

1 **Reviews and syntheses: VOC emissions from soil cover in boreal and temperate**
2 **natural ecosystems of the Northern Hemisphere**

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10 **A B S T R A C T**

11 Plant litter decomposition is a biogeochemical process underlying the carbon cycle in
12 terrestrial ecosystems and between the biosphere and the atmosphere. For the latter, it serves
13 as one of the most important sources of not only carbon dioxide, but also volatile organic
14 compounds (VOCs), which have not yet been taken into account in atmospheric models for
15 various purposes and scales, from local to large regional and global. This review owes its
16 appearance to the growing interest in decaying leaf litter and living forest floor cover as a
17 hitherto unaccounted-for source of photochemically active components of the Earth’s
18 atmosphere. This interest is understandable if we take into account the size of this source: for
19 terrestrial ecosystems, the global production of litter is at 10×10^{16} g dry matter. The living
20 vegetation cover of the soil on the forest floor, mainly comprising mosses and small shrubs,
21 should also be regarded as a potentially significant source of atmospheric VOCs, as its total
22 biomass may be comparable to or even exceed that of canopy foliage, which is considered the
23 main source of these compounds. This implies a need to integrate these sources into biogenic
24 VOC emission models, which in turn requires extensive research on these sources to
25 understand the conditions and factors that influence VOC emissions. The decomposition of

26 leaf litter, accompanied by the release of VOCs, is a very complex process that depends on a
27 number of biological, chemical and physical environmental factors, but little information is
28 currently available on the role each plays. Equally limited is information on the chemical
29 composition and emission rates of VOCs from these sources.

30 The review focuses on the main gaps in our knowledge of the sources of biogenic VOCs
31 under the forest canopy, and we are confident that filling them will make a significant
32 contribution to solving such an important task as closing the global organic carbon budget.

33

34 **Keywords:** leaf litter; living ground cover of forests; decomposition; litter-decomposing
35 microorganisms; volatile organic compounds; chemical composition; emission rate

36

37 **I. Introduction**

38 Terrestrial living vegetation is the main source of atmospheric VOCs that significantly affects
39 chemical processes in the boundary layer (Isidorov, 1990; Fehsenfeld et al., 1992; Guenther et
40 al., 1995; Navarro et al., 2014; Sindelarova et al., 2014). These emissions have received
41 considerable attention due to the fact that most of them are highly reactive and thus affect
42 atmospheric chemistry to a greater extent than comparable amounts of organic pollutants from
43 industrial and motor vehicle emissions (Bell and Ellis, 2004). In the atmosphere, VOCs
44 undergo gas-phase oxidation (Atkinson and Arey, 2003) or photo-stimulated oxidation on the
45 surface of solid atmospheric aerosols (Isidorov, 1992; Isidorov et al., 1997). Their reactions
46 with $\cdot\text{OH}$ radicals and NO_x result in the production of secondary photooxidants, such as
47 ozone, H_2O_2 , ROOH and peroxyacetyl nitrate (PAN). Furthermore, the oxidation of biogenic
48 VOCs initiates the production of secondary atmospheric aerosols, which influence the
49 radiative budget of the troposphere (Makkonen et al., 2012; Kulmala et al., 2001, 2013; Faiola
50 et al., 2014; Kourtchev et al., 2016; Lee et al., 2019). An increase in the tropospheric ozone

51 concentration can also affect the climate by perturbing the Earth's radiation budget as O₃ is
52 the third-most important greenhouse gas (Intergovernmental Panel on Climate Change, IPCC,
53 2013; Kim et al., 2015).

54 Exposure to elevated surface ozone concentration has detrimental impacts on human
55 health, natural vegetation and crop yield (Chuwah et al., 2015; Zhou et al., 2017; De Marco et
56 al., 2019). In particular, ground-level ozone pollution has become one of the top issues in
57 China and India. According to Feng et al. (2015), throughout China current and future O₃
58 levels will induce a wheat yield loss of 6.4–14.9% and 14.8–23.0%, respectively. Moreover,
59 economic losses from wheat and rice in India attributable to ozone are estimated at \$6.5
60 billion per year (Sharma et al., 2019). For these reasons, tropospheric ozone production,
61 temporal variations in its concentrations over different regions and examinations of future
62 near-surface air quality changes have been the subjects of numerous recent investigations and
63 publications (Vingarzan, 2004; Curci et al., 2009; Derwent et al., 2015; Dolwick et al., 2015;
64 Gaudel et al., 2015; Kim et al., 2015; Santurtún et al., 2015; Zong et al., 2018; Masiol et al.,
65 2019; Strode et al., 2019; Archibald et al., 2020; Zhang et al., 2021).

66 To examine the contribution of biogenic organic volatiles to ozone and other
67 secondary pollutant formations, various chemistry transport models have been developed,
68 with VOC and NO_x emissions as the input data. Accurate and reliable emission inventories
69 are essential for good model performance; any underestimation of VOCs in the emissions
70 inventory could cause an underestimation of ozone levels by photochemical models (Bell and
71 Ellis, 2004; Mogensen et al., 2015; Zhou et al., 2017). However, it is well known that the
72 estimation of biogenic VOC emissions is still characterised by considerable uncertainty, with
73 a factor of 3–5 for key species such as isoprene (Curci et al, 2009), although research in this
74 area has been continuously conducted for many years (Guenther et al., 2006; Karl et al.,
75 2009). This uncertainty can be partially connected with systematic errors in the VOC budget,

76 e.g. inadequate emission factors or omission of significant biological sources. Recent work on
77 the determination of the total reactivity of hydroxyl radicals, TOHRE in different types of
78 forests also indicate the existence of unaccounted for sinks of this radical (Di Carlo et al.,
79 2004; Sinha et al., 2010; Nölscher et al., 2013; Yang et al., 2016; Praplan et al., 2020), that is,
80 the presence of unaccounted sources of reactive biogenic VOCs in the atmosphere. This
81 implies the need to identify and quantitatively characterize sources of unknown reactive
82 VOCs in the atmosphere (Hellén et al., 2021).

83 Emissions from leaf litter and non-arboreal vegetation under the forest canopy – such
84 as mosses, lichens, grasses and small shrubs as well as the dead remains of grass in vast
85 steppes (steppe mat), prairies and savannahs – belong to this category of ‘lost’ or ‘omitted’
86 natural VOC sources (Isidorov, 1992; 1994; Isidorov et al., 1994; Tang et al., 2019). The
87 potential importance of this source of biogenic VOCs evidently results from its gigantic scale:
88 for land ecosystems, the litter mass is estimated to be 6×10^{16} g C (Bolin, 1983; Zlotin and
89 Bazilevich, 1993) and the global estimate of litter production is in the range $(9-10) \times 10^{16}$ g
90 yr^{-1} dry matter (Matthews, 1997). According to Liu et al. (2003) the annual leaf litter
91 production in the boreal forests of Eurasia is $(1.49 \pm 0.61) \cdot 10^{15}$ g yr^{-1} , with a total aboveground
92 litter production of $(2.07 \pm 0.85) \cdot 10^{15}$ g yr^{-1} . Depending on different factors, the litter layer can
93 develop to significant thicknesses, exemplified by the ~ 40 mm reported from 20 year
94 unburned *Eucalyptus marginata* forest in Western Australia or the ~ 60 mm reported under
95 *Pinus pinaster* in France. For five types of forest in seven southern states of the USA, it was
96 reported an average litter depth of ~ 37 mm. Larger litter thicknesses have also been reported,
97 including a mean of 86 mm under *Cryptomeria japonica* in Japan (Dunkerley, 2015 and ref.
98 in it).

99 Dead plant material contains substantial amounts of volatile organic compounds. A
100 recent study of the chemical composition of green, senescent leaves and partially decomposed

101 silver birch (*Betula pendula*) leaves in southern Finland showed that although the
102 concentration of many secondary metabolites is significantly reduced, almost all of them are
103 found in both senescent leaves and fresh litter (Paaso et al., 2017). Furthermore, Wood et al.
104 (1995) did not detect statistically significant differences in monoterpene yields in green,
105 yellow or newly fallen brown leaves of the hardwood tree *Umbellularia californica* and
106 concluded that there is a lack of catabolism of monoterpenes prior to leaf senescence.
107 However, the results of these isolated studies do not give grounds to state that aging leaves
108 enter the soil with almost the same yield of monoterpene as on the tree. Indeed, in one study,
109 the total monoterpene content was higher in the fresh needles of *Pinus monophylla* (5.6 ± 2.2
110 mg g^{-1} extracted air dry weight, d.w.) than in senescent needles ($3.6 \pm 1.8 \text{ mg g}^{-1}$ d.w.),
111 regardless of whether they were still attached to the tree or formed the freshest layer of the
112 understorey litter (Wilt et al., 1993). In another study, samples of Scots pine (*Pinus sylvestris*
113 L.) needles and needle litters collected in low-productive forests in eastern Siberia contained,
114 respectively, 7.9 ± 1.2 and $3.9 \pm 0.2 \text{ mg g}^{-1}$ (d.w.) of essential oils, mainly consisting of
115 volatile monoterpene hydrocarbons (Stepen' et al., 1987). About 15% of the total store of
116 essential oil in these forests is contained in litter, with a biomass of $12\text{--}15 \text{ t}\cdot\text{ha}^{-1}$. According
117 to Klemmedson et al. (1990), litter needle biomass comprises 20% of the live foliar biomass
118 in Canadian ponderosa pine forest. More productive forests of the Northern Hemisphere can
119 accumulate enormous amounts of 'dead' organic material. For example, total litter mass in a
120 100-year-old maritime pine (*P. pinaster*) forest in southern France was $43.1 \pm 12.0 \text{ t ha}^{-1}$, and
121 the depth of the needle compartment of the floor averaged 70 mm (Kurz et al., 2000). The
122 chemical composition of the litter was not determined by the authors, but it can be supposed
123 that the fallen needles in this maritime pine forest contain considerable amounts of terpenes.
124 Under the influence of external factors (both abiogenic and biogenic), decomposition of the

125 tissues and the cell structures of the needles takes place, resulting in the formation of volatile
126 compounds and their evolution into the gas phase.

127 The first authors of this review encountered this phenomenon in 1976 while studying
128 the composition of VOCs in the atmosphere of a city (Leningrad, former USSR), using gas
129 chromatography-mass spectrometry (GC-MS). Air samples were collected in a small public
130 garden at the end of October, i.e., when the vegetation period had finished. For this reason, it
131 was an absolute surprise to identify α -pinene, camphene and limonene in the air samples
132 (their peaks were among the more intensive peaks on the chromatograms) and six other less
133 abundant monoterpene hydrocarbons (Ioffe et al., 1977). In later investigations, it was
134 determined that fresh leaf litter of black poplar (*Populus nigra*) was the source of terpenes at
135 this sampling site. This was the second surprise, because the author's 1976 summer GC-MS
136 investigations of the volatiles emitted by the living foliage of this plant had demonstrated the
137 intensive evolution of isoprene into the gas phase, but the complete absence of any terpene
138 hydrocarbons among other volatiles. However, the author's attention was drawn to leaf litter
139 as a source of atmospheric VOCs, as reported by Zimmerman et al. (1978), who were the first
140 to pay attention to leaf litter and report the magnitude of the VOC release rate from this
141 source. According to their estimation, this averages $162 \mu\text{g m}^{-2} \text{h}^{-1}$ at 30°C . In spite of this
142 publication being cited more than 300 times (i.e., well known to the atmospheric chemistry
143 community), this natural source of reactive VOCs has remained unaccounted for and
144 unquantified (it was 'a hitherto unrecognised atmospheric source', Warneke et al., 1999). The
145 same is true for another component of forest ecosystems, namely living soil cover.

146 The purpose of this review is to draw the closer attention of atmospheric chemists to
147 the VOC emissions from these important components of terrestrial natural ecosystems. To our
148 mind, careful estimation of steppe- and forest floor-derived VOCs will help improve the
149 reliability of estimates of biogenic emissions so that they can be incorporated into chemistry

150 transport models as well as improve our understanding of land–atmosphere exchanges and
151 interactions.

152 In this review, we will focus only on forest floor emissions of non-methane VOCs
153 from boreal and temperate natural ecosystems in the Northern Hemisphere. This limitation is
154 due to the fact that at present there is almost no corresponding data for subtropical and
155 tropical forests in both hemispheres. The vegetation of boreal and sub-boreal forests (whose
156 area represents approximately $16,780 \cdot 10^3 \text{ km}^2$ or about 11.2% of the terrestrial area of our
157 globe) accumulates a substantial proportion of the planet's living matter: about $700 \cdot 10^6 \text{ t}$
158 (d.w.). Biomass in different types of forests varies from 10,000 to 40,000 t km^{-2} . Biomass
159 production in coniferous forests in the north taiga zone is equal to ca. 450 t km^{-2} , whereas in
160 the mixed and broad-leaved forests in the south taiga zone it reaches 800 and 900 t km^{-2} ,
161 respectively (Dobrovolsky, 1998).

162 Dying parts of plants fall off and form litter, the quantity of which is not proportional
163 to vegetation biomass. For example, south taiga forests with considerable biomass (more than
164 $30,000 \text{ t km}^{-2}$ d.w.) deposit approximately 500 t km^{-2} (d.w.) of litter in the soil yearly,
165 whereas meadow steppe vegetation with significantly lower amounts of biomass (ca. $2,500 \text{ t}$
166 km^{-2}) forms nearly $1,500 \text{ t km}^{-2}$ of litter (Dobrovolsky, 1998).

