 | 1 | 2 | 3 | n.q. |
| 25.05.99 02:00 | 285 | 71 | 0 | 1 | 1 | 1 | 0 | 1 | 4 | 0 |
| 25.05.99 03:00 | 285 | 78 | 0 | 1 | 2 | 2 | 0 | 1 | 2 | 1 |
| 25.05.99 04:00 | 286 | 95 | 0 | 1 | 2 | 2 | 0 | 1 | 2 | 0 |
| 25.05.99 05:00 | 286 | 102 | 0 | 1 | 2 | 2 | 0 | 1 | 2 | 0 |
| 25.05.99 06:00 | 286 | 106 | 1 | 2 | 2 | 2 | 0 | 1 | 9 | 0 |
| 25.05.99 07:00 | 287 | 97 | n.q. | 2 | 2 | 2 | 0 | 2 | 3 | 0 |
| 25.05.99 08:00 | 288 | 102 | 2 | 2 | 2 | 2 | 0 | 1 | 2 | 0 |
| 25.05.99 09:00 | 289 | 137 | n.q. | 2 | 2 | 3 | 1 | 2 | 1 | 0 |
| 25.05.99 10:00 | 289 | 144 | 1 | 2 | 2 | 3 | 1 | 2 | 2 | 0 |
| 25.05.99 11:00 | 292 | 225 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| 25.05.99 12:00 | 291 | 161 | n.q. | 2 | 2 | 3 | 2 | 2 | 7 | 1 |
| 25.05.99 14:00 | 299 | n.q. | 3 | 8 | 8 | 8 | 11 | 7 | 5 | 4 |
| 25.05.99 15:00 | 305 | n.q. | 5 | 21 | 27 | 15 | 16 | 14 | 13 | 8 |
| 25.05.99 16:00 | 301 | n.q. | 3 | 12 | 9 | 9 | 10 | 8 | 5 | 5 |
| 25.05.99 18:00 | 296 | 251 | 1 | 6 | 9 | 4 | 4 | 4 | 3 | 2 |
| 25.05.99 19:00 | 294 | 164 | 1 | 4 | 3 | 3 | 2 | 3 | 1 | 1 |
| 25.05.99 20:00 | 292 | 127 | 1 | 3 | 3 | 2 | 1 | 3 | 2 | 1 |
| 25.05.99 21:00 | 290 | 98 | 2 | 5 | 2 | 3 | 2 | 3 | 10 | 1 |
| 25.05.99 23:00 | 285 | 44 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 1 |
| 26.05.99 00:00 | 284 | 44 | 0 | 1 | 1 | 1 | 0 | n.q. | 1 | 0 |
| 26.05.99 01:00 | 283 | 37 | 0 | 1 | 1 | 1 | 0 | 1 | 2 | 0 |
| 26.05.99 09:15 | 301 | n.q. | 1 | 6 | 6 | 9 | 14 | 6 | 2 | 2 |
| 26.05.99 09:45 | 303 | n.q. | 3 | 12 | 14 | 13 | 20 | 9 | n.q. | n.q. |
| 26.05.99 10:15 | 305 | n.q. | 5 | 13 | 12 | 15 | 22 | 10 | 4 | 5 |
| 26.05.99 11:15 | 306 | n.q. | 4 | 16 | 15 | 14 | 27 | 12 | 5 | 6 |
| 26.05.99 11:45 | 306 | n.q. | 3 | 14 | 14 | 12 | 25 | 0 | 6 | 8 |
| 26.05.99 12:15 | 306 | n.q. | 4 | 15 | 11 | 12 | 23 | 1 | 6 | 7 |
| 26.05.99 13:15 | 308 | n.q. | 3 | 16 | 14 | 11 | 22 | 11 | 13 | 10 |
| 26.05.99 13:45 | 308 | 571 | 2 | 12 | 8 | 9 | 18 | 8 | 13 | 6 |
| 26.05.99 14:15 | 309 | n.q. | 5 | 16 | 12 | 12 | 22 | 12 | 5 | 10 |
| 26.05.99 14:45 | 309 | n.q. | 5 | 15 | 12 | 12 | 20 | 11 | 30 | 12 |
| 26.05.99 15:15 | 309 | n.q. | 3 | 12 | 10 | 10 | 16 | 8 | 7 | 11 |
| 26.05.99 15:45 | 309 | 703 | 6 | 21 | 20 | 22 | 21 | 18 | 20 | 14 |
| 26.05.99 16:15 | 308 | n.q. | 6 | 18 | 17 | 17 | 20 | 14 | 14 | 13 |
| 26.05.99 16:45 | 307 | n.q. | 5 | 17 | 17 | 20 | 19 | 14 | 14 | 11 |
| 26.05.99 17:15 | 305 | n.q. | 9 | 23 | 23 | 32 | 20 | 20 | 18 | 11 |
| 26.05.99 18:00 | 299 | n.q. | 4 | 10 | 10 | 16 | 1 | 6 | 1 | 0 |
| 26.05.99 20:00 | 293 | n.q. | 2 | 6 | 7 | 9 | 1 | 6 | 3 | 1 |
| 26.05.99 21:00 | 290 | n.q. | 2 | 5 | 6 | 8 | 1 | 4 | 2 | 1 |
| 26.05.99 22:00 | 287 | n.q. | 2 | 4 | 5 | 6 | 1 | 4 | 1 | 0 |
| 26.05.99 23:00 | 285 | n.q. | 1 | 2 | 3 | 4 | 0 | 2 | 2 | 1 |
| 27.05.99 01:00 | 284 | 159 | 1 | 2 | 2 | 4 | 0 | 2 | 1 | n.q. |
| 27.05.99 09:15 | 303 | n.q. | 18 | 42 | 61 | 62 | 26 | 22 | 6 | 3 |
| 27.05.99 10:15 | 307 | n.q. | 138 | 176 | 313 | 351 | 34 | 209 | 160 | 4 |
| 27.05.99 10:45 | 307 | n.q. | 40 | 121 | 223 | 242 | 37 | 127 | 74 | 11 |
| 27.05.99 11:15 | 308 | n.q. | 132 | 137 | 235 | 254 | 46 | 172 | 194 | 15 |
| 27.05.99 12:15 | 309 | n.q. | 125 | 125 | 223 | 286 | 42 | 174 | 182 | 22 |
| 27.05.99 12:45 | 310 | n.q. | 114 | 143 | 222 | 329 | 48 | 193 | 186 | 28 |
| 27.05.99 13:15 | 311 | n.q. | 108 | 124 | 191 | 263 | 48 | 163 | 145 | 28 |
| 27.05.99 13:45 | 311 | n.q. | 126 | 218 | 242 | 251 | 40 | 151 | 151 | 24 |
| 27.05.99 16:15 | 311 | n.q. | 7 | 12 | 16 | 25 | 3 | 12 | 17 | 1 |
| 28.05.99 01:00 | 292 | n.q. | 4 | 10 | 16 | 24 | 1 | 14 | 21 | 2 |
| 28.05.99 02:00 | 293 | n.q. | 4 | 9 | 15 | 23 | 1 | 12 | 12 | 1 |
| 28.05.99 03:00 | 292 | n.q. | 4 | 10 | 14 | 22 | 1 | 13 | 10 | 1 |
| 28.05.99 04:00 | 290 | n.q. | 3 | 8 | 13 | 20 | 1 | 11 | 10 | 1 |
| 28.05.99 05:00 | 289 | n.q. | 2 | 6 | 9 | 14 | 1 | 7 | 3 | 1 |
| 28.05.99 06:00 | 291 | n.q. | 5 | 9 | 13 | 21 | 1 | 10 | 3 | 0 |
| 28.05.99 07:00 | 292 | n.q. | 5 | 10 | 15 | 21 | 2 | 13 | 6 | 1 |
| 28.05.99 10:15 | 293 | n.q. | 4 | 11 | 18 | 26 | 2 | 15 | 10 | 2 |
| 28.05.99 10:45 | 294 | n.q. | 5 | 13 | 19 | 29 | 3 | 16 | 17 | 2 |
| 28.05.99 11:15 | 294 | n.q. | 5 | 12 | 20 | 29 | 2 | 16 | 14 | 1 |
| 28.05.99 12:15 | 295 | n.q. | 5 | 12 | 20 | 27 | 4 | 16 | 15 | 1 |
| 28.05.99 12:45 | 295 | 1107 | 5 | 12 | 13 | 23 | 3 | 14 | 7 | 1 |
| 28.05.99 13:15 | 294 | n.q. | 6 | 14 | 17 | 26 | 5 | 16 | 9 | 1 |
| 28.05.99 13:45 | 295 | n.q. | 4 | 11 | 17 | 26 | 5 | 15 | 13 | 2 |

