**Biogeosciences
Discussions**

Leaf level emissions of volatile organic compounds (VOC) from some Amazonian and Mediterranean plants

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Abstract

As volatile organic compounds (VOCs) significantly affect atmospheric chemistry (oxidative capacity) and physics (secondary organic aerosol formation and effects), emission inventories defining regional and global biogenic VOC emission strengths are important. The aim of this work was to achieve a description of VOC emissions from poorly described tropical vegetation to be compared with the quite well investigated and highly heterogeneous emissions from Mediterranean vegetation. For this task, common plant species of both ecosystems were investigated. Sixteen plant species from the Mediterranean area, which is known for its special diversity in VOC emitting plant species, were chosen. In contrast, little information is currently available regarding emissions of VOCs from tropical tree species at the leaf level. Twelve plant species from different environments of the Amazon basin, i.e. Terra firme, Várzea and Igapó, were screened for emission of VOCs at leaf level with a branch enclosure system. Analysis of the volatile organics was performed online by a proton-transfer-reaction mass spectrometer (PTR-MS) and offline by collection on adsorbent tubes and subsequent gas chromatographic analysis. Isoprene was quantitatively the most dominant compound emitted followed by monoterpenes, methanol and acetone. Most of the Mediterranean species emitted a variety of monoterpenes, whereas only five tropical species were monoterpene emitters exhibiting a quite conservative emission pattern (α-pinene > limonene > sabinene > β-pinene). Mediterranean plants showed additional emissions of sesquiterpenes, whereas in the case of plants from the Amazon region no sesquiterpenes were detected probably due to a lack of sensitivity in the measuring systems. On the other hand methanol emissions, an indicator of growth, were common in most of the tropical and Mediterranean species. A few species from both ecosystems showed acetone emissions. The observed heterogeneous emissions including reactive VOC species which are not easily detected by flux measurements, give reason to perform more screening at leaf level and, whenever possible, within the forests under ambient conditions.

1 Introduction

Vegetation is the main producer of Volatile Organic Compounds (VOCs) which can directly affect chemical and physical properties of the atmosphere (Atkinson and Arey, 2003). Biogenic VOCs regulate the oxidative capacity of the atmosphere and have an indirect impact on the lifetime of greenhouse gases and are also involved in the formation and growth of secondary organic aerosols (SOA) which in turn affect cloud development and precipitation (Andreae and Crutzen, 1997; Claeys et al., 2004; Collins et al., 2002; Lelieveld et al., 2002; Pöschl et al., 2010; Sjostedt et al., 2011; Wang et al., 1998).

Emission inventories and model calculations have been produced to define regional and global biogenic VOC emission strength, however they rely mostly on studies of VOC emissions from vegetation from temperate areas of North America and Europe (Guenther et al., 1995; Guenther et al., 2006; Kinnee et al., 1997; Simpson, 1999), or on studies of only one VOC species (Ferreira et al., 2010; Harley et al., 2004; Lerdau and Keller, 1997; Lerdau and Throop, 2000; Lerdau and Throop, 1999; Misztal et al., 2010; Oku et al., 2008; Pegoraro et al., 2006). Because of the heterogeneity of ecoregions, species diversity, inaccessibility, logistical difficulties, methodological difficulties, etc., the number of investigations made in tropical regions are limited (Geron et al., 2002; 2006b; Harley et al., 2004; Kesselmeier et al., 2002; Kuhn et al., 2002b, 2004). Yet, VOC emissions from tropical forests are of special interest because their contribution to the global VOC budget (estimated to be 30 %) is disproportional as compared to their terrestrial area fraction of 7 % (Guenther et al., 1995). In contrast to the tropics, Mediterranean plant species are known to emit a great variety of VOC, many of which have already been intensively studied (Kesselmeier and Staudt, 1999; Llusia et al., 2002; Owen et al., 1997, 2001, 2002; Simon et al., 2006).

In general, most of these studies concentrated on the emission of isoprene and monoterpenes. Less information is available on the emission of short-chain oxygenated compounds (oxVOCs) such as formaldehyde, acetaldehyde, acetone, methanol,

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ethanol and formic and acetic acids (Seco et al., 2007). Emissions of these oxygenated compounds were identified only recently as being a large source of carbon (150–$500\,Tg\,C\,yr^{-1}$) to the atmosphere Singh et al., 2001. Other compounds of high interest are sesquiterpenes (Jardine et al., 2011), but they are not easily measured due to their high reactivity (Fuentes et al., 2000). Sesquiterpenes and other highly reactive compounds may constitute a considerable amount of the missing VOCs (Goldstein et al., 2004) as evidenced by indirect approaches (Di Carlo et al., 2004; Kuhn et al., 2007).

The present study aims to contribute towards a more complete assessment of VOCs released at leaf level contrasting flux studies which may miss the more reactive VOC species. We chose the Amazonian vegetation because it is a poorly investigated region and compared it with the much better described Mediterranean ecosystem which exhibits a very heterogeneous emission composition. To enable a comparison of the VOC emissions between tropical and Mediterranean vegetation over a broad range of VOC species, several different methods for characterization and quantification of VOCs were used: a proton-transfer-reaction mass spectrometer (PTR-MS) for the detection of all VOCs with proton affinity higher than water; an online gas-chromatograph with a flame ionization detector (GC-FID) for the determination of isoprene emissions; and an offline GC-FID along with an offline gas-chromatograph coupled to a mass spectrometer (GC-MS) for the determination of higher VOCs including sesquiterpenes.

2   Material and methods

2.1   Plant material and environmental conditions

2.1.1   Tropical vegetation

Screening for VOC emissions was carried out with a total of twelve plant species common for terra firme and floodplain areas in the Amazonas region (Table 1). Three

representative trees from the upland forest (terra firme) ecosystem, eight from the floodplain region which is regularly inundated with nutrient rich and sediment loaded white-water during the flooding period (várzea) and three from the floodplain region inundated with black water rich in humic matter, or clear-water (igapó) were studied. For interregional comparison the species *Vatairea guianensis* and *Hevea spruceana* from both regions (igapó versus várzea) were measured.

The tropical vegetation screening experiment was a cooperative effort between the Max Planck Institute for Chemistry and the Instituto Nacional de Pesquisas da Amazônia (INPA, Manaus), which took place at the INPA Campus forest in Manaus, Brazil. One or two year old saplings of *Garcinia macrophylla*, *Hevea spruceana* and *Vatairea guianensis* from igapó, *Hura crepitans*, *Pouteria glomerata*, *Pseudobombax munguba*, *Ocotea cymbarum*, *Pachira insignis*, *Zygia jurana*, *Hevea spruceana* and *Vatairea guianensis* from várzea, and *Scleronema micranthum*, *Hevea brasiliensis* and *Hevea guianensis* from terra firme were measured in 2006 and 2007. The terra firme species *Hevea brasiliensis*, *Hevea guianensis* and *Scleronema micranthum* were collected at the Reserva Ducke, which is situated 40 km from Manaus. 90 % of the Reserva's area is covered by primary vegetation characteristic of the Central Amazon terra firme (Gomes and Mello-Silva, 2006). The várzea species *Hevea spruceana*, *Hura crepitans*, *Ocotea cymbarum*, *Pachira insignis*, *Pouteria glomerata*, *Pseudobombax munguba*, *Vatairea guianensis* and *Zygia juruana* were collected at the bank of the Ilha da Marchantaria (03° 15′ S, 59° 58′ W) an island located in the Solimões River. The igapó species *Garcinia macrophylla*, *Hevea spruceana* and *Vatairea guianensis* were collected at the bank of the Tarumã Mirim (03° 08′ S, 60° 01′ W) an affluent of the Rio Negro. The influence of different floodplain environments was investigated using plants that occur in várzea and igapó such as *Hevea spruceana* and *Vatairea guianensis*. After collection plants were potted in earth obtained from the sites of the plant's origin and allowed to adapt to the new conditions for at least one month before making measurements. Plants were kept under sunlight conditions, were protected by mosquito nets, and were irrigated daily. Daily mean temperature conditions of 29 °C ± 1.6 °C and

27.8 °C ± 1.3 °C and relative humidity values of 77 % ± 9 % and 91 ± 7 % were recorded during the dry and wet season, respectively. Ambient CO_2 concentrations were in the range of 335–408 ppm.

A total of three replicates for each species were measured with some exceptions (see Table 1). Dynamic flow-through-enclosures were installed at 08:00 p.m. on the evening before measurements were made to allow for adaptation to the enclosure system. Trace gas exchanges were measured during the next day.

2.1.2 Mediterranean vegetation

A total of sixteen potted plant species including deciduous and non-deciduous trees, shrubs, grasses and palm trees typical for the Mediterranean area and having different distribution ranges were studied at the CEFE-CNRS in Montpellier (France) during the months of April to July 2008 (Table 2). For each species there were three replicates.

The plants which were about 2–3 yr old were collected in March 2008 from the surroundings of Montpellier, France, and were potted and maintained in a greenhouse of the institute at an approximate day/night temperature of 25/15 °C.

