1   Reviews and syntheses: **VOC emissions from soil cover in boreal and temperate**

2   **natural ecosystems of the Northern Hemisphere**

4   Valery A. Isidorov[1*], Andrej A. Zaitsev[2]

5   [1]Institute of Forest Sciences, Białystok University of Technology, 15-351 Białystok, Poland

6   [2]Faculty of Geography of Perm State University, 614990 Perm, Russia

8   *Corresponding author: isidorov@uwb.edu.pl; ORCID: 0000-0001-8185-3301

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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

leaf litter, accompanied by the release of VOCs, is a very complex process that depends on a

number of biological, chemical and physical environmental factors, but little information is

currently available on the role each plays. Equally limited is information on the chemical

composition and emission rates of VOCs from these sources.

The review focuses on the main gaps in our knowledge of the sources of biogenic VOCs

under the forest canopy, and we are confident that filling them will make a significant

contribution to solving such an important task as closing the global organic carbon budget.

Keywords: leaf litter; living ground cover of forests; decomposition; litter-decomposing

microorganisms; volatile organic compounds; chemical composition; emission rate

I. Introduction

Terrestrial living vegetation is the main source of atmospheric VOCs that significantly affects

chemical processes in the boundary layer (Isidorov, 1990; Fehsenfeld et al., 1992; Guenther et

al., 1995; Navarro et al., 2014; Sindelarova et al., 2014). These emissions have received

considerable attention due to the fact that most of them are highly reactive and thus affect

atmospheric chemistry to a greater extent than comparable amounts of organic pollutants from

industrial and motor vehicle emissions (Bell and Ellis, 2004). In the atmosphere, VOCs

undergo gas-phase oxidation (Atkinson and Arey, 2003) or photo-stimulated oxidation on the

surface of solid atmospheric aerosols (Isidorov, 1992: Isidorov et al., 1997). Their reactions

with $^{\bullet}$OH radicals and NO_x result in the production of secondary photooxidants, such as

ozone, H_2O_2, ROOH and peroxyacetyl nitrate (PAN). Furthermore, the oxidation of biogenic

VOCs initiates the production of secondary atmospheric aerosols, which influence the

radiative budget of the troposphere (Makkonen et al., 2012; Kulmala et al., 2001, 2013; Faiola

et al., 2014; Kourtchev et al., 2016; Lee et al., 2019). An increase in the tropospheric ozone

concentration can also affect the climate by perturbing the Earth's radiation budget as O_3 is the third-most important greenhouse gas (Intergovernmental Panel on Climate Change, IPCC, 2013; Kim et al., 2015).

Exposure to elevated surface ozone concentration has detrimental impacts on human health, natural vegetation and crop yield (Chuwah et al., 2015; Zhou et al., 2017; De Marco et al., 2019). In particular, ground-level ozone pollution has become one of the top issues in China and India. According to Feng et al. (2015), throughout China current and future O_3 levels will induce a wheat yield loss of 6.4–14.9% and 14.8–23.0%, respectively. Moreover, economic losses from wheat and rice in India attributable to ozone are estimated at \$6.5 billion per year (Sharma et al., 2019). For these reasons, tropospheric ozone production, temporal variations in its concentrations over different regions and examinations of future near-surface air quality changes have been the subjects of numerous recent investigations and publications (Vingarzan, 2004; Curci et al., 2009; Derwent et al., 2015; Dolwick et al., 2015; Gaudel et al., 2015; Kim et al., 2015; Santurtún et al., 2015; Zong et al., 2018; Masiol et al., 2019; Strode et al., 2019; Archibald et al., 2020; Zhang et al., 2021).

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

silver birch (*Betula pendula*) leaves in southern Finland showed that although the concentration of many secondary metabolites is significantly reduced, almost all of them are found in both senescent leaves and fresh litter (Paaso et al., 2017). Furthermore, Wood et al. (1995) did not detect statistically significant differences in monoterpene yields in green, yellow or newly fallen brown leaves of the hardwood tree *Umbellularia californica* and concluded that there is a lack of catabolism of monoterpenes prior to leaf senescence. However, the results of these isolated studies do not give grounds to state that aging leaves enter the soil with almost the same yield of monoterpene as on the tree. Indeed, in one study, the total monoterpene content was higher in the fresh needles of *Pinus monophylla* (5.6 ± 2.2 mg g^{-1} extracted air dry weight, d.w.) than in senescent needles (3.6 ± 1.8 mg g^{-1} d.w.), regardless of whether they were still attached to the tree or formed the freshest layer of the understorey litter (Wilt et al., 1993). In another study, samples of Scots pine (*Pinus sylvestris* L.) needles and needle litters collected in low-productive forests in eastern Siberia contained, respectively, 7.9 ± 1.2 and 3.9 ± 0.2 mg g^{-1} (d.w.) of essential oils, mainly consisting of volatile monoterpene hydrocarbons (Stepen' et al., 1987). About 15% of the total store of essential oil in these forests is contained in litter, with a biomass of $12-15$ t·ha^{-1}. According to Klemmedson et al. (1990), litter needle biomass comprises 20% of the live foliar biomass in Canadian ponderosa pine forest. More productive forests of the Northern Hemisphere can accumulate enormous amounts of 'dead' organic material. For example, total litter mass in a 100-year-old maritime pine (*P. pinaster*) forest in southern France was 43.1 ± 12.0 t ha^{-1}, and the depth of the needle compartment of the floor averaged 70 mm (Kurz et al., 2000). The chemical composition of the litter was not determined by the authors, but it can be supposed that the fallen needles in this maritime pine forest contain considerable amounts of terpenes. 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 μg m^{-2} h^{-1} at 30$^{\text{o}}$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 $16,780 \cdot 10^3$ 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 $700 \cdot 10^6$ 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 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 t

166   km^{-2}) forms nearly 1,500 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 understorey 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.

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

190   *IIa. 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

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

Further decomposition of crushed litter is performed by microorganisms, bacteria, actinomycetes and fungi (Trowbridge et al., 2020). The last constitute a major component of soil biota and represent the primary decomposers in most environments. Indeed, fungi produce the enzymes (including extracellular enzymes) necessary to decompose the lignocellulose matrix of leaf litter and wood (Cox et al., 2001; Fioretto et al, 2007). Participating in the decomposition of organic matter of plant origin, these saprotrophic organisms produce their own, inherent metabolites; as part of these secondary products are volatile organic compounds, they can be transferred into the gas phase (Svendsen et al., 2018).

IIb. Abiotic processes

The microbial-zoological interactions mentioned above stimulate intense abiotic processes such as the evaporation of volatiles and the leaching of water-soluble compounds. Another abiotic process aiding the evolution of volatiles from plant tissues is their mechanical destruction, brought about by the freezing−thawing of dead organic material (Porchikalov 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 C_2–C_5

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 C_2–C_5 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 $60-100$ ^{o}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 $60-80$ ^{o}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 C_5 and C_6 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 C_5 and C_6 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 abiogenic 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

presented in this chapter allows us to conclude that substantial quantities of low molecular

weight C_5-C_6 VOCs can be formed as the result of the abiotic decomposition of plant litter.

Due to its importance in atmospheric chemistry, it can be concluded that much more research

should be devoted to this natural source of atmospheric VOCs. In particular, UV radiation,

heat and frost must be regarded as important triggers for seasonal emissions of these VOCs by

plant litter.

The second conclusion is related to the qualitative composition of leaf litter

emissions: one can expect among these emissions not only plant-derived compounds, but also

VOCs of microbial and animal origin.

III. Qualitative composition of plant litter and LSC emissions

Over the last few decades, the chemical composition of volatile emissions from some

thousands of plant species – including practically all forest-forming trees of the Northern

Hemisphere – has been investigated. For many hundreds of species, the emission rates of

principal biogenic VOCs, isoprenes and monoterpenes have also been determined

(Kesselmeier and Staudt, 1999). The available information on the chemical composition of

litter-derived compounds is much poorer. This chapter provides an overview of the current

knowledge, which is based on only a few publications.

Table 2 contains a list of 164 volatile organic compounds detected in emissions from the

leaf litter of 30 plants, including 25 arboreal species. The largest group is made up of

hydrocarbons (79 compounds), including mono- and sesquiterpenes (63 compounds), which

are more active in atmospheric processes. Isoprene, ethanol, acetaldehyde, acetone and

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 a., 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 μmol m^{-2} 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) 1,200–2,500 t km^{-2}, increasing to 7,600−8,100 t km^{-2}

387   in mature forests; at the same time interval, pine needle biomass decreased from 5,600−6,700

388   t km^{-2} to 3,200–4,700 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-ideae, 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   C_2−C_{19} 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   sesquitrepenoids (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-pinanone, 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 C_2–C_5 aliphatic alcohols and C_5–C_9 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, C_3–C_8 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

biosynthesis of metabolites with bactericidal properties has been found, while many types of

bacteria demonstrate fungicidal effects. These competitive relationships can manifest

themselves in the progressive decomposition of litter and determine the composition of VOCs

of microbial origin.

During leaf litter decomposition, microbial succession takes place, defined as *a directed*

change in the relative abundance and spatial pattern of species comprising communities

(Frankland, 1998). Undecomposed fallen leaves act as a carbon source for primary

saprotrophs, belonging to bacteria and/or fungi (Bonanomi et al., 2017). After use by the

primary colonisers of simple sugars, oligosaccharides, amino acids and other easy-

assimilating substances, litter is naturally colonised by other microbes, fungi and cellulolytic

bacteria (López-Mondéjar et al., 2016; Starke et al., 2016; Shao et al., 2017; Štursová et al.,

2020; Tennakoon et al., 2021). It is believed that more recalcitrant lignified hemicelluloses

and lignin are destroyed only by basidiomycetes, fungi capable of producing extracellular

lignolytic enzymes (Hobbie et al., 2012; Kirker et al., 2020).

The successional nature of fungal decomposition of the herbaceous litter of the Longleaf

Pine savanna ecosystem was noted by Lodato et al. (2021). Sequencing of fungi isolated by

the authors from the litter of *Schizachyrium scoparium* (little bluestem or beard grass) and *S.*

tenerum (slender bluestem) revealed the participation in the decomposition of several

phylotypes, among which representatives of Ascomycota (*Dothideomycetes*) and

Basidiomycota (*Agaricomycetes*) prevailed.

However, some groups of bacteria, which also have the ability to synthesize enzymes

suitable for these purposes, may be involved in the decomposition of recalcitrant biopolymers.

In particular, high lignolytic activity has been found in *Staphylococcus saprophyticus*,

Pseudomonas aeruginosa and certain bacteria from the genus *Bacillus* (Nahrowi et al., 2018).

According to Frankland (1998), fungal activity had almost ceased after 5 to 6 years when

472 Pokhylmycelial 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

litter, and only two (*Cladosporium herbarum* and *Pseudeurotium ovale*) were detected in

spruce needles. The observed disappearance of these fungi can be linked to the sharp decrease

in simple carbohydrates in the early stages of decomposition during the decay of leaf litter

(Kainulainen and Hopolainen, 2002; Osono and Takeda, 2005; Isidorov et al., 2010) due to

both use by microbes and leaching.

