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1 **Litter of Mediterranean species as a source of volatile organic compounds**

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5

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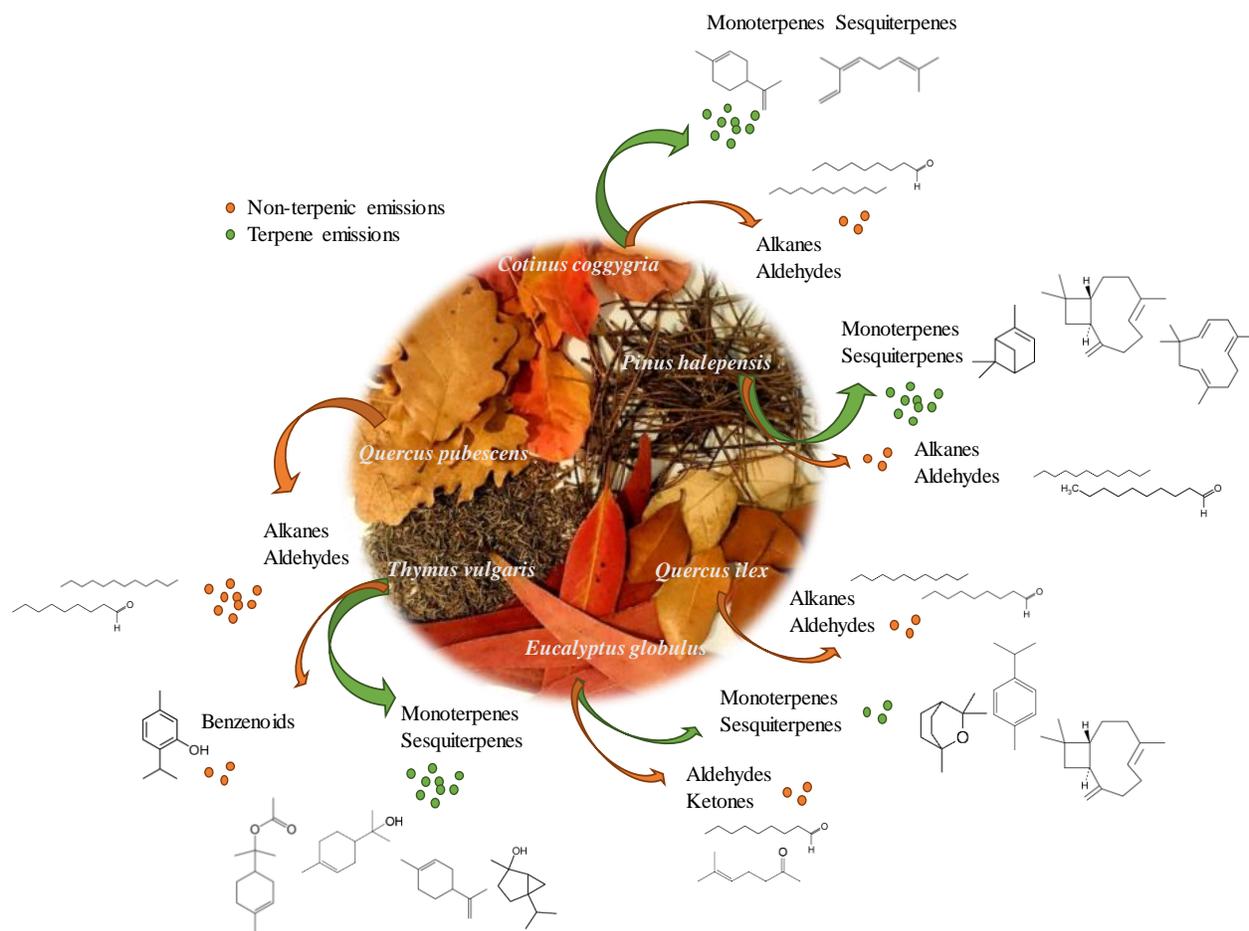
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## 8 Abstract

9 Leaf litter, at the interface between the soil and the atmosphere, releases Biogenic Volatile  
10 Organic Compounds (BVOC) which play an important role both in global atmospheric chemistry  
11 and plant ecology. Litter is especially important in the Mediterranean region, where it is produced  
12 in high amounts and decomposes slowly. Only leaf litter emissions of two dominant species (*Pinus*  
13 *halepensis* and *Eucalyptus* spp.) present in the Mediterranean region have been studied so far. The  
14 aim of this study is to characterize (quantitatively and qualitatively) the BVOC emissions (C10-  
15 C15) from litter (freshly fallen and non-decomposed leaves) under laboratory conditions. Sixteen  
16 species frequently found in the Mediterranean region were considered, nine of which possess  
17 terpene storage structures. Results show a large diversity of BVOC (87 compounds detected,  
18 terpenes, alkanes, alkenes, aldehydes, ketones, benzenoids), with terpene emission being higher  
19 than non-terpenic emission in most of the cases. Species were classified within 3 categories:  
20 negligible emitters (e.g. *Acer monspessulanum* and *Quercus ilex*,  $< 0.10 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ), low emitters  
21 (*Pinus pinea*, *Quercus pubescens*,  $0.1 - 1.0 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) and moderate emitters (*Thymus vulgaris*,  
22 *Cotinus coggygria* and *Pinus halepensis* between  $1.5$  to  $4.7 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ). Litter that possessed  
23 terpene storage structures and known to store high terpene concentration did not always release the  
24 highest terpene emission rates (e.g. *Eucalyptus globulus*, *Rosmarinus officinalis*). Species that do  
25 not possess such structures release only non terpenic emissions (e.g. alkanes, aldehydes).  
26 Estimation of the potential contribution of *P. halepensis* and *Q. pubescens* litter to  $\text{O}_3$  and  
27 secondary organic aerosol (SOA) formation in the atmosphere showed that *P. halepensis* has a  
28 larger potential impact on the global air quality than *Q. pubescens*. This study will contribute to  
29 build future BVOC emissions inventories on leaf litter for their further integration in atmospheric  
30 chemistry models.

31 **Keywords:** BVOC emissions, terpenes, storage structure, air quality, plant functional types

32 **Graphical abstract**



33 **Highlights**

- 34
- Litter emission rate ranges from  $< 0.1$  to  $4.7 \mu\text{g}\cdot\text{gDM}^{-1}\cdot\text{h}^{-1}$
- 35
- The highest emitters are *Thymus vulgaris*, *Cotinus coggygria* and *Pinus halepensis*
- 36
- Terpene emission rates are most often higher than non-terpene emissions
- 37
- Litter BVOC emissions of a species are not necessarily lower than green leaf BVOC
- 38
- Litter BVOC emissions contribute to air quality in a non-negligible way

39

## Introduction

40 Living plant species are well known to release a vast bouquet of Biogenic Volatile Organic  
41 Compounds (BVOC). Terrestrial living vegetation releases between 700 and 1000 TgC of BVOC  
42 every year to the atmosphere, of which 40 to 65% are terpenes, mainly isoprene (309–706 TgC  
43 yr<sup>-1</sup>), followed by monoterpenes (26–156 TgC yr<sup>-1</sup>) and sesquiterpenes (26 TgC yr<sup>-1</sup>) (Navarro et  
44 al., 2014). Higher BVOC emissions are probably released at the global scale since it has been  
45 estimated that soil (bare soil + litter) contributes to 1-20 % of total BVOC emission in different  
46 ecosystems (Asensio et al., 2007; Kramshøj et al., 2016; Tang et al., 2019). Quantification of leaf  
47 litter emissions at global or regional scales has not been performed using BVOC emission models  
48 due to data scarcity (Peñuelas et al., 2014). BVOC emissions from litter are important in ecological-  
49 related processes as they modify plant growth and germination, acting as volatile allelochemicals  
50 (Santonja et al., 2019) and in atmospheric chemistry by influencing the OH· budget, O<sub>3</sub> and  
51 secondary organic aerosol formation (Fehsenfeld et al., 1992; Spittler et al., 2006). As recently  
52 reviewed (Tang et al., 2019), a missing OH sink would be due to incomplete characterization of  
53 BVOC sources, particularly emissions from litter and soil.

54 Quantification of BVOC emissions at the ecosystem scale is not properly resolved with  
55 available models (Peñuelas et al., 2013) where only BVOC emission from the canopy are  
56 considered. In order to integrate litter in BVOC emission models, the first step it is to list BVOC  
57 emission rates of different plant species litter as previously carried out for living plants (Owen et  
58 al., 1997, 2001). The few studies that have reported litter BVOC emissions seem to support that  
59 litter is the second major source of BVOC after the canopy (Mäki et al., 2017; Tang et al., 2019)  
60 and releases higher emissions than bare soil (Ramirez et al., 2010). BVOC litter-related studies  
61 refer either to the layer of dead plant material present on the soil surface (Schade and Goldstein,  
62 2001; Gray et al., 2014) or dead plant material that is detached from a living plant (Isidorov et al.,  
63 2010; Isidorov et al., 2016), since ecologically the word litter has these two meanings (Krishna and  
64 Mohan, 2017).

65 It is difficult to evaluate if leaf litter of a given species releases higher or lower emission  
66 rates compared to its green leaves. For example, litter emission rate of *Pinus sylvestris* L., measured  
67 with a static system and SPME (Solid Phase Micro-Extraction), is 7.5 µg.g<sub>DM</sub><sup>-1</sup>.h<sup>-1</sup> (Isidorov et al.,  
68 2010) in good agreement with emissions from green litter (maximal emission rate 6 µg.g<sub>DM</sub><sup>-1</sup>.h<sup>-1</sup>;  
69 Vanhatalo et al., 2018). Emission rates of *Picea abies* (L.) H. Karst litter, also measured with a

70 static system and SPME, is  $1.3 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$  (Isidorov et al., 2010) contrast with green leaf emission  
71 ( $\sim 0.1\text{-}0.4 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ; Bourtsoukidis et al., 2014). Likewise, *Pinus taeda* L. litter showed an  
72 average emission rate of  $117 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$  (Ramirez et al., 2010) after litter conditioning (drying at  
73  $75^{\circ}\text{C}$  and incubation for 72 days), which is roughly 100 times higher compared to its green leaf  
74 emissions (Helmig et al., 2006). Litter conditioning and handling previous to measurements  
75 probably explain such differences. However, all these studies suggest that terpene emissions from  
76 litter are not negligible compared to green leaves.

77 Leaf litter emission varies according to decomposition stages (Gray et al., 2010; Isidorov  
78 et al., 2010) as terpenes volatilize from terpene pools and microbiota associated to litter releases  
79 and consumes BVOC. As a result, comparing leaf litter emission between species requires to  
80 consider litter from the same decomposition stage. Using fresh leaf litter that has not undergone  
81 microbial decomposition in soil allows to isolate BVOC emission from litter and is also the most  
82 accurate way to compare BVOC emission rates from green leaves and leaf litter.

83 Fresh litter could importantly contribute to BVOC emissions and the atmospheric chemistry  
84 in the Mediterranean region where climate is characterized by a long and hot summer period (2-5  
85 months; Polade et al., 2014) which could favor BVOC emissions from litter (Greenberg et al.,  
86 2012). Moreover, litter decomposes slowly (Hart et al., 1992) and many Mediterranean plant  
87 species including *Pinus* spp. and *Quercus* spp. produce important litter biomasses (e.g. *Pinus pinea*  
88 L., *Quercus coccifera* L., Arianoutsou and Radea, 2000). The Mediterranean area is also highly  
89 populated, leading to increases in anthropogenic pollutants, such as  $\text{NO}_x$ , necessary for  
90 tropospheric  $\text{O}_3$  formation, in the presence of BVOC and light (Atkinson and Arey, 2003). All  
91 these interacting phenomena highlight the importance of focusing on other biogenic sources of  
92 BVOC emission such as litter and not only living vegetation.

93 BVOC emissions from litter rely on both, soil microbial activity and specific BVOC  
94 reservoirs (such as glandular trichomes, secretory cavities) and cuticle where waxes are  
95 accumulated (Bondada et al., 1996). BVOC reservoirs (present only in some species) allow to store  
96 a high quantity of compounds resulting in toxic concentration for the other organisms (herbivore  
97 or phytopathogenic microorganisms) (Lange, 2015). BVOC reservoirs mostly contain terpenic  
98 compounds (Wagner, 1991) (excepting isoprene which is produced *de novo* and never stored in  
99 specific storing structures, Sharkey and Yeh, 2001), and are thus referred to as terpene storage  
100 structures. These structures can either be internal to the leaf such as the secretory cavities within

101 needles of resinous species or external to the leaf such as the glandular trichome (e.g. *Lamiaceae*  
102 spp). Numerous Mediterranean plant species (*Rosmarinus officinalis* L., *Pinus halepensis* Mill.,  
103 *Pinus sylvestris*, *Pinus nigra* R. Legay) possess remarkable terpene amounts in these leaf reservoirs  
104 ( $5\text{--}30\text{ mg}\cdot\text{g}_{\text{DM}}^{-1}$ ) presumably allowing these terpenes to be released in high amounts from leaf litter.  
105 Other species (*Cistus* spp, *P. pinea*) only store small amounts of terpenes ( $5\text{--}64.5\text{ }\mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}$ ) in these  
106 structures (Ormeño et al., 2009). While terpene reservoirs are present in some species only, all  
107 vascular species possess an upper cuticle layer which mainly stores low weight saturated and  
108 unsaturated aliphatic hydrocarbons ( $< \text{C}16$ ) (Bondada et al., 1996; Barik et al., 2004) but also a  
109 small fraction of terpene compounds in coniferous species (Joensuu et al., 2016). All these volatiles  
110 could thereby plausibly be released by leaf litter cuticle.

