Biogeosciences, 10, 5855–5873, 2013
www.biogeosciences.net/10/5855/2013/
doi:10.5194/bg-10-5855-2013

Biogeosciences Open Access

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

A. Bracho-Nunez[1,2], N. M. Knothe,[1], S. Welter[1,2], M. Staudt[2], W. R. Costa[3], M. A. R. Liberato[4], M. T. F. Piedade[3], and J. Kesselmeier[1]

[1]Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany
[2]Centre d'Ecologie Fonctionnelle et Evolutive, UMR5175, 54293 Montpellier, France
[3]Instituto Nacional de Pesquisas da Amazônia, Av. André Araújo, 2936 Manaus, Brazil
[4]Universidade do Estado do Amazonas, Av. Djalma Batista, Chapada, 69050-010 Manaus, AM, Brazil

Correspondence to: (j.kesselmeier@mpic.de)

Received: 17 August 2012 – Published in Biogeosciences Discuss.: 1 November 2012
Revised: 21 July 2013 – Accepted: 26 July 2013 – Published: 6 September 2013

Abstract. Emission inventories defining regional and global biogenic volatile organic compounds (VOC) emission strengths are needed to determine the impact of VOC on atmospheric chemistry (oxidative capacity) and physics (secondary organic aerosol formation and effects). The aim of this work was to contribute with measurements of tree species from the poorly described tropical vegetation in direct comparison with the quite well-investigated, highly heterogeneous emissions from Mediterranean vegetation. VOC emission from sixteen plant species from the Mediterranean area were compared with twelve plant species from different environments of the Amazon basin by an emission screening at leaf level using branch enclosures. 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 the most dominant compound emitted followed by monoterpenes, methanol and acetone. The average loss rates of VOC carbon in relation to the net CO_2 assimilation were found below 4 % and indicating normal unstressed plant behavior. Most of the Mediterranean species emitted a large variety of monoterpenes, whereas only five tropical species were identified as monoterpene emitters exhibiting a quite conservative emission pattern (α-pinene < limonene < sabinene < ß-pinene). Mediterranean plants showed additional emissions of sesquiterpenes. In the case of Amazonian plants no sesquiterpenes were detected. However, missing of sesquiterpenes may also be due to a lack of sensitivity of the measuring systems. Furthermore, our screening activities cover only 1 % of tree species of such tropical areas as estimated based on recent biodiversity reports. Methanol emissions, an indicator of growth, were found to be 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 (VOC) affecting chemical and physical properties of the atmosphere (Atkinson and Arey, 2003). Biogenic VOC regulates the oxidative capacity of the atmosphere and has an indirect impact on the lifetime of greenhouse gases. Furthermore, they are involved in the formation and growth of secondary organic aerosols (SOA), which in turn affect cloud development and precipitation (Andreae and Crutzen, 1997; Wang et al., 1998; Collins et al., 2002; Lelieveld et al., 2002; Claeys et al., 2004; Pöschl et al., 2010; Sjostedt et al., 2011).

Emission inventories and model calculations have been developed 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; Kinnee et al., 1997;

Simpson, 1999; Guenther et al., 2006), or on studies of only one VOC species, i.e. isoprene (Lerdau and Keller, 1997; Lerdau and Throop, 1999, 2000; Harley et al., 2004; Pegoraro et al., 2006; Oku et al., 2008; Ferreira et al., 2010; Misztal et al., 2010). Because of the heterogeneity of ecoregions, species diversity, inaccessibility, and logistical and methodological difficulties, the number of investigations made in tropical regions is limited (Geron et al., 2002; Kesselmeier et al., 2002, 2009; Kuhn et al., 2002a, b, 2004, 2007; Harley et al., 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 only 7 % (Guenther et al., 1995). In contrast to the tropics, Mediterranean plant species have already been intensively studied and are known to emit a great variety of VOC (Owen et al., 1997; Kesselmeier and Staudt, 1999; Owen et al., 2001, 2002; Llusia et al., 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, 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 unmeasured VOC (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 VOC 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. This study was performed as a doctoral thesis (Bracho-Nunez, 2010) which can be consulted at the given URL for more details. 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 VOC were used: a proton-transfer-reaction mass spectrometer (PTR-MS) for the detection of all VOC 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 VOC, including sesquiterpenes.

2 Material and methods

2.1 Plant material and environmental conditions

2.1.1 Tropical vegetation

VOC emission screening was carried out with a total of twelve different tree species common for terra firme and floodplain areas in the Amazonas region (Table 1). Three representative tree species were derived from the upland forest (terra firme) ecosystem, eight from the white water floodplain region (várzea) which is regularly inundated with nutrient-rich and sediment-loaded "white" water and three from the (igapó) floodplain region regularly inundated with nutrient-poor "black" water rich in humic matter, or clear-water with an intermediate amount of nutrients (Prance, 1979; Sioli, 1954, 1956). Two of the plant species, *Vatairea guianensis* and *Hevea spruceana*, are found in the igapó and várzea as well.

The tropical screening experiment was a cooperative effort between the Max Planck Institute for Chemistry and the Instituto Nacional de Pesquisas da Amazônia (INPA, Manaus), and was performed 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 Reserve'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. Effects of different floodplain environments on trace gas emission quality and quantity were investigated comparing plant individuals growing in várzea and igapó as well, such as *Hevea spruceana* and *Vatairea guianensis*. Collected plants were potted in soil 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 sunlit conditions, 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 were recorded during the dry and wet season, respectively. A total of three replicates for each species were measured with

Table 1. Plant species, family, functional type, ecosystem and distribution of the 12 investigated tropical plant species.

Plant species	Family	Functional type[1]	Distribution[2]
Garcinia macrophylla (Mart.) Planch. & Triana	Clusiaceae	evergreen tree	Tropical South America, Southeast Asia, United States
Hevea brasiliensis (Willd. ex. A.Juss.) Müll.Arg.	Euphorbiaceae	evergreen tree	Tropical South America, Central America, West Africa, Central Africa, South and SE Asia, south of North America
Hevea guianensis Aubl.	Euphorbiaceae	evergreen tree	Tropical South America
Hevea spruceana (Benth.) Müll.Arg.	Euphorbiaceae	deciduous/ brevi-deciduous tree	Tropical South America, Central America
Hura crepitans L.	Euphorbiaceae	brevi-deciduous tree	Tropical South America, Central America, West Africa, SE Asia, South of North America
Ocotea cymbarum Kunth	Lauraceae	brevi-deciduous/ evergreen tree	Tropical South America
Pachira insignis (Sw.) Sw. ex Savigny	Malvaceae	brevi-deciduous tree	Tropical South America, West Africa
Pouteria glomerata (Miq.) Radlk.	Sapotaceae	evergreen tree	Tropical South and Central America
Pseudobombax munguba (Mart. & Zucc.) Dugand	Malvaceae	deciduous tree	Tropical South America
Scleronema micranthum Ducke	Malvaceae	evergreen tree	Tropical South America
Vatairea guianensis Aubl.	Fabaceae	deciduous tree	Tropical South America
Zygia juruana (Harms) L. Rico	Fabaceae	evergreen tree	Tropical South America

[1] (Schöngart et al., 2002). [2] Global Biodiversity Information Facility: http://data.gbif.org and www.worldagroforestrycentre.org, *(v) Várzea (i) Igapó*

some exceptions (Table 7). Plant incubation in dynamic flow-through-enclosures started at 8.00 p.m. (local time) on the evening before measurements were performed the next day to allow tree individuals to adapt to the enclosure system.

2.1.2 Mediterranean vegetation

All plants 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. All together a total of sixteen plant species (all 2–3 yr old) including deciduous and non-deciduous trees, shrubs, grasses and palm trees typical for the Mediterranean area were studied at the CEFE-CNRS in Montpellier (France) during the months of April to July 2008 (Table 2). Again, for each species there were three replicates.

2.2 Enclosure techniques and gas exchange measurements

2.2.1 Tropical 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, b). 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 an ozone scrubber composed by ten copper nets coated with MnO_2 (Ansyco, Germany) placed in a Teflon tube to prevent oxidant inter-

Table 2. Plant species, family, functional type and occurrence of the 16 investigated Mediterranean plant species.

Plant species	Family	Functional type	Distribution
Brachypodium retusum Pers.	Poaceae	evergreen herb	Mediterranean region
Buxus sempervirens L.	Buxaceae	evergreen shrub	western and southern Europe, northwest Africa, southwest Asia
Ceratonia siliqua L.	Fabaceae	evergreen tree	Mediterranean region
Chamaerops humilis (L.) Cav.	Arecaceae	palm tree	western Mediterranean region
Cistus albidus L.	Cistaceae	evergreen shrub	southwest Europe to North Africa, Mediterranean region
Cistus monspeliensis L.	Cistaceae	evergreen shrub	southwest Europe
Coronilla valentina Pall. ex Bieb.	Fabaceae	evergreen shrub	Mediterranean region
Ficus carica L.	Moraceae	deciduous tree	southwest Asia and the eastern Mediterranean region
Olea europaea L.	Oleaceae	evergreen tree	Coastal areas of eastern Mediterranean region and Asia Minor; southern region of the Caspian Sea
Pinus halepensis Mill.	Pinaceae	evergreen tree	Mediterranean region
Prunus persica (L.) Batsch.	Rosaceae	deciduous tree	China, Iran, Mediterranean region
Quercus afares Pomel	Fagaceae	deciduous tree	Algeria and Tunisia
Quercus coccifera L.	Fagaceae	evergreen tree	western Mediterranean region, Morocco, Portugal, eastern Greece
Quercus suber L.	Fagaceae	evergreen tree	southwest Europe, northwest Africa
Rosmarinus officinalis L.	Lamiaceae	evergreen herb	Mediterranean region
Spartium junceum L.	Fabaceae	evergreen shrub	Mediterranean region

ferences 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 flow meter (EL-Flow, 50 L min^{-1}, Bronkhorst Hi-Tec, Germany). Two different cuvette sizes with volumes of 9 L and 100 L were used depending on the size of the plant to be enclosed. The cuvette 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.

Mixing of air within the cuvette was achieved with a Teflon-coated fan. Cuvette temperature and relative humidity was measured in bypassed air with a commercial sensor (Model Rotronics YA-100F, Walz, Germany). Exchange of VOC, 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 with a CO_2 / H_2O infrared gas analyzer (LI-COR Inc. 7000, Lincoln, Nebraska, USA). The analyzer 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, Freiburg, Germany) and adjusted to 0.5 L min^{-1} by a rotameter (Omega, USA). 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 channel (Li 610; LI-COR,

Table 3. Leaf temperature (T_{leaf}) and photosynthetic active radiation (PAR) of tropical plants measured under semi-controlled conditions. Enclosure temperatures were not significantly different as compared to leaf temperatures with 1 °C lower mean temperatures at most. Averages ± standard deviation of measurements with *n* tree individuals. Each replicate represents an average of data points measured every minute during one day measurement by a PAR $< 300\,\mu mol\,m^{-2}\,s^{-1}$ (this PAR value was determined with light curves (data not shown) and represents the photosynthetic saturation point of all tropical plants).

	n	T_{leaf} [°C]	PAR [$\mu mol\,m^{-2}\,s^{-1}$]
Garcinia macrophylla	3	36 ± 2	1259 ± 61
Hevea brasiliensis	3	34 ± 2	502 ± 4
Hevea guianensis	2	34 ± 1	499 ± 1
Hevea spruceana (v)	2	33 ± 1	498 ± 3
Hevea spruceana (i)	3	35 ± 2	1329 ± 138
Hura crepitans	3	32 ± 1	794 ± 92
Ocotea cymbarum	3	32 ± 2	607 ± 13
Pachira insignis	3	31 ± 1	595 ± 11
Pouteria glomerata	3	32 ± 1	573 ± 3
Pseudobombax munguba	3	33 ± 2	1171 ± 309
Scleronema micranthum	3	33 ± 1	607 ± 15
Vatairea guianensis (v)	2	31 ± 1	497 ± 1
Vatairea guianensis (i)	2	33 ± 1	499 ± 2
Zygia jurana	3	32 ± 1	612 ± 3

(v) várzea, (i) igapó

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 and temperature. Assimilation, transpiration and stomatal conductance were calculated according to Pearcy et al. (1989).

