
This is the **accepted version** of the journal article:

Yang, Kaijun; Llusia Benet, Joan; Preece, Catherine; [et al.]. «Exchange of volatile organic compounds between the atmosphere and the soil». *Plant and Soil*, Vol. 501, issue 1-2 (August 2024), p. 509-534. DOI 10.1007/s11104-024-06524-x

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1 **Exchange of volatile organic compounds between the atmosphere**
2 **and the soil**

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23 **Abstract**

24 *Background*

25 Volatile organic compounds (VOCs) play a crucial role in understanding soil ecology
26 and the atmospheric environment. However, the biochemical cycles of VOCs in soil
27 systems and their relationship to atmospheric VOC exchange remain unclear. The soil
28 system serves as a primary site for the generation, emission, and uptake of VOCs, yet
29 these processes lack sufficient understanding.

30

31 *Scope:*

32 This review aims to provide a comprehensive overview of the exchange of VOCs
33 between the soil and the atmosphere. We explore the mechanisms governing the
34 generation, emission, and uptake of VOCs in soils, quantitatively summarizing
35 available data on emission and uptake. Additionally, we highlight common and specific
36 VOCs emitted by various soil sources (litter, roots, bare soil, and soil microbes) and
37 examine their interactions.

38

39 *Conclusions:*

40 The composition and emission rates of VOCs display significant variability across
41 different soils, attributed in part to variations in the contributions of different VOC
42 sources within the soils. Litter and roots predominantly release terpenes, benzenoids,
43 and alcohols, while bare soil and microbes emit higher proportions of alkanes, esters,

44 and alcohols. Despite often being overlooked, soils serve as essential sinks for VOCs,
45 and global environmental changes may reshape patterns of soil VOC sources and sinks.

46 **Keywords:** Bidirectional exchange; Climate change; Ecosystems; Monoterpenes;
47 Litter; VOCs sink.

48 **Introduction**

49 Volatile organic compounds (VOCs) play vital roles in governing atmospheric
50 chemistry and climate, such as being involved in producing secondary organic aerosols
51 and photochemical ozone (Andreae and Crutzen 1997; Atkinson 2000; Williams 2004;
52 Tunved et al. 2006; Lelieveld et al. 2008). VOCs are also crucial in multiple interactions,
53 such as plant-animal, plant-microbe, and microbe-microbe communication (Insam and
54 Seewald 2010; Peñuelas et al. 2014; Honeker et al. 2021; Meredith and Tfaily 2022).

55 Terrestrial vegetation and anthropogenic activities are the main sources of VOCs
56 (Guenther et al. 1993), but soil may be an overlooked contributor (Peñuelas et al. 2014;
57 Bourtsoukidis et al. 2018; Llusia et al. 2022). Accurately estimating soil VOCs is
58 crucial for predicting global VOC emissions, however, these emissions from soils have
59 not been assessed (Guenther et al. 2012; Sindelarova et al. 2014).

60 Soils are widely recognized as a source of VOCs due to the continuous production
61 and release of VOCs from various contributors, including litter (Leff and Fierer 2008;
62 Gray et al. 2010; Viros et al. 2020; Isidorov and Zaitsev 2022), roots (Lin et al. 2007;
63 Mäki et al. 2017; Tsuruta et al. 2018), microorganisms (Bäck et al. 2010; Veres et al.
64 2014; Isidorov et al. 2016; Bourtsoukidis et al. 2018; Honeker et al. 2023) and soil
65 organic matter (SOM) (Leff and Fierer 2008; Insam and Seewald 2010; Monard et al.
66 2021). Generally, the concentration of atmospheric VOCs is higher than that of soil
67 VOCs. Although VOCs emission from soils have typically been reported to be 1-2

68 orders of magnitude lower than those from plant canopies (Peñuelas et al. 2014), soil
69 emissions can indeed be significant, depending on factors such as the habitat type
70 (Bourtsoukidis et al. 2018; Llusià et al. 2022) and season (Aaltonen et al. 2011; Mäki
71 et al. 2017). Different ecosystems vary significantly in the characteristics and
72 magnitudes of plant VOCs released due to variations in vegetation composition and
73 climate (Guenther et al. 2012), which directly affect the concentration of the
74 surrounding atmospheric VOCs. The concentration of atmospheric VOCs is
75 significantly negatively correlated with soil VOCs emission rate (Llusià et al. 2022;
76 Yang et al. 2024), indicating that aboveground vegetation VOCs may strongly
77 contribute to the VOCs that enter the soils (Mu et al. 2023). The high concentration
78 gradient between the atmosphere and the soil likely enhances the soil's capacity to act
79 as a sink for VOCs through physicochemical uptake (Li et al. 2019) or microbial
80 biodegradation (Pegoraro et al. 2006).

81 Soil VOC emissions are bidirectional; these processes are related to multiple
82 factors (Asensio et al. 2007c; Bachy et al. 2018; Trowbridge et al. 2020; Pugliese et al.
83 2023). Firstly, soil microorganisms can utilize VOCs as a carbon source for growth and
84 reproduction (Chaignaud et al. 2018; Shrestha et al. 2019; Abis et al. 2020; Carrión et
85 al. 2020). Accumulating evidence suggests that soils have the potential to act as a net
86 VOC sink and are also essential in controlling net fluxes (Isidorov et al. 1999;
87 Spielmann et al. 2017; Albers et al. 2018; Trowbridge et al. 2020), though the
88 magnitude of this sink capability remains uncertain (Cleveland and Yavitt 1997;
89 McGinity et al. 2018; Rinnan and Albers 2020; Honeker et al. 2023). Moreover,
90 different ecosystems vary significantly in the characteristics and magnitudes of plant
91 VOCs released due to variations in vegetation composition and climate (Guenther et al.
92 2012), which directly affect the concentration of the surrounding atmospheric VOCs.

93 The concentration of atmospheric VOCs is significantly negatively correlated with soil
94 VOCs emission rate (Llusià et al. 2022; Yang et al. 2024), indicating that aboveground
95 vegetation VOCs may strongly contribute to the VOCs that enter the soil (Mu et al.
96 2023). In the context of increasing global atmospheric concentration of VOCs induced
97 by vegetations (Peñuelas and Staudt 2010), it has also become imperative to understand
98 the balance of source-sink functions of soil VOCs. However, the absence of VOCs
99 uptake data, however, can lead to potentially incorrect calculations of net VOCs
100 emission (Rinnan and Albers.2020; Jiao et al. 2023; Pugliese et al. 2023).

101 Most studies focused on soil VOCs have not sampled directly from soils but from
102 soils plus short plant cover (Aaltonen et al. 2013; Tang et al. 2018; Zhang-Turpeinen et
103 al. 2020). The measurement of VOC fluxes from soils covered with surface vegetation
104 does not truly represent VOCs from soil sources, as this also contains contributions
105 from green leaves (Isidorov and Zaitsev 2022), which may mask or lead to
106 underestimations in the soil function of VOC uptake (Ramirez et al. 2010), resulting in
107 a significant bias for modeling global VOCs when integrated with the soil ecosystem.
108 So, distinguishing the VOCs from floor and soil is essential for understanding the
109 balance of VOCs between the soil and the atmosphere.