111 The main goal of this study is to characterize BVOC emissions from litter of 16  
112 Mediterranean species to identify those that could mostly contribute to biosphere-atmosphere  
113 interactions. Species belonging to different Plant Functional Types (PFT) are considered, including  
114 evergreen trees, deciduous trees and evergreen shrubs. This study considers fresh leaf litter  
115 (senescent leaves) that has not undergone decomposition by soil microorganisms and focuses on  
116 leaf terpene content (from literature data) to evaluate if this parameter could be an indicator of the  
117 potential of litter to release BVOC. Additionally, we aimed to estimate the potential impact of litter  
118 BVOC emissions on air quality. For this purpose, we focused on two tree species (*P. halepensis*  
119 and *Q. pubescens*) and calculated, for both plant species, three indicators of their influence on air  
120 quality: regional litter BVOC emissions, photochemical ozone creation potential (POCP) and  
121 secondary organic aerosol production (SOAP). These two plant species were chosen for this  
122 modelling exercise since they are major species in the Sud-PACA region where they occupy 197  
123 000 ha and 356 000 ha respectively (IGN – Inventory of 2014 to 2018).

## 124 **2. Material and Methods**

### 125 *2.1. Plant material*

126 Fresh leaf litter (hereafter referred to as litter) of 16 Mediterranean species was collected in  
127 2017 and 2018 in Southern France (Sud-PACA region). Litter consisted of both senescent leaves  
128 previous to abscission and senescent leaves freshly fallen from the plant (within the first days  
129 following leaf abscission) collected by means of a fine-mesh net previously placed in the field to  
130 avoid litter contact with soil (Santonja et al., 2018). The studied species were chosen in order to  
131 select a significant number of the most abundant Mediterranean species. We paid a special attention

132 to integrate both, species with leaf terpenic reservoirs and species that do not possess such

Species	Collection	GPS Coordinates	Storage structure	Plant Functional Type	Leaf litter production		Green leaves emission		
					g.m <sup>-2</sup> .y <sup>-1</sup>	Reference	µg.g <sup>-1</sup> .h <sup>-1</sup>	Type	Reference
<i>Q. ilex</i>	April	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	673	Rodriguez-Ramirez et al. (2017)	0.1 - 4.5	MT>ST	Owen & Ormeno
<i>Q. robur</i>	June	43°10'44.3"N 5°34'16.2"E	Glandular trichome	Shrub	Unknown		3.1	MT>ST	Owen et al.
<i>Q. pygmaea</i>	November	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	117	Unpublished data	Unknown	Unknown	
<i>Q. lobulus</i>	November	43°04'13.5"N 5°51'12.3"E	Subdermal oil glands	Evergreen broad leaf tree	250 - 370	Arianoutsou (1989)	5.4 - 42.0	MT>ST	He et al. & Pio (2000)
<i>Q. pedunculata</i>	August	43°14'27.1"N 5°40'33.3"E	Secretory cavities	Evergreen needle leaf tree	Unknown		0.5 - 2.3	Iso>MT>ST	Owen & Ormeno
<i>Q. pubescens</i>	August	43°56'06.0"N 5°42'37.7"E	Secretory cavities	Evergreen needle leaf tree	340 <sup>a</sup>	Arianoutsou & Radea (2000)	3.0 - 15.0	MT>ST	Ormeno & Llusia et al.
<i>Q. pubescens</i>	August	43°17'22.1"N 5°24'35.2"E	Secretory cavities	Evergreen needle leaf tree	240 - 790	Arianoutsou & Radea (2000)	3.4 - 8.8	MT>ST	Street et al. & Hewitt
<i>Q. officinalis</i>	August	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	385	Rodriguez-Ramirez et al. (2017)	2.2 - 5.0	MT>ST	Owen & Ormeno
<i>Q. robur</i>	July	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	Unknown		3.6	MT>ST	Parra et al.
<i>Q. sessiliflora</i>	November	43°56'06.0"N 5°42'37.7"E	None	Deciduous tree	55 - 125	Unpublished data	< 0.3	Iso, MT	Genard-Dejean (2014)
<i>Q. ilex</i>	June	43°10'44.3"N 5°34'16.2"E	None	Shrub	Unknown		19.0	Iso	Owen et al.
<i>Q. agrifolia</i>	September	43°56'06.0"N 5°42'37.7"E	None	Shrub	538	Arianoutsou (1989)	5.5 - 14.6	Iso>MT, ST	Owen & Staudt
<i>Q. pubescens</i>	June	43°14'27.1"N 5°40'33.3"E	None	Evergreen broad leaf tree	180 - 250	Bello et al. (1992)	15.0 - 21.0	MT>ST	Kesselmeier (1999)
<i>Q. pubescens</i>	January	43°10'44.3"N 5°34'16.2"E	None	Deciduous tree	166 <sup>b</sup>	Saunier et al. (2018)	90.0	Iso	Kesselmeier & Saunier
<i>Q. robur</i>	June	43°15'19.2"N 6°13'06.3"E	None	Evergreen broad leaf tree	349	Robert et al. (1996)	0.2 - 30.0	MT	Pio et al. & Osorio
<i>Q. robur</i>	June	43°21'54.9"N 5°25'30.9"E	None	Shrub	323	Rodriguez-Ramirez et al. (2017)	9.0 - 14.0	Iso	Owen et al.

133 structures, also species belonging to different plant functional types and finally taking into account  
134 their litter production. For example, *P. halepensis* is an *Evergreen needle leaf tree*, possesses  
135 terpene storage structures, occupies 231 000 ha in France and features a non-negligible litter  
136 production (150-530 g.m<sup>-2</sup>.y<sup>-1</sup>,

137 Table 1). *Q. pubescens* is a *Deciduous broad leaf tree* free of terpene storage structure,  
138 occupies 320 000 ha in the Sud-PACA region and features a moderate litter production (138 - 194  
139 g.m<sup>-2</sup>.y<sup>-1</sup>,

Species	Collection	GPS Coordinates	Storage structure	Plant Functional Type	Leaf litter production		Green leaves emission		
					$\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$	Reference	$\mu\text{g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	Type	Reference
<i>Quercus</i>	April	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	673	Rodriguez-Ramirez et al. (2017)	0.1 - 4.5	MT>ST	Owen & Ormeno
<i>Salix</i>	June	43°10'44.3"N 5°34'16.2"E	Glandular trichome	Shrub	Unknown		3.1	MT>ST	Owen et al.
<i>Pygmaea</i>	November	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	117	Unpublished data	Unknown	Unknown	
<i>Alnus</i>	November	43°04'13.5"N 5°51'12.3"E	Subdermal oil glands	Evergreen broad leaf tree	250 - 370	Arianoutsou (1989)	5.4 - 42.0	MT>ST	He et al. & Pio (2000)
<i>Cedrus</i>	August	43°14'27.1"N 5°40'33.3"E	Secretory cavities	Evergreen needle leaf tree	Unknown		0.5 - 2.3	Iso>MT>ST	Owen & Ormeno
<i>Pinus</i>	August	43°56'06.0"N 5°42'37.7"E	Secretory cavities	Evergreen needle leaf tree	340 <sup>a</sup>	Arianoutsou & Radea (2000)	3.0 - 15.0	MT>ST	Ormeno & Llusia et al.
	August	43°17'22.1"N 5°24'35.2"E	Secretory cavities	Evergreen needle leaf tree	240 - 790	Arianoutsou & Radea (2000)	3.4 - 8.8	MT>ST	Street et al. & Hewitt
<i>Pinus officinalis</i>	August	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	385	Rodriguez-Ramirez et al. (2017)	2.2 - 5.0	MT>ST	Owen & Ormeno
<i>Pinus maritima</i>	July	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	Unknown		3.6	MT>ST	Parra et al.
<i>Pinus sylvestris</i>	November	43°56'06.0"N 5°42'37.7"E	None	Deciduous tree	55 - 125	Unpublished data	< 0.3	Iso, MT	Genard-Dejean (2014)
<i>Salix</i>	June	43°10'44.3"N 5°34'16.2"E	None	Shrub	Unknown		19.0	Iso	Owen et al.
<i>Salix caprea</i>	September	43°56'06.0"N 5°42'37.7"E	None	Shrub	538	Arianoutsou (1989)	5.5 - 14.6	Iso>MT, ST	Owen & Staudt
	June	43°14'27.1"N 5°40'33.3"E	None	Evergreen broad leaf tree	180 - 250	Bello et al. (1992)	15.0 - 21.0	MT>ST	Kesselmeier (1999)
<i>Pinus peuceuntia</i>	January	43°10'44.3"N 5°34'16.2"E	None	Deciduous tree	166 <sup>b</sup>	Saunier et al. (2018)	90.0	Iso	Kesselmeier & Saunier
<i>Pinus</i>	June	43°15'19.2"N 6°13'06.3"E	None	Evergreen broad leaf tree	349	Robert et al. (1996)	0.2 - 30.0	MT	Pio et al. & Osorio
<i>Pinus brutia</i>	June	43°21'54.9"N 5°25'30.9"E	None	Shrub	323	Rodriguez-Ramirez et al. (2017)	9.0 - 14.0	Iso	Owen et al.

141 Litter was collected from 3 to 10 individuals in different locations and months according to  
 142 the time of the year when litter fall peak of each species occurs (

143 Table 1). Litter collection of each species took place in the same location and was never

Species	Collection	GPS Coordinates	Storage structure	Plant Functional Type	Leaf litter production		Green leaves emission		
					g.m <sup>-2</sup> .y <sup>-1</sup>	Reference	µg.g <sup>-1</sup> .h <sup>-1</sup>	Type	Reference
<i>Cistus</i>	April	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	673	Rodriguez-Ramirez et al. (2017)	0.1 - 4.5	MT>ST	Owen & Ormeno
<i>foliolus</i>	June	43°10'44.3"N 5°34'16.2"E	Glandular trichome	Shrub	Unknown		3.1	MT>ST	Owen et
<i>cogygia</i>	November	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	117	Unpublished data	Unknown	Unknown	
<i>globulus</i>	November	43°04'13.5"N 5°51'12.3"E	Subdermal oil glands	Evergreen broad leaf tree	250 - 370	Arianoutsou (1989)	5.4 - 42.0	MT>ST	He et al. Pio (200
<i>oxycedrus</i>	August	43°14'27.1"N 5°40'33.3"E	Secretory cavities	Evergreen needle leaf tree	Unknown		0.5 - 2.3	Iso>MT>ST	Owen &
<i>halepensis</i>	August	43°56'06.0"N 5°42'37.7"E	Secretory cavities	Evergreen needle leaf tree	340 <sup>a</sup>	Arianoutsou & Radea (2000)	3.0 - 15.0	MT>ST	Ormeno Llusia ar
	August	43°17'22.1"N 5°24'35.2"E	Secretory cavities	Evergreen needle leaf tree	240 - 790	Arianoutsou & Radea (2000)	3.4 - 8.8	MT>ST	Street et al. & Hewit
<i>officinalis</i>	August	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	385	Rodriguez-Ramirez et al. (2017)	2.2 - 5.0	MT>ST	Owen & Ormeno
<i>suber</i>	July	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	Unknown		3.6	MT>ST	Parra et
<i>monspessulanum</i>	November	43°56'06.0"N 5°42'37.7"E	None	Deciduous tree	55 - 125	Unpublished data	< 0.3	Iso, MT	Genard- (2014)
<i>arborea</i>	June	43°10'44.3"N 5°34'16.2"E	None	Shrub	Unknown		19.0	Iso	Owen et
<i>coccifera</i>	September	43°56'06.0"N 5°42'37.7"E	None	Shrub	538	Arianoutsou (1989)	5.5 - 14.6	Iso>MT, ST	Owen & Staudt &
	June	43°14'27.1"N 5°40'33.3"E	None	Evergreen broad leaf tree	180 - 250	Bello et al. (1992)	15.0 - 21.0	MT>ST	Kesselm (1999)
<i>pubescens</i>	January	43°10'44.3"N 5°34'16.2"E	None	Deciduous tree	166 <sup>b</sup>	Saunier et al. (2018)	90.0	Iso	Kesselm Saunier c
<i>suber</i>	June	43°15'19.2"N 6°13'06.3"E	None	Evergreen broad leaf tree	349	Robert et al. (1996)	0.2 - 30.0	MT	Pio et al. Osorio e
<i>suber</i>	June	43°21'54.9"N 5°25'30.9"E	None	Shrub	323	Rodriguez-Ramirez et al. (2017)	9.0 - 14.0	Iso	Owen et

144 carried out after rain events to avoid excess of humidity. Average litter humidity was  $9.6 \pm 1.2$  %  
 145 ( $\pm$  standard error).