**Table 8.18:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at pine No.8 in July 1999, n.q. = not quantified..*

| date, time | temperature | toluene | tricyclene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | α-phellandrene |
|---|---|---|---|---|---|---|---|---|---|
| 08.07.99 02:00 | 287 | 5 | 0 | 7 | 1 | 5 | 3 | 3 | n.q. |
| 08.07.99 03:00 | 286 | 5 | 1 | 8 | 2 | n.q. | 5 | 1 | n.q. |
| 08.07.99 04:00 | 286 | 2 | 0 | 8 | 1 | 2 | 6 | 1 | n.q. |
| 08.07.99 05:00 | 287 | 1 | 0 | 8 | 1 | 2 | 6 | 1 | n.q. |
| 08.07.99 06:00 | 288 | 4 | 1 | 11 | 2 | 2 | 7 | 1 | n.q. |
| 08.07.99 07:00 | 289 | 3 | 1 | 12 | 2 | 3 | 7 | 1 | n.q. |
| 08.07.99 08:00 | 290 | 2 | 1 | 20 | 5 | 1 | 8 | 1 | n.q. |
| 08.07.99 09:00 | 293 | 2 | 1 | 28 | 7 | 3 | 12 | 2 | n.q. |
| 08.07.99 10:00 | 295 | 3 | 2 | 27 | 6 | 4 | 14 | 2 | n.q. |
| 08.07.99 11:00 | 295 | 5 | 1 | 30 | 6 | 3 | 15 | 2 | n.q. |
| 08.07.99 12:00 | 296 | 5 | 1 | 27 | 6 | 3 | 13 | 2 | n.q. |
| 08.07.99 13:00 | 302 | 5 | 2 | 37 | 6 | 4 | 21 | 3 | n.q. |
| 08.07.99 14:00 | 302 | 4 | 2 | 48 | 8 | 5 | 25 | 4 | n.q. |
| 08.07.99 15:00 | 306 | 4 | 3 | 91 | 12 | 9 | 54 | 8 | n.q. |
| 08.07.99 17:00 | 306 | 6 | 4 | 93 | 15 | 8 | 44 | 7 | 0 |
| 08.07.99 18:00 | 302 | 6 | 4 | 79 | 17 | 9 | 33 | 8 | 1 |
| 08.07.99 19:00 | 297 | 6 | 3 | 56 | 15 | 12 | 24 | 6 | 1 |
| 08.07.99 21:00 | 293 | 2 | 1 | 24 | 7 | 3 | 10 | 2 | n.q. |
| 08.07.99 22:00 | 290 | 2 | 1 | 15 | 4 | 3 | 6 | 5 | n.q. |
| 08.07.99 23:00 | 289 | 1 | 1 | 13 | 3 | 2 | 5 | 1 | n.q. |
| 09.07.99 00:00 | 289 | 1 | 1 | 12 | 3 | 2 | 5 | 1 | 0 |
| 09.07.99 01:00 | 290 | 2 | 1 | 15 | 3 | 3 | 6 | 2 | n.q. |
| 09.07.99 09:00 | 305 | 3 | 3 | 71 | 12 | 7 | 35 | 4 | 0 |
| 09.07.99 10:00 | 307 | 5 | 3 | 92 | 12 | 7 | 50 | 4 | 0 |
| 09.07.99 11:00 | 309 | 14 | 3 | 101 | 14 | 15 | 58 | 20 | 0 |
| 09.07.99 12:00 | 310 | 9 | 3 | 99 | 15 | 15 | 61 | 5 | 1 |
| 09.07.99 13:00 | 311 | 6 | 3 | 80 | 10 | 9 | 41 | 4 | 0 |