2.2 Enclosure techniques and gas exchange measurements

Two different enclosure systems were used for the measurement of tropical and Mediterranean vegetation. For the measurement of tropical plants an enclosure system developed at the Max Planck Institute for Chemistry in Mainz, Germany was used. This enclosure system has been described in detail elsewhere (Schäfer et al., 1992; Kesselmeier et al., 1996; Kuhn et al., 2002a). Two identical branch cuvettes made of fully light permeable FEP Teflon foil (Norton, 50 µm thickness, Saint-Gobain Performance Plastics, Germany), were flushed with ozone free ambient air. One cuvette was used as the reference "empty" cuvette and a second cuvette enclosed a branch or the complete plant above ground. Ambient air was scrubbed of small particles using Teflon filters (Zefluor Teflon filters, 2 µm pore size, Gelman Science, USA) and of ozone with

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an ozone scrubber composed by ten copper nets coated with MnO_2 (Ansyco, Germany) placed in a Teflon tube to prevent oxidant interferences inside the enclosure. A combination of three Teflon membrane pumps (Vacuubrand, Germany) was used to pump the filtered ambient air to both cuvettes. The air flow to each cuvette was monitored by an in-line flowmeter (EL-Flow, 50 l min^{-1}, Bronkhorst Hi-Tec, Germany). Two different cuvette sizes were used depending on the size of the plant to be measured. For the small plants a 9 l cuvette was built and for the big plants a 100 l cuvette. The flow was controlled by a needle valve and adjusted to 10 l min^{-1} for the small cuvette and to 20–40 l min^{-1} for the larger cuvette.

A Teflon fan installed in the cuvette allowed a homogenous mixing of the air in the cuvette. Cuvette temperature and relative humidity was measured in bypassed air by a temperature/relative humidity sensor (Model Rotronics YA-100F, Walz, Germany). Exchange of VOCs, CO_2, and H_2O was monitored by direct sampling from the sample and reference cuvette. All sample tubing was made of Teflon and maintained at a constant temperature of 45 °C, which was always higher than the cuvette or ambient temperature in order to avoid condensation in the lines.

CO_2 and H_2O exchange were measured by using a CO_2/H_2O infrared gas analyzer (LI-COR inc. 7000, Lincoln, Nebraska, USA). This equipment was operated in differential mode receiving an analog signal of the absolute concentration measured by a second CO_2/H_2O infrared gas analyzer (LI-COR inc. 7000, Lincoln, Nebraska, USA) as reference. Pressurized nitrogen gas (N_2 5.0, Messer Griesheim, Germany) was used as the reference gas for the CO_2 and H_2O zero point calibration of the infrared gas analyzers. The gas flow to the instrument was supplied by a custom made pump unit (membrane pump, 12 Volt; KNF-NEUBERGER) and passed through a rotameter (Omega, USA) that adjusted the flow to 0.5 l min^{-1} placed up line of the analyzer inlet. Calibration of the analyzer was accomplished prior to the experiments by use of a calibration gas standard for the calibration of CO_2 (512 ± 2 ppm CO_2 in synthetic air, LI-COR, Lincoln, Nebraska, USA) and a dew point generator for the calibration of water vapor (Li 610; LI-COR, Lincoln, Nebraska, USA). At the end of each experiment

the calibration of the analyzer was checked and the signal response was corrected for sensitivity and zero drifts as a function of time. Furthermore, the signal response of the instrument was corrected for temperature effects and with regard to the offset of specified and measured reference concentrations. Assimilation, transpiration and stomatal conductance were calculated according to Pearcy, Schulze and Zimmermann (1989).

Measurements of tropical vegetation were performed under semi-controlled conditions following ambient relative humidity and temperature. During the measurements of *Garcinia macrophylla, Hevea spruceana* (igapó), *Hura crepitans*, and *Pseudobombax munguba* ambient light conditions were followed. In the case of the other plant species additional photosynthetic active radiation (PAR) was constantly provided by a LED system consisting of four double chains of a mixture of red, blue and white light constructed and designed by the electronics department of the MPI for Chemistry in Mainz, Germany. This LED system supported a maximum light regime of 500 $\mu mol\,m^{-2}\,s^{-1}$ (PAR) and was placed perpendicular to the cuvette. Gaps between the LED groups were closed with reflecting film in order to obtain a homogenous distribution of the light in the cuvette. The irradiation was checked with a quantum sensor (Model SB 190, Licor, USA) inside the cuvette at different heights before and after the measurements and found to be homogeneous for the area of the whole enclosed plant. The irradiation value determined in the center of the cuvette was taken as the incident PAR. In course of all other gas exchange measurements the same sensor was installed next to the chamber system. Light intensities and the cuvette and leaf temperatures measured with thermocouples of type E (Chrom-Constantan, OMEGA) were recorded with a datalogger CR23X (Campbell Scientific Ltd. Shepsherd, UK). All other micrometeorological and physiological parameters were monitored and recorded with a control unit (V25).

Gas exchange of Mediterranean vegetation was measured using a dynamic temperature and light controlled chamber system (Bracho-Nunez et al., 2011; Staudt et al., 2004). This custom made gas exchange chamber with a volume of approximately 105 ml was constantly flushed with air at a flow of 650 $ml\,min^{-1}$. The air was

purified and dried by a clean air generator (AIRMOPURE, Chromatotec, France) and then re-humidified by passing a variable portion of the air stream through a water bubbler. All tubing was made of Teflon and sample lines were maintained at a constant temperature of 45 °C. Chamber and plants were illuminated with white light (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 system. Leaf and chamber air temperatures were monitored with two thermocouples of type E (Chrom-Constantan, OMEGA). For all measurements of Mediterranean vegetation temperature and light was kept constant at standard conditions (leaf temperature = 30 ± 1 °C and PAR = 1055 ± 36 µmol m^{-2} s^{-1}). Relative humidity was also maintained constant at 48 ± 13 %. All data were stored on a 21X datalogger (Campbell Scientific Ltd., Shepsherd, UK). 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).

For the measurements, one or several terminal leaves of an individual plant were placed perpendicular to the light to ensure homogenous light distribution on the adaxial surface of the leaves. For most of the plants, it was necessary to remove some leaves to enable proper placement in the chamber; this was done at least one week before any measurements to minimize disturbance effects. In order to ensure adaptation of the plants to the chamber environment, all species were placed in the chamber at least 1 h before the measurements, or until the VOC signals measured with PTR-MS had become constant. Leaves of the conifer *Pinus halepensis* and the aromatic shrub *Rosmarinus officinalis* possess glands and ducts which store VOCs. It has been shown that mechanical stress can cause large bursts of VOCs from these plants leading to large overestimations of VOC emission rates normalized as standard emissions (E_s) at 30 °C and 1000 µmol m^{-2} s^{-1} (PAR) (Niinemets et al., 2011). Therefore, as based on our experiences during previous work the leaves of these species were enclosed at least 12 h before making measurements.

Projected leaf areas were determined either with an optical area meter (Delta-T Devices Ltd., Cambridge, UK) or, by copying the shape of the measured leaves on a sheet that was subsequently scanned using the software Size (Version 1.10R, Müller-Software) (Kesselmeier et al., 1996). To obtain leaf dry weights, leaves were dried at 60 °C for at least 48 h before weighing. Errors were estimated at 0.2 % and 2 % for dry weight and leaf area determination, respectively.

2.3 VOC measurements

VOC emissions from tropical vegetation were measured using two different methods, (i) by collection on cartridges using an automatic sampler and subsequent analysis with an offline gas chromatographic (GC) method equipped with a flame ionization detector (FID; Kesselmeier et al., 2002; Kuhn et al., 2002b) in the MPIC laboratory in Mainz, Germany, and (ii) by online PTR-MS as described below. In the case of Mediterranean vegetation four instruments were used: a PTR-MS (see detailed description below), an AirmoVOC C2-C6 online GC-FID (Chromatotec, France) for the detection of isoprene and light VOCs, a Chrompack CP9003 offline GC-FID equipped with a Chrompack TCT4002 thermo-desorber (all Varian Inc.) for the detection of higher VOCs such as monoterpenes and sesquiterpenes, and a Varian CP3800/Saturn2000 GC-MS equipped with a Perkin-Elmer Turbomatrix thermo-desorber to back identification of GC-FID peaks and PTR-MS signals. A detailed description of the GC systems is reported by Bracho-Nunez et al. (2011).

For real-time VOC monitoring, the PTR-MS (Ionicon Analytik, Austria) was operated in selected ion-monitoring mode at standard operational settings ($E/N = 130$ Td; E electric field strength, N buffer gas number density, 1 Td $= 10^{-17}$ cm^2 V molecule^{-1}) at a drift tube voltage of 600 V. A total of 27 mass signals (protonated masses; Molecular Weight $+1$) were measured by the PTR-MS with a dwell time of 1 s: m21, m29, m31, m32, m33, m39, m42, m45, m47, m55, m59, m61, m69, m71, m73, m75, m81, m83, m87, m93, m95, m107, m121, m137, m139, m151, m205. The measurement of one complete cycle took 27 s. The main compounds detected from tropical vegetation were

methanol (m33), acetone (m59), isoprene (m69), monoterpenes (m137, fragment on m81). On the other hand, Mediterranean vegetation showed emissions of the same compound classes and additional emissions of sesquiterpenes (m205). Different isomers of monoterpenes or sesquiterpenes cannot be distinguished with a PTR-MS, therefore PTR-MS based E_s for monoterpenes and sesquiterpenes always refers to the sum of all monoterpenes and sesquiterpenes, respectively.