146 Seven of the studied species do not possess specific terpene storage structures (*Acer*  
 147 *monspessulanum* L., *Erica arborea*, L., *Q. coccifera*, *Quercus ilex* L., *Quercus pubescens* Willd.,  
 148 *Quercus suber* L., *Ulex parviflorus* Pourr.). Nine species possess terpene storage structures internal  
 149 to the leaf (*Eucalyptus globulus* Labill., *Juniperus oxycedrus* L., *P. halepensis*, *P. pinea*) or external  
 150 to the leaf (*Cistus albidus* L., *Cistus salviifolius* L., *Cotinus coggygia* Scop., *R. officinalis*, *Thymus*  
 151 *vulgaris* L.,

Species	Collection	GPS Coordinates	Storage structure	Plant Functional Type	Leaf litter production		Green leaves emission		
					$\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$	Reference	$\mu\text{g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	Type	Reference
<i>...s</i>	April	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	673	Rodriguez-Ramirez et al. (2017)	0.1 - 4.5	MT>ST	Owen & Ormeno
<i>...folius</i>	June	43°10'44.3"N 5°34'16.2"E	Glandular trichome	Shrub	Unknown		3.1	MT>ST	Owen et al.
<i>...pygria</i>	November	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	117	Unpublished data	Unknown	Unknown	
<i>...lobulus</i>	November	43°04'13.5"N 5°51'12.3"E	Subdermal oil glands	Evergreen broad leaf tree	250 - 370	Arianoutsou (1989)	5.4 - 42.0	MT>ST	He et al. & Pio (2000)
<i>...cedrus</i>	August	43°14'27.1"N 5°40'33.3"E	Secretory cavities	Evergreen needle leaf tree	Unknown		0.5 - 2.3	Iso>MT>ST	Owen & Ormeno
<i>...nsis</i>	August	43°56'06.0"N 5°42'37.7"E	Secretory cavities	Evergreen needle leaf tree	340 <sup>a</sup>	Arianoutsou & Radea (2000)	3.0 - 15.0	MT>ST	Owen & Ormeno & Llusia et al.
	August	43°17'22.1"N 5°24'35.2"E	Secretory cavities	Evergreen needle leaf tree	240 - 790	Arianoutsou & Radea (2000)	3.4 - 8.8	MT>ST	Street et al. & Hewitt
<i>...officinalis</i>	August	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	385	Rodriguez-Ramirez et al. (2017)	2.2 - 5.0	MT>ST	Owen & Ormeno
<i>...aris</i>	July	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	Unknown		3.6	MT>ST	Parra et al.
<i>...ssulanum</i>	November	43°56'06.0"N 5°42'37.7"E	None	Deciduous tree	55 - 125	Unpublished data	< 0.3	Iso, MT	Genard-Dejeu & Pio (2014)
<i>...a</i>	June	43°10'44.3"N 5°34'16.2"E	None	Shrub	Unknown		19.0	Iso	Owen et al.
<i>...cifera</i>	September	43°56'06.0"N 5°42'37.7"E	None	Shrub	538	Arianoutsou (1989)	5.5 - 14.6	Iso>MT, ST	Owen & Staudt & Ormeno
	June	43°14'27.1"N 5°40'33.3"E	None	Evergreen broad leaf tree	180 - 250	Bello et al. (1992)	15.0 - 21.0	MT>ST	Kesselmeier et al. (1999)
<i>...escens</i>	January	43°10'44.3"N 5°34'16.2"E	None	Deciduous tree	166 <sup>b</sup>	Saunier et al. (2018)	90.0	Iso	Kesselmeier & Saunier et al.
<i>...er</i>	June	43°15'19.2"N 6°13'06.3"E	None	Evergreen broad leaf tree	349	Robert et al. (1996)	0.2 - 30.0	MT	Pio et al. & Osorio et al.
<i>...rus</i>	June	43°21'54.9"N 5°25'30.9"E	None	Shrub	323	Rodriguez-Ramirez et al. (2017)	9.0 - 14.0	Iso	Owen et al.

153 **Table 1** – Species studied, family they belong to, data when litter was collected and location, presence of storage structures in leaves, leaf litter  
 154 production, green leaf emission rate and type according to literature. Species are classified according to the presence or absence of specific terpene-  
 155 storage structures and alphabetically ordered.

	Species name	Collection	GPS Coordinates	Storage structure	Plant Functional Type	Leaf litter production		Green leaves emission		
						g.m <sup>-2</sup> .y <sup>-1</sup>	Reference	µg.g <sup>-1</sup> .h <sup>-1</sup>	Type	Reference
TERPENES STORING SPECIES	<i>Cistus albidus</i>	April	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	673	Rodriguez-Ramirez et al. (2017)	0.1 - 4.5	MT>ST	Owen & Hewit (2000); Ormeno et al. (2007a)
	<i>Cistus salviifolius</i>	June	43°10'44.3"N 5°34'16.2"E	Glandular trichome	Shrub	Unknown		3.1	MT>ST	Owen et al. (2001)
	<i>Cotinus coggygria</i>	November	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	117	Unpublished data	Unknown	Unknown	
	<i>Eucalyptus globulus</i>	November	43°04'13.5"N 5°51'12.3"E	Subdermal oil glands	Evergreen broad leaf tree	250 - 370	Arianoutsou (1989)	5.4 - 42.0	MT>ST	He et al. (2000); Nunes & Pio (2001)
	<i>Juniperus oxycedrus</i>	August	43°14'27.1"N 5°40'33.3"E	Secretory cavities	Evergreen needle leaf tree	Unknown		0.5 - 2.3	Iso>MT>ST	Owen & Hewit (2000)
	<i>Pinus halepensis</i>	August	43°56'06.0"N 5°42'37.7"E	Secretory cavities	Evergreen needle leaf tree	340 <sup>a</sup>	Arianoutsou & Radea (2000)	3.0 - 15.0	MT>ST	Ormeno et al. (2007a); Llusia and Peñuelas (2000)
	<i>Pinus pinea</i>	August	43°17'22.1"N 5°24'35.2"E	Secretory cavities	Evergreen needle leaf tree	240 - 790	Arianoutsou & Radea (2000)	3.4 - 8.8	MT>ST	Street et al. (1997); Owen & Hewit (2000)
	<i>Rosmarinus officinalis</i>	August	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	385	Rodriguez-Ramirez et al. (2017)	2.2 - 5.0	MT>ST	Owen & Hewit (2000); Ormeno et al. (2007a)
	<i>Thymus vulgaris</i>	July	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	Unknown		3.6	MT>ST	Parra et al. (2004)
NON TERPENES STORING SPECIES	<i>Acer monspessulanum</i>	November	43°56'06.0"N 5°42'37.7"E	None	Deciduous tree	55 - 125	Unpublished data	< 0.3	Iso, MT	Genard-Zielinski et al. (2014)
	<i>Erica arborea</i>	June	43°10'44.3"N 5°34'16.2"E	None	Shrub	Unknown		19.0	Iso	Owen et al. 1997
	<i>Quercus coccifera</i>	September	43°56'06.0"N 5°42'37.7"E	None	Shrub	538	Arianoutsou (1989)	5.5 - 14.6	Iso>MT, ST	Owen & Hewit (2000); Staudt & Lhoutellier (2011)
	<i>Quercus ilex</i>	June	43°14'27.1"N 5°40'33.3"E	None	Evergreen broad leaf tree	180 - 250	Bello et al. (1992)	15.0 - 21.0	MT>ST	Kesselmeier and Staudt (1999)
	<i>Quercus pubescens</i>	January	43°10'44.3"N 5°34'16.2"E	None	Deciduous tree	166 <sup>b</sup>	Saunier et al. (2018)	90.0	Iso	Kesselmeier et al. (1999); Saunier et al. (2017b)
	<i>Quercus suber</i>	June	43°15'19.2"N 6°13'06.3"E	None	Evergreen broad leaf tree	349	Robert et al. (1996)	0.2 - 30.0	MT	Pio et al. (2005); Sánchez - Osorio et al. (2019)
	<i>Ulex parviflorus</i>	June	43°21'54.9"N 5°25'30.9"E	None	Shrub	323	Rodriguez-Ramirez et al. (2017)	9.0 - 14.0	Iso	Owen et al. (2001)

156 Iso: isoprene; MT : monoterpenes, ST : sesquiterpenes

157 <sup>a</sup> calculated mean (150 -530 g.m<sup>-2</sup>.y<sup>-1</sup>) from Arianoutsou and Radea (2000)

158 <sup>b</sup> calculated mean (138 -194 g.m<sup>-2</sup>.y<sup>-1</sup>) from Saunier et al. (2018)

159 2.2. Collection of BVOC emissions from litter

160 A dynamic pull-push system was used to collect BVOC released by litter. This system is  
161 composed by 2 Pyrex® jars of 1.2 L each and a system that continuously flushes air inside these  
162 jars. The air flushed into each jar was previously filtered with both drierite (W.A.  
163 Hammond Drierite™ Indicating Absorbents Mesh size 8, USA) to avoid the excess of humidity  
164 inside the system, and activated charcoal (Untreated, Mesh 4-8, Sigma Aldrich, USA) to remove  
165 VOC from ambient air. Finally, the air goes through a particle filter treated with sodium thiosulfate  
166 to remove the O<sub>3</sub> that could interact with BVOC emitted by litter.

167 Ten grams of freshly collected litter were placed inside a jar, leaving the other one empty to  
168 check for the absence of VOC in the air flushed through the jars (blank measurement). We used  
169 between 3 to 10 replicates per species, and emissions were collected once for each replicate. The  
170 emission factor of litter (standardized emission rate at 30 °C; Guenther et al., 2006) was measured  
171 by placing the jars inside a stove at 30 °C. Temperature and air humidity were measured with an  
172 iButton ® (Hygrochron, Maxim Integrated iButtons, USA) placed inside each jar. Before  
173 measurements took place, air inside the jars was renewed (1 L.min<sup>-1</sup> during 30 min) to avoid  
174 sampling BVOC that would initially be inside the jar. During VOC sampling, flow inside and  
175 outside the jar was set up to 0.2 L.min<sup>-1</sup> for 20 min. We used Mass Flow Controllers (MFC, EL-  
176 Flow select, Bronkhorst France, 0-1 L. min<sup>-1</sup>) to control the flows. The air coming out of each jar  
177 was collected onto glass cartridges (20 cm height; 10.5 mm external diameter, Gerstel®, Germany)  
178 filled with two kind of adsorbents : Tenax TA (50 mg; Agilent technologies; 20 - 35 Mesh) and  
179 Carbotrap B (120 mg; Carbotrap Graphitized Carbon Black n°20287; Sigma Aldrich). Before use,  
180 cartridges were conditioned at 300 °C for 3 h with a constant nitrogen flow (Nitrogen 4.5, purity  
181 99.995 %) using a cartridge conditioner (TERA environment; RT-12-CN-3601-01). After BVOC  
182 collection, cartridges were sealed and put inside a freezer at -4 °C until being analyzed by GC-MS  
183 (see below).

184 Between samplings, the Pyrex jars were rinsed with water, then with ethanol (70 %) and  
185 finally put inside a muffle furnace for 4 h at 400 °C to ensure full VOC and plant debris removal  
186 that could influence the following samples. Blanks were performed for confirmation.

### 187 2.3. Chemical analysis

188 BVOC were analyzed using a Gas Chromatography (GC, 6890N, Agilent Technologies®)  
189 coupled to a Mass Spectrometer Detector (MSD 5973, Agilent Technologies ®). BVOC trapped  
190 in the cartridges were desorbed by a thermodesorber using a ramp of temperature from 50 °C to  
191 250 °C at the rate of 3 °C.s<sup>-1</sup> for 15 min (TDS3/CIS4, Gerstel®), using helium as carrier gas (50  
192 mL.min<sup>-1</sup>). BVOC were then trapped in the Cooled Injection System (CIS) at 6.8 Psi pressure at  
193 - 50 °C using liquid nitrogen. Then, the CIS was rapidly heated (25 s) from -50 °C to 250 °C  
194 allowing molecule passage to the chromatographic column (HP5-MS, 30 m length, 0.25 mm  
195 diameter, 0.25 µm film thickness, Agilent Technologies®). Molecules were separated using a ramp  
196 of temperature from 40 °C to 280 °C with a rate of 3 °C.min<sup>-1</sup> with a constant helium flow of 1.0  
197 mL.min<sup>-1</sup>. The method accuracy (101.27 %) and precision (4.7 %) were determined through  
198 replicate analyses (dodecane). The calibration linearity or coefficient of determination (R<sup>2</sup> =  
199 0.9935, CV = 0.0019) and the limit of detection (LOD = 0.10 ng) were determined using standard  
200 calibrations. Molecule identification in chromatograms (Suppl. Figure 2) was achieved using  
201 spectral libraries (NIST library), spectra from injected standards of high purity (> 99 %, Sigma  
202 Aldrich®, France, Suppl Table 1 & 2), and by comparison of our experimental and theoretical  
203 Kovats index from Adams (2007).

### 204 2.4. Scanning electron microscopy

205 Since we did not find any data on the type of leaf terpene storage structures in *C. coggygria*,  
206 we explored its litter surface (abaxial side) using a Scanning Electron Microscopy (SEM, model  
207 XL30 ESEM from FEI). Small surfaces of leaf litter were fastened with adhesive tape on brass  
208 stubs and then gold coated in a metallizer using a Cressington 108 Sputter Coater.