**Table 8.18:** *(continued)*

| date, time | temperature | 3-carene | α-terpinene | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | terpinolene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|---|---|
| 08.07.99 02:00 | 287 | 10 | n.q. | 1 | 1 | 0 | 0 | n.q. | 7 | 1 |
| 08.07.99 03:00 | 286 | 6 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | 1 |
| 08.07.99 04:00 | 286 | 12 | 0 | 1 | 1 | 0 | 0 | 0 | 3 | 0 |
| 08.07.99 05:00 | 287 | 13 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 |
| 08.07.99 06:00 | 288 | 16 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 0 |
| 08.07.99 07:00 | 289 | 16 | 0 | 1 | 1 | 0 | 0 | 1 | 2 | 0 |
| 08.07.99 08:00 | 290 | 19 | 0 | 1 | 1 | 0 | 1 | 1 | 3 | 0 |
| 08.07.99 09:00 | 293 | 28 | 0 | 1 | 1 | 1 | 2 | 1 | 8 | 0 |
| 08.07.99 10:00 | 295 | 33 | 0 | 1 | 1 | 1 | 2 | 1 | 7 | 0 |
| 08.07.99 11:00 | 295 | 36 | 1 | 1 | 1 | 1 | 4 | 2 | 4 | 1 |
| 08.07.99 12:00 | 296 | 32 | 1 | 1 | 1 | 1 | 2 | 1 | 3 | 0 |
| 08.07.99 13:00 | 302 | 51 | 0 | 2 | 1 | 1 | 2 | 1 | 4 | 1 |
| 08.07.99 14:00 | 302 | 71 | 0 | 2 | 2 | 1 | 3 | 1 | 2 | 1 |
| 08.07.99 15:00 | 306 | 182 | 2 | 6 | 4 | 2 | 4 | 1 | 8 | 1 |
| 08.07.99 17:00 | 306 | 163 | 2 | 6 | 4 | 2 | 5 | 2 | 11 | 2 |
| 08.07.99 18:00 | 302 | 107 | 1 | 4 | 3 | 2 | 7 | 1 | 6 | 2 |
| 08.07.99 19:00 | 297 | 67 | 0 | 5 | 4 | 2 | 6 | 2 | 27 | 1 |
| 08.07.99 21:00 | 293 | 29 | 0 | 1 | 1 | 0 | 1 | 1 | 3 | 1 |
| 08.07.99 22:00 | 290 | 17 | 1 | 2 | 1 | 1 | 1 | 1 | 4 | 1 |
| 08.07.99 23:00 | 289 | 15 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 0 |
| 09.07.99 00:00 | 289 | 14 | 0 | 1 | 1 | 0 | 0 | 0 | 2 | 1 |
| 09.07.99 01:00 | 290 | 17 | 0 | 1 | 1 | 0 | 1 | 1 | 2 | 0 |
| 09.07.99 09:00 | 305 | 115 | 1 | 4 | 2 | 1 | 10 | 1 | 1 | 1 |
| 09.07.99 10:00 | 307 | 177 | 2 | 7 | n.q. | 4 | 2 | 2 | 1 | 2 |
| 09.07.99 11:00 | 309 | 193 | 2 | 9 | 4 | 3 | 10 | n.q. | 31 | 2 |
| 09.07.99 12:00 | 310 | 205 | 2 | 9 | 5 | 2 | 11 | 2 | 9 | 2 |
| 09.07.99 13:00 | 311 | 139 | 1 | 7 | 3 | 2 | 8 | 1 | 2 | 2 |