167 Leaf litter is defined here as *the uppermost layer of the remains of dead leaves on the*
168 *soil surface of a forest, meadow or steppe, decomposed to varying degrees*. Living soil cover
169 (LSC), as we understand it, refers to *forest floor vegetation formed by understory dwarf*
170 *shrubs, mosses, lichens, herbs and ferns*. As a rule, in boreal and temperate regions, litterfall
171 is associated with the coming of cold, autumnal weather. However, we should also take into
172 account the transitory but intensive spring falling of bud scales, petals and flowers. This
173 material is characterised by significantly higher N and P levels but has lower concentrations
174 of lignin and cellulose compared to leaf litter (Wang et al., 2016). For this reason, fallen

175 flowers decompose much faster (within 1–1.5 months) than leaves. Many bud scales (for
176 example, protecting buds of different poplar species) are covered with a resinous or gummy
177 substance, mainly consisting of volatile terpenoids. Defoliation of deciduous trees can also
178 occur during the summer, as in July 2015 in the north-eastern region of Poland and in the
179 summer months of 2018 in Germany. Intensive summer litterfall (more than 15% of the
180 foliage store) is the result of an acute soil water deficit. Besides, many evergreen coniferous
181 trees shed their leaves all year round.

182 The following chapters will give an overview of the main processes governing litter
183 decomposition and litter-derived VOC emissions, their chemical composition and the
184 participation of litter-destroying microorganisms in their formation, available information
185 regarding the emission rates of separate VOCs. The Supplementary material to this article
186 provides data on litter and living soil biomass stocks in boreal and temperate forests of the
187 Northern Hemisphere that are useful for estimating the magnitude of VOC emissions.

188

189 **II. Biotic and abiotic controls of leaf litter decomposition**

190 *Ila. The role of biological processes*

191 The evolution of volatile organic compounds from dead plant tissues mostly takes place after
192 their more or less advanced decomposition. Two groups of factors controlling this process in
193 terrestrial ecosystems can be distinguished: abiotic and biotic ones (Swift et al., 1979; Berg,
194 2014; Krishna and Mohan, 2017). The latter group includes complex interactions between
195 litter-inhabiting saprotrophic (invertebrate and vertebrate) animals and microorganisms.

196 Leaf-eating insects can influence decomposition processes by modifying the quality
197 of litter. Many studies have demonstrated that soil fauna such as isopods, gastropods,
198 arthropods and other detritophages significantly affect the decomposition rate (Coulis et al.,
199 2013; David, 2014; Frouz et al., 2015; Hassall et al., 1987; Kozlov et al., 2016; Lukowski et

200 al., 2021; Pokhlyenko et al., 2020; Wang et al., 2015; Zimmer et al., 2003). Macroarthropods
201 are believed to enhance the decomposition rate of leaf litter and increase VOC emissions both
202 directly and indirectly. Their direct contribution includes the fragmenting of dead plant
203 material and increasing the surface area available for microbial colonisation, while their
204 indirect contribution consists in ingesting saprotrophic litter-colonising microbiota and
205 egesting their faeces in surface-increased substrate, thereby enhancing microbial activity
206 (Zimmer et al., 2003).

207 Further decomposition of crushed litter is performed by microorganisms, bacteria,
208 actinomycetes and fungi (Trowbridge et al., 2020). The last constitute a major component of
209 soil biota and represent the primary decomposers in most environments. Indeed, fungi
210 produce the enzymes (including extracellular enzymes) necessary to decompose the
211 lignocellulose matrix of leaf litter and wood (Cox et al., 2001; Fioretto et al., 2007).

212 Participating in the decomposition of organic matter of plant origin, these saprotrophic
213 organisms produce their own, inherent metabolites; as part of these secondary products are
214 volatile organic compounds, they can be transferred into the gas phase (Svendsen et al.,
215 2018).

216

217 *Iib. Abiotic processes*

218

219 The microbial-zoological interactions mentioned above stimulate intense abiotic
220 processes such as the evaporation of volatiles and the leaching of water-soluble compounds.
221 Another abiotic process aiding the evolution of volatiles from plant tissues is their mechanical
222 destruction, brought about by the freezing–thawing of dead organic material (Porchikalov
223 and Karelin, 2015). In some studies thermo- and photochemical reactions caused by direct

224 solar radiation are described as abiotic destruction processes; their role is much more
225 pronounced in forest-steppe and steppe landscapes than under the forest canopy.

226 The relative proportion of biotic and abiotic processes varies greatly, primarily
227 depending on climatic conditions, yet there is only scarce corresponding information available
228 in the literature (Kravchenko et al., 2019). According to Bazilevich et al. (1993), leaching
229 predominates among other abiotic factors in humid north taiga forests. To assess the role of
230 various natural factors in the decomposition of plant fall, these authors conducted field
231 experiments in different regions of Russia. The general conclusion was that there are two
232 principal factors limiting the intensity of organic matter destruction: in tundra-forest and north
233 taiga zones the key factor is a lack of heat, while in semi-arid steppe ecosystems it is a lack of
234 moisture. These authors' experiments, while supporting the phenomenon of the biological
235 decomposition of dead organic material, also highlight the important role of abiotic factors in
236 decomposition. The authors conducted experiments in two neighbouring ecosystems in the
237 central European part of Russia, finding that the proportions of biotic and abiotic factors differ
238 in forest and meadow steppe (Table 1). As can be seen, the contribution of abiotic processes
239 in the case of open landscapes (meadow steppe) significantly exceeds that in the oak forest,
240 and this difference is associated with different levels of solar radiation. Litter-bag experiments
241 with five degrees of solar light intensity (controlled by special screens) showed that the
242 decomposition rate of dead aspen and grass leaves declines gradually with decreases in solar
243 radiation intensity and short wavelength radiation (Bazilevich et al., 1993).

244 Bosco et al. (2016) found additive effects of ultraviolet (UV) radiation and soil water
245 on litter mass loss. Recent laboratory experiments have shown that the photodegradation of
246 plant litter driven by UV radiation is important in influencing mass loss, nutrient release and
247 the carbon balance in a broad range of terrestrial ecosystems (Austin et al., 2016; Li et al.,
248 2016). It can be assumed that the loss of litter mass under the action of solar radiation (light

249 and/or its thermal component) is at least partially related to the emission of VOCs, but at
250 present it is difficult to draw definite conclusions in this regard due to the limited number of
251 studies of this phenomenon.

252 Karl et al. (2005) did not see a significant influence of photosynthetically active
253 radiation (PAR) on emissions of VOCs from senescing grass crops. However, shortwave
254 radiation can stimulate different types of photochemical processes. UV-induced C₂–C₅
255 hydrocarbon emissions have been measured by Derendorp et al. (2011a,b) from the leaf litter
256 of some plant species, with the influence of experimental conditions determined. In the
257 absence of oxygen, no emissions of C₂–C₅ hydrocarbons were observed. When the litter was
258 placed in humid air, the emission rates approximately tripled compared with the emissions
259 from leaf litter in dry air. According to the authors, UV-induced hydrocarbon emissions from
260 leaf litter may have a small influence on atmospheric chemistry at the local scale, but do not
261 contribute significantly to their global budgets. However, it seems that this conclusion is
262 premature, because our knowledge about the influence of shortwave solar radiation on the
263 decomposition of dead plant material and VOC emissions is very limited.

264 Further field and laboratory measurements are needed to investigate the impact of
265 UV-B radiation (280–310 nm), together with UV-A (315–400 nm) and visible radiation (400–
266 700 nm). It is well worth remembering that senescent leaf matter photoproduces carbon
267 monoxide, which has an important effect on atmospheric composition (Tarr et al., 1995;
268 Derendorp et al., 2011c). In Tarr et al.'s (1995) study, leaf litter photoproduced CO at rates
269 that ranged from 1.3 to 5.4 times higher per unit area than did living leaves. According to
270 Bornman et al. (2015), UV radiation can also stimulate VOC emissions from both living plant
271 and leaf litter, although the magnitude, rates and spatial patterns of these (supposed)
272 emissions remain unknown at present.

273 On the other hand, there are experimental confirmations of the *de novo* synthesis of
274 partially oxidised volatile organic compounds in dead plant material under the action of the
275 heat component of solar radiation. Warneke et al. (1999) conducted experiments involving the
276 alternate 'roasting' (up to 60–100 °C) and wetting of dead beech leaves, demonstrating
277 multiple increases in the emission rates of oxidised VOCs such as methanol, acetone,
278 acetaldehyde, ethanol and butan-2-one. Moreover, these authors showed that even at room
279 temperature, considerable amounts of these volatiles are released over a period of days and
280 weeks. According to the authors' previous estimation, the decay of 1 g of leaf matter produces
281 at least 100 µg of acetone and 300–500 µg of methanol. Global annual emissions of acetone
282 and methanol from dead leaf matter may be at least 6–8 Tg and 18–40 Tg, respectively.
283 Considering the temperature dependence of the emission rates of the VOCs, Warneke et al.
284 (1999) predicted the largest emission rates to be in the late spring and early autumn.

285 Evidently, similar thermochemical processes can take place more intensively in
286 felted dead grass litter in semi-arid steppe ecosystems as well as on the outskirts of forests and
287 in open-canopy forests. The summer soil surface temperature can reach 60–80 °C in these
288 landscapes.

289 Paradoxically, the abiotic strengthening of VOC emissions can also be stimulated by the
290 process exactly opposite to 'roasting', namely freezing. Frequent freezing and thawing events,
291 especially characteristic in the last two decades for high-latitude regions, can positively
292 influence the decomposition rate (Porchikalov and Karelin, 2015; Jiang et al., 2016). Some
293 authors have presented the idea that a source of reactive VOCs are the wounding processes
294 that occur after leaves undergo freeze–thaw damage. Fukuj and Doskey (1998) measured
295 VOC emissions from a grassland site before and after frost events and reported morning frost-
296 enhanced emissions of acetaldehyde, acetone, methanol and ethanol. Fall et al. (2001)
297 detected the emissions of low-molecular-weight oxygenated VOCs during leaf drying,

298 senescence and following freeze–thaw damage. Leaves of beech, larch, clover, bluegrass and
299 fern wounded in this way released 1-penten-3-ol, 2- and 3-methylbutanal, 2(*E*)-penten-1-ol, 1-
300 penten-3-one, hexanal and some other minor compounds (supposedly, isomeric pentenals)
301 into the gas phase. Moreover, freeze–thawed C₅ and C₆ compounds were detected by GC-
302 PTR-MS and PTR-MS techniques in mid-November 1999 at the Sonnblick Observatory
303 (Austrian Alps, 3106 m a.s.l.). After a hard freeze had occurred in the central alpine valleys of
304 Austria, unprecedented levels of highly reactive C₅ and C₆ biogenic VOCs were registered in
305 ambient air transported from these valleys: isoprene, 2- and 3-methylbutanal, 1-penten-3-ol,
306 1-penten-3-one, hexanal, 3(*Z*)- and 2(*E*)-hexenal. These were the same VOCs seen in the
307 freeze–thaw wounding experiments. Fall et al. (2001) speculated that VOCs were released
308 from freeze-damaged local vegetation, larch and fir trees. This seems doubtful because living
309 frost-hardy trees are quite well protected from such kinds of wounding. However, saturated by
310 rainwater, dead plant matter (for example fallen larch and fir needles) is deprived of this
311 biological protection. After autumn rains, the litter can remain damp for a long time (Wood et
312 al., 1995). In frosty weather, the crystallisation of surplus water takes place, damaging cell
313 and tissue structures. Besides, freezing has a destructive effect on the resin canals in the litter
314 (Wu et al., 2010). All these forms of damage can increase the release and evolution of
315 volatiles.

316 At present, it is not possible to determine how various time or spatial features affect the
317 proportions of abiotic and biogenic processes in the emissions of VOCs from dead plant
318 material. According to some authors (Zhang et al., 2008; Gray et al., 2010), abiotic factors
319 play an additional role compared to litter microbial degradation and VOC emissions on a
320 global scale. The predominance of the microbiological production of volatile organics has
321 been demonstrated by Leff and Fierer (2008), who discovered a correlation between
322 respiration, microbial biomass and level of VOC emissions. However, the information

323 presented in this chapter allows us to conclude that substantial quantities of low molecular
324 weight C₅–C₆ VOCs can be formed as the result of the abiotic decomposition of plant litter.
325 Due to its importance in atmospheric chemistry, it can be concluded that much more research
326 should be devoted to this natural source of atmospheric VOCs. In particular, UV radiation,
327 heat and frost must be regarded as important triggers for seasonal emissions of these VOCs by
328 plant litter.

329 The second conclusion is related to the qualitative composition of leaf litter
330 emissions: one can expect among these emissions not only plant-derived compounds, but also
331 VOCs of microbial and animal origin.

332

333 **III. Qualitative composition of plant litter and LSC emissions**

334

335 Over the last few decades, the chemical composition of volatile emissions from some
336 thousands of plant species – including practically all forest-forming trees of the Northern
337 Hemisphere – has been investigated. For many hundreds of species, the emission rates of
338 principal biogenic VOCs, isoprenes and monoterpenes have also been determined
339 (Kesselmeier and Staudt, 1999). The available information on the chemical composition of
340 litter-derived compounds is much poorer. This chapter provides an overview of the current
341 knowledge, which is based on only a few publications.

342 Table 2 contains a list of 164 volatile organic compounds detected in emissions from the
343 leaf litter of 30 plants, including 25 arboreal species. The largest group is made up of
344 hydrocarbons (79 compounds), including mono- and sesquiterpenes (63 compounds), which
345 are more active in atmospheric processes. Isoprene, ethanol, acetaldehyde, acetone and
346 methanol belong to the more frequently detected litter-derived components. With the

347 exception of isoprene, these short-chain volatiles have relatively long atmospheric lifetimes
348 and reach concentrations in the ppb range.