### 209 2.5. Calculation of regional litter emission, global POCP and SOAP of *P. halepensis* and *Q.* 210 *pubescens*

211 In order to assess the impact of litter emission on air quality, we calculated three indicators.  
212 First, we estimated the regional litter BVOC emissions (t.y<sup>-1</sup>) for the Sud-PACA region according  
213 to the following equation:

$$214 \text{ Regional litter BVOC emissions} = \frac{ER \times 8760 \times \text{Litter production} \times \text{Surface}}{10^9} \quad (1)$$

215 where, *ER* refers to emission rates (µg.g<sub>DM</sub><sup>-1</sup>.h<sup>-1</sup>) reported in this study, 8760 refers to the hours in  
216 one year, *Litter production* refers to annual litter production (g.m<sup>-2</sup>) noted in Table 1, the *Surface*

217 refers to the forest area (m<sup>2</sup>) (IGN 2014-2018) occupied by each species in the Sud-PACA region  
218 and 10<sup>9</sup> is used to express results in ton. Second, for the two litter, we have calculated the  
219 photochemical ozone creation potential (POCP) and the potential secondary organic aerosol  
220 production (SOAP) using the following equations:

$$221 \quad POCP = \sum_{n=i} [contribution (\%)_i \times POCP_i] \quad (2)$$

$$222 \quad SOAP = \sum_{n=i} [contribution (\%)_i \times SOAP_i] \quad (3)$$

223 where, *contribution (%)<sub>i</sub>* refers to the relative contribution of the BVOC *i* to the litter emission  
224 under study, *POCP<sub>i</sub>* refers to the individual POCP of the BVOC *i* as reported in the Suppl. Table  
225 6 and *SOAP<sub>i</sub>* refers to individual SOAP of the BVOC *i* as reported in the Suppl. Table 6,

226 The POCP for individual VOC were reported from Dominutti et al. (2019). Unfortunately,  
227 POCP values were missing for monoterpenes and sesquiterpenes. Thus, as suggested by several  
228 authors, the isoprene POCP value (109.2) was also used for monoterpenes, because of their  
229 chemical similarity (Huang et al., 2017; Dominutti et al., 2019). The same reasoning was applied  
230 in this work for sesquiterpenes for which the isoprene value was used. Likewise, the SOAP for  
231 individual VOC were reported from Derwent et al., (2010) but SOAP values were available in  
232 literature for only two monoterpenes having similar values ( $\alpha$ -pinene: 17.4 and  $\beta$ -pinene: 18.1).  
233 They were missing for the other monoterpenes and sesquiterpenes. As suggested by Dominutti et  
234 al. (2019), the SOAP value of  $\beta$ -pinene was used in the present work for all the monoterpenes  
235 because of their similar chemical properties. The SOAP values of individual sesquiterpenes were  
236 estimated from their SOA Mass Yield, using SOAP and SOA Mass Yield of  $\alpha$ -pinene and isoprene  
237 as reference according to the following equation:

$$238 \quad SOAP_i = \frac{SOA\_M\_Y_i \times SOAP_{ref}}{SOA\_M\_Y_{ref}} \quad (4)$$

239 where, *SOAP<sub>i</sub>* and *SOA\_M\_Y<sub>i</sub>* are the SOAP and the SOA Mass Yield of the sesquiterpene *i*  
240 respectively, *SOAP<sub>ref</sub>* and *SOA\_M\_Y<sub>ref</sub>* are the SOAP and the SOA Mass Yield of the reference  
241 VOC. Because several SOA Mass Yields were available in literature for each sesquiterpene and  
242 reference VOC, the mean values were used (Suppl. Table 7). The calculated individual SOAP  
243 values obtained using the two reference VOC (isoprene and  $\alpha$ -pinene) were close and the mean  
244 values were used in the present work (Suppl. Table 7)

## 245 2.6. Statistical analysis

246 Differences and similarities in the BVOC emission profile between litter from different plant  
247 species were assessed using a Principal Component Analysis (PCA). The statistical analysis of the  
248 data was performed with R software (version 3.4.X, R Core Team 2017) using ade4, factoextra  
249 packages.

## 250 3. Results

### 251 3.1. BVOC emissions from leaf litter

252 Regarding total emissions, we identified a remarkable diversity with a total of 87 compounds,  
253 mainly terpenes (69 different compounds) followed by non-terpenic compounds (18 compounds)  
254 including alkanes, alkenes, aldehydes, ketones and benzenoids. Within each species, the bouquet  
255 of released compounds was also important for most species ranging from 4 emitted compounds in  
256 *Q. ilex* to 46 in *J. oxycedrus* (Suppl. Table 1 and 2). Terpene-storing species emitted an important  
257 diversity of compounds (mean:  $29 \pm 4$  compounds) with the most commonly emitted terpenes being  
258 limonene,  $\beta$ -caryophyllene,  $\alpha$ -pinene,  $\alpha$ -humulene and  $\alpha$ -terpinolene (Suppl. Table 1). By contrast,  
259 the non-terpene storing species emitted on average  $8 \pm 1$  compounds. Quantitatively, the studied  
260 species could be classified in 3 different groups based on their total emissions: *i*) negligible emitters  
261 ( $< 0.1 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) including *A. monspessulanum*, *Q. ilex*, *U. parviflorus*, *Q. suber* and *E. arborea*,  
262 *ii*) low emitters ( $0.1 < \text{emissions} < 1.0 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) including (in decreasing order) *R. officinalis*,  
263 *Q. pubescens*, *P. pinea*, *Q. coccifera*, *C. albidus*, *J. oxycedrus*, *C. salviifolius* and *E. globulus* and  
264 , *iii*) moderate emitters ( $1.0 < \text{emissions} < 5.0 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) including (in decreasing order) *T.*  
265 *vulgaris*, *C. coggygria* and *P. halepensis* (4.74; 3.37 and  $1.52 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$  respectively; Suppl.  
266 Table 3).

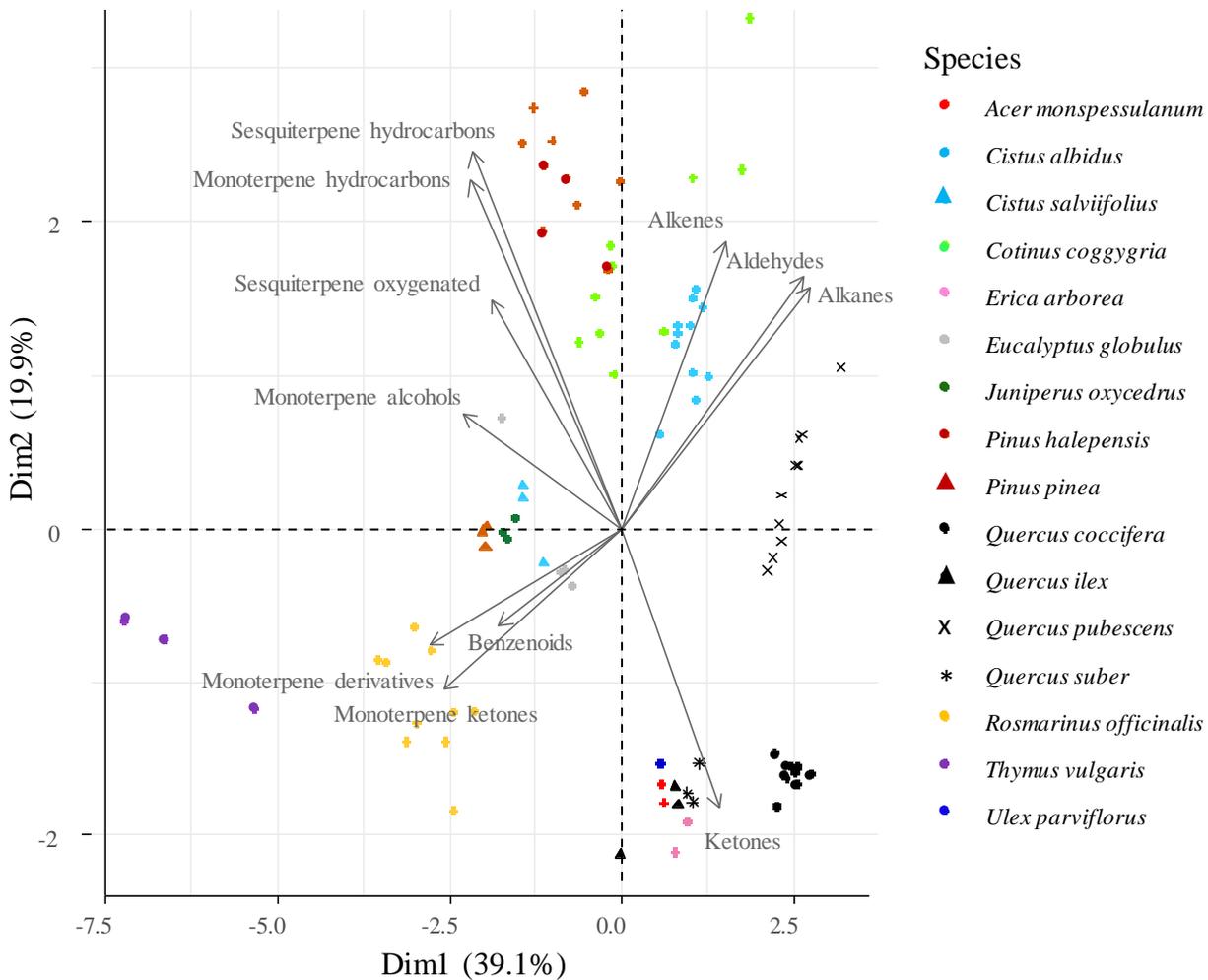
267 Terpene emissions only occurred from terpene-storing species. The highest terpene emitters  
268 were also *T. vulgaris*, *C. coggygria* and *P. halepensis* (4.74; 3.37;  $1.52 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$  respectively)  
269 whereas the remaining species emitted between 0.22 (*E. globulus*) and  $0.71 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$  (*R.*  
270 *officinalis*). Monoterpenes dominated emission from *T. vulgaris* ( $\alpha$ -terpinyl acetate,  $\alpha$ -terpineol,  
271 limonene, linalool and trans-4-thujanol) and *C. coggygria* (limonene, cis- $\beta$ -ocimene and myrcene)  
272 representing 98 % and 91 % respectively (Suppl. Table 1). By contrast, *P. halepensis* featured  
273 sesquiterpene emissions (61 % of total emissions), mainly  $\beta$ -caryophyllene and  $\alpha$ -humulene  
274 (Suppl. Table 1) and showed the highest sesquiterpene emission rates ( $0.92 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) of all  
275 species. Within each terpene emitter species, terpenes accounted for the major fraction in all

276 species, excepting *C. albidus* where terpene emissions ( $0.18 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) were close to non-  
277 terpenic emissions ( $0.11 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ; Suppl. Table 3).

278 All species released non-terpenic emissions (Suppl. Table 3; Suppl. Table 4), saturated  
279 aliphatic alkanes ( $\text{C}_{14}\text{H}_{30}$ ,  $\text{C}_{13}\text{H}_{28}$ ), followed by aldehydes (nonanal, decanal), representing the  
280 major fraction in most species (Suppl. Table 1 and 2). The most remarkable non-terpenic emissions  
281 occurred in *Q. pubescens* > *Q. coccifera* > *C. coggygia* ( $0.61$ ,  $0.32$  and  $0.23 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$   
282 respectively), followed by *P. halepensis* and *C. albidus* ( $0.16$  and  $0.11 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ , respectively).

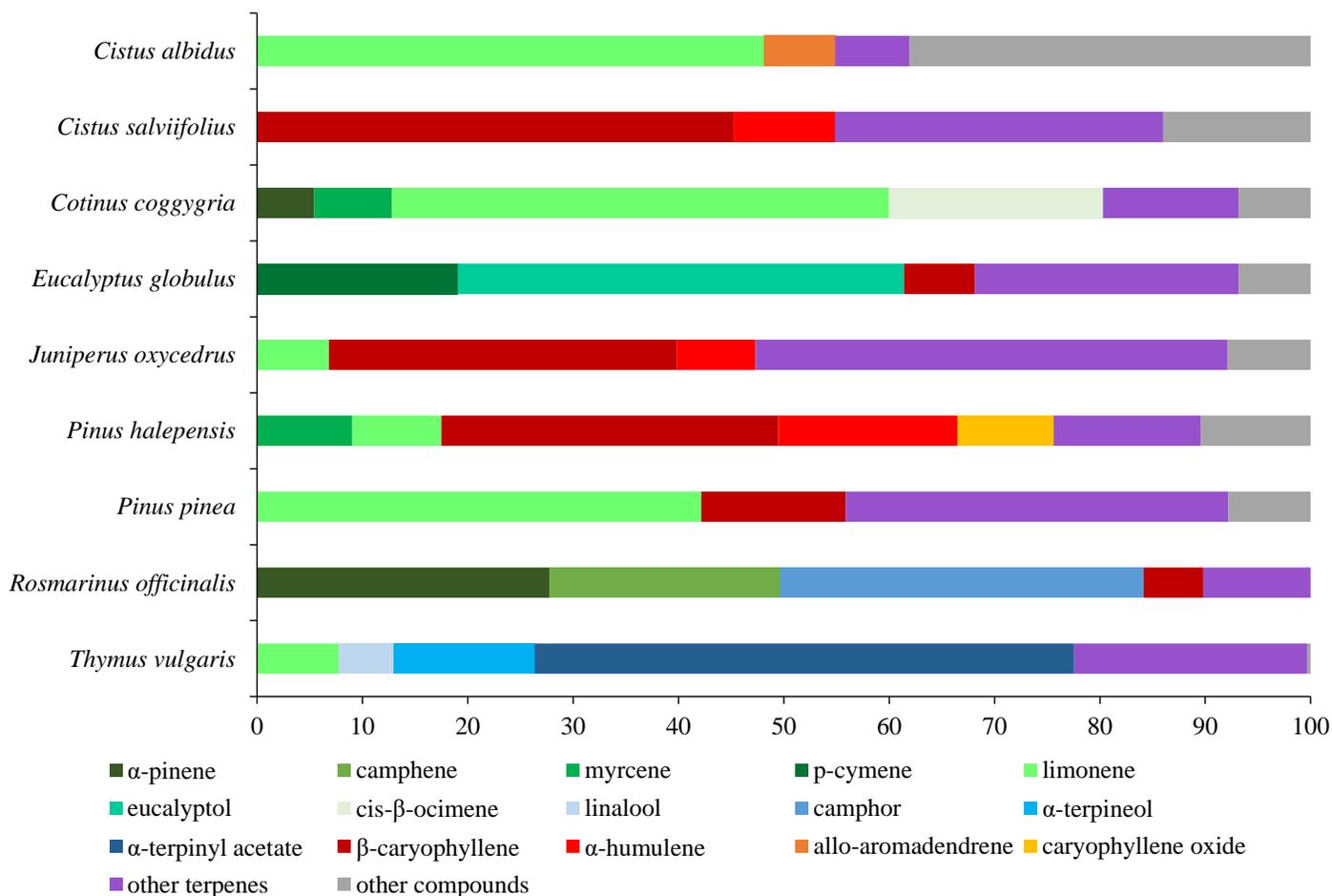
283 Species that do not possess terpene storage structures showed lower total BVOC emission  
284 rates than terpene storing species, with two exceptions, *Q. pubescens* and *Q. coccifera*, with total  
285 non-terpenic emission ( $0.61$  and  $0.32 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ , respectively) higher than total emissions of the  
286 terpene-storing species *C. albidus*, *C. salviifolius* and *J. oxycedrus*. ( $0.30$ ,  $0.21$  and  $0.21 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$   
287 <sup>1</sup>, respectively).

