Laboratory and field measurements of enantiomeric and non-enantiomeric biogenic VOCs and anthropogenic BTEX compounds

Dissertation zur Erlangung des Grades

„Doktor der Naturwissenschaften“

am Fachbereich Chemie, Pharmazie und Geowissenschaften

der Johannes Gutenberg-Universität Mainz

vorgelegt von

M.Sc. Wei Song

geboren in Shandong, VR China

Mainz, 2012

Abstract

This doctoral thesis was focused on the investigation of enantiomeric and non-enantiomeric biogenic organic compound (BVOC) emissions from both leaf and canopy scales in different environments. In addition, the anthropogenic compounds benzene, toluene, ethylbenzene, and xylenes (BTEX) were studied. BVOCs are emitted into the lower troposphere in large quantities (ca. 1150 Tg C $\cdot yr^{-1}$), approximately an order of magnitude greater than the anthropogenic VOCs. BVOCs are particularly important in tropospheric chemistry because of their impact on ozone production and secondary organic aerosol formation or growth. The BVOCs examined in this study were: isoprene, (-)/ (+)-α-pinene, (-)/ (+)-ß-pinene, Δ-3-carene, (-)/ (+)-limonene, myrcene, eucalyptol and camphor, as these were the most abundant BVOCs observed both in the leaf cuvette study and the ambient measurements.

In the laboratory cuvette studies, the sensitivity of enantiomeric enrichment change from the leaf emission has been examined as a function of light (0-1600 PAR) and temperature (20-45°C). Three typical Mediterranean plant species (*Quercus ilex* L., *Rosmarinus officinalis* L., *Pinus halepensis* Mill.) with more than three individuals of each have been investigated using a dynamic enclosure cuvette. The terpenoid compound emission rates were found to be directly linked to either light and temperature (e.g. *Quercus ilex* L.) or mainly to temperature (e.g. *Rosmarinus officinalis* L., *Pinus halepensis* Mill.). However, the enantiomeric signature showed no clear trend in response to either the light or temperature; moreover a large variation of enantiomeric enrichment was found during the experiment. This enantiomeric signature was also used to distinguish chemotypes beyond the normal achiral chemical composition method. The results of nineteen Quercus ilex L. individuals, screened under standard conditions (30°C and 1000 PAR) showed four different chemotypes, whereas the traditional classification showed only two.

An enclosure branch cuvette set-up was applied in the natural boreal forest environment from four chemotypes of Scots pine (*Pinus sylvestris*) and one chemotype of Norway spruce (*Picea abies*) and the direct emissions compared with ambient air measurements above the canopy during the HUMPPA-COPEC 2010 summer campaign. The chirality of α-pinene was dominated by (+)-enantiomers from Scots pine while for Norway spruce the chirality was found to be opposite (i.e.

(-)-enantiomer enriched) becoming increasingly enriched in the (-)-enantiomer with light.

Field measurements over a Spanish stone pine forest were performed to examine the extent of seasonal changes in enantiomeric enrichment (DOMINO 2008). These showed clear differences in chirality of monoterpene emissions. In wintertime the monoterpene (-)-α-pinene was found to be in slight enantiomeric excess over (+)-α-pinene at night but by day the measured ratio was closer to one i.e. racemic. Samples taken the following summer in the same location showed much higher monoterpene mixing ratios and revealed a strong enantiomeric excess of (-)-α-pinene. This indicated a strong seasonal variance in the enantiomeric emission ratio which was not manifested in the day/night temperature cycles in wintertime. A clear diurnal cycle of enantiomeric enrichment in α-pinene was also found over a French oak forest and the boreal forest. However, while in the boreal forest (-)-α-pinene enrichment increased around the time of maximum light and temperature, the French forest showed the opposite tendency with (+)-α-pinene being favored.

For the two field campaigns (DOMINO 2008 and HUMPPA-COPEC 2010), the BTEX were also investigated. For the DOMINO campaign, mixing ratios of the xylene isomers (meta- and para-) and ethylbenzene, which are all well resolved on the ß-cyclodextrin column, were exploited to estimate average OH radical exposures to VOCs from the Huelva industrial area. These were compared to empirical estimates of OH based on JNO_2 measured at the site. The deficiencies of each estimation method are discussed. For HUMPPA-COPEC campaign, benzene and toluene mixing ratios can clearly define the air mass influenced by the biomass burning pollution plume from Russia.

Zusammenfassung

Im Rahmen der vorgelegten Doktorarbeit wurden enantiomerische und nicht-enantiomerische biogene organische flüchtige Kohlenwasserstoffe auf unterschiedlichen Skalen studiert: die Emissionen einzelner Blätter und ganzer Wälder. Zusätzlich wurden anthropogene Substanzen, wie z. B. Benzol, Toluol, Ethylbenzol und Xylol untersucht. Biogene flüchtige Kohlenwasserstoffe werden in die untere Troposphäre in großen Mengen emittiert (ca. 1150 Tg yr^{-1}), etwa eine Größenordnung mehr als anthropogene Substanzen. Die biogenen flüchtigen Kohlenwasserstoffe sind insbesondere deshalb wichtig für die Chemie der Troposphäre, weil sie Einfluss nehmen auf Ozonproduktion sowie Bildung und Wachstum von sekundärem organischem Aerosol. In dieser Studie wurden folgende biogene Substanzen untersucht: Isopren, (-)/(+)-α-Pinen, (-)/(+)-β-Pinen, Δ-3-Caren, (-)/(+)-Limonen, Myrcen, Cineoll und Kampfer, da sie die am häufigsten beobachteten sind für sowohl Pflanzenkammer- als auch atmosphärische Messungen.

Mit Hilfe von Pflanzenkammermessungen wurde die Sensitivität der enantiomerischen Zusammensetzung der Blattemissionen als Funktion von Licht und Temperatur charakterisiert. Dafür wurden drei typisch mediterrane Pflanzen-Arten untersucht (*Quercus ilex* L., *Rosmarinus officinalis* L., *Pinus halepensis* Mill.). Jeweils mehr als drei individuelle Pflanzen pro Art wurden unter Verwendung einer dynamischen Kammer beobachtet. Die Terpenemissionen waren entweder direkt mit Licht und Temperatur gekoppelt oder hauptsächlich abhängig von der Temperatur. Die enantiomerische Signatur zeigte jedoch keine direkte Reaktion auf Licht und Temperaturvariationen. Vielmehr zeigten Enantiomere eine signifikante Varianz im Laufe des Experiments. Die enantiomerische Signatur wurde auch verwendet um zwischen „Chemotypen“ zu unterscheiden, was über die nicht-chirale chemische Kompositionsmethode hinausgeht. Unter 19 Quercus ilex L. Pflanzen, welche unter Standardbedingungen (30°C, 1000 PAR) beobachtet wurden, konnten 4 verschiedene „Chemotypes“ unterschieden werden. Die traditionelle Klassifikation zeigte nur zwei.

In der natürlichen Umgebung des borealen Walds wurden dynamische Küvetten für vier verschiedene Kiefer –„ Chemotypen“ und ein norwegische Fichte-„Chemotypen“ zur Untersuchung der primären Emissionen installiert. Diese wurden direkt mit atmosphärischen Messungen verglichen, welche über der

Baumkrone während der Sommerkampagne HUMPPA-COPEC 2010 durchgeführt wurden. Die Chiralität von α-Pinen der Kiefern wurde von seinem (+)-Enantiomer dominiert, während es sich umgekehrt bei der Fichte verhielt, die zusätzlich eine Lichtabhängigkeit vorwies.

Um saisonale Veränderungen der enantiomerischen Verteilung nachzuvollziehen, wurden Feldmessungen über einem spanischen Kiefernwald durchgeführt (DOMINO 2008). Hier konnte ein klarer Unterschied der Chiralität von Monoterpenemissionen festgestellt werden. Im Winter überstieg die Konzentration des Enantiomers (-)-α-Pinen die des (+)-α-Pinen nachts geringfügig, während tagsüber das Verhältnis ausgeglichen war. Proben des gleichen Walds während des folgenden Sommers zeigten insgesamt höhere Monoterpen Mischungsverhältnisse in der Atmosphäre, genauso wie einen klaren Überschuss an (-)-α-Pinen. Dies deutet auf eine starke Saisonalität der enantiomerischen Verhältnisse hin. Ein signifikanter Tagesgang in der Chiralität des α-Pinen konnte zudem in einem französischen Eichenwald und dem finnischen borealen Wald beobachtet werden. Während im borealen Wald (-)-α-Pinen gegenüber (+)-α-Pinen während des Tags zunahm und ein Maximum mit Licht- und Temperaturhöchstwerten erreichte, war die Tendenz im französischen Wald umgekehrt.

Für beide Feldmesskampagnen (DOMINO 2008 und HUMPPA-COPEC 2010) wurden zusätzlich Benzol, Toluol, Ethylbenzol und Xylol gemessen. Während der DOMINO Kampagne konnten die atmosphärischen Mischungsverhältnisse der Xylol Isomere (Meta- und Para-) sowie Ethylbenzol sehr gut mit Hilfe einer β-cyclodextrin Säule detektiert werden. Diese Substanzen halfen bei der Berechnung, wie lange die flüchtigen Kohlenwasserstoffe, welche aus dem Huelva Industriegebiet stammten, dem OH Radikal ausgesetzt wurden. Diese Ergebnisse wurden mit empirischen Abschätzungen der OH Konzentrationen, basierend auf JNO_2 Messungen, verglichen. Die Vor- und Nachteile beider Methoden werden hier diskutiert. Für die HUMPPA-COPEC Messkampagne konnten Benzol und Toluol Messungen den Einfluss der Emissionen russischer Waldbrände klar identifizieren.

Table of Contents

Chapter 1

Introduction

The troposphere, the lowermost region of the atmosphere, extends from the Earth's surface to 10-12 km. About 90% of the atmospheric mass is present in this layer. It is well mixed with 78% N_2, 21% O_2, 1% Ar, and 0.0.36% CO_2 with varying amount of water vapor dependent on temperature and altitude. At still lower mixing ratios the remaining compounds residing in the troposphere are the so called "trace gases" which include volatile organic compounds (VOCs). It has become increasingly apparent after the industrial revolution that human activities have changed the compositions of the troposphere with large amounts of emitted VOCs on both local and global scales, leading to increased ozone, increased temperature, and increased particle formation.

1.1 VOCs

Volatile organic compounds are known to be emitted from anthropogenic sources, soil, vegetation and ocean. They are organic chemicals that have high vapor pressures under standard conditions and to be found all around us as evidenced by the scents of gasoline, flowers, wine. They include hydrocarbons with only carbon and hydrogen (e.g. alkanes, alkenes, alkynes and aromatic compounds) as well as other elements such as oxygen and chlorine (e.g. ethers, alcohols and chlorofluorocarbons (CFCs)). They are important chemical species which can significantly affect the build-up and destruction of tropospheric ozone as well as the formation and growth of secondary aerosols and cloud condensation nuclei (FinlaysonPitts and Pitts, 1997). These compounds can impact human health directly, or indirectly after undergoing a complex series of atmospheric reaction cycles resulting in secondary pollutants such as peroxyacetyl nitrate (PAN), ozone (O_3) and aerosols (Williams, 2004). Moreover, they also play an important role in feedbacks inside the climate system contributing to the carbon cycle (Kulmala et al., 2004) and to land use (Lathiere et al., 2006; Purves et al., 2004).

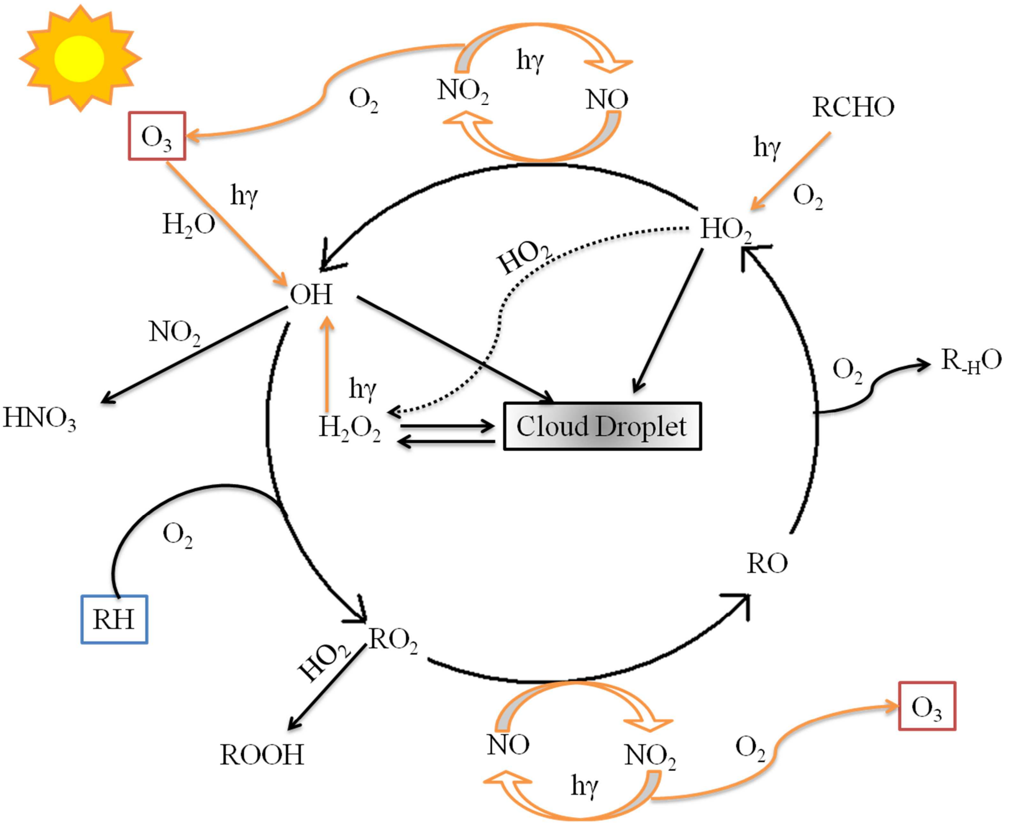


Fig. 1- 1 Schematic representation of the oxidation of saturated hydrocarbons, RH, during the daytime (adapted from Jenkin and Clemitshaw, 2000)

VOCs are emitted to the atmosphere from a variety of anthropogenic and biogenic sources with an emission estimated ca. 1300 Tg C •y^{-1} (Goldstein and Galbally, 2007). Although they are present at trace level in the troposphere, they have a great influence on the tropospheric oxidizing capacity which is determined by the total burden of O_3, hydroxyl radical (OH) and hydrogen peroxide (H_2O_2) (Thompson, 1992). Oxidative degradation of VOCs in the atmosphere is initiated by the reaction with OH radicals, NO_3 radicals, O_3, or direct photolysis depending on the structure of the VOC itself and the environmental conditions. Products resulting from these reaction processes are partially oxidized organic species and these can be viewed as an intermediate state between precursors and the ultimately gas phase fate of the oxidation carbon dioxide and water (Atkinson et al., 1994; Atkinson and Arey, 2003a). These intermediate oxidation products may be of low enough volatility that they will partition onto existing particulate matter, contributing significantly to fine particle mass as secondary organic aerosol formation and growth (Hallquist et al., 2009; Jacobson et al., 2000). Hydrocarbon oxidation (e.g. alkanes) is primarily initiated by the OH radical. These reaction mechanisms are complex but their essential feature is the radical chain carrying reactions between peroxy radicals (HO_2) and NO that regenerate OH and form NO_2. In the troposphere, The main route for OH formation in the atmosphere is the reaction of water vapor with atomic oxygen in the ^1D excited electronic state (O^1D) which is formed through the photolysis (λ<340 nm) of ozone:

$$O_3 + h\gamma = O(^1D) + O_2 \tag{1.1}$$

$$O(^1D) + H_2O = 2OH \tag{1.2}$$

Other minor processes forming OH are the photolysis of nitrous acid and ozonolysis of alkenes. The only significant formation route of O_3 in the troposphere is the photolysis of NO_2:

$$NO_2 + h\gamma = NO + O \tag{1.3}$$

$$O + O_2 + M = O_3 + M \tag{1.4}$$

The photolysis rate varies with latitude, altitude and season since it depends on the atmospheric path length of the incident sunlight. During the daytime, most of the photooxidation of VOC are initiated by OH, shown in Fig. 1-1 (Jenkin and Clemitshaw, 2000). The peroxy radicals formed perform a number of NO to NO_2 conversions, as they sequentially form alkoxy radicals and then further peroxy radicals depending on the structure. Each NO to NO_2 conversion leads to net ozone formation.

During the nighttime, in the absence of sunlight, the concentration of the OH radical is significantly suppressed while NO_3 which is readily photolysed can survive. Thus, the nitrate radical, NO_3, take over from OH as the dominant oxidant in the troposphere. Another important nocturnal sink for VOCs is O_3. The nocturnal chemistry of VOCs in troposphere is shown in Fig. 1-2 (based on Jenkin and Clemitshaw, 2000). The Tropospheric oxidation chemistry continues at night. However, this chemistry does not lead to ozone production but the opposite in fact, and it is important to produce the secondary pollutants as well. The main nighttime oxidant is thought to be the slow oxidation of NO_2 to NO_3 radical by O_3 and the equilibrium reaction of nitrogen pentoxide (N_2O_5) to NO_2 and NO_3. The NO_3 radical has somehow the range of reactivity to VOCs especially to the unsaturated ones such as isoprene and monoterpenes. The reactions between ozone and alkenes are also important when higher ozone level presents.

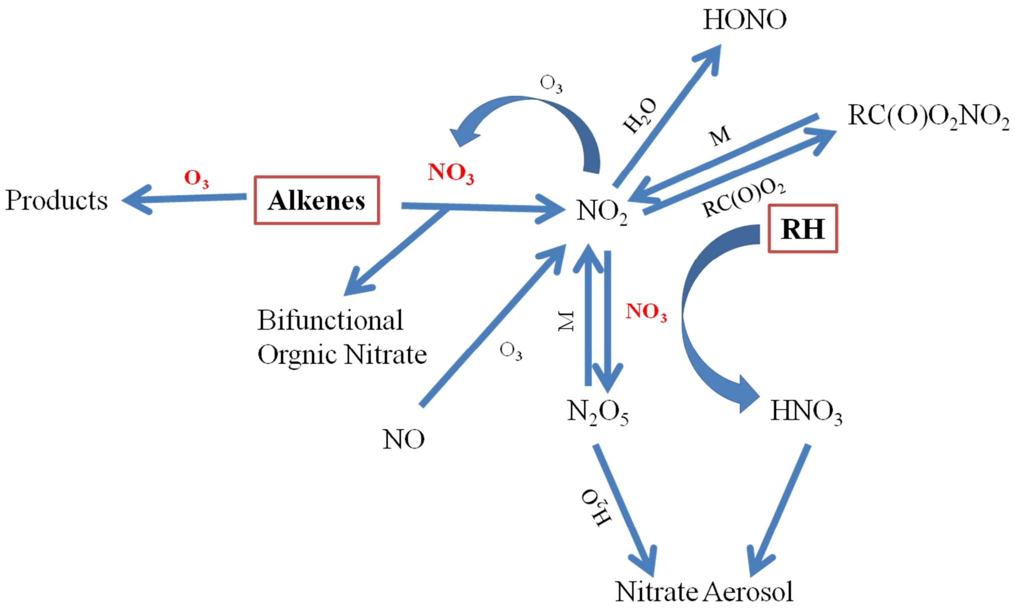


Fig. 1- 2 Schematic representation of the oxidation of saturated hydrocarbons, RH during the nighttime (based on Jenkin and Clemitshaw, 2000)

Although VOCs are removed from the atmosphere mainly through the reaction with OH, the reactions with O_3 and NO_3 also play an important role especially for those unsaturated compounds. The products from these reactions are less volatile and more susceptible to both wet (e.g. by rain) and dry removal. Thus, the specific lifetime (τ) of a VOC compound in the atmosphere depends on these physical and chemical processes. The chemical lifetime determined for how long the compound maintains its chemical identify after release (Holloway and Wayne, 2010). This can be expressed as the time needed for a chemical concentration reduced to 1/e times of its initial concentration (Finlayson-Pitts and Pitts, 1999). For a VOC compound (A), its chemical lifetime mainly depends on the reaction with OH, O_3 and NO_3:

$$\tau_A = \frac{1}{k_{OH}[OH]} + \frac{1}{k_{O_3}[O_3]} + \frac{1}{k_{NO_3}[NO_3]} \qquad (1.5)$$

Table 1-1 shows calculated lifetimes for selected anthropogenic and biogenic compounds which are the main focus of this thesis with respect to reaction with OH radical, NO_3 radical and O_3. The concentration of OH, O3 and NO3 used here are 0.08 ppt (2×10^{6} mol •cm^{-3}), 30 ppb (7×10^{11} mol •cm^{-3}) and 20 ppt (5×10^{8} mol •cm^{-3}). Generally the biogenic VOC have somewhat shorter lifetimes (minutes-hours) than the anthropogenic species (hours to days).

Table 1- 1 Reaction rate coefficients (Atkinson and Arey, 2003b) and estimated lifetimes for selected VOCs based on OH radicals (2×10^{6} mol •cm^{-3}), NO_3 radicals (5×10^{8} mol •cm^{-3}) and O_3 (7×10^{11} mol •cm^{-3}).

Species	$10^{12}\times k_{OH}$	$10^{17}\times k_{O3}$	k_{NO3}	τ_OH	τ_O_3	τ_NO_3
	(cm^3 ·mol^{-1} ·s^{-1})					
BTEX						
Benzene	1.22	$<1\times10^{-3}$	$<3\times10^{-17}$	4.7 d	+	>2 yr
Toluene	5.63	$<1\times10^{-3}$	7×10^{-17}	1.0 d	+	330.7 d
Ethylbenzene	7	$<1\times10^{-3}$	$<6\times10^{-16}$	0.8 d	+	>27.2 d
m-Xylene	23.1	$<1\times10^{-3}$	2.6×10^{-16}	6.0 h	+	62.8 d
p-Xylene	14.3	$<1\times10^{-3}$	5.6×10^{-16}	9.7 h	+	29.2 d
o-Xylene	13.6	$<1\times10^{-3}$	$<4.1\times10^{-16}$	10.2 h	+	>39.9 d
BVOCs						
Isoprene	100	1.27	7×10^{-13}	1.4 h	1.3 d	47.6 min
α-Pinene	52.3	8.4	6.16×10^{-12}	2.7 h	4.7 h	5.4 min
β-Pinene	74.3	1.5	2.51×10^{-12}	1.9 h	1.1 d	13.3 min
3-Carene	88	3.7	9.1×10^{-12}	1.6 h	10.7 h	3.7 min
Limonene	164	21	1.22×10^{-11}	50.8 min	1.9 h	2.7 min
Myrcene	215	47	1.1×10^{-11}	38.8 min	50.7min	3.0 min

+ The lifetime calculated from reaction with ozone was omitted here because of rather slow reaction rates

1.1.1 Anthropogenic VOCs

VOCs can be released to the atmosphere from a variety of human activities. Since the beginning of the industrial revolution human activities as a source of VOCs have become more and more important. Anthropogenic sources of VOCs dominate in the cities and the cities themselves have grown rapidly so that their emissions may also be significant on a regional scale. It is widely recognized that increases in economic development leads to photochemical air pollution (Lawrence et al., 2007) which results from increased emissions of NOx and VOCs (FinlaysonPitts and Pitts, 1997; Jacobson, 2002). The main sources of anthropogenic VOCs are vehicles, combustion of fossil fuel, industrial emissions, solvent use, and waste disposal (van Aardenne et al., 2001). It is estimated that every year the emission of anthropogenic VOCs are around 110-180 Tg carbons on a global scale (Piccot et al., 1992). Aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylenes (BTEX), halogenated compounds like CFCs, alkanes and alkenes are the main anthropogenic VOCs emitted into the atmosphere. In addition, an estimated 70~80 TgC come from biomass burning emissions (Andreae and Merlet, 2001; Ito and Penner, 2004; Wiedinmyer et al., 2011; Yokelson et al., 2008). This is characterized as an anthropogenic emission since most terrestrial fires are man-made.

BTEX compounds, which are mainly emitted from anthropogenic sources, are of great interest in urban and sub-urban studies because of their innate risk to human health (they are carcinogens) and their ozone forming potential (Durmusoglu et al., 2010). In urban areas, BTEX constitutes up to 60% of non-methane VOCs (Lee et al., 2002). By virtue of their hours-days lifetimes they may be transported a long distance from the sources and impact atmospheric chemistry during transportation. Note that the lifetimes of the BTEX compounds are subtly different, benzene reacting slowest with OH and the more substituted species reacting faster. The differences in reaction rate are exploited in chapter 3 of this thesis. *m*- and *p*-Xylene occurs naturally in petroleum. *o*-Xylene is found in coal tar, petroleum, forest-fire smoke-emissions and plant volatiles (Howard, 1990). Characteristic emission ratios of BTEX can be useful in identifying emission sources, age of air masses or characterizing the health impact (Baroja et al., 2005; Choi et al., 2009; Dutta et al., 2009; Ho et al., 2004; Hoque et al., 2008). For example in freshly polluted urban air toluene exceeds benzene (typically it is at a ratio of two to one) (Brocco et al., 1997; Perry and Gee, 1995; Wang et al., 2002). In biomass burning, however, benzene exceeds toluene by a ratio of two to one (Blake et al., 1994).

1.1.2 Terrestrial Biogenic VOCs

Terrestrial vegetation plays an important role as a source (ca. 1 $Pg \cdot yr^{-1}$) of a variety of reactive volatile organic compounds (Warneck, 1999). These are used by plants to transmit specific messages through the air and to attract or repel interacting organisms. Biogenic VOCs are a very heterogeneous group of compounds produced in different plant organs. Plants may use these VOCs to attract pollinators, fruit dispersers and parasitoids of herbivores, to repel herbivores, warn neighboring plants or neighboring parts of its own about attacks by herbivores and pathogens, and protect themselves from environmental stresses (Baldwin et al., 2006; Degenhardt and Gershenzon, 2000; Felton and Tumlinson, 2008; Gershenzon and Dudareva, 2007; Hopke et al., 1994;

Loreto et al., 1998; van Dam et al., 2010). Ambient concentrations of non-methane BVOCs typically range from a few pptv to several ppb (Kesselmeier and Staudt, 1999 and references therein). It has been estimated that circa 1150Tg carbon is emitted to the atmosphere worldwide every year from vegetation (Guenther et al., 1995), approximately, six times larger than the sum of anthropogenic VOCs emissions including fossil fuel and biomass burning. Plants produce a large variety of VOCs with diverse chemical structures, from relatively simple hydrocarbons, alcohols, carbonyls and acids to increasingly large, multifunctional and complex structures such as hexenal and the monoterpene family (see their structures in Fig.1-3).

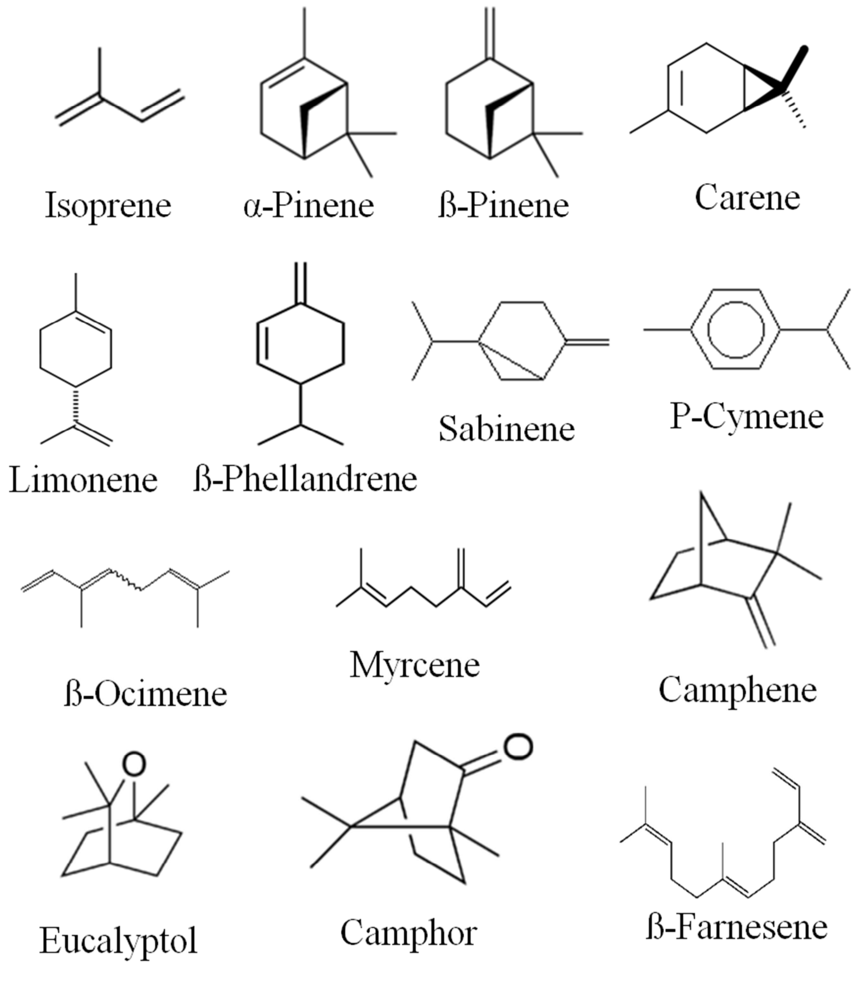


Fig. 1- 3 Skeletal structures of the selected BVOCs that have been identified in the troposphere, including isoprene, monoterpenes and sesqueterpenes

Among BVOCs, volatile isoprenoids, isoprene and methylbutenol (C5), monoterpenes (C10) and sesquiterpenes (C15), deserve special attention because of high volatility, reactivity in the atmosphere and their large contribution, often more than 90%, to total plant emissions (Aaltonen et al., 2011; Staudt and Lhoutellier, 2011). Isoprene and monoterpenes represent a large part of the NMVOC flux with global flux estimates between 454 and 601 $Tg{\cdot}C{\cdot}y^{-1}$ and between 32 and 127 $Tg{\cdot}C{\cdot}y^{-1}$, respectively (Arneth et al., 2008). Although there are large uncertainties in the magnitude of emission rates of individual and total BVOCs, in general, isoprene and monoterpenes, whose carbon skeletons are composed of characteristic C5 and C10 units (Mcgarvey and Croteau, 1995), are thought to be the dominant compounds and are the most commonly measured. These compounds consist of at least one olefinic double bonds, and structures of some selected monoterpenes and isoprene are given in Fig.1-3. These doubly bonded chemicals are much more reactive with atmospheric oxidizing agents (OH, NO_3, and O_3) compared to simple anthropogenic alkane-type hydrocarbons VOCs (see table 1-1).

Plants have the metabolic potential to produce and emit a large variety of VOCs. BVOCs are produced in various tissues and compartments above and below ground of the plant. Many have enough vapor pressure to be released into the atmosphere in significant amounts. Moreover, different plant families emit different subsets of these VOCs. In plants, all terpenoids are derived from geranyl diphosphate (GDP) which is synthesized by a common C5 precursor, isopentenyl pyrophosphate (IPP) and its allelic isomer dimethylallyl diphosphate (DMAPP) (Silver and Fall, 1991; Wise, 1999). Thus, the IPP and DMAPP are the central intermediate in the biosynthesis of isoprenoids and sometimes called ‘active isoprene’. There are two different routes that lead to IPP synthesis have been identified so far: (1) mevalonate (MVA) pathway according to the characteristic intermediate compound mevalonic acid in the cytosol (Hampel et al., 2007; Mcgarvey and Croteau, 1995; Meyer et al., 2003; Sanadze, 2004); and (2) methylerythritol phosphate (MEP) pathways in the plastids via the 1-deoxy-D-xylulose-5-phosphate (DXP) (Cassera et al., 2004; Eisenreich et al., 2004; Hampel et al., 2006; Meyer et al., 2003; Rohmer, 1999, 2003; Seemann et al., 2006). IPP can be reversibly transformed to its isomer DMAPP, which is the substrate for isoprene syntheses. Principally, both pathways for IPP synthesis require phosphorylation energy (ATP) and reduction power (NADPH, NADH) plus a carbon substrate like pyruvate, glyceraldehydes 3-phosphate, or acetate. A cross-talk between these two pathways has also been reported (Hampel et al., 2005). The chloroplastic enzyme produces isoprene by cleaving pyrophosphate (Monson et al., 1992; Sharkey and Yeh, 2001; Silver and Fall, 1991; Wildermuth and Fall, 1998). Many studies have established that isoprene is formed enzymatically from DMAPP in chloroplasts

(Fig.1-4 A). However, there were also studies showing that a small amount of isoprene may be formed by a nonenzymetic decomposition DMAPP (Fall and Wildermuth, 1998). The biosynthesis of several monoterpenes has been also worked out in detail (McCaskill and Croteau, 1995). It is generally accepted that the production of monoterpenes takes place within the plastids (Degenhardt et al., 2009; Dewick, 2002; Hampel et al., 2005; Hampel et al., 2007; McCaskill and Croteau, 1998; Mcgarvey and Croteau, 1995). By adding another IPP unit to DMAPP, the monoterpene geranylpyrophosphate (GPP) is formed, which is the starting unit for other monoterpenes. Based on the activities of different monoterpene cyclases, different types of monoterpenes will be synthesized (Croteau et al., 1988; Croteau et al., 1994; Satterwhite et al., 1985). It is also known that in many plants the initial monoterpene synthase products are converted to oxygenated monoterpenes, such as alcohols.

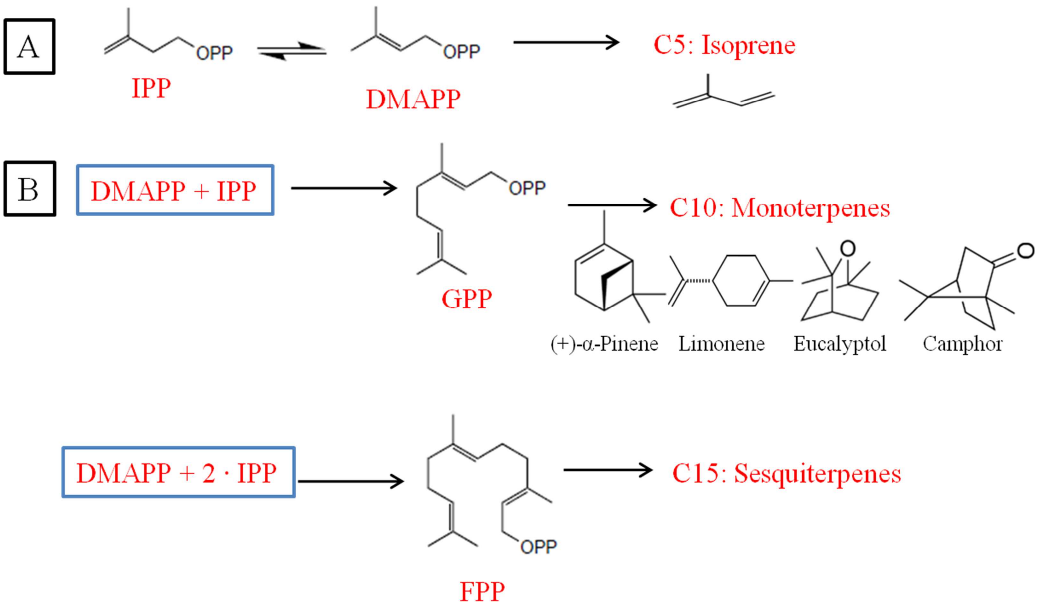


Fig. 1- 4 Overview of the terpenes biosynthesis in plants (adapted from Mahmoud and Croteau 2002). Abbreviations: IPP-isopentenyl pyrophosphate, DMAPP-dimethylallyl diphosphate, GPP-geranyl diphosphate, FPP-farnesyl diphosphate

Isoprene-emission occurs in many plants, but it is more often found in woody plant species than in herbs and crops (Harley et al., 1999). It is generally assumed that tropical forests are the main source of the global isoprene, with intermediate emissions from temperate forests, and low emissions from boreal forests, although the latter is an important source of monoterpenes (Guenther et al., 2006; Harley et al., 2004). Unlike isoprene which is rapidly lost by volatilization, monoterpenes are known to constitute the main fraction of ‘terpenic oils’ or ‘essential oils’ that are produced and stored in plant secretory organs like glandular trichomes and resin ducts. Usually, monoterpene-storing plants are also found to be monoterpene emitters; and for some coniferous species, a correlation has been observed between leaf concentration and leaf emission (Lerdau et al., 1994; Simon et al., 1994). In contrast, some European oak species emit high amounts of monoterpenes, but do not store them (Hansen and Seufert, 2003; Niinemets et al., 2002; Staudt and Seufert, 1995). This variety is reflected in the dependence of emission rates on a number of physicochemical, physiological and environmental factors, including radiation, temperature, phenology, water and nutrient availability, enzyme activity, plant species and physical structure, solubility and vapor pressure (Kesselmeier and Staudt, 1999; Laothawornkitkul et al., 2009; Niinemets et al., 2004).

In the past few decades, numerous studies have been conducted to quantify BVOC emission rates at leaf, plant and canopy levels in order to understand their temporal and spatial variations. It is recognized that light and temperature are the most important environmental drivers of isoprene and monoterpene emissions (Guenther et al., 2006; Laothawornkitkul et al., 2009; Niinemets et al., 2010a). Generally, isoprene emission responds to light following a rectangular hyperbola similar to that of photosynthesis, while its response to temperature resembles an Arrhenius function with an exponential increase at low temperatures, a temperature optimum typically lying around 40°C and a rapid decline at higher temperatures consistent with enzymatic denaturalization. In contrast, monoterpenes emissions from the storage pool show no clear responses to light variations and increase exponentially with temperature throughout the whole tested temperature ranges.

These findings have been used to develop leaf emission models and up-scaling procedures that estimate regional and global budgets of BVOC fluxes. The most frequently used modeling approach is that proposed by Guenther et al. (1995 and 2006) due to its robustness and simplicity. Various models exist to describe the emissions of VOCs from terrestrial vegetation scales (Grote and Niinemets, 2008 for a recent review). These models are based on the hypothesis that emissions of stored isoprenoids mainly result from diffusion processes out of storage organs independent of physiological processes, whereas the emissions of non-stored isoprenoids are essentially controlled by the rate of biosynthesis, where the light response would reflect the dependence of biosynthesis to primary substrates coming predominantly from photosynthetic processes, and the temperature response of the activity of rate-limiting enzymes, such as the isoprene synthesis within the BVOC biosynthesis pathway. Numerous studies of light and temperature responses of BVOC emissions have been performed on tens of different plant species (Penuelas and Staudt, 2010) to be better understand the controls over emissions. However, our understanding of the variability and correctness of these responses is still insufficient especially for those BVOCs other than isoprene (Niinemets et al., 2010). Even for emissions of isoprene, by far the best studied BVOC, the intra and inter-specific variability of the light and temperature responses is still far from being completely understood (Niinemets et al., 2010). Other environmental factors such as the effect of seasonality, the CO_2 level, the ozone level and drought also have been studied recently (Blanch et al., 2007; Curci et al., 2009; McKinney et al., 2011; Penuelas and Staudt, 2010; Staudt et al., 2002) and incorporated into emission models (Arneth et al., 2007; Grote et al., 2009; Keenan et al., 2009). In the past decades, great effort has been made to improve regional and global models which estimate the source strength of VOC (Grote and Niinemets, 2008; Guenther et al., 2006; Niinemets et al., 2002; Schurgers et al., 2009; Zimmer et al., 2000).

1.2 Chirality

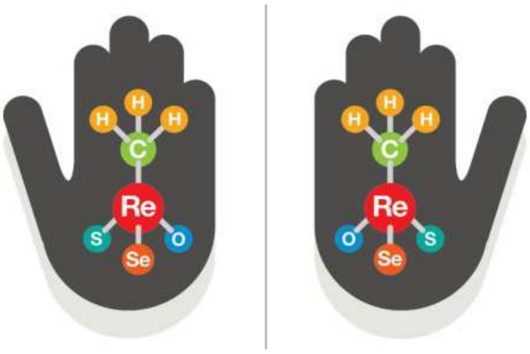


Fig. 1- 5 A left hand and a right hand are mirror images (Source: Thomas Porostocky / Nature News)

A chiral object is one that lacks an internal plane of symmetry and thus has a non-superposable mirror image. For instance, a left hand is a non-superposable mirror image of the right hand; no matter how the two hands are oriented, it is impossible for all the major features of both hands to coincide (see, Fig.1-5). Molecules may be chiral too. The two mirror image forms of a chiral molecule, called enantiomers, have identical physical and chemical properties. The feature that is most often the cause of chirality in molecules is the presence of an asymmetric carbon atom. Fig. 1-6 shows some of the enantiomeric monoterpenes which are also the main focus of this thesis. Despite being physically and chemically so similar on a biological level these species can elicit very different responses in plants and insects (Norin, 1996).