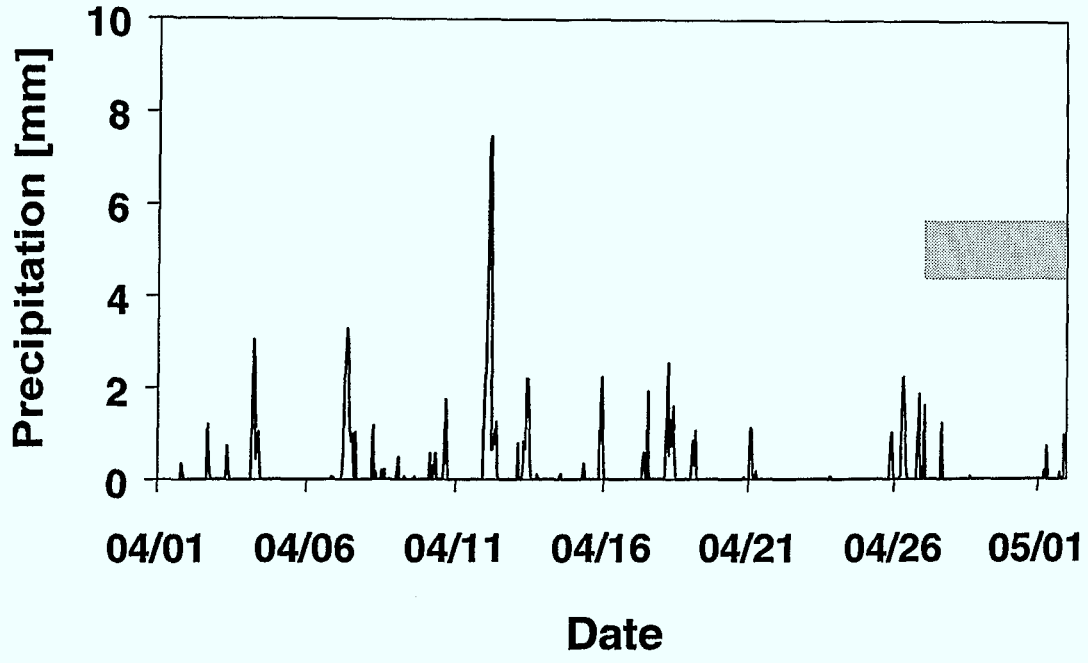
**Table 8.19:** *Emission rates in [ng g(dw)$^{-1}$ h$^{-1}$] measured at pine No.8 in August 1999, n.q. = not quantified..*

| date, time | temperature | toluene | tricyclene | α-pinene | camphene | sabinene | β-pinene | β-myrcene | α-phellandrene |
|---|---|---|---|---|---|---|---|---|---|
| 26.08.99 01:00 | 294 | 2 | 1 | 29 | 7 | 3 | 15 | 3 | n.q. |
| 26.08.99 02:00 | 294 | 2 | 1 | 30 | 7 | 2 | 15 | 3 | 0 |
| 26.08.99 03:00 | 293 | 3 | 1 | 22 | 6 | 3 | 11 | 6 | n.q. |
| 26.08.99 04:00 | 293 | 1 | 1 | 20 | 5 | 2 | 10 | 2 | n.q. |
| 26.08.99 05:00 | 293 | 2 | 1 | 25 | 6 | 2 | 12 | 3 | n.q. |
| 26.08.99 06:00 | 294 | 3 | 1 | 25 | 6 | 5 | 13 | 3 | n.q. |
| 26.08.99 07:00 | 294 | 3 | 1 | 25 | 6 | 3 | 13 | 6 | n.q. |
| 26.08.99 08:00 | 294 | 3 | 1 | 24 | 6 | 6 | 14 | 3 | n.q. |
| 26.08.99 10:00 | 297 | 2 | 2 | 47 | 12 | 4 | 24 | 6 | n.q. |
| 26.08.99 11:00 | 300 | 4 | 4 | 70 | 17 | 6 | 35 | 8 | n.q. |
| 26.08.99 12:00 | 300 | 3 | 4 | 67 | 15 | 5 | 34 | 7 | n.q. |
| 26.08.99 13:00 | 300 | 4 | 2 | 46 | 11 | 4 | 22 | 5 | n.q. |
| 26.08.99 14:00 | 300 | 3 | 3 | 65 | 14 | 5 | 31 | 8 | 0 |
| 26.08.99 15:00 | 298 | 2 | 2 | 40 | 9 | 3 | 19 | 5 | n.q. |
| 26.08.99 16:00 | 299 | 3 | 1 | 43 | 9 | 4 | 18 | 6 | n.q. |
| 26.08.99 18:00 | 297 | 6 | 2 | 55 | 11 | 13 | 30 | 7 | n.q. |
| 26.08.99 19:00 | 297 | 4 | 2 | 36 | 9 | 6 | 18 | 5 | n.q. |
| 26.08.99 21:00 | 293 | 2 | 2 | 30 | 10 | 4 | 13 | 3 | n.q. |
| 26.08.99 22:00 | 291 | 2 | 1 | 16 | 3 | 2 | 7 | 2 | n.q. |
| 26.08.99 23:00 | 291 | 2 | 1 | 13 | 4 | n.q. | 6 | 3 | n.q. |
| 27.08.99 00:00 | 290 | 1 | 1 | 13 | 3 | 2 | 6 | 1 | n.q. |
| 27.08.99 01:00 | 289 | 7 | 3 | 20 | 5 | 2 | 9 | 3 | n.q. |
| 27.08.99 08:56 | 295 | 5 | 4 | 52 | n.q. | 5 | 25 | 4 | n.q. |
| 27.08.99 10:00 | 303 | 4 | 4 | 66 | 14 | 9 | 34 | 9 | 1 |
| 27.08.99 11:00 | 303 | 4 | 4 | 86 | n.q. | 11 | 47 | 11 | 0 |
| 27.08.99 12:00 | 302 | 4 | 4 | 78 | n.q. | 9 | 40 | 9 | 1 |
| 27.08.99 13:00 | 303 | 6 | 4 | 73 | 16 | 9 | 36 | 8 | 1 |