288 Clear differences occurred between species, even when they belong to the same genus  
289 (Figure 1). In *Pinus* spp, *P. halepensis* mainly emitted sesquiterpenes (60 % of total emission),  
290 with a large diversity of volatiles (27 compounds) and a total emission rate 3-times higher ( $1.52$   
291  $\mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) than *P. pinea* ( $0.54 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) which mainly released monoterpenes (60 % of total  
292 emissions) with a higher diversity (43 compounds) (Suppl. Table 3). *Quercus* spp.- the main source  
293 of non-terpenic emissions - showed a poorer diversity of BVOC (4-10 compounds) compared to  
294 *Pinus* spp. *Q. suber* and *Q. ilex* showed lower emission rates ( $< 0.1 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) compared to *Q.*  
295 *coccifera* and *Q. pubescens* ( $0.32$  and  $0.61 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) (Suppl. Table 4). *C. albidus* and *C.*  
296 *salviifolius* emitted BVOC in similar rates (Suppl. Table 3), but *C. albidus* mostly released  
297 monoterpenes (50 % of total emission) (mainly limonene, Suppl. Table 1), while *C. salviifolius*  
298 mainly released sesquiterpenes (71 % of total emission,  $\beta$ -caryophyllene and  $\alpha$ -humulene). Litter  
299 emission rates also exhibited some quantitative differences between samples of the same species,  
300 up to 5-times different in samples of *E. globulus*.



301  
 302 **Figure 1** – Principal Component Analysis showing litter BVOC profiles of the different species studied.  
 303 Litter samples are represented with symbols and variables are represented with arrows. Variables with the  
 304 highest weight in Dim 1 are alkanes and aldehydes on the right part of PC1, and monoterpene derivatives  
 305 and monoterpene ketones on the left part of Dim 1. Variables with the highest weight in Dim 2 are  
 306 sesquiterpene hydrocarbons and monoterpenes hydrocarbons on the top part of Dim 2. Weights of all  
 307 variables is shown in Suppl Table 3.

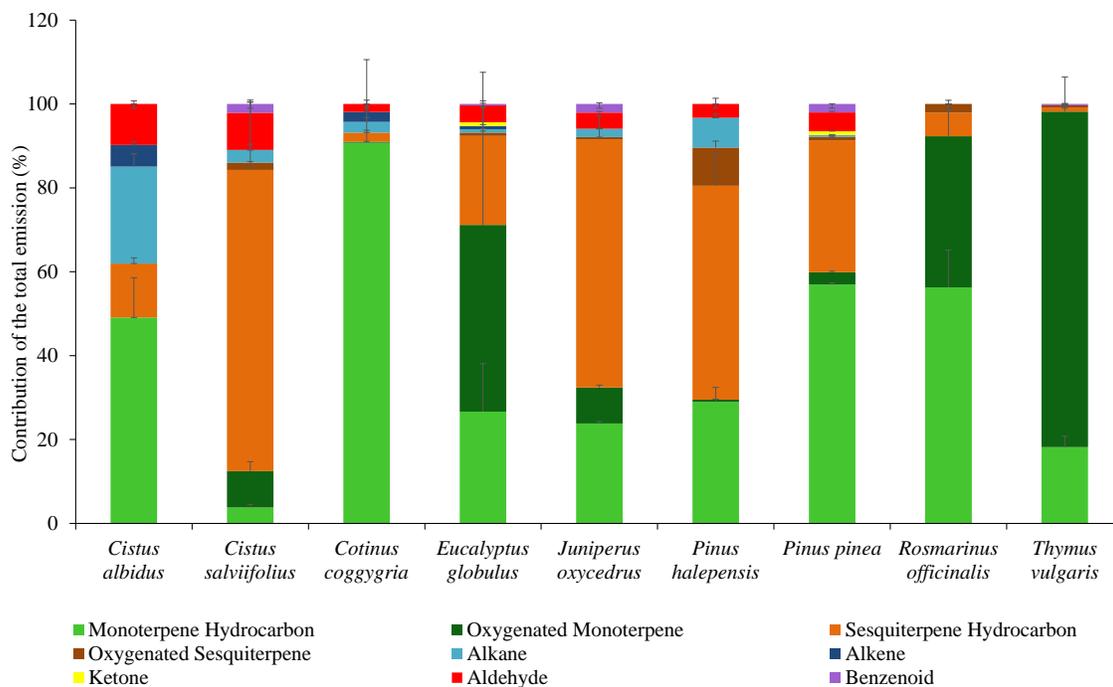
308 The sum of the most emitted terpenes (representing individually at least 5 % of the total  
 309 emission) contribute, at least, to half of the total emissions of a given species. For example, only  
 310 two and three terpenes account for ~ 50 % of total emissions from *J. oxycedrus* and the remaining  
 311 emissions were also characterized by terpene compounds, indicating that this species emits a large  
 312 diversity of terpenes in small quantities. By contrast, only four terpenes represent 90 % of total  
 313 emissions from *R. officinalis*, indicating few terpenes dominated emissions from this species  
 314 (Figure 2).



3\_\_

316 **Figure 2** – Contribution (%) of the major terpenes to the total emissions of nine plant species that possess  
 317 terpene storage structures. BVOC shown in the caption are ordered according to their molecular weight and  
 318 represent at least 5% of total emission of the species under study. Values are mean of n=3-10.

319 The contribution of each group of compounds to the total emission varied between species  
 320 (Figure 3 and Figure 4). Terpene emissions (monoterpene hydrocarbons, oxygenated  
 321 monoterpenes, sesquiterpene hydrocarbons and oxygenated sesquiterpenes) represented most of  
 322 the emissions for the species that possess terpene storage structures (Figure 3). For example, they  
 323 represent 62 % to 100 % of the total emission (*C. albidus* and *R. officinalis* respectively). By  
 324 contrast, for species that do not possess terpene storage structures, non terpenic emissions are the  
 325 most emitted compounds with alkanes and aldehydes being the major BVOC. *Quercus* spp. showed  
 326 major alkane emissions (54 % to 77 % of total emission for *Q. coccifera* and *Q. pubescens*) while  
 327 *A. monspessulanum*, *E. arborea* and *U. parviflorus* mostly emitted aldehydes (52 %, 46 % and  
 328 56 % respectively; Figure 4).

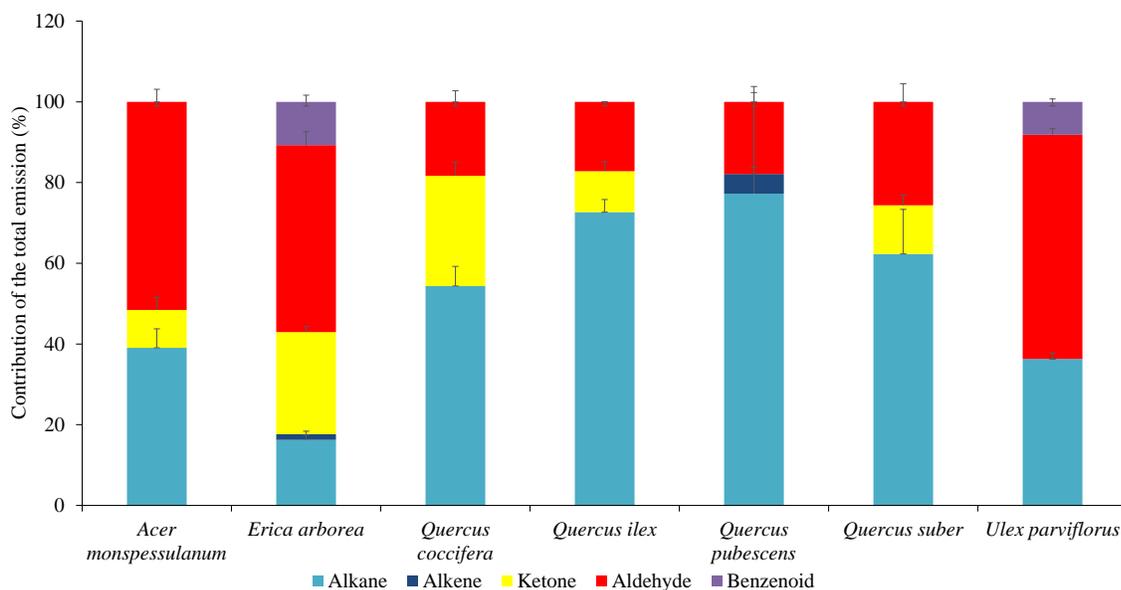


329

330

331 **Figure 3** – Contribution (%) of the compound groups (terpene and non-terpenic groups) to the total  
 332 emissions of nine species that possess terpene storage structures. Values are mean of n=3-10.

333



334

335 **Figure 4** – Contribution (%) of the compound groups to the total emissions of six species that do not possess  
 336 terpene storage structures. Values are mean of n=3-10.

337 3.2. Potential participation of *P. halepensis* and *Q. pubescens* litter BVOC to air quality at regional  
338 scale

339 The potential impact of the two main tree species in the Sud-PACA region on the regional  
340 air quality are assessed according to the three indicators previously described: their regional BVOC  
341 emissions ( $\text{t.y}^{-1}$ ) and their potential to form SOA and  $\text{O}_3$ . *P. halepensis* regional emissions represent  
342 almost 3 times those of *Q. pubescens* (8919 and 3158  $\text{t.y}^{-1}$  respectively, Table 2) and its POCP is  
343 2 times higher (96.2) than the POCP of *Q. pubescens* (47.7).

344 Despite the lower regional BVOC emissions from *Q. pubescens* litter, the SOAP calculated  
345 for both species is similar (36.9 and 37.5 for *P. halepensis* and *Q. pubescens* respectively). Indeed,  
346 on the one hand, *Q. pubescens* emissions are dominated by alkanes (pentadecane and tetradecane)  
347 which have the highest individual SOAP (54.5, Suppl. Table 6) but this high values are  
348 compensated by the SOAP value (zero) of aldehydes (second major group of BVOC from *Q.*  
349 *pubescens*). On the other hand, *P. halepensis* emissions are mainly constituted by monoterpenes  
350 and sesquiterpenes which have a lower individual SOAP (18 and 51.1 respectively, Suppl. Table  
351 6).