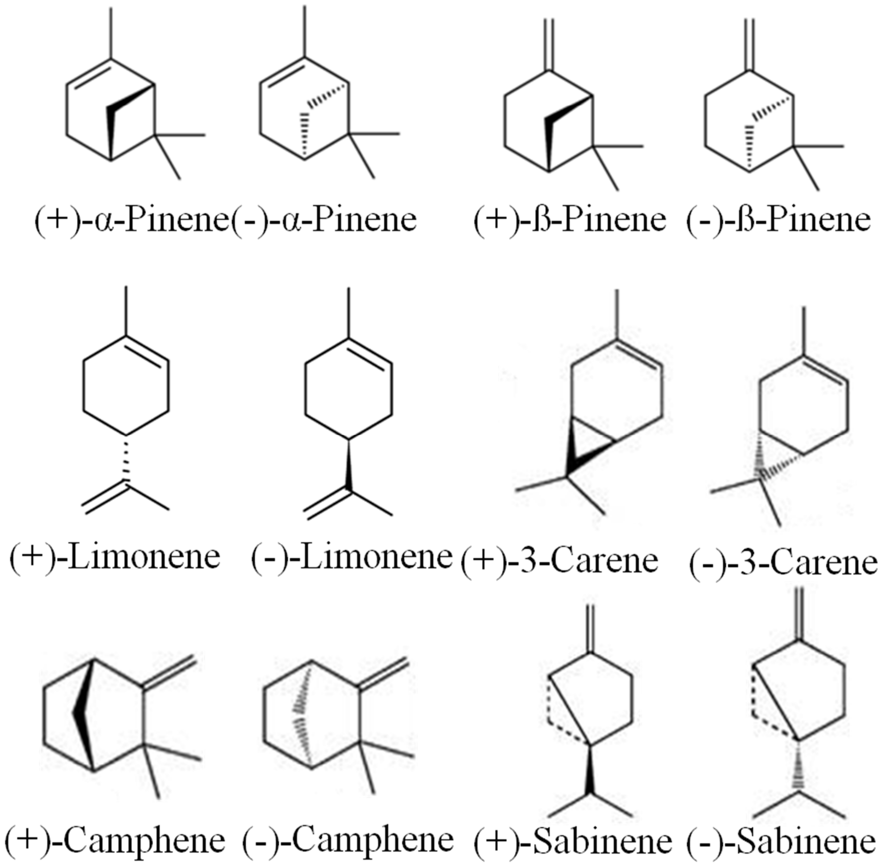


Fig. 1- 6 Mirror images of selected monoterpenes presented in the troposphere

In 1848, Louis Pasteur conducted an experiment in which he produced crystals of the sodium ammonium salt. The crystals were of two kinds, known as "+" and "-" forms, which were mirror images of one another. Pasteur shone polarised light through each solution, and found that the two solutions had equal but opposite optical activity. That is, the angle of polarization was rotated in each case by the same amount, but in opposite directions. If polarized light was shone through the original solution from which the crystals had been formed there was no rotation, the solution was optically inactive. An optical enantiomer can be named by the spatial configuration of its atoms. The D/L system does this by relating the molecule to glyceraldehyde. Glyceraldehyde is chiral itself, and its two isomers are labeled D and L. The system says whether the compound's stereochemistry is related to that of the dextrorotatory or levorotatory enantiomer of glyceraldehydes - the dextrorotatory isomer of glyceraldehyde is, in fact, the D- isomer. The definition is based on the interaction of the chemical with plane polarized light. Interestingly, all the amino acids in our body exist in one enantiomeric configuration, the L form, while the sugars that form the helical backbone of all living DNA and RNA are in the D form. The origin of homochirality for life on Earth is not currently understood, yet numerous theories have been proposed (Carroll, 2009).

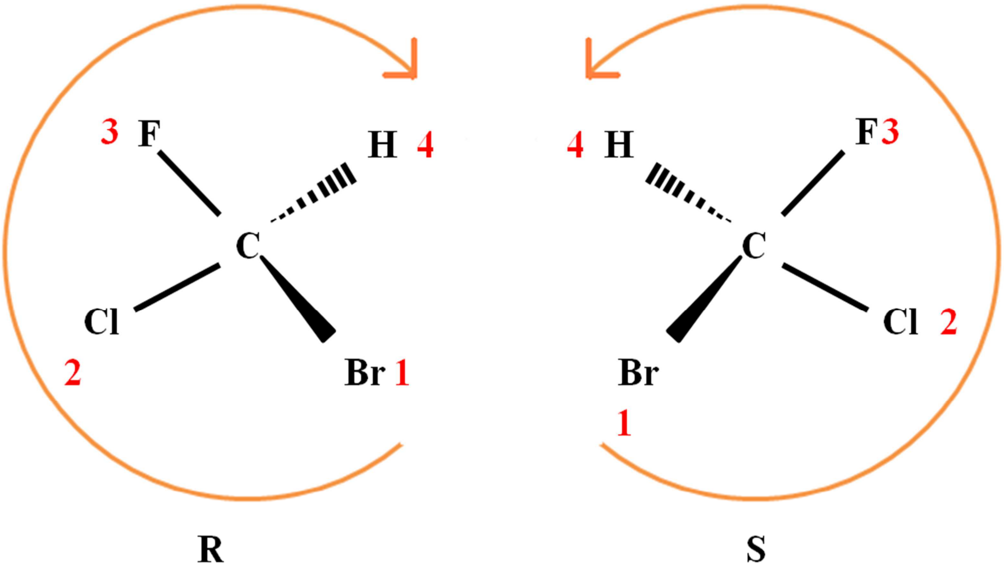


Fig. 1- 7 Tetrahedral chiral nomenclature: (R)-bromochlorofluoromethane and (S)-bromochlorofluoromethane

Another way to describe chiral structures is the R/S system, often called the CIP system, which was devised by Robert S. Cahn, Christopher Ingold, and Vladimir Prelog. In the CIP system, the chiral atom is based on an ordering of the four substituents attached. Taking bromochlorofluoromethane as an example (see Fig.1-7), the priority number is determined by the atomic number (the highest atomatic number equals to the highest priority, i.e.,1), the lowest one (4) is aligned to the rear of the structure and determining whether the priority order of the other three substituents shows a clockwise (R) or counterclockwise (S). The "+" and "-" forms of chiral molecules are known as dextrorotatory ("+" form) and levorotatory ("-" form). Dextrorotatory molecules rotate polarised light in a clockwise direction. In the case of levorotatory molecules, the direction of rotation is anti-clockwise.

Numerous monoterpenes and sesquiterpenes occur in two enantiomeric forms, for example α-pinene exists as (+)-α-pinene and (−)-α-pinene, see Fig.1-6. Since biogenic VOCs by definition are emitted from living organisms, one may expect some degree of enantiomeric expression beyond racemic mixtures to occur for the chiral compound emissions. Most atmospheric chemistry studies of monoterpenes and sesquiterpenes to date have not resolved the enantiomeric forms and report simply the sum e.g. as α-pinene (e.g Guenther et al. 1995). In the past this was because reliable separation methods such as cyclodextrin columns with gas chromatography were not readily available. Furthermore, since the rates of reaction of the enantiomers with the primary atmospheric oxidants OH, O_3 and NO_3 are identical in the gas phase, resolving the enantiomers represented unnecessary complication for both the measurement and ensuing model analysis. However, over the past 10 years more chiral studies have begun to emerge, providing captivating new information. Pioneering work on tree and plant emissions showed very distinct enantiomeric fingerprints in many trees so that information on vegetation abundance and influence can be gained from air measurements of enantiomers (Yassaa et al., 2000). Moreover, clear changes in enantiomeric ratios occur when trees are subjected to mechanical stress, again allowing processes upwind to be deduced (Eerdekens et al., 2009; Yassaa and Williams, 2007). Enantiomeric ratio measurements may also help improve the development of emission algorithms for monoterpenes for which light and temperature induce emissions via different mechanisms. Recently reported regiospecific enantiomeric ratios (Williams et al., 2007), enantiomeric signature constraints of aerosol formation from isoprene (Noziere et al., 2011), possible heterogeneous enantiomeric enrichment mechanisms on aerosols (Ebben et al., 2011; Stokes et al., 2009) and new marine sources of monoterpenes (Yassaa et al., 2008) provide exciting new information and questions for this emerging field. Most importantly though, the enantiomeric molecules emitted by vegetation represent an important nexus between plants, insects and the atmosphere. While enantiomers may be indistinguishable in their physical properties they often exhibit strong differences in biological activity, often eliciting very different responses in the detecting biota (Croteau, 1987). For example, when we smell the terpenoid enantiomer S-(+)-carvone we perceive the smell of caraway seeds whereas to us the R-(-)-carvone smells of spearmint. The enantiomers are used in nature as a “chemical language” for plant-to-plant and plant-to-insect communication whereby the atmosphere is used to transmit and to degrade the signals. The scent of a flower contains specific enantiomers that will attract pollinators but the atmosphere must rapidly oxidize or disperse such species to create concentration gradients that insects may follow. Certainly there are now strong reasons for examining chiral compounds especially to elucidate links between atmosphere and biosphere and it is hoped that this thesis will serve as a useful primer and guide to those entering this field.

1.3 Analytical techniques

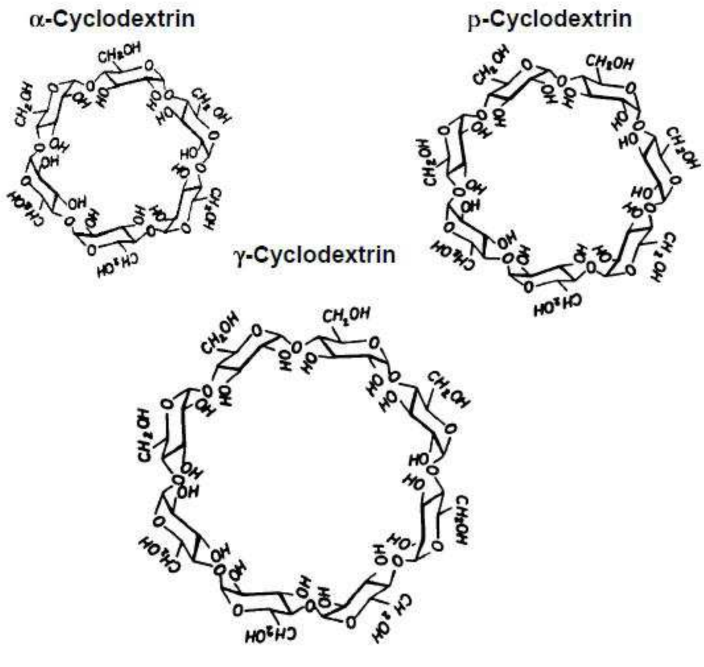


Fig. 1- 8 Chemical structure of the three main types of cyclodextrins (α-,ß-, and γ-cyclodextrins)

To study the characterization of the biogenic and anthropogenic VOCs in the ambient air, a range of different techniques such as differential optical absorption spectroscopy (DOAS), UV, Gas Chromatography Mass Spectrometry (GC-MS) and Proton

Transfer Reaction Mass Spectrometry (PTR-MS) have been employed by different groups (Warneck and Williams, 2012). Some techniques have the advantage of speed (e.g. PTR-MS, DOAS), making rapid, perhaps on-line measurements. In other techniques speed is sacrificed for greater specificity, accuracy and precision. In order to measure enantiomers of terpenes individually they must first be separated. Since the physical properties of the enantiomers are for the most part identical this appears to present a problem to the interested atmospheric chemist. Such measurements can, however, be made reliably using capillary gas chromatography.

Capillary gas chromatography is a simple, fast, accurate, sensitive, and reproducible technique for separating stereo and positional isomers of compounds that can be vaporized without decomposition. Chiral separations have been performed by gas chromatography for nearly three decades (Hinze, 1981; Koscielski et al., 1983; Mraz et al., 1984; Smolkovakeulemansova, 1982; Tanaka et al., 1983). First generation chiral GC columns were based on nonbonded and bonded amino acid moieties; the latest capillary GC columns are based on functionalized cyclodextrins. Cyclodextrins are cyclic oligosaccharides containing from six to twelve D-(+)-glucopyranose units bonded through α-(1, 4) linkages. They are produced by the action of Bacillus macerans amylase or cyclodextrin transglycosylase on starch. The latter enzyme can be made to produce cyclodextrins of specific sizes according to reaction conditions. Three sizes are commercially available alpha, beta and gamma corresponding to 6, 7 and 8 glucopyranose units respectively, see Fig. 1-9. The cyclodextrin molecule forms a truncated conical cavity the diameter of which depends on the number of glucopyranose units. This method relies on the chirality of the column to retain the two enantiomers to differing extents.

In this work, a ß-cyclodextrins column (30 m, 0.256 mm I.D., 0.25 µm film; J&W Scientific, CA, USA) has been used for the separation of enantiomeric and non-enantiomeric monoterpenes, xylene isomers as well as other VOCs. Column temperature was initially held for 5 min at 40 ºC and raised to 120 ºC at 1.5 $ºC·min^{-1}$ then to 200 ºC at a rate of 30 $ºC·min^{-1}$.

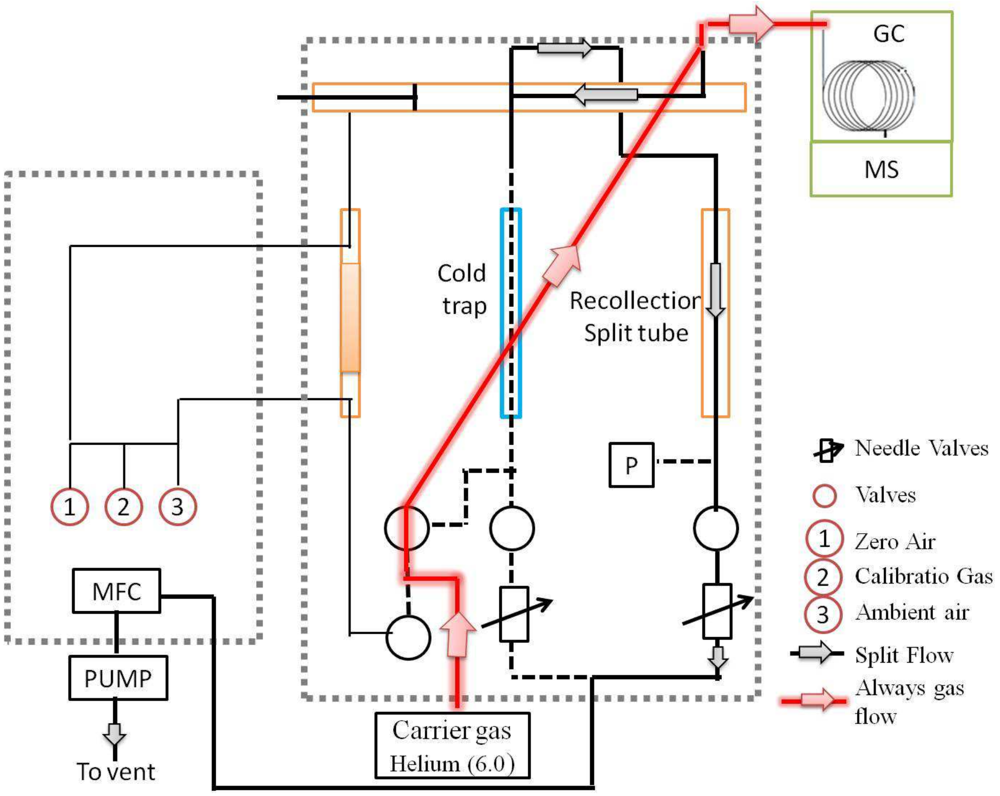


Fig. 1- 9 Thermal desorber with GC-MS for in situ online sampling

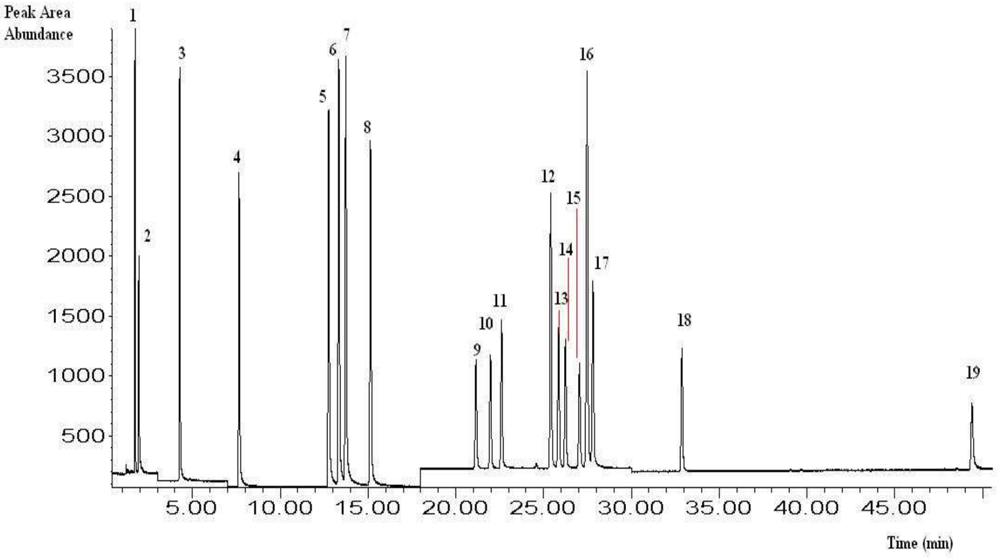


Fig. 1- 10 A chromatogram of the calibration gas (1: isoprenen, 2: acetone, 3: benzene, 4: toluene, 5: p-xylene, 6: m-xylene, 7: ethylbenzene, 8: o-xylene, 9: (-)-α-pinene, 10: (+)-α-pinene, 11: myrcene, 12: Δ3-carene, 13: (+)-β-pinene, 14: (-)-β-pinene, 15: ocimene, 16: (-)-limonene+p-cymene, 17: (+)-limonene, 18: eucalyptol, 19: camphor)

Both online and offline measurement technique were employed in this work. For on-line sampling the system consisted of a flow controller and a commercial thermal desorber (Markes International, Pontyclun, UK connected to a gas chromatograph (GC 6890, Agilent, Wilmington, CA, USA), equipped with a Mass Selective Detector (MS 5973 inert) from the same company. A more detailed setup for the online measurement is shown in Fig.1-9. Ambient VOCs were concentrated directly on the cold, adsorbent filled trap kept at 10 ºC of the thermal desorber by a membrane pump, which drew the sample air (about 2 L), through a Teflon manifold connection to the main sample line. The cold trap was 2 mm in diameter and filled by a 60 mm long bed of sorbent (Tenax TA and Carbograph I) supported by quartz wool. The cold trap was then heated to 200 ºC rapidly and then held there for 5 minutes while sample was transferred to the GC column. For offline measurements, adsorbent filled cartridges (Carbograph I/II or Tenax and carbograph) were used for this study. The cartridges were cleaned by purging with Heluim 6.0 for 2 h at 350°C and 30 min at 380°C prior to use. A sampling flow rate of 100 - 200 ml· min^{-1} was maintained for between 5-20 minutes to ensure a sampled volume of between 1-2 L. Directly before analysis, cartridges were pre-purged for 5 min with Helium to reduce the water content and were then thermally desorbed by flushing the heated tubes at 200°C for 10 min. The desorbed VOCs were cryogenically trapped at 10°C in the cold trap. From this point on the same GC-MS method was used as the on-line method described above.

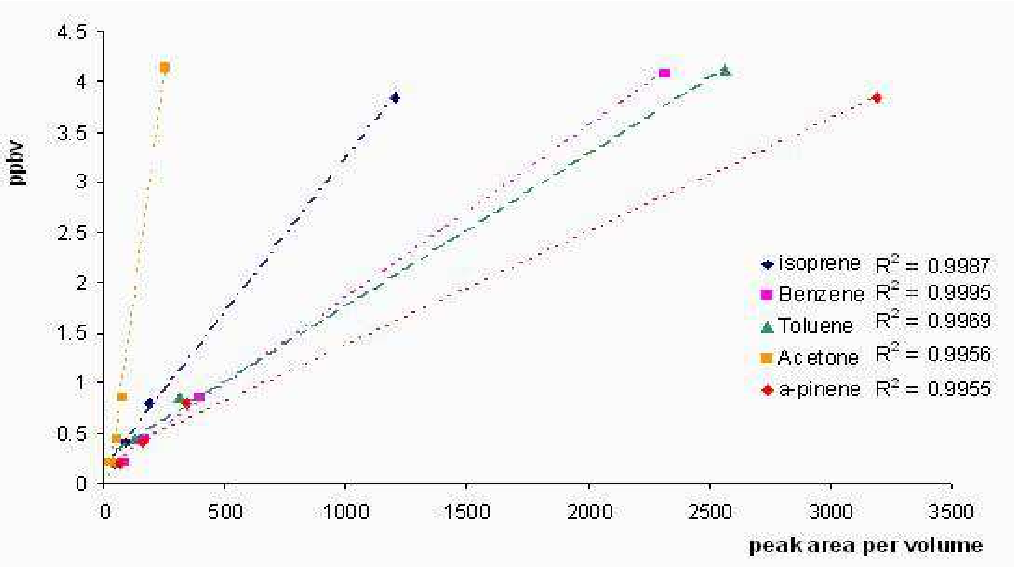


Fig. 1- 11 calibration curve of selected compounds (isoprene, benzene, toluene, acetone and α-pinene)

Table 1- 2 Overview of the measured compounds (note that on some occasions Δ3-carene and (+)-β-pinene were found co-eluted from the column. Since they have similar fragmentation it is impossible to calculate their ambient mixing ratios)

Compounds	Retention Time (min)	Precision (%)	Uncertainty (%)
Isoprene	1.724	10	11.2
Acetone	1.939	6.9	8.6
Benzene	4.273	8.3	9.7
Toluene	7.654	7.9	9.3
p-Xylene	12.757	6.6	8.2
m-Xylene	13.334	6.3	8
Ethylbenzene	13.729	6.6	8.3
o-Xylene	15.14	6.2	8
(-)-a-Pinene	21.146	9.5	10.7
(+)-a-Pinene	21.973	12.6	13.5
Myrcene	22.607	13.5	14.4
Δ3-Carene	25.404	17.7	18.4
(+)-b-Pinene	25.851	16.6	17.3
(-)-β-Pinene	26.237	18	18.7
Ocimene	27.05	19.3	19.9
(-)-Limonene	27.472	18.6	19.2
p-Cymene	27.477	18.1	18.7
(+)-Limonene	27.81	18.6	19.3
Eucalyptol	32.874	14.1	15
(-)/(+)-Camphor	49.39	33.5	33.9

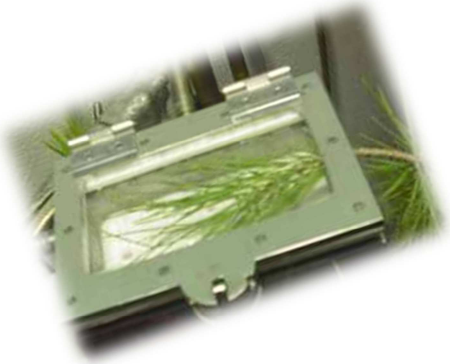
Blanks were conducted by flowing helium 6.0 (Messer-Griesheim, Germany) onto the cold trap or cartridges under the same conditions as for ambient air. In general, blanks were taken at least twice (the beginning and end of the measurements) and showed no high levels of the compounds discussed. Calibration was performed every 6-7 samples using prefilled compressed air for the first two years (2008 - May, 2009) and later using a commercial gravimetrically prepared standard containing approximately 2 ppb terpenes and BTEX respectively (National Physical Laboratory (NPL), Teddington Middlesex, UK). A typical chromatogram of the working standard is shown in Fig.1-10. The self-made working standard was prepared by filling an aluminum cylinder with ambient vegetation influenced air using a three-stage oil-free piston compressor (RIX Industry, Benicai CA, USA). The working cylinder was calibrated relative to a commercial primary standard (Apel-Riemer Environmental) containing 500ppb of the measured compounds (including isoprene, benzene, toluene, α-pinene and acetone). Note all monoterpenes were then calibrated as α-pinene. Laboratory multipoint calibrations for all reported species were completed prior to the field campaign and revealed a good linear dependency of peak area to the respective compound concentration (Fig. 1-11). Inlet line loss was tested by introducing different mixing ratios of the diluted calibration gas directly to the inlet line under the same conditions as ambient air. No significant loss during the sample collection was observed. Table 2 shows the retention time, precision and overall uncertainty of the selected BVOCs and BTEX which are the main focus of this thesis. The overall uncertainty was calculated based on the calibration standard (5%) and the precision of the chemical.

1.4 Summary

Within the introductory sections above, it has been described how both anthropogenic and biogenic VOCs play an important role in the chemistry of the troposphere and biogeochemistry. They may affect the tropospheric oxidant capacity from the local to the global scale by reacting with OH and O_3 although they are present only at relatively low concentrations (pmol/mol-nmol/mol or pptv-ppbv). Their source and emission strength as well as the enantiomeric monoterpenes and the measurement technique are described in detail in chapter1. From this start point this thesis explores several hitherto uninvestigated yet obvious questions to an atmospheric chemist interested in the potential of enantiomeric VOC to illuminate emission, transport or photochemical processes. The first key question to be addressed is whether the enantiomeric characteristics of the emission change predictably as a function of temperature and light. Chapter 2 shows the laboratory study of leaf emission as a function of temperature and light for three markedly different species. This is the first time such enantiomerically specific emissions have been studies in-vivo. A second question is whether the enantiomeric emission characteristics of a forest changes seasonally. This is addressed in Chapter 3 which presents the ambient measurement campaign (DOMINO, 2008) over a Spanish stone pine forest during winter time and in summer time. In Chapter 4 of this thesis the question of whether the enantiomeric leaf emissions and the ambient concentrations of these compounds are consistent during field measurements. The work in chapters 2 and 4 have both revealed the presence of numerous chemotypes of tree species monitored, uncovering unexpected complexity in the ecological system. The observations made in chapter 4 were made over a Boreal forest in Southern Finland, the HUMPPA-COPEC campaign, in the summer of 2010. This permitted a comparison with the enantiomeric monoterpene signatures measured some 5 years previously, and thereby to assess the consistency of the regional-specific nature of the enantiomeric signatures. Chapter 5 summarizes the major findings of this work and points out direction for potential research in the future.

Chapter 2

Laboratory determinations of the response of enantiomeric monoterpenes to temperature and light



2.1 Introduction

The main driving variables for the emission of biogenic VOCs are photosynthetically active radiation (PAR) and temperature which form the basis of most empirically derived emission models (Arneth et al., 2008; Grote and Niinemets, 2008; Guenther et al., 2006). However, other environmental factors such as the effect of seasonality, the CO_2 level, the ozone level and drought also have been studied (Blanch et al., 2007; Curci et al., 2009; McKinney et al., 2011; Penuelas and Staudt, 2010; Staudt et al., 2000; Staudt et al., 2002) and incorporated into emission models recently (Arneth et al., 2007; Grote et al., 2009; Keenan et al., 2009). In the past decades, great efforts have been made to improve regional and global models which estimate the source strength of VOC (Grote and Niinemets, 2008; Guenther et al., 2006; Niinemets et al., 2002; Schurgers et al., 2009; Zimmer et al., 2000). While there is a generally accepted emission algorithm for isoprene, which has been established to be proportional to both temperature and light (Guenther et al., 1995; Guenther et al., 2006), for the monoterpenes the situation is less clear – with some monoterpene emitters responding to temperature, and others to both light and temperature(Fuentes et al., 2000). In some species of plants, such as conifers, monoterpenes are synthesized and stored in secretory organs, such as the resin ducts within the leaves of conifers (Grote and Niinemets, 2008). In this case the emission rate of the monoterpene to the atmosphere is observed to be proportional to ambient temperature for the emissions rely on vaporization and diffusion from these extensive storage pools. In other species, it appears that the synthesis of the monoterpenes in the plant is instantaneous and the emission occurs (in similar fashion to isoprene) when light is present (Guenther et al., 1993; Kesselmeier and Staudt, 1999; Loreto et al., 2001).

Many of the monoterpenes considered in present atmospheric studies and models exist in two distinct forms that are mirror images called enantiomers. Typically they are measured and modeled together as one substance in ambient atmosphere studies as they react at the same rates with ozone and OH. However, for the biosphere (insect and plants) the two enantiomers are very different distinct molecules which may elicit opposite responses in pollinators and predators alike (Rostelien et al., 2005; Tooker and Hanks, 2004). Indeed, despite having the same mass and physical properties, enantiomers of the same compound may have different tastes or odors even in humans, and in plants the enantiomers may behave differently as plant growth regulators, insect pheromones, and enzyme substrates (Mori, 1998). If so, it might be advantageous to the plant to be able to alter the enantiomeric ratios it emits in order to communicate, via the atmosphere, to predators, pollinators and progeny. This implies the presence of an enantiomeric specific production in plants. Indeed several biochemical studies have shown that monoterpene producing enzymes (i.e. monoterpene synthases) are enantiomer specific (Martin et al., 2004) . Enzymes producing a similar blend of terpenes but with distinct chirality can co-exist in plants and may be subject to different environmental controls (Faldt et al., 2006). This implies the presence of more than one underlying mechanism in their production and this unresolved mechanistic complexity may help to explain the current difficulties encountered in establishing a reliable empirical monoterpene emission algorithm. The notion of enantiomerically selective emission is supported by previous work in which it was observed that remarkably distinct regional enantiomeric distributions exist for the generally most abundant monoterpene alpha pinene. Over Tropical it was observed that (-)-α-pinene predominated over (+)-α-pinene whereas over Boreal forests the reverse was true (Williams et al., 2007). Also in wounding experiments, plants have been seen to emit an enantiomerically distinctive response, a kind of “chemical scream” (Yassaa and Williams, 2007).

In this study we examine enantiomeric monoterpene emissions from several plants as a function of temperature and light under controlled laboratory conditions. In particular, focus is set on α-pinene whose enantiomeric ratios have been most commonly reported in field studies (Williams et al., 2007; Yassaa and Williams, 2005, 2007). The enantiomeric response will be examined with a view to explore the metabolic origins of monoterpenes. As mentioned above there are two possible pools of monoterpenes synthesized in the plant (Loreto and Schnitzler, 2010): (1) synthesis without storage in the chloroplasts of the green tissues; (2) synthesis in plastids of glandular organs (trichomes, resin ducts) with storage. Monoterpenes are synthesized from glyceraldehyde-3-phosphate and pyruvate via the 1- deoxy-D-xylulose-5-phosphate (DXP) pathway, which yields isopentenyl diphosphate (IPP, C5) and its isomer dimethylallyl diphosphate (DMAPP, C5). IPP and DMAPP condense to geranyl diphosphate (GPP, C10), which is the universal substrate of the last enzymatic step catalyzed by monoterpene syntheses, that convert GPP under phosphate cleavage to monoterpenes (Mahmoud and Croteau, 2002). In both cases it is thought that the monoterpenes are syntheised by the same MEP pathway but that the synthesis is localized in different organs. If enantiomeric signatures may be used to better understand monoterpene synthesis then better process based emission algorithms may emerge. Such models could consider the influence of environmental stress factors, as well as light and temperature in an enantiomerically specific way on the emission rates, and thus potentially improve predictive algorithms of monoterpene emission. For more accurate ecosystem response modeling in future it will be necessary to link atmospheric chemistry models to ecological models including biological stresses such as insect proliferation. Through this pioneering study, it is hoped to gain a better understanding of the character of enantiomeric monoterpene emissions and the processes which drive them. An improved understanding of monoterpene emission should allow us to better predict the linked response of atmosphere and ecosystem to future climate changes.

2.2 Experiment set-up

2.2.1 Plant material and the dynamic leaf enclosure cuvette set up

A total of three potted plant species (27 individuals) were studied at the CEFE-CNRS in Montpellier (France) during the months of April to July in 2009 and May to June in 2010, including deciduous and nondeciduous trees, and shrubs (*Quercus ilex* L., *Rosmarinus officinalis* L., *Pinus halepensis* Mill.). *Quercus ilex*, an evergreen sclerophyllous oak of great abundance in the Mediterranean basin, was chosen as a representative emitter of non-stored monoterpenes whose emission is essentially controlled by the rate of biosynthesis. The emitted monoterpenes predominantly come from photosynthetic processes that depend on the light intensity (Loreto et al., 1996a), and the temperature which can affect the activity of enzymes (Fischbach et al., 2002). In contrast the emission of *Pinus halepensis* and *Rosmarinus officinalis* is thought to mainly result from environmentally driven diffusion processes of the stored monoterpenes out of storage organs independent of physiological processes.

Plants were collected from the field (Southern France and Spain) and were potted at least one year before measurements were started. The individuals were 2-4 years old and more than three individuals of each species were studied. In March, the plants were put in a greenhouse in Montpellier at an approximate day/night temperature of 25/15°C to initiate bud break. In order to ensure adaptation of the plants to the chamber environment, all individuals of *Quercus ilex* were placed in the chamber at least 45min prior to the measurements. Since the leaves of the conifer *Pinus halepensis* and the aromatic shrub *Rosmarinus officinalis* possess glands and ducts storing VOCs, mechanical stress can cause large bursts of VOCs from these plants (Niinemets et al., 2010b) To avoid masking temperature and light driven effects by the stressed emission, these two species were enclosed at least 12 h before measurements began. The cuvette condition were varied in terms of light (0, 100, 200, 400, 800 and 1600 $\mu mol \cdot m^{-2} \cdot s^{-1}$ Photosynthetic Active Radiation (PAR)) and temperature (20, 25, 30, 35, 40, 45°C). The responses to light were determined by stepwise increases of 0 to approx. 1600 $\mu mol \cdot m^{-2} \cdot s^{-1}$ PAR at a constant temperature of 30±0.2°C. The responses to temperature were measured by increasing the enclosure temperature in 5°C increments from 20 to 45°C under 1000 PAR. In addition, as an assessment of chemotype variance within a given species, a total of nineteen *Quercus ilex* individuals were measured for enantiomeric monoterpenes in steady state under standard conditions (30°C and 1000 PAR).

A dynamic temperature and light controlled chamber system (see Fig. 2-1) was used to determine VOC exchanges at the leaf level. The enclosure chamber (approximately 105 ml in Volume) was constantly flushed with air at 500 $ml \cdot min^{-1}$ resulting in an air exchange of the enclosure system on average every 5 s. The in-flow air was first passed through a clean air generator (AIRMOPURE, Chromatotec, France) that purified and dried the ambient air. It was then re-humidified by passing a variable portion of the air stream through a washing bottle. Homogenous mixing of the air in the enclosure was maintained by a Teflon fan at the bottom of the cuvette.

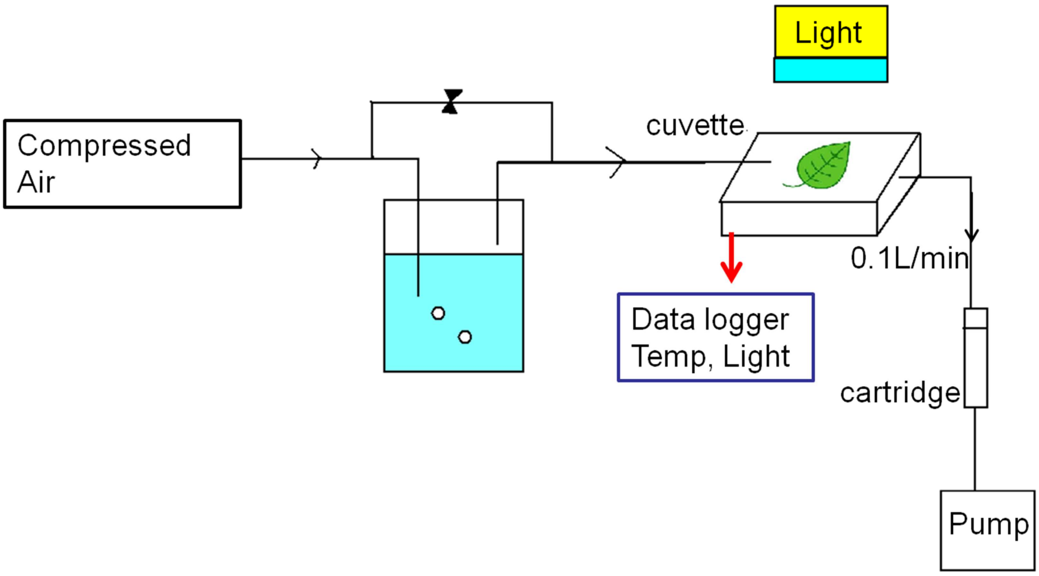


Fig. 2- 1 Dynamic leaves enclosure cuvette set up

Before experiments, terminal shoots consisting of 4 to 7 leaves were prepared for fixation in the cuvette by removing some leaves at the insertion point. This was done at least one week before the measurement to minimize disturbance effects. In order to ensure homogenous light repartition on the adaxial surface of the leaves, several terminal leaves of an individual plant were placed horizontal to the light. Leaf and cuvette temperatures were monitored with two thermocouples (Chrom-Constantan, OMEGA). These two temperatures were rather close with an average difference of 0.7°C during experiments. Cuvette and plants were illuminated with a white light source (OSRAM 1000 W) filtered by a 5-cm water bath. PAR was measured with a quantum sensor (Licor, PAR-SB 190, Lincoln, NE, USA) located next to the chamber. All sampling lines which were made of Teflon were maintained at a constant temperature of 45°C. Photosynthesis and transpiration were measured by directing a constant portion of the inlet and outlet air through a CO_2/H_2O infrared gas analyzer (LI-COR Inc. 7000, Lincoln, Nebraska, USA). At the end of each experiment the studied leaves were harvested and leaf area and dry weight were determined. Projected leaf area was determined with an optical area meter (Delta-T Devices Ltd., Cambridge, UK) and leaf dry weights after drying at 60°C for at least 48 h.

2.2.2 Sampling and analysis

Two types of cartridges (Carbograph I/II or Tenax and carbograph) were used for this study. Cuvette air was drawn at around 100 $ml \cdot min^{-1}$ through the cartridges and the sample flow passed over the sorbent for 10 min. This causes the emitted BVOCs to be selectively enriched on the sorbent surfaces while nitrogen and oxygen are not retained. The VOCs were then analyzed using the same method as described in chapter 1 (1.3).

The measurement systems were calibrated with either a pressurized gas standard mixture (NPL, UK) containing enantiomeric monoterpenes or liquid standards which were prepared from pure authentic standards (Fluka, Aldrich, Bedoukan) dissolved in MeOH. In the latter case, a microliter level liquid standard was injected into the cartridge and flushed with helium for 5 min. Calibrations were performed every 8-10 samples. Multipoint calibrations for all reported species for both gas and liquid standards revealed a good linear dependency of peak area to the respective compound concentration. Both datasets have been combined here. The second set of experiment made in 2010 had much shorter storage times as they were analyzed immediately at the site, however, no measurement basis was found to prefer one dataset and so both are included here. Empty cuvette air was measured each time before installing a new plant and this showed no significant levels of the compounds discussed.

2.3 Results and discussion

2.3.1 Monoterpene emission composition for *Quercus ilex*. L under standard conditions – an assessment of chemotype diversity

Quercus ilex is one of the most widespread tree species in the Mediterranean basin and act as a major source of volatile organic compounds (VOCs) in this region (Grote et al., 2006; Kesselmeier et al., 1996; Llusia et al., 2011; Penuelas and Llusia, 1999). It emits huge amounts of monoterpenes but small or not detectable amounts of isoprene (Plaza et al., 2005; Staudt and Bertin, 1998). The synthesis and emission of these monoterpenes is continuously modulated by environmental factors. However, the compositional profile of the emissions is mainly genetically controlled (Staudt et al., 2001; Staudt et al., 2003; Staudt et al., 2004). Figure 3-2 shows the percent composition of individual monoterpenes emitted from 19 *Quercus ilex* individuals which originated from two different areas (Southern Spain and France) at standard temperature (30°C) and light (1000 PAR) conditions. These contrasting emissions represent distinct chemotypes (genetically fixed) rather than environmental induced emission differences. The results provide a limited assessment of the geographic differences in the BVOC emission profile and an overview of potential chemotypes prevalent in the region. A total of 11 chiral and non-chiral monoterpene hydrocarbons including enantiomeric pairs of α-pinene, ß-pinene, camphene and limonene have been identified in all samples. The main monoterpene compounds emitted were α-pinene, ß-pinene, limonene, myrcene and sabinene. As can be seen in Figure 2-2, there are generally two types of emitter within this selection of Mediterranean *Quercus ilex*: a limonene dominated emitter (e.g. Q1) and a pinene dominated emitter (e.g. Q7). Within the six individuals originating from Spain both limonene and pinene dominated individuals were identified. Thus, if we ignore for a moment the enantiomeric speciation, no clear regiospecific monoterpene emission pattern exists within the group studied here. For those individuals from Spain identified as a limonene dominated emitter, (-)-limonene and (+)-α-pinene was the overwhelmingly dominant enantiomers. In contrast for the pinene chemotype, (-)-α-pinene and (+)-limonene (with some (-)-ß-pinene) are the predominant enantiomers. For those originally from France, almost all of the pinene dominated chemotype showed a clear (+)-enantiomer preference in the case of α-pinene and (+)-ß-pinene preference. Only two individuals from France were found to be limonene emitters, and showed an enantiomeric excess of (-)-enantiomer for all of the three chiral monoterpenes namely α-pinene, ß-pinene and limonene. Table 2-1 lists the chemotypes of studied individuals. As can be seen clearly, four types can be identified if the enantiomeric speciation was taken into account: (I) High limonene with high (-)-α-pinene (all were from France); (II) High limonene with high (+)-α-pinene (all were from Spain); (III) High pinene with high (-)-α-pinene (most were from Spain); (IV) High pinene with high (+)-α-pinene (all were from France).

