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### ► To cite this version:

E. Ormeño, C. Fernandez, C. Robles, Anne Bousquet-Mélou, B. Vila, et al.. Contribution of some Mediterranean plants to BVOC in the atmosphere of an open and a closed environment: a preliminary study. 14th International Conference on Modelling, Monitoring and Management of Air Pollution 2006 (AIR06), May 2006, The New Forest, United Kingdom. pp.629-636, 10.2495/AIR06062. hal-02094485

**HAL Id: hal-02094485**

**<https://hal.science/hal-02094485>**

Submitted on 9 Apr 2019

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## Contribution of some Mediterranean plants to BVOC in the atmosphere of an open and a closed environment: a preliminary study

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### Abstract

Terpenes (monoterpenes and sesquiterpenes) were measured under a closed environment (with a canopy structure) and an open environment (without a canopy structure). Terpenes were sampled both directly from vegetation (*Cistus albidus*, *Rosmarinus officinalis*, *Pinus halepensis* and *Quercus coccifera*) and in the atmosphere. Results show that the four species are influenced by the environmental structure. This influence is especially important for *Q. coccifera* and *R. officinalis* which present higher emission rates at the open and the closed environment, respectively. Of special interest is the fact that sesquiterpene emissions of *C. albidus* and *P. halepensis* are higher under the open environment, since it may indicate that these compounds are dependent on light. Terpenes do not follow a lengthwise gradient in the atmosphere. However, some exceptions have been found for  $\alpha$ -pinene and sesquiterpene concentrations. Monoterpene concentrations are significantly higher in the open atmosphere. This demonstrates that the canopy does not minimize terpene volatilization and that terpene concentration in the atmosphere is mostly dependent on plant contribution but litter seems to be another important source of terpenes.

*Keywords:* canopy, monoterpenes, sesquiterpenes, litter,  $\alpha$ -pinene, *Q. coccifera*, *R. officinalis*, *P. halepensis*, *C. albidus*.

### 1 Introduction

Biogenic volatile organic compounds (BVOC) from plants strongly contribute to the total release of VOC emissions to the atmosphere, mainly during summer



months, when they outstrip anthropogenic VOC emissions [1]. Among them, terpenes are precursors of some oxydative agents, such as ozone from the troposphere [2]. The Mediterranean region, with its climatic conditions, high emitter species and industrial and population concentration, is recognized as a major source of tropospheric ozone in Europe [3].

BVOC of plants are of great variability, partly because of the numerous factors influencing them. Thus, the scientific community all over the world and particularly in the Mediterranean Region (e.g. BEMA project [4], ESCOMPTE [5]), has devoted considerable effort on describing the effects of several abiotic and biotic factors on these emissions. Temperature, radiation [6] and seasonal cycles [7] are the factors most frequently studied. Many other factors, such as other pollutants ( $O_3$ ) [8], ecosystem type [9], age [10] or drought [11], have also been related to BVOC emissions.

Since canopy acts as a factor having an impact on light and temperature [12], we have studied the influence of the environmental structure (with or without canopy) on terpenes released from plants. We have also considered the possibility that canopy acts as a physical barrier to terpene volatilization. For this, we have measured terpene concentrations in the two types of atmosphere. For this second aim, measurements were developed following a lengthwise gradient in order to determine if terpene concentrations were or not homogenous at different levels.

Studying BVOC directly in the atmosphere is a new approach, since BVOC of plants are traditionally focalized on direct emissions from plants.

## 2 Materials and methods

### 2.1 Species, experimental site conditions and sampling description

Measurements were conducted in an open and a closed environment of a garrigue ecosystem in the south of France (Valabre) (distance between the two environments: 150 m). Vegetation for both environments was mainly represented by *Quercus coccifera* L., but *Rosmarinus officinalis* L., *Pinus halepensis* Mill, and *Cistus albidus* L., were also strongly widespread. The four studied species represented more than 80 % of total vegetation.

Two different measurements were made at each environment (i) direct terpene emissions of the studied species (ii) terpenes in the atmosphere. For direct emissions, seven plants per species were sampled between 13:00 and 15:00 (solar time). In the atmosphere, measurements were conducted at four levels (litter, few centimeters above plants, 4 meters and below canopy or the equivalent in the open environment) at 13:00 (s.t) for 1 hour. Four horizontal samples per level were taken. All measurements were conducted from July 16 to July 20. Climatic conditions of those days were similar: hot-clean sky, 1220-1600  $\mu\text{mol. m}^{-2} \text{ s}^{-1}$  PAR (photosynthetic active radiation), 36-40 °C at a sun exposed position and no or slight wind (max. 10  $\text{m.s}^{-1}$ ).