As mentioned above, for measurements of tropical vegetation a reference and a sample chamber were used. The PTR-MS was connected to the reference and the sample chamber with PFA tubing (1/8") heated to 45 °C. VOC determination occurred with ten cycles of the reference and sample chamber separately. The instrument background signals were determined with air samples after passing over a heated platinum catalyst maintained at 350 °C (Zero Air Generator, Parker Co., USA). The background signal was subtracted from the reference and sample chamber signals. This procedure was repeated from 08:00 p.m. to 06:00 p.m. of the following day. For VOC emission rate calculations the reference chamber signals (with background subtracted) were subtracted from the sample chamber signals (with background subtracted).

In the case of Mediterranean vegetation PTR-MS measurements were performed similarly as described above but with a slightly changed sampling protocol. Ten cycles of enclosure measurements switching between sample and empty reference cuvette were followed by three cycles of instrument background measurements. This process was repeated 3 to 10 times.

The PTR-MS instrument was calibrated using a VOC standard mixture in nitrogen (Deuste Steininger GmbH, Germany) containing some target VOCs (isoprene, α-pinene, methanol and acetone) at concentrations of $300\,\mathrm{nmol\,mol^{-1}} \pm 10\,\%$. For calibration, the gas was further diluted with synthetic air to final concentrations of 0.5–$10\,\mathrm{nmol\,mol^{-1}}$. For the quantification of sesquiterpenes a calculation of simple ion-molecule reaction kinetics was used as described elsewhere (Hansel et al., 1995; Wisthaler et al., 2001). Since the quantification of monoterpenes and sesquiterpenes with the PTR-MS is usually very difficult due to their tendency to fragment into different

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compounds depending on the VOC species (Demarcke et al., 2009; Tani et al., 2003), these data were always complemented by GC-FID or GC-MS (Bracho-Nunez et al., 2011). The detection limit of the PTR-MS was estimated as being 1.96 times the standard deviation of the empty chamber concentrations (at the 95 % confidence level) and was typically 1.6 nmol mol^{-1} for methanol, 579 pmol mol^{-1} for acetone, 493 pmol mol^{-1} for isoprene, 201 pmol mol^{-1} for monoterpenes, and 94 pmol mol^{-1} for sesquiterpenes, and the detection limits of the GCs ranged between 0.1 and 0.4 ng l^{-1}.

2.4 Data treatments

The emission rate E_s (µg g^{-1} h^{-1}) of each compound was calculated according to Eq. (1) based on the measured concentration difference ($\Delta c = c_{\text{sample chamber}} - c_{\text{empty or reference chamber}}$) in nmol l^{-1}, the chamber flush rate Q in l h^{-1}, the leaf dry weight (dw) in g and the molecular mass M in g mol^{-1}.

$$E_s = \Delta c \left(\frac{Q}{\text{dw}} \right) \cdot M \cdot 10^{-3} \tag{1}$$

For VOC emissions measured under non standard light and temperature conditions (the conditions for most of the measurements on tropical species), the phenomenological algorithm described by Guenther et al. (1993) was used to standardize the actual VOC emission rates to standard emission rates, often referred to as the basal emission rate. This algorithm describes the light and temperature dependencies for VOC originating from DMAPP (Dimethylallyl pyrophosphate), such as isoprene and monoterpenes and distinguishes between emissions from VOC storage pools and newly synthesized VOCs. Since acetone and methanol also showed light and temperature dependency during this study, emission rates of these compounds could also be described with the Guenther algorithm (Guenther et al., 1993). Methanol emission depends on stomatal conductance and accumulation occurs in the stomatal cavities during night. Thus, in the morning a methanol peak was detected on some occasions,

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due to the burst of the nocturnally accumulated methanol after stomatal opening. This morning peak observed for methanol was excluded for the calculation of E_s.

One-way anova tests were carried out in order to detect possible differences among two or more independent groups. Mean VOCs emissions (methanol, acetone, isoprene or monoterpenes separately) from tropical plant species were tested against those emitted from Mediterranean plant species and the same species from different ecosystems (igapó vs. várzea). The statistically significant difference effect in ANOVA was proven by the Tukey's test.

3 Results

3.1 Screening tropical vegetation

In the case of ten tropical plant species (*Garcinia macrophylla, Hevea brasiliensis, Hevea guianensis, Hevea spruceana, Hura crepitans, Pachira insignis, Pseudobombax munguba, Scleronema micranthum, Vatairea guianensis* and *Zygia jurana)*, out of the twelve plant species screened, we were able to identify VOC emissions. The other two plant species, *Pouteria glomerata* and *Ocotea cymbarum* did not show detectable emissons (Fig. 1). Considering the total amount of VOC emissions of the ten emitters, eight species were classified as high emitters (emission above $10 \, \mu g \, g^{-1} \, h^{-1}$) and two species, *Scleronema micranthum* and *Hevea guianensis*, were moderate-emitters (emission ranged between 1 and $10 \, \mu g \, g^{-1} \, h^{-1}$).

All isoprene emitting tree species were high emitters ($> 10 \, \mu g \, g^{-1} \, h^{-1}$). E_s for isoprene were estimated to range between 12.1 and $63.2 \, \mu g \, g^{-1} \, h^{-1}$ for *Garcinia macrophylla, Pachira insignis, Vatairea guianensis* and *Zygia jurana*. Only four tree species (*Hevea brasiliensis, Hevea guianensis, Hevea spruceana* from várzea and igapó and *Scleronema micranthum*) were found to emit monoterpenes. No monoterpene emission was detected in the other eight species. Monoterpene E_s varied from 0.3 to $67.1 \, \mu g \, g^{-1} \, h^{-1}$ (Fig. 1). The strongest monoterpene emitting tree was *Hevea*

spruceana from igapó followed by *Hevea brasiliensis*, *Hevea spruceana* from várzea, *Hevea guianensis* and *Scleronema micranthum*. The latter one was a very weak monoterpene emitter ($< 1\,\mu g\,g^{-1}\,h^{-1}$), *Hevea guianensis* a moderate emitter (emission ranged between 1 and $10\,\mu g\,g^{-1}\,h^{-1}$) and the other ones were high emitters ($> 10\,\mu g\,g^{-1}\,h^{-1}$). Interestingly, the geographic origin of the saplings may be of significance as indicated by marginally significant quantitative differences ($p < 0.08$) of the monoterpene E_s of *Hevea spruceana* from two floodplain ecosystems (várzea and igapó) (Fig. 1). No significant differences were found in the VOC emissions of *Vatairea guianensis* originating from várzea and igapó. Similarly, the relative composition of the monoterpenes emitted by *Hevea spruceana* saplings was similar for both provenances (Fig. 3). α-Pinene (63 %) was the most abundant monoterpene followed by limonene (14 %), sabinene (7.5 %), p-cymene (5.4 %) and β-pinene (2.8 %) (Fig. 3). α-Pinene was also the main monoterpene emitted by the rest of monoterpene emitting tree species (35–90 %). *Hevea brasiliensis* emitted α-pinene (57 %) followed by limonene (17 %), sabinene (7.4 %) and p-cymene (5.9 %), but in this case the emission of γ-terpinene (6.3 %) exceeded that of β-pinene (1.8 %). In the case of *Scleronema micranthum*, monoterpene species composition was similar to that of the *Hevea* species: α-pinene (35 %) was again the main monoterpene followed by limonene (26.6 %) and in this case β-pinene (15.9 %) and sabinene (9.1 %). In contrast, monoterpene emissions of *Hevea guianensis* were mainly composed of α-pinene (90.2 %) and camphene (9.8 %).

The oxygenated VOCs, methanol and acetone, were emitted from several of the investigated plant species. Methanol emissions were detected in seven species with emission rates varying between 1.5 to $20.2\,\mu g\,g^{-1}\,h^{-1}$ (Fig. 1). Five species (*Garcinia macrophylla*, *Hevea brasiliensis*, *Pachira insignis*, *Scleronema micranthum*, *Vatairea guianensis*) exhibited methanol emissions in the range of $1–10\,\mu g\,g^{-1}\,h^{-1}$ and the other two emitted $> 10\,\mu g\,g^{-1}\,h^{-1}$ (*Hura crepitans* and *Pseudobombax munguba*). Low emissions of acetone could be detected in the case of *Hevea spruceana* originating from both ecosystems ($< 1.5\,\mu g\,g^{-1}\,h^{-1}$).

A noticeable release of mass 73 was detected in the case of *Garcina macrophylla* during daytime conditions (light). Mass 73 could be the protonated methyl ethyl ketone (MEK), a known oxidation product of isoprene. This interpretation would be in accordance with the high emissions of isoprene found for this plant. But other compounds represented by this mass, such as methylgyoxal (Holzinger et al., 2007) or 2-methyl propanal suggested by Jardine et al. (2010) would also be reasonable.

3.2 Screening mediterranean vegetation

All sixteen Mediterranean plant species investigated were found to emit VOCs, nine of which being high emitters (*Brachypodium retusum, Buxus sempervirens, Chamaerops humilis, Coronilla valentine, Ficus carica, Quercus afares, Quercus coccifera, Quercus suber* and *Spartium junceum)* with emissions between 11.0 and 69.1 μg g^{-1} h^{-1}, whereas the rest of the plants were moderate emitters, showing VOC emissions in the range of 2.6 and 9.3 μg g^{-1} h^{-1}.

Emissions from five species were found to be dominated by isoprene, i.e. *Brachypodium retusum, Buxus sempervirens, Chamaerops humilis, Ficus carica* and *Spartium junceum.* Emission rates of these plant species ranged between 18.9 and 60.7 μg g^{-1} h^{-1} (Fig. 2). *Ceratonia siliqua, Coronilla valentina, Olea europaea, Pinus halepensis, Prunus persica, Quercus afares, Quercus coccifera* and *Quercus suber* could be classified as low isoprene emitters with $E_s < 1$ μg g^{-1} h^{-1} and *Cistus albidus, Cistus monspeliensis* and *Rosmarinus officinalis* as non isoprene emitters.