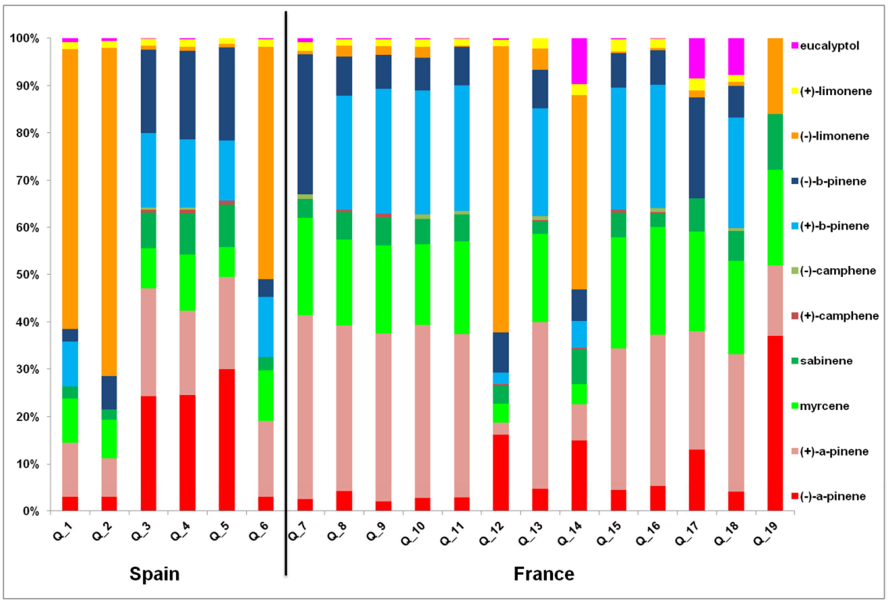


Fig. 2- 2 Screening of *Quercus ilex*. L originally from different areas (Southern Spain and France) at standard conditions

Therefore the enantiomeric signatures of monoterpenes from *Quercus ilex* originating from Spain and France appear to distinctly different. Interestingly, it would not be possible to distinguish the French and Spanish individual on the basis of non-enantiomerically resolved monoterpene emissions since both limonene and pinene dominated individuals exists in both groups. One may develop a hypothesis that the origin of a wood sample or individual plant may be identified on the basis of the enantiomeric emissions (using the table 2-1 below).

Table 2- 1 Chemotypes of the screened individuals

Chemotype	Emission signature	number of individuals	Origin
I	Limonene_(-)-α-pinene	2	France
II	Limonene_(+)-α-pinene	3	Spain
III	Pinene_(-)-α-pinene	4	* Spain(3), France (1)
IV	Pinene_(+)-α-pinene	10	France

* For chemotype III, it was found that three individuals were originally from Spain and one from France.

2.3.2 Light dependence

As described in the previous section (2.2.1), the emission rate of monoterpenes from *Q. ilex* is controlled by light (Bertin et al., 1997; Staudt and Seufert, 1995; Staudt and Bertin, 1998). Therefore, monoterpene emission should immediately follow synthesis, as for isoprene (Loreto et al., 1996b). This has been proven by isotopic labeling experiments as well (Loreto et al., 1996a). On the other hand, *P. halepensis* and *R. officinalis* produce and store monoterpenes in the secretory organs such as resin ducts (Ghirardo et al., 2010; Kesselmeier and Staudt, 1999). Thus, if no de-novo synthesis pools exist in the foliage of these plants, the effects of temperature on the gas vapor pressure in plant tissue and on the resistance along the emission pathway should be the dominant parameter of the emission rates. It is possible that in *P. halepensis* and *R. officinalis* two pools exit as it has been demonstrated for Norway spruce and Scots pine (Ghirardo et al., 2010). If two pools exist and produce exactly the same enantiomers, emissions should show some minor light dependence (i.e. there are emissions in the dark that somehow increase with light). However, minor light effects may be confounded with leaf temperature effects. If two pools exist and produce different enantiomers, the emissions of some enantiomers should express light dependency and others not.

Fig. 2-3 shows the emission from these three different plant species and assumed two different emission types (de-novo and stored), measured at 6 different levels of light using α-pinene as an example. For *Q. ilex*, a clear light dependent emission profile is shown with emission rates increasing with light. The dependence is strong with emissions increasing tenfold between 100 and 1000 µmol $\cdot m^{-2} \cdot s^{-1}$ PAR. However, the emissions from *P. halepensis* were much lower compared with that of *Q. ilex* and with little change with light (-16%-26% for (-)-α-pinene and 1%-17% for (+)-α-pinene).

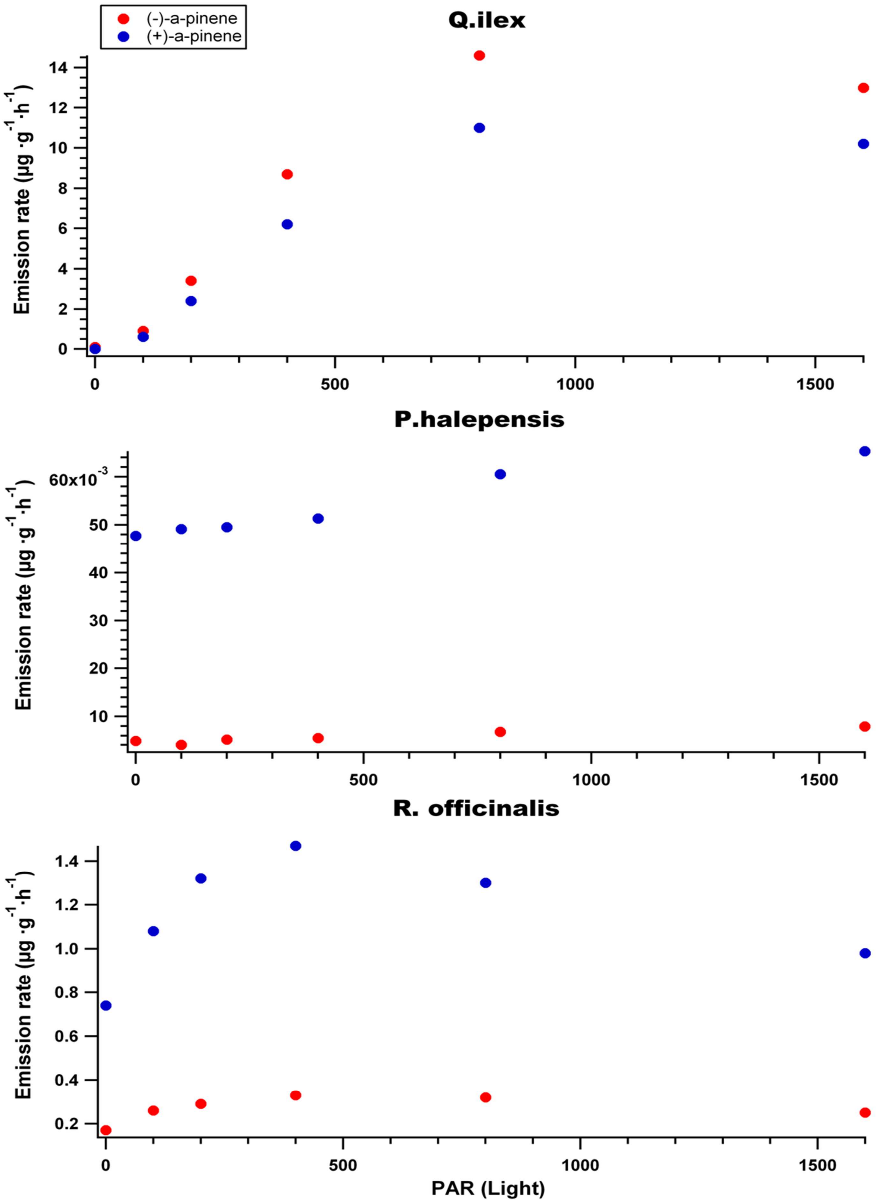


Fig. 2- 3 An example of emission rate (µg·g^{-1}·h^{-1}) of different plant species as a function of light

For *R.officinalis*, the emission rates were from 0.8-1.5 µg·g^{-1}·h^{-1} for (+)-α-pinene, and 0.2-0.3 µg·g^{-1}·h^{-1}for (-)-α-pinene. A rapid increase of emission at lower light intensity (from 0-100 PAR) and a much slower increase or decrease at higher light intensity was observed. Note that, the apparent slight increase of the emission rate might due to small undetected leaf temperature increases during the light dependence experiments. Pinene emissions from *R. officinalis* appear to increase from 100 to 400 PAR, (approximately doubling in rate) and decrease thereafter. Interestingly, the pinene enantiomers appear to show a different dependency to light. The enantiomeric response to light for all three plant species is discussed below.

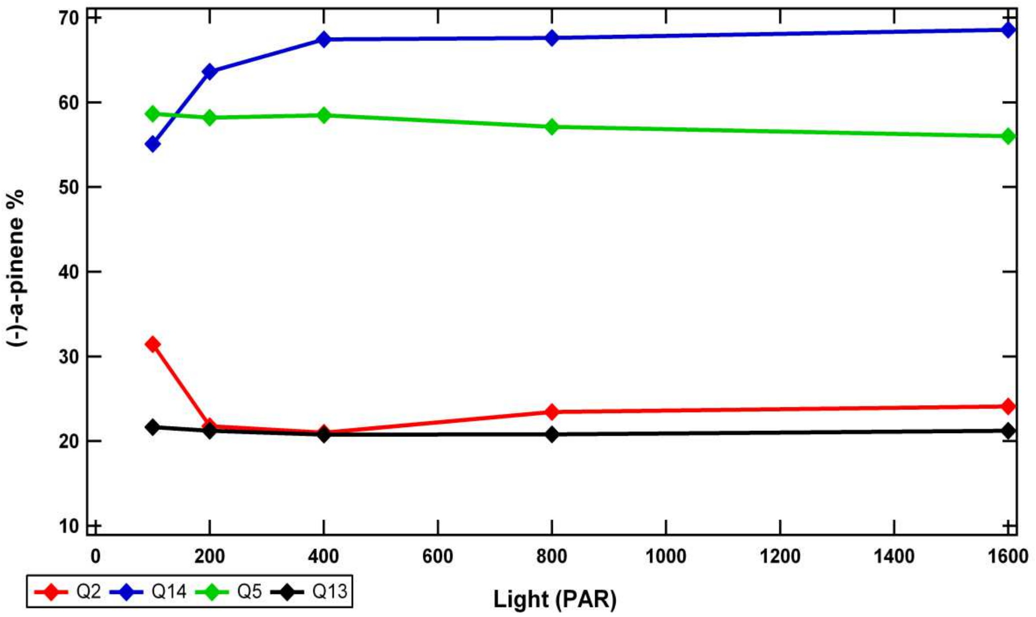


Fig. 2- 4 Enantiomeric enrichment ((-)-α-pinene%) of *Q.ilex* with light

Here we present the enantiomeric signature using the enantiomeric enrichment (i.e. (-)-enantiomer/ ((+)-enantiomer + (-)-enantiomer) ×100) of (-)-α-pinene. Between the replicates as a function of light, there were clear differences between the samples regarding the enantiomers ((-) and (+)-α-pinene). In the case of *Q.ilex* (Fig. 2-4), four replicates, including two originally from Spain (Q2 and Q5) and two from France (Q13 and Q14); two limonene emitters (Q2 and Q13) and two pinene emitters (Q5 and Q14), were analyzed for light responses. The result without light is excluded due to the low emission rate detected in the darkness. Two individuals (Q2 and Q13), which are the limonene dominated chemotype, showed a clear (+)-α-pinene dominance with only 20-30% (-)-α-pinene in the total α-pinene emission, moreover, the ratio was generally stable with light. For one pinene chemotype (Q5), the (-)-α-pinene was close to 50% (around 60-55%) meaning no significant enantiomeric preference. The enantiomer emission ratio was quite stable at low light intensity, but decreased slowly with increasing light levels. In contrast, the other pinene emitter, individual Q14, exhibited the reverse enantiomeric discrimination, namely that (-)-α-pinene predominated in the emission and the (-)-enantiomer increased preferentially with light.

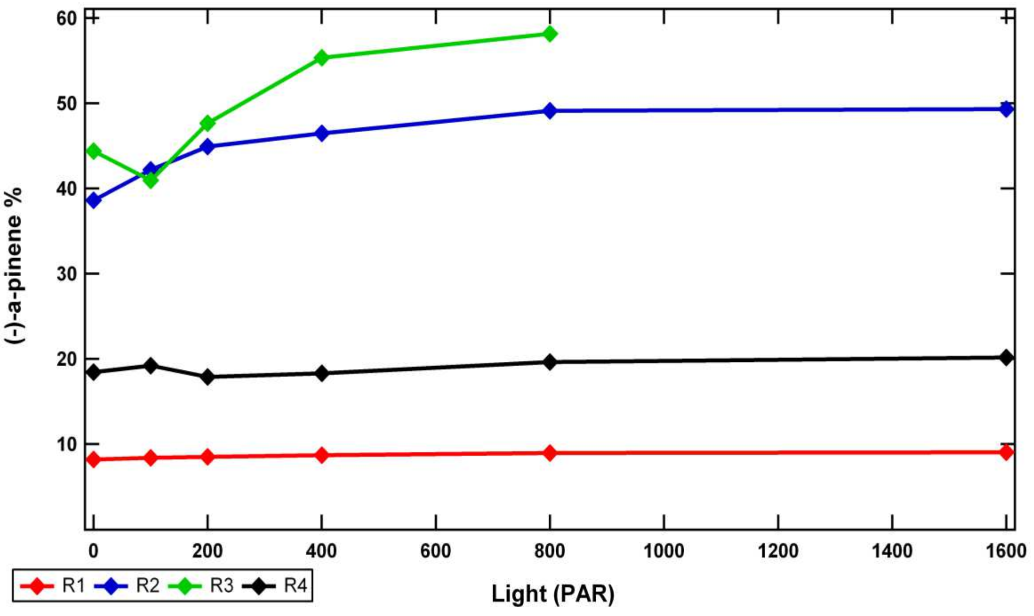


Fig. 2- 5 The enantiomeric enrichment of α-pinene emissions from *R.officinalis* as a function of light

For *R. officinalis* (Fig. 2-5), the (-)-α-pinene was generally lower than the (+)-α-pinene , that is the emission was dominated by (+)-α-pinene which is consistent with the only previous study (Yassaa and Williams, 2005). Nonetheless variation in emission strength and enantiomeric ratio for α-pinene can be seen. Individual R1, the one with strongest (+)-α-pinene predominance, showed no significant change with light (the (-)-α-pinene accounted for less than 10% and stayed stable with light). There was about 20% of (-)-α-pinene in the emission of individual R4, again relatively stable, with a very small tendency to increase (approximately 2%) at higher light intensity (from 200 to1600 PAR). In contrast the replicates R2 and R3 emitted much higher (-)-α-pinene than individual R1 and R4, from 39-49% and 41-58% respectively. These two replicates, with the higher fraction of (-)-α-pinene showed a clear increase with light.

Fig. 2-6 shows the enantiomeric profile of *P. halepensis* replicates as a function of light. Individual P1 began without any enantiomeric preference with around 50% of (-)-α-pinene in the darkness and showed (-)-enantiomer increasing strongly and preferentially in response to light (except one point at 400 PAR). Although the individual 2 started with 50% (-)-α-pinene as well, the response to light was found to be a decrease in the relative abundance of the (-)-enantiomer. Individual P3 emitted with strong (+)-α-pinene enantiomer predominance and showed almost no change in the (-)-enantiomer emission (9-11%) with light, and individual P4 shows a (-)-enantiomer preference (60-67%) and increase with light. Curiously the individuals of *P.halepensis* selected here for analysis have exhibited all possible variations in the α-pinene enantiomeric emission dependence on light namely: stable (+)-enantiomer dominated, stable (-)-enantiomer dominated, increasing (-)-enantiomer dominated with light and increasing (+)-enantiomer dominated with light.

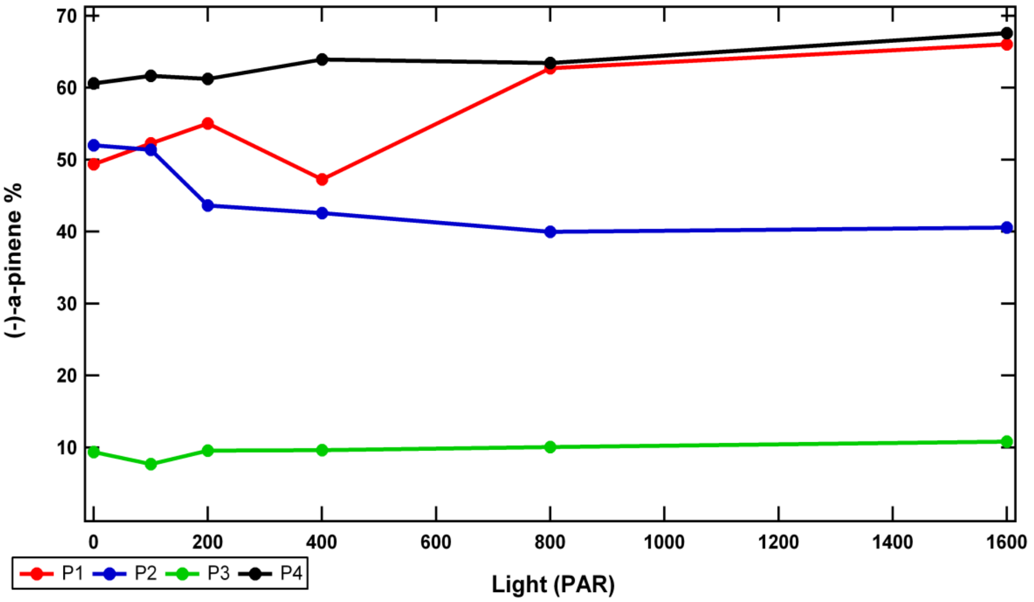


Fig. 2- 6 Enantiomeric enrichment of (-)-α-pinene of *P. halepensis* with light

2.3.3 Temperature dependence

As discussed above that *Q.ilex* emits monoterpenes right after they are synthesis inside the leaves, at constant light condition the production of monoterpenes in the plants will controlled by the activities of specific enzymes. As the temperature of the cuvette system is increased there are more energetic collisions between the enzymes within the reaction so that more enzymes per unit time will reach the activation energy. Thus the rate of the reaction may increase resulting increased monoterpenes in emission. However, above a certain temperature, there would be too much energy that some of the weak bonds determining the active proteins many be broken. The activity of enzymes begins to decline. Therefore, the rate of monoterpenes emission increases with temperature but then decreases at higher temperature as enzymes denature.

For those species which produce and store monoterpenes their monoterpenes emission should be in response to temperature. As temperature going up, more monoterpenes will volatilize from the storage pool to the atmosphere.

Measured emissions of monoterpenes responded to the temperature change clearly (see Fig. 2-7). High emission rates (5-25 µg·g^{-1}·h^{-1}) were found from *Q.ilex* which increased until 40°C, then exhibited a sharp decrease at the highest temperature of 45° C. The emission rates of *P. halepensis* were very low (0.02-0.2 µg·g^{-1}·h^{-1}), but a clear exponential increase with temperature, especially for (-)-α-pinene, was observed. Emission rates from *R. officinalis* were low (1 µg·g^{-1}·h^{-1}) and showed no clear temperature response except at highest temperatures.

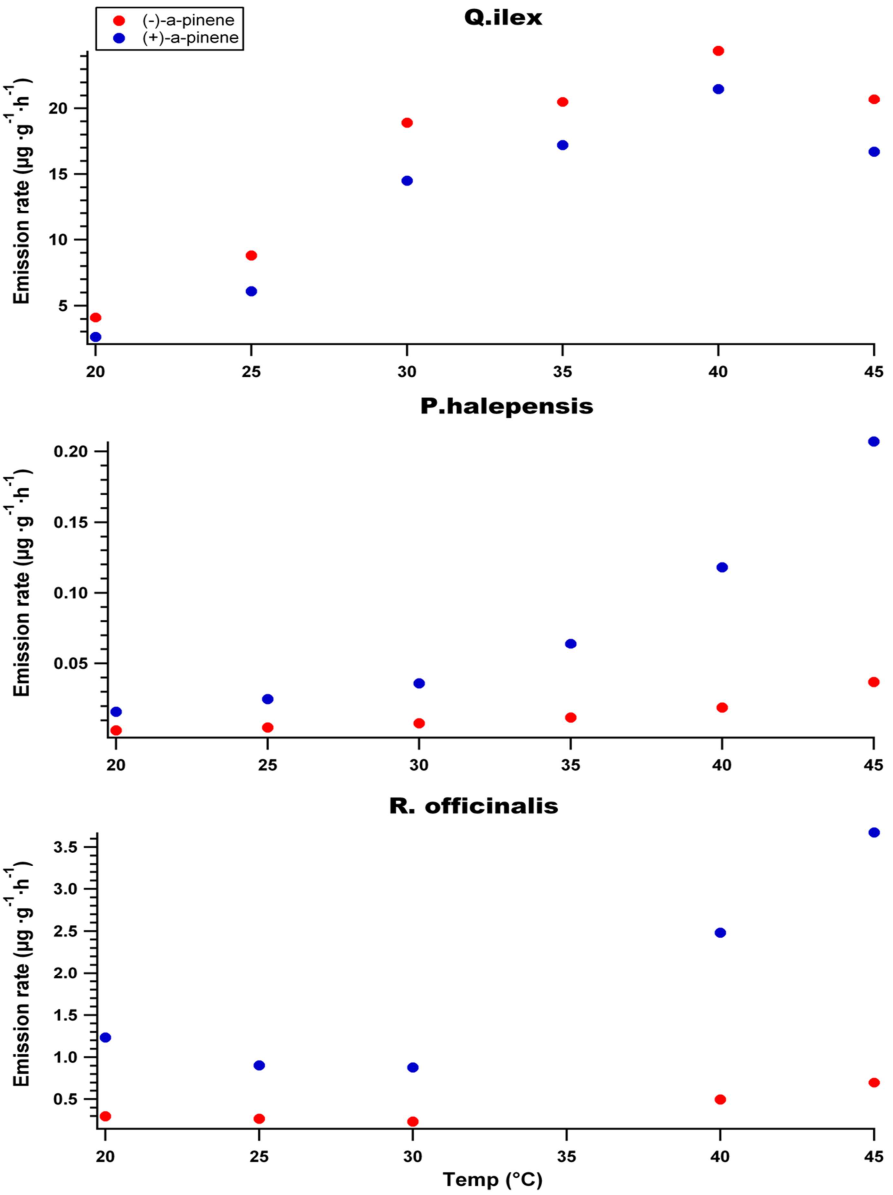


Fig. 2- 7 An example of Emission rate (µg·g^{-1}·h^{-1}) of different plant species as a function of temperature

Investigating the enantiomeric enrichments ((-)-enantiomer %) using α-pinene as the monoterpene representative among the replicates in terms of temperature, diverging effects in the enantiomeric enrichments can be seen in the results.

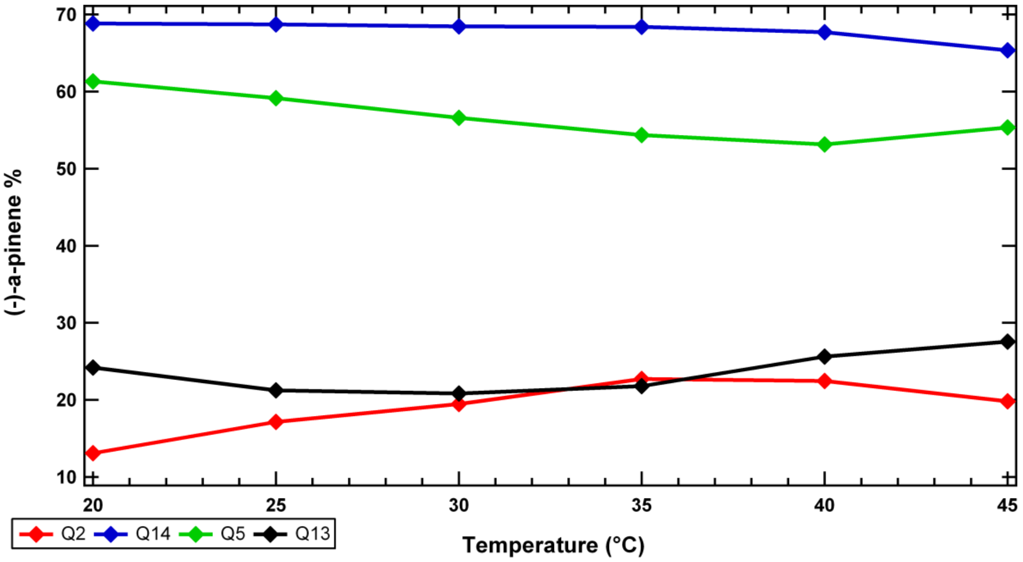


Fig. 2- 8 Enantiomeric enrichment of (-)-α-pinene in the emission of *Q.ilex* as a function of temperature

Regarding *Q.ilex* (Fig.2-8), individuals Q2 and Q13, limonene chemotype and two strong (+)-enantiomer emitters (less than 30% of (-)-enantiomer in total α-pinene emission) exhibited opposite enantiomeric trends in response to temperature: the (-)-enantiomer of individual Q2 was found to be decreased (more (+)-α-pinene enriched) at the highest temperatures (40-45°C) while the individual Q13 showed a increased (-)-α-pinene enrichment at the highest temperatures. For the pinene chemotype, the ratios of individual Q5 with weak (+)-enantiomeric preference were quite stable at the first two low temperature stages, and showed a tendency to decrease towards the higher temperatures, but increased slightly at the highest temperature point. However, the other pinene emitter (individual Q14) in which (-)-enantiomer predominated in the emission, was found to remain stable until 35°C and then rapidly decreased at the highest points (40-45°C).

Fig. 2-9 shows the enantiomeric profile of *R.officinalis* emission. Again with temperature there is a variety of responses in the enantiomeric enrichment. For replicates R1 and R4, there is a modest decrease in (-)-α-pinene emission in response to temperature from 25 to 45°C. Replicate R2 shows no clear dependence on temperature varying between 44 to 50% of (-)-α-pinene. Replicate R3 shows a weak increase in (-)-α-pinene with temperature. Thus the strongest impact on enantiomeric emission by temperature is shown for replicates R1 and R3.

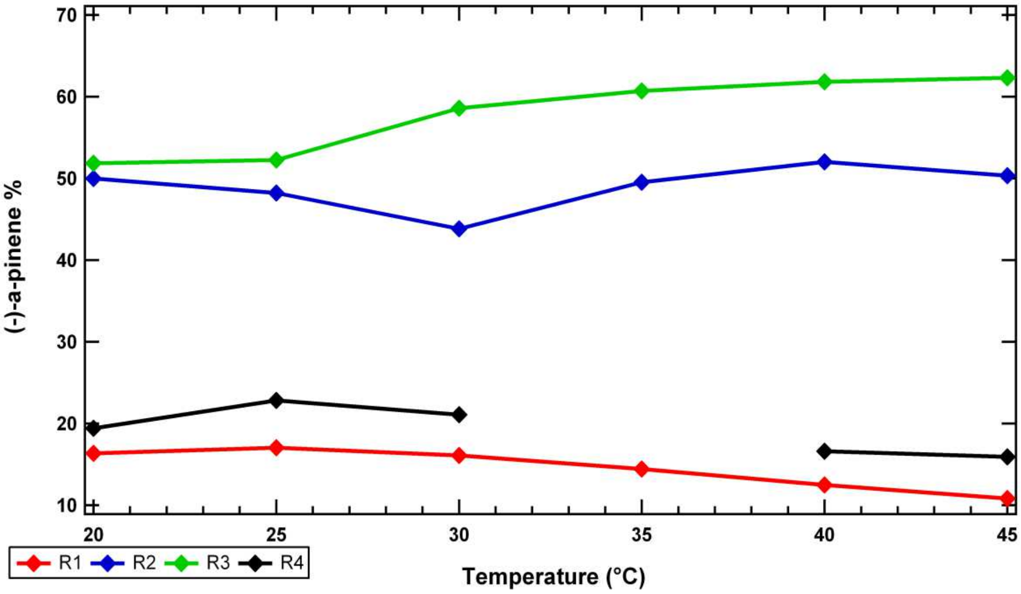


Fig. 2- 9 Enantiomeric enrichment of (-)-α-pinene in the emission of *R.officinalis* as a function of temperature

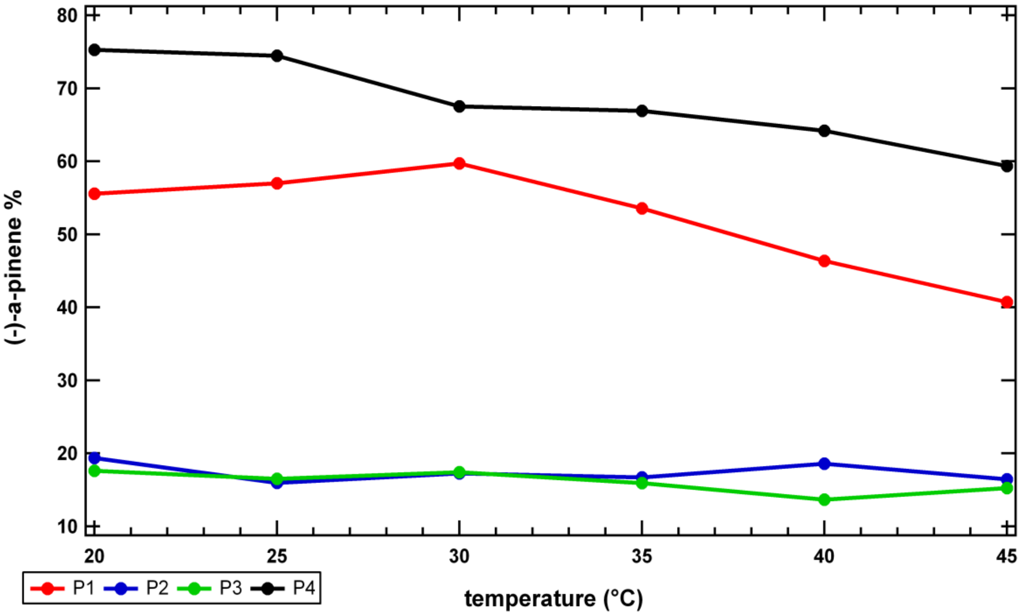


Fig. 2- 10 Enantiomeric enrichment of (-)-α-pinene in the emission of *P. halepensis* as a function of temperature

In the case of *P. halepensis* (Fig. 2-10), replicate P1 shows the (-)-enantiomer emission increasing strongly in response to temperature between 20-30°C but thereafter decreasing (becoming more (+)-enantiomer rich) at higher temperature, the enantiomeric enrichment of replicates P2 and P3 are strongly dominated by the (+)-enantiomer with less than 20% of (-)-enantiomer and show no clear dependence on temperatures, and replicate P4 shows the strongest (-)-enantiomer preference in all of the four replicates (the (-)-α-pinene accounts for 60-80% of the total (-)-α-pinene) but decreases with temeperature which is consistent with its change as a function of light.

2.3.4 One-day field measurements in a *Quercus ilex* .L forest

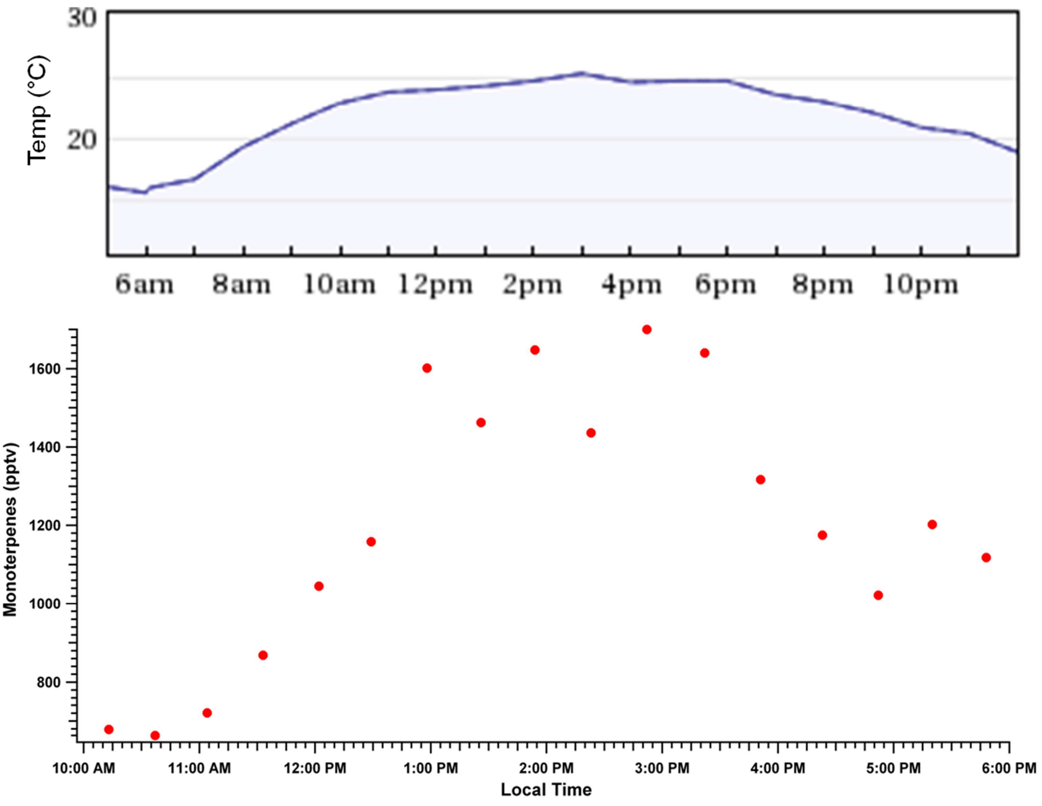


Fig. 2- 11 Monoterpene mixing ratios (sum of α-pinene, ß-pinene and limonene) measured over a *Q. ilex* forest, southern France

The field measurements took place over a *Q. ilex* forest in Puechabon, southern France. The Puechabon forest is a natural forest which was used to produce charcoal (coppice). The last cut was about 40 years ago. Therefore, each tree has usually several stems that represent resprouts from a several hundred-year-old root stock.

This was a one day measurement made during the daytime from 9:00 to 18:00 (local time). The temperature was from 16 to 21°C. The temperature and light reached its maxium value at around 14:00 (local time). The sampling line was placed about 2m above the canopy top.

The selected monoterpenes in the measurement were pinene enantiomeric pairs: (+)-α-pinene and (-)-α-pinene, (+)-ß-pinene and (-)-ß-pinene and limonene enantiomerc pairs: (+)-limonene and (-)-limonene which were the main monoterpenes observed over the forest. These monoterpenes ranged from 0.6ppbv to 1.8ppbv during the day, and peaked from 13:00 to 15:00.

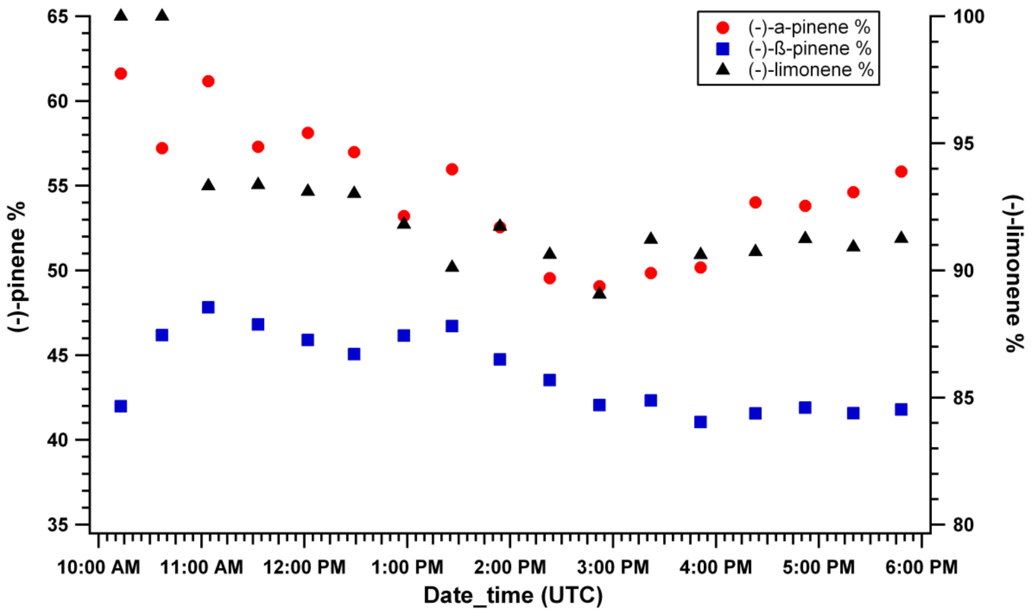


Fig. 2- 12 Enantiomeric enrichment of (-)-α-pinene, (-)-ß-pineen and (-)-limonene over the *Q. ilex* forest, southern France

The mixing ratio of monoterpenes, the sum of (-)/ (+)-α-pinene, (-)/ (+)-ß-pinene and (-)/ (+)-limonene, increased during the day and peaked in the afternoon (14:00-15:00 local time), see Fig. 2-11. However, for α-pinene and limonene the enantiomeric enrichment of (-)-enantimer had a clear decrease towards noon with the lowest value around 14:00-15:00. That is to say that the relative abundance of the (-)-enantiomer for α-pinene decreased throughout the morning with increasing light and temperature levels becoming (+)-enantiomer dominated at noon (Fig. 2-12). For limonene enantiomers, the (-)-limonene was always the predominant one by factor of circa 10. For ß-pinene, the enantiomeric ratios varies but the (+)-enantiomer predominants over the forest throughout the day.

Fig. 2-13 shows the mixing ratios of α-pinene, ß-pinene and limonene over the day. These three monoterpenes followed the same trend throughout the daytime and had the same level of mixing ratios over the canopy except in the morning. In the morning until 11:00, almost 80% of the monoterpenes observed were α-pinene and ß-pinene, while later in the day limonene accounted for approximately 30% in the total monoterpenes emission and α-pinene and ß-pinene were around 30% and 40%, respectively. In general, the abundance of a particular monoterpene in ambient air is dependent on (1) the emission source strength that is the absolute emission rate from forest tree species, (2) the atmospheric removing rates (i.e. reaction with OH radical, O_3 and NO_3), and (3) the distribution of the source trees relative to the measurement location. Limonene reacts much faster than α-pinene and ß-pinene in the free troposphere (the reaction rates and life time with OH and ozone are shown in table 1-2). From the mixing ratios point of view, the chemical compositions show that with more than 70% of pinene (α-pinene and ß-pinene) and around 30% of limonene, the forest is thought to be a mixture of chemotypes with slightly more pinene chemotype. These findings are also in agreement with the work of Staudt et al. (2001) for the same forest. Being a French forest, we would expect from the screening experiments, presented above that (+)-a-pinene would be the predominant enantiomer. However, the enantiomeric ratio of a-pinene does not vary consistently with the previously measured individual identified as French pinene chemotype (chemotype IV).

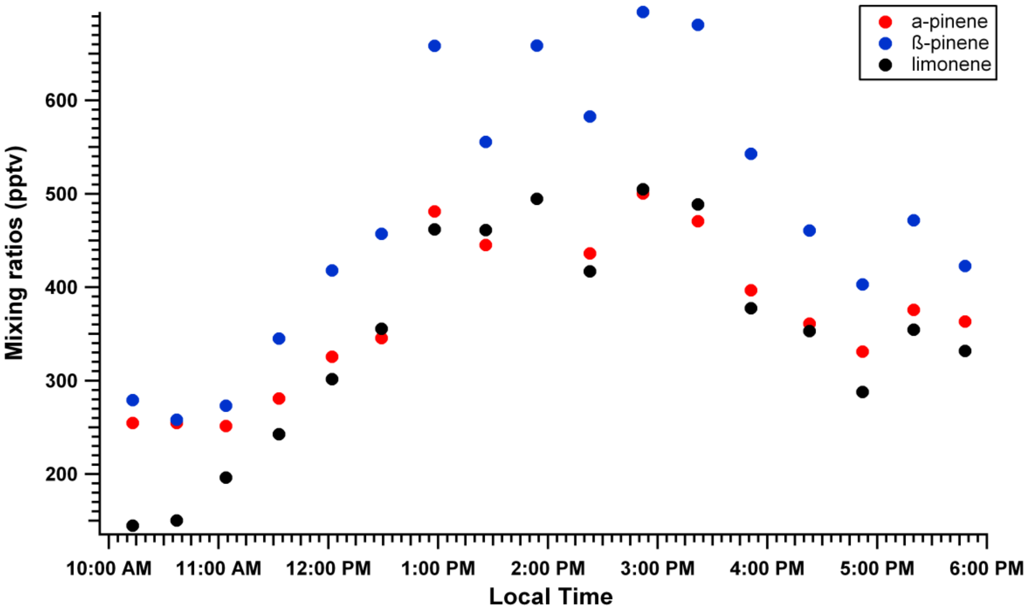


Fig. 2- 13 Monoterpes composition over the Q. ilex forest during the day time, late spring, 2010

The initial screening shown in Fig. 2-2 was performed at 30°C and 1000 PAR which corresponds approximately then ambient noon time conditions. In the ambient data, see Fig. 2-10, it can be seen that throughout the morning, with increasing temperature and light, the α-pinene enantiomeric ratio trends from (-)-α-pinene enrichment to racemic i.e. became more enriched in the (+)-α-pinene enantiomer. This behavior is only exhibited by the Spanish pinene chemotype (see Fig. 2-4). Therefore, we have to conclude that this forest is very likely a mixture of the Spanish pinene chemotype or at least have one such individual with strong emission rates close to the measurement tower. It appears initially disappointing that the ambient measurements do not correspond more closely to the emissions of the previously measured French chemotypes. However, it must be born in mind that the natural environment outside the laboratory contains many more stimuli than simply light and temperature. For example the effect of damage by insects may have been an additional driving force on the enantiomeric emissions.