352 **Table 2** – Emission rates (ER) of the litter of *P. halepensis* and *Q. pubescens* and the estimation of their  
353 litter emission at a regional scale ( $\text{t.y}^{-1}$ ), their litter production ( $\text{g.m}^{-2}.\text{y}^{-1}$ ) and the global litter POCP and  
354 SOAP attributed

Plant species	Emission type <sup>a</sup>	ER ( $\mu\text{g.gDM}^{-1}.\text{h}^{-1}$ ) <sup>b</sup>	Litter production ( $\text{gDM.m}^{-2}.\text{y}^{-1}$ )	ER ( $\mu\text{g.gDM}^{-1}.\text{y}^{-1}$ )	ER ( $\text{g.m}^{-2}.\text{y}^{-1}$ ) <sup>e</sup>	Assessed regional BVOC emission ( $\text{t.y}^{-1}$ ) <sup>f</sup>	POCP <sup>g</sup>	SOAP <sup>g</sup>
<i>P. halepensis</i>	ST > MT > Ald > Alk	1.5	340 <sup>c</sup>	13300	4,5	8919	96.2	36.9
<i>Q. pubescens</i>	Alk > Ald	0.6	166 <sup>d</sup>	5340	0,9	3158	47.7	37.5

MT: monoterpenes; ST: sesquiterpenes; Ald: Aldehydes; Alk: Alkanes

<sup>a</sup> Emissions that represent at least 1% of total emissions

<sup>b</sup> Results from this study

<sup>c</sup> Arianoutsou & Radea (2000)

<sup>d</sup> Saunier et al. (2018)

<sup>e</sup> Obtained by multiplying the emission rate ( $\mu\text{g.gDM}^{-1}.\text{y}^{-1}$ ) by litter production

<sup>f</sup> Obtained by multiplying emission rates ( $\text{g.m}^{-2}.\text{y}^{-1}$ ) by the surface occupied by the plant species in the Sud-PACA region: 197000 ha for *P. halepensis* and 356000 ha for *Q. pubescens* according to to IGN 2014-2018

<sup>g</sup> Refer to material and methods for calculations and Suppl. Table 6 for SOAP and POCP of each compound

## 355 **4. Discussion**

356 This study shows that fresh leaf litter is a source of BVOC emissions with important  
357 differences between species but also within litter of a given species (up to 5-times). BVOC  
358 emissions from green leaves are indeed also characterized by an important variability within a  
359 species under the same environmental conditions. For example, the study from Genard-Zielinski  
360 et al. (2014) reported important inter-canopy differences (up to 4-times) for *Q. pubescens* under  
361 very similar conditions of light, temperature and air relative humidity in the field.

362 Results are discussed in the following subsections for all the species grouped according to  
363 their PFT as used in BVOC emission models (Guenther et al., 2006; Messina et al., 2016). Before  
364 that, it is worth to mention that results in the present work were obtained at an averaged litter  
365 humidity of 9.6 % which is close to previous published data for senescent leaves (8 % in Isidorov  
366 2003, 5-7 % Romero et al., 2019). Different litter humidity values would have probably led to  
367 higher emission rates considering the laboratory results from Greenberg et al (2012) on *Pinus*  
368 *ponderosa* needle litter (specific values not reported in their paper). Excluding Greenberg et al  
369 (2012), all other litter BVOC-related studies in the laboratory have been performed using a single  
370 humidity (8 % litter humidity of *Pinus sylvestris* in Isidorov 2003, 0 % humidity in 12 species in  
371 Gray et al., 2010).

### 372 *4.1. BVOC emissions from litter of evergreen needle leaf tree species*

373 *P. halepensis* showed one of the highest litter emission rates in the present study ( $1.52 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ )  
374  $^1\cdot\text{h}^{-1}$ ), in agreement with previous results on *P. sylvestris* non decomposed litter  $1.96 \mu\text{g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$   
375 (Isidorov et al., 2010), and contrasting to *P. pinea* (~ 3-times less emission rates). This difference  
376 could be partly explained by the terpene content within their leaf litter which is negligible in *P.*  
377 *pinea* ( $0.064 \text{ mg}\cdot\text{g}_{\text{DM}}^{-1}$ ) and high in *P. halepensis* ( $5 \text{ mg}\cdot\text{g}_{\text{DM}}^{-1}$ , Ormeño et al., 2009). The moderate  
378 emission rates of *P. halepensis* litter could significantly contribute to BVOC emissions at the scale  
379 of the Mediterranean region where it shows a rather important leaf litter production ( $150\text{-}530$   
380  $\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ ),

381 Table 1). *P. halepensis* could also remarkably contribute to total BVOC in local areas such as

Species	Collection	GPS Coordinates	Storage structure	Plant Functional Type	Leaf litter production		Green leaves emission		
					g.m <sup>-2</sup> .y <sup>-1</sup>	Reference	µg.g <sup>-1</sup> .h <sup>-1</sup>	Type	Reference
<i>P. halepensis</i>	April	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	673	Rodriguez-Ramirez et al. (2017)	0.1 - 4.5	MT>ST	Owen & Ormeno
<i>P. halepensis</i>	June	43°10'44.3"N 5°34'16.2"E	Glandular trichome	Shrub	Unknown		3.1	MT>ST	Owen et al.
<i>P. halepensis</i>	November	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	117	Unpublished data	Unknown	Unknown	
<i>P. halepensis</i>	November	43°04'13.5"N 5°51'12.3"E	Subdermal oil glands	Evergreen broad leaf tree	250 - 370	Arianoutsou (1989)	5.4 - 42.0	MT>ST	He et al. & Pio (2000)
<i>P. halepensis</i>	August	43°14'27.1"N 5°40'33.3"E	Secretory cavities	Evergreen needle leaf tree	Unknown		0.5 - 2.3	Iso>MT>ST	Owen & Ormeno
<i>P. halepensis</i>	August	43°56'06.0"N 5°42'37.7"E	Secretory cavities	Evergreen needle leaf tree	340 <sup>a</sup>	Arianoutsou & Radea (2000)	3.0 - 15.0	MT>ST	Ormeno & Llusia et al.
<i>P. halepensis</i>	August	43°17'22.1"N 5°24'35.2"E	Secretory cavities	Evergreen needle leaf tree	240 - 790	Arianoutsou & Radea (2000)	3.4 - 8.8	MT>ST	Street et al. & Hewitt
<i>P. halepensis</i>	August	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	385	Rodriguez-Ramirez et al. (2017)	2.2 - 5.0	MT>ST	Owen & Ormeno
<i>P. halepensis</i>	July	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	Unknown		3.6	MT>ST	Parra et al.
<i>P. halepensis</i>	November	43°56'06.0"N 5°42'37.7"E	None	Deciduous tree	55 - 125	Unpublished data	< 0.3	Iso, MT	Genard-Dejeux et al. (2014)
<i>P. halepensis</i>	June	43°10'44.3"N 5°34'16.2"E	None	Shrub	Unknown		19.0	Iso	Owen et al.
<i>P. halepensis</i>	September	43°56'06.0"N 5°42'37.7"E	None	Shrub	538	Arianoutsou (1989)	5.5 - 14.6	Iso>MT, ST	Owen & Staudt et al.
<i>P. halepensis</i>	June	43°14'27.1"N 5°40'33.3"E	None	Evergreen broad leaf tree	180 - 250	Bello et al. (1992)	15.0 - 21.0	MT>ST	Kesselmeier et al. (1999)
<i>P. halepensis</i>	January	43°10'44.3"N 5°34'16.2"E	None	Deciduous tree	166 <sup>b</sup>	Saunier et al. (2018)	90.0	Iso	Kesselmeier & Saunier et al.
<i>P. halepensis</i>	June	43°15'19.2"N 6°13'06.3"E	None	Evergreen broad leaf tree	349	Robert et al. (1996)	0.2 - 30.0	MT	Pio et al. & Osorio et al.
<i>P. halepensis</i>	June	43°21'54.9"N 5°25'30.9"E	None	Shrub	323	Rodriguez-Ramirez et al. (2017)	9.0 - 14.0	Iso	Owen et al.

382 Southern France (PACA- Sud Region) were *P. halepensis* is especially present (231 000 ha,  
383 (Fernandez et al., 2013). Considering all the Western Mediterranean area, *P. halepensis* is more  
384 widespread (~3.5 million ha) than *P. pinea* (320 000 ha) (Quézel and Médail, 2003). Thereby, it is  
385 likely that litter from *P. halepensis* contributes more importantly to BVOC emissions than *P. pinea*  
386 in the Mediterranean region. Contrasting to leaf litter, literature shows higher emission rates from  
387 green leaves of *P. pinea* and *P. halepensis*, mainly represented by monoterpene compounds (

Species	Collection	GPS Coordinates	Storage structure	Plant Functional Type	Leaf litter production		Green leaves emission		
					$\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$	Reference	$\mu\text{g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	Type	Reference
<i>J. asperifolia</i>	April	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	673	Rodriguez-Ramirez et al. (2017)	0.1 - 4.5	MT>ST	Owen & Ormeno
<i>J. folius</i>	June	43°10'44.3"N 5°34'16.2"E	Glandular trichome	Shrub	Unknown		3.1	MT>ST	Owen et
<i>J. pygria</i>	November	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	117	Unpublished data	Unknown	Unknown	
<i>J. lobulus</i>	November	43°04'13.5"N 5°51'12.3"E	Subdermal oil glands	Evergreen broad leaf tree	250 - 370	Arianoutsou (1989)	5.4 - 42.0	MT>ST	He et al. Pio (200
<i>J. oxycedrus</i>	August	43°14'27.1"N 5°40'33.3"E	Secretory cavities	Evergreen needle leaf tree	Unknown		0.5 - 2.3	Iso>MT>ST	Owen &
<i>J. pensis</i>	August	43°56'06.0"N 5°42'37.7"E	Secretory cavities	Evergreen needle leaf tree	340 <sup>a</sup>	Arianoutsou & Radea (2000)	3.0 - 15.0	MT>ST	Ormeno Llusia ar
	August	43°17'22.1"N 5°24'35.2"E	Secretory cavities	Evergreen needle leaf tree	240 - 790	Arianoutsou & Radea (2000)	3.4 - 8.8	MT>ST	Street et al. & Hewit
<i>J. officinalis</i>	August	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	385	Rodriguez-Ramirez et al. (2017)	2.2 - 5.0	MT>ST	Owen & Ormeno
<i>J. parisi</i>	July	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	Unknown		3.6	MT>ST	Parra et
<i>J. sissulanum</i>	November	43°56'06.0"N 5°42'37.7"E	None	Deciduous tree	55 - 125	Unpublished data	< 0.3	Iso, MT	Genard- (2014)
<i>J. a</i>	June	43°10'44.3"N 5°34'16.2"E	None	Shrub	Unknown		19.0	Iso	Owen et
<i>J. cifer</i>	September	43°56'06.0"N 5°42'37.7"E	None	Shrub	538	Arianoutsou (1989)	5.5 - 14.6	Iso>MT, ST	Owen & Staudt &
	June	43°14'27.1"N 5°40'33.3"E	None	Evergreen broad leaf tree	180 - 250	Bello et al. (1992)	15.0 - 21.0	MT>ST	Kesselm (1999)
<i>J. escens</i>	January	43°10'44.3"N 5°34'16.2"E	None	Deciduous tree	166 <sup>b</sup>	Saunier et al. (2018)	90.0	Iso	Kesselm Saunier c
<i>J. er</i>	June	43°15'19.2"N 6°13'06.3"E	None	Evergreen broad leaf tree	349	Robert et al. (1996)	0.2 - 30.0	MT	Pio et al. Osorio e
<i>J. orus</i>	June	43°21'54.9"N 5°25'30.9"E	None	Shrub	323	Rodriguez-Ramirez et al. (2017)	9.0 - 14.0	Iso	Owen et

389 *J. oxycedrus* is a small tree found both in Mediterranean forest and garrigues. This species  
390 seems to contribute little to BVOC emissions since leaf litter emission rates ( $0.21 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) is  
391 low (

392 Table 1). This tree species possesses internal terpene storing structures and their content is

Species	Collection	GPS Coordinates	Storage structure	Plant Functional Type	Leaf litter production		Green leaves emission		
					$\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$	Reference	$\mu\text{g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	Type	Reference
<i>J. asperifolia</i>	April	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	673	Rodriguez-Ramirez et al. (2017)	0.1 - 4.5	MT>ST	Owen & Ormeno
<i>J. folius</i>	June	43°10'44.3"N 5°34'16.2"E	Glandular trichome	Shrub	Unknown		3.1	MT>ST	Owen et
<i>J. pygria</i>	November	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	117	Unpublished data	Unknown	Unknown	
<i>J. lobulus</i>	November	43°04'13.5"N 5°51'12.3"E	Subdermal oil glands	Evergreen broad leaf tree	250 - 370	Arianoutsou (1989)	5.4 - 42.0	MT>ST	He et al. Pio (200
<i>J. oxycedrus</i>	August	43°14'27.1"N 5°40'33.3"E	Secretory cavities	Evergreen needle leaf tree	Unknown		0.5 - 2.3	Iso>MT>ST	Owen &
<i>J. vasicis</i>	August	43°56'06.0"N 5°42'37.7"E	Secretory cavities	Evergreen needle leaf tree	340 <sup>a</sup>	Arianoutsou & Radea (2000)	3.0 - 15.0	MT>ST	Ormeno Llusia ar
	August	43°17'22.1"N 5°24'35.2"E	Secretory cavities	Evergreen needle leaf tree	240 - 790	Arianoutsou & Radea (2000)	3.4 - 8.8	MT>ST	Street et al. & Hewit
<i>J. officinalis</i>	August	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	385	Rodriguez-Ramirez et al. (2017)	2.2 - 5.0	MT>ST	Owen & Ormeno
<i>J. parisi</i>	July	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	Unknown		3.6	MT>ST	Parra et
<i>J. sssulanum</i>	November	43°56'06.0"N 5°42'37.7"E	None	Deciduous tree	55 - 125	Unpublished data	< 0.3	Iso, MT	Genard- (2014)
<i>J. a</i>	June	43°10'44.3"N 5°34'16.2"E	None	Shrub	Unknown		19.0	Iso	Owen et
<i>J. cifera</i>	September	43°56'06.0"N 5°42'37.7"E	None	Shrub	538	Arianoutsou (1989)	5.5 - 14.6	Iso>MT, ST	Owen & Staudt &
	June	43°14'27.1"N 5°40'33.3"E	None	Evergreen broad leaf tree	180 - 250	Bello et al. (1992)	15.0 - 21.0	MT>ST	Kesselm (1999)
<i>J. escens</i>	January	43°10'44.3"N 5°34'16.2"E	None	Deciduous tree	166 <sup>b</sup>	Saunier et al. (2018)	90.0	Iso	Kesselm Saunier c
<i>J. er</i>	June	43°15'19.2"N 6°13'06.3"E	None	Evergreen broad leaf tree	349	Robert et al. (1996)	0.2 - 30.0	MT	Pio et al. Osorio e
<i>J. orus</i>	June	43°21'54.9"N 5°25'30.9"E	None	Shrub	323	Rodriguez-Ramirez et al. (2017)	9.0 - 14.0	Iso	Owen et

393 often used to produce essential oil. However, terpene emissions from litter contrast with literature  
 394 on its needle essential oil content which is characterized by monoterpenes (41 % of total emission;  
 395 Dob et al., 2006) while its litter emits mostly sesquiterpenes (57 % of total emission; Figure 3).  
 396 The green leaves of *J. oxycedrus* also emits different types of BVOC including isoprene, which  
 397 can not be produced by the litter, monoterpenes and sesquiterpenes, its emission can reach 2.3  
 398  $\mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ . The difference of emission between green leaves and litter might also be explained by  
 399 the thickness of the cuticle of this species (Vasic and Dubak, 2012) that could act as a barrier for  
 400 the emission when still intact.