Fourteen out of the sixteen investigated Mediterranean plants emitted monoterpenes in significant amounts: *Brachypodium retusum, Buxus sempervirens, Ceratonia siliqua, Chamaerops humilis, Cistus albidus, Cistus monspeliensis, Coronilla valentine, Olea europaea, Pinus halepensis, Prunus persica, Quercus afares, Quercus coccifera, Quercus suber* and *Rosmarinus officinalis*. The species *Brachipodium retusum, Ceratonia siliqua, Cistus monspeliensis, Olea europaea, Pinus halepensis, Quercus afares, Quercus coccifera, Quercus suber*, and *Rosmarinus officinalis* were classified as moderate to high monoterpene emitters with emissions ranging between 1.03

and $35.6\,\mu g\,g^{-1}\,h^{-1}$. PTR-MS measurements indicated low monoterpene emissions also for *Chamaerops humilis, Cistus albidus, Coronilla valentina* and *Prunus persica* ($\leq 1\,\mu g\,g^{-1}\,h^{-1}$); however this could not be confirmed by GC analysis. This discrepancy might have been caused by decomposition of more labile monoterpene species,

5 an artifact of cartridge sampling for GC analysis, or by the emission of many different monoterpene species at rates below the detection limit for GC analysis. Alternatively, the masses classified as monoterpene (m81 and m137) with the PTR-MS might be related to other VOC species. For example, interferences of sesquiterpene fragments like β-caryophyllene (m81) and α-humulene (m137) have been reported to potentially

10 contribute 7.5 and 6 % for each mass (Demarcke et al., 2009).

The monoterpene composition of the emissions from Mediterranean vegetation was highly species specific (Fig. 4). *Cistus monspeliensis* released α-pinene as the major emitted monoterpene species with a contribution of 46 % to the total monoterpene emission rate, followed by β-pinene (25 %), *E*-β-ocimene (14 %), myrcene (11 %) and

15 camphene (4 %). *Quercus suber* emissions also showed a high contribution of α-pinene (33 %) and β-pinene (24 %), but were dominated by sabinene (37 %). Myrcene, limonene, camphene and others contributed less than 3 % to the monoterpene emissions of this species. *Pinus halepensis, Ceratonia siliqua* and *Olea europaea* showed emissions dominated by E-ocimene with 95, 80, and 90 %, respectively, followed by

20 *Z*-ocimene (10 %) in the case of *Olea europaea* and *Ceratonia siliqua* (10 and 19 %, respectively) and by myrcene (5 %) in the case of *Pinus halepensis*. The monoterpene emission pattern by *Rosmarinus officinalis, Quercus coccifera* and *Buxus sempervirens* was not comparable with the emission pattern of other plant species. These three species had very different and variable monoterpene emission patterns. In the

25 case of *Rosmarinus officinalis*, limonene represented the major contribution (40 %), whereas in the case of *Quercus coccifera* and *Buxus semprevirens* myrcene and α-phellandrene were the species with the highest contribution to the total monoterpene emission with 49 % and 95 %, respectively. It is noteworthy that Mediterranean plants showed a large number of monoterpene species, with up to a maximum of 14 different

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monoterpene species. Furthermore, the variability of monoterpene species among the different plant species was very high compared to tropical vegetation.

Low emissions of sesquiterpenes (0.1–$1.0\,\mu g\,g^{-1}\,h^{-1}$) were found in the case of *Cistus albidus, Cistus monspeliensis* and *Quercus coccifera*. In the case of *Buxus sempervirens, Ceratonia siliqua* and *Olea europaea* traces of this terpenoid ($< 0.1\,\mu g\,g^{-1}\,h^{-1}$) were observed, but only detectable by GC-FID, indicating that the GC-FID method may be more sensitive for these compounds than the PTR-MS.

(-)E-caryophyllene was the most frequently occurring sesquiterpene species and was the sole compound emitted in the case of *Ceratonia siliqua* and *Cistus monspeliensis.* For *Olea europaea* and *Quercus coccifera* (-)E-caryophyllene was the most abundant sesquiterpene emitted (78 and 77 %, respectively) followed by germacrene D (22 %). *Olea europaea* emitted β-bourbonene (15 %) and *Quercus coccifera* emitted α-cubebene (8 %) (Fig. 5). Emissions by *Buxus sempervirens* and *Pinus halepensis* were composed by (-)E-caryophyllene (33 and 25 %, respectively) and by α-humulene (67 %) and germacrene D (75 %), respectively. A great variety of sesquiterpene species were found in case of *Cistus albidus*. A total of eight different sesquiterpene species were detected (Fig. 5).

However, not only isoprenoids were emitted from Mediterranean plants. Oxygenated VOCs such as methanol and acetone were also found. Except for *Chamaerops humilis* all investigated plant species emitted methanol. The range of emission rates was very large (between 1.04 and $13.5\,\mu g\,g^{-1}\,h^{-1}$). For some species acetone emissions were detected, but at low rates (Fig. 2). Most of these emission rates were $< 1\,\mu g\,g^{-1}\,h^{-1}$, except for acetone emissions from *Brachipodium retusum* and *Ficus carica* with 1.77 and $4.17\,\mu g\,g^{-1}\,h^{-1}$, respectively.

3.3 Comparison of VOC emissions from tropical and Mediterranean plant species

Most of the investigated tropical and Mediterranean plants exhibited substantial VOC emissions. ANOVA results reflect no quantitatively significant differences between

monoterpenes ($p = 0.07$) and isoprene ($p = 0.2$) emissions from Mediterranean and tropical plant species. However, of striking difference was the higher number of monoterpene emitters in the Mediterranean vegetation. Of the tropical plants investigated, isoprene emitters equaled the monoterpene emitters. Four tropical plant species were isoprene emitting species and another four species emitted monoterpenes. In contrast, monoterpene emitters predominated the Mediterranean vegetation with fourteen out of 16 plants. Five species were classified as high and four as low isoprene emitters. Isoprene standard emission factors were usually higher than monoterpene emission factors in plants from both ecosystems, with mean values by the high emitting plants of $33.9\,\mu g\,g^{-1}\,h^{-1}$ and $25.6\,\mu g\,g^{-1}\,h^{-1}$ for isoprene and monoterpenes, respectively. Furthermore, the monoterpene species pattern emitted from the investigated tropical plants was quite constant, in contrast to the great variation of the monoterpene species pattern observed among Mediterranean plants. Sesquiterpenes were detected only in emissions from Mediterranean vegetation. However, although our experiments did not detect any sesquiterpene emissions from tropical vegetation, their existence in Amazonian forest air has been recently demonstrated (Jardine et al., 2011).

Next in ranking were methanol, acetone and mass 73. Emissions of methanol were found to be widely distributed in plants of both ecosystems. This can be understood as a consequence of growth (Fall, 2003). Since the investigated plants were still saplings, and probably in the growth period, such a high emission of methanol could be expected. In addition, acetone emissions were found only in one tropical plant species, whereas five from the investigated Mediterranean species emitted this VOC species. Interestingly, methanol and acetone emissions of the Mediterranean species investigated in this study were significantly lower ($p < 0.05$) than those detected for tropical vegetation.

4 Discussion

A robust assessment of regional and global VOC emissions is needed in order to understand their effects on atmospheric chemistry/physics and the carbon budget. For this purpose, we need more information at the plant species level to deal with processes and to contribute to the understanding on the ecosystem level, especially as flux studies covering larger terrains miss substantial amounts of emitted VOC because of their high reactivity. Therefore, this study contributes to the description of plant specific VOC emissions from plant species of two such special ecosystems, i.e. the Amazonian and the Mediterranean area. Investigation of Mediterranean plant species are numerous and demonstrate the domination of monoterpene emitting species. In contrast, screening of tropical plant species for the identification of VOCs on the species level is still rare, though compounds such as isoprene, monoterpenes, methanol and acetone have previously been detected above Amazonian forests in high concentrations (Eerdekens et al., 2009; Karl et al., 2004). For our screening study we chose plant species more or less by chance and the small numbers cannot lead to a final view but the results do indicate a trend and will at least improve data bases.

In both ecosystems we found plants that emit isoprene, monoterpenes, methanol and/or acetone as the main compounds. But there were qualitative differences. In contrast to the set of Amazonian plants, monoterpene emissions predominated for Mediterranean plant species. This is in close accordance with earlier investigations of VOC emissions from plants of Mediterranean ecosystems known to release high amounts of monoterpenes (Owen et al., 2001). Investigations of Amazonian plant species are fragmentary in terms of areas, plant species and analytical techniques (Kesselmeier et al., 2009). Several screenings of VOC emissions from tropical plant species from Africa (Harley et al., 2003), from Asia (Oku et al., 2008), or from America including Amazonia (Harley et al., 2004; Lerdau and Keller, 1997; Lerdau and Throop, 1999, 2000; Pegoraro et al., 2006) have been made but concentrated only on isoprene emissions. However, the question of how many trees emit monoterpenes and other volatiles has not

been answered with the exception of the screenings performed by Klinger et al. (2002) and by Geron et al. (2006b) which concentrated on tropical plant species of China but not of Amazonia. A few tree species were identified earlier as monoterpene emitters among them *Hevea brasiliensis* (Geron et al., 2006b; Klinger et al., 2002; Wang et al., 2007). Additionally, Wilske et al. (2007) identified six out of eight SE Asia tropical tree species as monoterpene emitters, though at low rates. For the Amazon region one more species was identified by Kuhn et al. (2002b, 2004) as a light dependent monoterpene emitter.