2.4 Summary and conclusions

During this laboratory study, conducted in 2009 and 2010, BVOCs comprising mainly of monoterpenes emissions from a dynamic leaves enclosure cuvette were measured applying GC-MS. During the two experimental sessions, two kinds of cartridges were used for the study, one with the sorbent material of Carbograph I and II and the other with Tenax and Carbograph. Both gas mixture standards and liquid ones were used as working standards. Multipoint calibrations for all reported species for both standards and they revealed a good linear dependency (r^2 >0.9) of peak area to the respective compound concentration.

Quercus ilex, which is the one of the most widespread tree species in the Mediterranean basin, emits huge amounts of monoterpenes. The screening experiments of *Q.ilex* emissions under standard condition together with the results from the light and temperature responses showed that the compositional profile of its emissions is mainly genetically controlled. Furthermore this limited sample set has provided an interesting hypothesis for regional identification according to enantiomeric chemotype.

Monoterpenes emission rates from *Q. ilex* were found to be controlled by light and temperature, while *R.officinalis* and *p.halepensis* emited monoterpene depending mostly on temperature. However, the enantiomeric excess of the main moneterpenes, namely (-)/ (+)-α-pinene, (-)/ (+)-β-pinene and (-)/ (+)-limonene is not manifested in the responses to light and temperature. The big differentiation of the enantiomeric excess was found within individuals even from the same species, for instance one *Q.ilex* showed a clear (-)-α-pinene predominant and increase as a function of light, while another one was found to be revealed a strong enantiomeric excess of (+)-α-pinene and showed no change with light. This suggests that the enantiomeric composition is inherent for a given individual and that several enantiomeric chemotypes exist within a given plant species. These enantiomeric variations have little impact on the overall emission of the monoterpenes which respond to temperature and light according to the existing algorithms reasonably well.

There is no clear evidence for an enantiomeric trend as a function of temperature or light in the leaf emission, however, generally it has been observed that where there is a strong dependence of the enantiomeric ratio with light, the (-)-α-pinene was predominant in the emission. A clear enantiomeric ratio diel cycle was observed in field measurements over different ecosystem, such as Mediterranean stone pine forest (chapter 3), oak forest and boreal forest (chapter 4). While the forests in Spain and Finland both show an enrichment of (-)-a-pinene at noon time, in France the opposite was observed (see the following chapter 3 and 4). Despite the discovery of many chemotypes with different sensitivity to light and temperature the overall diel cycle from this and other measurements (shown in the thesis) exhibit smooth cyclic behavior in the VOC mixing ratio. The enantiomeric ratio from the Stone pine forest and from Boreal forest showed no correlation with O_3 suggesting that the variation in the ratio comes from primary emissions. This raises an interesting question. Given the large number of enantiomeric chemotypes it is remarkable that the diel variation of these enantiomers follows such a clear cycle in the larger datasets. One may speculate whether the ecosystem is acting in unison to produce this cycle or indeed what use this cycle may be to the biological entities (insects, birds, plants) dwelling within the ecosystem.

In the future, temperature is predicted to increase. From the research presented above it can be seen that the overall enantiomeric signature of the forest will change as a consequence. Such effects may seem subtle, however, for insects and birds that use olfactory signals for their everyday life it may have important consequences.

Chapter 3

Domino 2008

Diel **O**xidant **M**echanisms **I**n relation to **N**itrogen **O**xides

GC-MS measurements

This chapter has been published as

Song, W., Williams, J., Yassaa, N., Martinez, M., Adame, J.A., Hidalgo, P.J., Bozem, H., Lelieveld, J. : Winter and summer characterization of biogenic enantiomeric monoterpenes and anthropogenic BTEX compounds at a Mediterranean Stone Pine forest site, J Atmos Chem, 68, 233-250, DOI 10.1007/s10874-012-9219-4, 2011

Parts of the results have also been used in the publications:

van Stratum, B. J. H., Vilà-Guerau de Arellano, J., Ouwersloot, H. G., van den Dries, K., van Laar, T. W., Martinez, M., Lelieveld, J., Diesch, J.-M., Drewnick, F., Fischer, H., Hosaynali Beygi, Z., Harder, H., Regelin, E., Sinha, V., Adame, J. A., Sörgel, M., Sander, R., Bozem, H., Song, W., Williams, J., and Yassaa, N.: Study of the diurnal variability of atmospheric chemistry with respect to boundary layer dynamics during DOMINO.Atmos. Chem. Phys. Discuss., 12, 6519-6550.
doi:10.5194/acpd-12-6519-2012, 2012

Crowley, J.N., Thieser, J., Tang, M.J., Schuster, G., Bozem, H., Beygi, Z.H., Fischer, H., Diesch, J.M., Drewnick, F., Borrmann, S., Song, W., Yassaa, N., Williams, J., Pohler, D., Platt, U., Lelieveld, J.: Variable lifetimes and loss mechanisms for NO(3) and N(2)O(5) during the DOMINO campaign: contrasts between marine, urban and continental air. Atmos. Chem. Phys. 11(21), 10853-10870 (2011).
doi:DOI 10.5194/acp-11-10853-2011

Within the ACP special issue: “DOMINO: the Diel Oxidant Mechanisms in relation to Nitrogen Oxides measurement campaign in El Arenosillo, Spain”

3.1 Introduction and site description

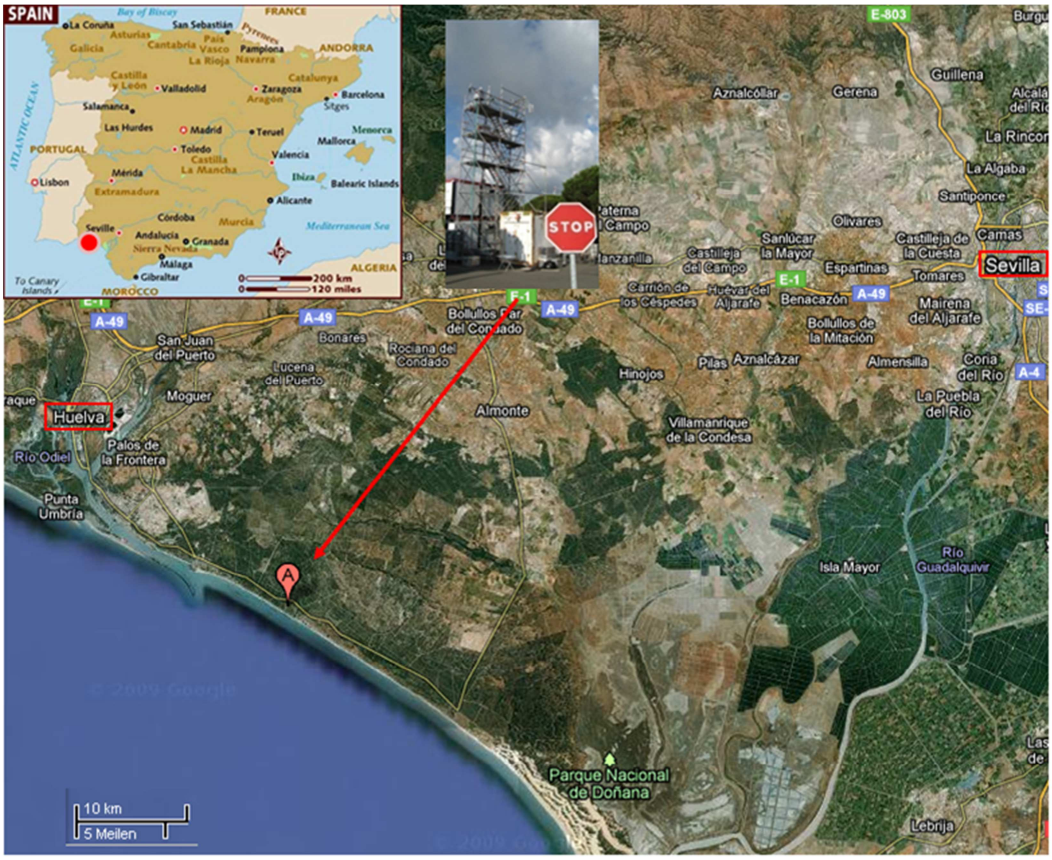


Fig. 3- 1 Map of Spain and the measurement site showed as a red dot. Major cities relevant to this study are Huelva and Seville

The aim of the DOMINO (Diel Oxidant Mechanisms In relation to Nitrogen Oxides) field measurement campaign made in November and December 2008 was to investigate relative rates of VOC oxidation by OH, NO_3 and ozone. As part of the field study an online TD-GC-MS measurements were carried out to characterize the biogenic and anthropogenic VOCs throughout the day during wintertime. In order to characterize the enantiomeric monoterpe emissions from the same ecosystem, additional samples were taken at the same site the following summer September, 2009.

The field campaign took place at the “Atmospheric Sounding Station - El Arenosillo” which is located at a rural zone in the southwestern coastline of the Iberian Peninsula (37.10°N, 6.70°W, 40m a.s.l). The El Arenosillo station, a platform of the Atmospheric Research and Instrumentation Branch of the Spanish National Institute for Aerospace Technology, is considered a representative site in this geographical area to perform atmospheric studies (Adame et al., 2010). The measurement site was located at a rural protected forested area (Donana National Park) and a coastal area, less than 1 km north of the Atlanic Ocean seashore, see Fig. 3-1. As can be seen in Fig. 3-2, the observatory is surrounded by forest, mostly stone pines *(Pinus pinea*. L, ~5-10m in height). In close proximity, there is a small village situated about 8 km to the west. The nearest and biggest city is Huelva at a distance about 35 km to the northwest (pop. 150,000 http://www.juntadeandalucia.es/institutodeestadistica). Huelva is one of the most industrialized areas in southern Spain. It houses one of the European's largest oil refineries. Another big city nearby is Seville at 70 km to the northeast (pop. 700,000 http://www.juntadeandalucia.es/institutodeestadistica). This city has a population of more than a million, the biggest in Andalusia. The Seville metropolitan area has the busiest roads in the south of Iberian Peninsula. Emissions from industrial areas around Huelva and Seville could contribute to increase the background levels at the measurement site for northwest and northeast winds. Thus it was expected that both anthropogenic and biogenic emissions would be detected providing contrasting photochemical regimes suitable for detailed mechanistic study.

Fig. 3- 2 View of Mediterranean forest from the top of the measurement tower towards the northeast

In this chapter, the meteorology conditions in the measurement area during the campaign would be described in the section 3.2. The detailed experimental methods are given in the following section 3.3. Results obtained from the field measurements would be shown in section 3.4: (1) VOC diel cycles and wind direction dependencies are used to establish the relative strength and temporal dominance of biogenic and anthropogenic VOC impacting the site. The biogenic species targeted in this study were isoprene and selected monoterpenes including the α-pinene enantiomers:

(+)-α-pinene and (-)-α-pinene, as well as (-)-limonene, eucalyptol and camphor. (2) We examine the ratio of the measured enantiomers, from this temperate Mediterranean forest in winter and summer, and then compare them to previously reported enantiomeric ratios from tropical and boreal forests (Williams et al. 2007). (3) The anthropogenic compounds studied here include benzene, toluene, ethylbenzene and xylenes. One advantage of using the GC-MS system configuration employed here (ß-cyclodextrin column) is that in addition to the enantiomeric separation of biogenic compounds, all isomers of xylene are separately quantified. These species are not resolved by most commonly used chromatography columns, however, due to their relatively constant emission ratios under traffic dominated conditions (Yassaa et al., 2006), and differing rates of reaction with OH, the measurements may be used to estimate the average OH concentration to which the VOCs have been exposed since emission (Roberts et al., 1984; Yassaa et al., 2006). (4) The aromatic VOCs are used to estimate OH which is then compared with an alternative empirical OH estimating approach using JNO_2. The results are then examined critically to assess the applicability of these methods at this location.

3.2 Site meteorology

For the campaign period (November-December 2008) the observatory site is mainly affected by both continental and oceanic meteorological conditions. Meteorological conditions (temperature, wind direction, wind speed, air pressure, relative humidity and precipitation) averaged over 10 minutes throughout the campaign are shown in Fig. 3-3. In general, the weather during the campaign changed from warm to cold. The temperatures measured at the site in this period were from 2 to 22°C. The warmer days (21st to 25th of November) showed a maximum temperature above 15°C during the day and around 10°C during night time. The temperature was below 15°C after that. The temperature had been shown a clear diurnal cycle from 21st to 28th of November, while variation between day and night was quite small in the middle (28th to 30th of November) and the end (4th to 7th of December) section of the campaign. Pressures varied between 996-1022 hPa. Precipitation was generally low in most days of the campaign, except for 28th, 29th and 30th of November when rain showers were experienced at the site. Fig. 3-4 shows the wind rose plot for the period of our measurements in the station. During the campaign the wind blew mostly from the northwest and the northeast wind sectors (see Fig. 3-4). The prevailing W-NW-NNE winds, served to advect anthropogenic VOC and NO_x emissions over the intervening forest from the cities of Huelva and Seville located 25 km and 70 km to the northwest and northeast of the site respectively. The windspeed averaged 3 m s^{-1}, corresponding to an approximate transport time of 2.3 h from Huelva and 6.5 h from Seville over the stone pine and eucalyptus forests in the national park. Air from southwesterly directions was of relatively clean marine origin.

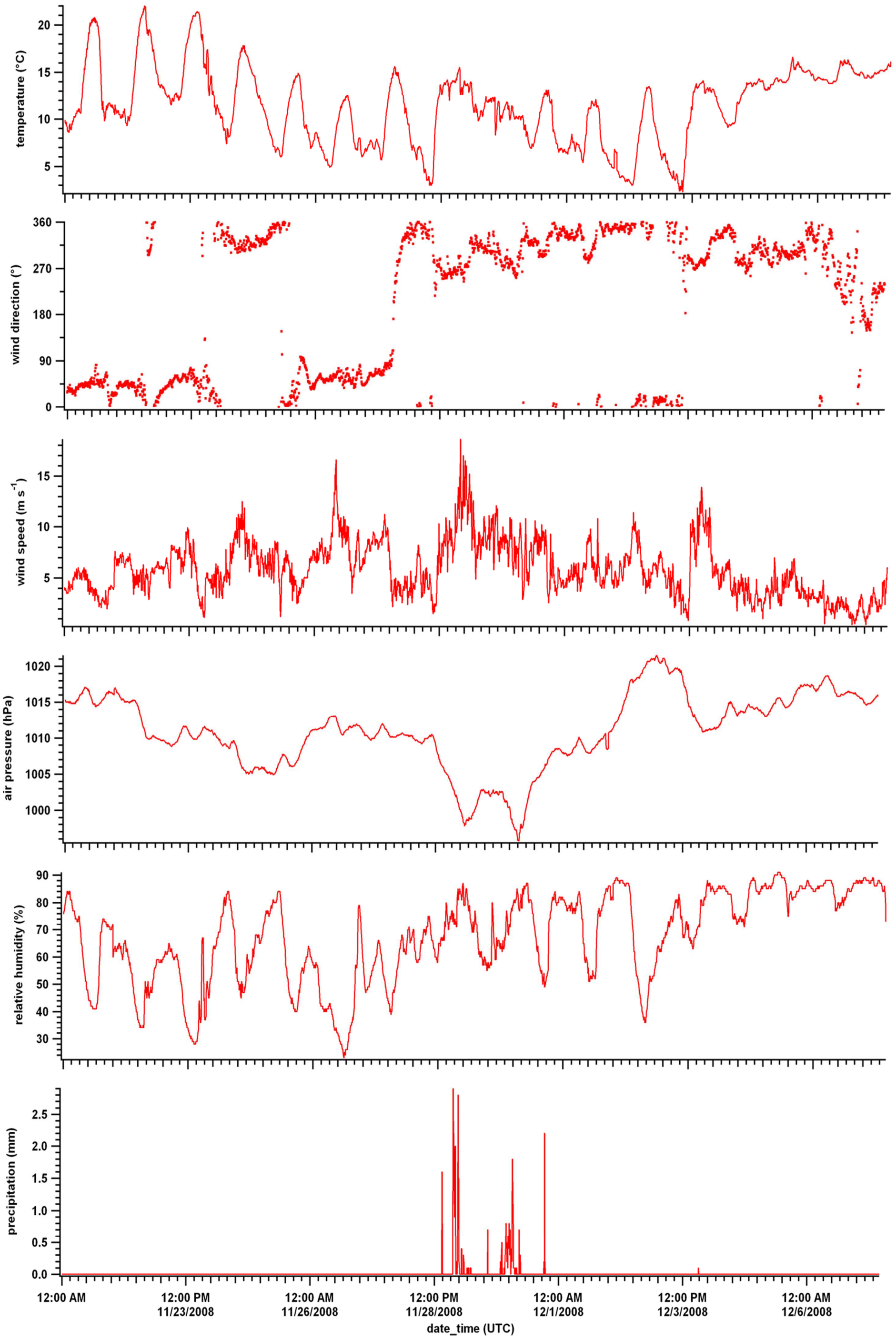


Fig. 3- 3 Meteorological data (temperature, wind direction, wind speed, air pressure, relative humidity and precipitation) during the campaign period

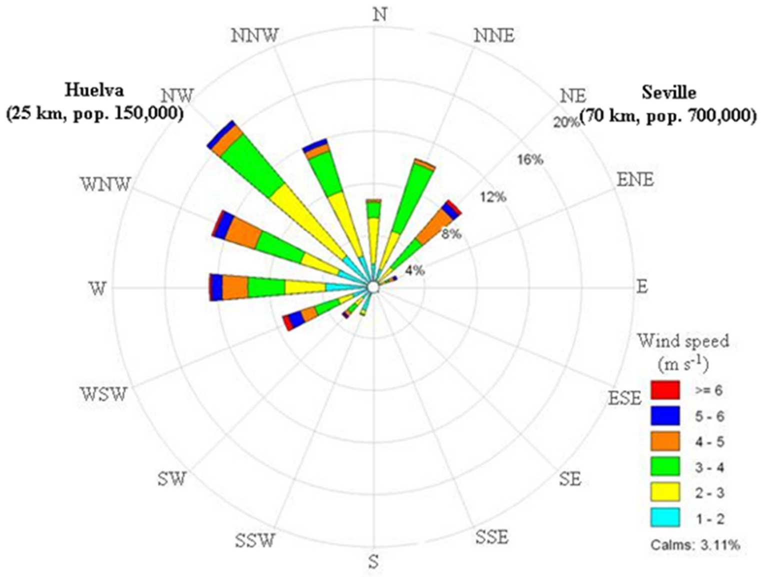


Fig. 3- 4 The distribution of windspeed and direction during the campaign in November and December at the measurement site

3.3 Experiment

An on-line sampling and TD-GC-MS measurement system was used for the in-situ observation of atmospheric VOCs during DOMINO campaign in winter. More details about the system can be found in 1.3. This experimental set-up allowed the measurement of anthropogenic VOCs such as ethylbenzene, and all xylene isomers as well as biogenic species such as isoprene and monoterpenes during the campaign. The air sampling line was fixed at 12 m above the ground, several meters above the canopy, and fitted with a Teflon filter to prevent particles from entering the inlet line. Ambient air was drawn continuously through a main sample line at about 10 L·min^{-1} by a high volume pump, the residence time of the inlet line was approximately 12 seconds. A sub-stream of sampled air was drawn at about 38 ml·min^{-1} through a Teflon manifold connection to the main sample line and concentrated directly on the cold (10 ºC), adsorbent filled trap by a membrane pump to give a total sample volume of about 2 L. An enantiomerically selective column (Cyclodex-B, 30 m, 0.256 mm I.D., 0.25 µm film; J&W Scientific, CA, USA) was used in this study. Further details about the instrumentation, as well as the identification and quantification of various compounds are given in chapter 1 (1.3). Daily pollen concentration was measured by means of a one-day pollen sampler (VPPS 1000 Lanzoni, Italy) placed at 15 m height.

For the summer measurements (21-23.09.2009), adsorbent cartridges (CarbographI /CarbographII; Markes International, Pontyclun, UK) were used (see details in section 1.3). Ambient temperatures during the summer measurements varied between 12.8°C to 31.3°C (average 20.8°C), and there was no rain during the summer sampling period.

3.4 Results and discussion

3.4.1 Overview

Measurements of VOCs were made from 21st November to 7th December. An overview of mean, median, maximum, minimum and standard deviation for the VOC data collected in this study is given in Table 3-1. Generally, levels of the biogenic compounds, namely the monoterpenes and isoprene, are low. The dominant tree species in the surrounding forest is *Pinus pinea.* L which has a strong seasonal emission variation with the lowest emission from November to February based on both chamber and model studies (Keenan et al. 2009; Staudt et al. 2000). Our study is therefore in keeping with the expected seasonal variations in net primary production and emission rates reported previously (Staudt et al. 1997; Staudt et al. 2000). Despite the measurement site being located in a forest and some 25 km from the nearest city and the industrial area of Huelva, anthropogenic VOCs namely benzene, toluene, ethylbenzene and the xylene isomers were found to be generally significantly higher than the biogenic species measured.

Table 3- 1 Summary of mean, median, and sample number for all VOC measured (n=231)

compound	mean (pptv)	sd (pptv)	max (pptv)	min (pptv)	median (pptv)
Benzene	182	299	3461	12	109
Toluene	156	238	2708	BLD	96
Ethylbenzene	16	19	219	BLD	11
p-Xylene	12	16	167	BLD	8
m-Xylene	34	62	766	BLD	19
o-Xylene	10	16	184	BLD	6
Isoprene	15	18	137	BLD	10
(-)-a-Pinene	4	3	34	BLD	3
(+)-a-Pinene	4	3	14	BLD	2
(-)-Limonene	6	5	43	BLD	5
1,8-Cineole	10	7	37	BLD	8
(-)/(+)-Camphor	11	9	51	BLD	7

BLD: Below detection limits

Fig. 3-5 presents the mixing ratios of selected BTEX throughout the campaign. The anthropogenic influences were highly variable as evidenced by the numerous pollution peaks. Generally though, the individual anthropogenic species exhibited similar trends and peaks throughout the campaign. Benzene and toluene showed higher levels during night time and in the early hours of Nov. 24th, Nov. 27th, Dec.1st and Dec. 6th which will be discussed further in section 3.3.3.

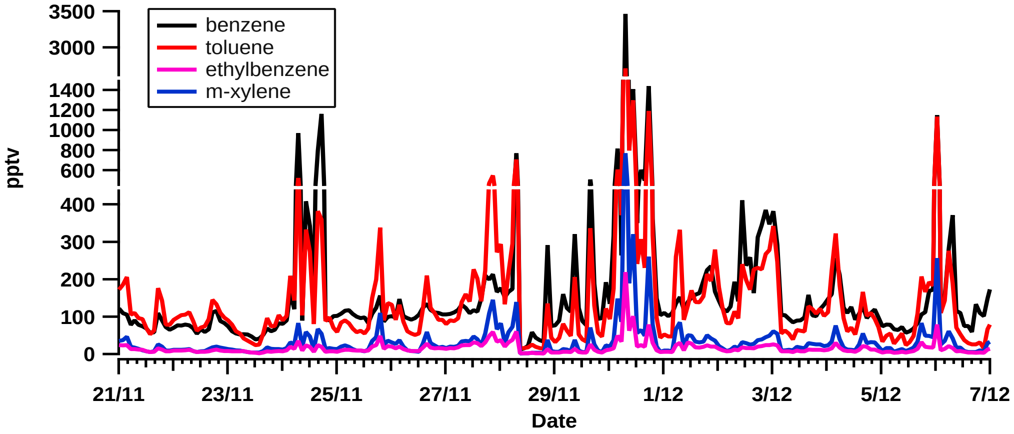


Fig. 3- 5 Mixing ratios of selected BTEX (benzene, toluene, ethylbenzene and *m*-xylene) during the DOMINO campaign

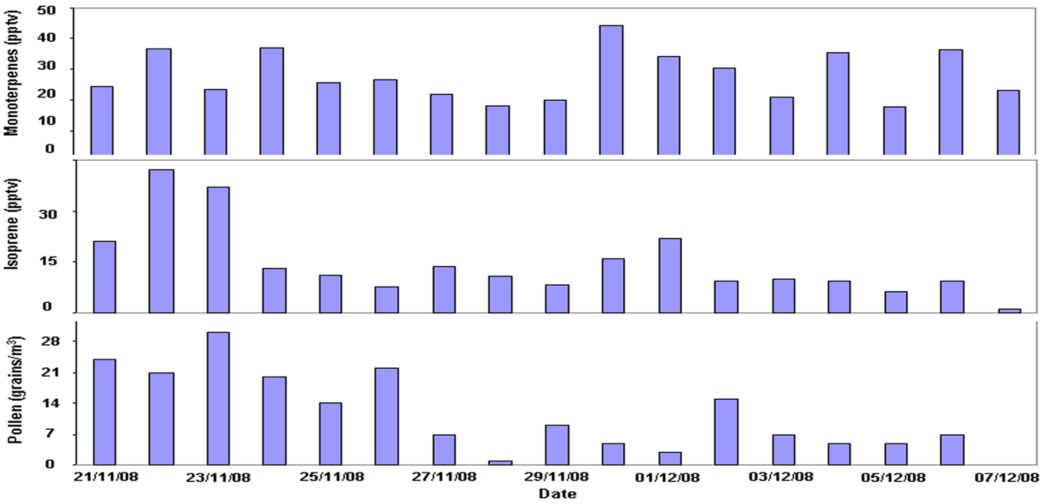


Fig. 3- 6 Average daily mixing ratios of isoprene, monoterpenes (α-pinene, limonene, 1, 8-cineole, camphor) and pollen concentration during the campaign

Fig. 3-6 shows average mixing ratios of isoprene and the monoterpenes (α-pinene, limonene, eucalyptol and camphor). These species are mainly biogenic and for comparison pollen data are included in the figure. In comparison to previous campaigns in both Tropical and summertime Boreal forest environments (Williams et al. 2007) the mixing ratios measured in DOMINO are low. Isoprene showed somewhat higher levels as well as diel cycles (see section 3.3.3) during the first week of the campaign. This supports the designation of the isoprene as biogenic emission. Interestingly, pollen counts show a similar temporal trend to isoprene, decreasing throughout the campaign (Fig 3-6). In contrast, daily average monoterpene levels remain stable throughout the campaign.

3.4.2 Wind dependency

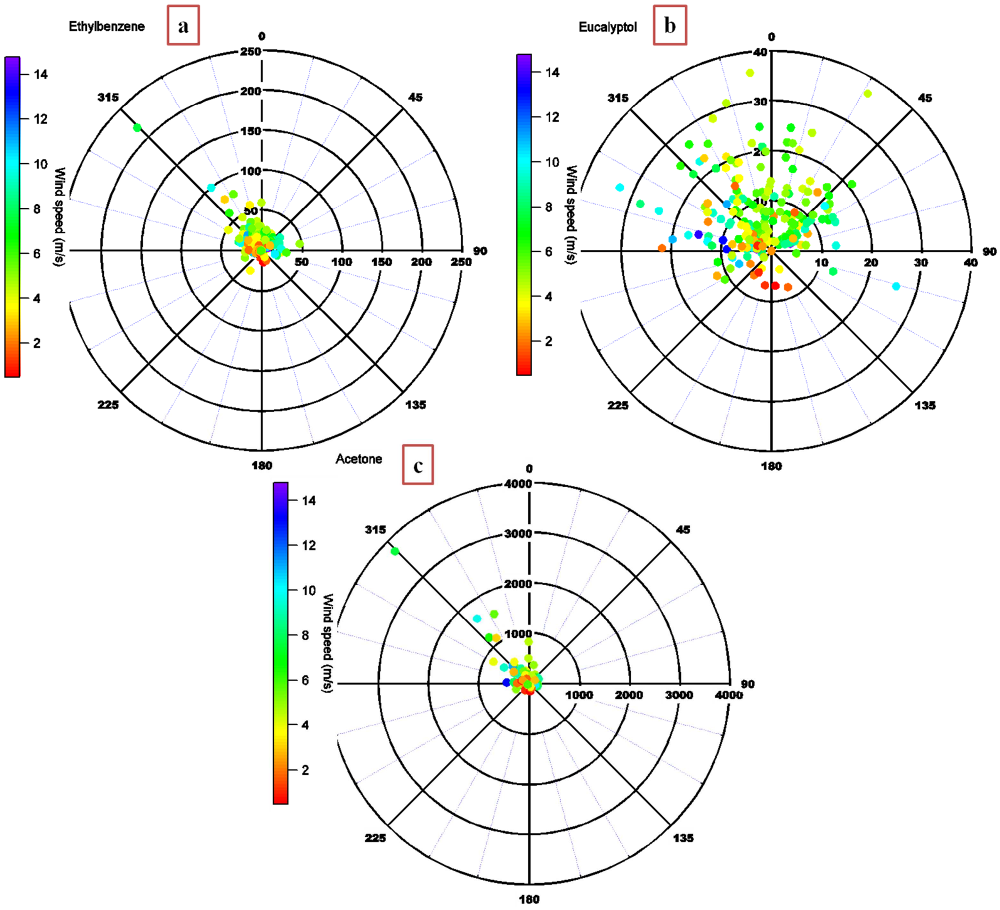


Fig. 3- 7 Dependence of VOC concentration on wind direction during the campaign is shown in the form of a wind rose: a: ethylbenzene (An anthropogenic species); b: eucalyptol (a biogenic species); c: acetone

The distinctly different source distribution patterns of the anthropogenic and biogenic VOC species can be clearly seen in Fig. 3-7 (a, b and c), which shows the dependence of VOC concentrations on wind direction and windspeed in the form of a windrose. Ethylbenzene is chosen to exemplify anthropogenic compounds (Fig. 3-7a), while eucalyptol is given as an examples of biogenic VOC (Fig. 3-7b). Ortho, meta and para xylene (not shown) show similar distributions to ethylbenzene while α-pinene (not shown) matches eucalyptol closely. For the biogenic VOCs there was no clear dependence of the measured mixing ratios on wind direction. This is unsurprising since the uniform stone pine forest extended for several tens of kilometers upwind of the site for all wind directions experienced during the campaign, see Fig. 3-1 and Fig.

3-4. For the anthropogenic species a clear dependence of the mixing ratio on wind direction was evident, the highest levels being measured in northwesterly winds. The most probable cause for the NW wind direction dependence are emissions from the city of Huelva and associated petrochemical processing plants which are located 25 km northwest of the measurement site. Huelva is also the closest conurbation to the site and its influence appears to dominate the larger but more distant city of Seville located 70 km to the northeast. In Fig. 3-7c the mixing ratios of acetone, also measured in this study, are plotted as a function of wind direction. Although acetone is known to be emitted from both biogenic and anthropogenic sources (Jacob et al., 2002) it is clear from the comparison with Figures 3-7a and 3-7b that the source distribution of acetone most closely resembles that of the anthropogenic species. Therefore we conclude that for this site, in winter, acetone mixing ratios may be considered to be predominantly influenced by anthropogenic sources.

3.4.3 Diel cycle

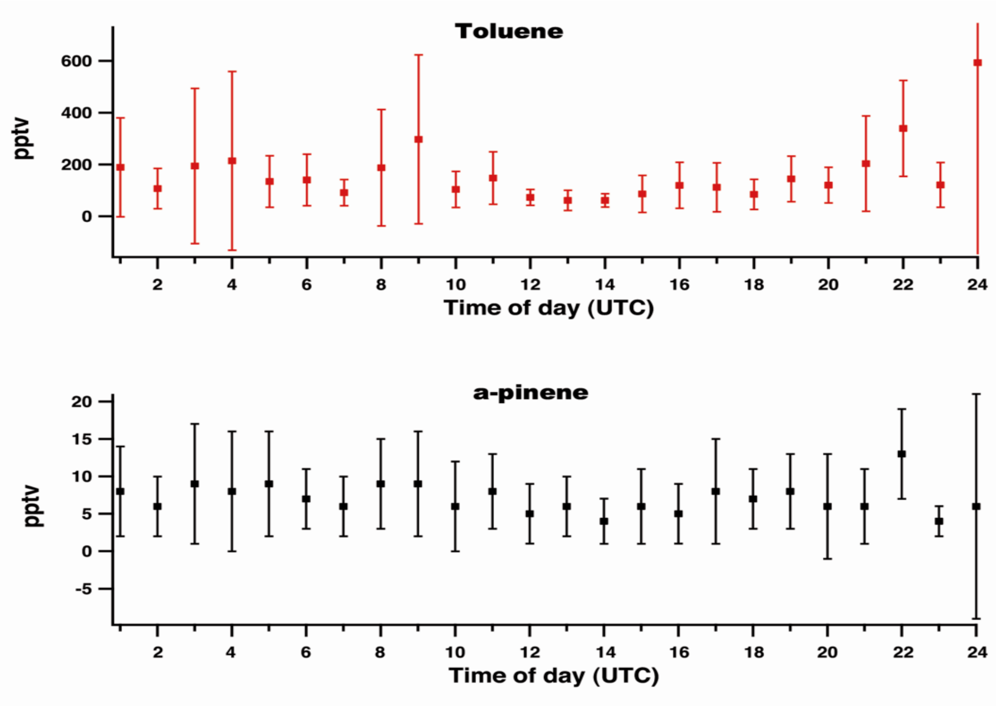


Fig. 3- 8 Campaign average diel cycles for selected anthropogenic (toluene) and biogenic (α-pinene) VOC (Note: In order to show the diurnal cycle clearly, we have truncated the standard deviation for the midnight. The high SD seen here was due to a single peak event.)

Figure 3-8 shows campaign average diel cycles for selected biogenic (α-pinene) and anthropogenic (toluene) VOC. The profiles of aromatic compounds (e.g. toluene) show elevated mixing ratios persisting from midnight to circa 3:00 UTC and a slightly decreasing before sunrise. Higher mixing ratios in the aromatic species from 7:00-8:00 UTC may be due to local traffic emission. After 8:00 UTC both biogenic and anthropogenic VOC mixing ratios were observed to decrease approximately exponentially, suggestive of a dilution effect of a deepening mixed layer. From 13:00 UTC until 21:00 UTC mixing ratios increased back to levels similar to those measured at 8:00 UTC, persisting thereafter for several hours. The daytime minimum in VOC mixing ratios measured at the site is likely to be caused by enhanced removal rates of the VOC by OH radicals which were estimated to reach maximum concentrations around 12:00-13:00 UTC (see section 3.5), and by variations of the mixed layer.

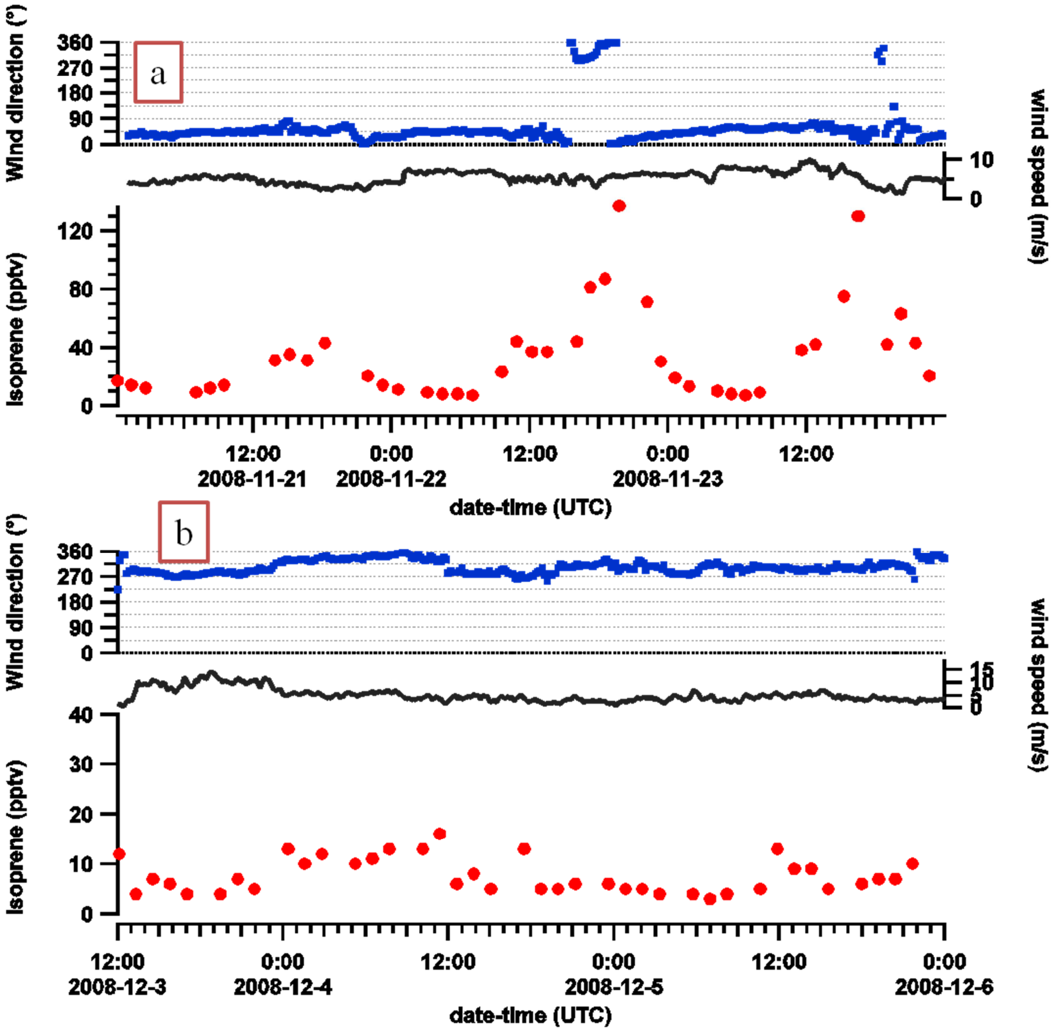


Fig. 3- 9 a: Isoprene observed when the wind came from northeast (direction of Seville); b: Isoprene observed when the wind came from northwest (direction of Huelva)

Biogenic α-pinene mixing ratios show high standard deviations (shown as vertical bars on graph) throughout the day and only a small difference between day and night. Slightly higher mixing ratios were observed around sunrise (7:00-8:00 UTC), sunset (16:00-18:00 UTC) and most of the night. The ambient mixing ratios of monoterpenes are influenced by the emission rate, the chemical sinks such as OH and ozone, and also by the height and stability of the boundary layer, i.e. the mixed layer. The slightly elevated mixing ratios of α-pinene observed during night time suggest a release of α-pinene from the storage pools of the needles that persists into the night when the mixed layer is low (Lerdau et al., 1997; Monson et al., 1995). It should be noted that the strength of this wintertime diel cycle is small in comparison to typical profiles taken in summer (e.g. Mckinney et al. 2011). Closer examination of the exponential decrease in mixing ratios of toluene and pinene observed between 10:00 and 14:00 revealed that the rate of decrease was independent of the OH lifetime of the species. Since VOC species with relatively slow OH reaction rates (e.g. toluene, OH lifetime ≈ 0.8 days) and those with faster rates (e.g. α-pinene, OH lifetime ≈ 2 hours) exhibit the same rate of decrease we conclude that the observed effect is dominated by the dynamically driven dilution caused by the deepening of the mixed layer.

The dominant tree species within Doñana National Park where the measurements were made, *Pinus pinea* L, is known mainly to emit monoterpenes, such as limonene, trans-β-ocimene, α-pinene and 1,8-cineole, but not isoprene (Davison et al., 2009; Kesselmeier et al., 1997; Owen et al., 1997; Sabillon and Cremades, 2001; Staudt et al., 1997; Staudt et al., 2000) . Therefore we assume that the higher isoprene mixing ratios observed at the beginning of the campaign are due to transport from emitting species further afield. This conclusion is supported by the isoprene diel cycle, see Figure 3-9a. While the time of maximum insolation was between 12:00-13:00 (UTC) and the maximum temperature between 13:00-14:00 (UTC), the peak values of isoprene were found at 16:00-18:00 (UTC). Previous studies have shown that isoprene maxima occur slightly (ca. 1 hour) after the maxima in light and temperature when OH levels have decreased and emissions are still high (e.g. McKinney et al. 2011). That the observed maximums are significantly later again suggests an isoprene source further upwind of the site (i.e. non-local). At the beginning of the campaign, the predominant wind direction was from the northeast. The transported air was advected from the direction of Seville and therefore would have passed over several other pine and eucalyptus forests, and orange groves, which emit isoprene before reaching the site (Street et al., 1997; Winters et al., 2009; Wolfertz et al., 2003). Fig. 3-9a shows the isoprene mixing ratio in the first 3 days of the campaign when the wind came from NE (direction of Seville) and highest isoprene levels were observed. However, when the wind came from the NW (direction of Huelva), the isoprene mixing ratio exhibited no clear diel trends (Fig. 3-9b).