**Table 8.19:** *(continued)*

| date, time | temperature | 3-carene | α-terpinene | p-cymene | limonene | β-phellandrene | 1,8-cineol | γ-terpinene | terpinolene | β-caryophyllene |
|---|---|---|---|---|---|---|---|---|---|---|
| 26.08.99 01:00 | 294 | 31 | 0 | 1 | 1 | 1 | 1 | 1 | 2 | 16 |
| 26.08.99 02:00 | 294 | 32 | n.q. | 1 | 1 | 1 | 1 | 1 | 1 | 15 |
| 26.08.99 03:00 | 293 | 24 | 0 | 2 | 1 | 0 | 1 | 3 | 2 | 14 |
| 26.08.99 04:00 | 293 | 20 | n.q. | 1 | 1 | 1 | 0 | 1 | 1 | 11 |
| 26.08.99 05:00 | 293 | 26 | n.q. | 1 | 1 | 1 | 1 | 1 | 3 | 13 |
| 26.08.99 06:00 | 294 | 26 | 0 | 1 | 1 | 1 | 0 | 1 | 1 | 13 |
| 26.08.99 07:00 | 294 | 27 | 0 | 1 | 1 | 1 | 0 | 1 | 3 | 11 |
| 26.08.99 08:00 | 294 | 26 | 0 | 1 | 1 | 1 | 0 | 2 | 6 | 8 |
| 26.08.99 10:00 | 297 | 53 | 1 | 2 | 1 | 1 | 3 | 1 | 2 | 13 |
| 26.08.99 11:00 | 300 | 84 | 0 | 3 | 2 | 2 | 6 | 2 | n.q. | 18 |
| 26.08.99 12:00 | 300 | 70 | n.q. | 2 | 2 | 2 | 5 | 2 | 8 | 25 |
| 26.08.99 13:00 | 300 | 52 | 0 | 2 | 2 | 1 | 2 | 1 | 9 | 15 |
| 26.08.99 14:00 | 300 | 80 | n.q. | 2 | 2 | 2 | 5 | 2 | 2 | 20 |
| 26.08.99 15:00 | 298 | 44 | n.q. | 1 | 1 | 1 | 3 | 1 | n.q. | 16 |
| 26.08.99 16:00 | 299 | 44 | 0 | 1 | 1 | 1 | 2 | 1 | 1 | 17 |
| 26.08.99 18:00 | 297 | 72 | 2 | 3 | 3 | 2 | 4 | 2 | 34 | 8 |
| 26.08.99 19:00 | 297 | 37 | n.q. | 2 | 1 | 1 | 2 | 1 | 2 | 12 |
| 26.08.99 21:00 | 293 | 31 | 0 | 2 | 1 | 3 | 1 | 12 | 5 | 13 |
| 26.08.99 22:00 | 291 | 15 | 0 | 1 | 1 | 1 | 0 | 1 | 1 | 5 |
| 26.08.99 23:00 | 291 | 12 | 1 | 1 | 0 | n.q. | 1 | 1 | 3 | 3 |
| 27.08.99 00:00 | 290 | 12 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 4 |
| 27.08.99 01:00 | 289 | 17 | 0 | 1 | 1 | 1 | 0 | 1 | 4 | 4 |
| 27.08.99 08:56 | 295 | 53 | 0 | 2 | 1 | 1 | 6 | 1 | 2 | 3 |
| 27.08.99 10:00 | 303 | 95 | 1 | 4 | 2 | 4 | 15 | 2 | 3 | 9 |
| 27.08.99 11:00 | 303 | 138 | 1 | 4 | 5 | 3 | 24 | 3 | 2 | 27 |
| 27.08.99 12:00 | 302 | 106 | n.q. | 5 | 2 | 3 | 23 | 3 | 5 | 23 |
| 27.08.99 13:00 | 303 | 92 | 0 | 4 | 4 | 2 | 21 | 3 | 6 | 25 |