401 4.2. BVOC emissions from litter of evergreen broad leaf tree species

402 Litter of *Q. ilex* and *Q. suber* released non-terpenic compounds only such as fatty acids  
403 derivatives (alkanes, alkenes) probably emitted by the cuticle present on top of the leaf litter  
404 (Maffei, 1994). Green leaves of these *Quercus* spp. are known to release high monoterpene  
405 emission which require photosynthesis to occur, own to the absence of monoterpene reservoirs  
406 within their foliage (Kesselmeier and Staudt, 1999). Such feature explains the absence of terpene  
407 emissions from their freshly collected leaf litter. It can be concluded that evergreen forests of  
408 *Quercus* ssp. are a remarkable source of terpene compounds from the canopy as shown in literature  
409 and a minor source of non-terpenic compounds from litter, although this could be moderated by  
410 their abundance and litter production.

411 *E. globulus* litter showed a rather low emission rate ( $0.20 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) dominated by  
412 monoterpenes. Contrastingly, Gray et al. (2010) showed that *Eucalyptus* litter released very high  
413 amounts of monoterpenes ( $0.4 \mu\text{mol}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ), which represents  $54.4 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ . In their study,  
414 litter had been previously oven-dried at  $60^\circ\text{C}$  and litter leaves were cut into small pieces triggering  
415 monoterpene emissions from litter and accumulation in the head space system they used (125 mL  
416 jars). It is important to note that the authors explicitly indicate that they aimed to compare litter  
417 emission rates between species not to accurately quantify them. *E. globulus* canopy is a major  
418 source of isoprene ( $38 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ; Keenan et al., 2009) with some monoterpene emissions too ( $2.7$   
419  $\mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ). Moreover, terpene content of green leaves of *E. globulus* is very high ( $25 \text{mg}\cdot\text{g}_{\text{DM}}^{-1}$ )  
420 contrasting with the leaf litter emission we measured. Since several authors (Wilt et al., 1993;  
421 Romero et al., 2019) showed a good agreement between terpene content in leaf litter and green  
422 leaves of numerous species, one can expect that terpene content in litter of *E. globulus* is also very  
423 high. We argue that such discrepancy (between low emission rates found in this study and high  
424 terpene content in green leaves reported in literature) is maybe due to the thick cuticles of fully  
425 expanded leaves of *E. globulus* (Johnson, 1926), since the cuticle limits BVOC diffusion from leaf  
426 tissues to the atmosphere (Joensuu et al., 2016).

#### 427 4.3 BVOC emissions from litter of deciduous tree species

428 Leaf litter from *Q. pubescens* showed a low emission rate ( $0.61 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) with only non-  
429 terpenic emissions, mostly low chain fatty acids derivatives (alkanes, alkenes). Contrastingly,  
430 green leaves of *Q. pubescens* are a remarkable source of isoprene emissions with emissions of fully  
431 expanded leaves ranging from 78.5 to  $124.3 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$  at  $30^\circ\text{C}$  (Genard-Zielinski et al., 2014;  
432 Saunier et al., 2017a). According to the European inventory of BVOC emissions (Keenan et al.,

433 2009), *Q. pubescens* is the second major isoprene emitting species. Isoprene requires *de novo*  
434 formation to be produced (Sharkey and Yeh, 2001) since there is no specific storage of isoprene in  
435 leaves (probably due to its very high vapor pressure) explaining that it is not released by leaf litter.  
436 However, isoprene can be synthesized from soil microorganisms (as shown in the data base mVOC  
437 2.0; Lemfack et al., 2018) which probably explains why Warneke et al. (1999) showed isoprene  
438 emission from oak, beech, spruce, grass litter (although the authors did not detail whether it was  
439 fresh or decomposed litter). Despite the low non-terpenic emissions we reported for *Q. pubescens*,  
440 this species grows in highly widespread deciduous forests where litter production is moderate (153  
441  $\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ ; Suppl. Table 3), suggesting that *Q. pubescens* litter could contribute to some extent to air  
442 chemistry during the leaf abscission period (December-March in Mediterranean ecosystems).  
443 *Q. pubescens* abundance is especially important in Southern France where it occupies more than 2  
444 million ha only in the Sud-PACA (Saunier et al., 2017b).

445 Forests dominated by *A. monspessulanum* are probably a negligible source of BVOC  
446 emissions independently of the ecological compartment considered, since litter released the lowest  
447 emission rates ( $< 0.01 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ , all of them being non-terpenic) and green leaves release only  
448 negligible terpene emissions ( $< 0.5 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ; Ormeño et al., 2020; Genard-Zielinski et al., 2014).

#### 449 4.4 BVOC emissions from litter of shrub species

450 *T. vulgaris* released the highest terpene emission rates ( $4.72 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) similar to green leaf  
451 emissions ( $3.6 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ; Parra et al., 2004). Accordingly, *T. vulgaris* contains remarkable  
452 monoterpene concentrations in the glandular trichome of green leaves ( $22.0 \text{mg}\cdot\text{g}_{\text{DM}}^{-1}$ ; Nielsen et  
453 al., 2015). This major aromatic plant species largely widespread in Mediterranean garrigues, is thus  
454 probably an important source of BVOC in these ecosystems.

455 Interestingly, BVOC emissions from litter or green leaves of *C. coggygria* have never been  
456 studied despite *C. coggygria* leaves have been largely used for medicinal purposes own to its  
457 essential oil (Matić et al., 2016). This species naturally coexists in the understory vegetation of  
458 Mediterranean forests (Genard-Zielinski et al., 2014) and is highly used as ornamental plant in  
459 urban vegetation. We observed, for the first time, the presence of a capitate sessile trichome, a type  
460 glandular trichome, on the leaf abaxial (bottom) surface (Suppl. Fig 1) in agreement with other  
461 Anacardiaceae species (Metcalf and Chalk, 1988). Despite the presence of these structures, *C.*  
462 *coggygria* stores poor amounts of terpenes ( $0.3 \text{mg}\cdot\text{g}_{\text{DM}}^{-1}$ ) both, in leaf litter (Santonja et al., 2018)  
463 and green leaves (Romero et al., 2019).

464 *R. officinalis* appeared to be a low emitter ( $0.71 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ) with numerous monoterpenes.  
465 Green leaves of *R. officinalis* release low to moderate terpene emission rates ( $2.2 - 5.0 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ;  
466 Owen and Hewitt, 2000; Ormeño et al., 2007b) and store high amounts of terpenes ( $6.0 \text{mg}\cdot\text{g}_{\text{DM}}^{-1}$ ;  
467 Peñuelas and Llusà, 1997; Ormeño et al., 2007b). This result reveals that the presence of an  
468 important storage of terpenes does not necessarily implies a high emission rate from leaf litter  
469 although the underlying processes remain to be tested.

470 *C. albidus* and *C. salviifolius* showed low emission rates of both terpene and non-terpenic  
471 compounds ( $0.30$  and  $0.21 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$  each). Accordingly, terpene emissions from green leaves of  
472 *Cistus spp.* are low to moderate ( $0.5-5.0 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ; Owen et al., 2001; Ormeño et al., 2007a), and  
473 store low terpene amounts ( $0.8 \text{mg}\cdot\text{g}_{\text{DM}}^{-1}$ ; Ormeño et al., 2007b). Epicuticular wax coverage (very  
474 long chained and saturated wax components) in leaves of *C. albidus* is very high ( $200 \mu\text{g}\cdot\text{cm}^{-2}$ )  
475 and represents about 3.5 % of the leaf dry weight (Hennig et al., 1988). Such coverage, which is a  
476 mechanism to cope with the relative aridity that characterizes macchias and garigues, probably  
477 limits leaf litter terpene emissions too. Although litter from *Cistus spp.* releases low emission rates,  
478 its contribution to BVOC emissions in Mediterranean garrigue ecosystems could be compensated  
479 by a high litter production ( $673 \text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ;

Species	Collection	GPS Coordinates	Storage structure	Plant Functional Type	Leaf litter production		Green leaves emission		
					$\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$	Reference	$\mu\text{g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	Type	Reference
<i>Q. ilex</i>	April	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	673	Rodriguez-Ramirez et al. (2017)	0.1 - 4.5	MT>ST	Owen & Ormeno
<i>Q. robur</i>	June	43°10'44.3"N 5°34'16.2"E	Glandular trichome	Shrub	Unknown		3.1	MT>ST	Owen et al.
<i>Q. pygmaea</i>	November	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	117	Unpublished data	Unknown	Unknown	
<i>Q. lobulus</i>	November	43°04'13.5"N 5°51'12.3"E	Subdermal oil glands	Evergreen broad leaf tree	250 - 370	Arianoutsou (1989)	5.4 - 42.0	MT>ST	He et al. & Pio (2000)
<i>Q. pedunculata</i>	August	43°14'27.1"N 5°40'33.3"E	Secretory cavities	Evergreen needle leaf tree	Unknown		0.5 - 2.3	Iso>MT>ST	Owen & Ormeno
<i>Q. ilex</i>	August	43°56'06.0"N 5°42'37.7"E	Secretory cavities	Evergreen needle leaf tree	340 <sup>a</sup>	Arianoutsou & Radea (2000)	3.0 - 15.0	MT>ST	Owen & Ormeno & Llusia et al.
<i>Q. ilex</i>	August	43°17'22.1"N 5°24'35.2"E	Secretory cavities	Evergreen needle leaf tree	240 - 790	Arianoutsou & Radea (2000)	3.4 - 8.8	MT>ST	Street et al. & Hewitt
<i>Q. officinalis</i>	August	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	385	Rodriguez-Ramirez et al. (2017)	2.2 - 5.0	MT>ST	Owen & Ormeno
<i>Q. robur</i>	July	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	Unknown		3.6	MT>ST	Parra et al.
<i>Q. sessiliflora</i>	November	43°56'06.0"N 5°42'37.7"E	None	Deciduous tree	55 - 125	Unpublished data	< 0.3	Iso, MT	Genard-Dejean (2014)
<i>Q. ilex</i>	June	43°10'44.3"N 5°34'16.2"E	None	Shrub	Unknown		19.0	Iso	Owen et al.
<i>Q. coccifera</i>	September	43°56'06.0"N 5°42'37.7"E	None	Shrub	538	Arianoutsou (1989)	5.5 - 14.6	Iso>MT, ST	Owen & Staudt & Ormeno
<i>Q. ilex</i>	June	43°14'27.1"N 5°40'33.3"E	None	Evergreen broad leaf tree	180 - 250	Bello et al. (1992)	15.0 - 21.0	MT>ST	Kesselmeier (1999)
<i>Q. ilex</i>	January	43°10'44.3"N 5°34'16.2"E	None	Deciduous tree	166 <sup>b</sup>	Saunier et al. (2018)	90.0	Iso	Kesselmeier & Saunier et al.
<i>Q. ilex</i>	June	43°15'19.2"N 6°13'06.3"E	None	Evergreen broad leaf tree	349	Robert et al. (1996)	0.2 - 30.0	MT	Pio et al. & Osorio et al.
<i>Q. robur</i>	June	43°21'54.9"N 5°25'30.9"E	None	Shrub	323	Rodriguez-Ramirez et al. (2017)	9.0 - 14.0	Iso	Owen et al.

481 *Q. coccifera* also showed low emission rates (only non-terpenic emissions) but, again, its  
482 important litter production (

483 Table 1) could compensate for such low emissions at the ecosystem scale. Finally, *U.*

Species	Collection	GPS Coordinates	Storage structure	Plant Functional Type	Leaf litter production		Green leaves emission		
					$\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$	Reference	$\mu\text{g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	Type	Reference
<i>Ulex</i>	April	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	673	Rodriguez-Ramirez et al. (2017)	0.1 - 4.5	MT>ST	Owen & Ormeno
<i>Lotus</i>	June	43°10'44.3"N 5°34'16.2"E	Glandular trichome	Shrub	Unknown		3.1	MT>ST	Owen et al.
<i>Pygmaea</i>	November	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	117	Unpublished data	Unknown	Unknown	
<i>Quercus</i>	November	43°04'13.5"N 5°51'12.3"E	Subdermal oil glands	Evergreen broad leaf tree	250 - 370	Arianoutsou (1989)	5.4 - 42.0	MT>ST	He et al. & Pio (2000)
<i>Quercus</i>	August	43°14'27.1"N 5°40'33.3"E	Secretory cavities	Evergreen needle leaf tree	Unknown		0.5 - 2.3	Iso>MT>ST	Owen & Hewitt
<i>Quercus</i>	August	43°56'06.0"N 5°42'37.7"E	Secretory cavities	Evergreen needle leaf tree	340 <sup>a</sup>	Arianoutsou & Radea (2000)	3.0 - 15.0	MT>ST	Owen & Llusia et al.
<i>Quercus</i>	August	43°17'22.1"N 5°24'35.2"E	Secretory cavities	Evergreen needle leaf tree	240 - 790	Arianoutsou & Radea (2000)	3.4 - 8.8	MT>ST	Street et al. & Hewitt
<i>Quercus officinalis</i>	August	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	385	Rodriguez-Ramirez et al. (2017)	2.2 - 5.0	MT>ST	Owen & Ormeno
<i>Quercus</i>	July	43°56'06.0"N 5°42'37.7"E	Glandular trichome	Shrub	Unknown		3.6	MT>ST	Parra et al.
<i>Quercus subulatum</i>	November	43°56'06.0"N 5°42'37.7"E	None	Deciduous tree	55 - 125	Unpublished data	< 0.3	Iso, MT	Genard-Dejean (2014)
<i>Quercus</i>	June	43°10'44.3"N 5°34'16.2"E	None	Shrub	Unknown		19.0	Iso	Owen et al.
<i>Quercus coccifera</i>	September	43°56'06.0"N 5°42'37.7"E	None	Shrub	538	Arianoutsou (1989)	5.5 - 14.6	Iso>MT, ST	Owen & Staudt & Hewitt
<i>Quercus</i>	June	43°14'27.1"N 5°40'33.3"E	None	Evergreen broad leaf tree	180 - 250	Bello et al. (1992)	15.0 - 21.0	MT>ST	Kesselmeier (1999)
<i>Quercus</i>	January	43°10'44.3"N 5°34'16.2"E	None	Deciduous tree	166 <sup>b</sup>	Saunier et al. (2018)	90.0	Iso	Kesselmeier & Saunier et al.
<i>Quercus</i>	June	43°15'19.2"N 6°13'06.3"E	None	Evergreen broad leaf tree	349	Robert et al. (1996)	0.2 - 30.0	MT	Pio et al. & Osorio et al.
<i>Quercus</i>	June	43°21'54.9"N 5°25'30.9"E	None	Shrub	323	Rodriguez-Ramirez et al. (2017)	9.0 - 14.0	Iso	Owen et al.

484 *parviflorus* and the *E. arborea* showed negligible BVOC emissions ( $<0.04 \mu\text{g}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ ), while  
485 green leaves release high isoprene emissions (Owen and Hewitt, 2000). Since these species are not  
486 the most commonly found in garrigues their litter is unlikely to contribute significantly to the whole  
487 BVOC budget at the ecosystem scale.

#### 488 4.5. Environmental implications of BVOC emissions from litter

489 According to our study, most emitted terpene compounds were limonene,  $\beta$ -caryophyllene,  
490  $\alpha$ -pinene and  $\alpha$ -humulene, in agreement with Leff and Fierer, (2008) and emissions from green  
491 leaves (Owen et al., 2001). We note that highly volatile compounds such as methanol,  
492 acetaldehyde, acetic acid, formic acid and acetone, are also commonly released by leaf litter alone  
493 (Gray et al., 2010; Greenberg et al., 2012; Tang et al., 2019) or soil and litter together (Schade and  
494 Goldstein, 2001) but these highly volatile compounds were not screened in our study.

495 The influence of BVOC emissions from soil (litter included) on secondary air pollution and  
496 the oxidizing capacity of the atmosphere are, by far, less well understood than their emission rates.  
497 Terpenes found in our study are known to take part of cloud condensation nuclei formation leading  
498 to the production of SOA (Hartz et al., 2005). The SOA mass yield (%) varies according to the  
499 species:  $\beta$ -caryophyllene,  $\alpha$ -humulene and  $\alpha$ -pinene have a high SOA mass yield (respectively  
500 45 %, 45 % and 41 %), while monoterpenes such as  $\beta$ -pinene or myrcene have a smaller SOA mass  
501 yield (17 % and 11 % respectively; Lee et al., 2006). It is important to highlight that BVOC from  
502 litter extend the seasonal period where BVOC are emitted from the ecosystem and so participate  
503 to SOA formation (Faiola et al., 2014) since the canopy of deciduous broadleaf species do not  
504 contribute to BVOC emissions through the entire seasonal cycle.

505 Although litter is a source of BVOC, part of the emission is adsorbed or assimilated through  
506 soil-related processes (Ramirez et al., 2010) and part readily reacts with atmospheric oxidants. For  
507 example, most commonly emitted terpenes in this study (limonene,  $\beta$ -caryophyllene,  $\alpha$ -pinene and  
508  $\alpha$ -humulene) feature high reactivity with OH (Atkinson and Arey, 2003). Accordingly, studies on  
509 OH reactivity in the forests highlight a missing OH sink own to incomplete characterization of  
510 BVOC sources (Di Carlo et al., 2004) and several authors suggest the missing source is soil  
511 (including litter) (Praplan et al., 2019 and citations therein).

512 It is worth to note that BVOC emissions from litter are not only important in atmospheric  
513 chemistry but also in ecological-driven processes. For instance, Santonja et al. (2019) recently  
514 showed that  $\beta$ -caryophyllene emissions from *P. halepensis* litter negatively affected the  
515 development of neighboring herbaceous plants, eventually shaping the ecosystem diversity.  
516 Moreover, terpenes impact the soil food web and slow down the litter decomposition process  
517 (Chomel et al., 2016).

518 It is important to highlight, that soil acts as a sink of BVOC (highly volatile compounds,  
519 isoprene and monoterpenes) through microbial uptake, dissolution in soil water and adsorption to  
520 soil particles (Misra et al., 1996; Ramirez et al., 2010). Independently of the underlying processes,  
521 several authors suggest that measuring BVOC emission from different compartments (litter alone,  
522 soil+litter, bare soil) can greatly benefit further model parametrization (Tang et al., 2019).  
523 Measuring BVOC emission rates from isolated leaf litter is thus necessary.

#### 524 4.6. Potential participation of *P. halepensis* and *Q. pubescens* litter BVOC to air quality at regional 525 scale

526 The regional emissions of *P. halepensis* and *Q. pubescens* litter (8.9 and 3.2 kt.y<sup>-1</sup>) could  
527 contribute to global forest BVOC emissions in France, which are estimated to 457 kt.y<sup>-1</sup> of  
528 isoprene, 350 kt.y<sup>-1</sup> of monoterpenes and 129 kt.y<sup>-1</sup> of other BVOC considering only the canopy  
529 BVOC emissions (Simon et al., 2001). It should however be highlighted that our estimations are  
530 preliminary since litter BVOC emission are likely to vary over the decomposition process as later  
531 discussed.

532 Although the SOAP of *P. halepensis* and *Q. pubescens* were similar, it is likely that *P.*  
533 *halepensis* litter contributes more than *Q. pubescens* to SOA formation at the regional scale since  
534 the amount of BVOC emitted by *P. halepensis* was more than 2-times higher. Similar, SOAP of  
535 the two tree species is explained by the emission chemical composition of their litter. While *P.*  
536 *halepensis* mainly releases sesquiterpenes (~ 60 % of total emissions) which are considered to have  
537 a high SOAP equal to 51.1, followed by monoterpenes with a SOAP equal to 18 (see Suppl Table  
538 6), *Q. pubescens* features alkane emissions (77 % of total emissions) which have the highest SOAP  
539 (54.5, Dominutti et al., 2019, Suppl Table 6). By contrast, litter emission of *P. halepensis* showed  
540 a 2-times higher POCP than *Q. pubescens*. This difference is due to the moderate POCP of alkanes  
541 (44.5, Suppl Table 6) which accounted for the major emissions of *Q. pubescens* (Dominutti et al.,  
542 2019, Suppl Table 6) whereas the individual POCP of monoterpenes and sesquiterpenes released  
543 by *P. halepensis* is much higher (109.2, Suppl Table 6). As described in material and methods, the  
544 POCP of terpenes actually lacks in literature. As a result, the isoprene POCP was used in the present  
545 study for all terpenes because of their similar chemical structure, thus further studies to calculate  
546 terpenes POCP would be useful to improve our estimates. With a moderate emission rate from the  
547 litter of *P. halepensis* and a high POCP, the litter of this species could contribute to the formation  
548 of O<sub>3</sub> and SOA in a non-negligible way.

549 According to our results, species that mostly release sesquiterpenes such as *P. halepensis*,  
550 *C. salviifolius* and *J. oxycedrus* (60 %, 74 % and 60 % of the total emission respectively, Figure 3)  
551 could be of special importance in terms of SOA formation. Moreover, species that emit both,  
552 monoterpenes and sesquiterpenes would have a higher potential of ozone formation assuming that  
553 terpenes possess a POCP as high as isoprene. These preliminary estimations thereby require further  
554 modelling exercises using models such as CHIMERE and ORCHIDE but also BVOC emission  
555 algorithms able to calculate BVOC litter emissions.

## 556 **5. Conclusion**

557 The forest canopy is known to be the main source of BVOC emissions. This study shows that  
558 litter emission of Mediterranean tree and shrub species should not be neglected in biosphere-  
559 atmosphere interactions. We also suggest that leaf terpene content shown in literature is not  
560 necessarily an indicator of the potential of litter to release BVOC. Of the three species known to  
561 possess rich terpene concentrations (*T. vulgaris*, *R. officinalis*, *E. globulus*), only *T. vulgaris*  
562 released high terpene amounts from litter. While litter of most species released low BVOC  
563 emission rates with a few exceptions (*T. vulgaris*, *C. coggygia*, *P. halepensis*), literature shows  
564 that litter is also a source of highly volatile compounds (methanol, ethanol, short-chained  
565 aldehydes, acids, acetone), which were not investigated in this study (Gray et al., 2010; Tang et al.,  
566 2019). Consequently, emission rates would have been higher if a more exhaustive BVOC  
567 screening had been carried out including compounds below C<sub>10</sub>.

568 We suggest future *in vitro* and *in situ* research tackles BVOC emission variability according  
569 to biotic (microorganisms) and abiotic factors (climatic conditions, soil). Since a couple of studies  
570 have reported that litter BVOC emissions vary with decomposition degree (Gray et al., 2010;  
571 Isidorov et al., 2010), soil properties (Gray et al., 2014; Mancuso et al., 2015; Chaignaud et al.,  
572 2018), and climatic conditions (Derendorp et al., 2011, Greenberg et al., 2012), future research  
573 should take into account these factors. For these purposes, BVOC from litter that has undergone  
574 decomposition in the field (using for example litterbags, Isidorov et al., 2010, Santonja et al., 2015)  
575 could be collected over different decomposition times ranging from several months to years. BVOC  
576 from these differently decomposed litter could be measured by combining *in vitro* measurements -  
577 using a controlled environment (at different temperatures and humidity) - and *in situ* measurements  
578 -using transparent dynamic enclosures equipped with temperature, humidity and light sensors as  
579 described by Svendsen et al. (2016). Transparency of the enclosure system would allow to take

580 into account weather variability (e.g. sunny, cloudy and so light conditions). Additionally, for *in*  
581 *vitro* measurements, BVOC emissions of litter free of microorganisms (using for example gamma  
582 irradiation as sterilization technique) could be compared to natural litter in order to assess  
583 microorganism-related BVOC and better estimate the contribution of litter itself. Characterization  
584 of microbiota litter (Wilkinson et al., 2002; Isidorov et al., 2016), could also help to explain BVOC  
585 emission variability over decomposition stages. These types of studies (combining decomposition  
586 processes and contribution of microbiota to BVOC emissions) will be compared to BVOC  
587 emissions from non-decomposed litter (our study). We also suggest that both, *in vitro* and *in situ*  
588 measurements are performed using litter plus soil, litter alone and soil alone to gain insight into  
589 soil capacity to act as a sink of BVOC as indicated by different authors (Isidorov et al., 1999;  
590 Chaignaud et al., 2018; Rinnan and Albers, 2020). It is particularly important to perform such  
591 studies with a focus on BVOC emissions from *P. halepensis* litter since it features a high litter  
592 production, occupies a high forest surface in the Mediterranean area and shows the highest litter  
593 BVOC emission rates among all tree species considered in this study. Results from this species  
594 could serve as a model to other *Pinus* spp.

595 To conclude, although litter BVOC emissions are roughly lower compared to green leaf  
596 emissions, litter accumulates in soil so BVOC emissions could occur all year round. This could be  
597 particularly true in the Mediterranean region where litter production of numerous species is rather  
598 high and decomposes slowly due to relative water scarcity during most part of the year (Quézel  
599 and Médail, 2003). Litter could thereby importantly contribute to BVOC emissions, O<sub>3</sub> and SOA  
600 formation in this region.

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## 610 **Data availability :**

611 The data used in this study is available on demand.

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