All measurements of tropical vegetation were performed under semi-controlled conditions following ambient relative humidity, temperature and CO_2. Relative humidity ranged between 77 ± 9 % and 91 ± 7 % during the dry and wet season and ambient CO_2 concentrations were found in the range of 340–404 ppm. Leaf temperatures varied between 31 to 36 °C (Table 3). *Garcinia macrophylla*, *Hevea spruceana* (igapó), *Hura crepitans*, and *Pseudobombax munguba* were measured under ambient light conditions (Table 3). For remaining plant species additional photosynthetic active radiation (PAR) was constantly provided by an 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 was placed perpendicular to the cuvette and supported a constant light regime around 500 $\mu mol\,m^{-2}\,s^{-1}$ (Table 3). 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 monitored 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 the 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 data logger CR23X (Campbell Scientific Ltd., Shepsherd, UK). All other micrometeorological and physiological parameters were monitored and recorded with a in-house control unit (V25, Max-Planck Institute for Chemistry, Mainz, Germany).

2.2.2 Mediterranean vegetation

Gas exchange of Mediterranean vegetation was measured using a dynamic temperature- and light-controlled chamber system (Staudt et al., 2004; Bracho-Nunez et al., 2011). 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 $\mu mol\,m^{-2}\,s^{-1}$). Relative humidity was also maintained constant at 48 ± 13 %. All data were stored on a 21X data logger (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). Ambient CO_2 concentrations varied between 318 and 380 ppm during the experiments.

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 were found constant. Leaves of the conifer *Pinus halepensis* and the aromatic shrub *Rosmarinus officinalis* possess glands and ducts

which store VOC. It has been shown that mechanical stress can cause large bursts of VOC 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.

2.3 VOC measurements

2.3.1 GC techniques

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 three GC-instruments were used: an AirmoVOC C2-C6 online GC-FID (Chromatotec, France) for the detection of isoprene and apolar 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 confirm PTR-MS signals by related GC peaks. A detailed description of the GC systems is reported by Bracho-Nunez et al. (2011).

2.3.2 PTR-MS techniques

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 mol^{-1}) at a drift tube voltage of 600 V. A total of 27 mass signals (protonated masses, i.e. Molecular Weight + 1) were measured by the PTR-MS with a dwell time of 1s: 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 seconds. The main compounds detected from tropical vegetation were methanol (m33), acetone (m59), isoprene (m69), and monoterpenes (m137, fragment on m81). 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.

In the case of tropical vegetation screening, the PTR-MS probing switched between the reference and the sample chamber, taking into account ten cycles of the reference and sample chamber, each. The instrument background signals were determined with air samples after passing over a heated platinum catalyst maintained at 350 °C (Parker Co., USA). The background signal was subtracted from the reference and sample chamber signals. This procedure was repeated from 8.00 p.m. to 6.00 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). Mediterranean vegetation screening by PTR-MS measurements were performed similarly as described above 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 nmol mol^{-1} ± 10 %. For calibration, the gas was further diluted with synthetic air to final concentrations of 0.5–10 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 compounds depending on the VOC species (Tani et al., 2003; Demarcke et al., 2009), 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 Leaf area and dry weight determination

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.

2.5 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}].

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

For VOC emissions measured under nonstandard light and temperature conditions (the conditions for most of the measurements on tropical species, Table 3), 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 VOC. Since acetone and methanol also showed light and temperature dependency during this study, emission rates of these compounds could also be described with this algorithm. 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, due to the burst of the nocturnally accumulated methanol after stomatal opening. Though this burst can reach higher emission rate values than observed during the rest of the day, it does not dominate the daily emissions as it lasts only a short time. Nevertheless, it could affect the determination of E_s derived from linear regression analysis according to the corresponding algorithm (Guenther et al., 1993). Therefore, this morning peak was excluded for the calculation of E_s. Our strategy implies that the VOC emitted from the tropical plants were de-novo-synthesized without substantial storage after production. This assumption could be confirmed by the absence of VOC emissions in the dark even at elevated temperatures.

2.6 Statistics

One-way Anova tests were carried out in order to detect possible differences among two or more independent groups. Mean VOC 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 ten out of twelve plant species screened, we were able to observe VOC emissions (Table 4). Considering the total amount of VOC emissions of the ten emitters, eight species were identified as high emitters ($< 10\,\mu g\,g^{-1}\,h^{-1}$) and two species, *Scleronema micranthum* and *Hevea guianensis*, as low to moderate emitters (1–10 $\mu g\,g^{-1}\,h^{-1}$). It is important to note that saplings were investigated. Mature, naturally growing plants may exhibit other emission qualities and quantities. However, their investigation in the field is difficult. Therefore, our screening results may be regarded as a first step adding to our current knowledge.

All isoprene-emitting plant species were high emitters ($< 10\,\mu g\,g^{-1}\,h^{-1}$) (Table 4). Four plant species were found to emit monoterpenes (Table 4). Only slight differences were found comparing one and the same species derived from várzea and igapó, i.e. *Hevea spruceana* and *Vatairea guianensis*. The relatively conservative composition of the monoterpenes emitted by all monoterpene-emitting tropical plant species studied was similar with α-pinene as the most abundant monoterpene followed by limonene, sabinene or β-pinene and other monoterpenes, except for *Hevea guianensis* that emitted only α-pinene and camphene (Table 5). It is interesting to see all *Hevea* species investigated so far being identified as monoterpene emitters in close agreement with earlier reports about *Hevea brasiliensis* (Klinger et al., 2002; Baker et al., 2005).

In addition to isoprenoid emissions a release of oxygenated VOCs, methanol and acetone, was found with several of the investigated plant species. Methanol emissions were detected in the case of seven species with emission rates varying between 1.5 to 20.2 $\mu g\,g^{-1}\,h^{-1}$ (Table 4). 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 from *Garcina macrophylla* during daytime conditions (light). Mass 73 may be regarded as the protonated methyl ethyl ketone (MEK), an oxidation product of isoprene. This interpretation would be in accordance with the high emissions of isoprene found for this plant. Furthermore, production within plants can no longer be excluded (Jardine et al., 2013). But other compounds, such as methylglyoxal (Holzinger et al., 2007) or 2-methyl propanal (Jardine et al., 2010) could also be made responsible for this mass.

3.2 Screening Mediterranean vegetation

As in the case of tropical plants, the Mediterranean plants investigated were also saplings showing emission rates that may differ as compared to mature, naturally growing individuals. All sixteen Mediterranean plant species investigated were found to emit VOC, nine of which being high emitters (11.0–69.1 $\mu g\,g^{-1}\,h^{-1}$), whereas the rest of the plants were moderate emitters, showing VOC emissions in the range of 2.6 and 9.3 $\mu g\,g^{-1}\,h^{-1}$ (Table 4).

Most of the Mediterranean plants emitted isoprene. Five of them could be classified as high emitters (E_s

Table 4. VOC emitted[a] from Mediterranean and tropical plant species measured with PTR-MS (Except for sesquiterpene emissions from *Buxus sempervirens*, *Ceratonia siliqua* and *Olea europaea* that were only detected with GC-FID). All averages ± standard errors are calculated from < 100 samples (tropical) or 18–83 samples (Mediterranean) from *n* tree individuals.

	n	Isoprene [$\mu g\,g^{-1}\,h^{-1}$]	Monoterpenes [$\mu g\,g^{-1}\,h^{-1}$]	Sesquiterpenes [$\mu g\,g^{-1}\,h^{-1}$]	Methanol [$\mu g\,g^{-1}\,h^{-1}$]	Acetone [$\mu g\,g^{-1}\,h^{-1}$]	m/z 73 [$\mu g\,g^{-1}\,h^{-1}$]
Tropical plant species							
Garcinia macrophylla	3	16.83 ± 3.45	–	–	1.86 ± 0.06	–	1.77 ± 0.93
Hevea brasiliensis	3	–	21.33 ± 14.66	–	2.20 ± 0.15	–	–
Hevea guianensis	2	–	9.45 ± 1.63	–	–	–	–
Hevea spruceana (v)	2	–	18.90 ± 16.26	–	–	1.4 ± 0.1	–
Hevea spruceana (i)	3	–	52.50 ± 13.35	–	–	0.66 ± 0.32	–
Hura crepitans	3	–	–	–	20.16 ± 0.38	–	–
Ocotea cymbarum	3	–	–	–	–	–	–
Pachira insignis	3	12.13 ± 3.84	–	–	4.00 ± 0.06	–	–
Pouteria glomerata	3	–	–	–	–	–	–
Pseudobombax munguba	3	–	–	–	13.53 ± 0.2	–	–
Scleronema micranthum	3	–	0.35 ± 0.07	–	1.53 ± 0.03	–	–
Vatairea guianensis (v)	2	63.20 ± 42.85	–	–	6.05 ± 0.07	–	–
Vatairea guianensis (i)	2	47.20 ± 3.53	–	–	2.30 ± 0.42	–	–
Zygia jurana	3	13.73 ± 8.78	–	–	–	–	–
Mediterranean plant species							
Brachypodium retusum	3	56.18 ± 20	1.1 ± 0.71	–	5.48 ± 1.99	1.77 ± 1.62	–
Buxus sempervirens	3	21.46 ± 5.21	0.13 ± 0.06	0.07 ± 0.05	1.04 ± 0.63	–	–
Ceratonia siliqua	3	0.52 ± 0.17	7.94 ± 5.41	0.03 ± 0.02	0.79 ± 0.23	–	–
Chamaerops humilis	3	18.93 ± 3.44	0.14 ± 0.03	–	–	–	–
Cistus albidus	3	–	0.3 ± 0.07	0.63 ± 0.32	8.2 ± 4.61	–	–
Cistus monspeliensis	3	–	1.03 ± 0.49	0.6 ± 0.18	7.46 ± 5.2	–	–
Coronilla valentina	3	0.43 ± 0.08	0.75 ± 0.45	–	13.48 ± 7.84	0.61 ± 0.07	–
Ficus carica	3	60.75 ± 4.79	–	–	4.22 ± 2.15	4.17 ± 1.18	–
Olea europea	3	0.12 ± 0.09	1.21 ± 0.95	0.09 ± 0.01	1.03 ± 0.2	0.11 ± 0.02	–
Pinus halepensis	3	0.1 ± 0.07	2.75 ± 0.94	–	2.95 ± 0.09	0.09 ± 0.01	–
Prunus persica	3	0.04 ± 0.03	0.36 ± 0.25	–	4,01 ± 1.3	0.32 ± 0.18	–
Quercus afares	2	0.88 ± 0.61	16.18 ± 10.13	–	1.27 ± 0.4	–	–
Quercus coccifera	3	0.64 ± 0.23	5.77 ± 6.42	0.24 ± 0.13	4.11 ± 3.9	0.25 ± 0.09	–
Quercus suber	3	0.26 ± 0.09	35.58 ± 5.46	–	1.83 ± 1.1	–	–
Rosmarinus officinalis	3	–	1.97 ± 1.36	–	2.03 ± 0.61	–	–
Spartium junceum	3	28.28 ± 6.13	–	–	3.74 ± 0.72	–	–

[a] Normalized to standard conditions (PAR: 1000 $\mu mol\,m^{-2}\,s^{-1}$ and leaf temperature: 30 °C) with R as a constant (= 8.314 $J\,K^{-1}\,mol^{-1}$) and the empirical coefficients a (= 0.0027), C_{L1} (= 1.066), C_T, (= 95 000 $J\,mol^{-1}$), C_{T2} (= 230 000 $J\,mol^{-1}$), C_{T3} (= 0.961) and T_M (= 314 K) according to Guenther et al. (1993) and Guenther (1997), (i) igapó, (v) várzea.