## 8.8 Environmental conditions prior and during the emission rate studies in Hartheim



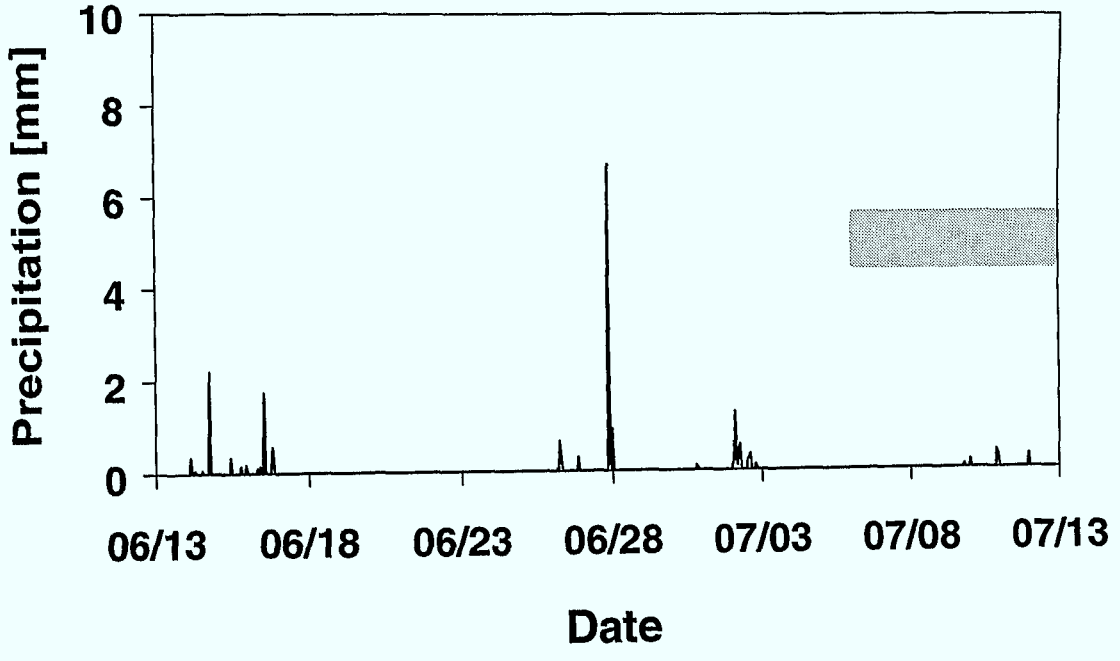
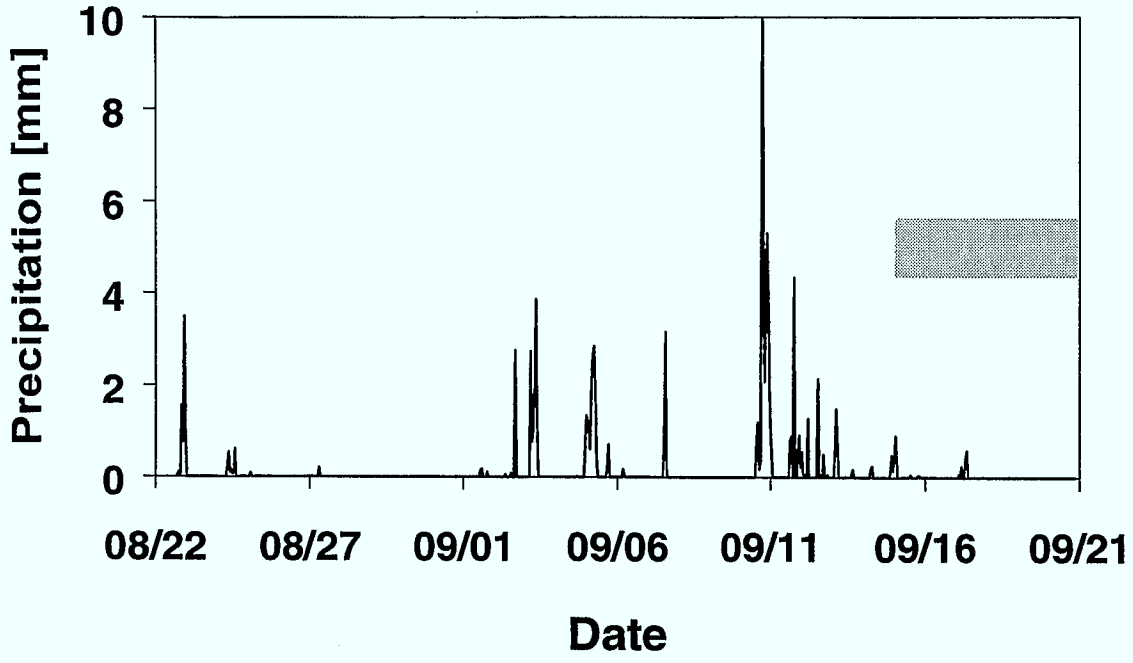




**Figure 8.2 a-b:** *Precipitation in mm before and during outdoor enclosure measurements with adult Scots pine. The grey bars mark the time period of emission rate measurements.*