3.4.4 Enantiomeric monoterpenes

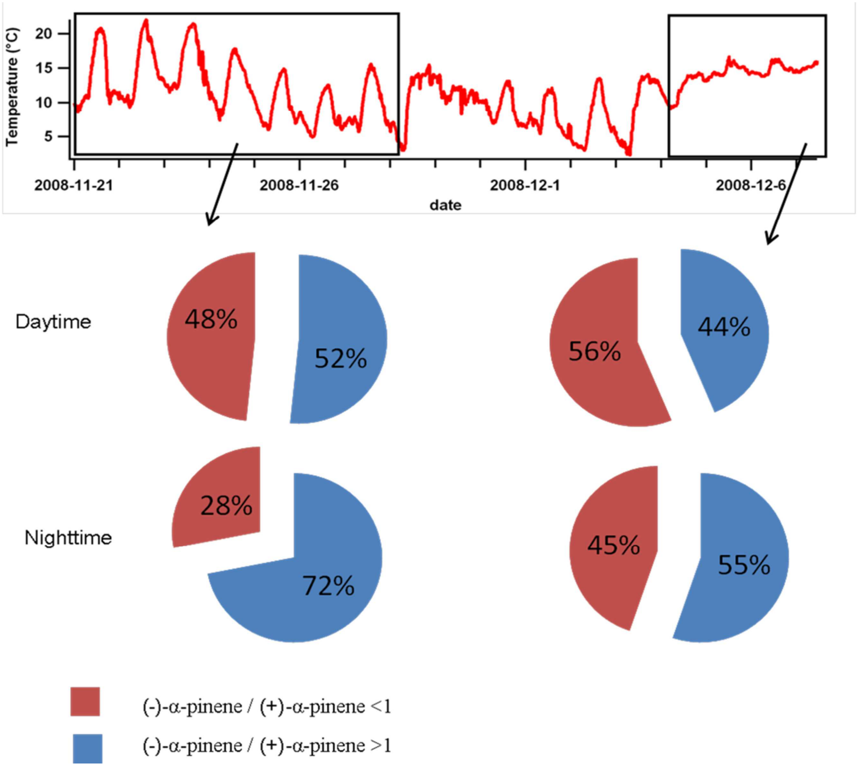


Fig. 3- 10 The distribution of (-)-α-pinene/ (+)-α-pinene within two distinct temperature regimes denoted by pink shading. The first regime shows clear diels cycles, the second a more constant temperature

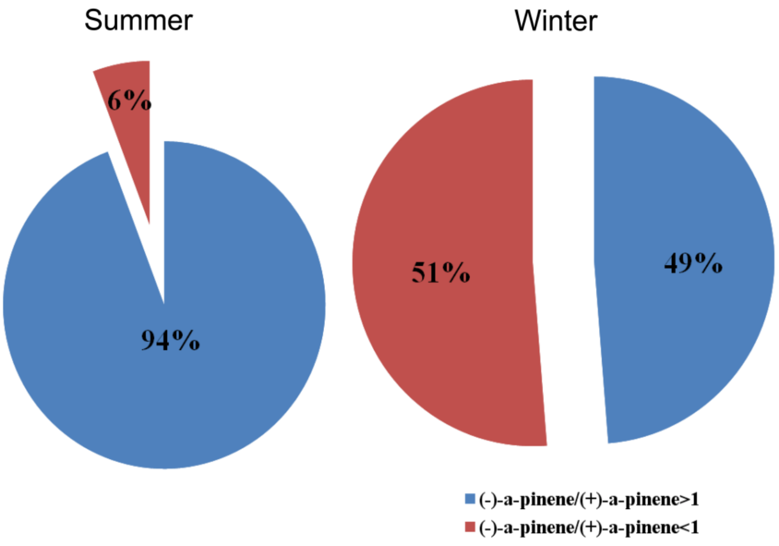


Fig. 3- 11 The daytime distribution of (-)-α-pinene/ (+)-α-pinene during summer time and winter time at the Atmospheric Sounding Station 'El Arenosillo'

In this section we examine the enantiomeric ratios of the monoterpenes from this

Mediterranean forest site. This is of interest since recently reported measurements of enantiomeric monoterpenes from the tropical rainforest and boreal forests (Williams et al. 2007) have shown surprisingly distinct ecosystem-wide enantiomeric signatures. In both tropical and boreal forests, α-pinene was found to be the most abundant monoterpene measured, and while (+)-α-pinene was always in enantiomeric excess over the boreal forest, (-)-α-pinene consistently predominated over the tropical rainforest. Fig. 3-10 shows the distribution ratio of the α-pinene enantiomers within the two distinct temperature regimes noted during the DOMINO campaign: namely an early period of clearly varying diel temperature cycles (21st - 28th November) and then a period of approximately constant temperature (4th - 7th December). At this Mediterranean pine forest site in November and December the (-)-α-pinene enantiomer was found to be in slight excess during the night time especially when there was a clear temperature diel cycle. This is in agreement with the reported (-)-/(+)-α-pinene enantiomeric ratio (e.g., 1.3) from the same plant species growing in Italy (Yassaa et al., 2001). There was no clear enantiomeric preference during daytime, however, (+)-α-pinene was in weak enantiomeric excess during the day time when ambient temperature remained approximately constant (from the 4th to 7th of December). Correlation coefficients for the measured biogenic VOC are shown in Table 3-2. A predominance of the (-)-α-pinene enantiomer, similar to that observed at night in this study, has been reported for daytime measurements over tropical rainforest (Williams et al. 2007). However, the rainforest campaign did not report any nighttime measurements with which to compare. Unlike the previously reported measurements from daytime tropical forest, the correlation of (-)-α-pinene with isoprene (r^2=0.43) from the Mediterranean site is significantly weaker than the correlation between the two α-pinene-enantiomers (r^2=0.75). It should be noted that the DOMINO measurements were made in winter and hence in a biologically quiescent period. Interestingly, subsequent daytime measurements made at the end of the following summer for comparison (21st -23rd September, 2009) showed a very strong preference to the (-)-α-pinene enantiomer (Fig. 3-11). The strongest correlations observed amongst the biogenic species during the DOMINO campaign were between camphor and (+)-α-pinene (r^2=0.8); and between (+)-α-pinene and (-)-α-pinene (r^2=0.75). Correlations of the other biogenic species with isoprene were generally weaker, (r^2<0.45), although interestingly the highest correlation coefficient with isoprene was that observed with (-)-α-pinene, again similar to the findings from the tropical rainforest (Williams et al. 2007).

Table 3- 2 Correlation coefficients (r^2) of biogenic species measured in the Stone pine forest in Southern Spain during the DOMINO campaign

	Isoprene	(-)-a-Pinene	(+)-a-Pinene	(-)-Limonene	1,8-Cineole	Camphor
Isoprene	1					
(-)-a-Pinene	0.421	1				
(+)-a-Pinene	0.256	0.749	1			
(-)-Limonene	0.326	0.621	0.517	1		
1,8-Cineole	0.244	0.503	0.618	0.358	1	
Camphor	0.161	0.602	0.8	0.386	0.552	1

3.4.5 OH estimation

In this section we examine the ratios of the anthropogenic VOC compounds more closely and exploit their variations to estimate the OH radical abundance. We then compare these VOC based estimates with an alternative approach to OH estimation using in-situ measured photolysis rates. VOC derived OH concentrations are calculated from the two different wind regimes (from Seville and from Huelva) as discussed in section 3.4.2 and shown in Fig. 3-9a and b. For this we adopt the photochemical method presented by Roberts et al. (1984), which uses a ratio of two aromatic compounds with significantly different lifetimes. This method assumes that the aromatic compounds used have negligible background levels and that reaction with OH radical is the only significant removal pathway from the atmosphere. Furthermore it critically assumes that the emission ratio is known and constant for all sources impacting the measurement location. Thus the mean OH concentration during the transportation could be calculated as follows:

$$\ln\left(\frac{C_a}{C_b}\right)_{t_2} - \ln\left(\frac{C_a}{C_b}\right)_{t_1} = (k_b - k_a) \times [\overline{OH}] \times (t_2 - t_1) \qquad (3.1)$$

where $(C_a/C_b)_{t1}$ and $(C_a/C_b)_{t2}$ are the ratio of two aromatic hydrocarbons at time $t_1$and t_2, k_a and k_b are the second order rate constants of the reaction of A and B with OH, and (t_2-t_1) is the transport time from the city source to the measurement site.

Previous studies of BTEX compounds have shown that the emission ratios of the isomers *m*-xylene and ethylbenzene are rather invariant from both traffic and industrial sources (Yassaa et al. 2006). Assuming these emission ratios to be applicable to Huelva and Seville we may exploit the measurements of ortho-, meta-, para-xylene and ethylbenzene according to the method of Roberts et al. (1984) in order to estimate the daytime average OH concentration since emission. It should be noted that in most VOC studies to date such an approach is not possible due to the co-elution of *meta*- and *para*-xylenes on all commonly used chromatography columns. The xylenes are, however, excellent candidates for such photochemical studies as they have relatively short lifetimes (hours) which limit any potential background in-mixing effect, and similar sources with little variability, see Table 1-1. Despite possessing similar structures the xylenes and ethylbenzene have significantly different reaction rates with OH owing to the different position of the alkyl groups on the aromatic ring. The reaction rate coefficients for these species and a lifetime based on the average measured daytime OH concentration are given in Table 1-1.

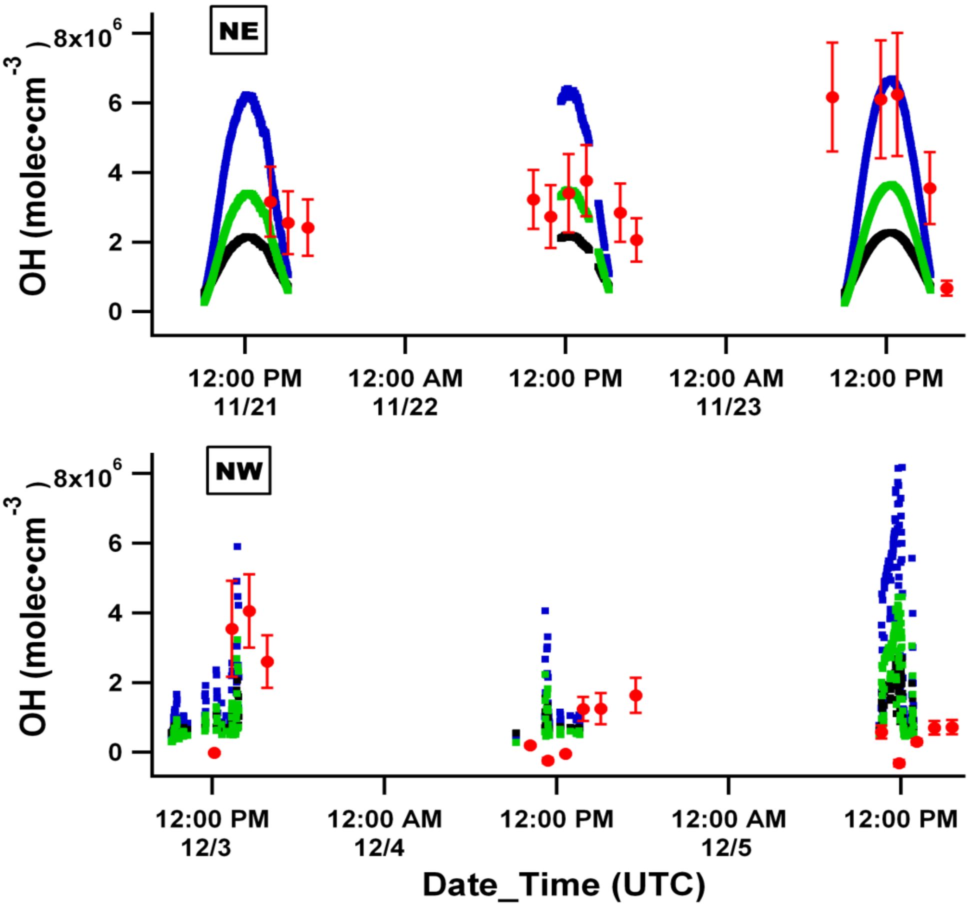


Fig. 3- 12 Estimated OH concentration in the two wind sectors shown in Fig. 3-9. The red dots show the OH concentration estimated from the ratio of ethylbenzene (lifetime 0.6 days) to *m*-xylene (lifetime 4.4 hours). Error bars denote the overall uncertainty calculated based on 20% error on the emission ratio, standard deviation of the wind speed over the averaging time, and 15% total error in the measurement. The JNO_2 estimated OH concentration in the two different wind sectors is shown as followed: the blue dots show OH concentration derived from the MINOS coefficients, the green dots show OH concentration derived from the POPCORN coefficients, the black dots show OH concentration derived from the BERLIOZ coefficients

In this study, for the first time, we compare the aforementioned VOC derived OH estimates with an additional approach based on measurements of the photodissociation frequency of NO_2 (JNO_2) (Ehhalt and Rohrer, 2000; Rohrer and Berresheim, 2006). In the DOMINO campaign JNO_2 was measured using a commercial filter radiometer (Meteorologieconsult GmbH, Germany). The JNO_2 was derived from the upward facing sensors. This photolysis rate was related to JO^1D (based on latitude and longitude of the site) using the 4.1 version of the NCAR-TUV model (http://cprm.acd.ucar.edu/Models/TUV/Interactive_TUV/). Note that in this concept JO^1D provides a proxy for primary OH formation through the photolytic production of O (^1D) and subsequent reaction with water vapor, yielding 2OH. The expression derived for JO^1D as a function of JNO_2 at the DOMINO site was:

$$JO^1D = -3.9908\times10^{-8} + 0.0001JNO_2 - 0.18545JNO_2^{\;2} + 57.609JNO_2^{\;3} \quad (3.2)$$

Minor corrections due to ozone columns and temperature variations are neglected in this case. Having derived JO^1D for the measurement campaign we use the relationship between OH and JO^1D (Rohrer and Berresheim, 2006) to estimate in-situ OH. In the aforementioned paper various coefficients have been derived for the best fit to OH measurements depending on the campaign conditions. In Fig. 3-12 we compare VOC based OH estimations to the OH derived from equation:

$$OH = a\times\left(\frac{JO^1D}{10^{-5}\bullet s^{-1}}\right)^b + c \quad (3.3)$$

using coefficients from: POPCORN (54°N, 12°E) and BERLIOZ (53°N, 13°E) both summer campaigns in central Germany; and MINOS a campaign on Crete (35°N,25°E) OH values have been derived. Fig. 3-12 shows the estimated daytime OH concentration according to ratios of ethylbenzene to *m*-xylene in two wind sectors (northeast and northwest) with the photolysis rate derived OH values according to the POPCORN, BERLIOZ and MINOS coefficients. The red dots show the OH concentration estimated from the ratio of ethylbenzene (lifetime ~0.6 days) to *m*-xylene (lifetime ~4.4 hours). Error bars denote the overall uncertainty calculated based on 20% error on the emission ratio, standard deviation of the wind speed over the averaging time, and 15% total error in the measurement. The JNO_2 estimated OH concentration in the two different wind sectors is shown as followed: the blue dots show OH concentration derived from the MINOS coefficients, the green dots show OH concentration derived from the POPCORN coefficients, the black dots show OH concentration derived from the BERLIOZ coefficients. All the coefficients are taken from Rohrer and Berresheim (2006). For the NE sector data, the VOC derived estimates correspond best with the POPCORN coefficient derived OH data for the first two days and then for the MINOS derived OH for the last day. For the NW sector data conditions were more overcast resulting in less continuous profiles for the photolysis derived data. Here again the comparison between derived OH values is inconsistent, the first day showing VOC based estimates to be higher than photolysis based estimates while on the subsequent two days this situation is reversed.

It is interesting to note that the effect of more photochemically aged air being mixed in from above during the transport from source to site would be to cause the OH to be overestimated by the VOC method. On December 3rd the VOC derived OH estimate is significantly higher than that of the photolysis method. From Fig. 3-9b, it can be seen that comparatively high windspeeds were experienced on this day. These strong winds are likely to have enhanced mixing of the surface layer with more aged air above causing the overestimate of the OH by the VOC based method. Another shortfall of the VOC method is that it is very reliant on assumed emission ratios. It should be noted that OH calculated using the *p*-xylene to *m*-xylene ratio (not shown) yielded unrealistic negative values. This suggests that emissions from non-traffic sources of one or both of these species have rendered the estimation method void. This is indeed likely since adjacent to Huelva is a very large petrochemical activities. When considering the photolysis derived OH coefficients one may reasonably expect those of the MINOS campaign to be most appropriate to the DOMINO campaign based on a comparison of latitude. From this limited comparison of two estimation methods this appears not to be the case. This corroborates that although the relationship between JO^1D and OH is robust, the coefficients can differ substantially for different locations and most importantly conditions. In turn this implies that OH formation is controlled both by primary production and recycling through reactions with NO_x and VOCs, the latter being specific for local atmospheric chemical conditions (Lelieveld et al., 2002; Lelieveld et al., 2008).

3.4 Conclusions and outlook

An online TD-GC-MS setup was used to measure ambient VOC mixing ratios on the coast of southern Spain during the DOMINO field campaign 2008. The use of beta-cyclodextrin column allowed a successful measurement of enantiomeric monoterpenes and geometrical xylene isomers. Mixing ratios of biogenic species were generally low, consistent with the low winter seasonal emission rates of *Pinus pinea* L. Anthropogenic VOCs were found to be generally higher than biogenic VOCs. High mixing ratios of anthropogenic VOCs were related to transport of air from the nearby city Huelva (to the west) which has a sizeable industrial quarter and high vehicle density and to Seville (to the northeast) which has a population of ca. 700,000. In winter, the (-)-α-pinene enantiomer was found to be in slight excess during the nighttime, but there was no clear enantiomeric preference during daytime. However, (-)-α-pinene strongly predominated during daytime in summer time when the mixing ratios of the α-pinene enantiomers were also higher. This is the first study of the seasonal variation in enantiomeric ratio for a forest ecosystem. The result suggested that the enantiomeric distribution markedly different in the summer and winter. Here we have compared two empirical methods for deriving OH levels in the field, namely by application of hydrocarbon ratios and from measured JNO_2 with an empirical relationship to JO^1D and OH from previous campaigns. These results highlight how such estimates depend critically on the source assumptions. For campaigns such as this in which the site is impacted by several strong but distinct hydrocarbon source types, the hydrocarbon based OH estimation method is of little practical value. The radiative approach of estimating OH using NO_2 is shown to be similarly uncertain, being also highly dependent on the choice of input coefficients. In short, when investigating photochemical processes related to OH there is no substitute for an accurate, direct in-situ measurement of OH.

Chapter 4

HUMPPA-COPEC 2010

Hyytiälä **U**nited **M**easurement of **P**hotochemistry and **Pa**rticles –

Comprehensive **O**rganic **P**article and **E**nvironmental **C**hemistry

GC-MS Measurements

Reproduced with permission from

Yassaa, N., Song, W., Lelieveld, J., Vanhatalo, A., Back, J., and Williams, J.: Diel cycles of isoprenoids in the emissions of Norway spruce, four Scots pine chemotypes, and in Boreal forest ambient air during HUMPPA-COPEC-2010, Atmos Chem Phys, 12, 7215-7229, DOI 10.5194/acp-12-7215-2012, 2012

Parts of the results have been used in the publication:

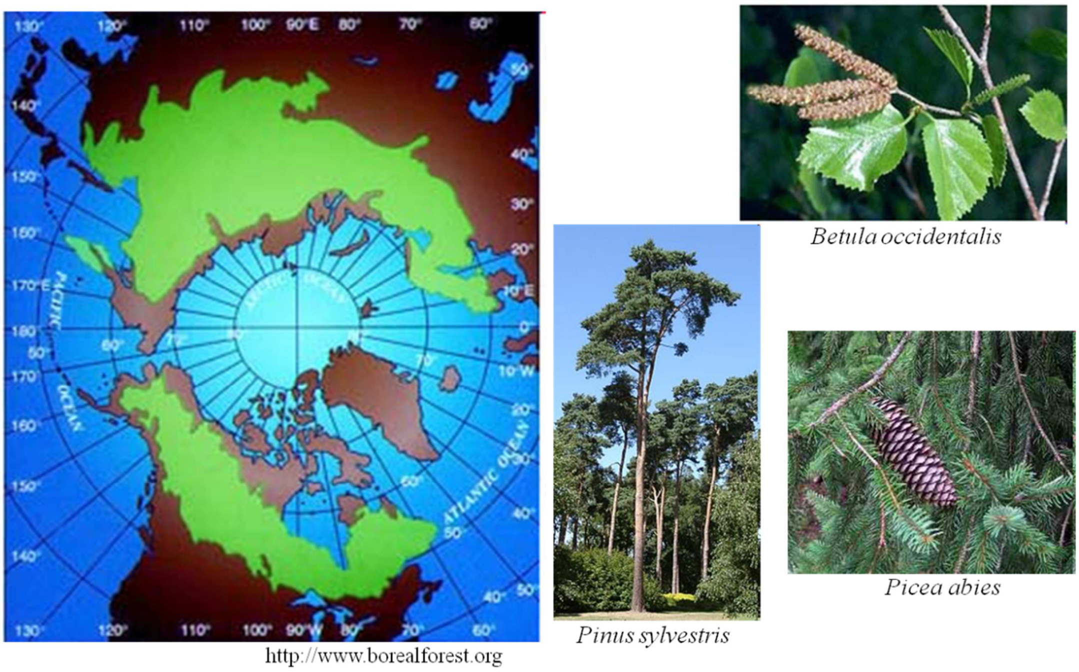
Williams, J., Crowley, J., Fischer, H., Harder, H., Martinez, M., Petaja, T., Rinne, J., Back, J., Boy, M., Dal Maso, M., Hakala, J., Kajos, M., Keronen, P., Rantala, P., Aalto, J., Aaltonen, H., Paatero, J., Vesala, T., Hakola, H., Levula, J., Pohja, T., Herrmann, F., Auld, J., Mesarchaki, E., Song, W., Yassaa, N., Nolscher, A., Johnson, A.M., Custer, T., Sinha, V., Thieser, J., Pouvesle, N., Taraborrelli, D., Tang, M.J., Bozem, H., Hosaynali-Beygi, Z., Axinte, R., Oswald, R., Novelli, A., Kubistin, D., Hens, K., Javed, U., Trawny, K., Breitenberger, C., Hidalgo, P.J., Ebben, C.J., Geiger, F.M., Corrigan, A.L., Russell, L.M., Ouwersloot, H.G., de Arellano, J.V.G., Ganzeveld, L., Vogel, A., Beck, M., Bayerle, A., Kampf, C.J., Bertelmann, M., Kollner, F., Hoffmann, T., Valverde, J., Gonzalez, D., Riekkola, M.L., Kulmala, M., Lelieveld, J.: The summertime Boreal forest field measurement intensive (HUMPPA-COPEC-2010): an overview of meteorological and chemical influences. Atmos Chem Phys 11(20), 10599-10618 (2011). doi:DOI 10.5194/acp-11-10599-2011

Ebben, C.J., Martinez, I.S., Shrestha, M., Buchbinder, A.M., Corrigan, A.L., Guenther, A., Karl, T., Petaja, T., Song, W.W., Zorn, S.R., Artaxo, P., Kulmala, M., Martin, S.T., Russell, L.M., Williams, J., Geiger, F.M.: Contrasting organic aerosol particles from boreal and tropical forests during HUMPPA-COPEC-2010 and AMAZE-08 using coherent vibrational spectroscopy. Atmos Chem Phys 11(20), 10317-10329 (2011). doi:DOI 10.5194/acp-11-10317-2011

Kampf, C. J., Corrigan, A. L., Johnson, A. M., Song, W., Keronen, P., Königstedt, R., Williams, J., Russell, L. M., Petäjä, T., Fischer, H. and Hoffmann, T.: First measurements of reactive -dicarbonyl concentrations on PM2.5 aerosol over the boreal forest in Finland during HUMPPA-COPEC 2010 – source apportionment and links to aerosol aging. Atmos. Chem. Phys. Discuss., 12, 723–751 (2012) doi:10.5194/acpd-12-723-2012

Within the ACP special issue: "Summertime boreal forest atmospheric chemistry and physics (HUMPPA-COPEC 2010)"

4.1 Introduction


Betula occidentalis

Pinus sylvestris

Picea abies

http://www.borealforest.org

Fig. 4- 1 A map of global boreal forest and pictures of the main plant species

Looking at the Earth from space, a green band spanning the uppermost Northern Hemisphere can be seen clearly. This is the boreal forest, also known as taiga, which extends in a broad band across North America and Eurasia (Fig. 4-1). The global boreal forest ecosystem covers approximately 15 million km^2 between 50 and 65 °N, about 8% of the Earth´s land surface, 27% of the world´s forest (FAO, 2010) presently and harbor half of the world’s remaining intact wilderness tracts. Many plant species are found in the boreal forest, but the most dominant ones are conifers such as Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*), as well as some broad leaf deciduous trees like birch (e.g. *Betula occidentalis*) (see plant pictures in Fig. 4-1).

The boreal forest ecosystem stores vast amounts of carbon, and their large annual net primary production (ca. 3.2 Pg) leads to a release of biogenic VOCs (Hakola et al., 2000; Hakola et al., 2003; Hakola et al., 2006; Tarvainen et al., 2005). Terpenenoids like monoterpenes can lead to aerosol formation through rapid oxidation to less volatile species in the troposphere (their reaction rates can be seen in Table 1-1). The Boreal forest contains almost 10% of the total carbon in the terrestrial ecosystem and has no parallel in the Southern hemisphere because there is little land area in the comparable latitude zone. In many places more than half of the sub-micron aerosol mass is dominated by biogenic VOCs (Hallquist et al., 2009). Thus, the boreal forest ecosystem is a very important source of atmospheric secondary organic aerosols

(SOA) from biogenic emissions (O'Dowd et al., 2002; Tunved et al., 2006). In the future, the global temperature is predicted to increase due to increased CO_2 concentration in the atmosphere (IPCC, 2007). As a result, the vegetation productivity may also increase give rise to more BVOCs that will enhance aerosol formation. This would result in a temperature decrease (a negative feedback) due to increased reflection of sunlight. Therefore the boreal forests, as sinks of CO_2 and sources of SOAs play an important role in global climate change (Carslaw et al., 2010; Kulmala et al., 2004). In order to be better understood the role of boreal forest for the climate change, it is important to conduct intensive field measurements. In particular the summer time needs to be well characterized as it represents the yearly maximum in VOC emissions and oxidants. Moreover, to date most studies in this region have focused on spring when nucleation events occur most frequently (Back et al., 2005; Bonn et al., 2008; Eerdekens et al., 2009; Lappalainen et al., 2009).

The HUMPPA-COPEC 2010 (Hyytiälä United Measurement of Photochemistry and Particles – Comprehensive Organic Particle and Environmental Chemistry) campaign was focused on comprehensively characterizing the atmospheric physics and chemistry over a Boreal forest site in summer. As part of this study an online TD-GC-MS system and an offline solid-phase microextraction (SPME)-GC-MS were used to characterize the enantiomeric and non-enantiomeric monoterpenes and isoprene emission above the forest canopy in ambient air, and directly from trees themselves via branch emission enclosures, respectively. Section 4.2 will describe the meteorology experienced at the site and the surrounding land cover; the detailed sampling and analysis methods are given in section 4.3; in section 4.4 both biogenic and anthropogenic VOCs measured during the campaign will be discussed, i.e. diel cycles of selected compounds, enantiomeric determinations and enantiomeric enrichment of both chamber and ambient study; a summary of this study is given in section 4.4.

4.2 Site description

The measurements took place from 12th of July-12th of August 2010 at the Boreal forest field station, SMEAR II (Station for Measuring Forest Ecosystem – Atmosphere Relation) in Hyytiälä, southern Finland (61° 51' N; 24° 17' E, 181m a.s.l., see Figure 4-2). The forest around the measurement site consists predominantly of pine, spruce (e.g. *Pinus sylvestris*, *Picea abies*) and some mixed forest (birch, willow). The height of the forest canopy was generally 20-21m though the land surrounding the site was slightly undulating so that the forest crown was not in one horizontal plane. These trees are known to emit significant quantities of reactive organic trace gases (e.g. monoterpenes) to the atmosphere as a function of temperature (Fuentes et al., 2000) and to a lesser extent light (Back et al., 2005;

Tarvainen et al., 2005).

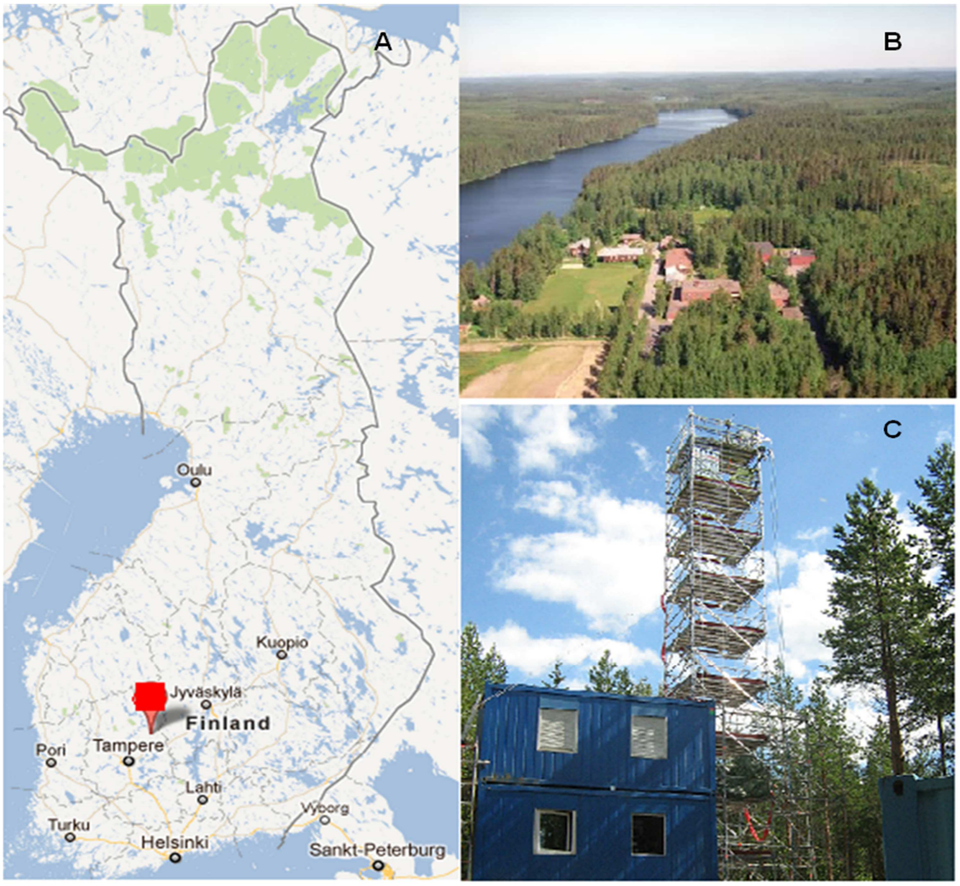


Fig. 4- 2 the Map of Finland (A), the red dot shows the location of SMEAR II station, B is the picture looking of the surrounding of the station, and C is the picture of the measurement container and tower

4.2.1 Site meteorology

The meteorological parameters (temperature, wind direction, wind speed, relative humidity and air pressure) measured at 33.6 m at the site during the campaign are shown in Fig. 4-3, the data is shown as 5 minutes averages. The Hyytiälä site was influenced by a high pressure region centered to the east of Finland and a sequence of weak frontal systems for the campaign period (July-August 2010). Pressures varied between 980-1005 hPa. Temperatures measured at the site in this period were anomalously high (T_{max}=31.8, T_{min}=10.1, T_{ave}=20.1 °C). This was an extremely hot summer in Finland and it established a new record for the temperature in Joensuu on 29th July when 37.2°C was reached. The previous high dated back to 1914. The measurements during these high temperature conditions may hold clues about the forest response to future warmer temperatures associated with climate change. The temperatures exceeded 25°C for several periods (e.g. 10-14th July, 27th-30th July) during the campaign. However, there were cooler periods (e.g. 23-25th July, average temperature 14°C) experienced during the campaign period as well, in particular associated with air from the northwest sector. It was generally dry for the summer, precipitation was low (< 2 mm/day) except for July 15th, July 27th and August 4th when heavier rain events were experienced at the site. On several occasions these rain events and associated lightning caused power disruption at the site, which is why there are a few gaps in the data set. It can be seen from Fig. 4-3 that temperature and relative humidity exhibited regular diel cycles throughout the campaign with peak values near local noon. Similar cycles can also be seen in the wind speed whereas the wind direction is driven primary by synoptic scale features (frontal passages).

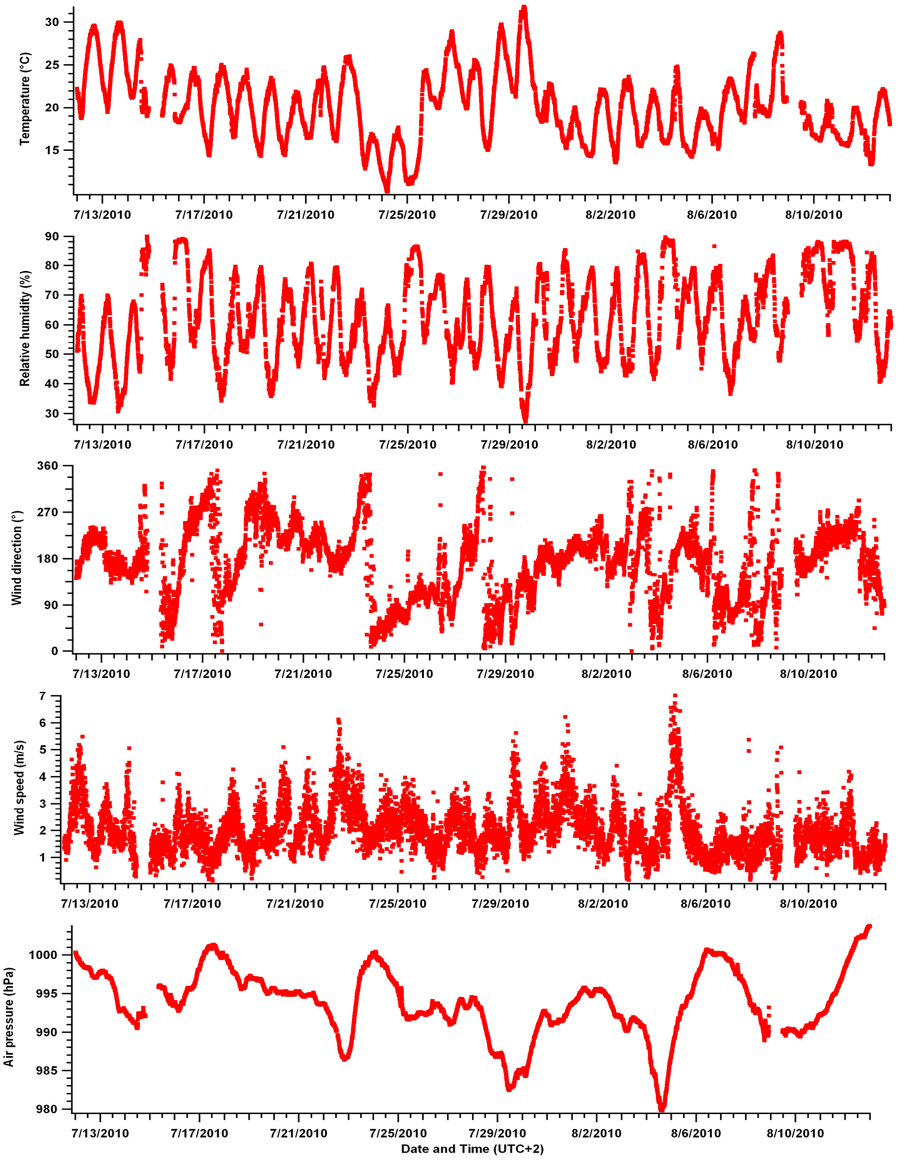


Fig. 4- 3 Meteorological parameters (temperature, relative humidity, wind direction, wind speed and air pressure) measured at 33.6m in 5 minutes averages during July 12th to August 12th, 2010

4.2.2 Land use

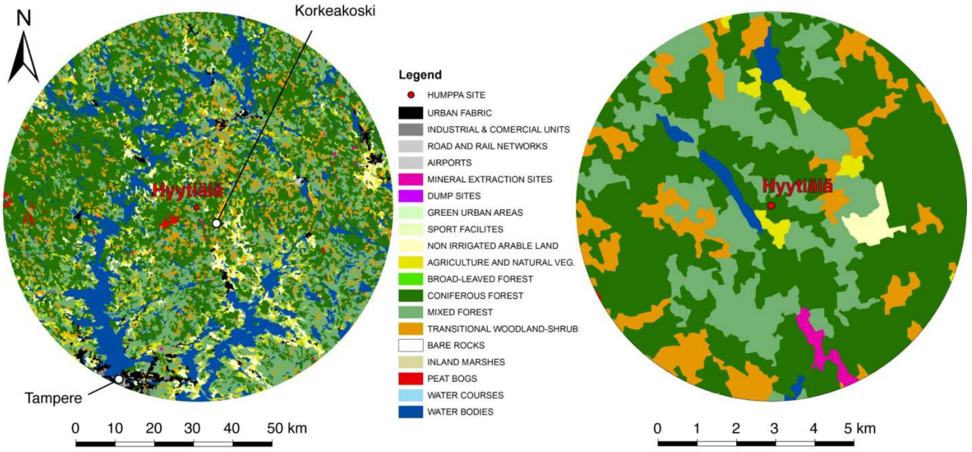


Fig. 4- 4 Land use in the surrounding areas of the measurement site with the radii of 50 km and 5km (Williams et al., 2011)

Fig. 4-4 (provided by Prof. Pablo J. Hidalgo) shows the distribution of land use within 50 and 5 km of the Hyytiälä site. The data used for the finger is from Corine land cover database (EEA Technical Report 2007), and were edited using the ArcGis 9.2 (Esri ©) Geographic Information Systems (GIS) software. These radii were chosen because of the typical summertime atmospheric lifetimes (2 hours) of α-pinene which is one of the most abundant biogenic species at the site. The lifetime calculation was based on the average OH concentration of 1x10^{6} and ozone of 1x10^{12} molecules·cm^{-3} (40 ppbv), and the laboratory measured rate coefficients(Atkinson and Arey, 2003b) shown in table 1-1. Wind speeds measured at 16.8 m during the campaign varied between 0.1-7.0 m·s^{-1} with an average of 2 m·s^{-1}. Thus the distances covered approximately to 5 km and 50 km at these wind speeds within 2 hours. As can be seen from Fig. 4-5, on both scales the surrounding area is mainly covered by vegetation. It should be noted that exact speciation is not given in this dataset. The only one significant urban centre which is visible on the 50km plot is Tampere (pop. 211 000) lying Southwest of the site. There is also a small village named Korkeakoski which has a saw mill and pellet factory in the southeast sector approximately 10 km away from the measurement site. The industrial VOC emissions originate from drying and processing softwood, mainly pine and spruce. The annual processed log volume in the local wood industry is ca. 950 000m^{3} (Lappalainen et al., 2009). Tables 4-1 and 4-2 give the detailed information about area covered by specific land use types within 50km and 5km of Hyytiälä respectively. The data is presented as a total and as a function of the wind sectors. From the 50km scale analysis, the coniferous forest and mixed forest account for over 65% of the land use surrounding Hyytiälä. Water bodies are also significant within the region comprising some 15% of the area within

50km. The northwest sector (corresponding to the prevailing wind) has the highest percentage of coniferous forest. This analysis is also in agreement with Tunved et al. (2006) who identified the NW sector as representing the pristine boreal forest with minimum anthropogenic influence. The southwest sector shows the largest percentage of urban fabric (4.3%), although this is still quite small in comparison to the combined total of coniferous and mixed forest. The dominance of the forest cover also extends to the southeast sector, although, this area has a slightly higher percentage of agriculture and arable land. Within 5 km of Hyytiälä the coverage of coniferous and mixed forest increases to approximately 80% in all sectors. This analysis shows that VOCs measured at the site will be most probably primarily influenced by biogenic sources.