The most substantial isoprene emissions were found for *Vatairea guianensis* from várzea and igapó as well as *Laetia corymbulosa* and *Salix martiana* from várzea, which reached values similar to those measured for several *Quercus* species Kesselmeier and Staudt, 1999. The results obtained here for the rest of the isoprene emitting species are consistent with emission rates reported for other tropical tree species (Harley et al., 2004; Padhy and Varshney, 2005). Also in the Mediterranean area high isoprene emitting species (*Brachypodium retusum, Buxus semprevirens, Chamaerops humilis, Ficus carica* and *Spartium junceum*) were found. High isoprene emissions for *Buxus sempervirens* were in close accordance with Owen et al. (2001). In contrast to our results, no isoprene emissions are reported in the case of *Ficus carica, Spartium junceum, Chamaerops humilis* and *Brachypodium retusum* in earlier studies (Benjamin et al., 1996; Owen et al., 2001; Pio et al., 1993). These differences could be due to the different origins of the plants within different Mediterranean areas, suggesting genetic differences. However, uncertain species identification, missing normalization of the data, and other technical aspects in previous studies cannot be ignored. In some cases no direct emission was reported, but assigned, based on genus average as in the case of the isoprene emission from *Ficus carica* and *Chamaerops humilis* reported by Benjamin et al. (1996) or from several tropical plant species (Harley et al., 2004).

Besides isoprene, monoterpenes make one of largest contributions to the global VOC flux. Together, isoprene and monoterpenes make up 55 % of the estimated global emissions (Guenther et al., 1995). During our experiments with tropical vegetation,

monoterpene emission was found to dominate in the group of *Hevea* species. The rubber tree *Hevea brasiliensis* showed a total monoterpene E_s of 10.9 to 38.1 μg g^{-1} s^{-1}, even exceeding the high emissions reported earlier (Geron et al., 2006b; Klinger et al., 2002; Wang et al., 2007). No information was found for the other monoterpene emitting *Hevea* species. Our data show that these species are also strong monoterpene emitters with emissions in the order of magnitude of *Hevea brasiliensis*, though *Hevea spruceana* from igapó and *Hevea spruceana* from várzea exhibited lower emission rates. No qualitative differences were observed for the monoterpene species emitted by all *Hevea* species except *Hevea guianensis*. Nearly all monoterpene emitting tropical trees of this work emitted α-pinene followed by limonene and sabinene. In contrast, the emission pattern reported previously for *Hevea brasiliensis* was dominated by sabinene followed by α-pinene and β-pinene (Wang et al., 2007). Further investigation is needed for a better understanding of these emission patterns of the dominant floodplain species *Hevea spruceana* and the terra firme species *Hevea guianensis*. Nevertheless, it is of special interest to note that all *Hevea* species investigated so far belong to the group of monoterpene emitters. In addition, this study revealed that the terra firme species *Scleronema micranthum* was a low monoterpene emitting species (< 1 μg g^{-1} s^{-1}) with a monoterpene emission pattern similar to *Hevea brasiliensis* and *Hevea spruceana* (Fig. 3). No bibliography data were found about the VOC emission pattern of this important tree of the Central Amazonian forest.

This study gives an impression of the domination of monoterpene emitting species in the Mediterranean area which is supported by the existence of a large number of aromatic plants. In a few cases, observed emission rates of monoterpene were comparable to literature data, e.g. the monoterpene emission from *Cistus albidus, Pinus halepensis, Quercus coccifera* and *Rosmarinus officinalis* of 0.2 ± 0.1, 2.0 ± 1.7, 5.7 ± 2.3 and 2.2 ± 0.3 μg g^{-1} h^{-1}, respectively, as reported by Owen et al. (2001). But in general, there were quantitative and qualitative differences reflecting the complex background for the emission and detection of this isoprenoid group. For example *Quercus suber* has been identified previously as a non isoprenoid emitter tree

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(Seufert et al., 1997; Steinbrecher et al., 1997), but this study found an emission factor of $35.6 \pm 5.5\,\mu g\,g^{-1}\,h^{-1}$, which corroborates more recent literature, showing typical summertime values of $10\text{--}30\,\mu g\,g^{-1}\,h^{-1}$ (Pio et al., 2005; Staudt et al., 2008, 2004). *Quercus afares* was found to emit high quantities of monoterpenes and low amounts of isoprene (see also Welter et al., 2012). Monoterpene emission by *Quercus coccifera* was observed in the range reported earlier between 1 and $5.5\,\mu g\,g^{-1}\,h^{-1}$ (Llusia and Penuelas, 2000; Ormeno et al., 2007a,c,d, 2009; Owen et al., 2001), though also higher rates of 11 to $14\,\mu g\,g^{-1}\,h^{-1}$ have been reported (Hansen and Seufert, 1996; Pio et al., 1993; Staudt and Lhoutellier, 2011). Monoterpene emissions as measured in our study for *Ceratonia siliqua* were in close accordance with other reports that showed emissions of $1.1\text{--}6.9\,\mu g\,g^{-1}\,h^{-1}$ (Llusia et al., 2002; Owen et al., 2001). Similarly, *Pinus halepensis* emitted monoterpenes in the range previously observed (Llusia and Penuelas, 2000; Ormeno et al., 2007a,b; Owen et al., 2001). But also in this case higher emissions between $14.8\text{--}86\,\mu g\,g^{-1}\,h^{-1}$ have been reported (Blanch, 2007; Llusia and Penuelas, 1998; Ormeno et al., 2007c; Penuelas and Llusia, 1999; Simon et al., 2005). *Ficus carica* and *Spartium junceum* could be classified as non monoterpene emitters, whereas low monoterpene emissions were detected in the case of *Prunus persica, Brachipodium retusum, Chamaerops humilis, Cistus albidus*, and *Coronilla valentina* though with PTR-MS only. For *Prunus persica, Brachipodium retusum, Cistus albidus* similar, lower ($0.2\text{--}1\,\mu g\,g^{-1}\,h^{-1}$) as well as higher ($11\text{--}45\,\mu g\,g^{-1}\,h^{-1}$) emission rates were reorted in earlier studies (Arey et al., 1991; Benjamin and Winer, 1998; Llusia and Penuelas, 2000; Ormeno et al., 2007a–d; Owen et al., 2001; Pio et al., 1993; Staudt et al., 2010; Winer et al., 1992). For *Chamaerops humilis* and *Coronilla valentina* no monoterpene emission was reported previously. Low, but still detectable emissions of monoterpenes ($< 2\,\mu g\,g^{-1}\,h^{-1}$) were found with *Buxus sempervirens, Cistus monspeliensis, Olea europaea*, and *Rosmarinus officinalis*. Monoterpene emissions by *Buxus sempervirens* were found for the first time. *Cistus monspeliensis* and *Rosmarinus officinalis* are already described as monoterpene emitters in the literature with high emission ($3.6\text{--}11.7\,\mu g\,g^{-1}\,h^{-1}$). We found low ($< 1\,\mu g\,g^{-1}\,h^{-1}$) or even

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no monoterpene emissions for *Cistus monspeliensis* and similar ranges as reported for *Rosmarinus officinalis* (Hansen et al., 1997; Lenz et al., 1997; Llusia and Penuelas, 1998; Olivier et al., 2011a; Ormeno et al., 2007b,c,d, 2009; Owen et al., 2002). It should be noted, however, that Owen et al. (2001) reports some emission rates twice the amount as found by us. This observed variability of monoterpene emissions may be understood to result from a variety of influences, such as different sampling and analytical methods, plant origin, plant developmental stages and environmental conditions or even questionable plant identification, making it difficult to use such data for emission models (Niinemets et al., 2011).

In contrast to the rather homogenous emission patterns as found for the tropical plants species in our study, the Mediterranean plants showed a high variability of monoterpene species composition. The monoterpene emission pattern found here for *Ceratonia siliqua* (myrcene, *Z*-ocimene, *E*-ocimene) was completely different than that reported by Owen et al. (2001) or by Llusia et al. (2002), who reported emissions of α-pinene and limonene or only α-pinene, respectively. Our results with *Cistus monspeliensis*, i.e. emissions of α-pinene, camphene and β-pinene, coincided with Owen et al. (2002) but not with Llusia et al. (1998) who reported an emission of α-phellandrene only. Furthermore, we could identify myrcene and *E*-ocimene in our study. For *Olea europaea* we found *Z*-ocimene and *E*-ocimene, the latter compound also reported by Arey et al. (1991) but this completely disagreed with the emission pattern reported in several other reports (Benjamin and Winer, 1998; Llusia et al., 2002; Owen et al., 2001; Pio et al., 1993; Winer, 1983). *Pinus halepensis* is one of the most intensively investigated conifers of the Mediterranean area with a large variety of emission patterns (Benjamin and Winer, 1998; Blanch, 2007; Corchnoy et al., 1992; Llusia and Penuelas, 1998, 2000; Ormeno et al., 2007a–d; Owen et al., 2001, 2002; Penuelas and Llusia, 1999; Simon et al., 2005). As in our studies, *Z*-ocimene and *E*-ocimene were also observed in previous work (Ormeno et al., 2007a,b,c; Owen et al., 2001), but the monoterpene terpinene-4-ol was found for the first time in our investigation. On the other hand a variety of compounds that were not detected in our study