< 10 $\mu g\,g^{-1}\,h^{-1}$) and the other eight as low emitters (E_s < 1 $\mu g\,g^{-1}\,h^{-1}$) (Table 4). Fourteen out of the sixteen investigated Mediterranean plants emitted monoterpenes in significant amounts (Table 4). Nine of them were classified as moderate to high monoterpene emitters with emissions ranging between 1 and 36 $\mu g\,g^{-1}\,h^{-1}$. Furthermore, PTR-MS measurements also indicated low monoterpene emissions for *Chamaerops humilis*, *Cistus albidus*, *Coronilla valentina* and *Prunus persica* (< 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, 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) by PTR-MS might be related to other VOC species. For example, interferences of sesquiterpene fragments like (−)*E*-caryophyllene (m81) and α-humulene (m137) have been reported to potentially 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 and very variable among the plant species, as summarized in Table 5. It should be noted that Mediterranean plants showed up to 14 different monoterpene species. Furthermore, the variability of monoterpene species among the different plant species was very high as compared to tropical vegetation.

Table 5. Monoterpene species emitted[a] from Mediterranean and tropical plant species measured with GC-FID. All averages ± standard errors are calculated from < 100 samples (tropical) or 18–83 samples (Mediterranean) from *n* tree individuals. Others include in *P. halepensis* (terpinene-4-ol), in *Q. afares* (linalool and allo-ocimene), in *Q. coccifera* (α-thujene, ß-phellandrene, eucalyptol and α-terpinene), in *Q. suber* (α-thujene, menthol, terpinolene, *o*-cymene, terpinene-4-ol, cis-sabinene hydrate, borneol and α-terpinene), in *R. officinalis* (eucalyptol and camphor) in *H. spruceana* (*i*) (3-carene), in *H. spruceana* (*v*) (3-carene).

	n	α−pinene [µg g^{-1} h^{-1}]	limonene [µg g^{-1} h^{-1}]	sabinene [µg g^{-1} h^{-1}]	ß-pinene [µg g^{-1} h^{-1}]	camphene [µg g^{-1} h^{-1}]	*p*-cymene [µg g^{-1} h^{-1}]	myrcene [µg g^{-1} h^{-1}]	γ-terpinene [µg g^{-1} h^{-1}]	α-phellandrene [µg g^{-1} h^{-1}]	*Z*-ocimene [µg g^{-1} h^{-1}]	*E*-ocimene [µg g^{-1} h^{-1}]	others [µg g^{-1} h^{-1}]
Tropical plant species													
Hevea guianensis	2	6.89 ± 4.87	–	–	–	0.75 ± 0.51	–	–	–	–	–	–	–
Hevea brasiliensis	3	15.03 ± 24.5	4.34 ± 7.52	7.94 ± 4.9	1.38 ± 0.78	0.54 ± 0.8	4.49 ± 4.0	1.05 ± 0.8	2.40 ± 2.24	0.81 ± 0.60	–	–	0.72 ± 0.84
Scleronema micranthum	3	0.27 ± 0.03	0.20 ± 0.13	0.07 ± 0.04	0.12 ± 0.04	–	–	0.03 ± 0.02	0.02 ± 0.01	–	–	–	–
Hevea spruceana (*v*)	3	22.38 ± 3.38	5.9 ± 1.61	2.34 ± 0.88	0.80 ± 0.01	0.84 ± 0.12	1.29 ± 0.91	0.45 ± 0.35	0.44 ± 0.27	–	–	–	0.04 ± 0.03
Hevea spruceana (*i*)	3	34.00 ± 7.70	5.81 ± 2.20	4.59 ± 3.80	1.83 ± 0.80	1.58 ± 0.50	3.94 ± 3.19	0.65 ± 0.3	2.06 ± 0.90	0.34 ± 0.26	–	–	0.04 ± 0.01
Mediterranean plant species													
Buxus sempervirens	3	–	–	–	–	–	–	–	–	0.12 ± 0.04	–	0.004 ± 0.0004	–
Ceratonia siliqua	3	–	–	–	–	–	–	0.06 ± 0.02	–	–	1.66 ± 1.30	7.08 ± 5.80	–
Cistus monspeliensis	3	0.11 ± 0.09	–	–	0.06 ± 0.05	0.01 ± 0.009	-	0.03 ± 0.02	–	–	–	0.03 ± 0.01	–
Olea europea	3	–	–	–	–	–	–	–	–	–	0.16 ± 0.24	1.48 ± 2.35	-
Pinus halepensis	3	–	–	–	–	–	–	0.11 ± 0.16	–	–	0.05 ± 0.03	2.23 ± 2.17	0.01 ± 0.009
Quercus afares	2	0.07 ± 0.07	3.74 ± 2.84	0.07 ±0.08	0.09 ± 0.03	–	–	0.36 ± 0.17	–	–	2.38 ± 2.11	4.12 ± 1.73	0.12 ± 0.12
Quercus coccifera	3	0.62 ± 0.62	0.72 ± 1.09	0.43 ± 0.50	0.32 ± 0.30	0.007 ± 0.008	0.01 ± 0.003	3.77 ± 6.60	0.02 ± 0.01	1.20 ± 1.60	–	–	0.80 ± 1.14
Quercus suber	3	15.04 ± 1.89	0.67 ± 0.07	17.13 ± 2.90	10.93 ± 1.50	0.44 ± 0.06	–	1.35 ± 0.38	0.01 ± 0.01	–	–	0.007	0.76 ± 0.10
Rosmarinus officinalis	1[b]	0.02	0.20	–	0.07	0.03	–	0.07	–	–	–	–	0.12

[a] Normalized to standard conditions (PAR: 1000 µmol m^{-2} s^{-1} and leaf temperature: 30 °C; Guenther et al., 1993; Guenther, 1997), [b] Due to technical reasons only data from one individual plant are available.

Table 6. Sesquiterpene species emitted[a] from Mediterranean and tropical plant species measured with GC-FID. Averages ± standard errors are calculated from *n* number of replicates. All averages ± standard errors are calculated from < 100 samples (tropical) or 18–83 samples (Mediterranean) from *n* tree individuals.

	n	(−)*E*-caryophyllene [µg g^{-1} h^{-1}]	α-humulene [µg g^{-1} h^{-1}]	α-copaene [µg g^{-1} h^{-1}]	ß-copaene [µg g^{-1} h^{-1}]	α-cubebene [µg g^{-1} h^{-1}]	ß-cubebene [µg g^{-1} h^{-1}]	δ-cadinene [µg g^{-1} h^{-1}]	ß-Bourboubene [µg g^{-1} h^{-1}]	*E*-ß-farnesene [µg g^{-1} h^{-1}]	germacrene D [µg g^{-1} h^{-1}]
Tropical plant species											
Hevea guianensis	2	–	–	–	–	–	–	–	–	–	–
Hevea brasiliensis	3	–	–	–	–	–	–	–	–	–	–
Scleronema micranthum	3	–	–	–	–	–	–	–	–	–	–
Hevea spruceana (v)	3	–	–	–	–	–	–	–	–	–	–
Hevea spruceana (i)	3	–	–	–	–	–	–	–	–	–	–
Mediterranean plant species											
Buxus sempervirens	3	0.02 ± 0.01	0.05 ± 0.03	–	–	–	–	–	–	–	–
Ceratonia siliqua	3	0.03 ± 0.02	–	–	–	–	–	–	–	–	–
Cistus albidus	–	0.11 ± 0.06	–	0.02 ± 0.02	0.01 ± 0.01	0.04 ± 0.004	0.06 ± 0.02	0.02 ± 0.02	0.02 ± 0.02	0.04 ± 0.03	–
Cistus monspeliensis	3	0.20 ± 0.14	–	–	–	–	–	–	–	–	–
Olea europea	3	0.09 ± 0.01	–	–	–	–	–	–	–	–	0.02 ± 0.01
Pinus halepensis	3	–	–	–	–	–	–	–	–	–	–
Quercus afares	2	–	–	–	–	–	–	–	–	–	–
Quercus coccifera	3	0.10 ± 0.09	–	–	–	0.01 ± 0.01	–	–	0.02 ± 0.02	–	–
Quercus suber	3	–	–	–	–	–	–	–	–	–	–
Rosmarinus officinalis	1[b]	–	–	–	–	–	–	–	–	–	–

[a] Normalized to standard conditions (PAR: 1000 µmol m^{-2} s^{-1} and leaf temperature: 30 °C; Guenther et al., 1993; Guenther, 1997); [b] Due to technical reasons only data from one individual plant are available; (i) igapó, (v) várzea.

Low emissions of sesquiterpenes (0.1–1.0 µg g^{-1} h^{-1}) were found in the case of *Cistus albidus*, *Cistus monspeliensis* and *Quercus coccifera* (Table 4). In the case of *Buxus sempervirens*, *Ceratonia siliqua* and *Olea europaea* traces of those terpenoids (< 0.1 µg 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 except for *Buxus sempervirens*, and was the sole compound emitted in the case of *Ceratonia siliqua* and *Cistus monspeliensis* (Table 6). A great variety of sesquiterpene species were found in the case of *Cistus albidus*. A total of eight different sesquiterpene species were detected (Table 6).

Not only isoprenoids were emitted from Mediterranean plants. Oxygenated VOC such as methanol and acetone were also observed. All investigated plant species except *Chamaerops humilis* emitted methanol (Table 4). The range of emission rates was very large (between 1 and 14 µg g^{-1} h^{-1}). For some species low acetone emissions were detected (Table 4). Most of these emission rates were < 1 µg g^{-1} h^{-1}, except for *Brachypodium retusum* and *Ficus carica*.

3.3 Comparison of VOC emissions from tropical and Mediterranean plant species

Most of the investigated tropical and Mediterranean plants exhibited substantial VOC emissions. Of striking difference was the higher number of monoterpene emitters in the case of the Mediterranean vegetation. Only four out of eight tropical plant species were emitting monoterpenes. In contrast, monoterpenes dominated emissions in 14 out

Table 7. Specific leaf weight (SLW), net photosynthetic rate (NPR), transpiration (E), and stomatal conductance (g_s) for Mediterranean and tropical plant species. Carbon loss (VOC carbon in relation net CO_2 assimilation) is estimated from the mean values of NPS (this table) and the sum of VOC carbon derived from the species listed in Table 4. Except for SLW, all averages ± standard errors are calculated from < 100 samples (tropical) or 5–125 samples (Mediterranean) from n tree individuals.

	n	SLW [$g\,m^{-2}$]	NPR [$\mu mol\,m^{-2}\,s^{-1}$]	E [$mmol\,m^{-2}\,s^{-1}$]	g_s [$mm\,s^{-1}$]	Carbon loss %
Tropical plant species						
Garcinia macrophylla	3	142	1.76 ± 0.55	1.55 ±0.25	1.94 ± 1.50	3.2
Hevea brasiliensis	3	33.4	5.53 ± 3.03	1.53 ± 0.32	3.97 ± 3.35	0.3
Hevea guianensis	2	39.6	2.35 ± 0.07	4 ± 1.27	6.35 ± 1.63	0.3
Hevea spruceana (v)	2	23.6	4.34 ± 0.46	0.80 ± 0.21	1.71 ± 0.31	0.2
Hevea spruceana (i)	3	42.9	7.20 ± 1.33	21.17 ±4.15	18.92 ± 7.66	0.6
Hura crepitans	3	45.2	8.19 ± 1.09	2.39 ± 0.44	4.86 ± 0.78	0.1
Ocotea cymbarum	3	76.0	4.57 ± 1.10	2.23 ± 0.51	4.87 ± 3.16	–
Pachira insignis	3	46.0	2.63 ± 0.15	1.03 ± 0.15	0.77 ± 0.90	0.5
Pouteria glomerata	3	67.7	4.74 ± 0.87	8.93 ± 2.83	17.93 ± 4.97	–
Pseudobombax munguba	3	65.0	4.71 ± 0.92	2.07 ±0.58	2.39 ± 0.74	0.2
Scleronema micranthum	3	76.9	3.03 ± 0.38	0.87 ±0.21	1.37 ± 0.23	0.1
Vatairea guianensis (v)	2	26.1	6.61 ± 0.92	1.04 ±0.55	4.68 ± 1.23	0.5
Vatairea guianensis (i)	2	36.4	3.50 ± 0.70	1.42 ±0.60	3.73 ± 1.53	1.0
Zygia jurana	3	41.9	3.70 ± 1.40	1.40 ± 0.65	3.47 ± 1.89	0.3
Mediterranean plant species						
Brachypodium retusum	3	85	6.16 ± 2.26	4.81 ± 2.91	10.69 ± 9.15	1.7
Buxus sempervirens	3	291	7.97 ± 0.82	2.83 ± 0.65	1.78 ± 0.46	1.6
Ceratonia siliqua	3	149	3.34 ± 0.66	1.01 ± 0.16	0.95 ± 0.17	0.8
Chamaerops humilis	3	240	10.21 ± 5.35	3.12 ± 2.35	6.90 ± 4.96	0.9
Cistus albidus	3	91	12.46 ± 5.43	5.92 ± 1.73	14.66 ± 5.39	0.1
Cistus monspeliensis	3	110	22.97 ± 7.19	9.40 ±3.58	20.61 ± 3.79	< 0.05
Coronilla valentina	3	73	14.99 ± 4.26	3.64 ± 1.65	4,13 ± 1.91	0.1
Ficus carica	3	66	8.89 ± 1.14	3.65 ± 0.98	11.91 ± 5.43	1.0
Olea europea	3	352	13.76 ± 1.76	3.69 ± 0.57	5.09 ± 1.28	0.1
Pinus halepensis	3	143	5.01 ± 1.21	1.85 ± 0.81	1.67 ± 1.07	0.2
Prunus persica	3	70	10.92 ± 2.27	2,23 ± 0.78	3,26 ± 1.27	< 0.05
Quercus afares	2	114	6,15 ± 1.19	2,24 ± 0.49	2.28 ± 0.48	3.6
Quercus coccifera	3	163	6.49 ± 1.58	1.87 ± 0.63	2.56 ± 1.10	3.7
Quercus suber	3	121	6,41 ± 1.15	1.03 ± 0.22	0,92 ± 0.22	1.4
Rosmarinus officinalis	3	215	14.77 ± 5.88	11.35 ±3.56	16.20 ± 7.5	0.1
Spartium junceum	3	135	7.53 ± 1.45	2,15 ± 0.32	2.77 ± 1.16	1.1

of 16 Mediterranean species. Furthermore, the monoterpene species composition emitted from the investigated tropical plants was quite conservative, in contrast to the great variation of the 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). 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). In addition, acetone emissions were found only in one tropical plant species, whereas five of the investigated Mediterranean species emitted this VOC species.

3.4 Plant physiology

The net exchange of CO_2 was monitored along all measurements to note the physiological activities of the enclosed plants. The data confirmed that all plants investigated were photosynthetically active (Table 7). Net photosynthetic rates (NPR) were found in the range of 1.8–8.2 $\mu mol\,m^{-2}\,s^{-1}$ and 3.3–23 $\mu mol\,m^{-2}\,s^{-1}$ for Amazonian and Mediterranean plants, respectively. Such rates have been reported for shade leaves of tropical C3-plants (Da Matta et al., 2001; Larcher, 2003) and for Mediterranean plants in spring or autumn (Llusia and Peñuelas, 2000). Mostly, the transpiration rates were < 6 $mmol\,m^{-2}\,s^{-1}$ except for *Cistus monspeliensis*, *Rosmarinus officinalis*, *Hevea spruceana* (igapó) and *Pouteria glomerata*, showing higher values (Table 7) and consequently

higher stomatal conductances. The other species exhibited transpiration rates and stomatal conductances in the range as reported before for tropical and temperate plant species (Parolin et al., 2001; Bazzaz, 1980). Monitoring the net CO_2 exchange data did not only enable a review of the physiological activities but also provided a data set to be compared with the carbon lost as VOC. Relating the mean values of photosynthetically driven net CO_2 uptake to the mean values of carbon emitted as VOC species identified so far, we estimated a carbon loss between 0–4 % of the net amount of carbon assimilated by the plants (Table 7).

4 Discussion

4.1 General remarks

Using phylogenetic reconstructions to explore the trait of isoprene emission, large gaps in our knowledge have been recently demonstrated (Monson et al., 2013; Sharkey, 2013), indicating the need to screen more plants even in the case of the most intensively investigated isoprene emission. The issue becomes much more complex by taking into account other VOC species. Furthermore, the mixture of emitted VOC species is highly dependent on multiple stress factors (Holopainen and Gershenzon, 2010) and is triggered by intra- and interspecific plant competition, economizing the loss of carbon in view of defense strategies (Kigathi et al., 2013). Therefore, 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. This study contributes to the description of plant-specific VOC emissions from plant species of two such special ecosystems, i.e. the Amazonian compared to 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 VOC on the species level is still rare, though compounds such as isoprene, monoterpenes, methanol and acetone have previously been detected in high concentrations above Amazonian forests (Karl et al., 2004; Eerdekens et al., 2009). For our screening study we chose plant species at random and the small numbers cannot lead to a final view, but the results do indicate a trend and will improve data bases.

4.2 Tropical plants

Investigations of Amazonian plant species are fragmentary in terms of areas, plant species and analytical techniques (Kesselmeier et al., 2009). Several screening projects of VOC emissions from tropical African (Harley et al., 2003), Asian (Klinger et al., 2002; Geron et al., 2006b; Oku et al., 2008; Llusia et al., 2013), or South American including Amazonia (Lerdau and Keller, 1997; Lerdau and Throop, 1999, 2000; Harley et al., 2004; Pegoraro et al., 2006) have been performed reporting on isoprene emissions. A few plant species were identified as monoterpene emitters, among them *Hevea brasiliensis* (Klinger et al., 2002; Baker et al. 2005; Geron et al., 2006b; 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 (*Apeiba tibourbou*) was identified by Kuhn et al. (2002b, 2004) as a light-dependent monoterpene emitter.

Within our investigation, the most substantial isoprene emissions of Amazonian plants were found for *Vatairea guianensis* from várzea and igapó, reaching values similar to those measured for several Mediterranean *Quercus* species (Kesselmeier and Staudt, 1999). Other isoprene-emitting species emissions were found to be consistent with emission rates reported for tropical tree species (Harley et al., 2004; Padhy and Varshney, 2005). Monoterpene emission was found to dominate in the group of *Hevea* species. The rubber tree *Hevea brasiliensis* showed a normalized monoterpene E_s of 10.9 to 38.1 $\mu g\, g^{-1}\, s^{-1}$, even exceeding the high emissions reported earlier (Klinger et al., 2002; Baker et al., 2005; Geron et al., 2006b; Wang et al., 2007). In addition to *Hevea brasiliensis*, we also identified *Hevea spruceana* and *Hevea guianensis* as strong monoterpene-emitters with some differences related to the origin of the species (igapó or várzea). All monoterpene-emitting tropical trees of this work emitted α-pinene followed by limonene and sabinene, contrasting the emission pattern reported previously for *Hevea brasiliensis* (Wang et al., 2007). Further investigation is needed for a better understanding of these differences. Nevertheless, it is of special interest to note that all *Hevea* species investigated so far belong to the group of monoterpene emitters. In addition to the *Hevea* species, the terra firme species *Scleronema micranthum* was found to be a low monoterpene-emitting species ($< 1\, \mu g\, g^{-1}\, s^{-1}$) with an emission pattern similar to *Hevea brasiliensis* and *Hevea spruceana* (Table 5). No bibliography data were found about the VOC emission pattern of this important tree of the Central Amazonian forest.

4.3 Mediterranean plants

In contrast to the set of Amazonian plants, Mediterranean plant species were found to be dominated by monoterpene emitters. These findings are in close accordance with earlier investigations of VOC emissions from Mediterranean ecosystems (Owen et al., 2001). Nevertheless, we identified several species such as *Ficus carica*, *Spartium junceum*, *Chamaerops humilis* and *Brachypodium retusum* to emit substantial amounts of isoprene in contrast to earlier studies (Pio et al., 1993; Benjamin et al., 1996; Owen et al., 2001).

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 an emission was not reported but assigned based on genus average as in the case of the isoprene emission from *Ficus carica* and *Chamaerops humilis* reported (Benjamin et al., 1996) or for some tropical species (Harley et al., 2004). Observed monoterpene emission rates were quantitatively comparable to literature data in a few cases only, e.g. for *Ceratonia siliqua*, *Pinus halepensis*, *Quercus coccifera* and *Rosmarinus officinalis* (Llusia and Peñuelas, 2000; Owen et al., 2001; Ormeno et al., 2007a, b, c, 2009; Staudt and Lhoutellier, 2011). *Quercus suber* has been identified previously as a non-isoprenoid-emitter tree (Seufert et al., 1997; Steinbrecher et al., 1997). But we estimated an emission factor of $35.6 \pm 5.5\,\mu g\,g^{-1}\,h^{-1}$, confirming more recent literature showing typical summertime values of 10–$43\,\mu g\,g^{-1}\,h^{-1}$ (Staudt et al., 2004; Pio et al., 2005; Staudt et al., 2008). A further oak species, *Quercus afares*, was found to emit high quantities of monoterpenes and low amounts of isoprene (see also Welter et al., 2012). Furthermore, we classified *Ficus carica* and *Spartium junceum* as non-monoterpene emitters contrasting earlier reports (Benjamin and Winer, 1998; Pio et al., 1993). Monoterpene emissions from *Chamaerops humilis*, *Coronilla valentina* and *Buxus sempervirens* were reported for the first time, though at low rates. Monoterpene emission rates found for *Olea europea* here were higher ($< 1\,\mu g\,g^{-1}\,h^{-1}$) than previously reported (Arey et al., 1991; Benjamin and Winer, 1998; Llusia et al., 2002; Owen et al., 2001; Pio et al., 1993; Winer et al., 1983, 1992). Such 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, biotic and abiotic stresses or even questionable plant identification, making it difficult to use such data for emission models (Niinemets et al., 2011).

4.4 Monoterpene species heterogeneity

Monoterpene species emission patterns as found for the tropical plants species were rather homogeneous, contrasting the high variability of monoterpene species in the case of the Mediterranean plants. The species pattern found here for *Ceratonia siliqua* (myrcene, *Z*-ocimene, *E*-ocimene) was completely different from that reported by Llusia et al. (1998), who reported an emission of α-phellandrene only, as well as by Owen et al. (2001) or by Llusia et al. (2002), who identified α-pinene and limonene or only α-pinene, respectively. Our results with *Cistus monspeliensis*, i.e. emissions of α-pinene, camphene and ß-pinene, coincided with Owen et al. (2002). Furthermore, we could additionally 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 our results completely disagreed with the emission pattern reported in several other reports (Winer, 1983; Pio et al., 1993; Benjamin and Winer, 1998; Owen et al., 2001; Llusia et al., 2002). *Pinus halepensis* is one of the most intensively investigated conifers of the Mediterranean area with a large variety of emission patterns (Corchnoy et al., 1992; Benjamin and Winer, 1998; Llusia and Peñuelas, 1998, 2000; Owen et al., 2001 2001; Simon et al., 2005; Blanch, 2007; Ormeno et al. 2007a, b, c, d). In our current study we detected Z-ocimene, E-ocimene, myrcene and at low concentration terpinen-4-ol, whereas α-pinene, ß-pinene, limonene, sabinene, and others were not found, a result which indicates the high emission variability of this plant species. In the case of *Quercus suber*, emissions of 15 different monoterpene species were found in our study, contrasting with other reports with only about 4 to 7 monoterpene species (Pio et al., 1993, 2005; Staudt et al., 2004; Staudt et al., 2008). Measurements of *Rosmarinus officinalis* confirmed the high variability of emissions as reported earlier (Hansen, et al., 1997; Seufert et al., 1997; Owen et al., 2002; Ormeno et al. 2007a, b, c, 2009; Olivier et al., 2011).

4.5 Sesquiterpenes

Sesquiterpene emissions were detected only in the case of Mediterranean vegetation and not for tropical plants. Due to their high reactivity and relatively low vapor pressure and emission rates, these compounds are easily missed or underestimated (Duhl et al., 2008). Special analytical adaptations can facilitate their quantification (Merfort, 2002; Helmig et al., 2004; Tholl et al., 2006). Bracho-Nunez et al. (2011) reported about a higher sensitivity by offline gas chromatographic methods as compared to online PTR-MS methods, the latter also being less specific. Other studies have confirmed the difficulty of PTR-MS for the measurements of sesquiterpenes, reporting high fragmentation patterns (Tani et al., 2003; Demarcke et al., 2009). 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 (Llusia and Peñuelas, 1998; Ciccioli et al., 1999; Hansen and Seufert, 1999; Ormeno et al., 2007b, d; Staudt and Lhoutellier, 2007; Staudt et al.; 2008). In the course of our work on Mediterranean vegetation we found a high variability for these compounds in close accordance with other reports (Duhl et al., 2008; Llusia and Peñuelas, 1998; Ormeno et al., 2007a, b, c, d, 2009). 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 (−)*E*-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 Peñuelas, 1998; Ormeno et al., 2007a, b, c, d) except for emissions of α- and ß-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 Peñuelas, 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 $(-)E-$caryophyllene by *Cistus monspeliensis* disagrees with the findings by Llusia and Peñuelas (1998). Such variation of sesquiterpene emissions 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 oxidative stress (Loreto and Schnitzler, 2010; Holopainen and Gershenzon, 2010). For example in a recent study on *Quercus coccifera*, Staudt and Lhoutellier (2011) observed that sesquiterpene emissions became 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. Similar trends were reported for *Cistus albidus* and *Pinus halepensis*. It has to be noted that the variability of sesquiterpene emissions is even more striking than that for monoterpenes. We have to take into account, however, potential interactions of oxidative stress and herbivory (Holopainen and Gershenzon, 2010), a complex interaction which will alter VOC emission qualities and quantities.

4.6 Oxygenated VOC

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). Regular environmental triggers such as inundation of large areas in the Amazon region may have substantial impact on oxygenated VOC species (ethanol, acetaldehyde) emitted (Bracho-Nunez et al., 2012). The technological improvement of using a PTR-MS has facilitated the study of such short-chain oxygenated VOC. The exchange of the oxygenated VOC like methanol and acetone has been detected for a variety of plant species (Isidorov et al., 1985; MacDonald and Fall, 1993a, b; Nemecek-Marshall et al., 1995; Kirstine et al., 1998; De Gouw et al., 1999; Holzinger et al., 2000; Hüve et al., 2007; 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 (Nemecek-Marshall et al., 1995; Galbally and Kirstine, 2002). The leaves we measured were mature but probably still in a 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 (MacDonald and Fall, 1993b; Holzinger et al., 2000; Janson and de Serves, 2001; Kreuzwieser et al., 2002; Villanueva-Fierro et al., 2004; Cojocariu et al., 2005; Geron et al., 2006a, b; Grabmer et al., 2006) as well as high concentrations of this compound in the troposphere above forested areas (Helmig et al., 1998; Pöschl et al., 2001; Geron et al., 2002; Karl et al., 2003; Müller et al., 2006). 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 to emit methanol and 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 during our studies. 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 different developmental stages of the measured leaves, 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 species released acetone, whereas seven Mediterranean plants were found to be acetone emitters. The metabolic pathway of acetone has not yet been proven. It was hypothesized that acetone is produced in spruce needles by the decarboxylation of acetoacetate (MacDonald and Fall, 1993b), whereas a cyanohydrin-lyase catalyzed reaction was found in cyanogenic plant species (Fall, 2003), leading to acetone release. *Hevea spruceana*, *Hevea guianensis* and *Hevea brasiliensis* are known as cyanogenic plants containing the cyanogenic ß-glucoside linamarin (Lieberei, 1986), but acetone emissions were found only with *Hevea spruceana*. Furthermore, a cyanogenic pathway causing acetone emission was also proposed for *Olea europaea*, *Coronilla glauca* and *Prunus persica* by Bracho-Nunez et al. (2011). On the other hand, it is known that in the presence of NO_x the atmospheric OH-oxidation of several monoterpenes, like α- and ß-pinene, appears to be a potentially relevant source of acetone (Wisthaler et al., 2001). NO_x data are not available but we cannot exclude a presence of this compound. Therefore, a contribution of this oxidation pathway to the measured acetone concentrations in the plant cuvette 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*, which emitted relevant quantities of α- and ß-pinene.

4.7 Unknown VOC species

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 (Isidorov et al., 1985; Kirstine et al., 1998; De Gouw et al., 1999; Jardine et al., 2010). Furthermore, a contribution to this mass by the volatile compound 2-methyl propanol cannot be excluded (Baraldi et al., 1999; Jardine et al., 2010). On the other hand, Holzinger et al. (2007) identified mass 73 as representing 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). But then emissions of MVK and/or methacrolein (primary oxidation products of isoprene) would have been expected, which was not the case. The detection of an unknown compound demonstrates the need for further investigation in order to identify compounds that probably have been overseen until now due to technical limitations. This is of special importance, as we seem to have a gap of knowledge in understanding the contributions of unmeasured and possibly unknown primary biogenic VOC species, which may contribute significantly to total OH reactivity in the atmosphere (Nölscher et al., 2013).

5 Conclusions

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). Such studies would contribute to our understanding of VOC, representing a substantial carbon loss for vegetation. The average loss rates below 4 %, as found in our study, are in close agreement with Kesselmeier et al. (2002) and indicate a normal unstressed plant behavior. The scientific community will not be able to screen all tree species. However, we should note that the role of biodiversity of a tropical forest may be overestimated. These communities are sometimes even regarded as not qualitatively different from temperate forest with a few dominating tree species (Montero et al., 2012; Pitmann et al., 2001; Ter Steege et al., 2003, 2006; Wittmann et al., 2002, 2010, 2013). Taking into account individuals with < 10 cm diameter at breast height (dbh) the number of tree species/ha can be estimated at 250 (terra firme), 172 (Várzea) and 79 (Igapó). In view of these numbers we screened more than 1 % of trees. This is definitely not enough but such estimates may reflect local features. Furthermore, without screening on a leaf area level we will not learn about the release of reactive chemical species and emission regulation processes. An enhanced understanding of VOC emission behavior from screening additional plant species will increase confidence in predictive models, although future investigations of possible sources of observed variability are warranted, including examining the role of biodiversity and plant competition, as well as comparing different measurement and analytical techniques.

Acknowledgements. This work was supported by the Max Planck Society, the European Science Foundation networking program VOCBAS and the French Environmental Agency (ADEME, No. 0575C0004). We greatly acknowledge the fundamental support by the Instituto Nacional de Pesquisas da Amazônia, Manaus (INPA) and the assistance of the PACE and TE platform staff in Montpellier. We thank Tracey W. Andreae for help with the manuscript.

The service charges for this open access publication have been covered by the Max Planck Society.

Edited by: P. Stoy

References

Andreae, M. O. and Crutzen P. J.: Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, Science, 276, 1052–1058, 1997.

Arey, J., Winer, A. M., Atkinson, R., Aschmann, S. M., Long, D. W., Lynn Morrison, C., and Olszyk, D. M.: Terpenes emitted from agricultural species found in California's Central Valley, J. Geophys. Res., 96, 9329–9336, 1991.

Atkinson, R. and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmos. Environ., 37, 197–219, 2003.

Baker, B., Bai, J. H., Johnson, C., Cai, Z. T., Li, Q. J., Wang J. F., Guenther, A., Greenberg, J., Klinger, L., Geron, C., and Rasmussen, R.: Wet and dry season ecosystem level fluxes of isoprene and monoterpenes from a southeast Asian secondary forest and rubber tree plantation, Atmos. Environ., 39, 381–390, 2005.

Baraldi, R., Rapparini, F., Rossi, F., Latella, A., and Ciccioli, P.: Volatile organic compound emission from flowers of the most occurring and economically important species of fruit trees, Phys. Chem. Earth, 24, 729–732, 1999.

Bazzaz, F. A.: Physiological ecology of tropical succession: A Comparative Review, Ann. Rev. Ecol. Syst., 11, 287–310, 1980.

Benjamin, M. T. and Winer, A. M.: Estimating the ozone-forming potential of urban trees and shrubs, Atmos. Environ., 32, 53–68, 1998.

Benjamin, M. T., Sudol, M., Bloch, L., and Winer, A. M.: Low-emitting urban forest: a taxonomic methodology for assigning isoprene and monoterpene emission rates, Atmos. Environ., 30, 1437–1452, 1996.

Blanch, J.-S.: Sensitivity of terpene emissions to drought and fertilization in terpene-storing Pinus halepenis and non-storing Quercus ilex, Physiol. Plantarum, 131, 211–225, 2007.

Bracho-Nunez, A.: Leaf level VOC emissions of single plants from Amazonian and Mediterranean ecosystems; Ontogeny and flooding as stress factor for VOC emissions, Doctoral Thesis, University Mainz, http://d-nb.info/1008612251/34, 2010.

Bracho-Nunez, A., Welter, S., Staudt, M., and Kesselmeier, J.: Plant specific volatile organic compound emission rates from young and mature leaves of Mediterranean vegetation, J. Geophys. Res., 116, D16304, doi:10.1029/2010JD015521, 2011.

Bracho-Nunez, A., Knothe, N., Costa, W. R., Liberato, M. A. R., Kleiss, B., Rottenberger, S., Piedade, M. T. F., and Kesselmeier, J.: Root Anoxia Effects on Physiology and Emissions of Volatile Organic Compounds (VOC) under Short and Long Term Inundation in Trees from Amazon Floodplains, Springerplus, 1:9, doi:10.1186/2193-1801-1-9, 2012.

Ciccioli, P., Brancaleoni, E., Frattoni, M., Di Palo, V., Valentini, R., Tirone, G., Seufert, G., Bertin, N., Hansen, U., Csiky, O., Lenz, R., and Sharma, M.: Emission of reactive terpene compounds from orange orchards and their removal by within-canopy processes, J. Geophys. Res.-Atmos., 104, 8077–8094, 1999.

Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O. Artaxo, P., and Maenhaut, W.: Formation of Secondary Organic Aerosol through Photooxidation of Isoprene, Science, 303, 1173–1176, 2004.

Cojocariu, C., Escher, P., Haberle, K. H., Matyssek, R., Rennenberg, H., and Kreuzwieser, J.: The effect of ozone on the emission of carbonyls from leaves of adult *Fagus sylvatica*, Plant Cell Environ., 28, 603–611, 2005.

Collins, W. J., Derwent, R. G., Johnson, C. E., and Stevenson, D. S.: The oxidation of organic compounds in the troposphere and their global warming potentials, Clim. Change, 52, 453–479, 2002.

Corchnoy, S. B., Arey, J., and Atkinson, R.: Hydrocarbon emissions from twelve urban shade trees of the Los Angeles, California, Air Basin, Atmos. Environ., 26, 339–348, 1992.

Da Matta, F. M., Loos, R. A., Rogrigues, R., and Barrons R. S.: Actual and Potential Photosynthetic Rates of Tropical Crop Species, R. Bras. Fisiol. Veg., 13, 24–31, 2001.

De Gouw, J., Howard, C. J., Custer, T. G., and Fall, R.: Emissions of volatile organic compounds from cut grass and clover are enhanced during the drying process, Geophys. Res. Lett., 26, 811–814, 1999.

Demarcke, M., Amelynck, C., Schoon, N., Dhooghe, F., Van Langenhove, H., and Dewulf, J.: Laboratory studies in support of the detection of sesquiterpenes by proton-transfer-reaction mass-spectrometry, Int. J. Mass Spectrom., 279, 156–162, 2009.

Di Carlo, P., Brune, W. H., Martinez, M., Harder, H., Lesher, R., Ren, X. R., Thornberry, T., Carroll, M. A., Young, V., Shepson, P. B., Riemer, D., Apel, E., and Campbell, C.: Missing OH reactivity in a forest: evidence for unknown reactive biogenic VOCs, Science, 304, 722–725, 2004.

Duhl, T. R., Helmig, D., and Guenther, A.: Sesquiterpene emissions from vegetation: a review, Biogeosciences, 5, 761–777, doi:10.5194/bg-5-761-2008, 2008.

Eerdekens, G., Ganzeveld, L., Vilà -Guerau de Arellano, J., Klüpfel, T., Sinha, V., Yassaa, N., Williams, J., Harder, H., Kubistin, D., Martinez, M., and Lelieveld, J.: Flux estimates of isoprene, methanol and acetone from airborne PTR-MS measurements over the tropical rainforest during the GABRIEL 2005 campaign, Atmos. Chem. Phys., 9, 4207–4227, doi:10.5194/acp-9-4207-2009, 2009.

Fall, R.: Abundant oxygenates in the atmosphere: A biochemical perspective, Chem. Rev., 103, 4941–4951, 2003.

Ferreira, J., Reeves, C. E., Murphy, J. G., Garcia-Carreras, L., Parker, D. J., and Oram, D. E.: Isoprene emissions modelling for West Africa: MEGAN model evaluation and sensitivity analysis, Atmos. Chem. Phys., 10, 8453–8467, doi:10.5194/acp-10-8453-2010, 2010.

Filella, I., Peñuelas, J., and Seco, R.: Short-chained oxygenated VOC emissions in Pinus halepensis in response to changes in water availability, Physiol. Plant, 31, 311–318, 2009.

Folkers, A., Huve, K., Ammann, C., Dindorf, T., Kesselmeier, J., Kleist, E., Kuhn, U., Uerlings, R., and Wildt, J.: Methanol emissions from deciduous tree species: dependence on temperature and light intensity, Plant Biol., 10, 65–75, 2008.

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. Meteor. Soc., 81, 1537–1575, 2000.

Galbally, I. E. and Kirstine, W.: The production of methanol by flowering plants and the global cycle of methanol, J. Atmos. Chem., 43, 195–229, 2002.

Geron, C., Guenther, A., Greenberg, J., Loescher, H. W., Clark, D., and Baker, B.: Biogenic volatile organic compound emissions from a lowland tropical wet forest in Costa Rica, Atmos. Environ., 36, 3793–3802, 2002.

Geron, C., Guenther, A., Greenberg, J., Karl, T., and Rasmussen, R.: Biogenic volatile organic compound emissions from desert vegetation of the Southwestern US, Atmos. Environ., 40, 1645–1660, 2006a.

Geron, C., Owen, S., Guenther, A., Greenberg, J., Rasmussen, R., Bai, J. H., Li, Q. J., and Baker, B.: Volatile organic compounds from vegetation in Southern Yunnan Province, China: emission rates and some potential regional implications, Atmos. Environ., 40, 1759–1773, 2006b.

Goldstein, A. H., McKay, M., Kurpius, M. R., Schade, G. W., Lee, A., Holzinger, R., and Rasmussen, R. A.: Forest thinning experiment confirms ozone deposition to forest canopy is dominated by reaction with biogenic VOCs, Geophys. Res. Lett., 31, L22106, doi:10.1029/2004GL021259, 2004.

Gomes, F. P. and Mello-Silva, R. D.: Flora da Reserva Ducke, Amazonas, Brasil: Cyclanthaceae, Rodriguésia, 57, 159–170, 2006.

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, 128–137, 2006.

Guenther, A. B.: Seasonal and Spatial Variations in Natural Volatile Organic Compound Emissions, Ecol. Appl., 7, 34–45, 1997.

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.

Guenther, A. B., 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, doi:10.5194/acp-6-3181-2006, 2006.

Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., and Lindinger, W.: Proton-transfer reaction mass-spectrometry – online trace gas-analysis at the ppb level, Int. J. Mass Spectrom., 150, 609–619, 1995.

Hansen, U. and Seufert, G.: Terpenoid emission from *Citrus sinensis* (L.) OSBECK under drought stress, Phys. Chem. Earth B, 24, 681–687, 1999.

Hansen, U., Van Eijk, J., Bertin, N., Staudt, M., Kotzias, D., Seufert, G., Fugit, J.-L., Torres, L., Cecinato, A., Brancaleoni, E., Ciccioli, P., and Bomboi, T.: Biogenic emissions and CO_2 gas exchange investigated on four Mediterranean shrubs, Atmos. Environ., 31, 157–166, 1997.

Harley, P., Otter, L., Guenther, A., and Greenberg, J.: Micrometeorological and leaf-level measurements of isoprene emissions from a Southern African savanna, J. Geophys. Res., 108, D138468, doi:10.1029/2002JD002592, 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, Glob. Change Biol., 10, 630–650, 2004.

Helmig, D., Balsley, B., Davis, K., Kuck, L. R., Jensen, M., Bognar, J., Smith Jr., T., Arrieta, R. V., Rodriguez, R., and Birks, J. W.: Vertical profiling and determination of landscape fluxes of biogenic nonmethane hydrocarbons within the planetary boundary layer in Peruvian Amazon, J. Geophys. Res., 103, 519–525, 1998.

Helmig, D., Bocquet, F., Pollmann, J., and Revermann, T.: Analytical techniques for sesquiterpene emission rate studies in vegetation enclosure experiments, Atmos. Environ., 38, 557–572, 2004.

Holopainen, J. K. and Gershenzon, J.: Multiple stress factors and the emission of plant VOCs, Trends in Plant Science, 15, 176–184, 2010.

Holzinger, R., Sandoval-Soto, L., Rottenberger, S., Crutzen, P. J., and Kesselmeier, J.: Emissions of volatile organic compounds from Quercus ilex L. measured by proton transfer reaction mass spectrometry under different environmental conditions, J. Geophys. Res.-Atmos., 105, 20573–20579, 2000.

Holzinger, R., Millet, D. B., Williams, B., Lee, A., Kreisberg, N., Hering, S. B., Jimenez, J., Allan, J. D., Worsnop, D. R., and Goldstein, A. H.: Emission, oxidation, and secondary organic aerosol formation of volatile organic compounds as observed at Chebogue Point, Nova Scotia, J. Geophys. Res., 112, D10S24, doi:10.1029/2006JD007599, 2007.

Hüve, K., Christ, M. M., Kleist, E., Uerlings, R., Niinemets, U., Walter, A., and Wildt, J.: Simultaneous growth and emission measurements demonstrate an interactive control of methanol release by leaf expansion and stomata, J. Exp. Bot., 58, 1783–1793, 2007.

Isidorov, V. A., Zankench, I. G., and Iofe, B. V.: Volatile organic compounds in the atmosphere of forests, Atmos. Environ., 19, 1–8, 1985.

Janson, R. and de Serves, C.: Acetone and monoterpene emissions from the boreal forest in Northern Europe, Atmos. Environ., 35, 4629–4637, 2001.

Jardine, K., Abrell, L., Kurc, S. A., Huxman, T., Ortega, J., and Guenther, A.: Volatile organic compound emissions from *Larrea tridentata* (creosotebush), Atmos. Chem. Phys., 10, 12191–12206, doi:10.5194/acp-10-12191-2010, 2010.

Jardine, K., Yanez-Serrano, A. M., Arneth, A., Abrell, L., Jardine, A., van Haren, J., Artaxo, P., Rizzo, L. V., Ishida, F. Y., Karl, T., Kesselmeier, J., Saleska, S., and Huxman, T.: Within-canopy sesquiterpene ozonolysis in Amazonia, J. Geophys. Res.-Atmos., 116, D19301, doi:10.1029/2011JD016243, 2011.

Jardine, K. J., Meyers, K., Abrell, L., Alves, E. G., Yanez-Serrano, A. M., Kesselmeier, J., Karl, T., Guenther, A., Chambers, J. Q., and Vickers, C.: Emissions of putative isoprene oxidation products from mango branches under abiotic stress, J. Experiment. Botany, 64, 3697–3709, 2013.

Karl, T., Guenther, A., Spirig, C., Hansel, A., and Fall, R.: Seasonal variation of biogenic VOC emissions above a mixed hardwood forest in Northern Michigan, Geophys. Res. Lett., 30, 2186, doi:10.1029/2003GL018432, 2003.

Karl, T., Potosnak, M., Guenther, A., Clark, D., Walker, J., Herrick, J. D., and Geron, C.: Exchange processes of volatile organic compounds above a tropical rain forest: implications for modeling tropospheric chemistry above dense vegetation, J. Geophys. Res., 109, D18306, doi:10.1029/2004JD004738, 2004.

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

Kesselmeier, J., Schäfer, 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., Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Andreae, M. O., Ciccioli, P., Brancaleoni, E., Frattoni, M., Oliva, S. T., Botelho, M. L., Silva, C. M. A., and Tavares, T. M.: Concentrations and species composition of atmospheric volatile organic compounds (VOCs) as observed during the wet and dry season in Rondonia (Amazonia), J. Geophys. Res.-Atmos., 107, 8053, doi:10.1029/2000JD000267, 2002.

Kesselmeier, J., Guenther, A., Hoffmann, T., Piedade, M. T. F., and Warnke, J.: Natural volatile organic compound emissions from plants and their roles in oxidant balance and particle formation, In: Amazonia and Global Change, Geophys. Monogr. Ser., vol. 186, edited by: Keller, M., Bustamante, M., Gash, J., and Silva Dias, P., AGU, Washington, DC, 183–206, doi:10.1029/2008GM000717, 2009.

Kigathi, R.N., Weisser, W.W., Veit, D., Gershenzon, J., and Unsicker, S.B.: Plants suppress their emission of volatiles when

growing with conspecifics. J. Chem Ecol, 39, 537–545, 2013.
Kinnee, E., Geron, C., and Pierce, T.: United States land use inventory for estimating biogenic ozone precursor emissions, Ecol. Appl., 7, 46–58, 1997.
Kirstine, W., Galbally, I. Y. Y., and Hooper, M.: Emissions of volatile organic compounds (primarily oxygenated species) from pasture, J. Geophys. Res., 103, 605–619, 1998.
Klinger, L. F., Li, Q. J., Guenther, A. B., Greenberg, J. P., Baker, B., and Bai, J. H.: Assessment of volatile organic compound emissions from ecosystem of China, J. Geophys. Res., 107, D214603, doi:10.1029/2001JD001076, 2002.
Kreuzwieser, J., Cojocariu, C., Jüssen, V., and Rennenberg, H.: Elevated atmospheric CO_2 causes seasonal changes in carbonyl emissions from Quercus ilex, New Phytol., 154, 327–333, 2002.
Kuhn, U., Rottenberger, S., Biesenthal, T., Ammann, C., Wolf, A., Schebeske, G., Oliva, S. T., Tavares, T. M., and Kesselmeier, J.: Exchange of short-chain monocarboxylic acids by vegetation at a remote tropical forest site in Amazonia, J. Geophys. Res.-Atmos., 107, D20, 8069, doi:10.1029/2000JD000303, 2002a.
Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Ciccioli, P., Brancaleoni, E., Frattoni, M., Tavares, T. M., and Kesselmeier, J.: Isoprene and monoterpene emissions of Amazonian tree species during the wet season: direct and indirect investigations on controlling environmental functions, J. Geophys. Res.-Atmos., Res. 107, D208071, doi:10.1029/2001JD000978, 2002b.
Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Ciccioli, P., Brancaleoni, E., Frattoni, M., Tavares, T. M., and Kesselmeier, J.: Seasonal differences in isoprene and light dependent monoterpene emission by Amazonian tree species, Glob. Change Biol., 10, 663–682, 2004.
Kuhn, U., Andreae, M. O., Ammann, C., Araujo, A. C., Brancaleoni, E., Ciccioli, P., Dindorf, T., Frattoni, M., Gatti, L. V., Ganzeveld, L., Kruijt, B., Lelieveld, J., Lloyd, J., Meixner, F. X., Nobre, A. D., Pöschl, U., Spirig, C., Stefani, P., Thielmann, A., Valentini, R., and Kesselmeier, J.: Isoprene and monoterpene fluxes from Central Amazonian rainforest inferred from tower based and airborne measurements, and implications on the atmospheric chemistry and the local carbon budget, Atmos. Chem. Phys., 7, 2855–2879, doi:10.5194/acp-7-2855-2007, 2007.
Larcher, W.: Physiological Plant Ecology, Ecophysiology and Stressphysiology of Functional Groups, Springer, Berlin, 2003.
Lee, A., Goldstein, A. H., Kroll, J. H., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, J. Geophys. Res., 111, D17305, doi:10.1029/2006JD007050, 2006.
Lelieveld, J., Peters, W., Dentener, F. J., and Krol, M.: Stability of tropospheric hydroxyl chemistry, J. Geophys. Res., 107, D234715, doi:10.1029/2002JD002272, 2002.
Lerdau, M. T. and Keller, M.: Controls on isoprene emission from trees in a subtropical dry forest, Plant Cell Environ., 20, 569–578, 1997.
Lerdau, M. T. and Throop, H. L.: Isoprene emission and photosynthesis in a tropical forest canopy: Implications for model development, Ecol. Appl., 9, 1109–1117, 1999.
Lerdau, M. T. and Throop, H. L.: Sources of variability in isoprene emission and photosynthesis in two species of tropical wet forest trees, Biotropica, 32, 670–676, 2000.
Lieberei, R.: Cyanogenesis of Hevea brasiliensis during infection with Microcyclus ulei, J. Phytopathol., 115, 134–146, 1986.
Llusia, J. and Peñuelas, J.: Changes in terpene content and emission in potted Mediterranean woody plants under severe drought, Can. J. Bot., 76, 1366–1373, 1998.
Llusia, J. and Peñuelas J.: Seasonal patterns of terpene content and emission from seven Mediterranean woody species in field conditions, Am. J. Botany, 87, 133–140, 2000.
Llusia, J., Peñuelas, J., and Gimeno, B. S.: Seasonal and species-specific response of VOC emissions by Mediterranean woody plant to elevated ozone concentrations, Atmos. Environ., 36, 3931–3938, 2002.
Llusia, J., Sardans, J., Niinemets, Ü., Owen, S. M., and Peñuelas, J.: A screening study of leaf terpene emissions of 43 rainforest species in Danum Valley Conservation Area (Borneo) and their relationships with chemical and morphological leaf traits, Plant Biosystems – An International Journal Dealing with all Aspects of Plant Biology, 1–11, doi:10.1080/11263504.2013.770803, 2013.
Loreto, F. and Schnitzler, J. P.: Abiotic stresses and induced BVOCs, Trends Plant Sci., 15, 154–166, 2010.
MacDonald, R. C. and Fall, R.: Detection of substantial emissions of methanol from plants to the atmosphere, Atmos. Environ. A, 27, 1709–1713, 1993a.
MacDonald, R. C. and Fall, R.: Acetone emission from conifer buds, Phytochemistry, 34, 991–994, 1993b.
Merfort, I.: Review of the analytical techniques for sesquiterpenes and sesquiterpene lactones, J. Chromatogr. A, 967, 115–130, 2002.
Misztal, P. K., Owen, S. M., Guenther, A. B., Rasmussen, R., Geron, C., Harley, P., Phillips, G. J., Ryan, A., Edwards, D. P., Hewitt, C. N., Nemitz, E., Siong, J., Heal, M. R., and Cape, J. N.: Large estragole fluxes from oil palms in Borneo, Atmos. Chem. Phys., 10, 4343–4358, doi:10.5194/acp-10-4343-2010, 2010.
Monson, R. K., Jones, R. T., Rosenstiel T. N., and Schnitzler, J. P.: Why only some plants emit isoprene, Plant, Cell and Environment, 36, 503–516, 2013.
Montero, J. C., Piedade, M. T. F., and Wittmann, F.: Floristic variation across 600 km of inundation forests (Igapó) along the Negro River, Central Amazonia, Hydrobiologia, 699, 1, do:10.1007/s10750-012-1381-9, 2012.
Müller, K., Haferkorn, S., Grabmer, W., Wisthaler, A., Hansel, A., Kreuzwieser, J., Cojocariu, C., Rennenberg, H., and Herrmann, H.: Biogenic carbonyl compounds within and above a coniferous forest in Germany, Atmos. Environ., 40, 81–91, 2006.
Nemecek-Marshall, M., MacDonald, R. C., Franzen, F. J., Wojciechowski, C. L., and Fall, R.: Methanol emission from leaves – enzymatic detection of gas-phase methanol and relation of methanol fluxes to stomatal conductance and leaf development, Plant Physiol., 108, 1359–1368, 1995.
Niinemets, Ü., Kuhn, U., Harley, P. C., Staudt, M., Arneth, A., Cescatti, A., Ciccioli, P., Copolovici, L., Geron, C., Guenther, A., Kesselmeier, J., Lerdau, M. T., Monson, R. K., and Peñuelas, J.: Estimations of isoprenoid emission capacity from enclosure studies: measurements, data processing, quality and standardized measurement protocols, Biogeosciences, 8, 2209–2246, doi:10.5194/bg-8-2209-2011, 2011.
Nölscher, A. C., Bourtsoukidis, E., Bonn, B., Kesselmeier, J., Lelieveld, J., and Williams, J.: Seasonal measurements of to-

tal OH reactivity emission rates from Norway spruce in 2011, Biogeosciences, 10, 4241–4257, doi:10.5194/bg-10-4241-2013, 2013.

Oku, H., Fukuta, M., Iwasaki, H., Tambunan, P., and Bab, S.: Modification of the isoprene emission model G93 for tropical tree *Ficus virgata*, Atmos. Environ., 42, 8747–8754, 2008.

Olivier, R., Lavoir, A. V., Ormeno, E., Mouillot, F., Greff, S., Lecareux, C., Staudt, M., and Fernandez, C.: Compost spreading in Mediterranean shrubland indirectly increases biogenic emissions by promoting growth of VOC-emitting plant parts, Atmos. Environ., 45, 3631–3639, doi:10.1016/j.atmosenv.2011.03.060, 2011.

Ormeno, E., Bousquet-Melou, A., Mevy, J. P., Greff, S., Robles, C., Bonin, A., and Fernandez, C.: Effect of intraspecific competition and substrate type on terpene emissions from some Mediterranean plant species, J. Chem. Ecol., 33, 277–286, 2007a.

Ormeno, E., Fernandez, C., Bousquet-Mélou, A., Greff, S., Morin, E., Robles, C., Vila, B., and Bonin, G.: Monoterpene and sesquiterpene emissions of three Mediterranean species through calcareous and siliceous soils in natural conditions, Atmos. Environ., 41, 629–639, 2007b.

Ormeno, E., Fernandez, C., and Mevy, J. P.: Plant coexistence alters terpene emission and content of Mediterranean species, Phytochemistry, 68, 840–852, 2007c.

Ormeno, E., Mevy, J. P., Vila, B., Bousquet-Melou, A., Greff, S., Bonin, G., and Fernandez, C.: Water deficit stress induces different monoterpene and sesquiterpene emission changes in Mediterranean species. Relation between terpene emissions and plant water potential, Chemosphere, 67, 276–284, 2007d.

Ormeno, E., Olivier, R., Mevy, J. P., Baldy, V., and Fernandez, C.: Compost may affect volatile and semi-volatile plant emissions through nitrogen supply and chlorophyll fluorescence, Chemosphere, 77, 94–104, 2009.

Owen, S. M., 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.

Owen, S. M., Boissard, C., and Hewitt, C. N.: Volatile organic compounds (VOCs) emitted from 40 Mediterranean plant species: VOC speciation and extrapolation to habitat scale, Atmos. Environ., 35, 5393–5409, 2001.

Owen, S. M., Harley, P., Guenther, A., and Hewitt, C. N.: Light dependency of VOC emissions from selected Mediterranean plant species, Atmos. Environ., 36, 3147–3159, 2002.

Padhy, P. K. and Varshney, C. K.: Isoprene emission from tropical tree species, Environ. Pollut., 135, 101–109, 2005.

Parolin, P., Junk, W., and Piedade, M. T. F.: Gas exchange of six tree species form Central Amazonian floodplains, Tropic. Ecol., 42, 15–24, 2001.

Pearcy, R. W., Schulze, E. D., and Zimmermann, R.: Measurement of transpiration and leaf conductance, in: Plant Physiological Ecology, Chapman and Hall, New York, 137–160, 1989.

Pegoraro, E., Rey, A., Abrell, L., Vanharen, J., and Lin, G. H.: Drought effect on isoprene production and consumption in Biosphere 2 tropical rainforest, Glob. Change Biol., 12, 456–469, 2006.

Pio, C., Nunes, T., and Brito, S.: Volatile Hydrocarbon Emissions from Common and Native Species of Vegetation in Portugal, Proceedings of Joint Workshop of CEC/BIATEX of EUROTRAC General Assessment of Biog, Emissions and Deposition of Nitrogen Compounds Sulphur Compounds and Oxidants in Europe, Air Pollution Research Report 47, edited by: Slanina, J., Angeletti, G., and Beilke, S., Aveiro, Portugal, 291–298, 1993.

Pio, C. A., Silva, P. A., Cerqueira, M. A., and Nunes, T. V.: Diurnal and seasonal emissions of volatile organic compounds from cork oak (Quercus suber) trees, Atmos. Environ., 39, 1817–1827, 2005.

Pitman, N. C. A., Terborgh, J. W., Silman, M. R., Núnpez, P. V., Neill, D. A., Cerón, C. E., Palacios, W. A., and Aulestia, M.: Dominance and distribution of tree species in upper Amazonian terra firme forests, Ecology, 82, 2101–2117, 2001.

Pöschl, U., Williams, J., Hoor, P., Fischer, H., Crutzen, P. J., Warneke, C., Holzinger, R., Hansel, A., Jordan, A., Lindinger, W., Scheeren, H. A., Peters, W., and Lelieveld, J.: High acetone concentrations throughout the 0–12 km altitude range over the tropical rainforest in Surinam, J. Atmos. Chem., 38, 115–132, 2001.

Pöschl, U., Martin, S. T., Sinha, B., Chen, Q., Gunthe, S. S., Huffman, J. A., Borrmann, S., Farmer, D. K., Garland, R. M., Helas, G., Jimenez, J. L., King, S. M., Manzi, A., Mikhailov, E., Pauliquevis, T., Petters, M. D., Prenni, A. J., Roldin, P., Rose, D., Schneider, J., Su, H., Zorn, S. R., Artaxo, P., and Andreae, M. O.: Rainforest aerosols as biogenic nuclei of clouds and precipitation in the Amazon, Science, 329, 1513–1516, 2010.

Prance, G. T.: Notes on the vegetation of Amazonia III. The terminology of Amazonian Forest Types subject to inundation, Brittonia, 31, 26–38, 1979.

Schäfer, L., Kesselmeier, J., and Helas, G.: Formic and acetic acid emission from conifers measured with a "cuvette" technique, in: Field Measurements and Interpretation of Species related to Photooxidants and Acid Deposition, edited by: Beilke, S., Slanina, J., and Angeletti, G., CEC Air Pollution Research 39, E. Guyot SA, Brussels, 1992.

Schöngart, J., Piedade, M. T. F., Ludwigshausen, S., Horna, V., and Worbes, M.: Phenology and stem-growth periodicity of tree species in Amazonian floodplain forest, J. Tropic. Ecol., 18, 581–597, 2002.

Seco, R., Penuelas, J., and Filella, I.: Short-chain oxygenated VOCs: emission and uptake by plants and atmospheric sources, sinks, and concentrations, Atmos. Environ., 41, 2477–2499, 2007.

Seufert, G., Bartzis, J., Bomboi, T., Ciccioli, P., Cieslik, S., Dlugi, R., Foster, P., Hewitt, C. N., Kesselmeier, J., Kotzias, D., Lenz, R., Manes, F., Perez Pastor, R., Steinbrecher, R., Torres, L., Valentini, R., and Versino, B.: An overview of the Castelporziano experiments, Atmos. Environ., 31, 5–17, 1997.

Sharkey, T. S.: Is it useful to ask why plants emit isoprene? Plant, Cell and Environment, 36, 517–520, 2013.

Simon, V., Dumergues, L., Solignac, G., and Torres, L.: Biogenic emissions from Pinus halepensis: a typical species of the Mediterranean area, Atmos. Res., 74, 37–48, 2005.

Simon, V., Dumergues, L., Ponche, J. L., and Torres, L.: The biogenic volatile organic compounds emission inventory in France – application to plant ecosystems in the Berre-Marseilles area (France), Sci. Total Environ., 372, 164–182, 2006.

Simpson, D., Winiwarter, W., Börjesson, G., Cinderby, S., Ferreiro, A., Guenther, A., Hewitt, N., Janson, R., Khalil, M. A. K., Owen, S., Pierce, T.E., Puxbaum, H., Shearer, M., Skiba, U., Stein-

brecher, R., Tarrasón, L., and Öquist, M. G.: Inventorying emissions from nature in Europe, Journal of Geophysical Research, 104, 8113–8152, 1999.

Singh, H., Chen, Y., Staudt, A., Jacob, D., Blake, D., Heikes, B., and Snow, J.: Evidence from the Pacific troposphere for large global sources of oxygenated organic compounds, Nature, 410, 1078–1081, 2001.

Sioli, H.: Beiträge zur regionalen Limnologie des Amazonasgebietes, Archiv für Hydrobiologie, 45, 267–283, 1954.

Sioli, H.: Über Natur und Mensch im brasilianischen Amazonasgebiet, Erdkunde, 10, 89–109, 1956.

Sjostedt, S. J., Slowik, J. G., Brook, J. R., Chang, R. Y.-W., Mihele, C., Stroud, C. A., Vlasenko, A., and Abbatt, J. P. D.: Diurnally resolved particulate and VOC measurements at a rural site: indication of significant biogenic secondary organic aerosol formation, Atmos. Chem. Phys., 11, 5745–5760, doi:10.5194/acp-11-5745-2011, 2011.

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, 2004.

Staudt, M. and Lhoutellier, L.: Volatile organic compound emission from holm oak infested by gypsy moth larvae: evidence for distinct responses in damaged and undamaged leaves, Tree Physiol., 27, 1433–1440, 2007.

Staudt, M., Ennajah, A., Mouillot, F., and Joffre, R.: Do volatile organic compound emissions of Tunisian cork oak (Quercus suber) populations originating from contrasting climatic conditions differ in their responses to summer drought?, Can. J. Forest Res., 38, 2965–2975, 2008.

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

Steinbrecher, R., Hauff, K., Rabong, R., and Steinbrecher, J.: Isoprenoid emission of oak species typical for the Mediterranean area: source strength and controlling variables, Atmos. Environ., 31, 79–88, 1997.

Tani, A., Hayward, S., and Hewitt, C. N.: Measurement of monoterpenes and related compounds by proton transfer reaction-mass spectrometry (PTR-MS), Int. J. Mass Spectrom., 223, 561–578, 2003.

Ter Steege, H., Pitman, N., Sabatier, D., Castellanos, H., Van der Hout, P., Daly, D. C., Silveira, M., Phillips, O., Vasquez, R., Van Andel, T., Duivenvoorden, J., De Oliveira, A. A., Ek, R., Lilwah, R., Thomas, R., Van Essen, J., Baider, C., Maas, P., Mori, S., Terborgh, J., Vargas, P. N., Mogollon, H., and Morawetz, W.: A spatial model of tree alpha-diversity and tree density for the Amazon, Biodiversity and Conservation, 12, 2255–2277, doi:10.1023/A:1024593414624, 2003.

Ter Steege, H., Pitman, N. C. A., Phillips, O. L., Chave, J., Sabatier, D., Duque, A., Molino, J. F., Prevost, M. F., Spichiger, R., Castellanos, H., von Hildebrand, P., and Vasquez, R.: Continental-scale patterns of canopy tree composition and function across Amazonia, Nature, 443, 444–447, doi:10.1038/nature05134, 2006.

Tholl, D., Boland, W., Hansel, A., Loreto, F., Röse, U. S. R., and Schnitzler, J. P.: Practical approaches to plant volatile analysis, Plant J., 45, 540–560, 2006.

Villanueva-Fierro, I., Popp, C. J., and Martin, R. S.: Biogenic emissions and ambient concentrations of hydrocarbons, carbonyl compounds and organic acids from ponderosa pine and cottonwood trees at rural and forested sites in Central New Mexico, Atmos. Environ., 38, 249–260, 2004.

Wang, Y. H., Jacob, D. J., and Logan, J. A.: Global simulation of tropospheric O_3-NOx-hydrocarbon chemistry 3, Origin of tropospheric ozone and effects of nonmethane hydrocarbons, J. Geophys. Res.-Atmos., 103, 10757–10767, 1998

Wang, Y. F., Owen, S. M., Li, Q. J., and Peñuelas, J.: Monoterpene emissions from rubber trees (Hevea brasiliensis) in a changing landscape and climate: chemical speciation and environmental control, Glob. Change Biol., 13, 2270–2282, 2007.

Welter, S., Bracho-Nunez, A., Mir, C., Zimmer, I., Kesselmeier, J., Lumaret, R., Schnitzler, J. P., and Staudt, M.: The diversification of terpene emissions in Mediterranean oaks – lessons from a study of *Quercus suber*, *Quercus canariensis*, and its hybridisation product *Quercus afares*, Tree Physiol., 32, 1082–1091, doi:10.1093/treephys/tps069, 2012.

Wilske, B., Cao, K. F., Schebeske, G., Chen, J. W., Wang, A., and Kesselmeier, J.: Volatile organic compound (VOC) emissions of trees in a tropical rainforest in Xishuangbanna, SW-China, Atmos. Environ., 41, 3748–3757, 2007.

Winer, A. M.: Investigation of the role of natural hydrocarbons in photochemical smog formation in California, Final Report, California Air Resources Board, Statewide Air Pollution Research, Center University of California, Riverside, California, 1983.

Winer, A. M., Arey, J., Atkinson, R., Aschmann, S. M., Long, D. W., Lynn Morrison, C., and Olszyk, D. M.: Emission rates of organics from vegetation in California's Central Valley, Atmos. Environ., 26, 2647–2659, 1992.

Wisthaler, A., Jensen, N. R., Winterhalter, R., Lindinger, W., and Hjorth, J.: Measurements of acetone and other gas phase product yields from the OH-initiated oxidation of terpenes by proton-transfer-reaction mass spectrometry (PTR-MS), Atmos. Environ., 35, 6181–6191, 2001.

Wittmann, F., Anhuf, D., and Junk, W. J.: Tree species distribution and community structure of central Amazonian várzea forests by remote-sensing techniques, Journal of Tropical Ecology, 18, 805–820, doi:10.1017/S0266467402002523, 2002.

Wittmann, F., Schöngart, J., and Junk, W. J.: Phytogeography, species diversity, community structure and dynamics of Amazonian várzea forests, In: Ecology and management of Amazonian floodplain forests, Ecological series 210, edited by: Junk, W. J., Piedade, M. T. F., Wittmann, F., Schöngart, J., and Parolin, P., Springer, Berlin, 61–102, 2010.

Wittmann, F., Householder, E., Piedade, M. T. F., De Assis, R. L., Schöngart, J., Parolin, P., and Junk, W. J.: Habitat specifity, edemism and the neotropical distribution of Amazonian white-water floodplain trees, Ecography, 36, 690–707, doi:10.1111/j.1600-0587.2012.07723.x, 2013.