349 It is plausible that α -pinene is widespread within litter-derived VOCs; however, the
350 accurate identification of this important monoterpene is impossible in certain cases. In some
351 of the investigations cited in Table 2, instead of 'traditional' GC-MS analyses, a relatively
352 novel and, in many aspects, convenient proton transfer reaction mass spectrometry (PTR-MS)
353 technique was used (Gray et al., 2010; Ramirez et al., 2010; Stoy et al., 2021). This method
354 has the undoubted advantage of being a tool for the simultaneous online registration of VOC
355 emissions. However, PTR-MS has limited identification possibilities as only a single
356 protonated ion, with a molecular weight corresponding to that of the neutral analyte molecule
357 plus 1 amu, $[M+1]^+$, is used as the sole analytical parameter. This hinders the precise
358 identification of isomers and the distinguishing of isobaric compounds, for example $C_{10}H_{16}$
359 monoterpenes and the numerous aromatic $C_9H_{12}O$ compounds, nor-terpenoids and furans with
360 a molecular weight of 136 amu. For this reason, in some cases, the identification of
361 monoterpenes (Gray et al., 2010; Ramirez et al., 2010; Greenberg et al., 2012) or isomeric
362 pentenols, methyl butanols and pentenals (Fall et al., 2001) has to be recognised as tentative.
363 The speciation (i.e., determination of the exact chemical structure) of VOCs is highly
364 important for atmospheric chemistry because even closely related compounds differ in their
365 reactivity (Atkinson and Arey, 2003). In recent years, a more advanced version of the method,
366 a Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-TOF-MS), has become
367 more frequently used, which makes it possible to determine the mass of a registered ion with
368 an accuracy of 0.01 amu (Viros et al., 2020; Crocker 2021). This significantly increased the
369 identification capability of the method, however, the much more time- and work-consuming
370 GC-MS method (which uses two independent analytical parameters for identification, full
371 mass spectrum and chromatographic retention index) maintains its significance.

372 Another component of forest floor cover worthy of attention as a source of atmospheric
373 VOCs is non-arboreal vegetation. Small shrubs, grasses, lichens and mosses considerably
374 contribute to the overall green biomass of many types of Northern Hemisphere forests
375 (Isidorov, 1994; Isidorov et al., 1994; Jagodzinski et al., 2016) and play an important role in
376 the photosynthetic production of boreal forests (Kolari et al., 2006). These plants are adapted
377 to low photosynthetically active radiation (PAR) and begin photosynthesis as early as at a
378 PAR level above $3 \mu\text{mol m}^{-2} \text{s}^{-1}$ (Morén and Lindroth, 2000). In boreal forests, different
379 feathermoss, peatmoss, and foliose lichen species often form a continuous layer on the forest
380 floor (Hageman and Moroni, 2015). Moreover, a significant fraction of the whole Earth's
381 land surface is dominated by bryophytes (Lindo and Gonzalez, 2010). Hence, mosses, lichens
382 and other forest floor plants can make up a principal part of total green biomass and VOC
383 emissions in forests, at least in subarctic and temperate regions of the Northern Hemisphere
384 (Isidorov, 1992; Isidorov et al., 1999; Mäki et al., 2017).

385 According to investigations performed in North European Russia, the LSC biomass in
386 20-year-old pine forests is (on average) $1,200\text{--}2,500 \text{ t km}^{-2}$, increasing to $7,600\text{--}8,100 \text{ t km}^{-2}$
387 in mature forests; at the same time interval, pine needle biomass decreased from $5,600\text{--}6,700$
388 t km^{-2} to $3,200\text{--}4,700 \text{ t km}^{-2}$ (Zyabchenko, 1984). The LSC composition of young (20–40-
389 year-old) pine forests in northern Russia is, as a rule, is dominated by grasses and ferns
390 (*Melampyrum sylvaticum*, *M. pratense*, *Maiantheum bifolium*, *Avenella flexuosa*, *Dryopteris*
391 *filix-max*, etc.) and small shrubs (*Vaccinium vitis-idaea*, *V. myrtilus*, *Calluna vulgaris*, *Ledum*
392 *palustre*, *Empetrum nigrum*, *Erica* sp., etc.), but in the oldest forests, they are replaced by
393 green mosses and lichens (*Pleurozium schreberi*, *Politrichum commune*, *Licopodium*
394 *clavatum*, *Cetraria islandica*, *Sphagnum* sp., etc.). The share of LSC in the current accretion
395 of biomass in pine forests reaches 30% in north taiga and 50% in middle taiga zones
396 (Zyabchenko, 1984). On a level with arboreal vegetation, LSC forms a litter mass which can

397 reach 1.8–2.3 t ha⁻¹. In spite of its importance as a component of forest biomass, LSC has not
398 been studied sufficiently as a source of atmospheric VOCs. Table 3 presents a list of volatile
399 organics registered in gas emissions from a limited number of these plants. It contains 206
400 C₂–C₁₉ compounds belonging to different classes. The compounds listed in the table are
401 divided into 11 groups, the most numerous of which are monoterpenoids (45 compounds) and
402 sesquiterpenoids (42 compounds). These VOCs are among the compounds with the highest
403 potential for secondary aerosol formation. Carbonyls form the third largest group, consisting
404 of 33 aldehydes and ketones.

405

406 **IV. VOCs from litter-decomposing microbes**

407 Not only the chemical composition of leaf litter-derived VOCs but also how it changes during
408 litter decomposition is of great interest. Such changes have been registered in a laboratory via
409 the use of head-space solid phase microextraction (HS-SPME) combined with GC-MS
410 (Isidorov et al., 2003) and since in long-term litterbag field experiments (Isidorov et al.,
411 2010). This study determined that during the decomposition of Scots pine (*Pinus sylvestris*)
412 and Norway spruce (*Picea abies*) litter, substantial changes in the number of compounds
413 emitted into the gas phase take place (Fig. 1).

414 Over the entire observation period, mono- and sesquiterpene hydrocarbons were the
415 main components of volatile emissions, but the ratio of these VOC groups varied greatly (Fig.
416 2). During decomposition, new compounds appeared in the composition of VOCs, mainly
417 represented by monoterpenoids, the oxidation products of α - and β -pinene (pinocarvone,
418 pinocampon, myrtenal, myrtenol, *cis*-3-pinane, verbenone) and aliphatic alcohols,
419 carbonyls and esters (Isidorov et al., 2010). Kainulainen and Hopolainen (2002) have also
420 reported the emission of verbenone and verbenol in decomposing pine needle litter. Most of
421 these 'additional' compounds were either not detected in the volatiles emitted by living pine

422 and spruce needles and in their essential oils or were present as minor and trace components.
423 For example, substantial quantities of acetone, butan-2-one, hexan-2-one, hexan-3-one, octan-
424 3-one and octan-4-one, as well as C₂–C₅ aliphatic alcohols and C₅–C₉ aldehydes, were only
425 registered in volatile emissions from pine and spruce needle litter after an experimental period
426 of four weeks. It has been proposed that all these volatiles are secondary products of litter-
427 destroying microorganisms (Isidorov et al., 2003). Therefore, the observed emission of VOCs
428 from leaf litter are the blend of volatiles stored in dead plant tissues, such as monoterpene
429 hydrocarbons and metabolites newly enzymatically synthesised by saprotrophic microbial
430 communities. In particular, C₃–C₈ carbonyl compounds, lower alcohols and their esters are the
431 main products of the enzymatic oxidative decomposition of unsaturated aliphatic acids
432 (Wurzenberg and Grosch, 1984).

433 It has long been known that diverse microorganisms grown on various nutritive artificial
434 media emit a broad range of VOCs into the gas phase (Norrman, 1969; Babich and Stotzky,
435 1974; Sunesson et al., 1995; Nilsson et al., 1996). Although the most labile primary and
436 secondary metabolites, such as mono- and oligosaccharides, amino acids and other organic
437 acids, are withdrawn by trees during leaf senescence, falling foliage still contains considerable
438 amounts of both volatile and non-volatile but easily degradable substances that can be
439 substrates for microorganisms (Tian et al., 2000; Isidorov et al., 2005; 2010). In Gray et al.'s
440 (2010) study, the cell-soluble fraction of the litter from 12 plant species was in the range of
441 28.9–74.6% of the litter carbon fraction. This material and more stable biopolymers
442 (cellulose, hemicelluloses, lignocellulose and lignin) can be used by various bacteria and
443 fungi. It can be assumed that these groups of microorganisms participate in the assimilation of
444 diverse substrates during the different stages of litter destruction; moreover, the composition
445 of microbial VOCs is species-specific. It is known that the relationship between bacteria and
446 fungi is characterized by antagonism. In most of the fungal cultures studied to date, the

447 biosynthesis of metabolites with bactericidal properties has been found, while many types of
448 bacteria demonstrate fungicidal effects. These competitive relationships can manifest
449 themselves in the progressive decomposition of litter and determine the composition of VOCs
450 of microbial origin.

451 During leaf litter decomposition, microbial succession takes place, defined as *a directed*
452 *change in the relative abundance and spatial pattern of species comprising communities*
453 (Frankland, 1998). Undecomposed fallen leaves act as a carbon source for primary
454 saprotrophs, belonging to bacteria and/or fungi (Bonanomi et al., 2017). After use by the
455 primary colonisers of simple sugars, oligosaccharides, amino acids and other easy-
456 assimilating substances, litter is naturally colonised by other microbes, fungi and cellulolytic
457 bacteria (López-Mondéjar et al., 2016; Starke et al., 2016; Shao et al., 2017; Štursová et al.,
458 2020; Tennakoon et al., 2021). It is believed that more recalcitrant lignified hemicelluloses
459 and lignin are destroyed only by basidiomycetes, fungi capable of producing extracellular
460 lignolytic enzymes (Hobbie et al., 2012; Kirker et al., 2020).

461 The successional nature of fungal decomposition of the herbaceous litter of the Longleaf
462 Pine savanna ecosystem was noted by Lodato et al. (2021). Sequencing of fungi isolated by
463 the authors from the litter of *Schizachyrium scoparium* (little bluestem or beard grass) and *S.*
464 *tenerum* (slender bluestem) revealed the participation in the decomposition of several
465 phylotypes, among which representatives of Ascomycota (*Dothideomycetes*) and
466 Basidiomycota (*Agaricomycetes*) prevailed.

467 However, some groups of bacteria, which also have the ability to synthesize enzymes
468 suitable for these purposes, may be involved in the decomposition of recalcitrant biopolymers.
469 In particular, high lignolytic activity has been found in *Staphylococcus saprophyticus*,
470 *Pseudomonas aeruginosa* and certain bacteria from the genus *Bacillus* (Nahrowi et al., 2018).
471 According to Frankland (1998), fungal activity had almost ceased after 5 to 6 years when

472 Pokhymycelial bacteria capable of degrading resistant substrates. Due to their slow growth,
473 these microorganisms are unable to compete with non-mycelial bacteria for readily available
474 substances, in the assimilation of which actinobacteria are actively involved (Mahajan et al.
475 2016). Three-year observations of litter-associated microbial organisms in northern Japan, in a
476 pioneer forest dominated by birch and a climax forest dominated by oak, confirmed that the
477 succession of microorganisms in the litter occurs from fungi to bacteria. In addition, in both
478 forest types, Gram-negative bacteria were replaced by Gram-positive bacteria (Otaki and
479 Tsuyuzaki, 2019). Noteworthy is the observation of the role of microbes associated with
480 deciduous litter in the rotting of aboveground wood: contact with litter leads to an increase in
481 the moisture content of the wood and its visually observed faster decomposition (Kirker et al.,
482 2020).

483 A propelling power and predominant regulator of the above microbial succession is the
484 change of litter quality, its chemical composition (Bray et al., 2012; Ge et al., 2017).
485 Therefore, it might be expected that the successive assimilation of different substrates by
486 different groups of microbes is accompanied by changes in the chemical composition of the
487 microbial emission of volatiles. Unfortunately, temporal changes in microbial VOC emission
488 profiles during litter decomposition remain uninvestigated. Recent single studies in this
489 direction are cited below.

490 During the course of a 690-day litterbag experiment in decaying pine (*P. sylvestris*) and
491 spruce (*P. abies*) needle litters, 92 fungi species were identified: 54 species in pine and 73 in
492 spruce litter (Isidorov et al., 2016). The composition of the fungal communities was
493 substantially specific, as only 38% of the species were found in both litter types. At the early
494 stage (30 days of the experiment), the typical primary colonisers from the orders of
495 *Capnodiales*, *Xylariales*, *Dothideales*, *Pleosporales*, *Eurotiales*, *Thelebolales* and
496 *Hypocreales* dominated. After 7 months, none of the primary colonisers were found in pine

497 litter, and only two (*Cladosporium herbarum* and *Pseudeurotium ovale*) were detected in
498 spruce needles. The observed disappearance of these fungi can be linked to the sharp decrease
499 in simple carbohydrates in the early stages of decomposition during the decay of leaf litter
500 (Kainulainen and Hopolainen, 2002; Osono and Takeda, 2005; Isidorov et al., 2010) due to
501 both use by microbes and leaching.

502 At the middle stage (280 days), *Penicillium purpurogenum* dominated in pine litter and
503 *Chloridium botryoideum* in spruce litter, whereas the late stage (490–690 days) was
504 characterised by the absolute predominance of *Trichoderma* species (*T. polysporum*, *T.*
505 *koningii* and *T. viride*). These filamentous fungi are producers of large amounts of cellulolytic
506 enzymes. Remarkably, in the late stage of the experiment, the recurrence of some primary
507 colonisers was also observed, which can be explained by the action of cellulolytic fungi,
508 producing readily available sugars released from the hemicelluloses. The recurrence of the
509 primary colonisers after approximately 350 days of *Pinus pinea* needle incubation was
510 previously documented by Virzo De Santo et al. (2002). Further degradation of more
511 recalcitrant lignified materials demands the participation of lignolytic fungi.