## 2.2 Sampling system and terpene analysis

A Teflon chamber enclosure system (0,5 l) was used to sample terpenes directly emitted from a single branch per plant. At the air stream inlet of each Teflon chamber pure air (99%) was flushed for 15 min at  $100 \text{ ml}\cdot\text{min}^{-1}$ . At the air stream outlet, one Tenax TA per Teflon chamber was used, and air was pumped for 10 min at  $80 \text{ ml}\cdot\text{min}^{-1}$  so that terpenes are trapped. The system was constructed to allow 14 measurements simultaneously.

The sampling system used to trap terpenes from the atmosphere, a part of the above described system, consisted of a 16 tube-system from which air is pumped. At the air stream outlet of each tube, a Tenax TA is used and pumping took place for 1h at  $30\text{-}80 \text{ ml}\cdot\text{min}^{-1}$  so that total sampled volume does not outstrip 3litres. We focussed on monoterpenes and sesquiterpenes which were analysed through thermal desorption by gas chromatography (GC) fitted with a flame ionization detector (FID). Most peak identification and quantitation was achieved by direct injection of terpene solutions in cyclohexane. These solutions were prepared from commercial authentic terpenes of high purity (~97 %).

## 3 Results and discussion

### 3.1 PAR and temperature under the open and the closed environment

Canopy structure has an effect on temperature. At the open environment it is  $4^{\circ}\text{C}$  (environmental temperature) or  $6^{\circ}\text{C}$  (chamber temperature) higher than at the closed environment. Though, canopy structure more particularly limits light. Light through PAR is between  $50\text{-}100 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  at the closed environment, while it is between  $1220\text{-}1600 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  at the open environment.

### 3.2 Direct terpene emissions of plants under the open and the closed environment

The four species are mainly monoterpene emitters (Figure 1) and their main emitted compound is the  $\alpha$ -pinene. Emissions of *Q. coccifera* (monoterpenes and total emissions), *C. albidus* (sesquiterpenes) and *P. halepensis* (sesquiterpenes) are significantly higher under the open environment (Figure 1, t Student test,  $p<0,05$ ), while emissions of *R. officinalis* (monoterpenes, sesquiterpenes and total emissions) are significantly higher under the closed environment (Figure 1, t Student,  $p<0,05$ ).

These results agree with previous studies. Thus, Mediterranean oaks (*Quercus* section *Sclerophylloides*), such as *Q. coccifera*, are known to produce monoterpenes in a light-dependent way, what agree with the fact that emissions of this species are higher at the open environment. Monoterpene emissions in a light-dependent way is apparently confined to the Mediterranean oaks, while it does not occur in other European or North American oaks [13]. In contrast, *R. officinalis* emissions are known to just depend on temperature [14, 15].



Although, even if temperature was lower at the closed environment, emissions of this species are higher under this environment. Indeed, each species presents a temperature up to which emissions increase and then, emissions decline at higher temperatures [16].

The fact that sesquiterpenes of *C. albidus* and *P. halepensis* are higher at the open environment is of special interest since it has never been shown their dependence neither to light nor to temperature. This dependence has just been demonstrated for monoterpenes [17]. Thus, traditional algorithms used to standardize monoterpene emissions [18–20], are also used to standardize sesquiterpene emissions [21].