Table 4- 1 Land use within 50km of the measurement site (Williams et al., 2011)

CLC code	Land use	50 km radius	%	NW	%	NE	%	SW	%	SE	%
112	URBAN FABRIC	147059823	1.87	8561787	0.44	35681430.1	1.82	84117096.3	4.29	18699326	0.95
121	INDUSTRIAL & COMERCIAL UNITS	23263609.3	0.3	310715	0.02	5679722	0.29	15786314.9	0.8	1486856.4	0.08
122	ROAD AND RAIL NETWORKS	1078139.48	0.01	-	0	-	0	1078139.6	0.05	-	0
124	AIRPORTS	3140464	0.04	-	0	2672769.4	0.14	467694.5	0.02	-	0
131	MINERAL EXTRACTION SITES	5397018	0.07	371601	0.02	2565526.7	0.13	952705.9	0.05	1507183.9	0.08
132	DUMP SITES	528365	0.01	-	0	-	0	528365.1	0.03	-	0
141	GREEN URBAN AREAS	2230216	0.03	-	0	-	0	2230217.3	0.11	-	0
142	SPORT FACILITES	1449950	0.02	317402	0.02	-	0	1132547.7	0.06	-	0
211	NON IRRIGATED ARABLE LAND	266247547	3.39	49464687	2.52	37493522.2	1.91	54722419.6	2.79	124560200	6.35
243	AGRICULTURE AND NATURAL VEG.	485324492	6.18	93758713.5	4.77	105836678	5.39	135220937	6.89	150493517	7.67
311	BROAD-LEAVED FOREST	3238747	0.04	1371977	0.07	1004467.2	0.05	862303.1	0.04	-	0
312	CONIFEROUS FOREST	3049435630	38.83	1057374360	53.84	795724597	40.52	642657656	32.74	553564167	28.2
313	MIXED FOREST	2070770468	26.37	343985492	17.51	530578014	27.02	523612082	26.68	672539186	34.26
324	TRANSITIONAL WOODLAND-SHRUB	547784642	6.97	111991924	5.7	211764041	10.78	114194451	5.82	109799004	5.59
332	BARE ROCKS	253594	0	253594	0.01	-	0	-	0	-	0
411	INLAND MARSHES	5544568	0.07	832045	0.04	303816.7	0.02	401174.9	0.02	4007531.8	0.2
412	PEAT BOGS	20906778	0.27	6261990	0.32	1687807.5	0.09	11745021.6	0.6	1209678.3	0.06
511	WATER COURSES	1143821	0.01	337685	0.02	806135.5	0.04	-	0	-	0
512	WATER BODIES	1219163143	15.52	288842593	14.71	232144854	11.82	373204642	19.01	324953469	16.56
TOTAL		7853961015	100	1964036565	100	1963943382	100	1962913768	100	1962820117	100

Table 4- 2 Land use within 5km of the measurement site (Williams et al., 2011)

CLC code	Land use	5 km radius	%	NW	%	NE	%	SW	%	SE	%
131	MINERAL EXTRACTION SITES	759476.8	1	-	-	-	-	-	-	759476.8	3.9
211	NON IRRIGATED ARABLE LAND	993627.8	1.3	-	-	124181.5	0.6	-	-	869446.7	4.4
243	AGRICULTURE AND NATURAL VEG.	1380030.9	1.8	329414.9	1.7	655524.6	3.3	138063.5	0.7	257028.4	1.3
312	CONIFEROUS FOREST	44814908.5	57.1	9620829.1	49	12241988.6	62.3	9901811.2	50.4	13050294.3	66.5
313	MIXED FOREST	18439426.1	23.5	6105694.9	31.1	4120920.1	21	4852368.5	24.7	3360450.7	17.1
324	TRANSITIONAL WOODLAND-SHRUB	10553201.9	13.4	2500133.5	12.7	2314404.8	11.8	4535634.9	23.1	1203032.6	6.1
412	PEAT BOGS	12096.1	0	-	-	-	-	12096.1	0.1	-	-
512	WATER BODIES	1584947.7	2	1077058.9	5.5	177866.9	0.9	194011.8	1	136011.6	0.7
TOTAL		78537715.8	100	19633131.4	100	19634886.4	100	19633986	100	19635741.2	100

4.3 Sampling and analysis

4.3.1 Ambient online measurements

The inlet line of the online TD-GC-MS instruments (see Chapter 1 (1.3) for further details) was set on the HUMPPA tower (24m), approximately 2-3m above the canopy top. The main sampling line was a 30 m, 9.6 cm i.d. Teflon line through which ambient air was drawn constantly at a flow rate of 7 L min^{-1}. The residence time was therefore circa 23 seconds. Air was drawn into the cold trap through a 3.175 mm Teflon line at a rate of 60ml·min^{-1} using a membrane pump. The sampling time was 30 min. More detailed sampling and analysis parameters are given in Chapter 1 (section 1.3). Blanks were taken 7 times during the campaign and showed no high levels of the compounds discussed. Calibration was performed every 6-7 samples using a 16 compound VOC standard (NPL, UK) which included the separate enantiomers of several species in the range of 2 ppbv. Laboratory multipoint calibrations were completed prior to the campaign and revealed a good linear dependency of peak area to the respective compound concentration.

4.3.2 Branch cuvette measurements

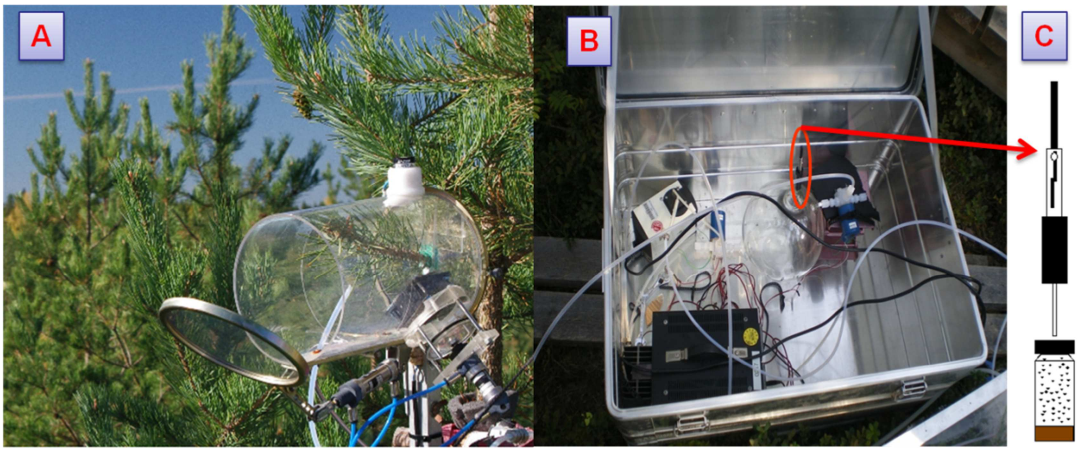


Fig. 4- 5 The encloure chamber set up for the plant direct emission measurement

In addition to the in-situ measurements of ambient gas phase monoterpenes, several branch cuvette enclosure systems were employed to measure the emission fluxes of monoterpenes and sesquiterpenes from several chemotypes of Scots pine and a spruce tree near the HUMPPA tower. This enabled the variations in the ambient concentrations and enantiomeric ratios to be compared with emissions directly from specific tree type sources.

The measured trees with an average height of 14 m were all growing in a natural forest environment. The dynamic branch enclosure chamber was installed at a height of approximately 13m from four branches belonging to four different chemotypes of Scots pine, and one branch from Norway spruce. A picture of the enclosure chamber is shown in Fig. 4-6 A.

The volume of the cylinderical Teflon enclosures was approximately 20 L and they were equipped with inlet and outlet ports and a thermometer inside the enclosure. The cover of the enclosures was made of transparent Teflon film. The photosynthetically active photon flux density (PPFD) was measured just above the enclosure. The flow through the enclosure was about 4 L per minute. Ozone was removed from the inlet air using MnO_2-coated copper nets (Pollmann et al., 2005). During the campaign a newly developed method based on sampling with SPME and analysis with (GC-MS) (Yassaa et al., 2010) has been used. The air exiting the plant cuvette chamber was continuously flushing the SPME chamber (Fig. 4-5 B) which consisted of a 5 L glass chamber containing a small septum (Sigma–Aldrich, Supelco, Germany) in the middle as well as two 0.64 cm (¼ inch) glass ports (inlet and outlet) connected to Teflon stopcocks. After a steady state was attained (minimum flushing time 1 hour, the stopcocks were closed isolating the collected air. The terpenes were sampled from the glass chamber by piercing the septum and exposing the SPME fibre (65 µm DVB-PDMS fibre coating, Sigma–Aldrich, Supelco, Germany) to the equilibrated air for a 20 min (Fig. 4-5 C). After sampling, the system was again flushed by re-opening the two stopcocks. At the same time, the SPME needle was introduced into the split/splitless injector of the gas chromatograph. A glass inlet liner with a narrow internal diameter (0.75 mm I.D., Supelco) was used in order to improve the GC resolution and the peak shape. Desorption was achieved in splitless mode at 250 °C for 5 min. These settings were found to be sufficient for a quantitative desorption of all analytes studied. This was established by subjecting the analysed fibre to a second desorption and observing no carry-over peaks. The DVB-PDMS response was calibrated under the same conditions in the glass SPME sampling chamber using a certified calibration gas (NPL, Teddington Middlesex, UK). The analysis was conducted using the same procedure as online measurements which were described in details in chapter 1 (1.3).

In order to determine the emission rates of terpenoids from each plant branch, air samples were collected onto SPME fibres from both the inlet and outlet ports which were sequentially connected to the SPME chamber. The emission rate is determined as the mass of compound per needle dry weight and time according to:

$$E = \frac{(C_2 - C_1) \bullet F}{m} \tag{4.1}$$

Here C_2 is the concentration in the outgoing air, C_1 is the concentration in the inlet air, and F is the flow rate into the enclosure. The dry weight of the biomass (m) was determined by drying the needles at 75 °C until constant weight was achieved.

4.4 Results and discussion

4.4.1 Temporal variation of VOCs

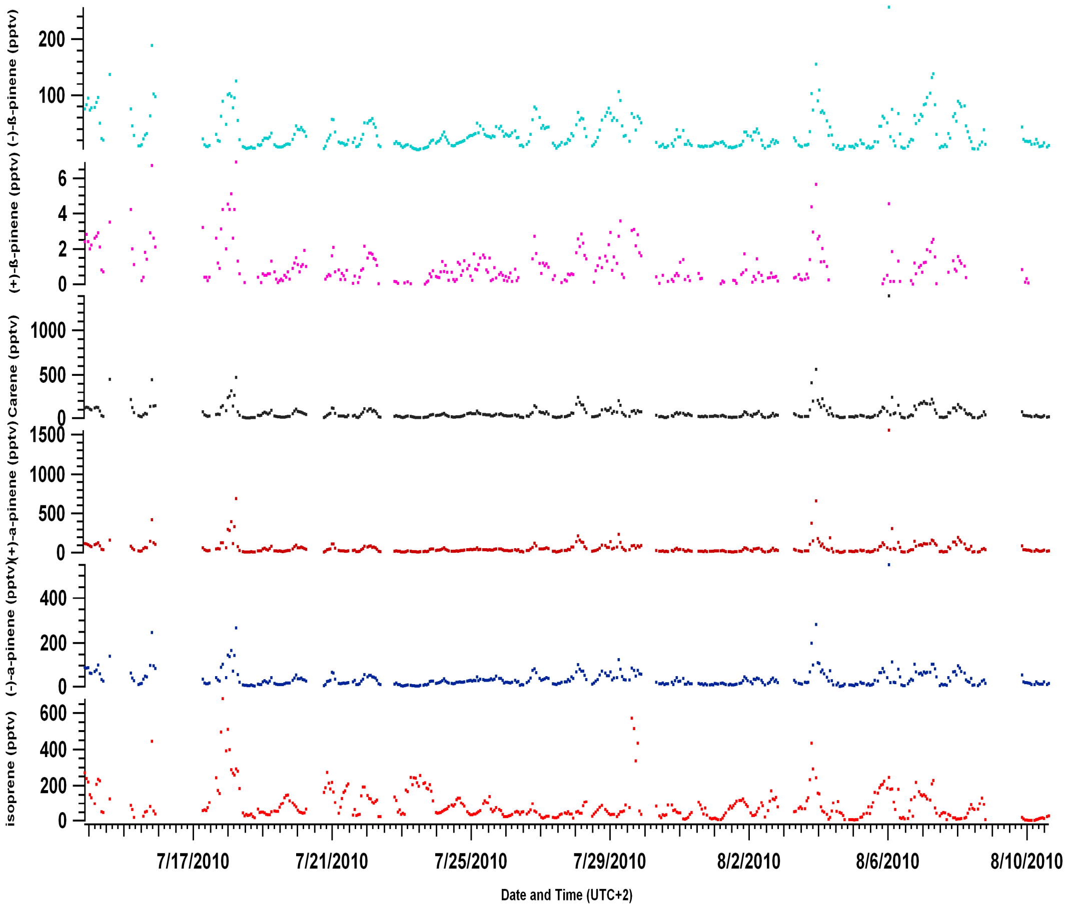


Fig. 4- 6 Mixing ratios of measured bigenic VOCs over the campaign. The marker represents the middle of the sampling time. The gaps were caused by calibration and blanks measurements, power failure or mixing ratios below detection limits

The measurement areas identified as coniferous forests in the landuse database were found to be Scot pine and Norway spruce. Scots pine is one of the most common tree species in the boreal forest. Its monoterpene emissions have been intensively studied during the past decade (Borg-Karlson et al., 1999; Holzke et al., 2006; Isidorov et al., 2010; Janson, 1992; Komenda and Koppmann, 2002; Räisänen et al., 2008, 2009; Shao et al., 2001; Thoss et al., 2007; Yassaa and Williams, 2007). The first estimated emission inventories for North European forests were published by Lindfores et al. (2000). Previous studies have established that α-pinene, ß-pinene, carene, and cineole are the most abundant emitted terpenes, with a strong contribution of isoprene and linalool during the summer months over the boreal forest (Lindfors et al., 2000). Ambient mixing ratios of α-pinene enantiomers over the boreal forest are dominated by the (+)-enantiomer, while ß-pinene exhibited the reverse enantiomeric preference with of the minus enantiomer (-)-ß-pinene being favoured (Williams et al., 2007). Studies have also shown that mechanical damage of the Scots pine can induce higher ratios of (+)-α-pinene (Yassaa and Williams, 2005, 2007). Although Scots pine and Norway spruce are found to emit monoterpenes mostly as a function of temperature, since the emissions originate from resin duct storage pools and essentially are evaporating from the needles (Grote and Niinemets, 2008; Tarvainen et al., 2005), there are still some monoterpenes emission being made de novo when the tree is sunlit (Grote and Niinemets, 2008; Shao et al., 2001). There are also a small number of decidous trees, such as birch (*Betula pendula* R) and aspen (*Populus tremula* L.) living around the measurement site, namely the mixed forest. The mixed forests and Norway spruce also emit siginificant amount of isoprene (Hakola et al., 2000; Janson and de Serves, 2001) again as a function of light (Ghirardo et al., 2010). It should be noted that in the summer time the daytime extends for circa 18 hours (04:00-23:00).

Fig. 4-6 presents the overview of the main Biogenic VOCs measured by TD-GC-MS from July 13th to August 10th, 2010. The data points represent the middle of the sampling period. The short gaps were caused by blanks or calibration measurements and the bigger ones were due to power failures at the station. (±)-α-Pinene, Δ3-carene, (±)-ß-pinene and isoprene are shown in Fig. 4-6. These were found to be the most abundant ambient biogenic compounds measured during the whole period of the HUMPPA-COPEC summer campaign. Small amounts of other monoterpenes such as myrcene and limonene were also observed. Generally, the predominant compounds were Δ3-carene and α-pinene with approximate relative contributions of 20-45% and 35-60% of the total observed monoterpenes, respectively. Other studies from boreal forest locations also have shown similarly large fractions of Δ3-carene and α-pinene over the boreal forest(Tarvainen et al., 2005). Δ3-Carene ranged from 5ppt to 1.4 ppb, (-)-α-pinene from 7 ppt to 0.5 ppb, and (+)-α-pinene is from 9 ppt to 1.5 ppb. Both enantiomers of α-pinene and ß-pinene were detected during the measurement period. Interestingly the mixing ratios of (+)-α-pinene were always higher than the (-)-enantiomer whereas the (-)-ß-pinene was always sigificantly higher than the (+)-ß-pinene enantiomer. The median values are for Δ3-carene 35 ppt, (-)-α-pinene 27 ppt, (+)-α-pinene 39 ppt, (-)-ß-pinene 20 ppt and isoprene 56 ppt. Isoprene mixing ratios, which were higher at the beginning and the end of the campaign, range from a few ppt to more than 600 ppt.

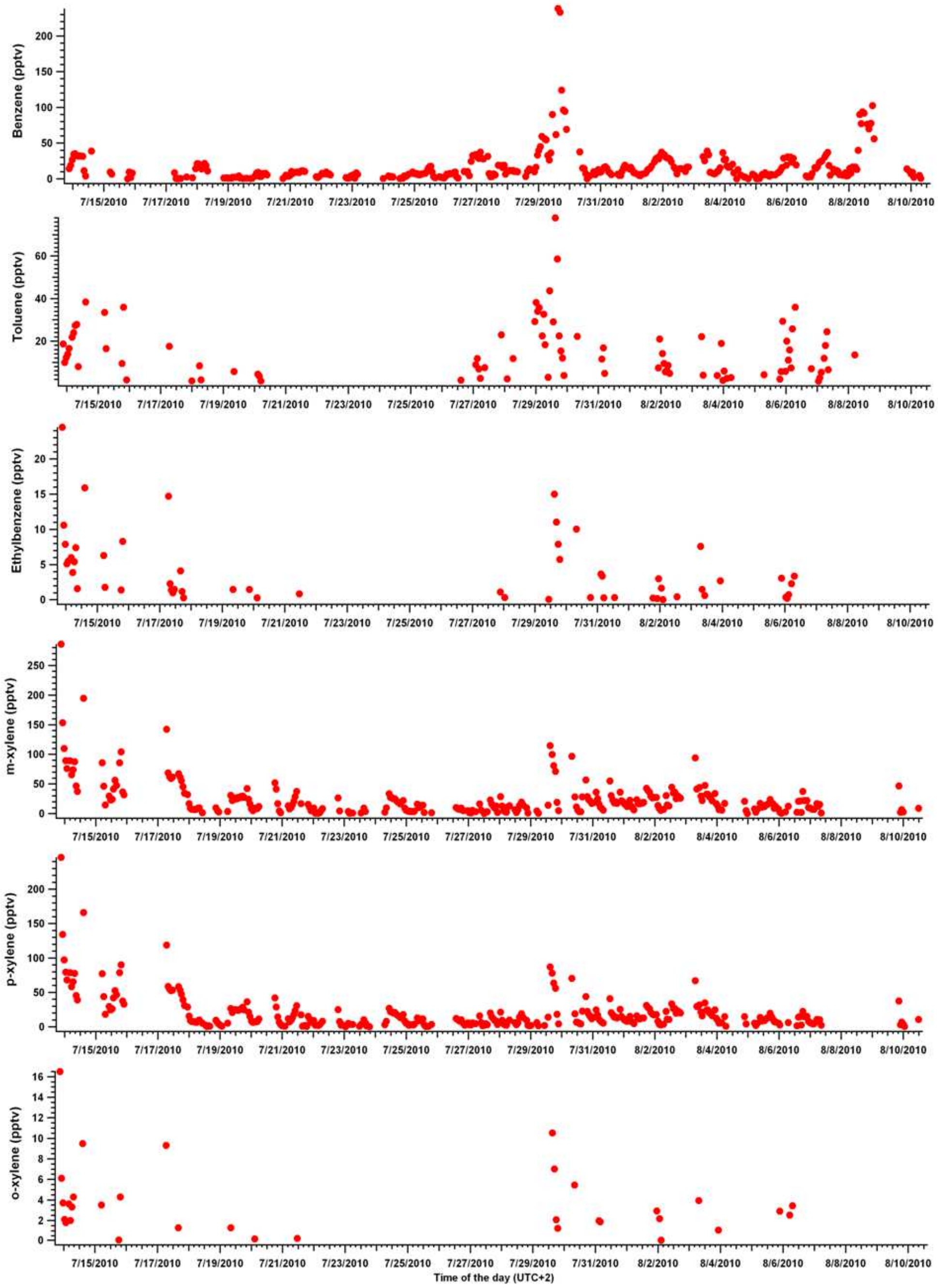


Fig. 4- 7 Mixing ratios of measured BTEX compounds over the campaign. The marker represents the middle of the sampling time. The gaps were caused by calibration and blanks measurements, power failure or mixing ratios below detection limits

The aromatic BTEX compounds such as benzene, toluene, ethylbenzene, *m-/p-/o-*xylene were also measured during the campaign. Ambient air measurements of these anthropogenic compounds are depicted in fig. 4-7. For the whole periods of the campaign, the mixing ratios of aromatic compounds were generally low. This is consistent with the vegetation dominated landuse results presented previously. The median mixing ratios for these compounds throughout the measurement period were found for benzene with 10 ppt, toluene with 12 ppt, ethylbenzene with 2 ppt, m-xylene with 16 ppt, p-xylene with 11 ppt and o-xylene with 3 ppt. The BTEX compounds discussed in this chapter originate mainly from fossil fuel burning (e.g. traffic exhaust) and are transported to the site from nearby cities and roadways. The highest mixing ratios of xylenes and ethylbenzene were observed near the beginning of the campaign (13th-19th July), while the lowest values occurred between 21st-27th July. Extremely high mixing ratios of benzene and toluene were recorded on the 29th of July and 8th of August and these were accompanied by high CO, SO2 and acetonitrile (Williams et al., 2011) indicating that they originated from a biomass burning event. This was identified by back trajectory and satellite analysis to be large regions of the Russian Federation southeast of Moscow (see details in Williams et al., 2011). This burning event destroyed nearly 6 million hectares of land and lasted from mid-July to mid-August.

4.4.2 Diel cycles

The diel cycles of selected biogenic VOCs analyzed during the HUMPPA-COPEC 2010 campaign are shown in Fig.4-8. The blue dots illustrate the median value of the mixing ratio, the open traingle represents the mean value, the upper and lower bars represent the maximum and minimum value and the box top and bottom show the percentile of 75th and 25th respectively.

All the monoterpenes follow a similar trend: a slow decrease of the mixing ratios starts in the morning around 8:00 (UTC+2) towards the daytime with the minimum around 12:00 (UTC+2), and after 15:00 or 16:00 the mixing ratio begins to increase again reaching a maximum after 21:00 (UTC+2), and remaining high and stable throughout the night until the following morning. Local noon was approximately 12:30 (UTC+2). Despite coniferous trees emitting monoterpenes as a function of temperature and light (Ghirardo et al., 2010) the maximum ambient concentrations are observed at night. This apparent paradox is due to changes in the boundary layer height and to the presence of higher levels of the primary atmospheric oxidant OH by day. Although the emission fluxes from the boreal forest are certainly higher by day (high light and temperature), the boundary layer into which they are mixing is some 15 times higher by day (ca. 1500m) than by night (ca. 100m). This and the attenuating effect of the OH reaction on concentration by day lead to the observed diel cycle. Isoprene has a different diel trend to the monoterpenes: there was a slow increase in concentration around 5:00 (UTC+2), a small peak around 07:00 UTC+2 is apparent and then a second larger peak in the afternoon around 19:00 (UTC+2). Thereafter it decrease until midnight and remains stable the whole night. Previous studies have shown that spruce and aspen are strong isoprene emitters (Fuentes et al., 1999;

Grabmer et al., 2006; Hakola et al., 2000; Janson and de Serves, 2001; Rinne et al., 2009) and that light is the primary driver for isoprene emission (Guenther et al., 1995; Guenther et al., 2006). Generally, the temperature reached its maximum around 15:00 (UTC+2) and the maximum radiation observed were from 11:00 to 14:00 (UTC+2). The two peaks observed in isoprene (07:00 and 19:00) may be explained by variation in the boundary layer height and the unusually long daylight time in the boreal summer. Illumination of the tree by the early morning sun (sunrise 04:00) may instigate isoprene emission before the break-up of the nocturnal boundary layer. Likewise under these conditions the sunlight may persist after the boundary layer has formed in the evening. In both cases emissions would occur into a shallow boundary layer and give rise to a peak in concentration.

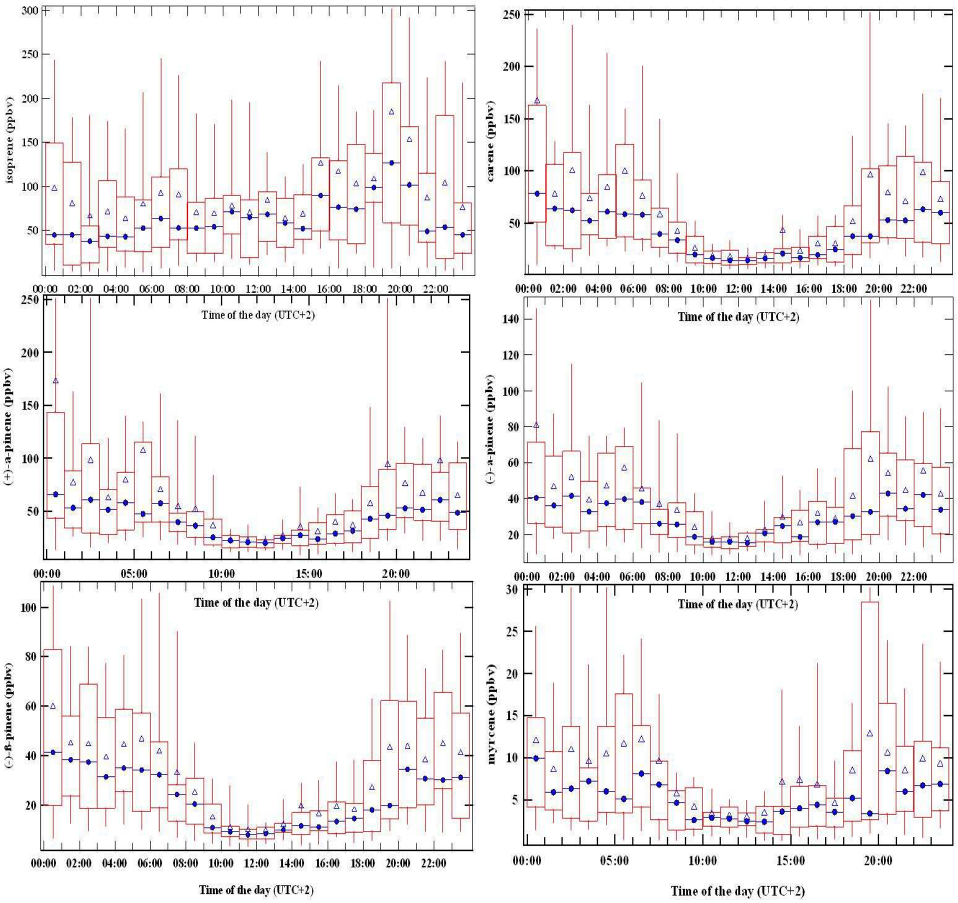


Fig. 4- 8 Diurnal cycles of BVOC compounds during the campaign. The dots represent the median value of every hour, the open traingle represents the mean value, and the box top and bottom represent the percentile of 75th and 25^{th}

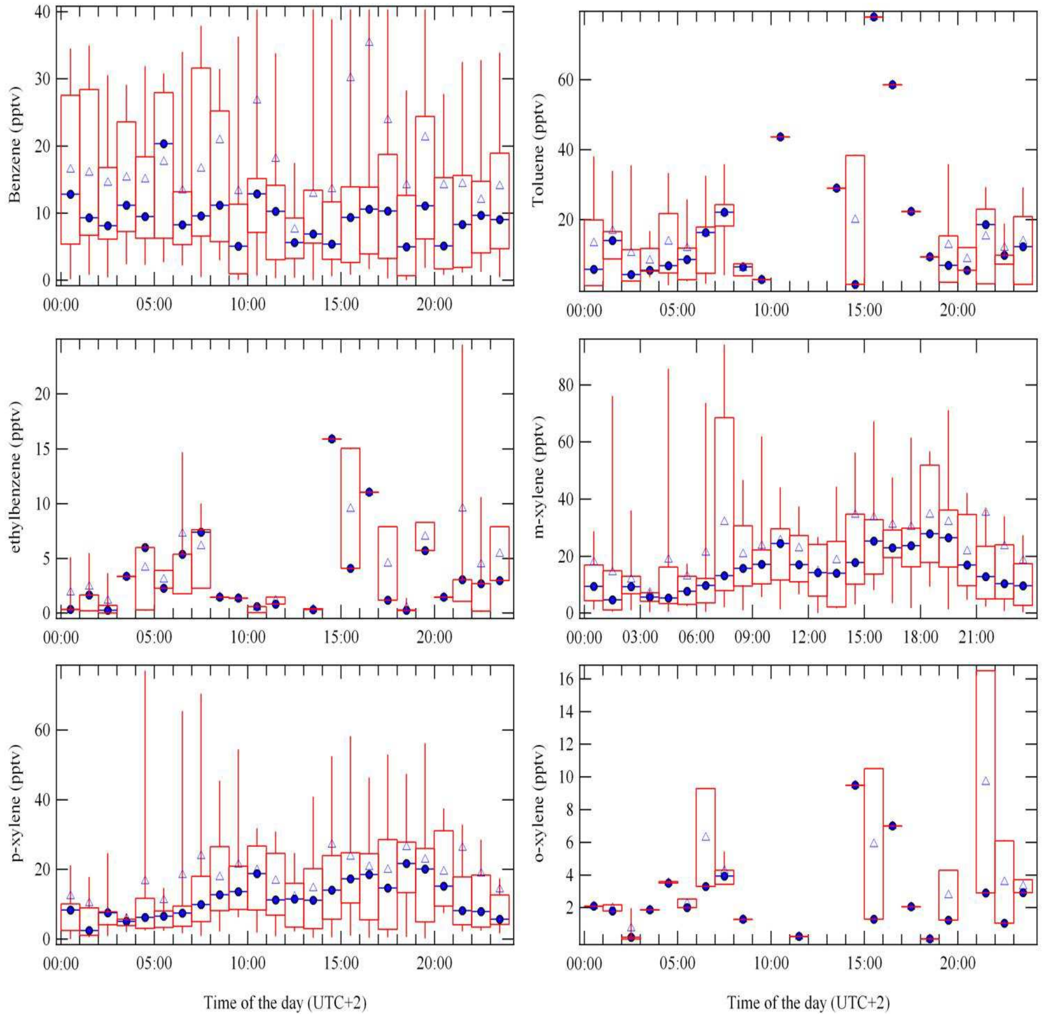


Fig. 4- 9 Diurnal cycles of BTEX compounds during the campaign. The dots represent the median value of every hour, the open traingle represents the mean value, and the box top and bottom represent the percentile of 75th and 25th

The anthropogenic BTEX componds show a totally different diel profile. The ethylbenzene and o-xylene concentrations were quite low most of the time during the campaign, they will not be discussed in this section although their diurnal cycles are presented in fig. 4-9. In general, the mixing ratios of benzene vary a lot. A short sharp peak in the morning appears around 5:00 (UTC+2), while this is not the case for the other BTEX compounds. During the daytime, it has two small peaks which are around 10:00 and 16:00 (UTC+2). This indicates a large source of benzene during summertime in Hyytiälä, such as local vehicle emission, pollution from the cities, biomass burning etc. For toluene, the peak around 15:00 (UTC+2) was due to the biomass burning which could also be seen in Fig. 4-6; the other small peak earlier around 10:00 accompanied with benzene, m-xylene and p-xylene at the same time may also be caused by the local vehicle emissions. For m-xylene and p-xylene they have the same trends: increase in the morning and reach their first maximum around

10:00, followed by a slow decrease with the minimum concentrations around 12:00 - 13:00, then the second maximum in the mixing ratios occurred at about 18:00 - 19:00 (UTC+2).

4.4.3 Enantiomers characterization: ambient and cuvette study

Conifers emit a large amount of monoterpenes. Many of these monoterpenes are chiral and most likely produced by specific enzymes within the plant (Martin et al. 2002 and references therein). Investigations of the enantiomeric distribution of monoterpenes in different tissues of Scots pine and Norway spruce based on solvent extraction methods showed clear differences between tissues. For example, the needles of Norway spruce were relatively rich in (-)-camphene compared with other tissues (such as xylem, phloem and oleoresin of branch), while (+)- and (-)-α-pinene and (-)-ß-pinene were found to be enriched in other tissues except needles (Borgkarlson et al., 1993; Persson et al., 1993; Persson et al., 1996). The enantiomeric composition was also found to change from more (-)-enantiomer (α-pinene and limonene) in the younger parts to more (+)-enantiomer in the older parts (Persson et al., 1993). The distribution of monoterpenes has also been used identify different chemotypes of the same tree species. These are trees of the same nominal species (e.g. Scots pine) but with distinctly different monoterpene emission characteristics. In Hyytiälä 4 different chemotypes of Scots Pine have been identified, with one chemotype predominatly emiting Δ3-carene, and another predominately pinene (α-pinene, ß-pinene) (Tavaine et al. 2005). The chemotypes of French and Spanish oaks are explored in chapter 2 of this thesis.

While the aforementioned studies examined single plants (or specific parts thereof) other studies have reported the regional enantiomeric signature (enantiomeric ratio or enantiomeric enrichment) of the whole boreal ecosystem by measuring in ambient air. The enantiomeric signature of monoterpenes in the atmosphere was determined for the first time in a Boreal forest during the Biosphere Aerosol Cloud Climate Interactions Quantification of Aerosol Nucleation in the European Boundary Layer (BACCI4-QUEST 2005) intensive field campaign conducted in Hyytiälä, Finland in April-May, 2005. (Williams et al, 2007, Eerdekens et al. 2009). By contrasting the results of this campaign with jet aircraft measurements of enantiomeric monoterpenes over a pristine rainforest conducted within the framework of the GABRIEL campaign (Guyanas Atmosphere-Biosphere exchange and Radicals Intensive Experiment with the Learjet, 2005). It has been established that distinct regional chiral signatures exist, and that ambient mixing ratios of the α-pinene enantiomers over the boreal forest always favours (+)-α-pinene (Williams et al., 2007). Results from the HUMPPA-COPEC campaign are in agreement with this previous study, although it should be noted the measurements were made at the same site at a different time of year. The summertime average mixing ratios of α-pinene found during HUMPPA-COPEC was 103 pptv and the (+)-enantiomer exceeded (–)-enantiomer in almost all samples with only 6 samples in which the ratio of (-)-enantiomer to (+)-enantiomer was close to 1, i.e. racemic. Interestingly, from the HUMPPA-COPEC dataset we see that the reverse appears to be true for ß-pinene. In this case the (-)-ß-pinene enantiomer dominates throughout the dataset, this is in agreement with the observation in the spring aircraft measurements (Williams et al., 2007). The (+)-ß-pinene enantiomer was often below detection limit suggesting a more enantiomerically selective mechanism is governing its production. This is supported by the results obtained in the branch chamber measurements where the emissions from the four chemotypes of Scots pine and Norway spruce were largely dominated by (-)-ß-pinene. Futhermore, the (-)-ß-pinene correlates (+)-α-pinene and (-)-α-pinene quite well, with r^2 value of 0.81 and 0.88 respectively.

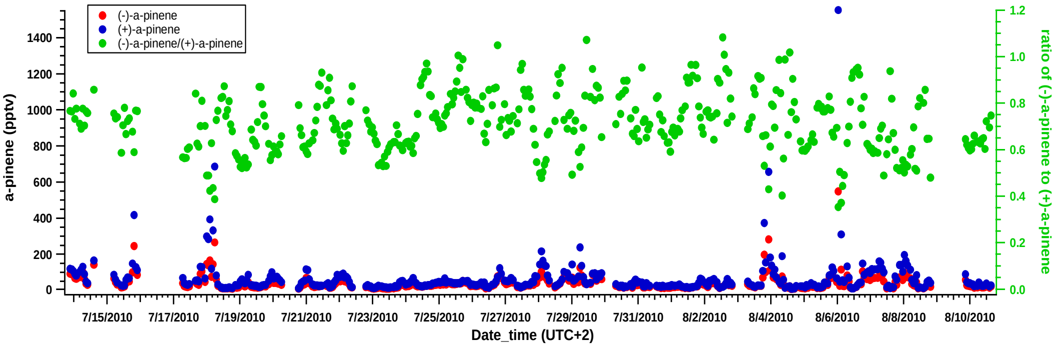


Fig. 4- 10 Enantiomeric ratio of α-pinene and mixing ratios of (-)-α-pinene and (+)-α-pinene over the HUMPPA-COPEC campaign

Damage to the needles of the Scots pine has been shown to induce higher ratios of the (+)-enantiomer of alpha pinene (Yassaa and Williams 2005, Yassaa and Williams 2007). This finding has proven useful in identifying emissions from a nearby sawmill (Eerdekens et al. 2009). This influence manifested itself as unusually high concentrations of monoterpenes and as a clear enrichment of (+)-α-pinene over its (-)-α-pinene enantiomer. These events were also associated with a southeasterly wind direction corresponding to the bearing of the mill from the site. Fig. 4-10 shows the mixing ratios of both α-pinene enantiomers and their ratio for the 2010 HUMPPA-COPEC campaign. On several occasions the peak concentrations are associated with enantiomeric ratio enrichments. These events (e.g. in the period 3th August 21:00-4th August 00:00) did coincide with short episodes of southeasterly winds suggesting that on this campaign sporadic influences of the sawmill on the dataset have been detected.

In order to minimum the effect of extreme high and low values and get a clear picture the diurnal cycles of the enantiomeric signature, the (-)-enantiomer enrichment is presented here using the calculation:

(-)-enantiomer % = (-)-enantiomer / ((-)-enantiomer + (+)-enantiomer) × 100

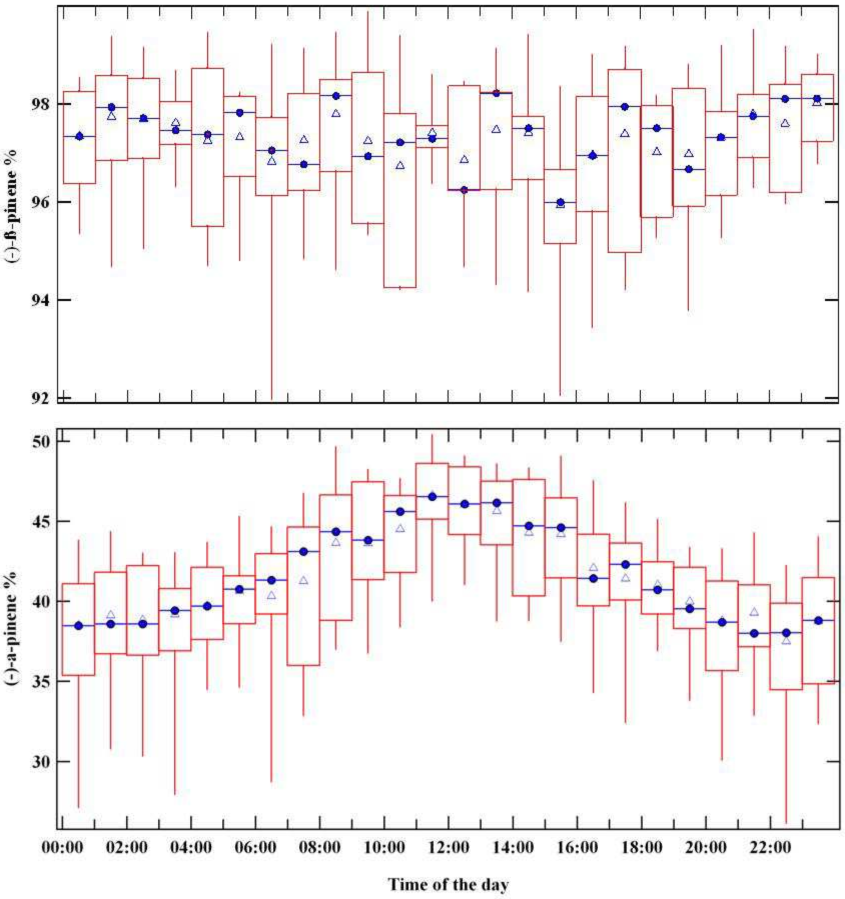


Fig. 4- 11 Diel cycle of enantiomeric enrichments of α-pinene and ß-pinene. The dots represent the median value of every hour, the open traingle represents the mean value, and the box top and bottom represent the percentile of 75th and 25th

Fig. 4-11 shows the diel cycle of enantiomeric enrichments during the campaign periods. As can be seen in the graph, (+)-α-pinene was dominant in the enantiomeric composition with the enrichment over 50% all the time, however, (-)-α-pinene did show small but significant increase throughout the day peaking around 11:00 to 14:00 (UTC+2). It is known that monoterpenes are emitted from resin ducts, which means the temperature controls the volatilization of hydrocarbons from strorage pools inside the leaf (Guenther et al., 1993). However, several studies have reported both light and temperature controlled terpenoids other than isoprene from Scots pines (Back et al., 2005; Ghirardo et al., 2010; Komenda et al., 2003; Shao et al., 2001; Taipale et al., 2011). Our study in Hyytiälä has provided further evidence that parts of the

(-)-α-pinene emitted from the boreal forest was controlled by both light and temperature. As can be seen from Fig. 4-12 which shows the (-)-α-pinene enrichments color coated with temperature, light and ozone concertration, the higher temperatures were always closely correlated with the higher emission of (-)-α-pinene, while there was a delay of one or two hours for the (-)-enantiomers enrichment peaks every day compared with the maximum radiation. Regard to ozone, the correlation is not very clear. So the reaction on the surface of aerosol appears to have little effect on the ambient enantiomeric composition. Recently laboratory studies have shown that ozone reacting with enantiomers on a surface can cause an abiological enrichment (Stokes et al. 2009). On the other hand, another chiral pinene, ß-pinene, shows a very strong (-)-enantiomer preference. The relative amount of (-)-enantiomer was over 90% of the total ß-pinene.

