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Review

Biogenic volatile emissions from the soil

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ABSTRACT

Volatile compounds are usually associated with an appearance/presence in the atmosphere. Recent advances, however, indicated that the soil is a huge reservoir and source of biogenic volatile organic compounds (bVOCs), which are formed from decomposing litter and dead organic material or are synthesized by underground living organism or organs and tissues of plants. This review summarizes the scarce available data on the exchange of VOCs between soil and atmosphere and the features of the soil and particle structure allowing diffusion of volatiles in the soil, which is the prerequisite for biological VOC-based interactions. In fact, soil may function either as a sink or as a source of bVOCs. Soil VOC emissions to the atmosphere are often 1–2 (0–3) orders of magnitude lower than those from aboveground vegetation. Microorganisms and the plant root system are the major sources for bVOCs. The current methodology to detect belowground volatiles is described as well as the metabolic capabilities resulting in the wealth of microbial and root VOC emissions. Furthermore, VOC profiles are discussed as non-destructive fingerprints for the detection of organisms. In the last chapter, belowground volatile-based bi- and multitrophic interactions between microorganisms, plants and invertebrates in the soil are discussed.

Key-words: Biogenic VOCs; microbial VOCs; plant root volatile emission; rhizobacteria; rhizosphere; soil fungi; volatile organic compounds (VOCs).

INTRODUCTION

The vast majority of studies examining the exchange of volatile organic compounds (VOCs) between terrestrial ecosystems and the atmosphere have focused on the production and emission of biogenic VOCs by plants and on the abiotic factors (mainly temperature, light intensity, water limitation, nutrition) that control these processes (Kesselmeier & Staudt 1999; Peñuelas & Llusià 2001; Peñuelas & Staudt 2010). As a result, even though the VOCs of soils could have an important influence on the abiotic processes and biotic interactions of soil, we know relatively little regarding the types and quantities of VOCs exchanged in the soil, their sources and sinks, the factors controlling their diffusion and emission, and their ecological and environmental effects.

Bacteria and fungi are present in all types of soils, which thus represent the greatest reservoir of biological diversity. As free-living organisms, these occur on (1) the soil surface; (2) in the soil core; (3) in association with the belowground parts of living plants; and (4) on organic material derived from dead plants or animals (Foster 1988). Due to the high heterogeneity of soil microenvironments, the number of bacterial cells per gram of soil can easily exceed 10^{11}, and estimates of the diversity reach 10^5 and 10^6 species of soil-dwelling bacteria and fungi, respectively (Gans *et al*. 2005; Giri *et al*. 2005; Egamberdieva *et al*. 2008). The majority of soil bacteria can be found in biofilms on roots, litter and soil particles (Burmølle *et al*. 2007). One of the most complex ecosystems on earth is the rhizosphere (Mendes *et al*. 2013), where root exudates influence the microbial habitat to yield bacterial cell numbers of 10^8 cells per gram of fresh root (Berg *et al*. 2002). Furthermore, more than 95% of the short roots of most terrestrial plants are colonized by symbiotic fungi, and these mycorrhizal fungi are surrounded by complex microbial communities, which are composed of mycorrhiza helper bacteria (Frey-Klett *et al*. 2007; Bonfante & Anca 2009; Rigamonte *et al*. 2010). The diversity and complexity of microbial communities in the rhizosphere, which comprise plant-beneficial, plant-pathogenic and human-pathogenic microorganisms, is shaped by the plant-derived nutrients (Mendes *et al*. 2013). These microbes fulfil diverse roles in the ecosystem, for example, they have an impact on plant growth, health and disease and are responsible for the decomposition and recycling of biomass (Drighton 2003; Giri *et al*. 2005). Some chemical compounds and signals that play a role in the inter- and intraspecies rhizosphere interactions have been characterized (Bais *et al*. 2006; Cesco *et al*. 2012; Chaparro *et al*. 2012); however, increasing attention has recently been drawn to the importance of biogenic VOCs in underground communications (Effmert *et al*. 2012; Junker & Tholl 2013).

The interactions between organisms within their biotic environment, such as plant-to-plant, plant-to-animal/microbe and microbe-to-microbe interactions, are universally mediated by VOCs. The biotic interactions in the soil involving VOCs are reported to occur in plant roots, fungi and bacteria, whereas nematodes, arthropods and amoeba receive signals (for a review, see Wenke *et al*. 2010). Biogenic VOCs play

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important functions in the development and formation of ecosystems. The communications mediated by volatile compounds help maintain the balance of the ecosystem (Gao *et al*. 2005) and the development of the community in a cooperative manner (Kai *et al*. 2009). Biogenic VOCs can function as info-chemicals for inter- and intra-organismic communication and as bioactive growth-promoting or growth-inhibiting agents (Baldwin & Preston 1999; Pichersky & Gershenzon 2002; Cardoza *et al*. 2003; Frost *et al*. 2007; Kai *et al*. 2009; Wenke *et al*. 2010; Falik *et al*. 2011; Effmert *et al*. 2012; Hung *et al*. 2012).

In this review, we outline the complexity of biogenic VOCs in the soil system and the known impacts of belowground interactions between multiple organismic groups. We provide insight into the methodological challenges associated with the analysis of belowground processes and the still-unexplored enormous biodiversity of soils. We also examine the multiple origins of VOCs from plants, fungi and microbes and summarize the current understanding of the underlying biochemical processes and responsible genes and how abiotic and biotic drivers regulate these. Additional insight into the fascinating complexity of the biotic interactions between various partners, that is, roots, fungi, microbes and arthropods, is also provided, with a particular focus on roots and their associated fungal and microbial communities. Overall, we aim to increase the scientific interest in the hidden importance of biogenic VOCs in a hitherto largely unknown ecosystem.

SOIL BIOGENIC VOCs

Soil acts as VOC source and sink

The non-methane soil VOCs present emissions or immissions in the soil as a result of multiple biotic and abiotic processes. Of the biotic processes, the microbial decomposition of soil organic matter is one of the most important contributions to soil VOC emissions (Leff & Fierer 2008). Several microbial VOCs are released as intermediate or end products of fermentative and respiratory (aerobic or anaerobic) microbial metabolic pathways (see section below). Because plant litter inputs (aboveground and belowground dead material) and root exudates contribute highly to soil organic matter (Kögel-Knabner 2002), a large fraction of soil VOCs results from the microbial degradation of plant-derived substrates. Schade & Goldstein (2001) measured the soil VOC fluxes with and without the top litter layer in a ponderosa pine (*Pinus ponderosa*) plantation and found that the litter layer in this ecosystem acts as the main source of methanol, whereas the acetone emissions are high in the bare soil without litter, indicating the existence of a different source of acetone in the subsoil. During their metabolism, plant roots, which have between one (fine roots) and two (total roots) orders of magnitude larger biomass than microbial biomass in most biomes (Jackson *et al*. 1997), also contribute to the release of VOCs with different chemical origins (Steeghs *et al*. 2004; Lin *et al*. 2007; Gfeller *et al*. 2013).

Of the abiotic processes contributing to soil VOC emissions, the evaporation of VOCs from plant litter storage pools or soil solutions and Maillard-type reactions have been described (Warneke *et al*. 1999; Gray *et al*. 2010; Greenberg *et al*. 2012). These physical processes contribute, for example, to the typical burst of VOCs from dry soils after a rain or dew event. Some VOCs in the soil pores can become quickly dissolved in water after the first drops (particularly polar oxygenated VOCs) and further evaporate from the soil solution into the atmosphere, giving rise to a flush of oxygenated VOCs from soils (Warneke *et al*. 1999; Greenberg *et al*. 2012). However, the fast activation of microbial activity during a rain event also contributes to this phenomenon (Wang *et al*. 2010).

Soils can also act as a sink of VOCs. The deposition of atmospheric VOCs has been often reported (Schade & Goldstein 2001; Pegoraro *et al*. 2006; Asensio *et al*. 2007a, 2008b; Greenberg *et al*. 2012; Aaltonen *et al*. 2013). One of the mechanisms explaining this sink activity is the microbial consumption of VOCs as a carbon source (Misra *et al*. 1996; Cleveland & Yavitt 1998; Owen *et al*. 2007; Ramirez *et al*. 2009). The abiotic physicochemical degradation of VOCs due to the action of NO_3 and OH radicals, ozone and hydrogen peroxide (reviewed by Insam & Seewald 2010) can also increase the sink potential of soils. Other physical processes that can 'trap' VOCs in the soil are their adsorption to soil mineral particle surfaces (Ruiz *et al*. 1998) and humic substances (Diamadopoulos *et al*. 1998).

Source and sink strengths

Due to the intrinsic complexity of soils and the diversity of these processes involved in the production, consumption and accumulation of VOCs in soil, it is difficult to assess the relative importance of each source and sink on the overall VOC fluxes in the field.

Roots represent a strong source of VOCs such as terpenes (Lin *et al*. 2007). However, the assessment of the contribution of root emissions to the overall soil VOC fluxes is difficult because of their linkage with soil microbes. Root litter and exudates can boost microbial activity in the soil, which can either increase the production or consumption of VOCs. Rinnan *et al*. (2013) performed a mesocosm experiment and found that soils with roots produced more VOCs than soils that were subjected to a root removal treatment. In contrast, Asensio *et al*. (2007b) performed a pot experiment and observed that the presence of roots decreased the soil VOC emissions compared with those obtained by soil without roots. Although the approach and methodologies used in these studies differ, both studies demonstrate that the VOC fluxes that originated from root-rhizosphere activity are very low.

The study conducted by Schade & Goldstein (2001) demonstrated that high amounts of terpenes are emitted from ponderosa pine litter (Table 1a). Other field studies also highlighted the importance of litter as a soil VOC source (Hayward *et al*. 2001; Hellen *et al*. 2006; Greenberg *et al*. 2012). The measurement of the contribution of biotic versus abiotic processes to soil VOC production in the field is difficult, and to the best of our knowledge, no study has directly addressed this question. Indirect proof of the high abiotic

Table 1a. Maximum or average biogenic volatile organic compound (VOC) fluxes measured in field

Ecosystem	Season	VOC source or sink	VOC type	Emission rate ($\mu g\ m^{-2}\ h^{-1}$)	Emission temperature (°C)	Immission rate ($\mu g\ m^{-2}\ h^{-1}$)	Immision temperature (°C)	Method	Contribution ecosystem or canopy fluxes (%)	Reference
Scots pine forest	Spring to autumn	Forest floor[a]	Ion *m/z* 137 monoterpenes (α-pinene)	936[b]	28[c]	-61[b]	15[c]	Dynamic chamber/PTR-MS	10-variable	Aaltonen *et al.* 2013
Ponderosa pine plantation	Summer and autumn	Forest soil pulse after rain	Acetone	806[b]	40[d]	NR	NR	Dynamic chamber/GC-FID	30–45	Schade & Goldstein 2001
Agricultural (cereal)	Summer	Bare soil	Methanol	533[b]	31[e]	NR	NR	EC/PTR-MS	NR	Schade & Custer 2004
Scots pine stand	Summer to autumn	Forest soil	Total monoterpenes	423[b]	8[f]	NR	NR	Variant of dynamic chamber/HSGC-FID	NR	Ketola *et al.* 2011
Scots pine forest	Spring to autumn	Forest floor[a]	Monoterpenes	373[b]	NR	NR	NR	static chamber/GC-MS and FID	NR	Hellen *et al.* 2006
Ponderosa pine plantation	Summer and autumn	Forest soil	Methanol	267[b]	36[d]	NR	NR	Dynamic chamber/GC-FID	20–40	Schade & Goldstein 2001
Ponderosa pine plantation	Summer and autumn	Forest soil	Acetone	258[b]	55[d]	NR	NR	dynamic Chamber/GC-FID	30–45	Schade & Goldstein 2001
Scots pine forest	Spring to autumn	Forest floor[a]	Monoterpenes (55% α-pinene, 29% Δ^3-carene, 15% camphene)	232[b]	10[c]	NR	NR	Static chamber/GC-ITD	20–40	Janson 1993
Scots pine forest	Spring to autumn	Forest floor[a]	Methanol	194[b]	30[c]	–31[b]	16[c]	Dynamic chamber/PTR-MS	10-variable	Aaltonen *et al.* 2013
Mediterranean shrubland	Winter to summer	Shrubland soil	Methanol	144[g]	24[e,h]	–6[g]	15[e,h]	Dynamic chamber/PTR-MS	NR	Asensio *et al.* 2008b
Scots pine stand	Summer to autumn	Forest soil	Total monoterpenes	112[i]	NR	NR	NR	Variant of dynamic chamber/HSGC-FID	NR	Smolander *et al.* 2006
Scots pine forest	Spring to autumn	Forest floor[a]	Acetaldehyde	101[b]	NR	–7[b]	NR	Dynamic chamber/PTR-MS	10-variable	Aaltonen *et al.* 2013
Mediterranean shrubland	Winter to summer	Shrubland soil	Acetaldehyde	82[g]	24[e,h]	–2.4[g]	15[e,h]	Dynamic chamber/PTR-MS	NR	Asensio *et al.* 2008b
Agricultural (cereal)	Summer	Bare soil	Acetone	81[b]	29.5[e]	~ –32[b]	29[e]	EC/PTR-MS	NR	Schade & Custer 2004
Scots pine forest	Spring to autumn	Forest floor[a]	Acetone	79[b]	NR	–14[b]	NR	Dynamic chamber/PTR-MS	10-variable	Aaltonen *et al.* 2013
Mediterranean shrubland	Winter to summer	shrubland soil	Ion *m/z* 73 (C_3 and C_4 carbonyls, MEK)	78[g]	25[e,h]	–2.6[g]	15[e,h]	Dynamic chamber/PTR-MS	NR	Asensio *et al.* 2008b
Ponderosa pine plantation	Summer and autumn	Forest soil	Acetaldehyde	73[b]	50[d]	NR	NR	Dynamic chamber/GC-FID	20–65	Schade & Goldstein 2001
Mediterranean shrubland	Winter to summer	Shrubland soil	Acetic acid	43[g]	25[e,h]	–2.2[g]	15[e,h]	Dynamic chamber/PTR-MS	NR	Asensio *et al.* 2008b
Norway spruce stand	Summer to autumn	Forest soil	Total monoterpenes	47[i]	NR	NR	NR	Variant of dynamic chamber/HSGC-FID	NR	Smolander *et al.* 2006
Sitka spruce plantation	Summer	Forest soil	Monoterpenes (~30% limonene, ~20% α-pinene, ~20% myrcene, ~20% camphene)	~38[b]	18[c]	NR	NR	Dynamic chamber/GC-FID	~3	Hayward *et al.* 2001
Holm oak forest	Spring to winter	Forest soil	Ion *m/z* 57 (hexenal)	20[g]	22.5[e,h]	–10[g]	8[e,h]	Dynamic chamber/PTR-MS	NR	Asensio *et al.* 2007c
Mediterranean shrubland	Winter to summer	Shrubland soil	Formaldehyde	5.4[g]	24[e,h]	–2.2[g]	15[e,h]	Dynamic chamber/PTR-MS	NR	Asensio *et al.* 2008b
Scots pine forest	Spring to autumn	Forest floor[a]	Total monoterpenes	6.6[g]	7.5[e,h]	NR	NR	Dynamic chamber/GC-MS	~10	Aaltonen *et al.* 2011
Ponderosa pine plantation	Summer	Forest soil	Acetone	4[b]	42[d]	NR	NR	Gradient flux/PTR-MS	~1	Greenberg *et al.* 2012
Ponderosa pine plantation	Summer	Forest soil	Methanol	3[b]	38[d]	NR	NR	Gradient flux/PTR-MS	~1	Greenberg *et al.* 2012
Holm oak forest	Spring to winter	Forest soil	Monoterpenes	2[g]	8[e,h]	~–5[g]	6[e,h]	Dynamic chamber/PTR-MS	NR	Asensio *et al.* 2007c
Scots pine forest	Spring to autumn	Forest floor[a]	Ethene, propane, propene, 2-methylpropene, *cis*-2-butene, pentane, hexane, heptane	<2[b]	NR	NR	NR	Static chamber/GC-MS and FID	NR	Hellen *et al.* 2006
Silver birch stand	Summer to autumn	Forest floor	Total monoterpenes	1.6[i]	NR	NR	NR	Variant of dynamic chamber/HSGC-FID	NR	Smolander *et al.* 2006
Ponderosa pine plantation	Summer	Forest soil	Acetaldehyde	1.7[b]	42[d]	NR	NR	Gradient flux/PTR-MS	~1	Greenberg *et al.* 2012
Ponderosa pine plantation	Summer	Forest soil	Terpenes	0.35[b]	32[d]	NR	NR	Gradient flux/PTR-MS	~1	Greenberg *et al.* 2012

Fluxes are not temperature normalized.
[a]Including ground vegetation.
[b]Maximum value during the study period.
[c]Air chamber temperature.
[d]Top soil temperature.
[e]Soil temperature at 5–10 cm.
[f]Organic soil layer temperature.
[g]Maximum seasonal average during the study period.
[h]Sampling date average temperature.
[i]Average value during the study period.
GC-FID, gas chromatography with flame ionization detector; GC-MS, gas chromatography–mass spectrometry; HSGC-FID, headspace gas chromatography with flame ionization detector; ITD, ion trap detector; MEK, methyl ethyl ketone; NR, not reported; NS, not significant; PTR-MS, proton-transfer reaction mass spectrometry.

release of methanol from agricultural soils was, however, provided by Schade & Custer (2004). Because the fluxes of methanol in the soil are well correlated with the sensible heat flux and solar irradiance but not with subsoil temperature, these authors suggested that methanol fluxes are mainly due to the physical desorption of the compound from the heated soil surface. Warneke *et al*. (1999) observed large quantities of short-chain oxygenated VOCs (acetone, acetaldehyde and methanol; Table 1b) emitted from beech leaf litter by abiotic processes after heating (from 20 to 100 °C) and rewetting cycles. In contrast, Gray *et al*. (2010) found that abiotic processes are less important for VOC emissions from different types of leaf litter samples (sterilized and not sterilized) incubated at a constant temperature of 22 °C (Table 1b). Because field litter and other sources of VOCs can experience strong environmental changes, such as high irradiation and rapid temperature increases following a rain event, it is possible that the contribution of abiotic processes to soil VOC emissions is particularly relevant over long-term periods. Additionally, different VOCs can have preferential mechanisms of emission, that is, abiotic or biotic, for example, methanol and terpenes prefer abiotic processes, and acetone is associated with biotic processes (Schade & Custer 2004; Gray *et al*. 2010).

Little information is available on the strength of soils as VOC sinks. Some field studies have reported significant VOC deposition fluxes (hexenal, methanol and monoterpenes) during the day (Asensio *et al*. 2007c, 2008b) and night (α-pinene, methanol and acetone; