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Seasonal variations in terpene emission factors of dominant species in four ecosystems in NE Spain

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HIGHLIGHTS

- ► Terpene emission factors were about 15 times higher in summer than in early spring.
- ► The maximum emission factors were recorded around midday.
- ► Minimum emission rates were recorded during the night.

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ABSTRACT

We studied the daily patterns in the rates of foliar terpene emissions by four typical species from the Mediterranean region in two days of early spring and two days of summer in 4 localities of increasing biomass cover in Northern Spain. The species studied were *Thymelaea tinctoria* (in Monegros), *Quercus coccifera* (in Garraf), *Quercus ilex* (in Prades) and *Fagus sylvatica* (in Montseny). Of the total 43 VOCs detected, 23 were monoterpenes, 5 sesquiterpenes and 15 were not terpenes. Sesquiterpenes were the main terpenes emitted from *T. tinctoria*. Total VOC emission rates were on average about 15 times higher in summer than in early spring. The maximum rates of emission were recorded around midday. Emissions nearly stopped in the dark. No significant differences were found for nocturnal total terpene emission rates between places and seasons. The seasonal variations in the rate of terpene emissions and in their chemical composition can be explained mainly by dramatic changes in emission factors (emission capacity) associated in some cases, such as for beech trees, with very different foliar ontogenical characteristics between spring and summer. The results show that temperature and light-standardised emission rates were on average about 15 times higher in summer than in early spring, which, corroborating other works, calls to attention when applying the same emission factor in modelling throughout the different seasons of the year.

1. Introduction

Many studies have shown the importance of environmental conditions, both abiotic and biotic, for the production and emission rates of VOCs (Langenheim, 1994; Takabayashi et al., 1994; Peñuelas and Llusia, 2001; Paris et al., 2010). Briefly, the main abiotic factors are irradiance and temperature (Sharkey and Loreto, 1993; Staudt and Bertin, 1998; Llusia and Peñuelas, 1999; Filella et al., 2007; Porcar-Castell et al., 2009; Peñuelas and Staudt, 2010) and the availability of water (Ebel et al., 1995; Bertin and Staudt, 1996; Llusia et al., 2008). These abiotic factors have strong effects, especially under Mediterranean conditions that are characterized by long dry summers, coinciding with high solar irradiation and high temperatures (Di Castri, 1973; Llusia et al., 2008). In addition, seasonality (Guenther, 1997; Llusia and Peñuelas, 1998; Peñuelas and Llusia, 1999a; Llusia and Peñuelas, 2000; Niinemets et al., 2010a,b) and the daily cycle also determine the production and emission of terpenes (Niinemets et al., 2010a,b; Llusia et al., 2012).

This study is part of a campaign to understand the interactions between forests and the atmosphere within the project MONTES. The campaigns of MONTES aimed to measure the emissions of VOCs in four different terrestrial ecosystems with increasing

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biomass (Peñuelas et al., 2011). The results of the measurements at the leaf level for the dominant species of each of the studied sites are here presented with the aim of providing emission factors useful for upscaling to landscape emission rates and discerning the potential need of using different emission factors for the different seasons of the year. The study also aimed to provide knowledge on seasonal and daily emission patterns including the assessment of the role of immediate temperature and PFD response relative to changes in emission factor due to phenology and ontogeny. We also conducted parallel measurements of photosynthesis and stomatal conductance. Since there was not a dominant species at the Monegros semidesertic site and for the Garraf shrubland, we measured one of the most characteristic and abundant species of the site, *Thymelaea tinctoria* in Monegros, and *Quercus coccifera* in Garraf. For Prades, a holm oak forest, the dominant species, *Quercus ilex*, was analysed and for Montseny beech forest, the dominant species, *Fagus sylvatica*, was analysed.

2. Material and methods

2.1. Study sites

2.1.1. Monegros

The region of Los Monegros is a mostly flat land ranging from the peak of the Sierra de Alcubierre (San Caprasio, 812 m) to the lowest altitude in Villanueva de Sigena (190 m). Most of the area is about 200–400 m. This great plain has a continental and arid climate that creates an extreme environment for organisms. The sampling location was near to the Santuario de Nuestra Señora de Magallón (Leciñena) at 41°48′03.22″N 0°35′17.58″W, and 531 m asl. The dominant vegetation there is composed by *T. tinctoria*, *Genista* sp., *Rosmarinus officinalis*, *Thymus vulgaris*, *Helichrysum* sp. and *Pinus halepensis*. *T. tinctoria* usually develops in degraded pine underwood, combining with *R. officinalis*, *Arctostaphylos uva-ursi*, and *T. vulgaris*.

2.1.2. Garraf

Garraf is a dry shrubland in Rosmarino-Ericion Natural Park, Barcelona, north-east Spain sampled here at 41°18′26.27″N 1°50′19.62″W at 335 m a.s.l. The climate of this site is typically Mediterranean. The site suffered big fires in the summers of 1982 and 1994. The soil is a petrocalcic calcixerept (Soil Survey Staff, 1998), thin (12–37 cm), with a loamy texture and abundant calcareous nodules. Currently the regenerating vegetation covers 50–60% with a maximum height of 70 cm. The dominant species at the study site, *Q. coccifera* (a dominant shrub species in Garraf (Folch, 1981)), *Erica multiflora* L., *Globularia alypum* L., *P. halepensis* L., *R. officinalis* L. and the less abundant *Pistacia lentiscus* L., are evergreen that typically occur on basic soils of the western Mediterranean Basin, where they are common components of the coastal shrubland.

2.1.3. Prades

The sampling location in Prades Mountains, also known as Muntanyes de Prades, was near to L'Espluga de Francolí, near to Casa del Paratge Natural, 41°21′38.84″N 1°05′26.27″W 872 asl. The Prades forest has typical Mediterranean vegetation. The forest is a holm oak forest (about 10 m tall), dominated by *Q. ilex* (the dominant plant species in Prades (Bolòs, 1983; Bolòs and Vigo, 1990)), with an important presence of other tree and shrub evergreen species (*Phillyrea latifolia*, *Arbutus unedo*, *Pinus sylvestris*, *Erica arborea*, *Juniperus oxycedrus*…) and other deciduous species such as *Sorbus torminalis* and *Acer monspessulanum*.

2.1.4. Montseny

The site of study was located within a densely forested natural park, Montseny, located about 60 km NNE of Barcelona (Catalonia, in the NE part of the Iberian Peninsula) and 25 km from the Mediterranean coast (Santa Fe del Montseny 41°46′26.37″N, 02°27′43.38″E, 1137 m above sea level). The site is highly representative of the montane forests in the Mediterranean regions of France, Italy, Greece and eastern Spain (Terradas, 1999). The site is covered by deciduous beech forest (about 20–25 m tall trees) *F. sylvatica* (Peñuelas and Boada, 2003; Bolòs, 1983; Bolòs and Vigo, 1990) with important presence of *Ilex aquifolium* and with a few patches of forest dominated by *Abies alba*.

2.2. Measurements of rates of gas exchange and sampling for leaf terpene emissions

Measurements were performed in spring 2010 (April 8 and 9 in Garraf, 14 and 15 in Monegros, 20, 21 and 22 in Prades, 27 and 28 in Montseny) and in summer 2010 (July 8 and 9 in Garraf, 14 and 15 in Monegros, 20 and 21 in Prades, 27 and 28 in Montseny). One branchlet in each plant with fully expanded, sunlit leaves of *Q. coccifera* in Garraf, *T. tinctoria* in Monegros, *Q. ilex* in *Prades*, and *F. sylvatica* in Montseny was used. Three or four plants were sampled five times daily for each sampling date (approximately three different of the most characteristic and abundant species of the site were sampled every 3 h (approximately one plant per hour) for 4 times daily). Measurements were conducted between 10 h and 22 h local time (7 am–18 pm solar time). Measurements of net photosynthetic rates, stomatal conductance and terpene levels were conducted using a gas-exchange system (CI-340 Hand-Held Photosynthesis System, CID, Inc., Camas, WA 98607, USA). Three to five leaves were enclosed in a 35-cm^2 clip-on gas-exchange cuvette. Air from the cuvette was pumped through a glass cartridge (8 cm long and 0.3 cm internal diameter) manually filled with terpene adsorbents Carbopack B, Carboxen 1003, and Carbopack Y (Supelco, Bellefonte, Pennsylvania) separated by plugs of quartz wool. Samples were taken using a Qmax air sampling pump (Supelco, Bellefonte, Pennsylvania). The hydrophobic properties of activated carbon minimized sample displacement by water. In these tubes, terpenes did not undergo chemical transformations as checked against trapped standards (α-pinene, β-pinene, camphene, myrcene, *p*-cymene, limonene, sabinene, camphor, α-humulene and dodecane). Prior to use for terpene sampling, these tubes were conditioned for 15 min at 350 °C with a stream of purified helium. The sampling time was 5–10 min, and the flow was around 450 mL min^{-1} depending on the glass tube adsorbent and quartz wool packing. The trapping and desorption efficiency of liquid and volatilized standards such as α-pinene, β-pinene or limonene was 99%. Blank air sampling on tubes was conducted for 10 min immediately before each measurement without the plants in the cuvette. The glass tubes were stored in a portable fridge at 4 °C and taken to the laboratory. There, glass tubes were stored at −28 °C until the analysis. For calculations of the terpene emission rates, terpene concentrations measured in the blank samples without the plants were subtracted from the samples measured with the plants.

2.3. Terpene analyses

Terpene analyses were performed by a GC–MS system (Hewlett Packard HP59822B, Palo Alto, CA, USA). The monoterpenes trapped in the tubes were processed with an automatic sample processor (Combi PAL, FOCUS-ATAS GL International BV 5500 AA Veldhoven, The Netherlands) and desorbed using an OPTIC3 injector (ATAS GL International BV 5500 AA Veldhoven, The Netherlands) into a 30 m × 0.25 mm × 0.25 μm film thickness capillary column (HP-5, Crosslinked 5% pH Me Silicone; Supelco Inc.). The injector temperature (60 °C) was increased at 16 °C s^{-1} to 300 °C. The injected