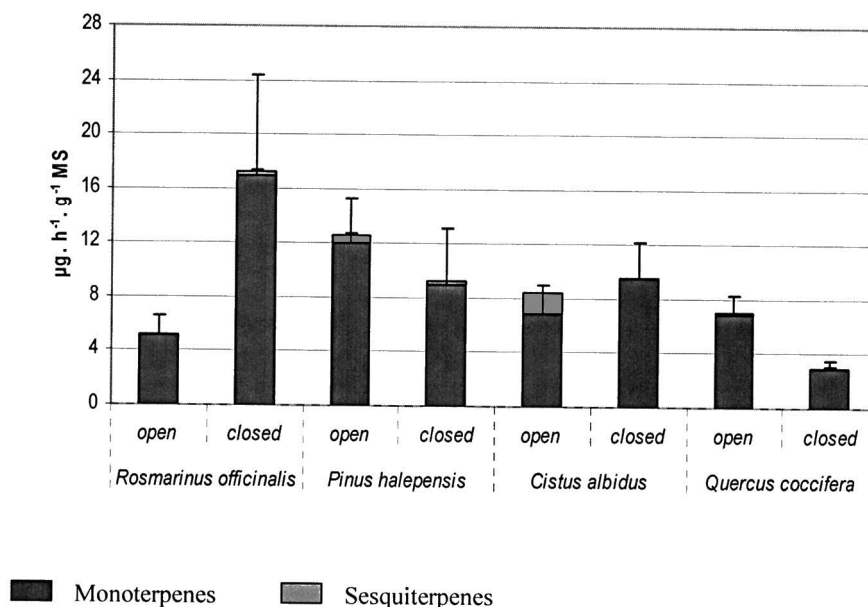


Figure 1: Monoterpenes and sesquiterpenes emitted by *C. albidus*, *R. officinalis*, *P. halepensis* and *Q. coccifera* under an open and a closed environment. (Bars indicate the standard error) (n=7).

### 3.3 Terpene concentrations in an open and a closed atmosphere

Globally terpene concentrations are homogenous both, at the open and the closed atmosphere (Figure 2, two factors ANOVA,  $p > 0,05$ ). Nevertheless, we have found two exceptions. Firstly, sesquiterpene concentrations are higher several cm above plants that 4m above ground, but this result has just been found in the open environment (Figure 2) (significant interaction between environment type and level sampling, one factor ANOVA, open environment,  $p < 0,05$ ). Moreover,  $\alpha$ -pinene, which represents 50% of total monoterpenes, reaches significant higher concentrations at the litter level (mean=  $0,37 \mu\text{g}\cdot\text{l}^{-1}$ ) than at the other three levels (mean=  $0,14 \mu\text{g}\cdot\text{l}^{-1}$ ) (Figure 2, two factors ANOVA, level,  $p < 0,05$ ) in the two atmospheres.



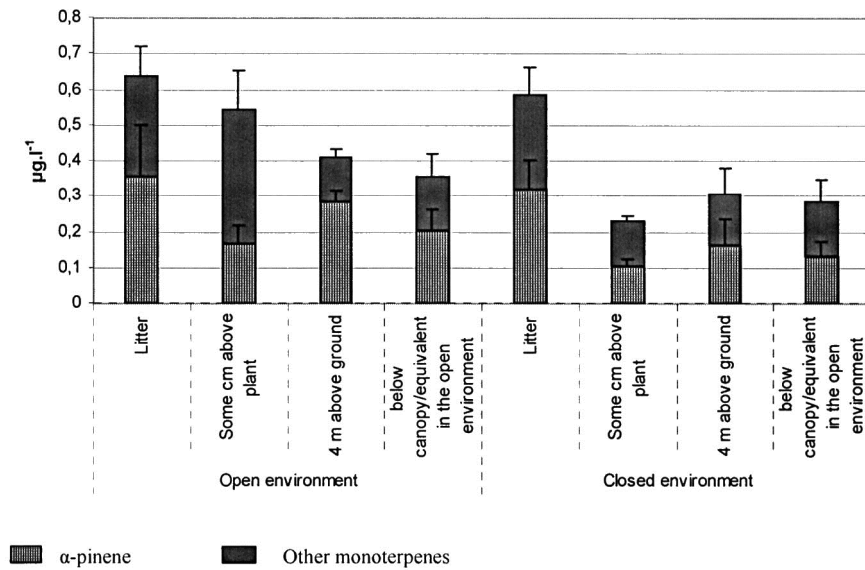


Figure 2: Mean concentrations of  $\alpha$ -pinene and total monoterpenes along a lengthwise gradient in an open and a closed atmosphere. (Bars indicate the standard error, n=4).