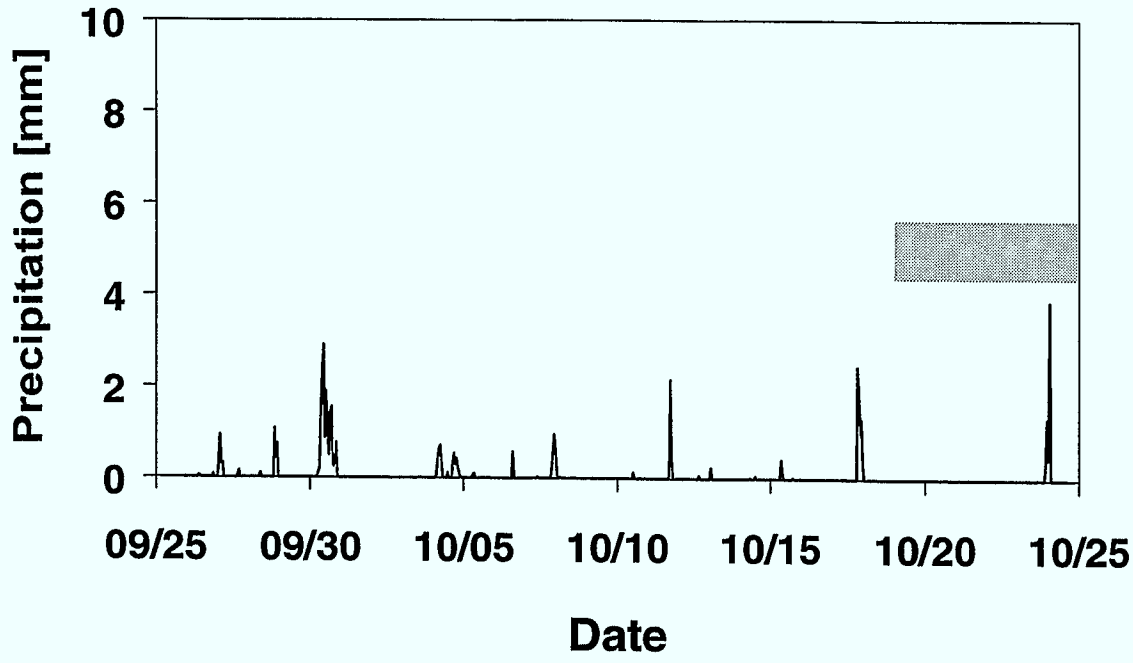
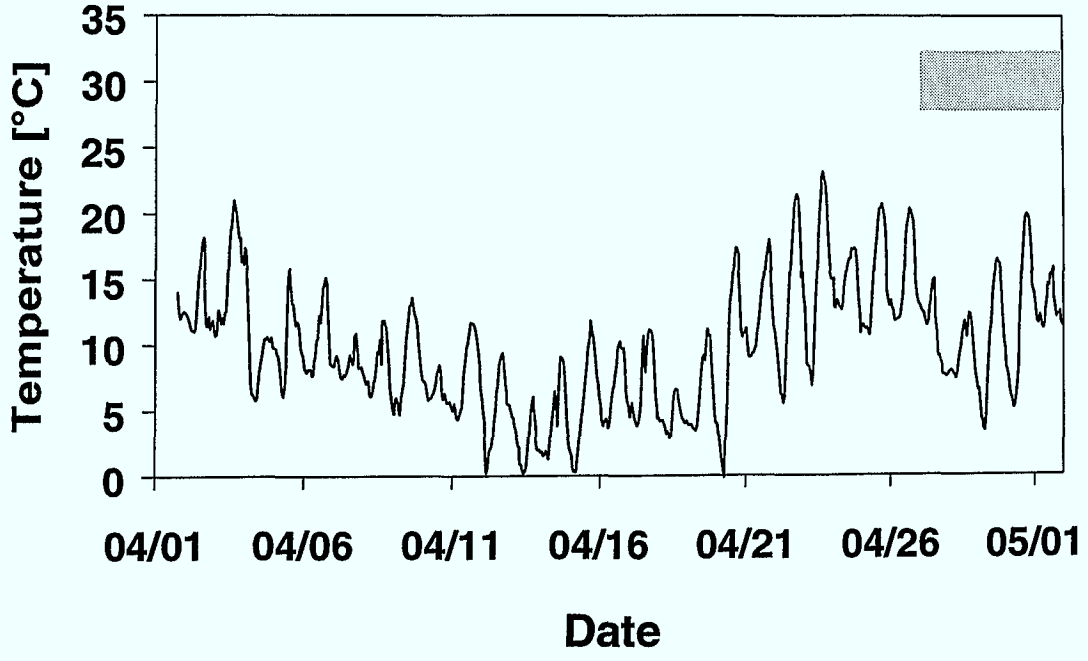




**Figure 8.2 c-d:** *Precipitation in mm before and during outdoor enclosure measurements with adult Scots pine. The grey bars mark the time period of emission rate measurements.*