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were reported previously, like *α*-pinene, *β*-pinene, limonene, sabinene, etc. (Blanch, 2007; Llusia and Penuelas, 1998; Owen et al., 2001). Monoterpene species emissions by *Quercus coccifera* were in close accordance with reports by Owen et al. (2001), Hansen and Seufert (1996), Llusia and Penuelas (2000), Ormeno et al. (2007a,c,d, 2009), Olivier et al. (2011b) and Staudt and Lhoutellier (2011). In the case of *Quercus suber*, emissions of 15 different monoterpene species were found in our study (Fig. 4) contrasting with other reports with only about 4 to 7 monoterpene species, such as *α*-pinene, sabinene, *β*-pinene, myrcene, limonene, camphene and eucalyptol (Pio et al., 1993, 2005; Staudt et al., 2008, 2004). Measurements from *Rosmarinus officinalis* confirmed the high variability of emissions as reported earlier (Hansen et al., 1997; Olivier et al., 2011a; Ormeno et al., 2007b,c,d, 2009; Owen et al., 2002; Seufert et al., 1997) coinciding only in the *α*-pinene emission which was the only monoterpene species reported in all studies. The shrub *Buxus sempervirens* has been described as a non monoterpene emitter by Owen et al. (2001) but our measurements show low emissions of *α*-phellandrene and *Z*-ocimene. On the other hand, we could not detect any monoterpene emission from *Spartium junceum* or *Ficus carica* in contrast to other authors who detected low monoterpene emissions (Benjamin and Winer, 1998; Owen et al., 1997, 2001; Pio et al., 1993; Seufert et al., 1997).

Today we understand that the variability of isoprenoid emissions is a consequence of many factors triggering plant secondary metabolism. Seasonality is one of the main factors, which can influence the amount of emissions and perhaps also the monoterpene species composition (Llusia and Penuelas, 2000; Owen et al., 2001; Penuelas and Llusia, 1997; Staudt et al., 2000, 2002) resulting in reports on dependency on the developmental stage of plants and ecosystems. However, even if we only compare data obtained during similar seasonal stages other factors of similar or even higher dominance, besides technical triggers, the genetic variability, the chemotype at the site of origin as well as hybridisation, and stress effects must be taken into account (Geron et al., 2000; Guenther et al., 1993; Niinemets et al., 2011; Staudt et al., 2010, 2004). Investigations performed with conifers demonstrated that the geographical variation

and population dynamics can exert genetic variations in trees within the same species (Hanover, 1992), leading to a differentiation in monoterpene composition. In the study of Hanover (1992), plant species from the South East French Mediterranean area were compared with studies performed in the Italian and Spanish Mediterranean area, Portu-
5 gal and California's Central Valley supposing different genetics due to evolutionary variation. Another possible source of variability can be expected by measurements outside standard light and temperature conditions which should be normalized if possible by mathematical algorithms such as the G93 (Guenther et al., 1995). However, such normalization was not performed in all studies and cannot be applied for all compounds.
10 Moreover, the emission responses to temperature and light are not constant but can vary considerably with time depending on prevailing weather conditions and interactions among environmental drivers (Staudt and Lhoutellier, 2011). However, without the normalization to common standard conditions a quantitative comparison has to be discussed carefully. Furthermore, the choice between an algorithm taking into account
15 temperature only or temperature and light may be of importance. Some estimates are based on the sole temperature normalization for plants species that have monoterpene storage organs such as *Pinus halepensis, Cistus monspeliensis* and *Rosmarinus officinalis*. Considerable emissions in darkness for *Rosmarinus officinalis* and *Cistus monspeliensis* (Owen et al., 2002) seem to support such an approach. But for example
20 in the case of *Pinus halepensis* and *Pinus pinea*, it has been demonstrated that the emission of some monoterpene species such as β-ocimenes are light dependent (Simon et al., 2005), though potentially supported by high temperature exposure (Staudt and Bertin, 1998; Staudt et al., 1997, 2000, 2003).

The sesquiterpenes were detected only in the case of Mediterranean vegetation
25 and not with tropical plants. Due to their high reactivity and relatively low vapour pressure and emission rates, these compounds are easily missed or underestimated (Duhl et al., 2008). Special analytical adaptations can facilitate their quantification (Helmig et al., 2004; Merfort, 2002; Tholl et al., 2006). Results previously published by Bracho-Nunez et al. (2011) reflect the difficulties depending on the VOC detection method.

Higher sensitivity by offline gas chromatographic methods as compared to online PTR-MS methods are observed, the latter being less specific, however. Other studies have confirmed the difficulty of PTR-MS for the measurements of sesquiterpenes, reporting high fragmentation patterns (Demarcke et al., 2009; Tani et al., 2003). The characterization of sesquiterpene emissions in the case of the Mediterranean area is sparse and only a few oaks, birches and pines typical for this region are reported to emit sesquiterpenes (Ciccioli et al., 1999; Hansen and Seufert, 1999; Llusia and Penuelas, 1998; Ormeno et al., 2007b,d; Staudt et al., 2008; Staudt and Lhoutellier, 2007, 2011). In the course of our work on Mediterranean vegetation we found a high variability for these compounds in close accordance with other reports (Ormeno et al. 2007a–d, 2009; Llusia et al., 1998; Duhl et al., 2008). However, sesquiterpene emissions from *Buxus sempervirens, Ceratonia siliqua* and *Olea europaea* could be reported for the first time here. Sesquiterpene emissions from *Quercus coccifera* were quantitatively but not qualitatively comparable. We found only β-caryophyllene emissions, whereas a variety of sesquiterpene species were reported in other studies (Ormeno et al., 2007a,c,d, 2009; Staudt and Lhoutellier, 2011). It is important to note that for *Cistus albidus* most of the sesquiterpene species identified here were partially in accordance with other studies performed in the Mediterranean region (Llusia and Penuelas, 1998; Ormeno et al., 2007a–d) except for emissions of α- and β-cubebene. Sesquiterpene emissions of *Cistus albidus* as low as $0.63 \pm 0.32\,\mu g\,g^{-1}\,h^{-1}$ were in concordance with Ormeno et al. (2007a,d) but contrasted significantly higher emissions found in other studies (Llusia and Penuelas, 1998; Ormeno et al., 2007b,c). We did not find any sesquiterpene emissions from *Pinus halepensis* and *Rosmarinus officinalis*, in contrast to observations reported by Ormeno et al. (2007a–d, 2009). The emission of β-caryophyllene by *Cistus monspeliensis* disagrees with the findings by Llusia et al., 1998. Such variation in the sesquiterpene emissions in the literature may be due to differences in analysis protocols and sampling and plant enclosure techniques. But other factors such as seasons, measuring conditions and overall stress effects may also contribute. Sesquiterpene emissions are known to be induced by a variety of stresses including heat and

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oxidative stress (Loreto and Schnitzler, 2010). For example in a recent study on *Quercus coccifera*, Staudt and Lhoutellier (2011) observed that sesquiterpene emissions become boosted during exposure to heat and high radiation, while at moderate temperatures sesquiterpene emissions were low or even undetectable in this species. In line with this, field studies by Ormeno et al. (2007d; 2009) observed the highest standard emissions of *Rosmarinus officinalis* in June, whereas lower emission rates were found in March or January suggesting a seasonal trend possibly associated with heat and oxidative stress occurring under Mediterranean summer conditions. However, similar trends were reported for *Cistus albidus* and *Pinus halepensis*. Thus it has to be noted that the variability of sesquiterpene emissions is even more striking than that for monoterpenes.

Despite their importance in plant physiology, ecology, and also in air chemistry (Fall, 2003) our information on oxygenated VOC compounds emission from vegetation is sparse, and their contribution to the global VOC budget has been poorly described (Eerdekens et al., 2009). The technological improvement of using a PTR-MS has facilitated the study of short-chain oxygenated VOCs. The exchange of the oxygenated VOCs like methanol and acetone has been detected for a variety of plant species (De Gouw et al., 1999; Holzinger et al., 2000; Hüve et al., 2007; Isidorov et al., 1985; Kirstine et al., 1998; MacDonald and Fall, 1993a,b; Nemecek-Marshall et al., 1995; Seco et al., 2007). Methanol is a product of the demethylation of pectin during cell wall formation and is produced by leaf growth, for example (Galbally and Kirstine, 2002; Nemecek-Marshall et al., 1995). The plants we investigated were young plants still in the growing period and a significant emission of methanol was found. However, the physiological background for methanol emission is still a matter of discussion (Folkers et al., 2008). In the case of acetone, several studies have reported leaf level acetone emissions from vegetation (Cojocariu et al., 2005; Geron et al., 2006a,b; Grabmer et al., 2006; Holzinger et al., 2000; Janson and de Serves, 2001; Kreuzwieser et al., 2002; MacDonald and Fall, 1993b; Nemecek-Marshall et al., 1995; Villanueva-Fierro et al., 2004) as well as high concentrations of this compound in the troposphere above