512 It can be noted that unlike the case of VOC emissions from living plants, there is little
513 knowledge regarding such emissions from litter-destroying microbes. The composition of
514 VOCs emitted into the gas phase by selected fungi isolated from Scots pine and Norway
515 spruce needles was determined after 490 days of incubation in one study (Isidorov et al.,
516 2016). Based on the results of HS-SPME/GC-MS analyses, as many as 75 C₂–C₁₅ volatile
517 organic compounds were identified. Table 4 presents the group composition of these VOCs
518 and the principal representatives of separate groups. As can be seen, VOC emissions are
519 species-specific: grown on the same cultivation media, the fungi differ in the qualitative and
520 quantitative composition of the volatiles produced. Even a representative of the same genus
521 (for example, *Trichoderma polysporum* and *T. koningi*, or *Penicillium minioluteum* and *P.*

522 *purpurogenum*) demonstrates considerable distinctions in VOC emissions. Striking
523 differences have also been observed by Nilsson et al. (1996): only three of 58 registered
524 VOCs were common for four *Penicillium* species.

525 Even less is known about VOC production by litter-destroying bacteria. However, the
526 emission of photochemical significant organic volatiles, including isoprene, by bacilli and
527 actinomycetes was discovered (Kuzma et al., 1997; Fall and Copley, 2000; Wilkins, 1996;
528 Wagner et al., 2000; Schöller et al., 2002). At present, the important role of bacteria in leaf
529 litter and coarse woody debris destruction is well documented (Kim et al., 2014; Urbanová et
530 al., 2015; López-Mondéjar et al., 2016; Mahajan et al., 2016; Purahong et al., 2016;
531 Bonanomi et al., 2017; Dolan et al., 2017; Hu et al., 2017). However, further studies are
532 required to understand their role in the litter-derived emission of VOCs into the atmosphere.

533 In terrestrial environments, algae represent the main component of the microbial flora.
534 Forest litter is also the place of the active development of microscopic algae, which form a
535 specific element of the living soil cover (Maltsev et al. 2017a,b). They participate in all
536 biogenic processes in leaf litter, together with other organisms. However, data on the algae of
537 leaf litter are scanty. Maltsev et al. (2017a) have recently studied the structural and dynamic
538 parameters of the algal communities of the anthropogenic and natural forests in the steppe
539 zone of Ukraine and found that the composition of communities varies by season and forest-
540 forming tree species. The authors identified 119 algae species belonging to six divisions:
541 *Chlorophyta* (68 species), *Xanthophyta* (21 species), *Cyanoprocarvota* (17 species),
542 *Bacillariophyta* (seven species), *Eustigmatophyta* and *Charophyta* (three species each). With
543 respect to species number and abundance, coniferous forest litter was predominated by green
544 (*Chlorophyta*) and yellow-green (*Xanthophyta*) algae, whereas leaf forest litter (*Q. robur* and
545 *Robinia pseudoacacia* plantations) was characterised by the significant participation of
546 oxygenic photosynthesising cyanobacteria *Cyanoprocarvota*. In the available literature, we

547 were unable to find information on the emission of VOCs by this group of photosynthetic
548 organisms of the soil cover.

549

550 **V. VOC emission rates: laboratory and field measurements**

551

552 In the past three and a half decades, many measurements of VOC emission rates have been
553 carried out both for the living foliage of individual plants and for various plant communities.

554 In particular, in a review covering the period from 1979 to 1997, 314 values of the emission
555 rates of isoprene and monoterpenes published in 52 articles are given. Another 126 values of
556 the emission rates of 39 non-terpene compounds from more than 50 plant species were
557 published from 1992 to 1999 (Kesselmeier and Staudt, 1999). Among the plants listed in this
558 review, only one species from the genus *Ericaceae*, which is part of the living soil cover of
559 boreal forests, is mentioned: blueberry (*Vaccinium uliginosum*). This shrub is one of the weak
560 sources of isoprene (emission rate $0.009 \mu\text{g g}^{-1} \text{h}^{-1}$). However, two other species of shrub from
561 the same genus – cassandra (*Chamaedaphne calyculata*) and Labrador tea (*Ledum*
562 *groenlandicum*) – are strong monoterpene emitters, with a release rate of more than $3 \mu\text{gC g}^{-1}$
563 h^{-1} (Isebrands et al., 1999).

564 Also limited are data in the literature on rates of VOC emissions from forest leaf litter in
565 natural environments, or even laboratory experiments. However, the few observations made
566 confirm the importance of the contribution of the forest floor to total VOC emissions with
567 regard to some forest types (Pettersson, 1988; Janson, 1993; Isidorov et al., 1994; Stepanov,
568 1999; Hayward et al., 2001). In addition to these early studies, several investigations have
569 been carried out in recent years as part of the SMEAR II (Station for Measuring Relationships
570 between Forest Ecosystems and the Atmosphere) research programme (Hari and Kulmala,
571 2005).

572 The information presented in Table 5 is remarkable in that almost all measurements
573 were carried out in boreal coniferous forests or in mixed forests with a predominance of
574 conifers. Meanwhile, there is no reason to believe that the decomposition of litter of small- or
575 broad-leaved species prevailing in the more southern forests contributes less to the total
576 emissions of biogenic VOCs than the northern, predominantly coniferous forests. However,
577 we were unable to find any publications on VOC emissions from deciduous forests. Besides,
578 plants of live soil cover were considered as a source of VOCs, along with litter, only in some
579 studies (Mäki et al., 2017; 2019a,b). It is also noteworthy that all but two studies were
580 conducted in forests of the Eastern Hemisphere (Hayward et al., 2001; Greenberg et al.,
581 2012).

582 Although this review focuses on the problems associated with VOC emissions from the
583 forest floor of the boreal and temperate zones of the Northern Hemisphere, Table 5 provides
584 the only information we know of these processes in tropical forests (Drewer et al., 2021). The
585 2-year exploration was carried out in a logged tropical forest and an oil palm plantation in
586 Malaysia on the island of Borneo. The amount of litter on the soil determined the level of
587 monoterpene fluxes, of which the main ones, as in the case of the floor of northern forests,
588 were α - and β -pinene as well as limonene (all other measured monoterpenoids, such as 3-
589 carene, camphene and eucalyptol, were emitted at lower rates). Fluxes from oilseed
590 plantations, which were practically devoid of litter, were low and increased only where litter
591 was present.

592 The results of the field experiments carried out to date and their conclusions can be
593 contradictory even within the same working group. For instance, Janson (1993) recorded a
594 fairly high rate (up to $580 \mu\text{gC m}^{-2} \text{h}^{-1}$) of terpene emission by litter in a mature pine forest in
595 southern Sweden, with significantly higher values in autumn than in summer. According to
596 the author's estimate based on these measurements, the flux of terpenes from the pine forest

597 litter accounted for 30% of the crown emissions. However, subsequent measurements (Janson
598 et al., 1999) in coniferous forests and wetlands in summer and early autumn yielded
599 considerably lower emission rates of monoterpenes ($19\text{--}90 \mu\text{g C m}^{-2} \text{ h}^{-1}$); it was concluded
600 that the flux of biogenic VOCs from the forest floor only accounts for a few percent of the
601 total forest flow. According to data obtained at the same time in western Russia (Stepanov,
602 1999), the emission rates of monoterpenes by spruce litter were higher ($21\text{--}402 \mu\text{g m}^{-2} \text{ h}^{-1}$),
603 and the highest values were recorded not in July–August at air temperatures of $22\text{--}25^\circ\text{C}$ but
604 in the second half of September at temperatures of $6\text{--}8^\circ\text{C}$. In both summer and autumn,
605 temporarily increased emission levels were observed immediately after rain events. The
606 strong effect of rain on VOC emissions from litter has been confirmed in a recent study
607 (Crocker, 2021). In the author's opinion, a short-term increase in emission by leaf litter of
608 *Clitoria fairchildiana* after its moistening occurs in accordance with Henry's law. The
609 concentration profile of monoterpenes, measured by Stepanov (1999) under the canopy of an
610 80-year-old spruce forest in summer in calm weather, showed the presence of two maxima,
611 one of which was located approximately at half the height of the crown tree, and the other
612 near the surface covered with coniferous litter at a height of 0.8 m.

613 In another study, monoterpene emissions from the boreal pine forest floor in Finland
614 varied from 0 to $373 \mu\text{g m}^{-2} \text{ h}^{-1}$ (Hellén et al., 2006), that is, its upper value was consistent
615 with that obtained by Stepanov (1999). According to the authors, emissions of terpenes from
616 the forest floor can be a significant source for the atmosphere, especially in spring.

617 Kivimäenpää et al. (2018) conducted a latitudinal experiment in Finland, involving a
618 1,000-km North–South transect, and concluded that emissions from the floor of pine forests
619 have a noticeable additive effect on total VOC emissions. The authors of an earlier study
620 (Räisänen et al., 2009), who measured the fluxes of monoterpenes in a pine forest in eastern
621 Finland, were inclined to the same conclusion. According to their estimates, the total flux of

622 monoterpenes in June–September was 502 mg m⁻², whereas the flux from the forest canopy
623 was only 374 mg m⁻². According to the authors, the difference of more than 25% can be
624 partially explained by the emission of terpenes from the forest floor.

625 The results of recent measurements – carried out mainly by Scandinavian researchers
626 (Mäki et al., 2017, 2019; Kivimäenpää et al., 2018; Wang et al., 2018) – and their conclusions
627 about the important role of VOC emissions from forest litter (primarily photochemically
628 active terpenes and sesquiterpenes with high potential for secondary aerosol formation) are at
629 odds with the earlier conclusion (Janson et al., 1999; Greenberg et al., 2012) that they only
630 slightly contribute to the total ecosystem flux of VOCs. To clarify the nature of such
631 discrepancies, it is necessary to continue research with a wider coverage of geographical and
632 climatic conditions and, first of all, to include forests formed by deciduous trees in the
633 research programme.

634 Table 5 also includes chamber measurements of mono- and sesquiterpene fluxes from
635 wet scrubland in northern Sweden, including an experiment that adds birch litter to the
636 chambers (Faubert et al. 2010). The relatively low emissions of terpenoids were doubled in
637 response to an air temperature increment of only 1.9–2.5 °C. This suggests that the predicted
638 warming of the climate in the subarctic and arctic regions is likely to lead to a significant
639 increase in the flux of reactive VOCs from plants of the living ground cover of the tundra.
640 The same conclusion was reached by the authors who studied the release of terpenes by plants
641 of the living soil cover of the high and low Arctic heaths and subarctic peatland (Lindwall et
642 al., 2015).

643 In addition to these field observations, the results of the small number of laboratory
644 measurements of the rates of VOC release by the litter of some species of woody and shrub
645 plants have been published. For example, the rates of terpene emission by fresh litter of
646 European larch as well as fresh and decaying litter of Norway spruce (*P. abies*) and Scots pine

647 (*P. sylvestris*) have been reported (Table 6). At the early stages of decomposition (2.5–5.5
648 months from the beginning of the experiment), the rates of terpene emission from pine and
649 spruce litter exceeded those observed for freshly fallen needles. Over the entire observation
650 period, in the case of spruce litter, camphene and α -pinene were released into the gas phase at
651 the highest rates, whereas in the case of pine litter, the main VOCs were α -pinene and 3-
652 carene.

653 In a recent study, the results of laboratory measurements of the rates of VOC release by
654 fresh (not decomposed) deciduous litter of 16 species of woody and shrub plants typical of the
655 Mediterranean region are presented (Viros et al., 2020). These species are divided by the
656 authors into two groups depending on the presence of terpene storage structures. Eighty-seven
657 VOCs were identified in the isolations of all the examined plants by GC-MS. The emission
658 rates of various VOCs at a temperature of 30°C ranged greatly. In the case of nine plants of
659 the terpene-storing species (*Eucalyptus globulus*, *Juniperus oxycedrus*, *Pinus pinea*, *P.*
660 *halepensis*, *Rosmarinus officinalis*, *Thymus vulgaris*, *Cistus albidus*, *C. salviifolius*, *Cotinus*
661 *corrygia*), the total emissions of monoterpenes, sesquiterpenes and non-terpene compounds
662 were in the range of < 0.01–4.62, 0.04–0.92 and < 0.01–0.23 $\mu\text{g g}^{-1} \text{h}^{-1}$, respectively (Table 7).
663 Emissions of seven non-terpene-storing species via litter (*Acer monspesulanum*, *Erica*
664 *arborea*, *Quercus ilex*, *Q. coccifera*, *Q. pubescens*, *Q. suber*, *Ulex parviflorus*) consisted
665 mainly of linear alkanes and carbonyl compounds and ranged from 0.01 to 0.61 $\mu\text{g g}^{-1} \text{h}^{-1}$
666 (Table 8).

667 A 15-month litter bag experiment was conducted to study the composition of VOCs
668 released by the decaying pine needles of *Pinus halepensis*, one of the main coniferous trees in
669 the Mediterranean (Viros et al., 2021). Material for laboratory studies was sampled every 3
670 months, and VOC emissions were determined both online (using the PTR-ToF-MS
671 instrument) and offline (GC-MS). During the observation period, 58 compounds were

672 registered in the composition of the fallen needle excretions. The maximum emission of 9.18
673 $\mu\text{g g}^{-1} \text{h}^{-1}$ was observed 3 months after the beginning of the experiment, with the main
674 components being α -pinene, terpinolene, 3-carene, limonene, sabinene and myrcene, whereas
675 the main sesquiterpenes were β -caryophyllene, α -humulene and copaene. In addition, at this
676 stage, the emission of highly volatile non-terpene compounds took place, with the main ones
677 being methanol, acetic acid and acetone. The maximum emission of oxidised monoterpenes
678 and sesquiterpenes occurred between the third and sixth months of the experiment.
679 Comparison of data on VOC emissions from green and decaying fallen needles *P. halepensis*
680 led the authors of the cited work to the conclusion that the contribution of litter to the total
681 emission in forests from this pine species (their area in the Western Mediterranean is about
682 3.5 million hectares) can be extremely high.

683 The data presented in this section indicate that VOC emissions from the forest floor are
684 not negligible. Moreover, during the spring and autumn seasons, the forest floor can be the
685 main source of these reactive components. However, to establish its effect on air quality,
686 additional studies are needed to determine the emission factors for different ecosystems and
687 biomes.

688 **VI. Conclusions**

689 It is recognised that a critical challenge for atmospheric chemistry is closing the
690 atmospheric organic carbon budget. This review shows that deciduous litter and plants of
691 living forest soil cover are an unaccounted source of large amounts of VOCs, for many of
692 which a high potential for the formation of ozone and other atmospheric photooxidants and/or
693 secondary aerosols has been postulated. The results of many studies indicate that these
694 elements of forest ecosystems are not negligible sources of atmospheric VOCs, especially in
695 spring and autumn. Based on their origin, they are a mixture of a variable composition of

696 products released as a result of various insufficiently studied physical and biological
697 processes.

698 There are serious knowledge gaps that prevent a quantitative assessment of the role of
699 VOC emissions from the forest floor in biospheric processes. These include the lack of
700 information on the composition and emission rates of litter VOCs in various forest types,
701 primarily those formed by deciduous tree species: the overwhelming majority of the
702 measurements were made in the coniferous forests of the northern belt. This applies to an
703 even greater extent to the dead parts of herbaceous plants of steppe and related ecosystems,
704 although the biomass of grass felt per unit area in them can significantly exceed that of
705 deciduous litter in forests. The participation of soil cover plants in the balance of these
706 compounds has hardly been studied, and it is unclear whether they serve as sources of VOCs
707 or as their absorbers (Mäki et al., 2017; Stoy et al., 2021). In some pioneering works, an
708 important influence on the rate of decomposition of litter of solar radiation, including in the
709 visible part of the spectrum, has been shown (Austin et al., 2016; Keiser et al., 2021).
710 However, the chemical composition of the resulting compounds, both volatile and easily
711 accessible for microbiological assimilation, has not been studied. Insufficient research has
712 focused on the impact of global changes on litter decomposition and VOC emissions by
713 ecosystems. There is also a lack of data on both litter and plants of the living ground cover of
714 forests in different geographic zones necessary for an inventory of VOC emissions on a
715 regional and global scale.

716 The study of the decomposition of leaf litter, the chemical composition and emission
717 rates of volatile organic compounds is of interest not only from the point of view of
718 atmospheric chemistry. Biogenic VOCs are involved in competitive interactions as both
719 allelochemicals and as neighbour detection signals (Kegge and Pierik, 2009). Volatile organic
720 compounds from leaf litter decomposition alter soil microbial communities and carbon

721 dynamics (McBride et al., 2020). However, it should be noted that this is not the only process
722 linking deciduous litter and soil biota. When litter decomposes, both labile and more stable
723 forms of dissolved organic matter are formed, significantly affecting the binding and
724 consumption of carbon in the soil (Hensgens et al., 2021); however, the chemical composition
725 of compounds leached from the litter and the very scale of this phenomenon remain
726 unexplored.

727 This review is limited to boreal and temperate natural ecosystems of the Northern
728 Hemisphere because of the almost complete absence of literature data on VOC emissions
729 from forest soil cover from other botanical-geographical zones. In particular, only a few
730 works are devoted to VOC emissions in subtropical and tropical forests (Drewer et al., 2021;
731 Crocker, 2021). We would like our review to serve as a stimulus for expanding the geography
732 of research and for a deeper study of the role of both 'dead' and living forest soil cover in the
733 release of organic compounds into the environment, which play an important role in many
734 ecological processes under the forest canopy and in the global atmosphere.

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737 **[http://www.biogeosciences.net/.....](http://www.biogeosciences.net/)**

738

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746

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1301 **Table 1.** Rate of decomposition of dead plant parts (%) during the warm season in two
1302 ecosystems of the forest-steppe zone of Russia (Bazilevich et al., 1993).

Factors	Oak forest	Meadow steppe
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Warm season		
Abiotic	14	72
Biotic		
– microorganisms	10	11
– mesofauna	30	9
– macrofauna	46	8
Whole year		
Abiotic	15	30
Biotic		
– microorganisms	45	55
– meso- and macrofauna	40	14

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1318 **Table 2.** Organic compounds in volatile emissions of leaves litter. Plant species: 1 - oriental beech (*Fagus*
1319 *orientalis*); 2 - sequoia (*Sequoiadendron giganteum*); 3 - cherry prinsepia (*Prinsepia sinenes*); 4 - aspen (*Populus*
1320 *tremula*); 5 - English oak (*Quercus robur*); 6 - maple (*Acer rubrum*); 7 - pine (*Pinus taeda*); 8 - poplar (*Populus*
1321 *balsamifera*); 9 - birch (*Betula pendula*); 10 - willow (*Salix* sp.); 11 - common beech (*Fagus sylvatica*); 12 -

1322 broad beech fern (*Phegopteris hexagonoptera*); 13 - northern red oak (*Q. rubra*); 14 - bur oak (*Q. macrocarpa*);
 1323 15 - lodgepole pine (*P. contorta*); 16 - ponderosa pine (*P. ponderosa*); 17 - eastern cottonwood (*Populus*
 1324 *deltooides*); 18 - quaking aspen (*Populus tremuloides*); 19 - green ash (*Fraxinus pennsylvanica*); 20 - great laurel
 1325 (*Rhododendron maximum*); 21 - eucalyptus (*Eucalyptus* sp.); 22 - spotted knapweed (*Centaurea maculosa*); 23 -
 1326 miscanth (*Miscanthus* sp.); 24 - wheatgrass (*Thinopyrum intermedium*); 25 - Scots pine (*P. sylvestris*); 26 -
 1327 Norway spruce (*Picea abies*); 27 - European larch (*Larix decidue*); 28 - clover (*Trifolium repens*); 29 - bluegrass
 1328 (*Poa pratensis*); 30 - European silver fir (*Abies alba*).
 1329 References: **a** - Derendorp et al. (2011); **b** - Isidorov et al. (2002); **c** - Ramirez et al. (2010); **d** - Warneke et al.
 1330 (1999); **e** - Fall et al. (2001); **f** - Gray et al. (2010); **h** - Isidorov et al. (2003); **i** - Isidorov et al. (2010); **j** -
 1331 Isidorov et al. (2005); **k** - Kesselmeier and Hubert (2002).
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Compound	Plant	Ref.
Aliphatic hydrocarbons		
Ethane	1,2	a
Ethylene	1-3	a
Propane	1-3	a
2-Butene	4,5	b
Butin	6,7	c
Pentane	1-3	a
Isoprene	4,5,8-24	b,d-f
Hexane	4,8	b
Heptane	4,5,8	b
Octane	4,5,8,9	b
Nonane	4,5,8-10	b
Decane	4,5,8-10	b
Undecane	4,5,8-10	b
Dodecane	4,5,8	b
Tridecane	4	b
Aromatic hydrocarbons		
Benzene	4,5,10,25,26	b,h,i
Toluene	4-10,13-24	b,f
Ethyl benzene	4,5,8-10	b
<i>p</i> -Xylene	4,5,9	b
<i>m</i> -Xylene	5,8,9	b
<i>o</i> -Xylene	5,9	b
Cumene	8	b
<i>n</i> -Propyl benzene	5	b
Mesitylene	5	b
<i>p</i> -Cymene	4,5,8-10,25,26	b, h, i
<i>p</i> -Cymenene	13	h
Monoterpene hydrocarbons		
Santene	26	h,i
Triicyclene	4,5,9,25,26	b, h, i
α -Thujene	25,26	g
α -Pinene	4,5,8-11,25-27	b,d, h-j
Camphene	4,5,8-10,25-27	b, h-j
Verbenene	25,26	h,i
Sabinene	25,26	i
β -Pinene	4,5,10,11,25-27	b,d,h-j
Myrcene	8,25-27	b,h-j
α -Phellandrene	9,25,26	b,i
3-Carene	4,10,25,26	b,h,i
α -Terpinene	8,25,26	b,i
β -Phellandrene	25,27	h,j
Limonene	4,5,8,9,25-27	b,h-j
β -(Z)-Ocimene	25,26	h,i
β -(E)-Ocimene	9,25,26	h,i

γ -Terpinene	25,26	h,i
<i>p</i> -Mentha-2,4(8)-diene	25	i
Terpinolene	25,26	h,i
Monoterpenoids		
1,8-Cineol, dehydro-	8,9	b
1,8-Cineol	5,26	h
Camphor	25,26	h,i
Fenchone	4	b
Linalool	25,26	h
Camphene hydrate	26	i
Limonene oxide	5	b
β -Terpineol	26	h
Borneol	26	h,i
<i>cis</i> -3-Pinanone	25	h
Terpin-4-ol	25,26	h
α -Terpineol	25,26	h,i
Myrtenol	25,26	i
<i>p</i> -Cymen-8-ol	25	h
Verbenone	25	h,i
<i>cis</i> -Carveol	25	h
Myrtanol	26	h
Linalyl acetate	26	h
α -Terpenyl acetate	25,26	i
Bornyl acetate	25,26	b, i
Sesquiterpene hydrocarbons		
δ -Elemene	26	h
α -Cubebene	25,26	h
α -Longipinene	26	h,i
Longicyclene	26	h
Ylangene	25	i
α -Copaene	25,26	h,i
β -Bourbonene	25,26	h,i
β -Cubebene	25	h,i
β -Elemene	25	h,i
D-Longifolene	25,26	i
(Z)-Caryophyllene	25	i
α -Gurjunene	25	h
β -Caryophyllene	25,26	h,i
Aromadendrene	25,26	i
β -Humulene	25,26	h
α -Humulene	25,26	h,i
γ -Muurolene	25,26	h,i
Germacrene D	25	i
β -Selinene	25	h,i
α -Selinene	25	h,i
α -Muurolene	25,26	h,i
γ -Cadinene	25,26	h,i
Cadina-1,4-diene	25,26	h,i
α -Calacorene	25	i
Sesquiterpenoids		
Spathulenol	25	h
Caryophyllene oxide	25	h,i
<i>epi</i> - α -Cadinol	25	h
α -Muurolol	25	h
τ -Cadinol	25	i
α -Cadinol	25	h,i
Carbonyl compounds		
Acetaldehyde	11,13-26	d,f-h

α -Methylacroleine	4,5	b
Propanal	13-24	f
Isobutanal	5	b
2-Methyl butanal	28	e
3-Methyl butanal	8,28,29	b,e
Pentanal	4,8,26	b,i
Hexanal	25,26,28	e,i
2-Hexenal	5,8,10	b
3-(Z)-Hexenal	11,29	e
Nonanal	25,26	i
Benzaldehyde	4,5,8-10,26	b,i
Furfural	4	b
Anis aldehyde	26	h
Vanillin	6,7	c
Acetone	5-7,10,11,13-26	b-d,f-i
Butan-2-one	5,10,11,13-26	b,d,f-i
1-Penten-3-one	12,28-30	e
2-Pentanone	25	i
3-Hexanone	25	i
4-Octanone	25,26	i
3-Octanone	25,26	i
6-Methyl-5-hepten-2-one	25,26	i
2-Decanone	25	i
Alcohols		
Methanol	6,7,11,13-24	c,d,f
Ethanol	4,5,8-11,13-26	b,d,f,i
1-Propanol	11,13-24	d,f
1-Butanol	4,5,8,13-24	b,f
2-Methyl-1-butanol	25,25	h
3-Methyl-1-butanol	4,25,26	b,h
1-Penten-3-ol	12,28-30	e
2-(Z)-penten-1-ol	12,28-30	e
1-Pentanol	25	h
2-Ethyl-1-hexanol	25,26	i
Phenol	25,26	i
Benzyl alcohol	25,26	i
Esters		
Methyl formate	8	b
Methyl acetate	4	b
Ethyl acetate	4,5,10,25	b,h
Methyl tiglate	4	b
Butyl acetate	5,8,10,25,26	b,i
Ethyl butanoate	25,26	i
Allyl butyrate	4	b
Isopentyl acetate	4,10	b
Isopentyl butanoate	25	i
<i>sec</i> -Pentyl acetate	4	b
Allyl isopentanoate	4	b
Hexenyl acetate	28	e
Ethyl 3-methylbutanoate	7	c
Isopentyl butanoate	25	i
Sulfur and chlorine containing compounds		
Methyl mercaptane	8	a
Ethyl mercaptane	8	a
Dimethyl sulfide	11	k
Diethyl sulfide	4	a
Ethyl isopropyl sulfide	4	a

Methyl chloride	1-4	a,b
Dichloromethane	4,25,26	b,i
Trichloromethane	4,26	b,i
Trichloroethylene	25,26	i
Tetrachloromethane	4,5,8	a
Other VOCs		
Formic acid	13-24	f
Acetic acid	5,8,13-24	b,f
Diethyl ether	4,9,10	b
2-Methylfuran	5,9,10,25,26	b,i
3-Methylfuran	25,26	i
Thymol, methyl ether	25	i
<i>o</i> -Cresol	5	b
Anisol	8	b
Methoxy phenol	8	b

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Table 3. VOCs composition of some LS plants (forests and bog forests). Plants: 1 - lichen (*Cetraria islandica*); 2 - heather (*Calluna vulgaris*); 3 - moss (*Pleurozium schreberi*); 4 - club moss (*Lycopodium clavatum*); 5 - red bilberry (*Vaccinium vitis-idaea*); 6 - bilberry (*Vaccinium myrtillus*); 7 - moss (*Polytrichum commune*); 8 - marsh tea (*Ledum palustre*); 9 - male fern (*Dryopteris filix-max*); 10 - soft tree fern (*Dicksonia antarctica*); 11 - Japanese beech fern (*Thelypteris decursive-pinnata*); 12 - southern shield fern (*Thelypteris kunthii*); 13 - cottongrass (*Eriophorum* sp.); 14 - red raspberry (*Rubus idaeus*); 15- Labrador tea (*Rhododendron groenlandicum*); 16 - bog heather (*Erica tetralix*); 17 - sphagnum (*Sphagnum fuscum*); 18 - thick stemmed wood fern (*Dryopteris crassirhizoma*); 19 - marsh andromeda (*Andromeda polifolia*); 20 – lichen (*Cladonia arbuscular*); 21 – moss (*Dicranum polysetum*); 22 – moss (*Hylocomnium splendens*); 23 – moss (*Leucobrium glaucum*); 24 – moss (*Sphagnum fallax*); 25 – pipsissewa (*Chimaphilla umbellate*); 26 - European clefthoof (*Asarum europaeum*); 27 – catsfoot (*Antennaria dioica*); 28 – fern (*Pteridium aquilium*).
Ref.: a - Isidorov et al. (1994); b - Isidorov et al. (1992); c - Isidorov et al. (1985); d – Isidorov et al. (2022); e- Tingey et al. (1987); f - Drewitt et al. (1998); g - Helmig et al. (1999); h - Mochizuki et al. (2014); i - Rinnan et al. (2005).

Compound	Plant	Ref.
Aliphatic hydrocarbons		
Ethane	1,3,5	a
Propane	2-4	a
Butene	1-4	a
2-Methylbutane	1,2,4-9	a-c
<i>n</i> -Pentane	1-4	a
Pentene	5-7,9	b
Penta-1,3-diene	7,9	c
Isoprene	1,2,4-15,17-19	a-c,e-i
2,3-Dimethylbutane	17	i
2,3-Dimethylbutadiene	8	b
<i>n</i> -Hexane	20-28	d
2-Methylpentane	23	d
<i>n</i> -Heptane	1,21	a,d
4,8-Dimethyl-1,3,5-nonatriene	6,27	d
1-Octene	22,27	d
1,3-Octadiene	28	d
2,6-Dimethyl-2,4,6-octatriene	6	d
3,7,7-Trimethyl-1,3,5-cycloheptatriene	22,24	d
<i>n</i> -Decane	1	a
<i>n</i> -Undecane	1,2,27	a,d
<i>n</i> -Tetradecane	6,20	d

<i>n</i> -Pentadecane	22,24,26	d
<i>n</i> -Hexadecane	24	d
<i>n</i> -Heptadecane	21,24	d
<i>n</i> -Nonadecane	24	d
<i>n</i> -Heneicosane	25	d
Methyl cyclopetane	3,23	d
Cyclohexane	3,20,21	d
Aromatic hydrocarbons		
Benzene	1-3	a
Toluene	1-3,20,21,25-28	a,d
<i>m</i> -Cymene	21,24,27,28	d
<i>p</i> -Cymene	1,2,14-16,20-28	a,d,g
<i>p</i> -Cymenene	15	f
Monoterpenes		
Bornylene	5	b
Tricyclene	7	b
α -Thujene	5,15,16	b,g
α -Pinene	2-14,16,19, 21-23, 26-28	a-g,i
β -Pinene	1,7,8,15,16,21,24,26	a-d,g
Sabinene	7,21,26	d
α -Fenchene	5,15	b,g
Camphene	2,5,7,8,15,17,21,22,26,27	a-d,g
Myrcene	2,6-8,14-16,22,26,27	a-d,g
2-Carene	24,28	d
3-Carene	3,6-8,16,21,22,24-28	b,c,d,g
α -Phellandrene	5,15,16	b,d,g
α -Terpinene	25,28	d
Limonene	1,7,8,13-16,19-28	a-d,g,i
Alloocimene	8	b,c
(<i>Z</i>)-Ocimene	6,25-27	d
(<i>E</i>)-Ocimene	6,15,25-27	d,g
<i>neo-allo</i> -Ocimene	6	d
α -Terpinene	15,16,25,28	d,g
γ -Terpinene	15,24-28	d,g
Terpinolene	6,8,14,24,26,28	b-d,g
Isoterpinolene	28	d
Isobornyl acetate	15,16	g
1,8-Cineol	22,24	d
Linalool	3,6,25	d
Campholenal	21	d
(<i>E</i>)-Verbenol	25	d
Camphor	22,26	d
Pinocarvone	24	d
Isoborneol	25,26	d
Borneol	22,26	d
4-Terpineol	6,26	d
Myrtenol	25	d
Myrtenal	24	d
Verbenone	25	d
(<i>E</i>)-Carveol	25	d
β -Cyclocitral	24	d
Geraniol	6	d
Dihydromyrcenol	3,25,26	d
α -Terpineol	3,6,20,23,25	d
Linalyl acetate	26	d
Bornyl acetate	25,26	d
(<i>Z</i>)-Ethyl linalool	20-22	d
(<i>E</i>)-Ethyl linalool	20-22	d

α -Terpenyl acetate	25	d
Sesquiterpenes		
Silphinene	27	d
α -Cubebene	6,27	d
α -Ylangene	6,25	d
Moderphene	27	d
α -Isocomene	27	d
β -Isocomene	27	d
β -Bourbonene	6,21,24	d
α -Copaene	6,21,24	d
β -Copaene	26	d
β -Cubebene	6	d
α -Chamipineneq	25	d
Longifolene	21,22,24,25	d
α -Humulene	6,21,26,27	d
(<i>E</i>)- β -Farnesene	27	d
(<i>E</i>)-Muuurola-4(14),5-diene	26	d
Alloaromadendrene	24,25	d
(<i>E</i>)-Cadina-1(6),4-diene	6	d
α -Amorphene	25	d
γ -Muurolene	6,26	d
Germacrene D	6,26,27	d
α -Curcumene	27	d
δ -Selinene	26	d
Bicyclosesquiphellandrene	6	d
Bicyclogermacrene	26	d
A-Zingiberene	27	d
γ -Amorphene	6,25	d
β -Himachalene	25	d
Cuparene	25	d
(<i>E,E</i>)-Farnesene	6	d
(<i>Z</i>)-Calamenene	6	d
(<i>E</i>)-Calamenene	25	d
γ -Cadinene	6,21,25,26	d
δ -Cadinene	24,26	d
α -Cadinene	6,26	d
β -Sesquiphellandrene	27	d
α -Copaen-8-ol	25	d
Caryophyllene oxide	25	d
Humulene epoxide II	25	d
β -Eudesmol	25	d
α -Eudesmol	25	d
Caryophylla-3,8(13)diene-5 α -ol	25	d
Caryophylla-3,8(13)diene-5 β -ol	25	d
Carbonyls		
Propanal	9	b,c
Butanal	9	b,c
Isobutenal	7,9	c
α -Methylacrolein	7,9	b
Pentanal	21	d
Hexanal	3,9,20-24,26	c,d
(<i>E</i>)-2-Hexenal	23,24,28	d
Heptanal	3,20-22,24	d
(<i>E</i>)-2-Heptenal	23,24	d
(<i>E,E</i>)-2,4-Heptadienal	23	d

Octanal	3,12,20-22,24	d,f
Benzaldehyde	2,3,16,23,24	a,d,f
Benzeneacetaldehyde	23,24	d
(E)-2-Octenal	23,24	d
(2E,4Z)-Decadienal	23,24	d
(2E,4E)-Decadienal	25	d
Undecanal	24	d
(E)-2-Undecenal	24	d
Acetone	1-3,5-9,14,20-28	a-d,f
Butan-2-one	9	b,c
2-Methylbutan-3-one	8	c
3-Methyl-3-buten-2-one	9	b
Pentan-2-one	5-7,9,22	b-d
Pentan-3-one	6,7,23,24	b-d
6-Methyl-5-hepten-2-one	3,12,21,22	d,f
5-Methyl-3-hepten-2-one	17,20	d,f
Octan-3-one	7,9	c
1-Octen-3-one	7,9	b
3-Octanone	24	d
(E,E)-3,5-Octadien-2-one	23	d
(E,Z)-3,5-Octadien-2-one	23,24	d
Acetophenone	27	d
β -Ionone	6,23,24	d
Furans		
2-Methyl furan	5-9,12	b,c,f
3-Methyl furan	6	b,c
2-Ethyl furan	5-7,9,12,23,24	b-d,f
Vinyl furan	8	b,c
2-Pentenyl-2-furan	23	d
2-Pentylfuran	23,24	d
Hexyl furan	8	b
Furan, 3-(4-methyl-3-pentenyl)-	8	c
Alcohols		
Ethanol	1-7,9,20-25,28	a-d
Butan-1-ol	1	a
1-Penten-3-ol	24	d
1-Pentanol	20,24	d
(Z)-2-Pentenol	23,24	d
1-Octen-3-ol	24	d
1-Octanol	3,20-22,24	d
1-Nonanol	20,24,25	d
(Z)-3-Hexen-1-ol	5,6,8,14,19,24,28	b-d,f,h
2,5-Dimethylcyclohexanol	24	d
6-Methyl-5-hepten-2-ol	12,20	d,f
Acids		
Acetic acid	3,20-24	d
Isopentanoic acid	23,26	d
Hexanoic acid	20,23,25,26	d
Octanoic aci	3,21,23	d
Nonanoic acid	23	d
Esters		
Ethyl acetate	1-3,5-7,20-22	a-d
(Z)-3-Hexen-1-nyl acetate	5,6,12,16	b,c,f
2-Hexen-1-ol acetate	23,26	d
(Z)-3-Hexenyl isobutyrate	6	d
(Z)-3-Hexenyl butyrate	6	d
(E)-2-Hexenyl butyrate	6,25	d

Octyl acetate	20	d
(Z)-3-Hexenyl isovalerate	6	d
(Z)-3-Hexenyl tyglate	6	d
(Z)-3-Hexenyl (3Z)-hexenoate	6	d
Benzyl acetate	3	d
Methyl salicylate	6,25	d
Phenyl ethyl acetate	3	d
(Z)-3-Hexenyl benzoate	6	d
Lactones		d
γ -Butyrolactone	23	d
γ -Valerolactone	20	d
γ -Caprolactone	20	d
Other		
Diethyl ether	1-4	a
Methyl chloride	1,4	a
Chloroform	7	c
Dimethyl sulfide	9	b
2-Cyanobutane	6	d
Isoamyl nitrile	6	d
Methyl carvacrol	25	d
Methylthymol	26	d
Thymol	25	d
Carvacrol	25	d
Dihydroactinidiolide	24	d
Benzothiazole	20	d

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Table 4

Relative composition (% of TIC) of volatile compounds emission from "fresh" pine and spruce litter and isolated from litter fungi after 490 days of the needle incubation)

Compound	Pine litter	Spruce litter	<i>Trichoderma polysporum</i>		<i>Trichoderma koningii</i>	<i>Mortirella isabellina</i>	<i>Penicillium purpurogenum</i>	<i>Penicillium minioluteum</i>	<i>Absidia glauca</i>	<i>Thielavia terricola</i>	Non-spore forming
			Pine	Spruce	Spruce	spruce	spruce	pine	pine	spruce	
Monoterpenes	8.0	10.2	69.8	22.5	34.8	72.2	1.1	4.0	44.1	67.9	56.3
- α -pinene	3.5	4.6	17.0	5.9	15.1	10.1	0.5	0.1	4.1	14.6	8.4
- camphene	0.2	0.5	0.7	-	trace	0.3	trace	-	-	-	0.1
- myrcene	-	trace	26.4	trace	8.2	24.5	-	0.1	1.8	-	3.2
- 3-carene	2.8	3.2	trace	8.7	9.9	1.5	0.6	3.4	33.1	36.9	37.1
- limonene	1.0	1.0	13.3	5.8	0.6	26.1	trace	trace	4.6	10.0	5.5
- terpinolene	-	-	6.1	-	0.2	4.6	-	0.4	0.5	0.2	-
Monoterpenoids	-	5.0	3.6	6.6	3.2	0.1	-	-	8.0	-	11.2
- linalool	-	1.2	-	-	1.2	-	-	-	-	-	-
- menthone	-	-	2.3	6.6	0.8	-	-	-	-	-	8.1
- menthol	-	-	0.7	2.1	1.2	-	-	-	-	-	2.5
- verbenone	-	-	-	0.1	0.1	-	-	-	-	-	0.5
Sesquiterpenes	2.1	1.3	16.5	0.3	19.0	9.0	-	-	-	-	0.4
- longifolene	2.1	1.3	-	-	1.5	-	-	-	-	-	-
- β -caryophyllene	-	-	15.2	0.3	14.2	9.0	-	-	-	-	0.4
Alcohols	13.2	7.2	2.8	51.8	39.5	3.6	8.4	-	0.8	16.2	10.5
- ethanol	-	-	-	25.0	22.5	2.8	trace	-	-	16.2	4.3
- isopentanol	-	-	0.8	8.5	12.6	0.7	trace	-	-	-	2.7
- 1-octen-3-ol	-	-	0.2	0.1	9.2	0.1	8.4	trace	-	-	-
Carbonyls	34.6	38.9	2.5	9.7	13.9	8.8	82.5	50.3	41.3	8.8	12.9
- acetaldehyde	-	-	0.5	0.1	2.0	-	-	-	trace	-	-
- acetone	26.8	36.8	2.0	9.7	6.9	8.8	82.5	46.0	18.7	8.8	12.9
- 2-butanone	-	-	-	trace	-	-	-	2.8	22.6	-	-
- 3-octanone	-	-	trace	trace	2.4	-	trace	trace	-	-	-

Esters	trace	-	-	1.2	1.5	0.9	-	-	-	0.8	4.8
Furans	-	-	-	2.5	3.0	-	3.6	6.1	-	2.0	0.3
Chlorohydrocarbons	12.5	4.9	-	trace	-	0.2	0.9	3.9	-	-	-
- chloroform	-	-	-	trace	-	0.2	0.9	3.9	-	-	-
Aromatic hydrocarbons	19.5	10.5	3.0	0.7	3.8	4.4	0.2	5.7	0.6	2.3	1.9
- benzene	7.0	3.1	-	-	2.1	0.2	-	0.9	-	-	-
- toluene	7.3	5.2	0.2	trace	0.7	0.5	0.1	1.1	0.4	1.6	0.8
- xylenes	1.0	1.2	0.1	0.2	trace	0.2	0.1	0.7	-	0.1	0.1
- <i>p</i> -cymene	0.7	0.5	2.7	0.5	0.5	3.5	-	2.6	0.2	0.3	1.0
Alkanes	12.3	8.3	0.7	0.7	0.4	0.9	1.1	14.3	-	1.6	0.7

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Table 5. Field measurements of VOC emission from forest floor

Method	Forest/sampling site type	Time of experiments	Emission rates	References
Static flow chamber technique. Sampling in sorption tubes with Tenax TA. GC-MS analysis of VOCs after thermal desorption.	VOCs emission from pine forest floor on two plots in the 140-year-old stand of Scots pine in the southern Sweden.	VII and X.1992	The terpene emission rate in July normalized to 20°C was 21 µgC m ⁻² h ⁻¹ . In October, the emission rate at the two test sites was 104 and 580 µgC m ⁻² h ⁻¹ . According to the author's estimates, the emission from the bottom of a pine forest reaches 30% of the emission from tree crowns.	Janson, 1993
Static flow chamber technique. VOC concentration in dual-bed sorption tubes with Tenax GC and Carbotrap. GC-MS analysis of VOCs after thermal desorption	Middle taiga pine (<i>P. sylvestris</i>) forest in Karelia (62° 07' N, 33° 56' E) with soil cover with green mosses (<i>Pleurocium schreberi</i> , <i>Politrichum commune</i>), lichens (<i>Cetraria islandica</i> , <i>Cladonia rangiferina</i>), shrubs (<i>Calluna vulgaris</i>) and club moss.	VII–VIII. 1993	Depending on the temperature (16–28°C) within 6.1–40.5 µgC g ⁻¹ h ⁻¹ (based on the dry weight of pine litter and living plants inside the static chamber).	Isidorov et al., 1994
Static chamber technique. VOC concentration on Tenax TA; whole air sampling of light hydrocarbons; sample analysis by GC-FID.	Southern boreal zone in Sweden. Mixed pine (<i>P. sylvestris</i>) and spruce (<i>P. abies</i>) forest, about 50 years of age, and a <i>Sphagnum</i> fen.	VI–IX.1995	The monoterpene flux from forest floor made up only a few percent of total forest flux, reaching 50 µgC m ⁻² h ⁻¹ . The highest flux was observed from the moss plots. Small emission of ethene and propane was registered. Sphagnum fen emitted isoprene at the average rate 55±45 µgC m ⁻² h ⁻¹ in June and 408±240 µgC m ⁻² h ⁻¹ in August. Monoterpene fluxes were 19±9 µgC m ⁻² h ⁻¹ .	Janson et al., 1999

			$^2 \text{ h}^{-1}$ in June and $90 \pm 60 \mu\text{gC m}^{-2} \text{ h}^{-1}$ in August.	
Static chamber technique. VOC concentration in sorption tubes with Tenax TA. GC-MS analysis of VOCs after thermal desorption.	Leningrad region ($59^\circ 57' \text{ N}$, $29^\circ 51' \text{ E}$). Coniferous forest with a predominance of Norway spruce (<i>Picea abies</i>). The soil cover is formed by litter of spruce needles and green mosses.	VII-IX.1997	The monoterpenes fluxes from fallen spruce needles at $6-25^\circ \text{ C}$ was $20.9-402.0 \mu\text{g m}^{-2} \text{ h}^{-1}$. The share of α -pinene in the total emission of terpenes is 82%. The highest emission rates were recorded shortly after rainfall.	Stepanov, 1999
PTR-MS system was used for simultaneous monitoring of the VOCs concentration.	Semi-natural experiment on VOC emission by decaying beech leaves	IV.1997	The observed emission rate of methanol, acetaldehyde and acetone at 19° C was 1.0, 0.23 and $0.1 \mu\text{g g}^{-1}(\text{dw}) \text{ h}^{-1}$, respectively	Warneke et al., 1999
Dynamic soil enclosure technique. Air samples were collected on dual-bed adsorption trap (Tenax TA + Carbotrap). GC-MS analysis of VOCs after thermal desorption.	Sitka spruce (<i>Picea sitchensis</i>) commercial plantation ($54^\circ 20' \text{ N}$, $3^\circ 2' \text{ W}$). The trees on the plantation are 35 years old.	VII.1999	The average rate of terpene emission from the undisturbed forest floor was $33.6 \mu\text{g m}^{-2} \text{ h}^{-1}$ (30° C). Limonene and α -pinene dominated the emission of monoterpenes; camphene, β -pinene and myrcene were also present in significant quantities. According to authors, the surface needle litter was the most likely source of soil emissions to the atmosphere.	Hayward et al., 2001
Static chamber technique. VOC concentration in sorption tubes with Tenax TA-Carbopack B adsorbent. GC-MS analysis of VOCs after thermal desorption.	Boreal wetland and a Scots pine forests at the SMEAR II station ($61^\circ 51' \text{ N}$, $24^\circ 17' \text{ E}$) in southern Finland. Forest is dominated by <i>P. sylvestris</i> with admixture of aspen (<i>P. tremula</i>) and birches (<i>B. pendula</i> and <i>B. pubescens</i>). The ground vegetation consists mainly of shrubs. Northern ribbed fen is dominated by mosses (<i>Sphagnum</i> sp.), sedges and Rannoch-rush.	VI-X.2014; IV-VI, VIII.2015	Isoprene was main hydrocarbon emitted by the wetland with the mean emission potential $224 \mu\text{g m}^{-2} \text{ h}^{-1}$ for the whole season. Monoterpene emission from boreal forest floor varied from 0 to $373 \mu\text{g m}^{-2} \text{ h}^{-1}$ ($0-0.8 \mu\text{g m}^{-2} \text{ h}^{-1}$ of β -caryophyllene). Comparison with Scots pine emission showed that forest floor may be an important monoterpene source, especially in spring	Hellén et al., 2006
Dynamic PVC soil cuvette system. VOCs released by soil and litter were concentrated in sorption tubes with Carbotrap C, Carbotrap B, and Carbosieve S-II separated by quartz	Mediterranean mountains environment in the Prades region of Southern Catalonia dominated by evergreen oak <i>Quercus ilex</i>	Spring 2003–spring 2004	The measured monoterpene emission in summer was $1.67 \pm 1.57 \mu\text{g m}^{-2} \text{ h}^{-1}$ normalised to 30° C .	Asensio et al., 2007

wool. GC-MS analysis after thermal desorption.				
The air was sampled using a transparent polycarbonate chamber placed on an aluminum collar. VOCs were concentrated in sorption tubes filled with a combination of Tenax TA and Carbopack B adsorbents. GC-MS analysis of VOCs after thermal desorption	Wet dwarf shrub heath in northern Sweden (68° 21' N, 18° 49' E; 385 m a. s. l.). The vascular vegetation consist mainly of the sedge (<i>Carex vaginata</i>) and the evergreen shrubs <i>Empetrum hermaphroditum</i> and <i>Andromeda polifolia</i> . Additionally, an experiment was carried out to study the effect of the addition of <i>Betula pubescens</i> ssp. <i>czerepanovii</i> litter.		The measured monoterpene hydrocarbons emission rate varied from 1.5 to 9.8 $\mu\text{g m}^{-2} \text{h}^{-1}$. The relatively low emissions of terpenoids were doubled in response to an air temperature increment of only 1.9–2.5°C, while litter addition had a minor influence.	Faubert et al., 2010
Steady-state chamber system. VOC concentration in sorption tubes with Tenax-Carbopack-B adsorbent. GC-MS analysis of VOCs after thermal desorption.	Scots pine forest floor at the SMEAR II station in southern Finland.	IV–XI.2008	Emission rates: $\text{C}_{10}\text{H}_{16}$ – 5.04 $\mu\text{g m}^{-2} \text{h}^{-1}$; $\text{C}_{15}\text{H}_{24}$ – 0.045 $\mu\text{g m}^{-2} \text{h}^{-1}$; C_5H_8 – 0.05 $\mu\text{g m}^{-2} \text{h}^{-1}$. Seasonal variations were recorded with a maximum in early summer and autumn.	Aaltonen et al., 2011
Static enclosure technique. PTR-MS system was used for simultaneous monitoring of methanol, acetaldehyde, acetone and propanal, acetic acid, mono- and sesquiterpenes emission.	The Manitou Experimental Forests (39° 6' N, 150° 5'30" W) with mixed-age ponderosa pine up to 100 years old and a sparse vegetation surface cover of grasses, sage and forbs.	VI–VII.2010	Litter fluxes made only a minor contribution to the above-canopy flux for the VOCs measured. In the case of methanol, acetaldehyde, acetone, and the sum of monoterpenes, the average daily flux is 1.3, 0.3, 0.3, and 3.1 $\mu\text{g m}^{-2} \text{h}^{-1}$, respectively. The litter emission clearly follow the trend in temperature; the dependence of litter moisture is of lesser importance, however, VOC emissions increased immediately after the rain.	Greenberg et al., 2012
BVOC emissions were measured during 24-hour periods in the field using a push-pull chamber technique and collection of volatiles in adsorbent cartridges followed by analysis with GC-MS	Five arctic vegetation communities were examined: high arctic (74°30' N, 21°00' W) heaths dominated by <i>Salix arctica</i> and <i>Cassiope tetragona</i> , low arctic (69°14' N, 53°32' W) heaths dominated by <i>Salix glauca</i> and <i>Betula nana</i> and a subarctic peatland (67°22' N,	The subarctic site was measured on 23–24 July and 5–6 August 2008; The high and low arctic sites were measured on June and July 2013	The total monoterpene fluxes in high Arctic <i>Salix</i> -heath and high Arctic <i>Cassiope</i> -heat were 0.01 and 7 $\mu\text{g m}^{-2} \text{h}^{-1}$, respectively. Warming by open top chambers increased the emission rates both in the high and low arctic sites, forewarning higher emissions in a future warmer climate in the	Lindwall et al., 2015

	26°38' E) dominated by the moss <i>Warnstorfia exannulata</i> and the sedge <i>Eriophorum russeolum</i> .		Arctic.	
Static chamber technique. Concentration of VOCs in sorption tubes filled with Tenax TA and Carbopack B. GC-MS analysis of VOCs after thermal desorption.	55-year old Scots pine forest in southern Finland with <i>Sorbus aucuparia</i> , <i>B. pendula</i> , <i>Picea abies</i> grow below canopy. LSC was formed by shrubs (<i>Vaccinium</i> sp. and <i>Caluna vulgaris</i>), mosses (<i>P. schreberi</i> , <i>Dicranum</i> sp., <i>H. splendens</i>), and grasses (<i>Deschampsia flexuosa</i> , <i>Melampyrum sylvaticum</i>).	IV–X.2015	Monoterpenes flux range from the forest floor was 0.40–221.0 $\mu\text{g m}^{-2} \text{h}^{-1}$ (average 23 $\mu\text{g m}^{-2} \text{h}^{-1}$); the most dominant compounds: α -pinene and 3-carene. Sesquiterpene flux range was 0.01–10.9 $\mu\text{g m}^{-2} \text{h}^{-1}$; the most abundant waere β -caryophyllene and aromadendrene. Isoprene flux range was 0.005–99.8 $\mu\text{g m}^{-2} \text{h}^{-1}$	Mäki et al., 2017
Static chamber technique. Concentration on sorption tubes(Tenax TA). GC-MS analysis after thermal desorption.	VOC emissions from forest floor were studied in a latitudinal (over a 1000 km South-North transect) provenance experiments. The provenances studied were Saarema (58° 22' N), Korpilahti (62° 0' N), Suomussalmi (65 ° 10') and Muonio (67° 56' N).	VIII.2010	The main compounds emitted by forest floor were α -pinene, 3-carene, and camphene. Average unstandardised VOC emission rate from forest floor was 50 $\mu\text{g m}^{-2} \text{h}^{-1}$. Total emission rates were 65% higher in Korpilahti than in Muonio. High emission rates were explained by the high amount of decomposing needle litter and low moss coverage. α -Pinene and 3-carene contributed a major fraction of the emissions from the forest floor.	Kivimäenpää et al., 2018
Dynamic soil chambers. . Concentration on sorption tubes(Tenax TA + Carbograph 1). GC-MS analysis after thermal desorption.	Norway spruce and Scots pine 120yr old forests in Sweden.	VI–X.2015	The VOC emissions from the forest floor ranged from 0.4 to 66.6 $\mu\text{g m}^{-2} \text{h}^{-1}$. The emission rates peaked in October when the air temperature was <10 ° C. However, monoterpene emission rate increased exponentially with air temperature inside the soil chambers. It was concluded that needle litter may be an important source of VOC emission.	Wang et al., 2018
Glass steady-state flow-through chambers. . Concentration on sorption tubes (Tenax	(1) 60 yr old <i>P. sylvestris</i> and <i>P. abies</i> forests in Finland (boreal, 61° 51' N, 24°	V–X. 2017; IV–VI.2018	The total terpene fluxes were higher from the Scots pine forest floor (boreal 23 $\mu\text{g m}^{-2} \text{h}^{-1}$)	Mäki et al., 2019a

TA + Carbopack B). GC-MS analysis after thermal desorption.	17' E); (2) <i>P. sylvestris</i> , <i>P. abies</i> , <i>Betula</i> sp. forests Estonia (hemiboreal, 58° 25' N, 27° 46' E); (3) 100 yr old <i>P. abies</i> forest; SMEAR II rural background site.		and from the mixed forest floor (hemiboreal, 32 $\mu\text{g m}^{-2} \text{h}^{-1}$) compared to the Norway spruce forest floor in both boreal (12 $\mu\text{g m}^{-2} \text{h}^{-1}$ and hemiboreal (9 $\mu\text{g m}^{-2} \text{h}^{-1}$) climates. Due to higher litterfall production, the forest floor seems to be a greater source of monoterpenoids and sesquiterpenes in the hemiboreal mixed stand dominated by Scots pine compared to the boreal Scots pine stand.	
Static flux chambers. Concentration on sorption tubes (Tenax TA + Carbopack B). GC-MS analysis after thermal desorption.	Measurement of monoterpene emissions every 2 months over 2 years from logged tropical forests and oil palm plantation floor in Malaysian Borneo (4 °49 'N, 116 °54 'E).	I. 2015–XI. 2016	The main emitted monoterpenes were α - and β -pinene and limonene. Mean α -pinene fluxes were around 2.5-3.5 $\mu\text{g m}^{-2} \text{h}^{-1}$ from the forest floor with occasional fluxes exceeding 100 $\mu\text{g m}^{-2} \text{h}^{-1}$. Fluxes from the oil palm plantation were on average 0.5-2.9 $\mu\text{g m}^{-2} \text{h}^{-1}$ and only higher when litter was present. No seasonal trends could be identified for all monoterpenes (the climate is wet tropical with a wet season typically from October to February and a dry season typically from March to September).	Drewer et al., 2021

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Table 6. Laboratory measurements of emission rates of monoterpene hydrocarbons from fresh and decaying litter of Norway spruce and Scots pine (Isidorov et al., 2010) as well as from fresh litter of European larch, *Larix decidue* (Isidorov et al., 2005).

Terpene	Emission rate at 20°C ($\mu\text{g g}^{-1} \text{h}^{-1}$, dw) vs. decomposition time (days)										Larch litter*
	Spruce litter					Pine litter					
	0	77	165	282	490	0	77	165	282	490	
α -Pinene	0.06	0.56	0.44	0.16	0.09	1.15	5.13	1.01	0.18	0.06	0.50

β -Pinene	0.02	0.07	0.06	trace	trace	0.09	0.24	0.04	0.01	trace	0.18
Camphene	0.10	0.63	0.76	0.28	0.10	0.18	0.47	0.15	0.03	0.04	0.10
3-Carene	-	0.03	0.02	0.02	trace	0.53	1.65	0.42	0.10	0.10	-
Limonene	0.02	0.16	trace	0.05	0.02	0.01	0.03	0.02	trace	trace	0.11
Terpinolene	0.01	-	-	-	-	0.01	0.02	-	-	-	-
Myrcene	-	-	-	-	-	-	-	-	-	-	0.05
β -Phellandrene	-	-	-	-	-	-	-	-	-	-	0.12
Total	0.20	1.46	1.28	0.51	0.21	1.96	7.54	1.64	0.32	0.20	1.08

1376 * Emission at 22°C.

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1378 **Table 7.** Emission rates of volatile organic compounds ($\text{ng g}^{-1} \text{h}^{-1}$) from litter of nine terpene storing species.

1379 Values are mean \pm SE ($n=3$ to 10) (Viros et al., 2020).

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Compound	<i>Cistus albidus</i>	<i>Cistus salviifolius</i>	<i>Cotinus coggygria</i>	<i>Eucalyptus globulus</i>	<i>Juniperus oxycedrus</i>	<i>Pinus halepensis</i>	<i>Pinus pinea</i>	<i>Rosmarinus officinalis</i>	<i>Thymus vulgaris</i>
α -thujene	-	-	-	-	-	4.35 \pm 1.11	-	-	10.47 \pm 4.87
α -pinene	2.99 \pm 0.21	-	181.64 \pm 43.11	4.26 \pm 1.86	6.17 \pm 2.14	61.63 \pm 10.61	24.85 \pm 18.61	197.91 \pm 30	21.17 \pm 2.8
camphene	-	-	27.37 \pm 4.44	-	-	-	1.34 \pm 0.66	155.84 \pm 25.51	24.3 \pm 3.17
sabinene	-	-	-	-	3.19 \pm 0.3	36 \pm 9.3	-	-	40.98 \pm 33.66
β -pinene	-	-	17.38 \pm 4.46	2.85 \pm 0.58	-	-	15.75 \pm 0.58	31.03 \pm 6.98	11.8 \pm 2.52
myrcene	-	-	250.3 \pm 69.87	1.39 \pm 0.3	5.46 \pm 0.65	137.67 \pm 24.79	-	-	48.9 \pm 7.46
α -phellandrene	-	-	-	3.47 \pm 0.65	0.67 \pm 0.17	-	13.68 \pm 1.01	-	8.69 \pm 2.79
δ -3-carene	-	-	0.84 \pm 0.2	-	-	5.7 \pm 1.35	7.53 \pm 2.5	-	36.61 \pm 16.6
α -terpinene	-	-	1.69 \pm 0.85	-	-	-	-	-	-
limonene	142.94 \pm 28.14	5.15 \pm 1.14	1591.51 \pm 315.27	2.78 \pm 1.01	14.21 \pm 0.09	128.95 \pm 21.37	226.98 \pm 5.3	-	368.38 \pm 169.09
eucalyptol	-	-	-	82.85 \pm 68.64	-	-	-	-	-
<i>cis</i> - β -ocimene	-	-	686.08 \pm 217.7	-	2.95 \pm 0.15	3.07 \pm 0.41	3.16 \pm 0.05	-	-
<i>trans</i> - β -ocimene	-	-	148.33 \pm 49.28	-	0.99 \pm 0.13	5.89 \pm 1.72	1.49 \pm 0.07	-	5.85 \pm 1.47
γ -terpinene *	-	-	6.71 \pm 2.49	-	2.49 \pm 0.13	14.14 \pm 2.5	1.26 \pm 0.14	-	56.98 \pm 34.51
<i>trans</i> -4-thujanol	-	-	-	-	-	-	-	-	228.32 \pm 28.77
α -terpinolene	-	2.75 \pm 0.68	77.93 \pm 20.61	-	5.43 \pm 0.18	42.58 \pm 11.77	3.58 \pm 2.41	-	99.38 \pm 51.21
linalool	-	5.02 \pm 2.07	-	-	2.03 \pm 0.22	-	1.71 \pm 0.08	-	244 \pm 123.55
α -campholenal	-	-	-	-	1.04 \pm 0.15	-	-	-	2.59 \pm 0.15

Compound	<i>Cistus albidus</i>	<i>Cistus salviifolius</i>	<i>Cotinus coggygria</i>	<i>Eucalyptus globulus</i>	<i>Juniperus oxycedrus</i>	<i>Pinus halepensis</i>	<i>Pinus pinea</i>	<i>Rosmarinus officinalis</i>	<i>Thymus vulgaris</i>
<i>allo</i> -ocimene	-	-	72.56 ± 22.92	-	-	-	-	-	-
<i>cis</i> -p-mentha-2.8-dien-1-ol	-	-	-	-	-	-	-	-	1.53 ± 0.15

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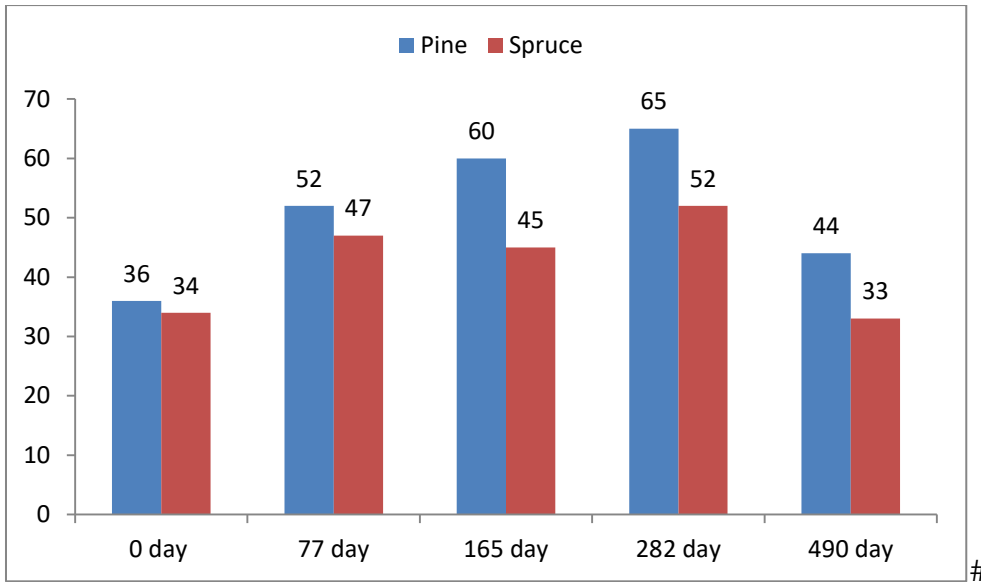
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1386 **Table 8.** Emission rates of compounds ($\text{ng g}^{-1} \text{h}^{-1}$) from litter of seven non-terpene storing
 1387 species. Values are mean \pm SE (n=3 to 10) (Viros et al., 2020).

Compound	<i>Acer monspessulanum</i>	<i>Erica arborea</i>	<i>Quercus coccifera</i>	<i>Quercus ilex</i>	<i>Quercus pubescens</i>	<i>Quercus suber</i>	<i>Ulex parviflorus</i>
Aliphatic carbonyls							
- benzaldehyde	-	4.06 ±0.22	-	-	-	-	-
- 6-methyl-5-hepten-2-one	0.59 ±0.20	10.61 ±0.55	6.08 ±2.70	0.9 ±0.54	-	2.45 ±0.49	-
- octanal	-	-	-	-	-	0.20 ±0.31	0.84 ±0.02
- nonanal	2.76 ±0.18	11.85 ±0.39	27.32 ±3.90	1.48 ±0.74	55.37 ±13.61	3.84 ±0.84	4.65 ±0.29
- decanal	0.54 ±0.06	1.31 ±0.86	32.19 ±5.3	-	52.7 ±10.87	1.05 ±0.38	1.96 ±0.08
- 2,4-heptadienal. (E,E)	-	2.16 ±0.58	-	-	-	-	-
Alkane and alkene							
- undecane	-	-	2.32 ±0.45	-	6.56 ±3.52	-	-
- dodecane	1.67 ±0.10	4.66 ±0.39	4.97 ±0.77	5.19 ±2.62	6.86 ±3.96	9.49 ±1.78	1.03 ±0.01
- tridecane	0.32 ±0.14	1.59 ±0.1	26.03 ±5.68	0.98 ±0.49	47.08 ±22.19	2.88 ±0.40	0.91 ±0.07
- 1-tetradecene	-	0.55 ±0.28	-	-	-	-	-
- tetradecane	0.52 ±0.21	-	87.21 ±7.09	-	163.19±50.51	-	1.48 ±0.16
- 1-pentadecene	-	-	-	-	29.62 ±9.91	-	-
- pentadecane	-	-	38.42 ±10.26	-	217.48±93.11	-	-
- hexadecane	-	0.54 ±0.27	17.45 ±1.99	-	26.42 ±6.04	-	1.52 ±0.02
Other							
- 3-methyl-2(5H)-	-	-	82.59 ±10.63	-	-	-	-

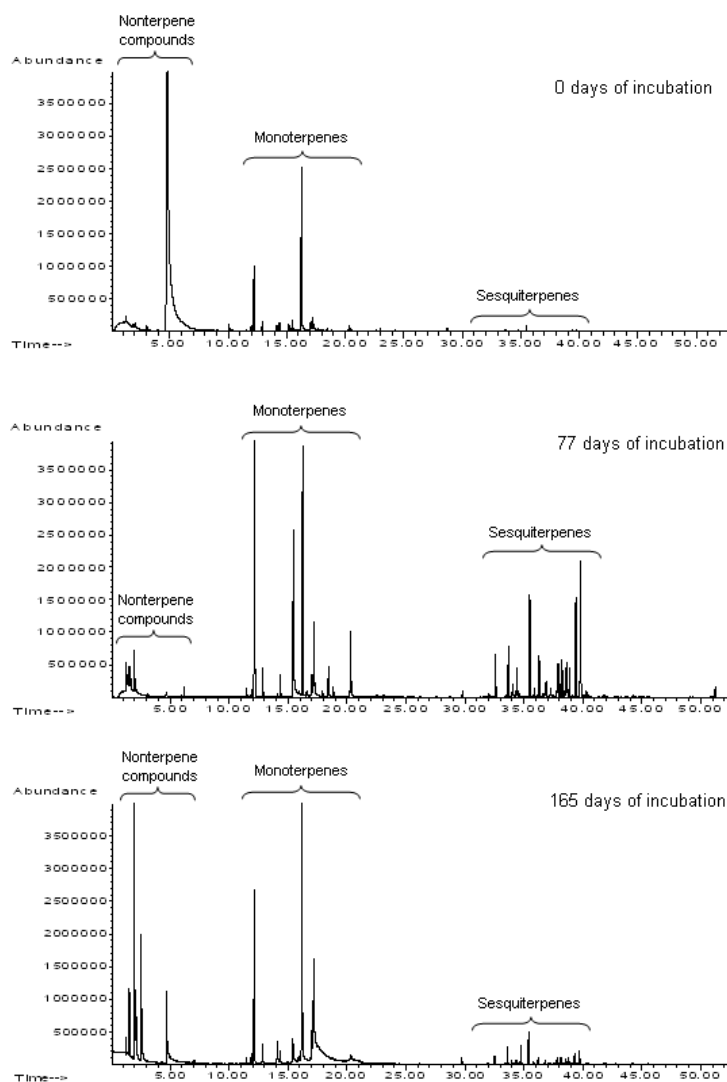
furanone							
- phenyl ethyl alcohol	-	3.58 ±0.56	-	-	-	-	1.05 ±0.11
Total emission, µg g⁻¹ h⁻¹	0.01±0.01	0.04±0.01	0.32±0.03	0.01±0.01	0.61±0.16	0.02±0.01	0.01±0.01

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Fig. 1. Changes in the number of different VOCs registered in emissions from decomposing Scots pine and Norway spruce needles (Isidorov et al., 2010).



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 1411 **Fig. 2.** Changes in the profiles of volatile emissions of pine litter at the first stages of
 1412 decomposition in natural conditions. HS-SPME/GC-MS chromatograms from pine needle
 1413 litter emissions concentrated on polydimethylsiloxane (PDMS) fibre (Isidorov et al., 2010).
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