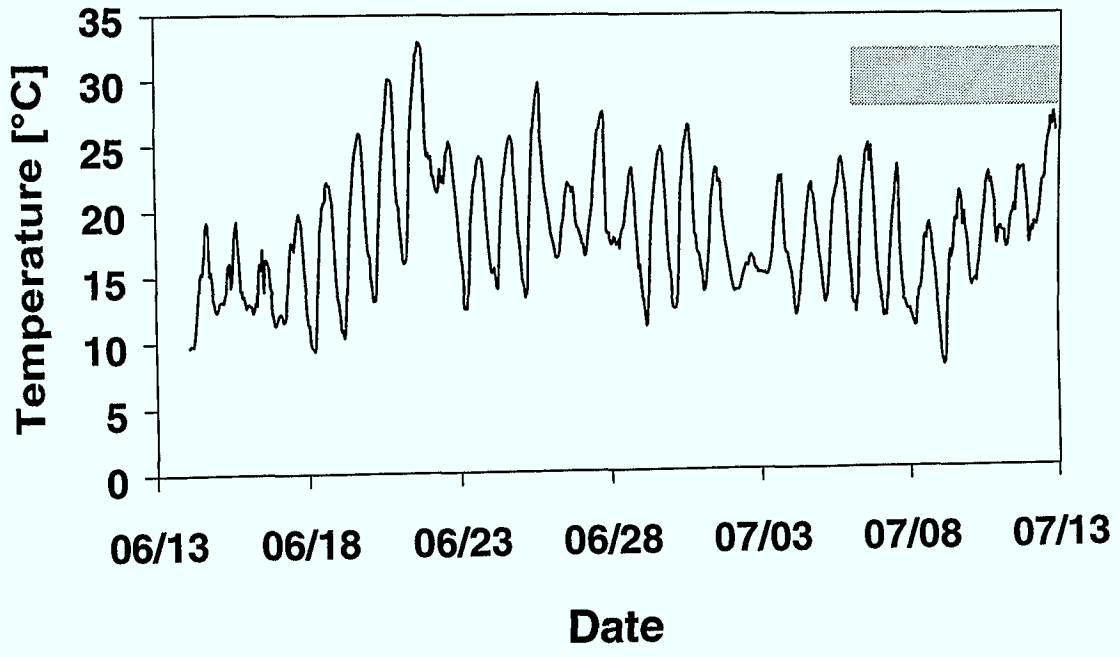
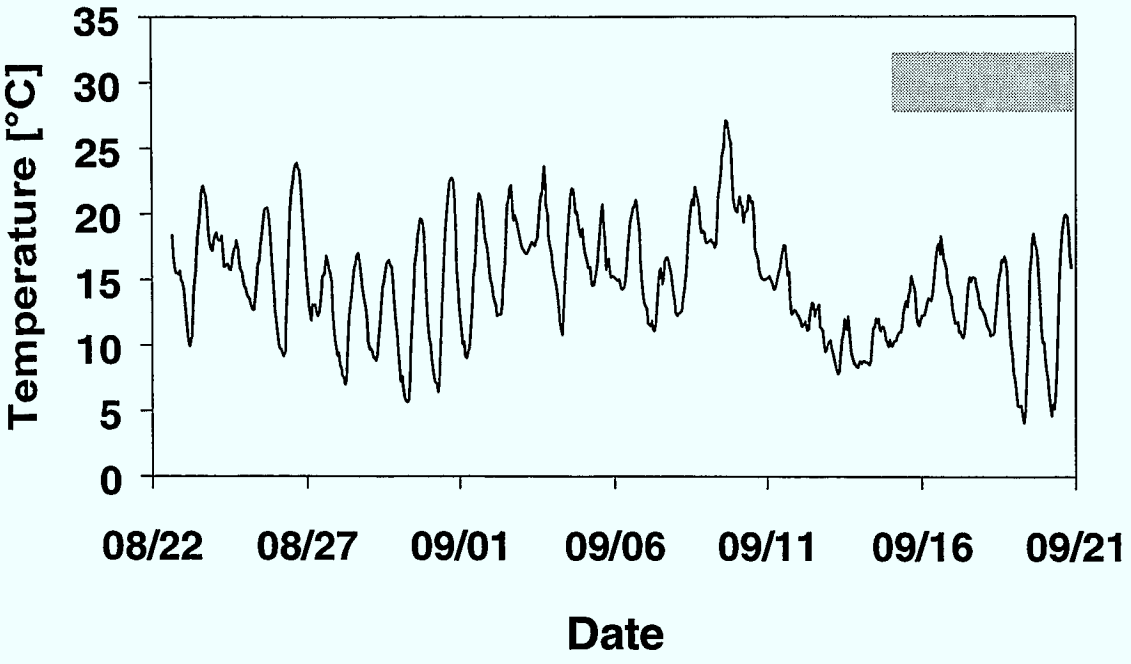




**Figure 8.3 a-b:** *Temperature in °C before and during outdoor enclosure measurements with adult Scots pine. The grey bars mark the time period of emission rate measurements.*



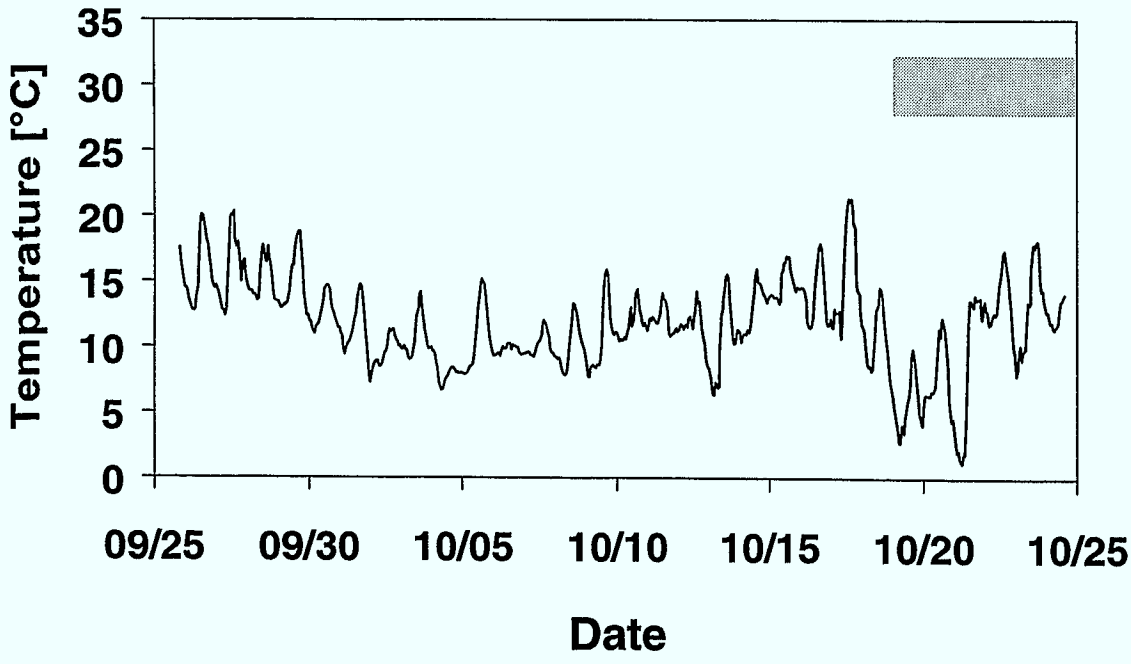




**Figure 8.3 c-d:** *Temperature in °C before and during outdoor enclosure measurements with adult Scots pine. The grey bars mark the time period of emission rate measurements.*

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