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forested areas (Geron et al., 2002; Helmig et al., 1998; Karl et al., 2003; Müller et al., 2006; Pöschl et al., 2001). In our study, emissions of methanol and acetone were demonstrated for the chosen plant species for the first time, except for the Mediterranean tree *Pinus halepensis* which has been reported earlier to emit methanol and
5 acetone (Filella et al., 2009). Though the tropical tree *Hevea brasiliensis* has been described as an acetone emitter by Geron et al. (2006b) we did not find acetone emissions in this case. Interestingly, emissions of methanol by the Mediterranean species investigated in this study were significantly lower ($p < 0.05$) than those detected for our tropical vegetation species. We may understand that difference as being due to differ-
10 ent developmental stages of the plants. The tropical plants investigated were younger than the Mediterranean plant species, although in both experiments fully expanded mature leaves were measured. On the other hand, the light dependent acetone emissions found in this study are supposed to be direct emissions from the leaves; only one tropical plant released acetone, whereas seven Mediterranean plants were found to be
15 acetone emitters. The metabolic pathway of acetone has not yet been proven. It was hypothesised that acetone is produced in spruce needles by the decarboxylation of acetoacetate (MacDonald and Fall, 1993b), whereas a cyanohydrin-lyase catalysed reaction was found in cyanogenic plant species (Fall, 2003) leading to acetone release. *Hevea spruceana*, *Hevea guianensis* and *Hevea brasiliensis* are known to be cyanogenic
20 plants containing the cyanogenic β-glucoside linamarin (Lieberei, 1986), but acetone emissions were found only in *Hevea spruceana*. Furthemore, the emissions of acetone could be inferred from the cyanogenic pathway in *Olea europaea*, *Coronilla glauca* and *Prunus persica* as already speculated by Bracho-Nunez et al. (2011). On the other hand, it is known that the atmospheric OH-oxidation of several monoterpenes, like
25 α- and β-pinene, in the presence of NO_x appears to be a potentially relevant source of acetone (Wisthaler et al., 2001). Though NO_x data for our measurements are not available, a contribution of this oxidation pathway to the measured acetone concentrations could not be excluded, particularly in the case of all tropical plant species and

the Mediterranean species *Cistus monspeliensis, Quercus afares, Quercus suber* and *Rosmarinus officinalis*, that emitted relevant quantities of α- and β-pinene.

Diurnal emissions of an unknown compound with mass 73 have been detected from the tropical plant species *Garcinia macrophylla*. This mass might be considered to be protonated methyl ethyl ketone (MEK), also known as 2-butanone. Not much is known about the biosynthetic pathways leading to the formation of MEK and its emission mechanisms, but it has been reported to be emitted by a variety of plants and grasses (De Gouw et al., 1999; Isidorov et al., 1985; Jardine et al., 2010; Kirstine et al., 1998). Furthermore, the contribution of 2-methyl propanal to the mass 73 being a known floral volatile compound (Baraldi et al., 1999) can not be excluded (Jardine et al., 2010). On the other hand, Holzinger et al. (2007) identified mass 73 as being protonated methylglyoxal, a secondary oxidation product of isoprene (Lee et al., 2006). Since *Garcinia macrophylla* is a high isoprene emitter, formation of such an oxidation product could be plausible (Jardine et al., 2011). The detection of an unknown compound demonstrates the need of further investigation in order to identify compounds that probably have been overseen until now due to technical limitations.

This study provides a categorization of VOC emissions from common tropical and Mediterranean plant species to further the understanding on interactions between vegetation and the atmosphere. Screening should be continued in the future, since the characterization of VOC emissions from representative species will support our understanding of emission processes, regulation and development. In particular more attention should be given to sesquiterpenes and oxygenated compounds whose emissions are highly variable and uncertain due perhaps to methodological limitations and their inherent association with stress and phenology (Bracho-Nunez et al., 2011, 2012). The better understanding of VOC emission patterns from plant species will significantly contribute to the confidence in prediction models.

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Table 1. Plant species, number of individuals measured (n), specific leaf weight (SLW), family, functional type, ecosystem and distribution of the 12 investigated tropical plant species.

Plant species	n	SLW (gm^{-2})	Family	Functional type[c]	Ecosystem[a]	Distribution[b]
Garcinia macrophylla (Mart.) Planch. and Triana	3	142	*Clusiaceae*	evergreen tree	a, b[d], c, d, i	Tropical South America, South-East Asia, United States
Hevea brasiliensis (Willd. ex A. Juss.) Müll. Arg.	3	33.4	*Euphorbiaceae*	evergreen tree	b, c[d], i, j	Tropical South America, Central America, Western Africa, Central Africa, South and SE-Asia, South of North-America
Hevea guianensis Aubl.	2	39.6	*Euphorbiaceae*	evergreen tree	b, c[d], d	Tropical South America
Hevea spruceana(Benth.) Müll. Arg.	3[f], 2[e]	42.9[f], 23.6[e]	*Euphorbiaceae*	deciduous/brevi-deciduous tree	a[d], b[d], d	Tropical South America, Central America
Hura crepitans L.	3	45.2	*Euphorbiaceae*	brevi-deciduous tree	a[d], c, i	Tropical South-America, Central America, Western Africa, SE-Asia, South of North-America.
Ocotea cymbarum Kunth	3	76.0	*Lauraceae*	brevi-deciduous /evergreen tree	a[d], d	Tropical South America
Pachira insignis (Sw.) Sw. ex Savigny	3	46.0	*Malvaceae*	brevi-deciduous tree	a[d], c	Tropical South America, Western Africa
Pouteria glomerata (Miq.) Radlk.	3	67.7	*Sapotaceae*	evergreen tree	a[d], c, d, e, f, g, h	Tropical South and Central America
Pseudobombax munguba (Mart. and Zucc.) Dugand	3	65.0	*Malvaceae*	deciduous tree	a[d], b, d	Tropical South America
Scleronema micranthum Ducke	3	76.9	*Malvaceae*	evergreen tree	c[d]	Tropical South America
Vatairea guianensis Aubl.	2[f], 2[e]	36.4[f], 26.1[e]	*Fabaceae*	deciduous tree	a[d], b[d], c, d, e	Tropical South America
Zygia juruana (Harms) L. Rico	3	41.9	*Fabaceae*	evergreen tree	a[d], c	Tropical South America

[a] Missouri Bot Garden, New Bot. Garden, Royal Bot. Gardens Kew, INPA-Herbarium and F. Wittmann, personal communication, 2011.

[b] Global Biodiversity Informations Facility: http://data.gbif.org and www.worldagroforestrycentre.org.

[c] Schöngart et al., 2002.

[d] Indicates the plant's environment selected for the measurement.

[e] Várzea

[f] Igapó

a) Várzea of Central Amazonian
b) Igapó of Central Amazonian
c) Amazonian Terra Firme
d) Orinoco basin
e) Atlantic rainforest (non-flooded)
f) Brazilian Pantanal (non-flooded)
g) Brazilian Pantanal (flooded)
h) Cerrado
i) Central America
j) West Africa, Asia

Table 2. Plant species, number of individuals measured (n), specific leaf weight (SLW), family, functional type and occurrence of the 16 investigated Mediterranean plant species.

Plant species	n	SLW $(\mathrm{g\,m^{-2}})$	Family	Functional type	Distribution
Brachypodium retusum Pers.	3	85	*Poaceae*	evergreen herb	Mediterranean Region
Buxus sempervirens L.	3	291	*Buxaceae*	evergreen shrub	Western and Southern Europe, North-West Africa, South-West Asia
Ceratonia siliqua L.	3	149	*Fabaceae*	evergreen tree	Mediterranean Region
Chamaerops humilis (L.) Cav.	3	240	*Arecaceae*	palm tree	Western Mediterranean Region
Cistus albidus L.	3	91	*Cistaceae*	evergreen shrub	South West Europe to North Africa, Mediterranean Region
Cistus monspeliensis L.	3	110	*Cistaceae*	evergreen shrub	South West Europe
Coronilla valentina Pall. ex Bieb.	3	73	*Fabaceae*	evergreen shrub	Mediterranean Region
Ficus carica L.	3	66	*Moraceae*	deciduous tree	South-West Asia and the Eastern Mediterranean Region
Olea europaea L.	3	352	*Oleaceae*	evergreen tree	Coastal Areas of Eastern Mediterranean Region, Lebanon, Syria and the maritime parts of Asia Minor and Northern Iran at the south end of the Caspian Sea
Pinus halepensis Mill.	3	143	*Pinaceae*	evergreen tree	Mediterranean region
Prunus persica (L.) Batsch.	3	70	*Rosaceae*	deciduous tree	China, Iran, Mediterranean region
Quercus afares Pomel	3	114	*Fagaceae*	deciduous tree	Algeria and Tunisia
Quercus coccifera L.	3	163	*Fagaceae*	evergreen tree	Western Mediterranean region, Morocco, Portugal, East Greece
Quercus suber L.	3	121	*Fagaceae*	evergreen tree	South-West Europe, North -West Africa
Rosmarinus officinalis L.	3	215	*Lamiaceae*	evergreen herb	Mediterranean Region
Spartium junceum L.	3	135	*Fabaceae*	evergreen shrub	Mediterranean Region

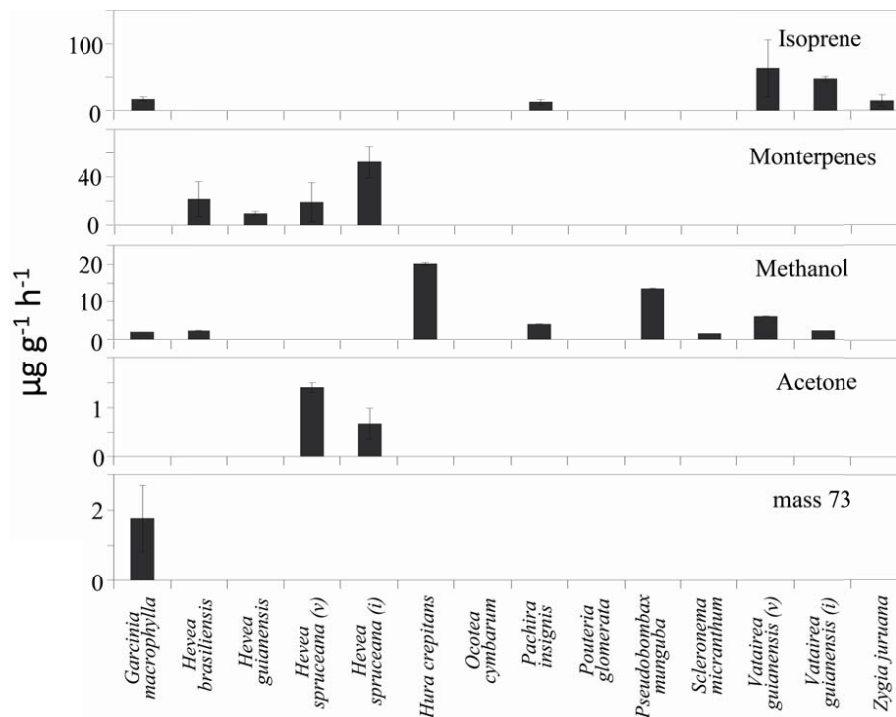**Fig. 1.** VOC emitted from 12 plant species of the tropical ecosystems ((v) várzea and (i) igapó) in $\mu g\, g^{-1}\, h^{-1}$. Standard error bars are given.

Fig. 2. VOCs emitted from 16 Mediterranean plant species in $\mu g\, g^{-1}\, h^{-1}$. Standard error bars are given.

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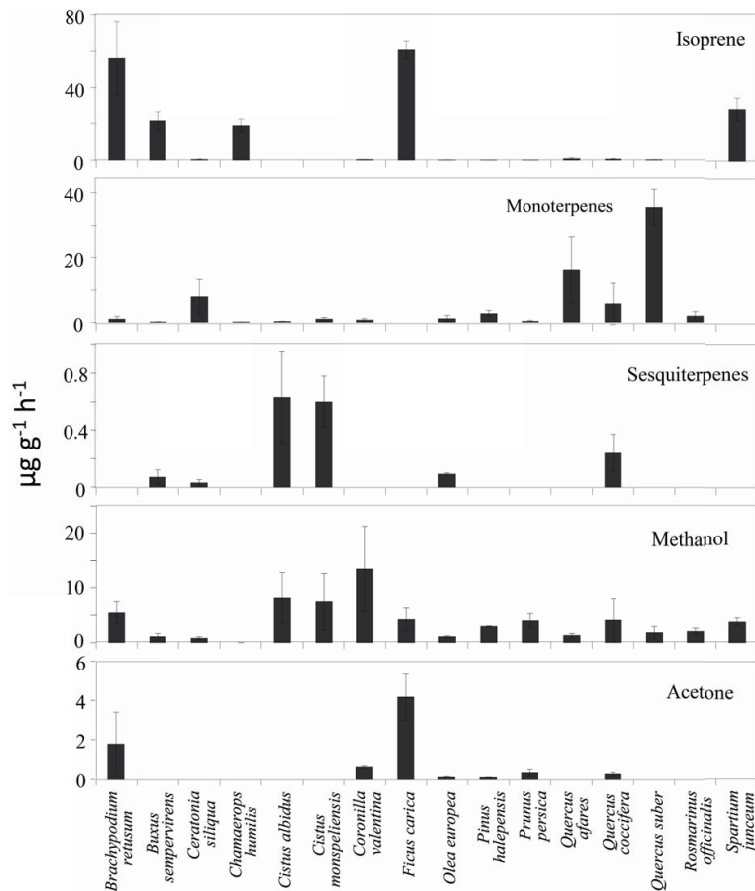Full Screen / Esc

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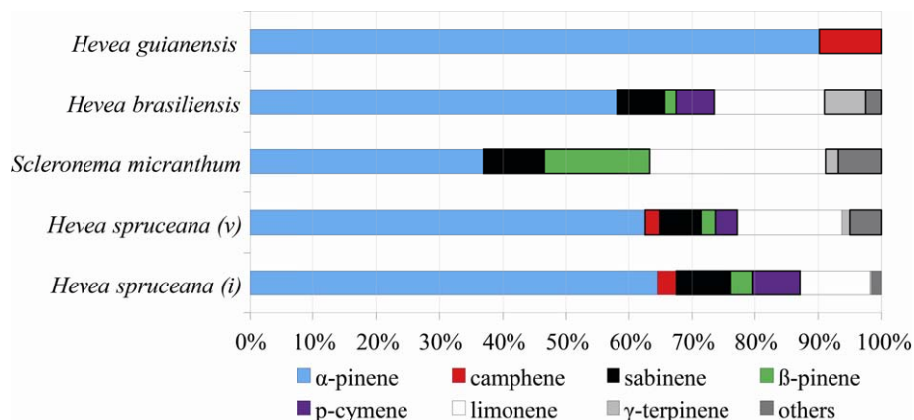
Fig. 3. Relative composition (%) of monoterpenes emitted from tropical plant species ((v) várzea, (i) igapó). Others include for *H. spruceana* (i) (myrcene, α-phellandrene and 3 carene) for *H. spruceana* (v) (myrcene, 3 carene and γ-terpinene) for *S. micranthum* (myrcene and γ-terpinene) and for *H. brasiliensis* (myrcene and α-phellandrene).
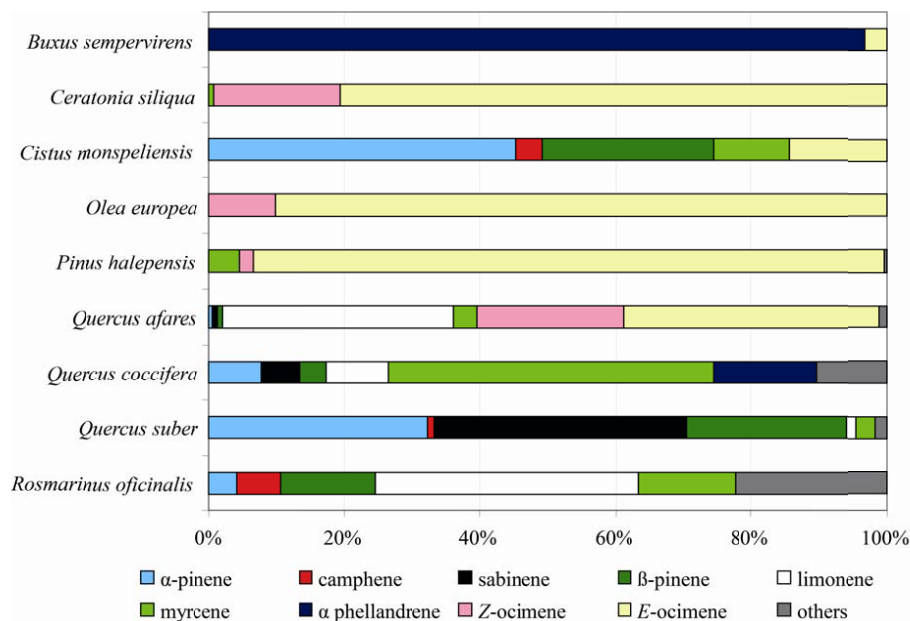
Fig. 4. Relative composition (%) of monoterpenes emitted from Mediterranean plant species. Others include in *P. halepensis* (terpinene-4-ol), in *Q. afares* (linalol and allo-ocimene), in *Q. coccifera* (α-thujene, β-phellandrene, eucalyptol, α-terpinene, p-cymene and γ-terpinene), in *Q. suber* (α-thujene, menthol, terpinolene, o-cymene, terpinene-4-ol, cis-sabinenehydrat, borneol, α-terpinene and γ-terpinene) and in *R. officinalis* (eucalyptol and camphor).
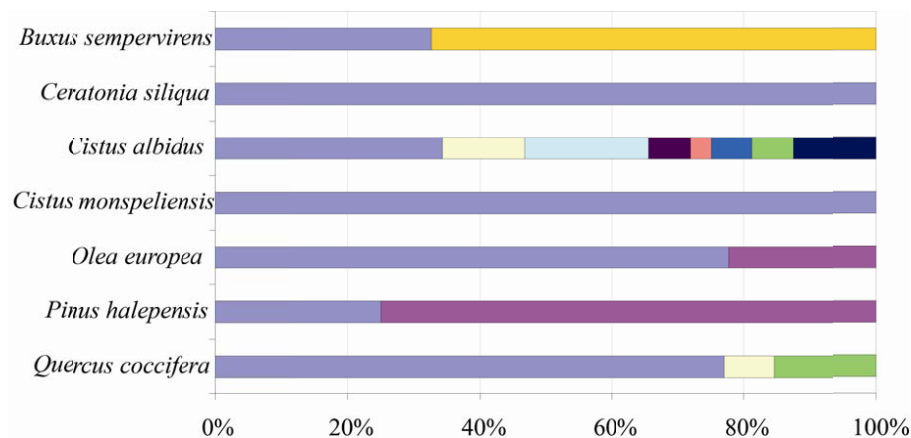
Fig. 5. Relative composition (%) of sesquiterpenes emitted from Mediterranean plant species.