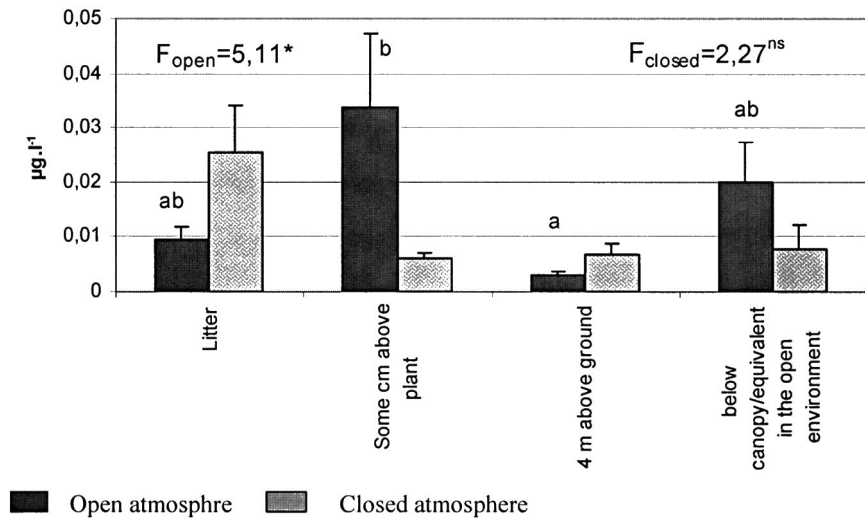


Figure 3: One factor ANOVA about mean sesquiterpene concentrations along a lengthwise gradient in an open and a closed atmosphere. (Bars indicate the standard error, n=4). Results of post hoc Tukey test are also shown. Different letters indicate that valeurs are significantly different at 95% of confidence. a < b.



Little information is available about BVOC released from litter. However, some authors have pointed out the importance of taking litter into account for obtaining more accurate terpene estimations [22].

While we have found no differences for sesquiterpenes between the two atmospheres (Two factor ANOVA, environmental structure,  $p > 0,05$ ), monoterpene concentrations are significantly higher at the open atmosphere, (Two factor ANOVA, environmental structure,  $p < 0,05$ ). Thus, mean monoterpene concentrations is:  $0,49 \pm 0,06 \mu\text{g.l}^{-1}$  at the open atmosphere (standard error) and  $0,35 \pm 0,06 \mu\text{g.l}^{-1}$ ; at the closed atmosphere, when all (Figure 4).

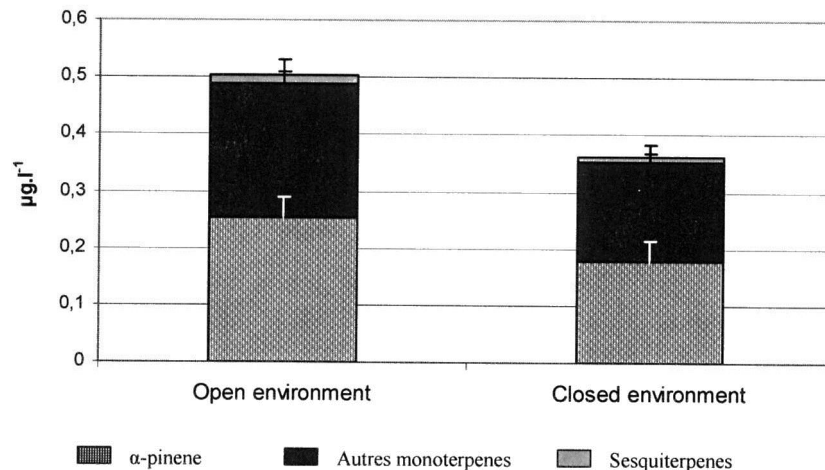


Figure 4: Mean concentrations of  $\alpha$ -pinene, total monoterpenes and sesquiterpenes in an open and a closed atmosphere, all level samplings taken together (Bars indicate the standard error,  $n=12$ ).

In conclusion, the four studied species are directly influenced by the presence or the absence of a canopy structure, since it strongly modifies temperature and light conditions. Moreover, canopy structure does not act as a physical barrier for terpenes, since monoterpene concentrations are higher at the open atmosphere. Therefore, plant contribution appears to be the main source of terpenes in the atmosphere, but litter could also be an important source of atmospheric BVOC. Thus, concentrations and composition of BVOC in the atmosphere are likely different depending on species composition and abundance. In consequence, the higher monoterpene concentrations here found in the open atmosphere, seem to be linked to the fact that the two environments are mainly represented by *Q. coccifera*, and that monoterpene emissions of this species are strongly favoured by light. In consequence, linking both, plant composition and species-specific emission variation according to light and temperature, could be of great interest for estimating BVOC concentrations in open (e.g. shrub environment) and closed environments (e.g. pine forest).



These scenarios at the environmental scale, emphasizes the need for detailed information about (i) factors affecting BVOC emissions for different species (ii) other biogenic emission sources (e.g. litter), in order to improve inputs of BVOC emissions to tropospheric chemistry model.

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