At the middle stage (280 days), *Penicillium purpurogenum* dominated in pine litter and

Chloridium botryoideum in spruce litter, whereas the late stage (490–690 days) was

characterised by the absolute predominance of *Trichoderma* species (*T. polysporum, T.*

koningii and *T. viride*). These filamentous fungi are producers of large amounts of cellulolytic

enzymes. Remarkably, in the late stage of the experiment, the recurrence of some primary

colonisers was also observed, which can be explained by the action of cellulolytic fungi,

producing readily available sugars released from the hemicelluloses. The recurrence of the

primary colonisers after approximately 350 days of *Pinus pinea* needle incubation was

previously documented by Virzo De Santo et al. (2002). Further degradation of more

recalcitrant lignified materials demands the participation of lignolytic fungi.

It can be noted that unlike the case of VOC emissions from living plants, there is little

knowledge regarding such emissions from litter-destroying microbes. The composition of

VOCs emitted into the gas phase by selected fungi isolated from Scots pine and Norway

spruce needles was determined after 490 days of incubation in one study (Isidorov et al.,

2016). Based on the results of HS-SPME/GC-MS analyses, as many as 75 C_2–C_{15} volatile

organic compounds were identified. Table 4 presents the group composition of these VOCs

and the principal representatives of separate groups. As can be seen, VOC emissions are

species-specific: grown on the same cultivation media, the fungi differ in the qualitative and

quantitative composition of the volatiles produced. Even a representative of the same genus

(for example, *Trichoderma polysporum* and *T. koningi*, or *Penicillium minioluteum* and *P.*

purpurogenum) demonstrates considerable distinctions in VOC emissions. Striking

differences have also been observed by Nilsson et al. (1996): only three of 58 registered

VOCs were common for four *Penicillium* species.

Even less is known about VOC production by litter-destroying bacteria. However, the

emission of photochemical significant organic volatiles, including isoprene, by bacilli and

actinomycetes was discovered (Kuzma et al., 1997; Fall and Copley, 2000; Wilkins, 1996;

Wagner et al., 2000; Schöller et al., 2002). At present, the important role of bacteria in leaf

litter and coarse woody debris destruction is well documented (Kim et al., 2014; Urbanová et

al., 2015; López-Mondéjar et al., 2016; Mahajan et al., 2016; Purahong et al., 2016;

Bonanomi et al., 2017; Dolan et al., 2017; Hu et al., 2017). However, further studies are

required to understand their role in the litter-derived emission of VOCs into the atmosphere.

In terrestrial environments, algae represent the main component of the microbial flora.

Forest litter is also the place of the active development of microscopic algae, which form a

specific element of the living soil cover (Maltsev et al. 2017a,b). They participate in all

biogenic processes in leaf litter, together with other organisms. However, data on the algae of

leaf litter are scanty. Maltsev et al. (2017a) have recently studied the structural and dynamic

parameters of the algal communities of the anthropogenic and natural forests in the steppe

zone of Ukraine and found that the composition of communities varies by season and forest-

forming tree species. The authors identified 119 algae species belonging to six divisions:

Chlorophyta (68 species), *Xanthophyta* (21 species), *Cyanoprocaryota* (17 species),

Bacillariophyta (seven species), *Eustigmatophyta* and *Charophyta* (three species each). With

respect to species number and abundance, coniferous forest litter was predominated by green

(*Chlorophyta*) and yellow-green (*Xanthophyta*) algae, whereas leaf forest litter (*Q. robur* and

Robinia pseudoacacia plantations) was characterised by the significant participation of

oxygenic photosynthesising cyanobacteria *Cyanoprocaryota.* 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 μg g^{-1} 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 μgC 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 (Petersson, 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).

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

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

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

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

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

Kivimäenpää et al. (2018) conducted a latitudinal experiment in Finland, involving a 1,000-km North–South transect, and concluded that emissions from the floor of pine forests have a noticeable additive effect on total VOC emissions. The authors of an earlier study (Räisänen et al., 2009), who measured the fluxes of monoterpenes in a pine forest in eastern 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. salviiflius, 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 $\mu g \ g^{-1} \ h^{-1}$, 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 $\mu g \ g^{-1} \ h^{-1}$

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

registered in the composition of the fallen needle excretions. The maximum emission of 9.18

$\mu g \ g^{-1} \ h^{-1}$ was observed 3 months after the beginning of the experiment, with the main

components being α-pinene, terpinolene, 3-carene, limonene, sabinene and myrcene, whereas

the main sesquiterpenes were β-caryophyllene, α-humulene and copaene. In addition, at this

stage, the emission of highly volatile non-terpene compounds took place, with the main ones

being methanol, acetic acid and acetone. The maximum emission of oxidised monoterpenes

and sesquiterpenes occurred between the third and sixth months of the experiment.

Comparison of data on VOC emissions from green and decaying fallen needles *P. halepensis*

led the authors of the cited work to the conclusion that the contribution of litter to the total

emission in forests from this pine species (their area in the Western Mediterranean is about

3.5 million hectares) can be extremely high.

The data presented in this section indicate that VOC emissions from the forest floor are

not negligible. Moreover, during the spring and autumn seasons, the forest floor can be the

main source of these reactive components. However, to establish its effect on air quality,

additional studies are needed to determine the emission factors for different ecosystems and

biomes.

VI. Conclusions

It is recognised that a critical challenge for atmospheric chemistry is closing the

atmospheric organic carbon budget. This review shows that deciduous litter and plants of

living forest soil cover are an unaccounted source of large amounts of VOCs, for many of

which a high potential for the formation of ozone and other atmospheric photooxidants and/or

secondary aerosols has been postulated. The results of many studies indicate that these

elements of forest ecosystems are not negligible sources of atmospheric VOCs, especially in

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.

735

736 **Supplementary material related to this article is available online at:**

737 **http://www.biogeosciences.net/......................**

738

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References

746

747 **References**

748 Aaltonen, H., Pumpanen, J., Pihlatie, M., Hakola, H., én, H., Kulmala, L., Vesala, T., and

749   Bäk, J.: Boreal pine forest floor biogenic volatile organic compound emissions peak in

750   early summer and autumn. Agricul. Forest Meteorol. 151, 682–691; doi:

751   10.1016/j.agrformet.2010.12.010, 2011.

752 Archibald, A.T., Neu, J.L., Elshorbany, Y.F., et al.: Tropospheric Ozone Assessment Report:

753   A critical review of changes in the tropospheric ozone burden and budget from 1850 to

754   2100. Elementa-Sci. Anthrop. 8(1), doi: 10.1525/elementa.2020.034, 2020.

755 Asensio, D., Peñuelas, J., Ogaya, R., and Llusià, J.: Seasonal soil VOC exchange rates in a

756   Mediterranean holm oak forest and their responses to drought conditions. Atmos. Environ.

757   41, 2456–2466, doi: 10.1016/j.atmosenv.2006.05.007, 2007.

758 Atkinson, R., and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic

759   compounds: A review. Atmos. Environ. 31(S2), 197–219, doi: 10.1016/S1352-

760   2310(03)00391-1, 2003.

761 Austin, A.T., Mendez, M.S., and Ballaré, C.L.: Photodegradation alleviates the lignin

762   bottelneck for carbon turnover in terrestrial ecosystems. Proc. Nat.. Acad. Sci. USA, 113,

763   4392–4397, 10.1073/pnas.1516157113, 2016.

764 Babich, H., and Stotzky, G.: Air pollution and microbial ecology. CRC Crit. Rev. Microbiol.

765   4, 353–421; doi: 10.1080/10643387409381619, 1974.

766 Bazilevich, N.I., Drozdov, A.V., and Zlotin, R.I.: Geographical peculiarities of the

767   production–destruction–processes in Northern Eurasia. In: SCOPE Conf. Pap. 18. Ed. by

768   A. Breymeyer, Warszaw, pp. 51–79, 1993.

769   Bell, M., and Ellis, H.: Sensitivity analysis of tropospheric ozone to modified biogenic

770   emissions for the Mid–Atlantic region. Atmos. Environ. 38, 1879–1889, doi:

771   10.1016/j.atmosenv.2004.01.012, 2004.

772   Berg, B.:. Decomposition patterns for foliar litter – A theory for influencing factors. Soil Biol.

773   Biochem. 78, 222–232; doi:10.1016/j.soilbio.2014.08.005, 2014.

774   Bolin, B.: The carbon cycle. In: Bolin B., Cook R.B. (Eds.), SCOPE 21 – The Major

775   Biogeochemical Cycles and Their Interactions. Wiley, Chichester; doi: 10.1016/0016-

776   7037(84)90418-6, 1983.

777   Bonanomi, G., Cesarano, G., Lombardi, N., Motti, R., Scala, F., Mazzoleni, S., and Incerti,

778   G.: Litter chemistry explains contrasting feeding preferences of bacteria, fungi, and higher

779   plants. Sci. Rep. 7: 9208, 1–13, doi: 10.1038/s41598-017-09145-w, 2017.

780   , J.F., Barnes, P.W., Robinso, S.A., Ballaré, C.L., Flint, S.D., and Caldwell, M.M.: Solar

781   ultraviolet radiation and ozone depletion-driven climate change: effects on terrestrial

782   ecosystems. Photochem. Photobiol. Sci. 14, 88 Shao107, doi: 10.1039/C4PP90034K, 2015.

783   Bosco, T., Bertiller, M.B., and Carrera A.L.: Combined effects of litter features, UV radiation,

784   and soil water on litter decomposition in denuded areas of the arid Patagonian Monte. Plant

785   Soil 406, 71–82, doi: 10.1007/s11104-016-2864-7, 2016.

786   Bray, S.R., Kitajima, K., and Mack, M.C.: Temporal dynamics of microbial communities on

787   decomposing leaf litter of 10 plant species in relation to decomposition rate. Soil Biol.

788   Biochem. 49, 30–37; doi: 10.1016/j.soilbio.2012.02.009, 2012.

789   Chuwah, C., van Noije, T., van Vuuren, D.P., Stehfest, E., and Hazeleger, W.: Global impact

790   of surface ozone changes on crop yields and land use. Atmos. Environ. 49, 11–13, 2015.

791   Coulis, M., Hättenschwiler, F.N., and David, J.F.: Macroarthropod–microorganism interaction

792   during the decomposition of Mediterranean shrub litter at different moisture levels. Soil

793   Biol. Biochem. 64, 114–121; doi: 10.1016/j.soilbio.2013.04.012, 2013.

794 Cox, P., Wilkinson, S.P., and Anderson, J.M.: Effects of fungal inocula on the decomposition

795   of lignin and structural polysaccharides in *Pinus sylvestris* litter. Biol. Fertil. Soils 33, 246–

796   251; doi: 10.1007/s003740000315, 2001.

797 Crocker, L.N.: The Composition and Diversity of Volatile Organic Compounds (VOCs) from

798   Leaf Litter in the Biosphere 2 Tropical Rainforest. The University of Arizona, ProQuest

799   Dissertations Publishing, 2021. 28870239.

800 Curci, G., Beekmann, M., Vautard, R., Smiatek, G., Steinbrecher, R., Theloke, J., and

801   Friedrich, R.: Modelling study of the impact of isoprene and terpene biogenic emissions on

802   European   ozone   levels.   Atmos.   Environ.   43,   1444–1455;   doi:

803   10.1016/j.atmosenv.2008.02.070, 2009.