110 Global models currently exclude soil VOC fluxes due to insufficient data
111 (Guenther et al. 2012). With the increase in soil-related VOC studies in recent decades,
112 the variations of soil VOC exchange among ecosystems due to differences in climate
113 (Kramshøj et al. 2016; Mäki et al. 2019b; Huang et al. 2021; Llusià et al. 2022; Romero-
114 Olivares et al. 2022; Yang et al. 2024), vegetation composition (Kivimäenpää et al.
115 2018; Mäki et al. 2019c; Ghirardo et al. 2020) and soil organisms (Bourtsoukidis et al.
116 2018; Trowbridge et al. 2020) have been uncovered. However, even more field data are

117 needed across various ecosystems, especially in soils with high microbial activity in
118 subtropical and tropical regions (Llusia et al. 2022; Mu et al. 2023; Pugliese et al. 2023).

119

120 VOC fluxes between the soil and the atmosphere are predominantly influenced by
121 isoprenoids, as indicated by studies such as Asensio et al. (2007) and Mäki et al. (2019).

122 In this review, we classify isoprenoids into four main classes: isoprene, monoterpenes,
123 sesquiterpenes, and other VOCs, aligning with categories commonly utilized in
124 previous studies (Kramshøj et al. 2016; Mäki et al. 2017). Our discussion encompasses
125 recent developments in soil VOC research, offering insights into potential soil VOC
126 emissions and uptake. Additionally, we present an analysis of soil VOC characteristics
127 across diverse ecosystems, examine the sources of VOCs in soil ecosystems, outline
128 the primary mechanisms governing the return of atmospheric VOCs to soils, and assess
129 the impact of climate change on the exchange of soil VOCs.

130

131 **Materials and methods**

132 *Data collation*

133 In the paper, we are focused on the VOCs released from soils with litter cover. Hence,
134 the soil is defined as comprising decomposing organic matter (mainly consisting of leaf
135 litter), roots, bare soil, and soil microbes (Figure 1). We collected data related to VOCs
136 from soil-related sources by searching the Web of Science and Google Scholar for peer-
137 reviewed journal articles published until the end of 2021. The search terms were
138 (volatile organic compound* OR VOC OR isoprenoids OR monoterpene OR
139 sesquiterpene) AND (soil OR plant litter OR plant root) contained in the title, keyword,
140 or abstract. The VOC data are divided into two subsets: quantitative and qualitative.
141 For the quantitative analysis of VOCs, we included field experiments of soil VOCs flux

142 and concentration and studies of VOC release rates from decaying plant litter in the
143 laboratory. In contrast, for the qualitative data on VOCs, we focused on VOCs release
144 species from different soil sources under laboratory conditions. Therefore, different
145 collection strategies were used for the two datasets. The quantitative data collected
146 compounds that appeared in each article and had a corresponding rate. The qualitative
147 data recorded every compound released from the different sources reported in each
148 article.

149 Quantitative data of VOCs from soil-related sources article was cross-checked to
150 determine whether the studies met the following criteria: (1) the flux and concentration
151 of VOCs in soils or soil profiles were studied in field conditions; (2) the flux of VOC
152 was directly sampled from soil sources (including soil with litter, without litter, without
153 root, without understory); (3) the rate value of litter VOCs was available or could be
154 extracted from figures; (4) the VOC flux could be extracted directly from the text, table,
155 figure or published supplementary material. The Engauge Digitizer version 12.1
156 (<http://markum mitchell.github.io/engauge-digitizer>) was assisted to digitally estimate
157 from the figures in the published literature when the results were graphically reported.
158 After the aforementioned criteria, these studies could be used for data analysis (for more
159 details, see Table S1 in the appendix), representing three ecosystems (forest, tundra,
160 and cropland). For the forest ecosystem, six different vegetation types are included
161 (boreal forest, subalpine forest, Mediterranean forest, temperate forest, subtropical
162 forest and tropical forest). Additionally, six papers are shown for comparison of litter
163 VOC rates in Table 3.

164 For the qualitative analysis, each article was cross-checked to determine whether
165 the studies met the following criteria: (1) plant litter material, either from falling leaves
166 or decomposing litter on the floor; (2) root samples must be living roots; (3) microbes

167 are extracted from within the soil or in the litter habitat; (4) the bare soil source VOCs
168 could be from (sterile) cultured soil, which removed roots and litter; (5) the VOC data
169 was able to be extracted directly from the text, table, figure and/or published
170 supplementary material. Following the aforementioned criteria, these studies could be
171 used for the qualitative analysis (for more details, see Table S2), representing four soil
172 sources (plant litter, roots, bare soil, and soil microbes).

173

174 *Data analysis*

175 Before the statistical analysis, conversions were made of all necessary data so they were
176 fully comparable. In the literature, VOC exchange rates reported with other units (e.g.,
177 $\text{pmol m}^{-2} \text{ s}^{-1}$ and $\text{nmol m}^{-2} \text{ h}^{-1}$) were converted to $\text{ug m}^{-2} \text{ h}^{-1}$. To compare soil VOC
178 exchange in various ecosystems, the range of rates for the main VOC classes (isoprene,
179 monoterpenes, sesquiterpenes, other VOCs) was summarized. PubChem
180 (<https://pubchem.ncbi.nlm.nih.gov/>) was used to verify molecular formulas and
181 chemical classes for these VOCs not classified in the original paper. Additionally, to
182 highlight the uptake capacity of soils, studies that found uptake rates are shown
183 separately.

184 To explore the correlations of VOCs among different soil sources, all components
185 underwent certification by Pubchem and mVOCs 3.0 (<https://bioinformatics.charite.de/mvoc/>), with verification of the molecular formula, PubChem ID and chemical
186 classification. Those compounds that could not be certified were rejected in the
187 following analysis. The relative abundance of VOCs from the different soil sources,
188 such as decomposing litter, roots, bare soil and soil microbe, were summarized in pie
189 charts as the ratio between the number of VOCs in that chemical class and the total
190 number of VOCs in all classes. An additional graphical representation was made

192 (Cytoscape 3.9.1) to highlight the associations between groups of VOCs and their
193 sources. The Venn diagrams were generated using EVenn (<http://www.ehbio.com/test/venn>) (Chen et al. 2021).

195

196 **Results**

197 **Main detectable VOCs emitted from soils**

198 The global VOC emissions from terrestrial vegetation are estimated to be 500, 89 and
199 36 Tg C y^{-1} for isoprene, monoterpenes and sesquiterpenes, respectively (Guenther et
200 al. 2012; Acosta Navarro et al. 2014), based on the Model of Emissions of Gases and
201 Aerosols from Nature (MEGAN). Their emissions from soil sources, however, have
202 received considerably less attention and are rarely estimated at a global scale (Tang et
203 al. 2019).

204

205 *Isoprene*

206 Isoprene is the most globally abundant VOC emitted from aboveground sources
207 (Guenther et al. 1993), but its flux rate in soil systems needs to be clarified (McGenity
208 et al. 2018). Plant litter and soil microbes serve as the primary sources of isoprene in
209 soils (Guenther et al. 1993; Insam and Seewald 2010; Gray et al. 2010; Mancuso et al.
210 2015; Svendsen et al. 2018), which have higher concentrations in topsoil (Table 1). In
211 contrast, plant roots seem to produce less isoprene, as shown by a laboratory study in
212 which isoprene emissions below the limits of quantification from the bare roots of 15
213 different tree species (Tsuruta et al. 2018). Isoprene emissions from litter occur mainly
214 during the initial phase of decomposition (Gray et al. 2010; Svendsen et al. 2018). This

215 can be attributed to the ability of some cells in fresh leaf litter to maintain isoprene
216 synthesis.

217 Compared to aboveground sources, isoprene emissions from soils have been
218 reported to be relatively low (Gray et al. 2014; Mäki et al. 2019b), with the highest rate
219 observed in cropland being $5.7 \mu\text{g m}^{-2} \text{ h}^{-1}$ (Figure 2 and Table 2). Other ecosystems,
220 such as forests in the boreal and Mediterranean, have shown low emission rates and
221 low concentrations in the soil horizon (Tables 1 and 2) (Asensio et al. 2007b; Mäki et
222 al. 2017, 2019b). Moreover, isoprene emission is not always detectable in soil samples
223 because it depends heavily on the litter plant species and microbes present (Veres et al.
224 2014).

225 Although generally in low concentrations, isoprene appears in a wide variety of
226 soil ecosystems, generated by bacteria, fungi, protists, algae and animals (Scholler et
227 al. 2002; Murrell et al. 2020). Some bacteria and fungi, such as *Bacillus* sp.,
228 *Burkholderia* sp. and *Tuber borchii* have been found to release isoprene as a means of
229 defense and communication (Lemfack et al. 2018). However, the role of soil microbes
230 in isoprene emission may be insignificant, possibly due to the consumption of soil
231 isoprene-degrading bacteria that can exceed its production in soil ecosystems
232 (Cleveland and Yavitt 1998; Carrión et al. 2020; Trowbridge et al. 2020; Mu et al. 2023).
233 This phenomenon will be discussed further in a subsequent section.

234

235 *Monoterpenes*

236 Globally, monoterpenes make up the second largest class of atmospheric VOCs
237 (Guenther et al. 2012). In soils, monoterpene concentrations were highest in the litter
238 layer and O-horizon compared to others (Table 1), due to the high levels of organic
239 matter that accelerates microbial decomposition and typically releases α -pinene

240 (Asensio et al. 2012; Svendsen et al. 2018). Monoterpenes tend to have relatively high
241 emissions from soils and constitute a substantial proportion of soil VOCs, particularly
242 in forest soils, except for subalpine forests (Table 2). Extensive research has been
243 conducted on the emissions of monoterpenes in boreal forest floors (Hellén et al. 2006;
244 Aaltonen et al. 2011; Wang et al. 2018b; Mäki et al. 2019b), but there is less research
245 for other soil types (Mäki et al. 2017). Boreal forest soils reveal considerable emissions
246 of monoterpenes with rates ranging from 38.4 to 49.5 $\mu\text{g m}^{-2} \text{h}^{-1}$, with the variability
247 influenced by seasons, soil characteristics and litter cover characteristics (Mäki et al.
248 2017).

249 For temperate forests, Staudt et al. (2019) measured significantly higher
250 monoterpane emissions (from 558.3 to 4548.1 $\mu\text{g m}^{-2} \text{h}^{-1}$) from soils with litter during
251 summer in a *Pinus pinaster* forest in France. There was high heterogeneity in the
252 emission of monoterpenes among different plots, which was partially caused by
253 variations in the quantity and traits of litter present (Leff and Fierer 2008; Viros et al.
254 2020). Litter is a strong emitter of monoterpenes, and the amount of litter biomass
255 strongly affects the emission rate of monoterpenes. This also helps to explain the
256 difference in emission rates of monoterpenes reported by Staudt et al. (2019) and Mäki
257 et al. (2017), as litter biomass in the former study (740 g dry weight m^{-2}) was around
258 60 times higher than that in the latter study (12 g dry weight m^{-2}). However, the soil in
259 the study by Staudt et al. (2019) still maintained a high rate of monoterpane emission
260 (245 $\mu\text{g m}^{-2} \text{h}^{-1}$) after litter removal, indicating that other soil characteristics (e.g., SOM
261 and soil microbes), as well as litter, are also essential sources of monoterpenes (Llusia
262 et al. 2022).

263 Compared to boreal and temperate forests, the emission rates of soil monoterpenes
264 are relatively low in tundra, subalpine and Mediterranean forests (Table 2). According

265 to a study by Kramshøj et al. (2016), the mean emission rate of monoterpenes in tundra
266 soil during the growing season was $1.73 \mu\text{g m}^{-2} \text{ h}^{-1}$, and α -terpineol was found to be
267 the primary compound. The low emission of monoterpenes in tundra soil may be
268 attributed to the absence of litter cover in combination with the low temperature, which
269 can reduce microbial decomposition. Similarly, subalpine forest soils are also weak
270 emitters of monoterpenes with emission rates ranging from 0.05 to $0.7 \mu\text{g m}^{-2} \text{ h}^{-1}$ due
271 to low temperatures and slow microbial activity (Greenberg et al. 2012; Gray et al. 2014;
272 Trowbridge et al. 2020). However, in Mediterranean soils, the low monoterpenene
273 emissions seem to be limited by soil water content (Asensio et al. 2007c, b), and a
274 strong uptake by soil was observed in a recent study (Yang et al. 2024).

275 Lastly, tropical forest soils are generally predicted to be considerable sources of
276 monoterpenes due to their abundant litter cover, high root density and relatively high
277 temperature. But their fluxes of monoterpenes much lower than those in boreal and
278 temperate forest soils, which range from -2.4 to $23.3 \mu\text{g m}^{-2} \text{ h}^{-1}$ (Table 2).
279 Bourtsoukidis et al. (2018) revealed that monoterpenes in tropical forest soils were
280 weakly emitted under high water conditions and moderately consumed in the low-
281 moisture range, which was also confirmed by Llusià et al. (2022), who found a
282 significant shift from source to sink of terpenoids in the wet and the dry season. The
283 low emission of monoterpenes in tropical forest soils can be attributed to high
284 consumption by soil microbes, which utilize VOCs as a carbon source and energy
285 supply (Albers et al. 2018; Bourtsoukidis et al. 2018; Pugliese et al. 2023).

286

287 *Sesquiterpenes*

288 The concentration of sesquiterpenes has been shown to be higher in the A-horizon
289 compared to the O- and B-horizons Mäki et al. (2019) (Table 1). This is due to the fact

290 that sesquiterpene production in soils is strongly associated with high emissions from
291 plant roots (Mäki et al. 2017; Tsuruta et al. 2018) and soil fungi (Asensio et al. 2008a;
292 Horváth et al. 2011; Bourtsoukidis et al. 2018). In Amazonian soils, sesquiterpene
293 production of soil microbes is also higher in the O- and A-horizons than in the B-
294 horizon (Bourtsoukidis et al. 2018). The high concentration of sesquiterpenes in the
295 litter layer in the *Pinus halepensis* tree (Table 1) can be attributed to the high amount
296 of fungal hyphae growing on the litter (Asensio et al. 2008a).

297 A wide variety of sesquiterpenes is generated in the soil horizons of the boreal
298 forest, such as α -gurjunene, α -humulene and β -farnesene. However, due to their low
299 volatility, their emission rates to the atmosphere are typically low, ranging from 0.4 to
300 $17.5 \mu\text{g m}^{-2} \text{h}^{-1}$ (Mäki et al. 2017, 2019b). Table 2 shows that other ecosystems, such
301 as tundra and Mediterranean forests, also exhibit low emissions of sesquiterpenes. For
302 instance, a study on tundra soils detected only one sesquiterpene during the growing
303 season, with an emission rate of $0.14 \mu\text{g m}^{-2} \text{h}^{-1}$ (Kramshøj et al. 2016). Similarly, an
304 experiment in Mediterranean forest soils found the highest rate of soil sesquiterpenes
305 to be $2.40 \mu\text{g m}^{-2} \text{h}^{-1}$ (Asensio et al. 2007b). Compared with those low emissions of
306 sesquiterpenes, tropical forest soils were found to have high sesquiterpene emissions (a
307 maximum of $210 \mu\text{g m}^{-2} \text{h}^{-1}$) in recent studies (Bourtsoukidis et al. 2018; Llusià et al.
308 2022), which highlights the potential source of sesquiterpenes inherent in this soil type.
309 The substantial variation in sesquiterpene emissions among different ecosystem soils
310 may be attributed, in part, to differences in soil microorganism communities, which are
311 the primary contributors of sesquiterpenes in soils (Horváth et al. 2011, 2012; Weikl et
312 al. 2016). Additionally, some studies have suggested that high microbial biomass in
313 soils may result in higher emissions of sesquiterpenes (Weikl et al. 2016; Bourtsoukidis
314 et al. 2018; Kramshøj et al. 2018).

315

316 *Other VOCs*

317 Most of the research on soil VOC exchanges has focused on terpenoids. Notably, other
318 VOCs seem to have a stronger emission than isoprenoids (Table 2). Other VOCs, such
319 as methanol (Asensio et al. 2007b; Mu et al. 2022), carbonyl compounds (e.g., acetone,
320 acetaldehyde and acetic acid) (Asensio et al. 2008a; Gray et al. 2014; Mielnik et al.
321 2018), benzenoids (Zheng et al. 2015), sulphurous compounds (e.g., dimethyl sulphide,
322 carbon disulphide and dimethyl disulphide) (Yi et al. 2010) and formaldehyde (Gray et
323 al. 2014; Li et al. 2016) have also been reported as being emitted from soils, but are
324 rarely studied.

325 The annual global emissions of methanol, acetone, formic and acetic acids from
326 terrestrial ecosystems are estimated to be 187 Tg y^{-1} (Stavrakou et al. 2011), 95 Tg y^{-1}
327 (Jacob et al. 2002), 57 Tg y^{-1} and 85 Tg y^{-1} (Poulton et al. 2011), respectively. Some of
328 these compounds have high emission rates in a specific type of soil (Kramshøj et al.
329 2016; Bourtsoukidis et al. 2018; Mäki et al. 2019b). For example, aldehydes (octanal,
330 nonanal, and hexanal) are found in tundra soils and account for about 75% of the total
331 VOC emissions in that ecosystem ($78.4 \mu\text{g m}^{-2} \text{ h}^{-1}$) (Kramshøj et al. 2016), and
332 methanol is predominant in cropland soils (Bachy et al. 2018).

333 Methanol is mainly emitted by soil bacteria and the decomposition of residual
334 organic matter, so methanol synthesis is likely driven by temperature-dependent
335 enzymatic activity and microbial community structure. In fact, methanol emission is
336 generally positively correlated with temperature (Schade and Goldstein 2001), but
337 recent experiments have suggested that this relationship could also be affected by soil
338 water content. In one study, methanol emissions under dry conditions were strongly
339 positively correlated with soil temperature, but methanol was taken up under wet

340 conditions in the same cropland, and the amount taken up increased with temperature
341 (Bachy et al. 2018). Similarly, in Mediterranean forest soils, methanol emission was
342 high during a dry summer, and uptake was strong in a wet autumn (Asensio et al. 2008b).

343

344 **Sources of VOCs in soils**

345 The profiles of VOCs from the same soil sources are vary widely due to different
346 species. Therefore, the focus of this section is to examine the diversity of VOCs
347 originating from soil compartments and compare them among different sources to
348 determine if distinct characteristics exist in the VOC profiles that can be helpful in
349 understanding the belowground information network formed by various soil sources
350 through VOCs.

351

352 *VOC emissions from decomposing litter*

353 Comparisons of sterile and non-sterile litters could give an insight into the VOCs
354 derived from plant litter and or microbes (Gray et al. 2010). Litter produces abundant
355 VOCs during its decomposition process, and the emission rate and diversity of these
356 VOCs vary with changes in the environment (Schade and Goldstein 2001; Gray et al.
357 2010; Isidorov et al. 2016; Svendsen et al. 2018; Viros et al. 2021). While early field
358 studies suggested that litter may be a minor source of VOCs compared to aboveground
359 plant emitters (Schade and Goldstein 2001; Faubert et al. 2010; Greenberg et al. 2012),
360 a recent study emphasized that a thick litter layer above the soil may be a large potential
361 source, with the removal of that litter layer substantially reducing (by 81%) total soil
362 VOC emissions in that system (Staudt et al. 2019). Results from laboratory litter
363 incubation experiments show that litter emission rates range from 0.1 to 265.5 $\mu\text{g g}$
364 $(\text{dw})^{-1} \text{ h}^{-1}$ (Table 3), depending on litter types, degree of decomposition and incubation

365 conditions (Leff and Fierer 2008; Gray et al. 2010; Isidorov et al. 2016; Svendsen et al.
366 2018). It is worth mentioning that decomposing litters seem to be a particularly
367 important source of methanol (Warneke et al. 1999), which, in one study with litter
368 from 12 different plant species, accounted for the majority litter emissions (Gray et al.
369 2010).

370 In general, the decomposition of broadleaf litter is faster than other types of litter;
371 thus, the emission rate of VOCs may be higher in broadleaf forest soils than in others.
372 For instance, the VOC emission rates of broadleaf litters (e.g., *Eucalyptus* sp., *Fraxinus*
373 sp. and *Populus* sp.) are shown to be higher than from litters of conifer (e.g., *Pinus*
374 *contorta*), grasses (e.g., *Miscanthus* sp.) and shrubs (e.g., *Cassiope* sp.) (Table 3), and
375 that is partly attributed to litter quality. On the other hand, conifer litters strongly
376 correlate with terpenoids, while for deciduous tree trends are much weaker (Table 3).
377 One possible reason is that conifer leaf litter contains structures for storing terpenoids,
378 which benefits terpenoid emissions (Viros et al. 2020).

379 Incubation experiments have shown that the VOC emission rates in the early stage
380 of decomposition are positively related to the amount of labile C in the litter and the
381 presence of terpene storage structures (Leff and Fierer 2008; Ramirez et al. 2010; Gray
382 et al. 2010; Svendsen et al. 2018; Viros et al. 2020). However, there is a burst of VOC
383 emissions in the litter during the early decomposition stage, possibly due to the
384 contribution of green leaf volatile compounds, which can constitute more than 75% of
385 the emissions from *Betula pendula* litter (Holopainen et al. 2010). Overall, the VOC
386 emission rate of litter decreases with the time of decomposition (Ramirez et al. 2010;
387 Isidorov et al. 2010; Viros et al. 2021; Isidorov and Zaitsev 2022). Increased
388 temperature can stimulate emission rates, especially for alkenes and terpenoids
389 (Svendsen et al. 2018). The profiles of litter VOCs are also highly associated with the

390 community structure of microbes in the litter (Isidorov et al. 2016; Svendsen et al. 2018),
391 with litter in different decomposition stages being dominated by different fungi,
392 accounting for some of the differences in emitted VOCs that are found (Isidorov et al.
393 2016).

394 The full range of VOCs emitted by litter is still unclear. Here, we collected
395 references of VOCs emitted from litter from 40 plant species, encompassing 285
396 different VOCs belonging to twelve chemical groups (Figure 3a). These VOCs included
397 106 terpenes (37% of those described), 46 benzenoids (16%), 25 alkanes (9%), 19
398 alcohols (7%), 16 aldehydes (6%), 16 esters (6%), 13 ketones (4%), 13 alkenes (4%),
399 nine halogenated compounds (3%), eight furans (3%), seven ethers (2%), six sulphur
400 (S) compounds (2%), four acids (1%) and one nitrogen (N) compound (0.4%). The first
401 four classes, which comprise 68% of the measured VOCs, represented the major classes
402 of litter VOCs. After comparing VOCs from litter with VOCs emitted from other
403 sources (root, bare soil and microbes), our Venn diagram revealed that litter emitted
404 147 unique VOCs not shared by any other sources (Figure 4), with most belonging to
405 terpenes (60) and benzenoids (21) and alkanes (10 VOCs) (Table 4).

406 *VOC emissions from active roots*

407 Plants allocate 40–73% of the photosynthesized C for root metabolism, root growth and
408 to root-associated microbes in the rhizosphere (Grayston et al. 1997). Roots are known
409 to produce VOCs for defence and communication (Schenkel et al. 2015), but little is
410 known about the production and emission rates (Lin et al. 2007; Asensio et al. 2008a;
411 Tsuruta et al. 2018). Furthermore, evidence has suggested that the rate of production of
412 root VOCs might correlate with morpho-anatomical traits of roots, such as root
413 taxonomy and mycorrhizal type (Tsuruta et al. 2018). Otherwise, the presence of roots
414 in soils have an inconsistent effect on soil VOC emissions (Rinnan 2013; Gray et al.

415 2014), with positive, negative and no impacts, which are related to individual VOCs
416 (Asensio et al. 2007a; Mäki et al. 2017).

417 The low number of papers published on root VOCs is likely due to the technical
418 difficulties in sampling VOCs in soil matrices (Peñuelas et al. 2014; Tsuruta et al. 2018).
419 We collected six papers focused on root VOCs and found a total of 153 different
420 compounds produced by the roots of 24 plant species (Table S1). The majority (71%)
421 of the identified VOCs were terpenes (57 VOCs), alcohols (27 VOCs), aldehydes (13
422 VOCs) and alkenes (12 VOCs) (Figure 3b), and the remaining 29% was composed of
423 ten groups (Figure 3b). Moreover, most VOCs from roots are shared with VOCs
424 measured from soil microbes (74 VOCs, Figure 4), with the remaining 57 unique VOCs
425 including 23 terpenes (most belong to sesquiterpenes), 13 alcohols and seven alkanes
426 (Table 4).

427 In the few that studies have tried to quantify the rate of VOC emission by roots, a
428 mean emission rate of $24.3 \mu\text{g g}^{-1} \text{h}^{-1}$ for eight monoterpenes (mainly α -pinene, β -
429 pinene, and limonene) was found for the washed roots of *Pinus spp.* growing in pots
430 (Lin et al. 2007), and another study using a similar method with *Pinus densiflora* roots
431 found the same monoterpenes but a higher emission rate ($122.6 \mu\text{g g}^{-1} \text{h}^{-1}$) (Tsuruta et
432 al. 2018). This difference may be associated with root traits such as oleoresin content
433 and stored terpenoid pools (Tsuruta et al. 2018). Oleoresin consists of a mixture of
434 terpenoids and is produced by specialized secretory tissues of coniferous tree roots
435 (Lewinsohn et al. 1991). Large differences were also found amongst the emission rates
436 of monoterpenes and sesquiterpenes from the roots of 15 tree species, with the roots of
437 gymnosperms associated with ectomycorrhiza having a strong potential for releasing
438 monoterpenes. In contrast, angiosperm roots emitted low amounts of monoterpenes
439 regardless of mycorrhizal type (Tsuruta et al. 2018).

440 A field trenching experiment in a forest dominated by *Pinus contorta* estimated
441 that roots contributed to 53% of total soil VOC emissions. However, the removal of
442 roots did not affect the rate of emission of soil monoterpenes (Gray et al. 2014), which
443 could indicate that the roots of the study species are a minor emitter of monoterpenes.
444 Currently, assessing the contribution of root emissions in situ to overall soil VOC fluxes
445 is difficult because of their linkages with soil organisms, which inevitably impact the
446 potential soil sink and source of VOCs (Trowbridge et al. 2020).

447

448 *VOC emissions from soil organic matter*

449 Although soil organic matter (SOM) could emit a series of VOCs naturally, given that
450 the strengths and composition of VOC emissions are always associated with microbial
451 activities, it is a challenge for researchers to verify the source of VOCs derived from
452 SOM or soil microbes (Veres et al. 2014; Monard et al. 2021). SOM-derived VOCs are
453 emitted during the SOM breakdown and decomposition processes, which are
454 dominated by different pathways of microbial metabolism, such as aerobic
455 decomposition, fermentation, and terpenoid biosynthesis (Tang et al. 2019). Therefore,
456 the community and function of microbes in soils play a vital role in determining the
457 production and emission of SOM-derived VOCs (Leff and Fierer 2008; Mancuso et al.
458 2015). Additionally, soil microbes are an essential contributor to the diversity of VOCs,
459 summarized in the mVOC 3.0 database, which has documented about 2000 microbial
460 VOCs emitted by almost 1000 microbial species (Lemfack et al. 2018).

461 Use of experimental methods combining litter removal and root trenching could
462 potentially estimate the contribution of SOM to VOC emissions from field soils,
463 although it appears that the emission rates of VOCs derived from SOM only are small
464 compared to the rates from litter and roots (Lin et al. 2007; Leff and Fierer 2008). For

465 example, one study detected an obvious emission of formic acid from sterilized soil
466 with an average rate of $\sim 6 \times 10^{-3}$ nmol m $^{-2}$ s $^{-1}$ (Li et al. 2019). Rossabi et al. (2018)
467 incubated three distinct ecosystem soils (agricultural soil, grassland soil and subalpine
468 soil) at room temperature and measured the rates of VOCs emission ranging from 25 to
469 190 ng g $^{-1}$ dry soil h $^{-1}$. These rates are lower than the emission of litter in the same
470 region, which varied from 81 to 960 ng g $^{-1}$ dry soil h $^{-1}$, which is caused by the litter
471 decomposition periods and incubation temperature (Svendsen et al. 2018). The amount
472 of VOC production from bare soils was 10-100 folds lower than from litter emitters
473 (Leff and Fierer 2008).

474 The profiles of VOCs from bare soils were also dramatically changed by incubation
475 temperature and soil water content. One incubation study suggested that higher
476 temperature can increase the emission of soil VOCs emission, but soil water had the
477 opposite effect (Raza et al. 2017). Incubated permafrost soils with different water
478 conditions (drained and non-drained) under two temperature levels (10 °C and 20 °C)
479 resulted in total VOC measurements ranging from 2.5 to 42.7 ng g $^{-1}$ dry soil h $^{-1}$, also
480 demonstrating that higher temperature and drained soils produced more VOCs
481 (Kramshøj et al. 2019). Besides soil temperature and water, the quantity of VOCs
482 emitted from bare soils positively correlates with SOC and microbial biomass
483 (Mancuso et al. 2015). For example, ethanol and methanol are strongly emitted from
484 soils with high SOM content and active microbes (Kramshøj et al. 2018).

485 In this review, a total of 170 VOCs were found emitted from bare soils, with the
486 main chemical classes comprising alkanes (49), benzenoids (42), terpenes (12), ketones
487 (12), alcohols (11), alkenes (11), acids (10), totaling 86% of the sum of VOCs (Figure
488 3c). The VOC profile of bare soils in chemical classes differs from that of litter and
489 roots, which are dominated by terpenes (Figure 3a-c). Compared with other sources,

490 bare soils have 78 unique volatiles not shared by other sources (Figure 4), and these
491 VOCs include alkanes (30 VOCs), benzenoids (19 VOCs), ketones (five VOCs), but
492 no ethers and furans were found (Table 4).

493

494 *VOC emissions from soil microorganisms*

495 Microbial VOCs (mVOCs) are produced by various microorganisms ranging from
496 bacteria to fungi. VOC profiles emitted by microorganisms are usually consistent,
497 relating to microbial traits, culture conditions, and environments (Bäck et al. 2010). The
498 measurement of species-specific mVOC emissions, even when grown on the same
499 cultivation media, indicates that soil microbes differ in the qualitative and quantitative
500 composition of their volatiles produced (Isidorov and Zaitsev 2022). Nutrient
501 availability may have an impact on emissions, with a laboratory experiment finding
502 parallel changes in soil VOC emissions and the composition of fungal communities
503 after the application of different fertilizers (Insam and Seewald 2010). Moreover, the
504 emission of sesquiterpenes by fungi (e.g., *Alternaria alternata*) was strongly related to
505 fungal growth phases rather than its biomass, with fungi in the early stages of growth
506 being able to emit much higher amounts of sesquiterpenes than in their mature stages,
507 with higher biomass (Weikl et al. 2016). Another study noted that bacteria may be as
508 important as fungi in releasing sesquiterpenes in Amazonian soils (Bourtsoukidis et al.
509 2018).

510 The mVOC 3.0 database has summarized 2061 VOCs emitted by microbes,
511 including human pathogens, plant pathogens and soil microorganisms (Lemfack et al.
512 2014, 2018), identifying more than 841 VOCs that are known to be produced by soil
513 microbes from different soil habitats (e.g., rhizosphere, bulk soil) (Schenkel et al. 2015).
514 High amounts of VOCs are released from microbes as end and intermediate products

515 of primary metabolism, and some are emitted as secondary metabolites (Insam and
516 Seewald, 2010). From the recently updated database of mVOC 3.0, the profiles of
517 bacterial VOCs are dominated by (in descending order) alkenes, alcohols, ketones,
518 terpenes, benzenoids, pyrazines, acids and esters. The profiles of fungal VOCs are
519 dominated by alcohols, benzenoids, aldehydes, alkenes, acids, esters, and ketones. We
520 summarised 22 papers related to soil microbe-only incubations and found a total of 416
521 VOCs produced by 36 microbial species. Our data show that soil microbes have higher
522 production of alcohols (64 VOCs), esters (61 VOCs), terpenes (57 VOCs), ketones (45
523 VOCs) and alkanes (41 VOCs), which comprised 64% of total VOCs (Figure 3d).
524 Moreover, there are 270 unique VOCs, shared with neither litter, roots or bare soils
525 (Figure 4), with most of them belonging to esters (31 VOCs), alcohols (30 VOCs) and
526 ketones (33 VOCs) (Table 4).

527 In soil ecosystems, VOCs are important for information communication among
528 organisms, and they are “ambassadors” linking understory root-microorganism-SOM
529 cycle and carbon flow, which are of great ecological significance (Honeker et al. 2021;
530 Minerdi et al. 2021; Meredith and Tfaily 2022). Soil sources share general VOCs while
531 retaining their unique components, forming a complex network (Figure 5), which
532 themselves vary between different ecosystems. This diversity of soil-derived VOCs, as
533 well as their specific functions in soils, are potential mechanisms for shedding light on
534 the counter-intuitive nature of certain soil processes (Honeker et al. 2021; Meredith and
535 Tfaily 2022). For example, the home-field advantage of decomposition of litter may be
536 attributed to the changes in decomposers dominated by the characteristics of VOCs
537 released from decomposing litter (Austin et al. 2014; Isidorov et al. 2016).

538

539 **Soil's capacity to uptake VOCs**

540 Field chamber and continuous-flow studies have demonstrated that soils are a potential
541 biological sink for VOCs at environmentally relevant concentrations (Table 5)
542 (McGenity et al. 2018; Trowbridge et al. 2020; Abis et al. 2020; Jiao et al. 2023).
543 VOCs can also be taken up by soils and subjected to biotic and abiotic processes,
544 including microbial degradation (Cleveland and Yavitt 1997; Gray et al. 2015),
545 chemical oxidation (Insam and Seewald 2010), and physical desorption (Ruiz et al.
546 1998). Recent studies have highlighted that the capacity of soils to act as a sink for
547 VOCs is affected by the diversity, community structure, biomass and growth phases
548 of soil microbes (Trowbridge et al. 2020; Abis et al. 2020). Microorganisms can
549 metabolize and utilize VOCs as carbon and energy sources (Cleveland and Yavitt 1998;
550 Owen et al. 2007; Albers et al. 2018), and soil microbes have been shown to consume
551 the majority of VOCs released by other sources (Ramirez et al. 2010; Bachy et al.
552 2018). Moreover, soils containing high SOC may have a stronger potential ability to
553 take up VOCs than mineral soils (Kramshøj et al. 2018). A recent study demonstrated
554 that VOC metabolism (e.g., of methanol and acetone) in soils may be a previously
555 unrecognized carbon sequestration pathway by contributing to the accumulation of
556 soil labile C and increasing the immobilization of N (McBride et al. 2019).

557 An initial attempt to quantify the rate of isoprene uptake in a laboratory setting
558 soils led to an estimate of $-97.3 \mu\text{g m}^{-2} \text{ h}^{-1}$ and global isoprene sink strength was
559 calculated as 20.4 Tg C y^{-1} under a given isoprene concentration (385 ppb), which is
560 higher than the current atmospheric concentration (Cleveland and Yavitt 1997). Much
561 higher estimates of rates of isoprene uptake have since been calculated (from -4168.9
562 to $-987.7 \mu\text{g m}^{-2} \text{ h}^{-1}$) using higher concentrations of isoprene under mesocosm
563 conditions (up to 1000 ppb) (Pegoraro et al. 2005). The isoprene concentrations used

564 in that study, however, greatly exceeded those in the atmosphere, which is generally
565 lower than ten ppb. The clear positive correlation between air isoprene concentration
566 and the rate of isoprene deposition suggests that an increasing isoprene gradient can
567 increase the rate of deposition of isoprene in soils (Pegoraro et al. 2005; Spielmann et
568 al. 2017). Although such a high atmospheric concentration of isoprene is not realistic,
569 a recent study conducted in a subtropical *Eucalyptus urophylla* plantation reported a
570 high rate of isoprene uptake ($-80.88 \mu\text{g m}^{-2} \text{ h}^{-1}$) measured under ambient conditions
571 (Mu et al. 2023), which was close to the estimates by Cleveland et al. (1997). This
572 high uptake rate can be attributed to the high ambient concentrations of isoprene (17.5
573 ng L⁻¹) and high soil microbial consumption following long-term adaptation of soil
574 microbes to the *Eucalyptus urophylla* plantation, which is a high emitter of isoprene.
575 Overall, the capacity of soils to take up isoprene has likely been overestimated (Table
576 5).

577 The highest reported uptake rate of monoterpenes was $37.55 \mu\text{g m}^{-2} \text{ h}^{-1}$ in
578 subtropical forest soils (without litter) (Mu et al. 2023). Similarly, net uptake of
579 monoterpenes by soils has been demonstrated in Mediterranean forest soil, where the
580 rate of uptake was highest ($27.96 \mu\text{g m}^{-2} \text{ h}^{-1}$) in summer (Yang et al. 2024), and a
581 simulated drought generally enhanced the capability of sinking monoterpenes
582 (Asensio et al. 2007c; Yang et al. 2024).

583 The uptake of sesquiterpenes and whether microbes can directly consume them is
584 unclear, as they are quickly oxidized into other compounds (Tang et al. 2019).
585 However, an increasing number of field experiments have shown that soils are also
586 weak sinks for sesquiterpenes (Table 5). It is interesting to point out that tropical
587 rainforest soils were previously reported to be a significant source of sesquiterpenes
588 (Bourtsoukidis et al. 2018); subsequent reports, however, have also demonstrated that

589 tropical forest soils can uptake a large amount of sesquiterpenes (Llusià et al. 2022).
590 Such variability in tropical forests is partly related to season, elevation and topography
591 (Llusià et al. 2022).

592 Other VOCs, such as acetaldehyde and methanol, are readily taken up by soils
593 (Asensio et al. 2007b; Bachy et al. 2018; Albers et al. 2018; Jiao et al. 2023). Field
594 studies showed that cropland soils take up methanol at high rates and that the net
595 uptake is high in summer ($306.0 \mu\text{g m}^{-2} \text{ h}^{-1}$) and autumn ($243.0 \mu\text{g m}^{-2} \text{ h}^{-1}$) (Bachy
596 et al. 2018). The differences in uptake ability between seasons may be due to
597 environmental factors, especially soil water content. For example, soils can switch
598 between releasing methanol when dry and taking up methanol when wet (Bachy et al.
599 2018; Bourtsoukidis et al. 2018). Regarding other compounds, a study in a subtropical
600 pine forest detected high uptakes of undecane ($-66.2 \mu\text{g m}^{-2} \text{ h}^{-1}$) and dodecane (-36.2
601 $\mu\text{g m}^{-2} \text{ h}^{-1}$) by soils during sampling in spring (Zhang et al. 2017). Additionally, 2-
602 hexenal was taken up in the highest amounts in a Mediterranean forest in autumn
603 ($-26.0 \mu\text{g m}^{-2} \text{ h}^{-1}$), even under drought conditions, but was not stored in soils in other
604 seasons (Asensio et al. 2007b, c).

605

606 **Main pathways of atmospheric VOCs into the soils**

607 The main pathways of how the soils can act as a sink can be divided into abiotic
608 processes (e.g., adsorption and deposition) and biotic processes (e.g., microbial
609 consumption and mineralization). The mechanisms of the uptake of VOCs into soils
610 likely differ between compounds due to their high heterogeneity and specificity
611 (Cleveland and Yavitt 1997; Ruiz et al. 1998; Asensio et al. 2007a; Albers et al. 2018;
612 Li et al. 2019). The abiotic processes are primarily driven by concentration gradients
613 and soil properties, which generally do not change the VOCs, and balance is

614 established with the surrounding air concentrations over time (Rinnan and Albers
615 2020). The biotic processes, however, are mostly the result of microbial activity and
616 VOCs are ultimately degraded to CO₂ (Albers et al. 2018; Carrión et al. 2020).

617

618 *VOC deposition*

619 An estimated 130–270 Tg C y⁻¹ of atmospheric VOCs are deposited on vegetation and
620 soil surfaces (Goldstein and Galbally 2007), which accounts for 17–36% of annual
621 terrestrial vegetation emissions of VOCs (760 Tg C y⁻¹) (Sindelarova et al. 2014). The
622 deposition of VOCs to vegetation is ubiquitous, but it has become clear that deposition
623 onto soils also plays a more important role than previously thought (Goldstein and
624 Galbally 2007; Hallquist et al. 2009; Laffineur et al. 2012; Park et al. 2013; Spielmann
625 et al. 2017). Atmospheric VOC deposition includes wet deposition (hydrophilic VOCs
626 dissolved in precipitation) and dry deposition (VOCs deposited onto the soil surface)
627 (Nguyen et al. 2015; Rinnan and Albers 2020). It has been suggested that the process
628 of wet deposition of VOCs is dependent on the physico-chemical properties of
629 atmospheric water and surrounding air temperatures (Šoštarić et al. 2017; Stojić et al.
630 2019), whereas dry deposition of VOCs is affected by the aboveground plant species,
631 surrounding VOC concentrations and light (Spielmann et al. 2017; Staudt et al. 2019).
632 There are reports of several chemical classes of VOC, including aldehydes, ketones,
633 aromatic hydrocarbons and isoprenoids, being deposited on various soil types
634 (Asensio et al. 2008a; Gray et al. 2014).

635

636 *Adsorption and dissolution*

637 VOCs can be adsorbed to SOM or dissolved in the vapor and water phases of soils
638 (English and Loehr 1991; Tang et al. 2019). They can be adsorbed by soils directly,

639 or indirectly by first reacting with ozone and hydroxyl radicals on the soils surface (Li
640 et al. 2016). The soil surface area and other properties regulate the capacity of soils to
641 adsorb VOCs (Petersen et al. 1994; Ruiz et al. 1998). A soil surface that is completely
642 covered with water molecules can increase VOC adsorption and dissolution, and
643 characteristic hydrophilic VOCs such as methanol, ethanol, formaldehyde, and
644 acetone can be adsorbed onto the soils at high levels and can then diffuse into the soil
645 water (Li et al. 2016; Bachy et al. 2018). Under dry conditions, however, soil
646 properties such as aggregate structure and SOC content are important for affecting the
647 strength of VOC adsorption (Ruiz et al. 1998; Hamamoto et al. 2009). For example,
648 in dry soil, soil macroaggregates and a high SOC content can increase the adsorption
649 of VOCs (e.g., isohexane) (Van Roon et al. 2005; Hamamoto et al. 2009). Also, the
650 capacity of VOCs to be adsorbed can be an order of magnitude higher for clay than
651 for sand and two orders of magnitude higher than for limestone (Ruiz et al. 1998).

652

653 *Biodegradation of VOCs by soil microbes*

654 The microbial sink of VOCs in soils is potentially highly important to both carbon
655 cycling and the atmospheric concentrations of these gases (Owen et al. 2007; Albers et
656 al. 2018). Several isoprene-degrading bacteria have been detected in various
657 ecosystems (Cleveland and Yavitt 1997, 1998; El Khawand et al. 2016; Carrión et al.
658 2020). For example, the following genera have been linked to isoprene degradation:
659 *Rhodococcus*, *Nocardia*, *Arthrobacter*, *Gordonia*, *Mycobacterium*, *Leifsonia*,
660 *Alcaligenes*, *Alcanivorax*, *Pseudomonas*, *Alcaligenes*, and *Klebsiella* (Gray et al. 2015;
661 El Khawand et al. 2016; Carrión et al. 2020). However, there seem to be no anaerobes,
662 archaea or fungi that have been isolated from soils that can grow on isoprene as a C
663 source (McGenity et al. 2018).

664 Soil microorganisms seem to be more in favour of the biodegradation of small
665 compounds with lower reactivity in the atmosphere, such as methanol and methane
666 (Jacob et al. 2005). Methylotrophs are microorganisms that can consume these small
667 compounds as their sole source of C (Kolb 2009), and soil methylotrophic communities
668 can vary with ecosystem type and soil pH (Stacheter et al. 2013). Methanol uptake in a
669 Mediterranean forest was higher in rhizosphere soils than in bare soils, indicating that
670 rhizosphere microorganisms can consume methanol (Asensio et al. 2007a). Moreover,
671 Trowbridge et al. (2020) have uncovered that soil parameters related to different
672 mycorrhizal communities are important for affecting exchanges of VOC, and
673 ectomycorrhizal (EMC) soils exhibited greater uptake of methanol than arbuscular
674 mycorrhiza (AM) dominated soils due to high methylotrophic taxa in EMC soil.
675 Although the microbial degradation of VOCs in soils is widely recognized to occur
676 (Albers et al. 2018), it is challenging to estimate the degradation rate due to the
677 variability of rates based on compound specificity and various soil types.

678

679

680 **Measurements of soil VOCs**

681 Experimental studies typically employ three primary approaches to investigate the
682 composition and flux of VOCs in soil: direct thermal desorption gas chromatography-
683 mass spectrometry (TD-GC-MS), proton transfer reaction mass spectrometry (PTR-MS)
684 and solid-phase microextraction (SPME).

685 TD-GC-MS can identify various compounds, but it cannot be continuously
686 monitored in real-time (Mäki et al. 2019a, b; Ghirardo et al. 2020; Llusià et al. 2022).
687 PTR-MS can perform real-time measurements of VOC rate but is limited to discerning

688 compounds with the same mass, isomers, and isobaric compounds, such as
689 monoterpenes and furans with a molecular weight of 136 amu (Veres et al. 2014;
690 Mancuso et al. 2015; Isidorov and Zaitsev 2022). SPME is similar to TD-GC-MS; using
691 it alone cannot quantify the flux of VOCs, although it can analyze all targeted and non-
692 targeted compounds. Moreover, based on the targeted VOCs, fibres made from
693 different polymers can be chosen for different research purposes (James and Stack 1996;
694 Brown et al. 2021a, b). Therefore, the PTR-MS method can be combined with TD-GC-
695 MS or SPME, which are beneficial to the complementarity of a single method, and
696 ensure simultaneous qualitative and quantitative analysis. This combination method has
697 been effectively applied in laboratory and field soil experiments in recent studies
698 (Faiola et al. 2014; Bourtsoukidis et al. 2018; Ghirardo et al. 2020; Viros et al. 2021;
699 Rezaie et al. 2023).

700 It can be difficult to measure VOC uptake capacity in soil, as oxidants (e.g., ozone
701 and hydroxyl radicals) rapidly degrade VOCs, and the chamber-based method of
702 removing VOCs from the air of the sampling tube using active materials typically
703 cannot reveal soil sink activity (Aaltonen et al. 2011, 2013; Mäki et al. 2019a). Thus, it
704 is important to adopt a suitable sampling method to characterize the uptake capacity of
705 soil VOCs and their emission rates. The method of concentration difference is, so far,
706 an effective method to study the exchange flux of soils and atmospheric VOCs (Asensio
707 et al. 2007b; Trowbridge et al. 2020; Mu et al. 2020; Huang et al. 2021; Yang et al.
708 2024). This method separately obtains the air VOC concentration during the
709 measurement period and the soil source VOC concentration after mixing the air VOCs.
710 The concentration resulting from the difference between the former and the latter shows
711 whether the soil is a source or a sink for compounds.

712 The sampling method and sampling date also significantly affect the source-sink
713 pattern of soil VOCs. To better uncover the source-sink function of soil VOCs, we first
714 recommend avoiding the inclusion of green plants in the chamber when measuring soil
715 VOCs. The presence of plants leads to overestimates of the VOC emission from soil
716 sources and may also cover up the potential sink function of soils (Mäki et al. 2017).
717 We therefore recommend removing the surface plants at least one day in advance before
718 sampling soil VOCs. Second, the dynamic chamber method is generally used for
719 studying soil VOCs exchange rate; that is, the VOCs in the inlet and outlet are collected,
720 or the blank sample of the chamber on the film is collected while collecting soil VOCs.
721 So, a purified inlet air by an activated charcoal filter is not recommended as it can mask
722 the sink function of soil VOCs (Aaltonen et al. 2011, 2013; Mäki et al. 2019a). Third,
723 the source-sink function of soil VOCs has obvious seasonal characteristics (Asensio et
724 al. 2007c; Llusia et al. 2022), so long-term or across-season samplings should be
725 performed in field soil VOC studies, and extreme weather (e.g., rainy) should also be
726 avoided as it may significantly affect VOC emissions (Staudt et al. 2019). Lastly, there
727 is high heterogeneity in soil VOC characteristics in the field, as the litter traits and
728 surface roots affect not only the release of VOCs but also the micro-habitat (e.g.,
729 rhizosphere) they form, which is an active place for microorganisms producing and
730 consuming VOCs. Therefore, it is recommended to try to avoid excessive heterogeneity
731 between VOC sampling points, especially in studies where the effects of climate factors
732 are simulated.

733

734 **Conclusions and prospects**

735

736 The exchange rate between the soil and the atmosphere is a dynamic process. Changes
737 in aboveground VOC concentrations due to global change can directly impact the
738 potential for soil sinks, as highlighted by studies such as Llusià et al. (2022) and Yang
739 et al. (2024). However, given the current limitations in research on soil VOC exchange,
740 quantifying the magnitude of soil VOC sources and sinks remains challenging. Thus,
741 there is a need for more field studies on soil VOCs.

742

743 Ecosystems, vegetation types, and rhizobacterial types may significantly influence soil
744 VOC source-sink characteristics, given the substantial differences in VOC release from
745 various soil sources (Gray et al. 2014; Mäki et al. 2017; Staudt et al. 2019; Mu et al.
746 2023) and the potential of the soil microbial community to consume VOCs (Ramirez et
747 al. 2010; Albers et al. 2018). Therefore, we recommend simultaneous investigation of
748 both soil biotic factors (e.g., microbial characteristics) and abiotic factors (e.g., soil
749 water content) to unveil soil VOC patterns.

750

751 Furthermore, soil VOCs exhibit temporal dynamics with alternating source-sink
752 processes (Asensio et al. 2007b; Mäki et al. 2019b). Thus, cross-seasonal and long-term
753 monitoring prove more informative than a single observation date for understanding
754 soil VOC source-sink function.

755

756 VOCs in soils impact biogeochemical cycling processes (Smolander et al. 2006)
757 and microbial community structure and function (Asensio et al. 2012; McBride et al.
758 2023), coordinating various ecological interactions between species and organism
759 groups (Meredith LK and Tfaily MM. 2022). Our results reveal shared and specific
760 VOCs among soil sources, indicating that linkages through VOC within soils are

761 complex and overlapping (Schenkel et al. 2015). Overall, a better understanding of the
762 mechanisms underlying VOC exchange between soils and the atmosphere is crucial for
763 elucidating global biogeochemical cycles and ecosystem function.

764

765 **Declaration on interest**

766 All authors declare that there are no conflicts of interest relevant to this work.

767

768 **Acknowledgments**

769 This research was financially supported by the Catalan government grant SGR221-
770 1333, the TED2021-132627B-I00 grant funded by the Spanish MCIN,
771 AEI/10.13039/501100011033 and by the European Union NextGenerationEU/PRTR,
772 and the Fundación Ramón Areces project CIVP20A6621. Kaijun Yang is grateful for
773 the financial support from the China Scholarship Council (201806910060).

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