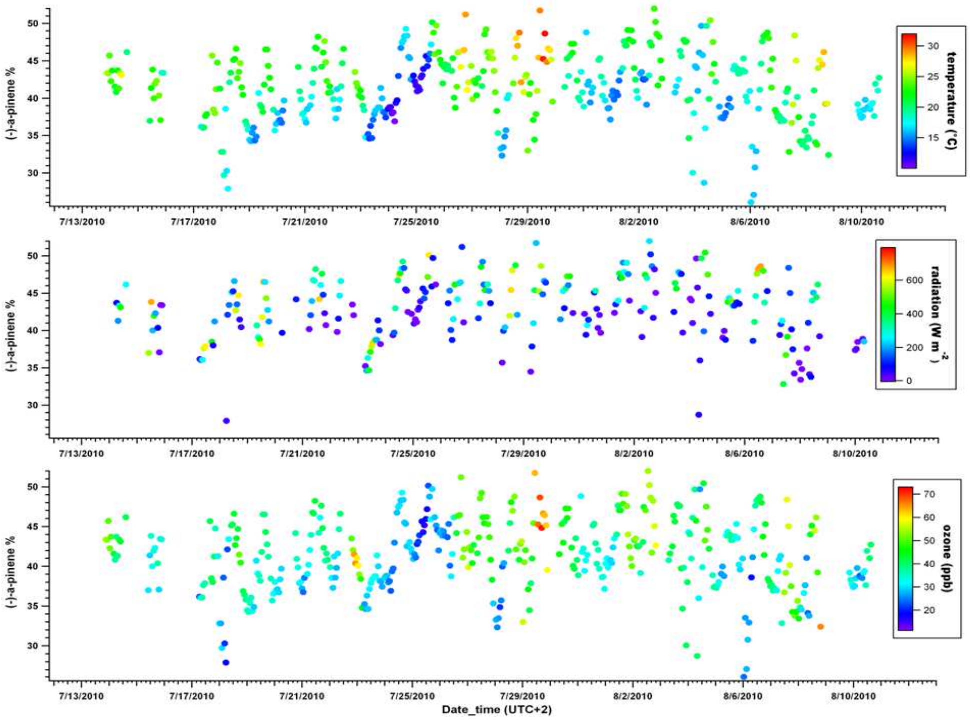


Fig. 4- 12(-)-α-pinene enrichment color coated with temperature, radiation, and ozone concerntration during the HUPPA_COPEC campaign

To further understand the origin of the ambient enantiomeric distribution, chamber studies were carried on during the campaign periods as well. This enabled the variations in the ambient concentrations and enantiomeric enrichments to be compared with emissions directly from specific tree type sources. Here we examine for the first time to what extent the chemotypic diversity of Scots pine can affect the chemical composition, the chirality and emission strength of mono-and sesquiterpenes through experiments performed from plant chambers. Diel cycles of emitted mono-and sesquiterpenes were also followed from four chemotypic individuals of Scots pine and Norway spruce.

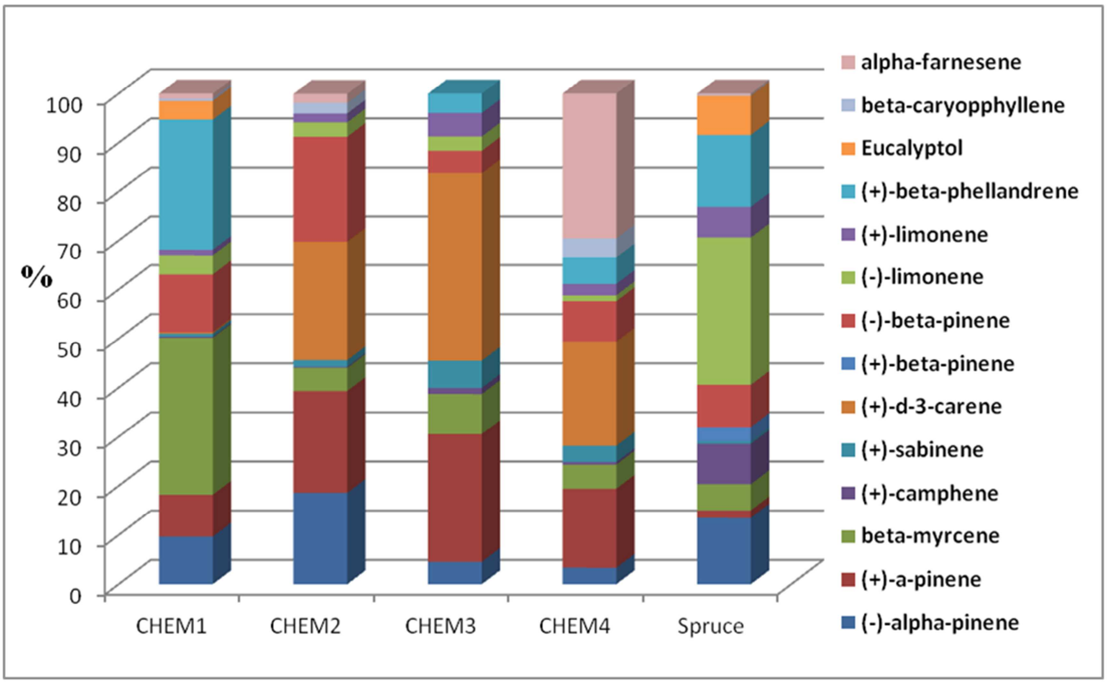


Fig. 4- 13 Chemical composition determined as percentage of total mono-and sesquiterpenes in the emissions of four chemotypes of Scots pine and Norway spruce

Most of the branch scale studies that have been performed in Hyytiäla SMEAR II sattion have focused on short-term emissions of monoterpenes (Janson et al., 2001; Rinne et al., 2000; Rinne et al., 2007) or on their seasonal variations (Hakola et al., 2006) from Scots pine. In number of studied Scots pine, Δ-3-carene was identified as the major terpene making up more than 60 % of the terpenoid emissions. α-and ß-Pinene and a suite of other mono-and sesquiterpenes were present at moderate or low levels. It is important to note, that myrcene, a reactive organic trace gas had not been previously identified due its coelution with ß-pinene in most of the chromatographic analyses. The present study represents the first intensive investigation on the chirality of monoterpenes present in direct plant emissions from the Boreal forest. Four different chemotypes of Scot pine and one Norway spruce were investigated (Fig. 4-13) during the campaign. As can be seen from Fig. 4-13 where isoprenoid compositions in each Scots pine chemotype and in Norway spruce are displayed, there is a large intra-specific variation. According to the variation of the emission blends and in particular the Δ-3-carene content, the four studied Scots pines can be classified as no- Δ-3-carene chemotype (i.e. chemotype 1), Δ-3-carene chemotype (i.e. chemotype 3) and intermediate chemotypes (i.e. chemotypes 2 and 4). The chemotype 1 presented no- Δ-3-carene in its emission but exhibited a suit of monoterpenes and sesquiterpenes (α-and ß-pinene, myrcene, ß-phellandrene, limonene, eucalyptol, caryophyllene and α-farnesene) and revealed the strongest fluxes of mono- and sesquiterpenes. Interestingly, myrcene and ß-Phellandrene, both very reactive organic species, were the predominant compounds accounting for 32% and 27 % of total mono-and sesquiterpenes respectively. The mixing ratios of these two species were reletively low in the ambient atmosphere. For chemotype 2, Δ-3-carene and ß-pinene were the most species. It should be noted that chemotype 2 was the only one that was found to be high in ß-pinene emission. Chemotype 3 (Δ-3-carene chemotype), was the weakest emitter of mono-and sesquiterpenes in comparison with others investigated. In chemotype 4, the emission of α-farnesene, made up more than 30 % of total mono- and sesquiterpene emissions, while the emission of Δ-3-carene, α-pinene and ß-pinene with 21 %, 19 % and 8 %, respectively composed almost all the remaining of total mono- and sesquiterpenes. Whereas Chemotype 1 and chemotype 2 showed a recemate for a-pinene, chemotype 3 and chemotype 4 revealed high preference for (+)-α-pinene,, almost 6 and 5 times enriched in chemotype 3 and chemotype 4, respectively. ß-Pinene, even though weakly emitted in most of the cases, was almost exclusively present as (-)-enantiomer in the emission of the four chemotypes. In contrast, Norway spruce exhibited a strong preference for the (-)-enantiomeric form for both α- and ß-pinene, on average (-)-α-pinene was 9 times higher than (+)-α-pinene and (-)-ß-pinene was 3 times higher (+)-ß-pinene. These chiral characterizations underline that not only the chemical composition is distinct between the four chemotypic individuals but also the stereochemistry of emitted monoterpenes. This also suggests that the chemical composition and enantiomeric preference are genetically controlled. Whether the transition from native Scots pines with high preference for (+)-α-pinene to new genotypic trees without enantiomeric discrimination for a-pinene is good or bad to the boreal forest ecosystem, is an issue that has to be considered in future forest management. Although the diel cycles of (+)- and (-)-α-pinene emitted from the four chemotypic individuals of Scots pine did not reveal any clear profiles with light and temperature, those determined in the emission of Norway spruce are particularly interesting (Fig. 4-14). Whilst (+)-α-pinene fluxes remained stable over time, (-)-a-pinene showed a nice Gaussian profile and peaked between 16:00 and 18:00 local time (UTC+2). The maximum (-)-a-pinene emission rates seem to be slightly delayed from the photosynthetic light maximum. It could be that there is a time shift between the photosynthetic production of (-)-α-pinene and its release from the plant, although monoterpenes are not stored in special pools in Norway spruce.

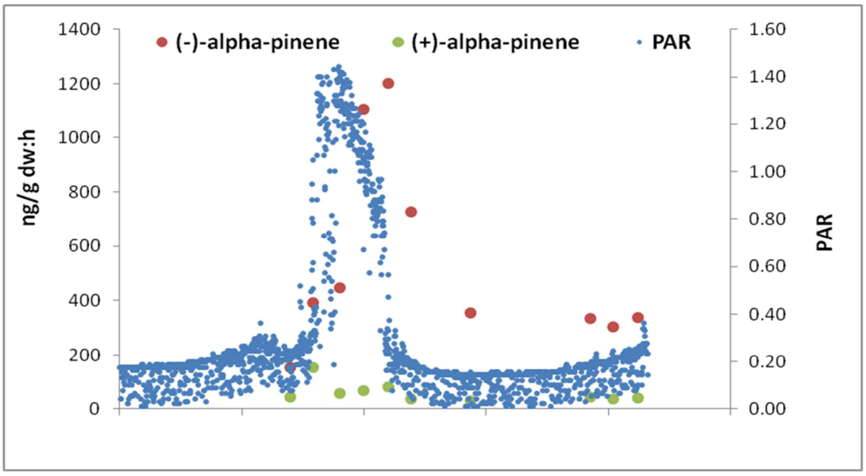


Fig. 4- 14 Diel cycle of (+)- and (-)-a-pinene in the emission of Norway spruce plotted with PAR

In the results from the branch chamber experiments, the emissions from Norway spruce, one of the second common tree species, manifested a reverse enantiomeric preference for α-pinene where (-)-enantiomer was 9 times more enriched than (+)-enantiomer. Furthermore, it showed a diel cyle where (-)-α -pinene peaked around 4 pm and 6 pm (UTC+2) and (+)-a-pinene remained constant over the time. It could be that the diel cycle in the ambient air enrichment of (-)-α-pinene shown in Fig. 4-11 is a combination of the temperature and radiation effects as being examined in chapter 2 under laboratory conditions. Alternatively it may simply be a changing (-)-enantiomer contribution from the emission of spruce to the ambient mix even though the peaks in the direct spruce emission and ambient air did not coincide at the same time. The latter assumption is supported by the fact that the measured isoprene in ambient air during the campaign comes very likely from Norway spruce as Scots pine is not an isoprene emitter and (-)-α-pinene did not show any clear diel cyles in any of the four studied chemotypes of Scots pine. This is further supported by the plot showed in Fig. 4-15 where the enantiomeric enrichment of (-)-α-pinene is associated with a southwesterly wind direction indicating that more Norway spruce trees distributing southwest of the site, leading to the diel cycles favouring the (-)-α-pinene. It implies that the enantiomeric signature of monoterpenes may play a great role in reconciling the ambient BVOC mixing ratios to the emission sources. It can also help in correcting the existing discrepancies between the measured branch scale emission patterns and above-canopy concentrations which indicates that measurements of emissions on the branch scale represent incorrectly the sources at stand, population or footprint scale.

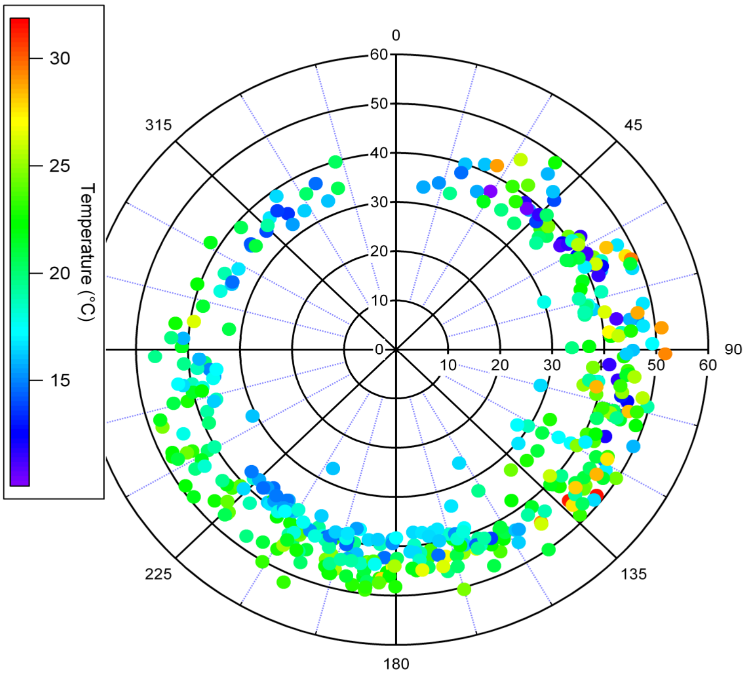


Fig. 4- 15 The variation of (-)-α-pinene enantiomeric enrichment color coated with temperature and wind direction

4.4 Conclusions and outlook

In order to better understand the atmospheric chemistry in the boreal forest region, during the field HUMPPA-COPEC campaign at Hyytiälä SMEAR II station from July 12th until August 12th in 2010, a suite of key biogenic and some anthropogenic VOCs were measured by online TD-GC-MS.

The total monoterpenes (including α-pinene, Δ3-carene, ß-pinene and myrcene) measured during the campaign varied in mixing ratio from a few ppt to over one ppb. The main biogenic BOVCs measured above the canopy were α-pinene and Δ3-carene and these two compounds together contribute more than 50% of the total monoterpenes. Isoprene mixing ratios were also detected during the summer campaign with the median value of 56 ppt, especially high mixing ratio (over 600 ppt) at the beginning of the campaign when it was very hot. The main emitter of isoprene was the spruce (based on the cuvette studies), as well as willows and aspens (Jason and serves 2001; Hakola et al.,2000). The anthropogenic BTEX compounds were generally low except during the period influenced by the Russian wildfires. Pronounced diel cycles in the ambient data were found for the monoterpenes and for isoprene. For the BTEX compounds, benzene was affected by the biomass burning events and other local emissions, so the mixing ratios varied thorough the day, while toluene and xylenes followed a similar trend which reached a first maximum value late in the morning and a second one in the early evening. Both biogenic VOCs and anthropogenic BTEX mixing ratios stay relatively stable and high during the night. This is due to the low emission and a low and stable boundary layer.

Cuvette measurements of direct plant emission from four chemotypes of Scots pine revealed that these chemotypes can be classified as Δ-3-carene chemotype, no Δ-3-carene chemotype and intermediate chemotype. Chemodiversity was found to affect not only the chemical composition of emitted terpenes but also their stereoisomery. While Δ-3-carene chemotype manifested strong preference for (+)-α-pinene, the no Δ-3-carene chemotype was a racemic for a-pinene. All chemotypes emit almost exclusively (-)-ß-pinene. Norway spruce showed strong preference for (-)-enantiomers for both α-pinene and ß-pinene. In the ambient measurements, in the case of α-pinene, the (+)-enantiomer was discovered to be dominant in ambient air which is in keeping with the previous study at the same site (Williams et al., 2007). This also suggests that d-3-carene chemotypes of Scots pine, which emits preferentially (+)-a-pinene are dominant and widespread in the Hyytiala Boreal forest. While for ß-pinene, the (-)-enantiomer was predominant over the boreal forest, which enriched relative to the (+)-enantiomer over 80% of the total measured ß-pinene. This is also consistent with the branch enclosure measurements. As can be seen from the ambient diel cycle of the enantiomeric enrichment of (-)-α-pinene, the (-)-enantiomer had an increasing fraction as the light and temperature rose through the day. This might be the contribution from the spruce or Scot pines not only emit (-)-α-pinene from the storage pools which controlled by temperature, but also has other emission path ways as a function of light.

Chapter 5

Summary

VOCs are so called “trace gases”, which are present only at relatively low concentrations (<1%) in the atmosphere, but they play an important role in tropospheric chemistry because of their high reactivity with the main atmospheric oxidants OH, NO_3 and O_3. Globally, biogenic VOCs are much more abundant and reactive than those produced by human activities. For years BVOCs have been of special interest to both atmospheric chemists and biogeochemists who have investigated their sources, emission strengths, sinks and reactions in the atmosphere. This thesis pursues a greater understanding of the chiral signature of the most abundant BVOCs, namely α-pinene. In the past few decades, scientists have made great efforts to investigate the biosynthesis of non-enantiomeric terpenoids in plants and their emission algorithms which have been used in the models to estimate the global or regional emission inventories. Before this work little was known of the source characteristics and distribution of enantiomeric monoterpenes in ambient air.

Chapter 1 gives a global scale overview of both anthropogenic BTEX and biogenic VOCs (enantiomeric and non-enantiomeric ones) detailing known sources and sinks as well as the measurement technique used for all the analyses in this thesis.

Chapter 2 presents an attempt to understand whether the enantiomeric characteristics of the emission change predictably as a function of temperature and light. In this chapter, we investigated leaf emission as a function of temperature and light for three markedly different Mediterranean species (*Quercus ilex*, *Rosemarrie officinalis* and *Pinus halepensis*) using a dynamic leaves enclosure cuvette in the laboratory. This is the first time that such enantiomerically specific emissions have been studies in-vivo.

The screening experiments of nineteen *Q.ilex* emissions under standard conditions (30°C and 1000 PAR) showed the compositional profile of its emissions is mainly genetically controlled, for instance the French limonene chemotype emitted more (-)-α-pinene than the (+)-enantiomer, while the Spanish limonene chemotype individuals had an opposite preference with the enrichment of (+)-enantiomer. This is the first experiment in which additional chemotypes have been distinguished with the enantiomeric compositions. Despite the limited sample set, an interesting hypothesis for regional identification according to enantiomeric chemotype has been formulated.

The main purpose of this section of the thesis work was to investigate the enantiomeric profile as a function of light and temperature. *Q. ilex* was found to emit monoterpenes depending on light and temperature, but the monoterpene emissions from *R.officinalis* and *P.halepensis* were mainly controlled by temperature but with some compounds emitted right after the photosynthesis. However, the enantiomeric excess of the main moneterpenes, namely (-)/ (+)-α-pinene, (-)/ (+)-β-pinene and (-)/

(+)-limonene showed no clear trends in the responses to light and temperature. Moreover, there were large variations of the enantiomeric excess behavior within individuals no matter what kind of species they were. One typical example was *Q.ilex*, for which chemotype IV (French-pinene-(+)-α-pinene) showed a strong (+)-α-pinene predominance and no change as a function of light, whereas for chemotype I (French-limonene-(-)-α-pinene) revealed a clear preference of (-)-α-pinene and showed enriched (-)-α-pinene with light. There appears to be no common enantiomeric behavior across the species measured as a function of temperature and light. The response behavior also varies greatly within a given plant species. It should be noted that these enantiomeric variations have little impact on the overall emission of the monoterpenes yet for biological entities within the forest they may provide important cues.

What is the enantiomeric characterization in the real world? Does it compare to the laboratory results or are there other parameters affecting it?

In Chapter 3 the seasonal variation of enantiomeric characterization in the forest environment is examined. Here we present results of ambient air measurements (DOMINO campaign, 2008) over a Spanish *Pinus Pinea*. L forest in winter and in summer. An online TD-GC-MS setup was used during the winter measurements. At this time mixing ratios of biogenic species were generally low, in keeping with the previously determined low winter seasonal emission rates of *Pinus pinea* L. Anthropogenic VOCs were found to be generally higher and were related to transport of air from the nearby cities such as Huelva (to the west) and Seville (to the northeast). Despite the low emission rates, the (-)-α-pinene enantiomer was found to be in excess during the nighttime but with no clear enantiomeric preference during daytime in winter. The offline cartridge measurements were used for the following summer studies at the same site. A clear (-)-α-pinene consistently predominated signature was found during daytime in summer time. This suggested that the enantiomeric preferences vary markedly through the different seasons.

In addition to the chiral seasonality, two empirical methods for deriving OH levels in the field, namely by application of hydrocarbon ratios and from measured JNO_2 with an empirical relationship to JO^1D and OH from previous campaigns, have been employed in this chapter in order to get a better view of the OH radial in the ambient. For this study, both methods show shortcomings in estimating OH thus there is no better substitute for an accurate, direct in-situ measurement of OH.

Chapter 4 presents the study of both enantiomeric leaf emissions and the ambient concentrations of these compounds measured at the same time over a Boreal forest in Southern Finland, the HUMPPA-COPEC field measurements campaign, in the summer of 2010. The ambient VOCs were measured with online TD-GC-MS and the cuvette emissions were made by offline GC-MS using SPME. The total monoterpenes (including α-pinene, Δ3-carene, ß-pinene and myrcene) observed during the campaign were from a few ppt to over one ppb. More than 50% of the measured monoterpenes above the canopy were α-pinene and Δ3-carene. Although the main tree species (Scots pine) are not isoprene emitters in the site, isoprene mixing ratios were still detected during the summer time with a maximum mixing ratio over 600ppt and median value of 56 ppt. The cuvette studies conducted at the same site during the campaign showed that Norway spruce was one of the main isoprene emitters. The Scots pines around the site can be classified as three different chemotypes according to Δ-3-carene, they are a high Δ-3-carene chemotype, a no Δ-3-carene chemotype and an intermediate chemotype. It is found that chemotype diversity not only affects the chemical composition of emitted terpenes but also their stereoisomery. The Δ-3-carene chemotype manifested strong preference for (+)-α-pinene which is in a good agreement with the previous studies taken at the same time of year (Williams et. al., 2007). However, the no Δ-3-carene chemotype was racemic for a-pinene. For ß-pinene, all chemotypes show enrichment with (-)-enantiomer, this was also the case in the ambient. For Norway spruce monoterpene emissions of both α-pinene and ß-pinene were found to be predominated by the (-)-enantiomers. From the emission composition and strength we can conclude that Δ-3-carene chemotypes of Scots pine, which emit preferentially (+)-α -pinene, are dominant and widespread in the Hyytiala Boreal forest. Interestingly, the ambient diel cycle of the enantiomeric enrichment of (-)-α-pinene showed that the (-)-enantiomer had an increasing fraction as the light and temperature rose through the day. This might be the contribution from the spruce via light controlled (-)-enantiomer enrichment of emissions from Scots pines.

In general, the BTEX compounds were much lower than BVOCs except during the period influenced by Russian wildfires. Outside this period benzene was also affected by other local emissions, such that the mixing ratios varied thorough the day, with toluene and xylenes following a similar trend which reached a first maximum value late in the morning and a second one in the early evening.

So far, no clear evidence has been found for predictable enantiomeric signatures in response to temperature or light in the leaf emissions under the laboratory conditions or in the natural environment. However, generally (not without exception) throughout this thesis work it has been observed that where there is a strong dependence of the enantiomeric ratio with light, the (-)-α-pinene was predominant in the emission. All the field measurements made over different ecosystems show clear enantiomeric ratio diel cycles (oak forest and boreal forest), and a clear seasonal change (Mediterranean stone pine forest). While the forests in Spain and Finland both show an enrichment of (-)-a-pinene at noon time, the French oak forest was observed to express a (+)-enantiomer enrichment at midday (see chapters 2, 3 and 4). The enantiomeric ratio from the Boreal forest showed no correlation with O_3 suggesting that the variation in the ratio is very likely coming from primary emissions. Despite the variety of enantiomeric signatures from individual emissions and the great chemodiversities, the diel variation of these enantiomers follows remarkably clear cycles in the larger datasets. This raises some interesting questions: do the ecosystems act to harmonize their emissions? Are other biological entities such as insects and neighboring plants affecting or affected by this diurnal cycle? Are there any other underlying mechanisms for the enantiomeric monoterpenes synthesis inside the plants? How may we benefit from the knowledge of this enantiomeric signature? It is clear the when suffering from stress (biotic or abiotic) plants will change their emission pattern leading to one enantiomer enrichment, for instance the saw mill activities or insects attacking induced the increased emissions of (+)-α-pinene in the Scots pine. One can speculate that this enantiomeric characterization could be used as an early warning for whether the forests are attacking by insects or not. If, as is expected,global temperatures will increase in the future, it can be seen from this work that the overall enantiomeric signature of the forest will change subtly as a consequence. This may lead to problems for other forest living entities, such as insects, using olfactory signals for their everyday life in the forests.

List of Figures

List of Tables

Abbreviation Index

Ar	Argon
ATP	Phosphorylation energy
BTEX	Acronym that stands for benzene, toluene, ethylbenzene, and xylenes
BVOC	Biogenic volatile organic compounds
CFC	Chlorofluorocarbon
CIP	(Name after Robert Sidney Cahn, Christopher Kelk Ingold and Vladimir Prelog) Describe chiral structures is the R/S system
CO2	Carbon dioxide
DMAPP	Dimethylallyl diphosphate
DOAS	Differential Optical Absorption Spectroscopy
DOMINO	Diel Oxidant Mechanisms In relation to Nitrogen Oxides
DVB-PDMS	Polydimethylsiloxane/Divinylbenzene
DXP	1- Deoxy-D-xylulose-5-phosphate
FAO	Food and Agriculture Organization of the United Nations
FPP	Farnesyl diphosphate
GC-MS	Gas chromatography–mass spectrometry
GDP	Geranyl diphosphate
GPP	Geranylpyrophosphate
H2O2	Hydrogen peroxide
HO2	Hydroperoxyl
HUMPPA-C OPEC	Hyytiälä United Measurement of Photochemistry and Particles – Comprehensive Organic Particle and Environmental Chemistry
IPCC	Intergovernmental Panel on Climate Change
IPP	Isopentenyl pyrophosphate
MEP	Methylerythritol phosphate
MVA	Cytosolic mevalonate
N2	Nitrogen
NADH	An enzyme used as a reducing agent to donate electrons
NADPH	An enzyme, used as reducing power for the biosynthetic reactions in the Calvin cycle to assimilate carbon dioxide.
NO x	Refers to NO and NO2
NO2	Nitrogen dioxide
NO3	nitrate radical
O2	Oxygen
OH	Hydroxyl radical
PAN	Peroxyacetyl nitrate
PAR	Photosynthetically active radiation
ppb	Parts-per-billion, 10–9
ppt	Parts-per-trillion, 10–12
PTR-MS	Proton-transfer-reaction mass spectrometry
RH	Saturated hydrocarbons

SPME	Solid Phase Microextraction
TD	Thermal desorption
UV	Ultraviolet
VOC	Volatile organic compounds

Bibliography

Aaltonen, H., Pumpanen, J., Pihlatie, M., Hakola, H., Hellen, H., Kulmala, L., Vesala, T., and Back, J.: Boreal pine forest floor biogenic volatile organic compound emissions peak in early summer and autumn, Agr Forest Meteorol, 151, 682-691, 10.1016/j.agrformet.2010.12.010, 2011.

Adame, J. A., Serrano, E., Bolivar, J. P., and de la Morena, B. A.: On the Tropospheric Ozone Variations in a Coastal Area of Southwestern Europe under a Mesoscale Circulation, J Appl Meteorol Clim, 49, 748-759, Doi 10.1175/2009jamc2097.1, 2010.

Andreae, M. O., and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biogeochem Cy, 15, 955-966, 2001.

Arneth, A., Niinemets, U., Pressley, S., Back, J., Hari, P., Karl, T., Noe, S., Prentice, I. C., Serca, D., Hickler, T., Wolf, A., and Smith, B.: Process-based estimates of terrestrial ecosystem isoprene emissions: incorporating the effects of a direct CO(2)-isoprene interaction, Atmos Chem Phys, 7, 31-53, 2007.

Arneth, A., Monson, R. K., Schurgers, G., Niinemets, U., and Palmer, P. I.: Why are estimates of global terrestrial isoprene emissions so similar (and why is this not so for monoterpenes)?, Atmos Chem Phys, 8, 4605-4620, 2008.

Atkinson, R., Arey, J., Tuazon, E. C., Aschmann, S. M., and Hakola, H.: Products of the Oh Radical and O3 Reactions with Isoprene and Monoterpenes, Abstr Pap Am Chem S, 207, 160-ENVR, 1994.

Atkinson, R., and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmos Environ, 37, S197-S219, 2003a.

Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem Rev, 103, 4605-4638, Doi 10.1021/Cr0206420, 2003b.

Back, J., Hari, P., Hakola, H., Juurola, E., and Kulmala, M.: Dynamics of monoterpene emissions in Pinus sylvestris during early spring, Boreal Environ Res, 10, 409-424, 2005.

Baldwin, I. T., Halitschke, R., Paschold, A., von Dahl, C. C., and Preston, C. A.: Volatile signaling in plant-plant interactions: "Talking trees" in the genomics era, Science, 311, 812-815, DOI 10.1126/science.1118446, 2006.

Baroja, O., Rodriguez, E., de Balugera, Z. G., Goicolea, A., Unceta, N., Sampedro, C., Alonso, A., and Barrio, R. J.: Speciation of volatile aromatic and chlorinated hydrocarbons in an urban atmosphere using TCT-GC/MS, J Environ Sci Heal A, 40, 343-367, 2005.

Bertin, N., Staudt, M., Hansen, U., Seufert, G., Ciccioli, P., Foster, P., Fugit, J. L., and Torres, L.: Diurnal and seasonal course of monoterpene emissions from Quercus ilex (L.) under natural conditions - Applications of light and temperature algorithms, Atmos Environ, 31, 135-144, 10.1016/s1352-2310(97)00080-0, 1997.

Blake, D. R., Smith, T. W., Chen, T. Y., Whipple, W. J., and Rowland, F. S.: Effects of Biomass Burning on Summertime Nonmethane Hydrocarbon Concentrations in the Canadian Wetlands, J

Geophys Res-Atmos, 99, 1699-1719, 1994.

Blanch, J. S., Penuelas, J., and Llusia, J.: Sensitivity of terpene emissions to drought and fertilization in terpene-storing Pinus halepensis and non-storing Quercus ilex, Physiol Plantarum, 131, 211-225, DOI 10.1111/j.1399-3054.2007.00944.x, 2007.

Bonn, B., Kulmala, M., Riipinen, I., Sihto, S. L., and Ruuskanen, T. M.: How biogenic terpenes govern the correlation between sulfuric acid concentrations and new particle formation, J Geophys Res-Atmos, 113, -, Artn D12209

Doi 10.1029/2007jd009327, 2008.

Borg-Karlson, A. K., Persson, M., Christansson, A., Faldt, J., Langstrom, B., Li, T., Liu, H., Zhou, N., and Lieutier, F.: Relative amounts and enantiomeric compositions of monoterpene hydrocarbons in Pinus yunnanensis Fr. and Pinus sylvestris L., Colloq Inra, 101-110

374, 1999.

Borgkarlson, A. K., Lindstrom, M., Norin, T., Persson, M., and Valterova, I.: Enantiomeric Composition of Monoterpene Hydrocarbons in Different Tissues of Norway Spruce, Picea-Abies (L) Karst - a Multidimensional Gas-Chromatography Study, Acta Chem Scand, 47, 138-144, 1993.

Brocco, D., Fratarcangeli, R., Lepore, L., Petricca, M., and Ventrone, I.: Determination of aromatic hydrocarbons in urban air of Rome, Atmos Environ, 31, 557-566, 1997.

Carroll, J. D.: A New Definition of Life, Chirality, 21, 354-358, Doi 10.1002/Chir.20590, 2009.

Carslaw, K. S., Boucher, O., Spracklen, D. V., Mann, G. W., Rae, J. G. L., Woodward, S., and Kulmala, M.: A review of natural aerosol interactions and feedbacks within the Earth system, Atmos Chem Phys, 10, 1701-1737, 2010.

Cassera, M. B., Gozzo, F. C., D'Alexandri, F. L., Merino, E. F., del Portillo, H. A., Peres, V. J., Almeida, I. C., Eberlin, M. N., Wunderlich, G., Wiesner, J., Jomaa, H., Kimura, E. A., and Katzin, A. M.: The methylerythritol phosphate pathway is functionally active in all intraerythrocytic stages of Plasmodium falciparum, Journal of Biological Chemistry, 279, 51749-51759, 10.1074/jbc.M408360200, 2004.

Choi, S. W., Park, S. W., Lee, C. S., Kim, H. J., Bae, S., and Inyang, H. I.: Patterns of VOC and BTEX concentration in ambient air around industrial sources in Daegu, Korea, J Environ Sci Heal A, 44, 99-107, 2009.

Croteau, R.: BIOSYNTHESIS AND CATABOLISM OF MONOTERPENOIDS, Chem Rev, 87, 929-954, 10.1021/cr00081a004, 1987.

Croteau, R., Satterwhite, D. M., Cane, D. E., and Chang, C. C.: BIOSYNTHESIS OF MONOTERPENES - ENANTIOSELECTIVITY IN THE ENZYMATIC CYCLIZATION OF (+)-LINALYL AND (-)-LINALYL PYROPHOSPHATE TO (+)-PINENE AND (-)-PINENE AND (+)-CAMPHENE AND (-)-CAMPHENE, Journal of Biological Chemistry, 263, 10063-10071, 1988.

Croteau, R., Alonso, W. R., Koepp, A. E., and Johnson, M. A.: BIOSYNTHESIS OF MONOTERPENES - PARTIAL-PURIFICATION, CHARACTERIZATION, AND MECHANISM OF ACTION OF 1,8-CINEOLE SYNTHASE, Arch Biochem Biophys, 309, 184-192, 10.1006/abbi.1994.1101, 1994.

Curci, G., Beekmann, M., Vautard, R., Smiatek, G., Steinbrecher, R., Theloke, J., and Friedrich, R.: Modelling study of the impact of isoprene and terpene biogenic emissions on European ozone levels, Atmos Environ, 43, 1444-1455, DOI 10.1016/j.atmosenv.2008.02.070, 2009.

Davison, B., Taipale, R., Langford, B., Misztal, P., Fares, S., Matteucci, G., Loreto, F., Cape, J. N., Rinne, J., and Hewitt, C. N.: Concentrations and fluxes of biogenic volatile organic compounds above a Mediterranean macchia ecosystem in western Italy, Biogeosciences, 6, 1655-1670, 2009.

Degenhardt, J., and Gershenzon, J.: Demonstration and characterization of (E)-nerolidol synthase from maize: a herbivore-inducible terpene synthase participating in (3E)-4,8-dimethyl-1,3,7-nonatriene biosynthesis, Planta, 210, 815-822, 2000.

Degenhardt, J., Kollner, T. G., and Gershenzon, J.: Monoterpene and sesquiterpene synthases and the origin of terpene skeletal diversity in plants, Phytochemistry, 70, 1621-1637, DOI 10.1016/j.phytochem.2009.07.030, 2009.

Dewick, P. M.: The biosynthesis of C-5-C-25 terpenoid compounds, Natural Product Reports, 19, 181-222, 10.1039/b002685i, 2002.

Durmusoglu, E., Taspinar, F., and Karademir, A.: Health risk assessment of BTEX emissions in the landfill environment, J Hazard Mater, 176, 870-877, DOI 10.1016/j.jhazmat.2009.11.117, 2010.

Dutta, C., Som, D., Chatterjee, A., Mukherjee, A. K., Jana, T. K., and Sen, S.: Mixing ratios of carbonyls and BTEX in ambient air of Kolkata, India and their associated health risk, Environmental Monitoring and Assessment, 148, 97-107, 2009.

Ebben, C. J., Zorn, S. R., Lee, S. B., Artaxo, P., Martin, S. T., and Geiger, F. M.: Stereochemical transfer to atmospheric aerosol particles accompanying the oxidation of biogenic volatile organic compounds, Geophysical Research Letters, 38, Artn L16807

Doi 10.1029/2011gl048599, 2011.

Eerdekens, G., Yassaa, N., Sinha, V., Aalto, P. P., Aufmhoff, H., Arnold, F., Fiedler, V., Kulmala, M., and Williams, J.: VOC measurements within a boreal forest during spring 2005: on the occurrence of elevated monoterpene concentrations during night time intense particle concentration events, Atmos Chem Phys, 9, 8331-8350, 2009.

Ehhalt, D. H., and Rohrer, F.: Dependence of the OH concentration on solar UV, J Geophys Res-Atmos, 105, 3565-3571, 2000.

Eisenreich, W., Bacher, A., Arigoni, D., and Rohdich, F.: Biosynthesis of isoprenoids via the non-mevalonate pathway, Cellular and Molecular Life Sciences, 61, 1401-1426, 10.1007/s00018-004-3381-z, 2004.

Faldt, J., Solheim, H., Langstrom, B., and Borg-Karlson, A. K.: Influence of fungal infection and wounding on contents and enantiomeric compositions of monoterpenes in phloem of Pinus sylvestris, Journal of Chemical Ecology, 32, 1779-1795, DOI 10.1007/s10886-006-9109-9, 2006.

Fall, R., and Wildermuth, M. C.: Isoprene synthase: From biochemical mechanism to emission algorithm, J Geophys Res-Atmos, 103, 25599-25609, 1998.

FAO: Food and Agriculture Organsation: Global forest resources assessment, FAO Forestry paper 2010.

Felton, G. W., and Tumlinson, J. H.: Plant-insect dialogs: complex interactions at the plant-insect interface, Curr Opin Plant Biol, 11, 457-463, DOI 10.1016/j.pbi.2008.07.001, 2008.

Finlayson-Pitts, B. J., and Pitts, J. N.: Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications Academic Press, 1999.

FinlaysonPitts, B. J., and Pitts, J. N.: Tropospheric air pollution: Ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles, Science, 276, 1045-1052, 1997.

Fischbach, R. J., Staudt, M., Zimmer, I., Rambal, S., and Schnitzler, J. P.: Seasonal pattern of monoterpene synthase activities in leaves of the evergreen tree Quercus ilex, Physiol Plantarum, 114, 354-360, 2002.

Fuentes, J. D., Wang, D., and Gu, L.: Seasonal variations in isoprene emissions from a boreal aspen forest, Journal of Applied Meteorology, 38, 855-869, 10.1175/1520-0450(1999)038<0855:sviief>2.0.co;2, 1999.

Fuentes, J. D., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J. W., Ciccioli, P., Lamb, B., Geron, C., Gu, L., Guenther, A., Sharkey, T. D., and Stockwell, W.: Biogenic hydrocarbons in the atmospheric boundary layer: A review, B Am Meteorol Soc, 81, 1537-1575, 2000.

Gershenzon, J., and Dudareva, N.: The function of terpene natural products in the natural world, Nat Chem Biol, 3, 408-414, DOI 10.1038/nchembio.2007.5, 2007.

Ghirardo, A., Koch, K., Taipale, R., Zimmer, I., Schnitzler, J. P., and Rinne, J.: Determination of de novo and pool emissions of terpenes from four common boreal/alpine trees by 13CO(2) labelling and PTR-MS analysis, Plant Cell Environ, 33, 781-792, 10.1111/j.1365-3040.2009.02104.x, 2010.

Goldstein, A. H., and Galbally, I. E.: Known and unexplored organic constituents in the earth's atmosphere, Environ Sci Technol, 41, 1514-1521, 2007.

Grabmer, W., Kreuzwieser, J., Wisthaler, A., Cojocariu, C., Graus, M., Rennenberg, H., Steigner, D., Steinbrecher, R., and Hansel, A.: VOC emissions from Norway spruce (Picea abies L. [Karst]) twigs in the field - Results of a dynamic enclosure study, Atmos Environ, 40, S128-S137, DOI 10.1016/j.atmosenv.2006.03.043, 2006.

Grote, R., Mayrhofer, S., Fischbach, R. J., Steinbrecher, R., Staudt, M., and Schnitzler, J. P.: Process-based modelling of isoprenoid emissions from evergreen leaves of Quercus ilex (L.), Atmos Environ, 40, S152-S165, DOI 10.1016/j.atmosenv.2005.10.071, 2006.

Grote, R., and Niinemets, U.: Modeling volatile isoprenoid emissions - a story with split ends, Plant Biology, 10, 8-28, 2008.

Grote, R., Lavoir, A. V., Rambal, S., Staudt, M., Zimmer, I., and Schnitzler, J. P.: Modelling the drought impact on monoterpene fluxes from an evergreen Mediterranean forest canopy, Oecologia, 160, 213-223, DOI 10.1007/s00442-009-1298-9, 2009.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A Global-Model of Natural Volatile Organic-Compound Emissions, J Geophys Res-Atmos, 100, 8873-8892, 1995.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos Chem Phys, 6, 3181-3210, 2006.

Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and Monoterpene Emission Rate Variability - Model Evaluations and Sensitivity Analyses, J Geophys Res-Atmos, 98, 12609-12617, 1993.

Hakola, H., Laurila, T., Rinne, J., and Puhto, K.: The ambient concentrations of biogenic hydrocarbons at a northern European, boreal site, Atmos Environ, 34, 4971-4982, 10.1016/s1352-2310(00)00192-8, 2000.

Hakola, H., Tarvainen, V., Laurila, T., Hiltunen, V., Hellen, H., and Keronen, P.: Seasonal variation of VOC concentrations above a boreal coniferous forest, Atmos Environ, 37, 1623-1634, Doi 10.1016/S1352-2310(03)00014-1, 2003.

Hakola, H., Tarvainen, V., Back, J., Ranta, H., Bonn, B., Rinne, J., and Kulmala, M.: Seasonal variation of mono- and sesquiterpene emission rates of Scots pine, Biogeosciences, 3, 93-101, 2006.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos Chem Phys, 9, 5155-5236, 2009.

Hampel, D., Mosandl, A., and Wust, M.: Biosynthesis of mono- and sesquiterpenes in carrot roots and leaves (Daucus carota L.): metabolic cross talk of cytosolic mevalonate and plastidial methylerythritol phosphate pathways, Phytochemistry, 66, 305-311, DOI 10.1016/j.phytochem.2004.12.010, 2005.

Hampel, D., Mosandl, A., and Wust, M.: Biosynthesis of mono- and sesquiterpenes in strawberry fruits and foliage: H-2 labeling studies, J Agr Food Chem, 54, 1473-1478, Doi 10.1021/Jf0523972, 2006.

Hampel, D., Swatski, A., Mosandl, A., and Wust, M.: Biosynthesis of monoterpenes and norisoprenoids in raspberry fruits (Rubus idaeus L.): The role of cytosolic mevalonate and plastidial methylerythritol phosphate pathway, J Agr Food Chem, 55, 9296-9304, 10.1021/jf071311x, 2007.

Hansen, U., and Seufert, G.: Temperature and light dependence of beta-caryophyllene emission rates, J Geophys Res-Atmos, 108, Artn 4801

Doi 10.1029/2003jd003853, 2003.

Harley, P., Vasconcellos, P., Vierling, L., Pinheiro, C. C. D., Greenberg, J., Guenther, A., Klinger, L., De Almeida, S. S., Neill, D., Baker, T., Phillips, O., and Malhi, Y.: Variation in potential for isoprene emissions among Neotropical forest sites, Global Change Biol, 10, 630-650, 10.1111/j.1529-8817.2003.00760.x, 2004.

Harley, P. C., Monson, R. K., and Lerdau, M. T.: Ecological and evolutionary aspects of isoprene emission from plants, Oecologia, 118, 109-123, 10.1007/s004420050709, 1999.

Hinze, W. L.: APPLICATIONS OF CYCLODEXTRINS IN CHROMATOGRAPHIC SEPARATIONS AND PURIFICATION METHODS, Sep. Purif. Methods, 10, 159-237, 10.1080/03602548108066011, 1981.

Ho, K. E., Lee, S. C., Guo, H., and Tsai, W.: Seasonal and diurnal variations of volatile organic compounds (VOCs) in the atmosphere of Hong Kong, Science of the Total Environment, 322, 155-166, 2004.

Holloway, A. M., and Wayne, R. P.: Atmospheric Chemistry Royal Society of Chemistry, 2010.

Holzke, C., Hoffmann, T., Jaeger, L., Koppmann, R., and Zimmer, W.: Diurnal and seasonal variation of monoterpene and sesquiterpene emissions from Scots pine (Pinus sylvestris L.), Atmos Environ, 40, 3174-3185, 10.1016/j.atmosenv.2006.01.039, 2006.

Hopke, J., Donath, J., Blechert, S., and Boland, W.: Herbivore-Induced Volatiles - the Emission of Acyclic Homoterpenes from Leaves of Phaseolus-Lunatus and Zea-Mays Can Be Triggered by a Beta-Glucosidase and Jasmonic Acid, Febs Lett, 352, 146-150, 1994.

Hoque, R. R., Khillare, P. S., Agarwal, T., Shridhar, V., and Balachandran, S.: Spatial and temporal variation of BTEX in the urban atmosphere of Delhi, India, Science of the Total Environment, 392, 30-40, 2008.

Howard, P. H.: Handbook of Environmental Fate and Exposure Data for Organic Chemicals, CRC Press 1990.

IPCC: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change 2007.

Isidorov, V. A., Smolewska, M., Purzynska-Pugacewicz, A., and Tyszkiewicz, Z.: Chemical composition of volatile and extractive compounds of pine and spruce leaf litter in the initial stages of decomposition, Biogeosciences, 7, 2785-2794, 10.5194/bg-7-2785-2010, 2010.

Ito, A., and Penner, J. E.: Global estimates of biomass burning emissions based on satellite imagery for the year 2000, J Geophys Res-Atmos, 109, Artn D14s05

Doi 10.1029/2003jd004423, 2004.

Jacob, D. J., Field, B. D., Jin, E. M., Bey, I., Li, Q. B., Logan, J. A., Yantosca, R. M., and Singh, H. B.: Atmospheric budget of acetone, J Geophys Res-Atmos, 107, Artn 4100

Doi 10.1029/2001jd000694, 2002.

Jacobson, M. C., Hansson, H. C., Noone, K. J., and Charlson, R. J.: Organic atmospheric aerosols: Review and state of the science, Reviews of Geophysics, 38, 267-294, 2000.

Jacobson, M. Z.: Atmospheric Pollution: History, Science and Regulation, Cambridge University Press, NewYork, 2002.

Janson, R.: Monoterpene Concentrations in and above a Forest of Scots Pine, J Atmos Chem, 14, 385-394, 1992.

Janson, R., and de Serves, C.: Acetone and monoterpene emissions from the boreal forest in northern Europe, Atmos Environ, 35, 4629-4637, 10.1016/s1352-2310(01)00160-1, 2001.

Janson, R., Rosman, K., Karlsson, A., and Hansson, H. C.: Biogenic emissions and gaseous precursors to forest aerosols, Tellus B, 53, 423-440, 2001.

Jenkin, M. E., and Clemitshaw, K. C.: Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer, Atmos Environ, 34, 2499-2527, 2000.

Keenan, T., Niinemets, U., Sabate, S., Gracia, C., and Penuelas, J.: Seasonality of monoterpene emission potentials in Quercus ilex and Pinus pinea: Implications for regional VOC emissions modeling, J Geophys Res-Atmos, 114, 10.1029/2009jd011904, 2009.

Kesselmeier, J., Schafer, L., Ciccioli, P., Brancaleoni, E., Cecinato, A., Frattoni, M., Foster, P., Jacob, V., Denis, J., Fugit, J. L., Dutaur, L., and Torres, L.: Emission of monoterpenes and isoprene from a Mediterranean oak species Quercus ilex L measured within the BEMA (Biogenic Emissions in the Mediterranean Area) project, Atmos Environ, 30, 1841-1850, 1996.

Kesselmeier, J., Bode, K., Hofmann, U., Muller, H., Schafer, L., Wolf, A., Ciccioli, P., Brancaleoni, E., Cecinato, A., Frattoni, M., Foster, P., Ferrari, C., Jacob, V., Fugit, J. L., Dutaur, L., Simon, V., and Torres, L.: Emission of short chained organic acids, aldehydes and monoterpenes from Quercus ilex L. and Pinus pinea L. in relation to physiological activities, carbon budget and emission algorithms, Atmos Environ, 31, 119-133, 1997.

Kesselmeier, J., and Staudt, M.: Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology, J Atmos Chem, 33, 23-88, 1999.

Komenda, M., and Koppmann, R.: Monoterpene emissions from Scots pine (Pinus sylvestris): Field studies of emission rate variabilities, J Geophys Res-Atmos, 107, Artn 4161

Doi 10.1029/2001jd000691, 2002.

Komenda, M., Kobel, K., Koppmann, R., and Wildt, J.: Comparability of biogenic VOC emission rate measurements under laboratory and ambient conditions at the example of monoterpene emissions from Scots pine (Pinus sylvestris), J Atmos Chem, 45, 1-23, 2003.

Koscielski, T., Sybilska, D., and Jurczak, J.: Separation of Alpha-Pinene and Beta-Pinene into Enantiomers in Gas-Liquid-Chromatography Systems Via Alpha-Cyclodextrin Inclusion Complexes, J Chromatogr, 280, 131-134, 1983.

Kulmala, M., Suni, T., Lehtinen, K. E. J., Dal Maso, M., Boy, M., Reissell, A., Rannik, U., Aalto, P., Keronen, P., Hakola, H., Back, J. B., Hoffmann, T., Vesala, T., and Hari, P.: A new feedback mechanism linking forests, aerosols, and climate, Atmos Chem Phys, 4, 557-562, 2004.

Laothawornkitkul, J., Taylor, J. E., Paul, N. D., and Hewitt, C. N.: Biogenic volatile organic compounds in the Earth system, New Phytol, 183, 27-51, 10.1111/j.1469-8137.2009.02859.x, 2009.

Lappalainen, H. K., Sevanto, S., Back, J., Ruuskanen, T. M., Kolari, P., Taipale, R., Rinne, J., Kulmala, M., and Hari, P.: Day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors, Atmos Chem Phys, 9, 5447-5459, 2009.

Lathiere, J., Hauglustaine, D. A., Friend, A. D., De Noblet-Ducoudre, N., Viovy, N., and Folberth, G. A.: Impact of climate variability and land use changes on global biogenic volatile organic compound emissions, Atmos Chem Phys, 6, 2129-2146, 2006.

Lawrence, M. G., Butler, T. M., Steinkamp, J., Gurjar, B. R., and Lelieveld, J.: Regional pollution potentials of megacities and other major population centers, Atmos Chem Phys, 7, 3969-3987, 2007.

Lee, S. C., Chiu, M. Y., Ho, K. F., Zou, S. C., and Wang, X. M.: Volatile organic compounds (VOCs) in urban atmosphere of Hong Kong, Chemosphere, 48, 375-382, 2002.

Lelieveld, J., Peters, W., Dentener, F. J., and Krol, M. C.: Stability of tropospheric hydroxyl chemistry, J Geophys Res-Atmos, 107, Artn 4715

Doi 10.1029/2002jd002272, 2002.

Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737-740, 10.1038/nature06870, 2008.

Lerdau, M., Dilts, S. B., Westberg, H., Lamb, B. K., and Allwine, E. J.: Monoterpene Emission from Ponderosa Pine, J Geophys Res-Atmos, 99, 16609-16615, 1994.

Lerdau, M., Litvak, M., Palmer, P., and Monson, R.: Controls over monoterpene emissions from boreal forest conifers, Tree Physiol, 17, 563-569, 1997.

Lindfors, V., Laurila, T., Hakola, H., Steinbrecher, R., and Rinne, J.: Modeling speciated terpenoid emissions from the European boreal forest, Atmos Environ, 34, 4983-4996, 10.1016/s1352-2310(00)00223-5, 2000.

Llusia, J., Penuelas, J., Alessio, G. A., and Ogaya, R.: Species-specific, seasonal, inter-annual, and historically-accumulated changes in foliar terpene emission rates in Phillyrea latifolia and Quercus ilex submitted to rain exclusion in the Prades Mountains (Catalonia), Russ J Plant Physl+, 58, 126-132, Doi 10.1134/S1021443710061020, 2011.

Loreto, F., Ciccioli, P., Cecinato, A., Brancaleoni, E., Frattoni, M., Fabozzi, C., and Tricoli, D.: Evidence of the photosynthetic origin of monoterpenes emitted by Quercus ilex L leaves by C-13 labeling, Plant Physiology, 110, 1317-1322, 1996a.

Loreto, F., Ciccioli, P., Cecinato, A., Brancaleoni, E., Frattoni, M., and Tricoli, D.: Influence of environmental factors and air composition on the emission of alpha-pinene from Quercus ilex leaves, Plant Physiology, 110, 267-275, 1996b.

Loreto, F., Forster, A., Durr, M., Csiky, O., and Seufert, G.: On the monoterpene emission under heat stress and on the increased thermotolerance of leaves of Quercus ilex L. fumigated with selected monoterpenes, Plant Cell Environ, 21, 101-107, 1998.

Loreto, F., Fischbach, R. J., Schnitzler, J. P., Ciccioli, P., Brancaleoni, E., Calfapietra, C., and Seufert, G.: Monoterpene emission and monoterpene synthase activities in the Mediterranean evergreen oak Quercus ilex L. grown at elevated CO2 concentrations, Global Change Biol, 7, 709-717, 2001.

Loreto, F., and Schnitzler, J. P.: Abiotic stresses and induced BVOCs, Trends Plant Sci, 15, 154-166, DOI 10.1016/j.tplants.2009.12.006, 2010.

Mahmoud, S. S., and Croteau, R. B.: Strategies for transgenic manipulation of monoterpene biosynthesis in plants, Trends Plant Sci, 7, 366-373, 2002.

Martin, D. M., Faldt, J., and Bohlmann, J.: Functional characterization of nine Norway spruce TPS genes and evolution of gymnosperm terpene synthases of the TPS-d subfamily, Plant Physiology, 135, 1908-1927, DOI 10.1104/pp.104.042028, 2004.

McCaskill, D., and Croteau, R.: Some caveats for bioengineering terpenoid metabolism in plants, Trends Biotechnol, 16, 349-355, 1998.

Mcgarvey, D. J., and Croteau, R.: Terpenoid Metabolism, Plant Cell, 7, 1015-1026, 1995.

McKinney, K. A., Lee, B. H., Vasta, A., Pho, T. V., and Munger, J. W.: Emissions of isoprenoids and oxygenated biogenic volatile organic compounds from a New England mixed forest, Atmos Chem Phys, 11, 4807-4831, DOI 10.5194/acp-11-4807-2011, 2011.

Meyer, O., Grosdemange-Billiard, C., Tritsch, D., and Rohmer, M.: Isoprenoid biosynthesis via the MEP pathway. Synthesis of (3R,4S)-3,4-dihydroxy-5-oxohexylphosphonic acid, an isosteric analogue of 1-deoxy-D-xylulose5-phosphate, the substrate of the 1-deoxy-D-xylulose5-phosphate reducto-isomerase, Organic & Biomolecular Chemistry, 1, 4367-4372, 10.1039/b312193c, 2003.

Monson, R. K., Jaeger, C. H., Adams, W. W., Driggers, E. M., Silver, G. M., and Fall, R.: Relationships among Isoprene Emission Rate, Photosynthesis, and Isoprene Synthase Activity as Influenced by Temperature, Plant Physiology, 98, 1175-1180, 1992.

Monson, R. K., Lerdau, M. T., Sharkey, T. D., Schimel, D. S., and Fall, R.: Biological Aspects of Constructing Volatile Organic-Compound Emission Inventories, Atmos Environ, 29, 2989-3002, 1995.

Mori, K.: Semiochemicals - Synthesis, stereochemistry, and bioactivity, European Journal of Organic Chemistry, 1479-1489, 1998.

Mraz, J., Feltl, L., and Smolkovakeulemansova, E.: CYCLODEXTRINS AND METHYLATED CYCLODEXTRINS AS STATIONARY PHASES IN GAS-SOLID CHROMATOGRAPHY, J Chromatogr, 286, 17-22, 10.1016/s0021-9673(01)99165-4, 1984.

Niinemets, U., Seufert, G., Steinbrecher, R., and Tenhunen, J. D.: A model coupling foliar monoterpene emissions to leaf photosynthetic characteristics in Mediterranean evergreen Quercus species, New Phytol, 153, 257-275, 2002.

Niinemets, U., Loreto, F., and Reichstein, M.: Physiological and physicochemical controls on foliar volatile organic compound emissions, Trends Plant Sci, 9, 180-186, DOI 10.1016/j.tplants.2004.02.006, 2004.

Niinemets, U., Arneth, A., Kuhn, U., Monson, R. K., Penuelas, J., and Staudt, M.: The emission factor of volatile isoprenoids: stress, acclimation, and developmental responses, Biogeosciences, 7, 2203-2223, DOI 10.5194/bg-7-2203-2010, 2010a.

Niinemets, U., Monson, R. K., Arneth, A., Ciccioli, P., Kesselmeier, J., Kuhn, U., Noe, S. M., Penuelas, J., and Staudt, M.: The leaf-level emission factor of volatile isoprenoids: caveats, model algorithms, response shapes and scaling, Biogeosciences, 7, 1809-1832, 10.5194/bg-7-1809-2010, 2010b.

Norin, T.: Chiral chemodiversity and its role for biological activity. Some observations from studies on insect/insect and insect/plant relationships, Pure Appl Chem, 68, 2043-2049, 1996.

Noziere, B., Gonzalez, N. J. D., Borg-Karlson, A. K., Pei, Y. X., Redeby, J. P., Krejci, R., Dommen, J., Prevot, A. S. H., and Anthonsen, T.: Atmospheric chemistry in stereo: A new look at secondary organic aerosols from isoprene, Geophysical Research Letters, 38, Artn L11807

Doi 10.1029/2011gl047323, 2011.

O'Dowd, C. D., Aalto, P., Hameri, K., Kulmala, M., and Hoffmann, T.: Aerosol formation - Atmospheric particles from organic vapours, Nature, 416, 497-498, 10.1038/416497a, 2002.

Owen, S., Boissard, C., Street, R. A., Duckham, S. C., Csiky, O., and Hewitt, C. N.: Screening of 18 Mediterranean plant species for volatile organic compound emissions, Atmos Environ, 31, 101-117, 1997.

Penuelas, J., and Llusia, J.: Seasonal emission of monoterpenes by the Mediterranean tree Quercus ilex in field conditions: Relations with photosynthetic rates, temperature and volatility, Physiol Plantarum, 105, 641-647, 1999.

Penuelas, J., and Staudt, M.: BVOCs and global change, Trends Plant Sci, 15, 133-144, 10.1016/j.tplants.2009.12.005, 2010.

Perry, R., and Gee, I. L.: Vehicle Emissions in Relation to Fuel Composition, Science of the Total Environment, 169, 149-156, 1995.

Persson, M., Borgkarlson, A. K., and Norin, T.: Enantiomeric Composition of 6 Chiral Monoterpene Hydrocarbons in Different Tissues of Picea-Abies, Phytochemistry, 33, 303-307, 1993.

Persson, M., Sjodin, K., BorgKarlson, A. K., Norin, T., and Ekberg, I.: Relative amounts and enantiomeric compositions of monoterpene hydrocarbons in xylem and needles of Picea abies, Phytochemistry, 42, 1289-1297, 1996.

Piccot, S. D., Watson, J. J., and Jones, J. W.: A Global Inventory of Volatile Organic-Compound Emissions from Anthropogenic Sources, J Geophys Res-Atmos, 97, 9897-9912, 1992.

Plaza, J., Nunez, L., Pujadas, M., Perrez-Pastor, R., Bermejo, V., Garcia-Alonso, S., and Elvira, S.: Field monoterpene emission of Mediterranean oak (Quercus ilex) in the central Iberian Peninsula measured by enclosure and micrometeorological techniques: Observation of drought stress effect, J Geophys Res-Atmos, 110, Artn D01105

Doi 10.1029/2004jd005168, 2005.

Pollmann, J., Ortega, J., and Helmig, D.: Analysis of atmospheric sesquiterpenes: Sampling losses and mitigation of ozone interferences, Environ Sci Technol, 39, 9620-9629, Doi 10.1021/Es050440w, 2005.

Possanzini, M., Di Palo, V., Gigliucci, P., Concetta, M., Sciano, T., and Cecinato, A.: Determination of phase-distributed PAH in Rome ambient air by denuder/GC-MS method, Atmos Environ, 38, 1727-1734, DOI 10.1016/j.atmosenv.2003.12.024, 2004.

Purves, D. W., Caspersen, J. P., Moorcroft, P. R., Hurtt, G. C., and Pacala, S. W.: Human-induced changes in US biogenic volatile organic compound emissions: evidence from long-term forest inventory data, Global Change Biol, 10, 1737-1755, DOI 10.1111/j.1365-2486.2004.00844.x, 2004.

Räisänen, T., Ryyppö, A., and Kellomäki, S.: Effects of elevated CO2 and temperature on monoterpene emission of Scots pine (Pinus sylvestris L.), Atmos Environ, 42, 4160-4171, 10.1016/j.atmosenv.2008.01.023, 2008.

Räisänen, T., Ryyppö, A., and Kellomäki, S.: Monoterpene emission of a boreal Scots pine (Pinus sylvestris L.) forest, Agr Forest Meteorol, 149, 808-819, 10.1016/j.agrformet.2008.11.001, 2009.

Rinne, J., Hakola, H., Laurila, T., and Rannik, U.: Canopy scale monoterpene emissions of Pinus sylvestris dominated forests, Atmos Environ, 34, 1099-1107, 2000.

Rinne, J., Taipale, R., Markkanen, T., Ruuskanen, T. M., Hellen, H., Kajos, M. K., Vesala, T., and Kulmala, M.: Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modeling, Atmos Chem Phys, 7, 3361-3372, 2007.

Rinne, J., Back, J., and Hakola, H.: Biogenic volatile organic compound emissions from the Eurasian taiga: current knowledge and future directions, Boreal Environ Res, 14, 807-826, 2009.

Roberts, J. M., Fehsenfeld, F. C., Liu, S. C., Bollinger, M. J., Hahn, C., Albritton, D. L., and Sievers, R. E.: Measurements of Aromatic Hydrocarbon Ratios and Nox Concentrations in the Rural Troposphere - Observation of Air-Mass Photochemical Aging and Nox Removal, Atmos Environ, 18, 2421-2432, 1984.

Rohmer, M.: The discovery of a mevalonate-independent pathway for isoprenoid biosynthesis in bacteria, algae and higher plants, Natural Product Reports, 16, 565-574, 10.1039/a709175c, 1999.

Rohmer, M.: Mevalonate-independent methylerythritol phosphate pathway for isoprenoid biosynthesis. Elucidation and distribution, Pure Appl Chem, 75, 375-387, 10.1351/pac200375020375, 2003.

Rohrer, F., and Berresheim, H.: Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, Nature, 442, 184-187, Doi 10.1038/Nature04924, 2006.

Rostelien, T., Stranden, M., Borg-Karlson, A. K., and Mustaparta, H.: Olfactory receptor neurons in two heliothine moth species responding selectively to aliphatic green leaf volatiles, aromatic compounds, monoterpenes and sesquiterpenes of plant origin, Chem Senses, 30, 443-461, DOI 10.1093/chemse/bji039, 2005.

Sabillon, D., and Cremades, L. V.: Diurnal and seasonal variation of monoterpene emission rates for two typical Mediterranean species (Pinus pinea and Quercus ilex) from field measurements-relationship with temperature and PAR, Atmos Environ, 35, 4419-4431, 2001.

Sanadze, G. A.: Biogenic isoprene - (A review), Russ J Plant Physl+, 51, 729-741, 2004.

Satterwhite, D. M., Wheeler, C. J., and Croteau, R.: BIOSYNTHESIS OF MONOTERPENES - ENANTIOSELECTIVITY IN THE ENZYMATIC CYCLIZATION OF LINALYL PYROPHOSPHATE TO (-)-ENDO-FENCHOL, Journal of Biological Chemistry, 260, 3901-3908, 1985.

Schurgers, G., Hickler, T., Miller, P. A., and Arneth, A.: European emissions of isoprene and monoterpenes from the Last Glacial Maximum to present, Biogeosciences, 6, 2779-2797, 2009.

Seemann, M., Bui, B. T. S., Wolff, M., Miginlac-Maslow, M., and Rohmer, M.: Isoprenoid biosynthesis in plant chloroplasts via the MEP pathway: Direct thylakoid/ferredoxin-dependent photoreduction of GcpE/IspG, Febs Lett, 580, 1547-1552, 10.1016/j.febslet.2006.01.082, 2006.

Shao, M., Czapiewski, K. V., Heiden, A. C., Kobel, K., Komenda, M., Koppman, R., and Wildt, J.: Volatile organic compound emissions from Scots pine: Mechanisms and description by algorithms, J Geophys Res-Atmos, 106, 20483-20491, 2001.

Sharkey, T. D., and Yeh, S. S.: Isoprene emission from plants, Annual Review of Plant Physiology and Plant Molecular Biology, 52, 407-436, 10.1146/annurev.arplant.52.1.407, 2001.

Silver, G. M., and Fall, R.: ENZYMATIC-SYNTHESIS OF ISOPRENE FROM DIMETHYLALLYL DIPHOSPHATE IN ASPEN LEAF EXTRACTS, Plant Physiology, 97, 1588-1591, 10.1104/pp.97.4.1588, 1991.

Simon, V., Clement, B., Riba, M. L., and Torres, L.: The Landes Experiment - Monoterpenes Emitted from the Maritime Pine, J Geophys Res-Atmos, 99, 16501-16510, 1994.

Smolkovakeulemansova, E.: CYCLODEXTRINS AS STATIONARY PHASES IN CHROMATOGRAPHY, J Chromatogr, 251, 17-34, 10.1016/s0021-9673(00)98506-6, 1982.

Staudt, M., and Seufert, G.: Light-Dependent Emission of Monoterpenes by Holm Oak (Quercus-Ilex L), Naturwissenschaften, 82, 89-92, 1995.

Staudt, M., Bertin, N., Hansen, U., Seufert, G., Ciccioli, P., Foster, P., Frenzel, B., and Fugit, J. L.: Seasonal and diurnal patterns of monoterpene emissions from Pinus pinea (L.) under field conditions, Atmos Environ, 31, 145-156, 1997.

Staudt, M., and Bertin, N.: Light and temperature dependence of the emission of cyclic and acyclic monoterpenes from holm oak (Quercus ilex L.) leaves, Plant Cell Environ, 21, 385-395, 1998.

Staudt, M., Bertin, N., Frenzel, B., and Seufert, G.: Seasonal variation in amount and composition of monoterpenes emitted by young Pinus pinea trees - Implications for emission modeling, J Atmos Chem, 35, 77-99, 2000.

Staudt, M., Mandl, N., Joffre, R., and Rambal, S.: Intraspecific variability of monoterpene composition emitted by Quercus ilex leaves, Can J Forest Res, 31, 174-180, 2001.

Staudt, M., Rambal, S., Joffre, R., and Kesselmeier, J.: Impact of drought on seasonal monoterpene emissions from Quercus ilex in southern France, J Geophys Res-Atmos, 107, Artn 4602

Doi 10.1029/2001jd002043, 2002.

Staudt, M., Joffre, R., and Rambal, S.: How growth conditions affect the capacity of Quercus ilex leaves to emit monoterpenes, New Phytol, 158, 61-73, DOI 10.1046/j.1469-8137.2003.00722.x, 2003.

Staudt, M., Mir, C., Joffre, R., Rambal, S., Bonin, A., Landais, D., and Lumaret, R.: Isoprenoid emissions of Quercus spp. (Q-suber and Q-ilex) in mixed stands contrasting in interspecific genetic introgression, New Phytol, 163, 573-584, DOI 10.1111/j.1469-8137.2004.01140.x, 2004.

Staudt, M., and Lhoutellier, L.: Monoterpene and sesquiterpene emissions from Quercus coccifera exhibit interacting responses to light and temperature, Biogeosciences, 8, 2757-2771, 10.5194/bg-8-2757-2011, 2011.

Stokes, G. Y., Chen, E. H., Buchbinder, A. M., Paxton, W. F., Keeley, A., and Geiger, F. M.: Atmospheric Heterogeneous Stereochemistry, J Am Chem Soc, 131, 13733-13737, Doi 10.1021/Ja904206t, 2009.

Street, R. A., Hewitt, C. N., and Mennicken, S.: Isoprene and monoterpene emissions from a Eucalyptus plantation in Portugal, J Geophys Res-Atmos, 102, 15875-15887, 1997.

Taipale, R., Kajos, M. K., Patokoski, J., Rantala, P., Ruuskanen, T. M., and Rinne, J.: Role of de novo biosynthesis in ecosystem scale monoterpene emissions from a boreal Scots pine forest, Biogeosciences, 8, 2247-2255, 10.5194/bg-8-2247-2011, 2011.

Tanaka, M., Kawano, S., and Shono, T.: APPLICABILITY OF MODIFIED BETA-CYCLODEXTRIN STATIONARY PHASES FOR GAS-CHROMATOGRAPHY, Fresenius Zeitschrift Fur Analytische Chemie, 316, 54-55, 10.1007/bf00487590, 1983.

Tarvainen, V., Hakola, H., Hellen, H., Back, J., Hari, P., and Kulmala, M.: Temperature and light dependence of the VOC emissions of Scots pine, Atmos Chem Phys, 5, 989-998, 2005.

Thompson, A. M.: The Oxidizing Capacity of the Earths Atmosphere - Probable Past and Future Changes, Science, 256, 1157-1165, 1992.

Thoss, V., O'Reilly-Wapstra, J., and Iason, G. R.: Assessment and implications of intraspecific and phenological variability in monoterpenes of Scots pine (Pinus sylvestris) foliage, Journal of Chemical Ecology, 33, 477-491, 10.1007/s10886-006-9244-3, 2007.

Tooker, J. F., and Hanks, L. M.: Stereochemistry of host plant monoterpenes as mate location cues for the gall wasp Antistrophus rufus, Journal of Chemical Ecology, 30, 473-477, 2004.

Tunved, P., Hansson, H. C., Kerminen, V. M., Strom, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P. P., Komppula, M., and Kulmala, M.: High natural aerosol loading over boreal forests, Science, 312, 261-263, DOI 10.1126/science.1123052, 2006.

van Aardenne, J. A., Dentener, F. J., Olivier, J. G. J., Goldewijk, C. G. M. K., and Lelieveld, J.: A 1 degrees x 1 degrees resolution data set of historical anthropogenic trace gas emissions for the period 1890-1990, Global Biogeochem Cy, 15, 909-928, 2001.

van Dam, N. M., Qiu, B. L., Hordijk, C. A., Vet, L. E. M., and Jansen, J. J.: Identification of Biologically Relevant Compounds in Aboveground and Belowground Induced Volatile Blends, Journal of Chemical Ecology, 36, 1006-1016, DOI 10.1007/s10886-010-9844-9, 2010.

Wang, X. M., Sheng, G. Y., Fu, J. M., Chan, C. Y., Lee, S. G., Chan, L. Y., and Wang, Z. S.: Urban roadside aromatic hydrocarbons in three cities of the Pearl River Delta, People's Republic of China, Atmos Environ, 36, 5141-5148, 2002.

Warneck, P.: Chemistry of the Natural Atmosphere, Academic Press; 2 edition (October 29, 1999), 1999.

Warneck, P., and Williams, J.: The Atmospheric Chemist's Companion: Numerical Data for Use in the Atmospheric Sciences, Springer Netherlands, 2012.

Wiedinmyer, C., Akagi, S. K., Yokelson, R. J., Emmons, L. K., Al-Saadi, J. A., Orlando, J. J., and Soja, A. J.: The Fire INventory from NCAR (FINN): a high resolution global model to estimate the emissions from open burning, Geosci Model Dev, 4, 625-641, DOI 10.5194/gmd-4-625-2011, 2011.

Wildermuth, M. C., and Fall, R.: Biochemical characterization of stromal and thylakoid-bound isoforms of isoprene synthase in willow leaves, Plant Physiology, 116, 1111-1123, 10.1104/pp.116.3.1111, 1998.

Williams, J.: Organic Trace Gases in the Atmosphere: An Overview, Environ Chem, 1, 125-136, Doi 10.1071/En04057, 2004.

Williams, J., Yassaa, N., Bartenbach, S., and Lelieveld, J.: Mirror image hydrocarbons from Tropical and Boreal forests, Atmos Chem Phys, 7, 973-980, 2007.

Williams, J., Crowley, J., Fischer, H., Harder, H., Martinez, M., Petaja, T., Rinne, J., Back, J., Boy, M., Dal Maso, M., Hakala, J., Kajos, M., Keronen, P., Rantala, P., Aalto, J., Aaltonen, H., Paatero, J., Vesala, T., Hakola, H., Levula, J., Pohja, T., Herrmann, F., Auld, J., Mesarchaki, E., Song, W., Yassaa, N., Nolscher, A., Johnson, A. M., Custer, T., Sinha, V., Thieser, J., Pouvesle, N., Taraborrelli, D., Tang, M. J., Bozem, H., Hosaynali-Beygi, Z., Axinte, R., Oswald, R., Novelli, A., Kubistin, D., Hens, K., Javed, U., Trawny, K., Breitenberger, C., Hidalgo, P. J., Ebben, C. J., Geiger, F. M., Corrigan, A. L., Russell, L. M., Ouwersloot, H. G., de Arellano, J. V. G., Ganzeveld, L., Vogel, A., Beck, M., Bayerle, A., Kampf, C. J., Bertelmann, M., Kollner, F., Hoffmann, T., Valverde, J., Gonzalez, D., Riekkola, M. L., Kulmala, M., and Lelieveld, J.: The summertime Boreal forest field measurement intensive (HUMPPA-COPEC-2010): an overview of meteorological and chemical influences, Atmos Chem Phys, 11, 10599-10618, DOI 10.5194/acp-11-10599-2011, 2011.

Winters, A. J., Adams, M. A., Bleby, T. M., Rennenberg, H., Steigner, D., Steinbrecher, R., and Kreuzwieser, J.: Emissions of isoprene, monoterpene and short-chained carbonyl compounds from Eucalyptus spp. in southern Australia, Atmos Environ, 43, 3035-3043, DOI 10.1016/j.atmosenv.2009.03.026, 2009.

Wise, M. L. a. C., R.: Comprehensive Natural Products Chemistry, Isoprenoids Including Caroteinoids and Steroids, vol. 2

Elsevier, Amsterdam, 1999.

Wolfertz, M., Sharkey, T. D., Boland, W., Kuhnemann, F., Yeh, S., and Weise, S. E.: Biochemical regulation of isoprene emission, Plant Cell Environ, 26, 1357-1364, 10.1046/j.0016-8025.2003.01059.x, 2003.

Yassaa, N., Meklati, B. Y., and Cecinato, A.: Evaluation of monoterpenic biogenic volatile organic compounds in ambient air around Eucalyptus globulus, Pinus halepensis and Cedrus atlantica trees growing in Algiers city area by chiral and achiral capillary gas chromatography, Atmos Environ, 34, 2809-2816, 2000.

Yassaa, N., and Williams, J.: Analysis of enantiomeric and non-enantiomeric monoterpenes in plant emissions using portable dynamic air sampling/solid-phase microextraction (PDAS-SPME) and chiral gas chromatography/mass spectrometry, Atmos Environ, 39, 4875-4884, 2005.

Yassaa, N., Brancaleoni, E., Frattoni, M., and Ciccioli, P.: Isomeric analysis of BTEXs in the atmosphere using beta-cyclodextrin capillary chromatography coupled with thermal desorption and mass spectrometry, Chemosphere, 63, 502-508, 2006.

Yassaa, N., and Williams, J.: Enantiomeric monoterpene emissions from natural and damaged Scots pine in a boreal coniferous forest measured using solid-phase microextraction and gas chromatography/mass spectrometry, J Chromatogr A, 1141, 138-144, DOI 10.1016/j.chroma.2006.12.006, 2007.

Yassaa, N., Peeken, I., Zollner, E., Bluhm, K., Arnold, S., Spracklen, D., and Williams, J.: Evidence for marine production of monoterpenes, Environ Chem, 5, 391-401, Doi 10.1071/En08047, 2008.

Yassaa, N., Custer, T., Song, W., Pech, F., Kesselmeier, J., and Williams, J.: Quantitative and enantioselective analysis of monoterpenes from plant chambers and in ambient air using SPME, Atmos Meas Tech, 3, 1615-1627, 10.5194/amt-3-1615-2010, 2010.

Yokelson, R. J., Christian, T. J., Karl, T. G., and Guenther, A.: The tropical forest and fire emissions experiment: laboratory fire measurements and synthesis of campaign data (vol 8, pg 3509, 2008), Atmos Chem Phys, 8, 4497-4497, 2008.

Zimmer, W., Bruggemann, N., Emeis, S., Giersch, C., Lehning, A., Steinbrecher, R., and Schnitzler, J. P.: Process-based modelling of isoprene emission by oak leaves, Plant Cell Environ, 23, 585-595, 2000.

Curriculum Vitae

Wei Song
Born on 10. 12. 1982 in Shandong, China

Contact Information
Max Planck Institute for Chemistry
Hahn-Meitner-Weg 1
D-55128 Mainz, Germany
Telephone: +49-6131 305 4541
E-mail: wei.song@mpic.de

Education

01/2008 - present	PhD student at the Max Planck Institute for Chemistry, Mainz, Germany
08/2006 - 05/2009	Graduate School of Chinese Academy of Sciences Master of Science in Environmental Science
07/2005 - 07/2007	State Key laboratory of Organic Geochemistry (SKLOG) Guangzhou Institute of Geochemistry (Possanzini et al.), Chinese Academy of Sciences (CAS)
09/2002 - 07/2006	University of Science and Technology of China (*USTC*) B. Sc. in Environmental Sciences

Publication

- Song, W., Williams, J., Yassaa, N., Martinez, M., Carnero, J. A. A., Hidalgo, P. J., Bozem, H., and Lelieveld, J.: Winter and summer characterization of biogenic enantiomeric monoterpenes and anthropogenic BTEX compounds at a Mediterranean Stone Pine forest site, J Atmos Chem, 68, 233-250, DOI 10.1007/s10874-012-9219-4, 2011

- Yassaa, N., Song, W., Lelieveld, J., Vanhatalo, A., Back, J., and Williams, J.: Diel cycles of isoprenoids in the emissions of Norway spruce, four Scots pine chemotypes, and in Boreal forest ambient air during HUMPPA-COPEC-2010, Atmos Chem Phys, 12, 7215-7229, DOI 10.5194/acp-12-7215-2012, 2012

- van Stratum, B. J. H., Vilà-Guerau de Arellano, J., Ouwersloot, H. G., van den Dries, K., van Laar, T. W., Martinez, M., Lelieveld, J., Diesch, J.-M., Drewnick, F., Fischer, H., Hosaynali Beygi, Z., Harder, H., Regelin, E., Sinha, V., Adame, J. A., Sörgel, M., Sander, R., Bozem, H., Song, W., Williams, J., and Yassaa, N.: Study of the diurnal variability of atmospheric chemistry with respect to boundary layer dynamics during DOMINO, Atmos. Chem. Phys. Discuss., 12, 6519-6550, doi:10.5194/acpd-12-6519-2012, 2012

- Kampf, C. J., Corrigan, A. L., Johnson, A. M., Song, W., Keronen, P., Königstedt, R., Williams, J., Russell, L. M., Petäjä, T., Fischer, H. and Hoffmann, T.: First measurements of reactive -dicarbonyl concentrations on PM2.5 aerosol over the boreal forest in Finland during HUMPPA-COPEC 2010 – source apportionment and links to aerosol aging. Atmos. Chem. Phys. Discuss., 12, 723–751 (2012) doi:10.5194/acpd-12-723-2012

- Crowley, J.N., Thieser, J., Tang, M.J., Schuster, G., Bozem, H., Beygi, Z.H., Fischer, H., Diesch, J.M., Drewnick, F., Borrmann, S., Song, W., Yassaa, N., Williams, J., Pohler, D., Platt, U., Lelieveld, J.: Variable lifetimes and loss mechanisms for NO(3) and N(2)O(5) during the DOMINO campaign: contrasts between marine, urban and continental air. Atmos Chem Phys 11(21), 10853-10870 (2011). doi:DOI 10.5194/acp-11-10853-2011
- Ebben, C.J., Martinez, I.S., Shrestha, M., Buchbinder, A.M., Corrigan, A.L., Guenther, A., Karl, T., Petaja, T., Song, W.W., Zorn, S.R., Artaxo, P., Kulmala, M., Martin, S.T., Russell, L.M., Williams, J., Geiger, F.M.: Contrasting organic aerosol particles from boreal and tropical forests during HUMPPA-COPEC-2010 and AMAZE-08 using coherent vibrational spectroscopy. Atmos Chem Phys 11(20), 10317-10329 (2011). doi:DOI 10.5194/acp-11-10317-2011

- Williams, J., Crowley, J., Fischer, H., Harder, H., Martinez, M., Petaja, T., Rinne, J., Back, J., Boy, M., Dal Maso, M., Hakala, J., Kajos, M., Keronen, P., Rantala, P., Aalto, J., Aaltonen, H., Paatero, J., Vesala, T., Hakola, H., Levula, J., Pohja, T., Herrmann, F., Auld, J., Mesarchaki, E., Song, W., Yassaa, N., Nolscher, A., Johnson, A.M., Custer, T., Sinha, V., Thieser, J., Pouvesle, N., Taraborrelli, D., Tang, M.J., Bozem, H., Hosaynali-Beygi, Z., Axinte, R., Oswald, R., Novelli, A., Kubistin, D., Hens, K., Javed, U., Trawny, K., Breitenberger, C., Hidalgo, P.J., Ebben, C.J., Geiger, F.M., Corrigan, A.L., Russell, L.M., Ouwersloot, H.G., de Arellano, J.V.G., Ganzeveld, L., Vogel, A., Beck, M., Bayerle, A., Kampf, C.J., Bertelmann, M., Kollner, F., Hoffmann, T., Valverde, J., Gonzalez, D., Riekkola, M.L., Kulmala, M., Lelieveld, J.: The summertime Boreal forest field measurement intensive (HUMPPA-COPEC-2010): an overview of meteorological and chemical influences. Atmos Chem Phys 11(20), 10599-10618 (2011). doi:DOI 10.5194/acp-11-10599-2011

- Yassaa, N., Custer, T., Song, W., Pech, F., Kesselmeier, J., Williams, J.: Quantitative and enantioselective analysis of monoterpenes from plant chambers and in ambient air using SPME. Atmos Meas Tech 3(6), 1615-1627 (2010). doi:DOI 10.5194/amt-3-1615-2010

- Xu, H., Wang, X., Pöesch, U., Feng, S., Wu, D., Yang,L., Li, S., Song, W., Sheng, G., Fu, J.: Genotoxicity of total and fractionated extractable organic matter in fine air particulate matter from urban Guangzhou: comparison between haze and nonhaze episodes. Environmental Toxicology & Chemistry, 27 (2008), pp. 206–212

Poster

- “In-situ Volatile Organic Compounds Measurements with GC-MSD during the DOMINO campaign in Spain, December 2008”, W. Song, N. Yassaa, J. Williams, European Geosciences Union, 19.-24. April 2009, Vienna, Austra

- “Laboratory and field measurements of enantiomeric monoterpenes in plant emissions”, W. Song , M. Staudt, N. Yassaa, J. Williams, European Geosciences Union, 03.-08. April 2011, Vienna, Austra