804 David, J.F.: The role of litter-feeding macroarthropods in decomposition process: A

805   reappraisal common views. Soil Biol. Biochem. 76, 109–118; doi: 10.1016/J.

806   SOILBIO.2014.05.009, 2014.

807 De Marco, A., Proietti, C., Anav, A., et al.: Impacts of air pollution on human and ecosystem

808   health, and implications for the National Emission Ceilings Directive: Insights from Italy.

809   Environ. Intern. 125, 320–333, doi: 10.1016/j.envint.2019.01.064, 2019.

810 Derendorp, L., Holzinger, R., Wishkerman, A., Keppler, F., and Röckmann, Th.: Methyl

811   chloride and C_2–C_5 hydrocarbons emissions from dry leaf litter and their dependence on

812   temperature. Atmos. Environ. 45, 3112–3119; doi: 10.1016/j.atmosenv.2011.03.016 ,

813   2011a.

814 Derendorp, L., Holzinger R., and Röckmann, T.: UV induced emissions of C_2–C_5

815   hydrocarbons from leaf litter. Environ. Chem. 8, 622–611; doi: 10.1071/EN11024, 2011b.

816 Derendorp, L., Quist, J.B., Holzinger R., and Röckmann, T.: Emissions of H_2 and CO from

817   leaf litter of *Sequoidendron giganteum,* and their dependence on UV radiation and

818   temperature. Atmos. Environ. 45, 7520–7524; doi: 10.1016/j.atmosenv.2011.09.044,

819   2011c.

820 Derwent, R.G., Utembe, S.R., Jenkin, M.E., and Shallcross, D.E.: Tropospheric ozone

821   production regions and the intercontinental origins of surface ozone over Europe. Atmos.

822   Environ. 112, 216–224; doi: 10.1016/j.atmosenv.2015.04.049, 2015.

823 Di Carlo, P., Brune, W.H., Martinez, M., Harder, H., Lesher, R., Ren, X., Thornberry, T.,

824   Carroll, M.A., Young, V., Shepson, P.B., Riemer, D., Apel, E., and Campbell, C.: Missing

825   OH reactivity in a forest: Evidence for unknown reactive biogenic VOCs. Science 304,

826   722–725, doi: 10.1126/science.1094392.2004, 2004.

827 Dobrovolsky, V.V.: Elements of Biogeochemistry. Moscow, High School Publ., 1998 (in

828   Russian).

829 Dolan, K.L., Peña, J., Allison, S.D., and Martiny, J.B.H.: Phylogenetic conservation of

830   substrate use specialization in leaf litter bacteria. PLoS ONE 12 (3): e0174472,

831   doi:10.1371/journal.pone.0174472, 2017.

832 Dolwick, P., Akhtar, F., Baker, K.R., Possiel, N., Simon, H., and Tonnesen, G.: Comparison
833   of background ozone estimates over the western United States based on two separate
834   model methodologies. Atmos. Environ. 109, 282–296; doi:
835   10.1016/j.atmosenv.2015.01.005, 2015.
836 Drewer, J., Leduning, M.M., Purser, G., Cash, J.M., Sentian, J., and Skiba, U.M.:

837   Monoterpenes from tropical forest and oil palm plantation floor in Malaysian

838   Borneo/Sabah: emission and composition. Environ. Sci. Pollut. Res. 28 (24), 31792–

839   31802; doi: 10.1007/s11356-021-13052-z, 2021.

840 Drewitt, G.B., Curren, K., Steyn, D.G., Gillespie, T.J., and Niki, H.: Measurement of biogenic

841   hydrocarbon emissions from vegetation in the Lower Fraser Valley, British Columbia.

842   Atmos. Environ. 32, 3457–3466; doi: 10.1016/S1352-2310(98)00043-0, 1998 .

843 Dunkerley, D.: Percolation through leaf litter: What happens during rainfall events of varying

844   intensity? J. Hydrol. 525, 737–746; doi: 10.1016/j.jhydrol.2015.04.039, 2015.

845   Faiola, C.L., VanderSchelden, G.S., Wen, M., Elloy, F.C., Cobos, D.R., Watts, R.J., Jobson,

846   B.T., and VanReken,, T.M.: SOA formation potential of emissions from soil and leaf litter.

847   Environ. Sci. Technol. 48, 938–946, doi: 10.1021/es4040045, 2014.

848   Fall, R., and Copley, S.D.: Bacterial sources and sinks of isoprene, a reactive atmospheric

849   hydrocarbon. Environ. Microbiol. 2, 123–130; doi: 10.1046/j.1462-2920.2000.00095.x,

850   2000.

851   Fall, R., Karl, T., Jordan, A., and Lindinger, W.: Biogenic C5 VOCs: release from leaves after

852   freeze–thaw wounding and occurrence in air at a high mountain observatory. Atmos.

853   Environ. 35, 3905–3916; doi: 10.1016/S1352-2310(01)00141-8, 2001.

854   Faubert, P., Tiiva, P., Rinnan, Å., Michelsen, A., Holopainen, J.K., and Rinnan, R.: Doubled

855   volatile organic compound emissions from subarctic tundra under simulated climate

856   warming. New Phytol. 187, 199–208, doi: 10.1111/J.1469-8137.2010.03270.X, 2010.

857   Feng, Z., Hu, E., Wang, X., Jiang, L., and Liu, X.: Ground–level O_3 pollution and its impacts

858   on food crops in China: A review. Atmos. Environ. 199, 42–48; doi:

859   10.1016/j.envpol.2015.01.016, 2015.

860   Fehsenfeld, F.C., Calvert, J., Fall, R., Goldan, P., , A.B., Hewitt, C.N., Lamb, B., Liu, S.,

861   Trainer, M., Westberg, H., and Zimmerman, P.: Emissions of volatile organic compounds

862   from vegetation and the implications for atmospheric chemistry. Glob. Biogeochem.

863   Cycles 6, 398–420; doi: 10.1029/92GB02125, 1992.

864   Fioretto, A., Papa, S., Pellegrino, A., and Fuggi, A.: Decomposition dynamics of *Myrtus*

865   *communis* and *Quercus ilex* leaf litter: Mass loss, microbial activity and quality change.

866   Appl. Soil Ecol. 36, 32–40; doi: 10.1016/j.apsoil.2006.11.006, 2007.

867   Frankland, J.C.: Fungal succession – unraveling the unpredictable. Mycol. Res. 102, 1–15;

868   doi: 10.1017/S0953756297005364, 1998.

869 Frouz, J., Roubíčková, A., Heděnec, P., and Tajovský, K.: Do soil fauna really hasten litter

870   decomposition? A meta-analysis of enclosure studies. Eur. J. Soil Biol. 68, 18–24; doi:

871   10.1016/j.ejsobi.2015.03.002, 2015.

872 Fukuj, Y., and Doskey, P.V.: Air–surface exchange of non-methane organic compounds as a

873   grassland site: seasonal variations and stressed emissions. J. Geophys. Res. 103, 13153–

874   13168; doi: 10.1029/98JD00924, 1998.

875 Gaudel, A., Ancellet, G., and Godin–Beekmann, S.: Analysis of 20 years of tropospheric

876   ozone vertical profiles by lidar and ECC at Observatoire dr Haute Provence (OHP) at

877   44^oN, 6.7^oE. Atmos. Environ. 113, 78–89; doi: 10.1016/j.atmosenv.2015.04.028, 2015.

878 Ge, J., Xie, Z., Xu, W., and Zhao, Ch.: Controls over leaf litter decomposition in a mixed

879   evergreen and deciduous broad-leaved forests, Central China. Plant Soil, 412,345–355,

880   doi: 10.1007/s11104-016-3077-9, 2017.

881 Gray, C.M., Monson, R.K., and Fierer, N.: Emission of volatile organic compounds during

882   the decomposition of plant litter. J. Geophys. Res. 115, G03015, doi:

883   10.1029/2010JG001291, 2010.

884 Greenberg, J.P., Asensio, D., Turnipseed, A., Guenther, A.B., Karl, T., and Gochin, D.:

885   Contribution of leaf and needle litter to whole ecosystem BVOC fluxes. Atmos. Environ.

886   59, 302–311; doi: 10.1016/j.atmosenv.2012.04.038, 2012.

887 Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger,

888   L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamrajan, R.,

889   Tailor, J., and Zimmerman, P.R.: A global model of natural volatile organic compounds

890   emission. J. Geophys. Res. 100, 8873–8892; doi: 10.1029/94JD02950, 1995.

891 Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of

892   global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and

893   Aerosols from Nature). Atmos. Chem. Phys. 6, 3181–3210; doi: 10.5194/ACP-7-4327-

894   2007, 2006.

895   Hageman, U., and Moroni, M.T.: Moss and lichen decomposition in old-growth and harvested

896   high-boreal forests estimated using the litterbag and minicontainer methods. Soil Biol.

897   Biochem. 87, 10–24, doi: 10.1016/j.soilbio.2015.04.002, 2015.

898   Hari, P., and Kulmala, M.: Station for Measuring Ecosystem-Atmosphere Relations (SMEAR

899   II). Boreal Environ. Res. 10, 315–322, 2005.

900   Hassall, M., Turner, J.G., and Rands, M.R.W.: Effects of terrestrial isopods on the

901   decomposition of woodland leaf litter. Oecologia 72, 597–604; doi: 10.1007/BF00378988,

902   1987.

903   Hayward, S., Muncey, R.J., James, A.E., Halsall, C.J., and Hewitt, C.N.: Monoterpene

904   emissions from soil in Sitka spruce forest. Atmos. Environ. 35, 4081–4087; doi:

905   10.1016/S1352-2310(01)00213-8, 2001.

906   Hellén, H., Hakola, H., Pystynen, K.-H., Rinne, J., and Haapanala, S:. C_2–C_{10} hydrocarbon

907   emissions from a boreal wetland and forest floor. Biogeosciences 3, 167–174; 10.5194/bg-

908   3-167-2006 , 2006.

909   Hellén, H., Praplan, A.P., Tykkä, T., Helin, A., Schallhart, S., Schiestl-Aalto., P.P., Bäck, J.,

910   and Hakola, H.: Sesquiterpenes and oxygenated sesuiterpenes dominate the VOC (C5-C20)

911   emission of downy birches. Atmos. Chem. Phys. 21, 8045–8066, doi: 10.5194/acp-21-

912   8045-2021, 2021.

913   Helmig, D., Klinger, L.F., Guenther, A., Vierling, L., Geron, Ch., and Zimmerman, P.:

914   Biogenic volatile organic compound emissions (BVOCs). I. Identifications from three

915   continental sites in the U.S. Chemosphere 38, 2163–2187; doi: 10.1016/S0045-

916   6535(98)00425-1, 1999.

917 Hensgens, G., Lechtenfeld, O.J**.,** Guillemette, F**.,** Laudon, H**.,** and Berggren, M.: Impacts of

918 litter decay on organic leachate composition and reactivity. Biogeochemistry 154 (1), 99–

919 117; doi: 10.1007/s10533-021-00799-3, 2021.

920 Hewins D.B., Lee, H., Barnes, P.W., McDowell, N.G., Pockman, W.T., Rahn, T., and Throop,

921 H.L.: Early exposure to UV radiation overshadowed by precipitation and litter quality as

922 drivers of decomposition in the northern Chihuahuan Desert. PLOS ONE, 14 (2),

923 e0210470, doi: 10.1371/journal.pone.0210470, 2019.

924 Hobbie, S., Eddy, W.C., Buyarsku, CR., Adair, C., Ogdahl, M.L., and Weisenhorn, P.:

925 Response of decomposing litter and its microbial community to multiple forms of nitrogen

926 enrichment. Ecol. Monogr. 82, 389–405; doi: 10.2307/41739376, 2012.

927 Hu, Z., Xu, C., McDowell, N.G., Jonson D.J., Wang, M., Luo, Y., Zhou, X., and Huang, Z.:

928 Linking microbial community composition to C loss rates during wood decomposition.

929 Soil Biol. Biochem. 104, 108–116, doi: 10.1016/j.soilbio.2016.10.017, 2017.

930 Ioffe, B.V., Isidorov, V.A., and Zenkevich, I.G.: Gas chromatographic–mass spectrometric

931 determination of volatile organic compounds in an urban atmosphere. J. Chromatogr. 142,

932 787–795; doi: 10.1016/S0021-9673(01)92086-2, 1977.

933 IPCC: Climate Change 2013: the Physical Science Basis. Contribution of working group in

934 to the fifth assessment report of the intergovernmental panel on climate change. Cambridge

935 Univ. Press, Cambridge, 2013.

936 Isebrands, J.D., Guenther, A.B., Harley, P., Helmig, D., Klinger, L., Vierling, L.,

937 Zimmerman, P., and Geron, C.: Volatile organic compound emission rates from mixed

938 deciduous and coniferous forests in Northern Wisconsin, USA. Atmos. Environ. 33, 2527–

939 2536; doi: 10.1016/S1352-2310(98)00250-7, 1999.

940 Isidorov, V.A., Zenkevich, IG., and Ioffe, B.V.: Volatile organic compounds in the

941   atmosphere of forests. Atmos. Environ. 19,1–8; doi: 10.1016/0004-6981(85)90131-3,

942   1985.

943 Isidorov, V.A.: Organic Chemistry of the Earth's Atmosphere. Springer, Berlin, 1990.

944 Isidorov, V.A.: Non-methane hydrocarbons in the atmosphere of boreal forests: composition,

945   emission rates, estimation of regional emission and photocatalytic transformation. Ecol.

946   Bull. 42, 71–76; https://www.jstor.org/stable/20113107, 1992.

947 Isidorov, V.A.: Volatile Emissions of Plants: Composition, Emission Rate, and Ecological

948   Significance. Alga Publ., St. Petersburg, 1994.

949 Isidorov, V.A., Povarov, V.G., Klokova, E.M., Prilepsky, E.B., and Churilova Yu.Yu.:

950   Estimation of photochemically active VOC emission by forests of the European part of the

951   former USSR. In: Angeletti, G. and Restelli, G. (Eds.), Physico-Chemical Behaviour of

952   Atmospheric Pollutants. ECSC-EC-EAEC, Brussels, Luxembourg, pp. 31–40, 1994.

953 Isidorov, V.A, Klokova, E.M., Povarov, V.G., and Kolkova, S.: Photocatalysis on

954   atmospheric aerosols: Experimental studies and modelling. Catal. Today, 39 (3), 233–242;

955   doi: 10.1016/S0920-5861(97)00104-1, 1997.

956 Isidorov, V., Povarov, V., and Stepanov, A.: Forest soil cover: VOC sink or source? In: Proc.

957   EUROTRAC Symp. Borrell, P.M. and Borrel,P. (eds). WIT Press, Southampton, pp. 158–

958   162, 1999.

959 Isidorov, V., and Jdanova, M.: Volatile organic compounds from leaves litter. Chemosphere

960   48, 975–979; 10.1016/s0045-6535(02)00074-7, 2002.

961 Isidorov, V.A., Vinogorova, V.T., and Rafałowski, K.: HS–SPME analysis of volatile organic

962   compounds of coniferous needle litter. Atmos. Environ. 37, 4645–4650;

963   10.1016/j.atmosenv.2003.07.005, 2003.

964 Isidorov, V., Vinogorova, V., and Rafałowski, K.: Gas chromatographic determination of

965   extractable compounds composition and emission rate of volatile terpenes from larch

966   needle litter. J. Atmos. Chem. 50, 263–278; doi: 10.1007/s10874-005-5078-6, 2005.

967 Isidorov, V.A., Smolewska, M., Purzyńska–Pugacewicz, A., and Tyszkiewicz, Z.: Chemical

968   composition of volatile and extractive compounds of pine and spruce litter in the initial

969   stages of decomposition. Biogeosciences 7, 2785–2794; doi: 10.5194/bg–7–1–2010, 2010.

970 Isidorov, V., Tyszkiewicz, Z., and Pirożnikow, E.: Fungal succession in relation to volatile

971   organic compounds emissions from Scots pine and Norway spruce leaf litter–destroying

972   fungi. Atmos. Environ. 131, 301–316, doi: 10.1016/j.atmosenv.2016.02.015, 2016.

973 Isidorov, V.A., Pirożnikow, E., Spirina, V.L., Vasyanin, A.N., Kulakova, S.A., Abdulmanova,

974   I.F., Zaitsev, A.A. (2022) Emission of volatile organic compounds by plants of the floor of

975   boreal and mid-latitude forests. J. Atmos. Chem. doi: 10.1007/s10874-22-09434-3.

976 Jagodzinski, A.M., Dyderski, M.K., Rawlik, K., and Katna, B.: Seasonal variability of

977   biomass, total leaf area and specific leaf area of forest understory herbs reflects their life

978   strategies. Forest Ecol. Manage. 374, 71–81, doi: 10.1016/j.foreco.2016.04.050, 2016.

979 Jiang, L.P., Yue, K., Yang Y.L., and Wu, Q.G.: Leaching and freeze-thaw events contribute to

980   litter decomposition - A review. Sains Malays. 4, 1041–1047, 2016.

981 Janson, R.W.: Monoterpene emissions from Scots pine and Norwegian spruce. J. Geophys.

982   Res. 98, 2839–2850, doi:10.1029/92JD02394, 1993.

983 Janson, R., De Serves C., and Romero R.: Emission of isoprene and carbonyl compounds

984   from a boreal forest and wetland in Sweden. Agricul. Forest Meteorol. 98–99, 671–681;

985   doi: 10.1016/S0168-1923(99)00134-3, 1999.

986 Kainulainen, P., and Holopainen, J.K.: Concentration of secondary compounds in Scots pine

987   needles at different stages of decomposition. Soil Biol. Biochem. 34, 37–42; doi:

988   10.1016/S0038-0717(01)00147-X, 2002.

989 Karl, T., Harren,F., Warneke, C., de Gouw, J., Grayless, C., and Fall, R.: Senescing grass

990   crops as regional sources of reactive volatile organic compounds. J. Geophys. Res. 110,

991   D15302; doi:10.1029/2005JD005777, 2005.

992 Karl, M., Guenther, A., Köble, R., Leip, A., and Seufert, G.: A new European plant-specific

993   emission inventory of biogenic volatile organic compounds for use in atmospheric

994   transport models. Biogeosciences 6, 1059–1087; doi: 10.5194/bg-6-1059-2009, 2009.

995 Kegge, W., and Pierik, R.: Biogenic volatile organic compounds and plant competition.

996   Trends Plant Sci. 15 (3) 1263–132; doi: 10.1016/j.trplants.2009.11.007, 2009.

997 Keiser, A.D., Warren, R., Filley, T., and Bradford, M.A.: Signatures of an abiotic

998   decomposition pathway in temperate forest leaf litter. Biogeochemistry, 153 (2), 177–190;

999   doi: 10.1007/s10533-021-00777-9, 2021.

1000 Kesselmeier, J., and Staudt, M.: Biogenic volatile organic compounds (VOC): An overview

1001   on emission, physiology and ecology. J. Atmos. Chem. 33, 23–88; doi:

1002   10.1023/A:1006127516791, 1999.

1003 Kesselmeier, J., and Hubert, A.: Exchange of reduced volatile sulfur compounds between leaf

1004   litter and the atmosphere. Atmos. Environ. 36, 4679–4686; doi: 10.1016/S1352-

1005   2310(02)00413-2, 2002.

1006 Kim, M.J., Park, R.J., Ho, C.–H., Choi, K.–C., Song, C.–K., and Lee, J.–B.: Future ozone and

1007   oxidants change under RCP scenarios. Atmos. Environ. 101, 103–115; doi:

1008   10.1016/j.atmosenv.2014.11.016, 2015.

1009 Kim, M., Kim, W.–S., Tripathi, B.M., and Adams, J.: Distinct bacterial communities

1010   dominate tropical and temperate zone leaf litter. Microb. Ecol. 67, 837–848;

1011   doi:10.1007/s00248-014-0380-y, 2014.

1012   Kirker G.T., Bishell A., Cappellazzi J., Palmer J., Bechle N., Lebow P., and Lebow S.: Role

1013   of leaf litter in above-round wood decay. Microorganisms, 8, 696; doi:

1014   10.3390/microorganisms8050696, 2020.

1015   Kivimäenpää M., Markkanen J.-M., Ghimire R. P., Holopainen T., Vuorinen M., and

1016   Holopainen J. K.: Scots pine provenance affects the emission rate and chemical

1017   composition of volatile organic compounds of forest floor. Can. J. For. Res. 48, 1373–

1018   1381. DOI: 10.1139/cjfr-2018-0049, 2018.

1019   Klemmedson, J.O., Meier, C.E., and Campbell, R.E.: Litter fall transfers of dry matter and

1020   nutrients in ponderosa pine stand. Canadian J. For. Res. 20, 1105–1115; doi: 10.1139/x90-

1021   146, 1990.

1022   Kolari, P., Pumpanen, J., Kulmala, L., Ilvesniemi, H., Nikinmaa, E., Grönholm, T., and Hari,

1023   P.: Forest floor vegetation plays an important role in photosynthetic production of boreal

1024   forests. For. Ecol. Manage. 221, 241–248; doi:10.1016/j.foreco.2005.10.021, 2006.

1025   Kourtchev, I., Giorgio,C., Manninen,A., Wilson, E., Mahon, B., Alto, J., et al.: Enhanced

1026   volatile organic compounds emissions and organic aerosol mass increase the oligomer

1027   content of atmospheric aerosols. Sci. Rep. 6, 35038, doi: 10.1038/srep35038, 2016.

1028   Kozlov, M.V., Zverev, V., and Zvereva E.L.: Shelters of leaf-tying herbivores decompose

1029   faster than leaves damaged by free-living insects: Implications for nutrient turnover in

1030   polluted habitats. Sci. Total Environ. 568, 946–951; doi: 10.1016/j.scitotenv.2016.04.121,

1031   2016.

1032   Kravchenko I.K., Tikhonova E.N., Ulanova R.V., Menko E., and Sukacheva M.V.: Effect of

1033   temperature on litter decomposition, soil microbial community structure and biomass in

1034   mixed-wood forest in European Russia. Curr. Sci., 116, 765–772; doi:

1035   10.18520/cs/v116/i5/765-772, 2019.

1036 Krishna, M.P., and Mohan, M.: Litter decomposition in forest ecosystems: a review. Energy

1037   Ecol. Environ., 2, 236–249; doi:10.1007/s40974-017-0064-9, 2017.

1038 Kulmala, M., Hämeri, K., Aalto, P.P., Mäkelä, J.M., Pirjola, L., Nilsson, E., Douglas, E.,

1039   Buzorius, G., Rannik, Ü., Dal Maso, M., Seidl, W., Hoffmann, T., Janson, R., Hansson,

1040   H.C., Viisanen, Y., Laaksonen, A., and O'Dowd, C.D.: Overview of the international

1041   project on biogenic aerosol formation in the boreal forest (BIOFOR). Tellus B 53, 324–

1042   343; doi: 10.1034/j.1600-0889.2001.530402.x, 2001.

1043 Kulmala, M., Kontkanen,J., Junninen, H., et al.: Direct observation of atmospheric aerosol

1044   nucleation. Science, 339, 943–946, doi: 10.1126/science.1227385, 2013.

1045 Kuzma, J., Nemecek-Marshall, M., Pollock, W.H., and Fall, R.: Bacteria produce of volatile

1046   hydrocarbon isoprene. Curr. Microbiol. 30, 97–103; doi: 10.1007/BF00294190"00294190,

1047   1995.

1048 Kurz, C., Coûteaux, M.–M., and Thiéry, J.M.: Residence time and decomposition rate of

1049   *Pinus pinaster* needles in a forest floor from direct field measurements under a

1050   Mediterranean climate. Soil Biol. Biochem. 32, 1197–1206; doi: 10.1016/S0038-

1051   0717(00)00036-5, 2000.

1052 Lee, S.H., Gordon, H., Yu, H., Lehtipalo, K., Haley, R., Li, Y., and Zhang, R.: New particle

1053   formation in the atmosphere: From molecular clusters to global climate. J. Geophys. Res.:

1054   Atmospheres, 124, 7098–7146. https://doi.org/10.1029/2018JD029356, 2019.

1055 Leff, J.W., and Fierer, N.: Volatile organic compound (VOC) emissions from soil and litter

1056   samples. Soil. Biol. Biochem. 40, 1629–1636; doi: 10.1016/j.soilbio.2008.01.018, 2008.

1057 Li, Y.L., Huang, H.Y., Wu, G.F., Yan, S.Z. Chang, Z.Z., Bi, J.H., and Chen, L.: The effect of

1058   UV-A on dry rice straw decomposition under controlled laboratory conditions.

1059   Bioresources, 11, 2568–2582; doi: 10.15376/biores.11.1.2568-2582, 2016.

1060 Lindo, Z., and Gonzalez, A.: The bryosphere: an integral and influential component of the

1061   earth's biosphere. Ecosystems 13, 612e627. doi: 10.1007/s10021-010-9336-3, 2010.

1062 Lindwall, F., Faubert, P., and Rinnan, R.: Diel variation of biogenic volatile organic

1063   compound emissions - field study in the sub, low and high arctic on the effect of

1064   temperature and light. PLoS One 10(4):e0123610, doi: 10.1371/journal.pone.0123610,

1065   2015.

1066 Liu, C., Ilvesniemi, H., Berg, B., Kutsch, W., Yang, Y., Ma, X., and Westman, C. J.:

1067   Aboveground litterfall in Eurasian forests J. Forest. Res. 14(1), 27–34; doi:

1068   10.1007/BF02856758, 2003.

1069 Lodato, M.B., Boyette, J.S., Smilo, R.A., Jackson, C.R., Halvorson, H.M., and Kuehn, KA.:

1070   Functional importance and diversity of fungi during standing grass litter decomposition.

1071   Oekologia, 195 (2), 499–512; doi: 10.1007/s00442-020-04838-y, 2021.

1072 López-Mondéjar, R., Zühlke, D., Becher, D., Riedel, K., and Baldrian, P.: Cellulose and

1073   hemicellulose decomposition by forest soil bacteria proceeds by the action of structurally

1074   variable enzymatic systems. Sci. Rep. 6:25279, doi: 10.1038/srep25279, 2016.

1075 Lukowski, A., Giertych, M.J., Zmuda, M., Maderek, E., Adamczyk, D., and Karolewski, P.:

1076   Decomposition of herbivore-damaged leaves of understory species growing in oak and

1077   pine stands. Forests 12(3), Article Number 304; doi: 10.3390/f12030304, 2021.

1078 Mahajan, R., Nikitina, A., Litti, Y., Nozhevnikova, A., and Goel, G.: Autochthonous

1079   microbial community associated with pine needle forest litterfall influences its degradation

1080   under natural environmental conditions. Environ. Monit. Assess. 188, 417; doi

1081   10.107/s10661-016-5421-1, 2016.

1082 Makkonen, R., Asmi, A., Kerminen, V.M., Boy, M., Arneth, A., Guenther, A., and Kulmala,

1083   M.: BVOC-aerosol-climate interactions in the global aerosol-climate model ECHAM5.5-

1084   HAM2. Atmos. Chem. Phys. 12, 10077–10096, doi: 10.5194/acp-12-10077-2012, 2012.

1085   Maltsev, Ye,I., Pakhomov, A. Ye., and Maltseva, I.A.: Specific features of algal communities

1086   in forest litter of forest biogeocenoses of the steppe zone. Contemp. Prob. Ecol. 10, 71–76;

1087   doi:10.1134/s1995425517010085, 2017a.

1088   Maltsev, Ye,I., Didovich, S.V., and Maltseva, I.A.: Seasonal changes in the communities of

1089   microorganisms and algae in the litters of tree plantations in the steppe zone. Euras. Soil

1090   Sci. 50, 935–942; doi: 10.1134/S1064229317060059, 2017b.

1091   Mäki, M., Heinonsalo, J., Hellèn, H., and Bäck, J.: Contribution of understorey

1092   vegetation and soil processes to boreal forest isoprenoid exchange. Biogeosciences

1093   14(5), 1055–1073. doi: 10.5194/bg-14-1055-2017, 2017.

1094   Mäki M., Krasnov, D., Hellen, H., Noe, S ., and Back, J.: Stand type affects fluxes of

1095   volatile organic compounds from the forest floor in hemiboreal and boreal climates. Pant

1096   and Soil. 441 (1–2), 363–381, doi: 10.1007/s11104-019-04129-3, 2019a.

1097   Mäki, M., Aalto, J., Hellèn, H., Pihlatie, M., and Bäck, J.: Interannual and seasonal dynamics

1098   of volatile organic compounds fluxes from the boreal forest floor. Front. Plant Sci. 10:191,

1099   doi: 10.3389/fpls.2019.00191, 2019b.

1100   Masiol, M., Squizzato, S., Chalupa, D., Rich, D.Q., and Hopke, P.K.: Spatial-temporal

1101   variations of summertime ozone concentrations across a metropolitan area using a network

1102   of low-cost monitors to develop 24 hourly land-use regression models. Sci. Total Environ.

1103   654, 1167–1178, doi: 10.1016/j.scitotenv.2018.11.111, 2019.

1104   McBride S.G., Choudoir M., Fierer N., and Strickland, M.: Volatile organic compounds from

1105   leaf litter decomposition alter soil microbial communities and carbon dynamics. Ecology

1106   101:e03130, doi: 10.1002/ecy.3130, 2020.

1107   Mochizuki, T., Tani, A., Takahashi, Y., Saigusa N., and Ueyama, M.: Long–term

1108   measurement of terpenoid flux above a *Larix kaempferi* forest using a relaxed eddy

1109   accumulation method. Atmos. Environ. 83, 53–61; doi:10.1016/j.atmosenv.2013.10.054,

1110   2014.

1111   Mogensen, D., Gierens, R., Crowley, J.N., et al.: Simulation of atmospheric OH, O3 and NO3

1112   reactivities within and above the boreal forest. Atmos. Chem. Phys. 15, 3909–3932, doi:

1113   10.5194/acp-15-3909-2015, 2015.

1114   Morén, A.-S., and Lindroth A.: CO2 exchange at the floor of boreal forests. Agric. For.

1115   Meteorol. 101, 1–14; doi: 10.1016/S0168-1923(99)00160-4, 2000.

1116   Nahrowi M.B., Susilowati A., and Setyaningsih R.: Screening and identification of lignolytic

1117   bacteria from the forest at eastern slope of Lawu Mountain. AIP Conf. Proc. 2002, 020028;

1118   https://doi.org/10.1063/1.5050138, 2018.

1119   Navarro J.C.A, Smolander S., Struthers H. et al.: Global emissions of terpenoid VOCs from

1120   terrestrial vegetation in the last millennium. J. Geophys. Res. Atmos. 119, 6867–6885; doi:

1121   10.1002/2013jd021238, 2014.

1122   Nilsson, T., Larsen, T.O., Montanarella, L., and Madsen, J.Ø.: Application of head–space

1123   solid–phase microextraction for the analysis of volatile metabolites emitted by *Penicillium*

1124   species. J. Microbiol. Meth**.** 25**,** 245–255; doi: 10.1016/0167-7012(95)00093-3, 1996.

1125   Norrman, J.: Production of volatile organic compounds by the yeast fungus *Dipodascus*

1126   *aggregatus.* Arch. Microbiol. 68, 133–149; doi: 10.1007/BF00413873, 1969.

1127   Nölscher, A.C., Bourtsoulidis, E., Bonn, B., Kesselmeier, J., Lelieveld, J., and Williams, J.:

1128   Seasonal measurements of total OH reactivity emission rates from Norway spruce in 2011.

1129   Biogeosciences 10, 4241–4257, doi: 10.5194/bg-10-4241-2013, 2013.

1130   Osono, T., and Takeda, H.: Decomposition of organic chemical components in relation to

1131   nitrogen dynamics in leaf litter of 14 tree species in a cool temperate forests. Ecol. Res. 20,

1132   41–49; doi: 10.1007/s11284-004-0002-0, 2005.

1133   Otaki M., and Tsuyuzaki S.: Succession of litter-decomposing microbial organisms in

1134   deciduous birch and oak forests, northern Japan. Acta Oecol., 101, 103485; doi: 1-

1135   16/j.actao.2019.103485, 2019.

1136   Paaso, U., Keski-Saari, S., Keinänen, M., Karvinen, H., Silfrer, T., Rousi, M., and Mikola, J.:

1137   Interpopulation genotypic variation of foliar secondary chemistry during leaf senescence

1138   and litter decomposition in silver birch (*Betula pendula*). Front. Plant Sci. 8, 1074. doi:

1139   10.3389/fpls.2017.01074, 2017.

1140   Petersson, G.: High ambient concentration of monoterpenes in Scandinavian pine forests.

1141   Atmos. Environ. 22, 2617–2619; doi: 10.1016/0004-6981(88)90497-0, 1988.

1142   StarkeInfluence of saprophages (Isopoda, Diplopoda) on leaf litter decomposition under

1143   different levels of humidification and chemical loading. Biosyst. Divers. 28 (4), 384–389;

1144   doi: 10.15421/012049, 2020.

1145   Porchikalov, A.V., and Karelin, D.V.: A field study of tundra plant litter decomposition rate

1146   via mass loss and carbon dioxide emission: The role of biotic and abiotic controls, biotope,

1147   season of year, and spatial–temporal scale. Biol. Bull. Rev. 5, 1–16; doi:

1148   10.1134/S2079086415010077, 2015.

1149   Praplan, A.P, Tykkä, T., Schallhart, S., Tarvainen, V., Bäck, J., and Hellén, H.: OH reactivity

1150   from the emissions of different tree species: investigating the missing reactivity in a boreal

1151   forest. Biogeosciences 17, 4681–4705, doi: 10.5194/bg-17-4681-2020, 2020.

1152   Purahong, W., Wubet, T., Lentendu, G., Schloter, M., Pecyna, M.J., Kapturska, D.,

1153   Hofrichter, M., Kruger, D., and Buscot, F.: Life in leaf litter: novel insights into

1154   community dynamics of bacteria and fungi during litter decomposition. Mol. Ecol. 26,

1155   4059–4074, doi: 10.1111/mec.13739, 2016.

1156   Ramirez, K.S., Lauber, C.L., and Fierer, N.: Microbial consumption and production of

1157   volatile compounds at the soil–litter interface. Biogeochemistry 99, 97–107, 2010.

1158 Räisänen, T., Ryyppö, A., and Kellomäki, S.: Monoterpene emission of a boreal Scots pine

1159 (*Pinus sylvestris* L.) forest. Agric. For. Meteor., 149(5), 808–819, doi:

1160 10.1016/j.agrformet.2008.11.001, 2009.

1161 Rinnan, R., Rinnan, Å., , Holopainen, T, Holopainen, J.K., and Pasanen, P.: Emission of non-

1162 methane volatile organic compounds (VOCs) from boreal peatland microcosms—effects of

1163 ozone exposure. Atmos. Environ 39, 921–930; doi: 10.1016/j.atmosenv.2004.09.076, 2005.

1164 Santurtún, A., González–Hildago, J.C., Sanchez–Lorenzo, A., and Zarrabeitia, M.T.: Surface

1165 ozone concentration trends and its relationship with weather type in Spain (2001–2010).

1166 Atmos. Environ. 101, 10–22; doi: 10.1016/j.atmosenv.2014.11.005, 2015.

1167 Sharma, A., Ojha, N., Pozzer, A., Gufran Beig, G., Sachin S., and Gunthe, S.S.: Revisiting the

1168 crop yield loss in India attributable to ozone. Atmos. Environ., doi:

1169 10.1016/j.aeaoa.2019.100008, 2019.

1170 Schöller, C.E.G., Gurtler, H., Pedersen, R., Molin, S., and Wilkins, K. Volatile metabolites

1171 from actinomycetes. J. Agric. Food Chem. 50, 2615–2621; doi: 10.1021/jf0116754, 2002.

1172 Shao, S., Zhao, Y., Zhang, W., Hu, G., Xie, H., Yan, J., Han, S., He, H., and Zhang, X.:

1173 Linkage of microbial residue dynamics with soil organic carbon accumulation during

1174 subtropical forest succession. Soil Biol. Biochem. 114, 114–120, doi:

1175 10.1016/j.soilbio.2017.07.007, 2017.

1176 Sindelarova, K., Granier, C., Bouarar, I., Guenther, A., Tilmes, S., Stavrakou, T., Müller, J.F.,

1177 Kuhn U., Stefani, P., and Knorr. W.: Global data set of biogenic VOC emissions calculated

1178 by the MEGAN model over the last 30 years. Atmos. Chem. Phys. 14, 9317–9341;

1179 doi:10.5194/acp-14-9317-2014, 2014.

1180 Sinha, V., Williams, J., Lelieveld, J., Ruuskanen, T., Kajos, M., Patokoski, J., Hellen, H.,

1181 Hakola, H., Mogensen, D., Boy, M., Rinne, J., and Kulmala, M.: OH reactivity

1182   measurements within a boreal forests: Evidence of unknown reactive emissions. Enviro.

1183   Sci. Technol. 44, 6614–6620, doi: 10.1021/es101780b.2010, 2010.

1184   Starke, R., Kermer, R., Ullmann-Zeunert, L., Baldwin, I.T., Seifert, J., Bastida, F., von

1185   Bergen, M., and Jehmlich N.: Bacteria dominate the short-term assimilation of plant-

1186   derived N in soil. Soil Biol. Biochem. 96, 30–38, doi: 10.1016/J.soilbio.2016.01.09, 2016.

1187   Stepanov A.: Formation of concentration fields of phytogenic volatile organic compounds

1188   under the canopy of the boreal forest. PhD Thesis, St. Petersburg University, 1999.

1189   Stepen', R.A., Vershnyak, V.M., and Peryshkina, G.I.: The store of essential oil in Yakut pine

1190   (*Pinus sylvestris* L.) forests. Rastit. Res. № 1, 81–86, 1987 (in Russian).

1191   Strode, S.A., Ziemke, J.R., Oman, L.D., Lamsal, L.N., Olsen, M.A., and Liu, J.H.: Global

1192   changes in the diurnal cycle of surface ozone. Atmos. Environ. 199, 323-333, doi:

1193   10.1016/j.atmosenv.2018.11.028, 2019.

1194   Stoy, P.C., Trowbridge, A.M., Siqueira, M.B., Freire, L.S., Phillips, R.P., Jacobs, L., Wiesner,

1195   S., Moonson, R.K., and Novick, K.A.: Vapor pressure deficit helps explain biogenic

1196   volatile organic compound fluxes from the forest floor and canopy of a temperate

1197   deciduous forest. Oecologia, doi: 10.1007/s00442-21-04891-1.

1198   Štursová, M., Šnajdr, J., Koukol, O., Tláskal, V, Cajthaml, T., and Baldrian, P.: Long-term

1199   decomposition of litter in the montane forest and the definition of fungal traits in the

1200   successional space. Fungal Ecol., 46, 100913; doi: 10.1016/j.funeco.2020.100913, 2020.

1201   Sunesson, A.L., Vaes, W.H.J., Nilsson, C.A., Blomquist, G., Andersson, B., and Carlson, R.:
1202   Identification of volatile metabolites from five fungal species cultivated on two media.
1203   Appl. Environ. Microbiol., 61, 2911–2918; doi: 10.1128/AEM.61.8.2911-2918.1995,
1204   1995.

1205   Svendsen, S.H., Prieme, A., Voriskova, J., Kramshoj, M., Schostag, M., Jacobsen, C S., and

1206   Rinnan, R.: Emissions of biogenic volatile organic compounds from arctic shrub litter are

1207   coupled with changes in the bacterial community composition. Soil Biol. Biochem., 120, :

1208   80–90. doi: 10.1016/j.soilbio.2018.02.001, 2018.

1209   Swift, M.J., Heal, O.W., and Anderson, J.M.: Decomposition in Terrestrial Ecosystems.

1210   Blackwell Sci. Publ., Oxford,1979.

1211   Tang J., Schurgers G., and Rinnan R.: Process understanding of soil BVOC fluxes in natural

1212   ecosystems: a review. Rev. Geophys. 57, 966–986; doi: 10.1029/2018rg000634,2019.

1213   Tarr, M.A., Miller, W.L., and Zepp, R.G.: Direct carbon monoxide photoproduction from

1214   plant matter. J. Geophys. Res. 100(D6), 11,403–11,413, 1995.

1215   Tennakoon, D.S., Gentekaki, E., Jeewon, R., Kuo, C.H., Promputtha, I., and Hyde, K.D.: Life

1216   in leaf litter: Fungal community succession during decomposition. Mycosphere, 12(1),

1217   406–429; doi: 10.5943/mycosphere/12/1/5, 2021.

1218   Tian, X., Takeda, H., and Azuma, J.: Dynamics of organic-chemical components in leaf litters

1219   during a 5.5-year decomposition. Eur. J. Soil. Biol. 36, 81–89; doi: 10.1016/S1164-

1220   5563(00)01049-9, 2000.

1221   Tingey, D.T., Evans, R.C., Bates, E.H., and Gumpertz, M.L.: Isoprene emissions and

1222   photosynthesis in three ferns. The influence of light and temperature. Physiol. Plant. 69,

1223   609–616; doi: 10.1111/J.1399-3054.1987.TB01974.X, 1987.

1224   Trowbridge, A. M., Stoy, P. C., and Phillips, R. P. (2020). Soil biogenic volatile organic

1225   compound flux in a mixed hardwood forest: Net uptake at warmer temperatures and the

1226   importance of mycorrhizal associations. Journal of Geophysical Research: Biogeosciences,

1227   125(4). doi:10.1029/2019jg005479.

1228   Urbanová, M., Šnajdr, J., and Baldrian, P.: Composition of fungal and bacterial communities

1229   in forest litter and soil is largely determined by dominant trees. Soil Biol. Biochem. 84,

1230   53–64;.doi: 10.1016/j.soilbio. 2015.02.011, 2015.

1231 Vingarzan, R.: A review of surface ozone background levels and trends. Atmos. Environ. 38,

1232 3431–3442; doi: 10.1016/j.atmosenv.2004.03.030, 2004.

1233 Viros, J., Fernandez, C., Wortham, H., Gavinet, J., Lecareux, C., and Ormeño, E.: Litter of

1234 mediterranean species as a source of volatile organic compounds. Atmos. Environ. 242,

1235 117815; doi: 10.1016/j.atmosenv.2020.117815, 2020.

1236 Viros, J., Santonja, M., Temime-Roussel, B., Wortham, H., Fernandez, C., and Ormeño, E.:

1237 Volatilome of Aleppo Pine litter over decomposition process. Ecol. Evol., doi:

1238 10.1002/ece3.7533, 2021.

1239 Virzo De Santo, A., Rutigliano, F.A., Berg, B., Fioretto, A., Puppi, G., and Alfani, A.: Fungal

1240 mycelium and decomposition of needle litter in three contrasting coniferous forests. Acta

1241 Oecol. 23, 247–259; doi: 10.1016/S1146-609X(02)01155-4, 2002.

1242 Wagner, W.P., Helmig, D., and Fall, R.: Isoprene biosynthesis in *Bacillus subtilis* via the

1243 methylerythritol phosphate pathway. J. Nat. Prod. 63, 37–40; doi: 10.1021/np990286p,

1244 2000.

1245 Wang, Z., Yin, X., and Li, X.: Soil mesofauna effects on litter decomposition in the

1246 coniferous forest of the Chanbai Mountains, China. Appl. Soil Biol. 92, 64–71; doi:

1247 10.1016/j.apsoil.2015.03.010, 2015.

1248 Wang, J.N., Xu, B., Wu, Y., Gao, J., and Shi, F.S.: Flower litters of alpine plants affect soil

1249 nitrogen and phosphorus rapidly in the eastern Tibetan Plateau. Biogeosciences 13, 5619-

1250 5631, doi: 10.5194/bg-13-5619-2016, 2016.

1251 Wang, M., Schurgers, G., Hellèn, H., Lagergren, F., and Holst, T.: Biogenic volatile organic

1252 compound emission from a boreal forest floor. Boreal Environ. Res. 23, 249–265, 2018.

1253 Warneke, C., Karl, Th., Judmaier, H., Hansel, A., Jordan, A., Lindinger, W., and Crutzen,

1254 P.J.: Acetone, methanol, and other partially oxidized volatile organic emissions from dead

1255   plant matter by abiological processes: significance for atmospheric HO_x chemistry. Glob.

1256   Biogeochem. Cycl. 13, 9–17; doi: 10.1029/98GB02428, 1999.

1257   Wilkins, K.: Volatile metabolites from actinomycetes. Chemosphere 32, 1427–1434; doi:

1258   10.1016/0045-6535(96)00051-3, 1996.

1259   Wilt, F.M., Miller, G.C., Everett, R.L., and Hackett , M.: Monoterpene concentrations in

1260   fresh, senescent, and decaying foliage of singleleaf pinyon (*Pinus monophylla* Torr. &

1261   Frem.: Pinaceae) from the western Great Basin. J. Chem. Ecol. 19, 185−194; doi:

1262   10.1007/BF00993688, 1993.

1263   Wood, S.E., Gaskin, J.F., and Langenheim, J.H.: Loss of monoterpenes from *Umbellularia*

1264   *californica* leaf litter. Biochem. System. Ecol. 23, 581–591; doi: 10.1016/0305-

1265   1978(95)00087-9, 1995.

1266   Wu, F., Yang, W., Zhang, J., and Deng, R.: Litter decomposition in two subalpine forests

1267   during the freeze–thaw season. Acta Oecol. 36, 135–140; doi:

1268   10.1016/j.actao.2009.11.002, 2010.

1269   Wurzenberger, M., and Ghosch, W.: Origin of the oxygen in the products of the enzymatic

1270   cleavage reaction of linoleic acid to 1-octen-3-ol and 10-oxo-*trans*-8-decenoic acid in

1271   mushrooms (*Psalliota bispora*). Biochim. Biophys. Acta 794, 18–24; 10.1016/0005-

1272   2760(84)90292-3, 1984.

1273   Yang, Y., Shao, M., Wang, X., Nölscher, A.., Kessel, S., Guenther, A., and Williams, J.:

1274   Towards a quantitative understanding of total OH reactivity: A review. Atmos. Environ.

1275   134, 147–161, doi: 10.1016/j.atmosenv.2016.03.010, 2016.

1276   Zhang, D., Hui, D., Luo, Y., and Zhou, G.: Rates of litter decomposition in terrestrial

1277   ecosystems: global patterns and controlling factors. J. Plant Ecol. 1, 85–93; doi:

1278   10.1093/jpe/rtn002, 2008.

1279   Zhang, Y.Q., West, J.J., Emmons, L.K., et al.: Contributions of world regions to the global

1280   tropospheric ozone burden change from 1980 to 2010. Geophys. Res. Let. 48(1), article

1281   number e2020GL089184, doi: 10.1029/2020GL089184, 2021.

1282   Zhou, P., Ganzeveld, L., Rannik, Ü., et al.: Simulating ozone dry deposition at a boreal

1283   forests with a multi-layer canopy deposition model. Atmos. Chem. Phys. 17, 1361–1379,

1284   doi: 10.5194/acp-17-1361-2017, 2017.

1285   Zimmer, M., Kautz, G., and Topp, W.: Leaf litter–colonizing microbiota: supplementary food

1286   source or indicator of food quality for *Porcellio scaber* (Isopoda: Oniscidea)? Eur. J. Soil

1287   Biol. 39, 209–216; doi: 10.1016/S0038-0717(02)00065-2, 2003.

1288   Zimmerman, P.R., Chatfield, R.B., Fishmann, J., Crutzen, P.J., amd Hanst, P.L.: Estimation

1289   of production of CO and H_2 from the oxidation of hydrocarbon emissions from vegetation.

1290   Geophys. Res. Lett. 5, 679–682; doi: 10.1029/GL005i008p00679, 1978.

1291   Zlotin, R.I., and Bazilevich, N.I.: Global maps of organic matter structure in terrestrial

1292   ecosystems. In: Breymeyer A. (Ed.), Geography of Organic Matter Production and Decay.

1293   SCOPE Seminar, Conference Papers 18, Warsaw, 1993, pp. 7–20.

1294   Zong, R.H., Yang, X., Wen, L., et al.: Strong ozone production at a rural site in the North

1295   China Plain: Mixed effects of urban plumes and biogenic emissions. J. Envir. Sci. 71, 261–

1296   270, doi: 10.1016/j.jes.2018.05.003, 2018.

1297   Zyabchenko, S.S., 1984. North European Pine Forests. Nauka Publ., Leningrad (in Russian).

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1303 **Table 1**. Rate of decomposition of dead plant parts (%) during the warm season in two

1304 ecosystems of the forest-steppe zone of Russia (Bazilevich et al., 1993).

Factors	Oak forest	Meadow steppe
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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Table 2. Organic compounds in volatile emissions of leaves litter. Plant species**:** 1 - oriental beech (*Fagus orientalis*); 2 - sequoia (*Sequoiadendron giganteum*); 3 - cherry prinsepia (*Prinsepia sinenes*); 4 - aspen (*Populus tremula*); 5 - English oak (*Quercus robur*); 6 - maple (*Acer rubrum*); 7 - pine (*Pinus taeda*); 8 - poplar (*Populus balsamifera*); 9 - birch (*Betula pendula*); 10 - willow (*Salix* sp.); 11 - common beech (*Fagus sylvatica*); 12 - broad beech fern (*Phegopteris hexagonoptera*); 13 - northern red oak (*Q. rubra*); 14 - bur oak (*Q. macrocarpa*); 15 - lodgepole pine (*P. contorta*); 16 - ponderosa pine (*P. ponderosa*); 17 - eastern cottonwood (*Populus deltoides*); 18 - quaking aspen (*Populus tremuloides*); 19 - green ash (*Fraxinus pennsylvanica*); 20 - great laurel (*Rhododendron maximum*); 21 - eucalyptus (*Eucalyptus* sp.); 22 - spotted knapweed (*Centaurea maculosa*); 23 - miscanth (*Miscanthus* sp.); 24 - wheatgrass (*Thinopyrum intermedium*); 25 - Scots pine (*P. sylvestris*); 26 - Norway spruce (*Picea abies*); 27 - European larch (*Larix decidue*); 28 - clover (*Trifolium repens*); 29 - bluegrass (*Poa pratensis*); 30 - European silver fir (*Abies alba*).

References: **a** - Derendorp et al. (2011); **b** - Isidorov et al. (2002); **c** - Ramirez et al. (2010); **d** - Warneke et al. (1999); **e** - Fall et al. (2001); **f** - Gray et al. (2010); **h** - Isidorov et al. (2003); **i** - Isidorov et al. (2010); **j** - Isidorov et al. (2005); **k** - Kesselmeier and Hubert (2002).

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
p-Xylene	4,5,9	b
m-Xylene	5,8,9	b
o-Xylene	5,9	b
Cumene	8	b
n-Propyl benzene	5	b
Mesytilene	5	b
p-Cymene	4,5,8-10,25,26	b, h,i
p-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
p-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
cis-3-Pinanone	25	h
Terpin-4-ol	25,26	h
α-Terpineol	25,26	h,i
Myrtenol	25,26	i
p-Cymen-8-ol	25	h
Verbenone	25	h,i
cis-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
epi-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-Methy 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
sec-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
o-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 (*Licopodium clavatum*); 5 - red
bilberry (*Vaccinium vitis-ideae*); 6 - bilberry (*Vacinnium 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 – Isisorov 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
n-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
n-Hexane	20-28	d
2-Methylpentane	23	d
n-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
n-Decane	1	a
n-Undecane	1,2,27	a,d
n-Tetradecane	6,20	d
n-Pentadecane	22,24,26	d
n-Hexadecane	24	d
n-Heptadecane	21,24	d
n-Nonadecane	24	d
n-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
m-Cymene	21,24,27,28	d
p-Cymene	1,2,14-16,20-28	a,d,g
p-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
(Z)-Ocimene	6,25-27	d
(E)-Ocimene	6,15,25-27	d,g
neo-allo-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
(E)-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
(E)-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
(Z)-Ethyl linalool	20-22	d
(E)-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
(E)-β-Farnesene	27	d
(E)-Muuurola-4(14),5-	26	d

diene		
Alloaromadendrene	24,25	d
(E)-Cadina-1(6),4-diene	6	d
α-Amorphene	25	d
γ-Muurolene	6,26	d
Germacrene D	6,26,27	d
ar-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
(E,E)-Farnesene	6	d
(Z)-Calamenene	6	d
(E)-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-5α-ol	25	d
Caryophylla-3,8(13)diene-5β-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
(E)-2-Hexenal	23,24,28	d
Heptanal	3,20-22,24	d
(E)-2-Heptenal	23,24	d
(E,E)-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-Hexe-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
Isoamylnitrile	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	Trichoderma polysporum		Trichoderma koningii	Mortirella isabellina	Penicillium purpurogenum	Penicillium minioluteum	Absidia glauca	Thielavia terricola	Non-spore forming
			Pine	Spruce	Spruce	spruce	spruce	pine	pine	spruce	pine
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
- *p*-cymene	0.7	0.5	2.7	05	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**

1427 **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 (*P. sylvestris*) forest in Karelia (62° 07' N, 33° 56' E) with soil cover with green mosses (*Pleurocium schreberi, Politrichum commune*), lichens (*Cetraria islandica, Cladonia rangiferina*), shrubs (*Calluna vulgaris*) 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 (*P. sylvestris*) and spruce (*P. abies*) forest, about 50 years of age, and a *Sphagnum* 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} in June and 90±60 μgC m^{-2} h^{-1} in August.	Janson et al., 1999
Static chamber technique. VOC concentration in sorption tubes with Tenax TA. GC-MS analysis of VOCs after thermal desorption.	Leningrad region (59° 57' N, 29° 51' E). Coniferous forest with a predominance of Norway spruce (*Picea abies*). 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 °C was 20.9–402.0 μg m^{-2} h^{-1}. The share of a-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	Warneke et al., 1999

			and 0.1 μg g^{-1}(dw) h^{-1}, respectively	
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 (*Picea sitchensis*) commercial plantation (54° 20' N, 3° 2' 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 μg m^{-2} 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° 51' N, 24° 17' E) in southern Finland. Forest is dominated by *P. sylvestris* with admixture of aspen (*P. tremula*) and birches (*B. pendula* and *B. pubescens*). The ground vegetation consists mainly of shrubs. Northern ribbed fen is dominated by mosses (*Sphagnum* 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 μg m^{-2} h^{-1} for the whole season. Monoterpene emission from boreal forest floor varied from 0 to 373 μg m^{-2} h^{-1} (0−0.8 μg m^{-2} 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 wool. GC-MS analysis after thermal desorption.	Mediterranean mountains environment in the Prades region of Southern Catalonia dominated by evergreen oak *Quercus ilex*	Spring 2003– spring 2004	The measured monoterpene emission in summer was 1.67±1.57 μg m^{-2} h^{-1} normalised to 30 ∘ C.	Asensio et al., 2007
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 (*Carex vaginata*) and the evergreen shrubs *Empetrum hermaphrodium* and *Andromeda polifolia.* Additionally, an experiment was carried		The measured monoterpene hydrocarbons emission rate varied from 1.5 to 9.8 μg m^{-2} 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

	out to study the effect of the addition of *Betula pubescens* ssp. *czerepanovii* litter.			
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: $C_{10}H_{16}$ – 5.04 $\mu g\ m^{-2}\ h^{-1}$; $C_{15}H_{24}$ – 0.045 $\mu g\ m^{-2}\ h^{-1}$; C_5H_8 – 0.05 $\mu g\ m^{-2}\ h^{-1}$. 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 $\mu g\ m^{-2}\ h^{-1}$, 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 *Salix arctica* and *Cassiope tetragona*, low arctic (69°14' N, 53°32' W) heaths dominated by *Salix glauca* and *Betula nana* and a subarctic peatland (67°22' N, 26°38' E) dominated by the moss *Warnstorfia exannulata* and the sedge *Eriophorum russeolum*.	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 *Salix*-heath and high Arctic *Cassiope*-heat were 0.01 and 7 $\mu g\ m^{-2}\ h^{-1}$, 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 Arctic.	Lindwall et al., 2015
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 *Sorbus aucuparia, B. pendula, Picea abies* grow below canopy. LSC was formed by shrubs (*Vaccinium* sp. and *Caluna vulgaris*), mosses (*P. schreberi, Dicranum* sp., *H.*	IV–X.2015	Monoterpenes flux range from the forest floor was 0.40–221.0 $\mu g\ m^{-2}\ h^{-1}$ (average 23 $\mu g\ m^{-2}\ h^{-1}$); the most dominant compounds: α-pinene and 3-carene. Sesquiterpene flux range was 0.01–10.9 $\mu g\ m^{-2}\ h^{-1}$; the most abundant waere β-caryophyllene	Mäki et al., 2017

	splendens), and graces (*Deschampsia flexuosa, Melampyrum sylvaticum*).		and aromadendrene. Isoprene flux range was 0.005–99.8 µg m^{-2} h^{-1}	
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 µg m^{-2} 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 + Carbongraph 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 µg m^{-2} 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 TA + Carbopack B). GC-MS analysis after thermal desorption.	(1) 60 yr old *P. sylvestris* and *P. abies* forests in Finland (boreal, 61° 51' N, 24° 17' E); (2) *P. sylvestris, P. abies, Betula* sp. forests Estonia (hemiboreal, 58° 25' N, 27° 46' E); (3) 100 yr old *P. abies* forest; SMEAR II rural background site.	V–X. 2017; IV–VI.2018	The total terpene fluxes were higher from the Scots pine forest floor (boreal 23 µg m^{-2} h^{-1}) and from the mixed forest floor (hemiboreal, 32 µg m^{-2} h^{-1}) compared to the Norway spruce forest floor in both boreal (12 µg m^{-2} h^{-1} and hemiboreal (9 µg m^{-2} 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	Mäki et al., 2019a

			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 μg m^{-2} h^{-1}from the forest floor with occasional fluxes exceeding 100 μg m^{-2} h^{-1}. Fluxes from the oil palm plantation were on average 0.5-2.9 μg m^{-2} 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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1437 **Table 6**. Laboratory measurements of emission rates of monoterpene hydrocarbons from
1438 fresh and decaying litter of Norway spruce and Scots pine (Isidorov et al., 2010) as well as
1439 from fresh litter of European larch, *Larix decidue* (Isidorov et al., 2005).

Terpene	Emission rate at 20ºC (μg g^{-1} 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

1440 * Emission at 22ºC.
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Table 7. Emission rates of volatile organic compounds (ng g^{-1} h^{-1}) from litter of nine terpene storing species. Values are mean ± SE (*n*=3 to 10) (Viros et al., 2020).

Compound	Cistus albidus	Cistus salviifolius	Cotinus coggygria	Eucalyptus globulus	Juniperus oxycedrus	Pinus halepensis	Pinus pinea	Rosmarinus officinalis	Thymus vulgaris
α-thujene	-	-	-	-	-	4.35 ±1.11	-	-	10.47 ±4.87
α-pinene	2.99 ± 0.21	-	181.64 ±43.11	4.26 ±1.86	6.17±2.14	61.63±10.61	24.85±18.61	197.91 ±30	21.17 ±2.8
camphene	-	-	27.37 ±4.44	-	-	-	1.34 ± 0.66	155.84±25.51	24.3 ±3.17
sabinene	-	-	-	-	3.19 ± 0.3	36 ± 9.3	-	-	40.98 ±33.66
β-pinene	-	-	17.38 ±4.46	2.85 ± 0.58			15.75 ±0.58	31.03 ±6.98	11.8 ±2.52
myrcene	-	-	250.3 ±69.87	1.39 ± 0.3	5.46 ± 0.65	137.67 ± 24.79	-	-	48.9 ±7.46
α-phellandrene	-	-	-	3.47 ± 0.65	0.67 ± 0.17	-	13.68 ±1.01	-	8.69 ±2.79
δ-3-carene	-	-	0.84 ±0.2	-	-	5.7 ± 1.35	7.53 ±2.5	-	36.61 ±16.6
α-terpinene	-	-	1.69 ± 0.85	-	-	-	-	-	-
limonene	142.94±28.14	5.15 ±1.14	1591.51±315.27	2.78 ±1.01	14.21±0.09	128.95±21.37	226.98±5.3	-	368.38 ± 169.09
eucalyptol	-	-	-	82.85±68.64	-	-	-	-	-
cis-β-ocimene	-	-	686.08 ±217.7	-	2.95 ± 0.15	3.07 ± 0.41	3.16 ± 0.05	-	-
trans-β-ocimene	-	-	148.33 ±49.28	-	0.99 ± 0.13	5.89 ± 1.72	1.49 ± 0.07	-	5.85 ± 1.47
γ-terpinene *	-	-	6.71 ±2.49	-	2.49 ±0.13	14.14 ±2.5	1.26 ± 0.14	-	56.98 ± 34.51
trans-4-thujanol	-	-	-	-	-	-	-	-	228.32 ± 28.77
α-terpinolene	-	2.75 ±0.68	77.93 ± 20.61	-	5.43 ±0.18	42.58 ±11.77	3.58 ±2.41	-	99.38 ±51.21
linalool	-	5.02 ±2.07	-	-	2.03 ±0.22	-	1.71 ±0.08	-	244 ±123.55
α-campholenal	-	-	-	-	1.04±0.15	-	-	-	2.59 ± 0.15
allo-ocimene	-	-	72.56 ± 22.92	-	-	-	-	-	-
cis-p-mentha-2.8-dien-1-ol	-	-	-	-	-	-	-	-	1.53 ± 0.15

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

Compound	*Acer monspessulanum*	*Erica arborea*	*Quercus coccifera*	*Quercus ilex*	*Quercus pubescens*	*Quercus suber*	*Ulex parviflorus*
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 ±010	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)-furanone	-	-	82.59 ±10.63	-	-	-	-
- 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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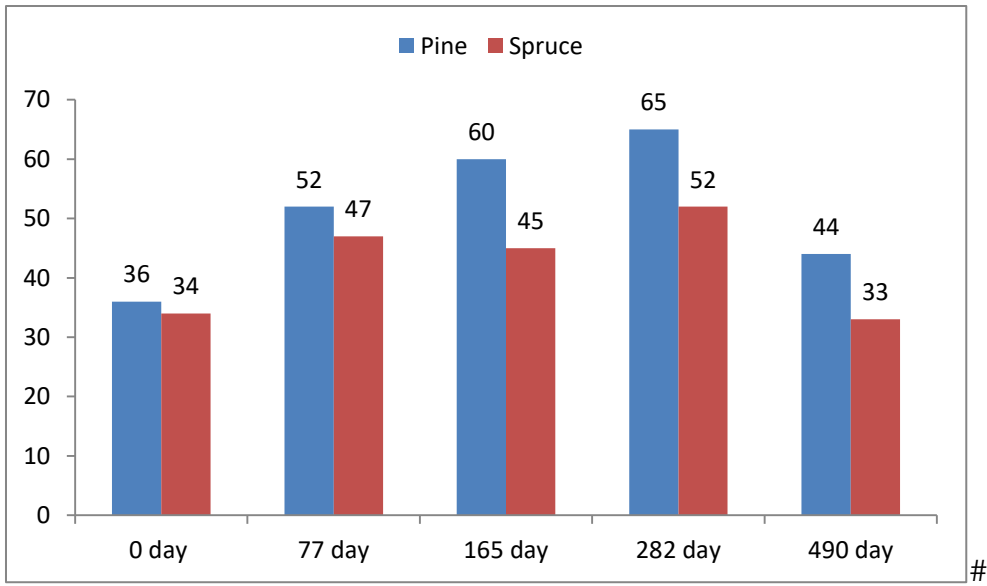
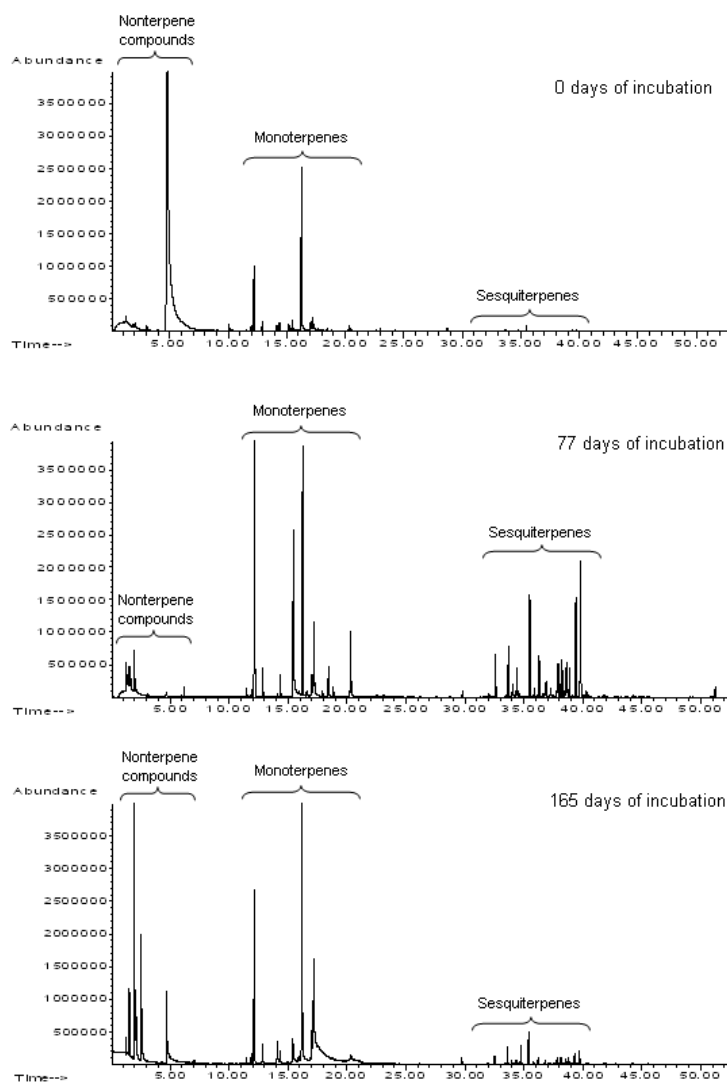


Fig. 1. Changes in the number of different VOCs registered in emissions from decomposing

Scots pine and Norway spruce needles (Isidorov et al., 2010).

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1479 **Fig. 2**. Changes in the profiles of volatile emissions of pine litter at the first stages of

1480 decomposition in natural conditions. HS-SPME/GC-MS chromatograms from pine needle

1481 litter emissions concentrated on polydimethylsiloxane (PDMS) fibre (Isidorov et al., 2010).

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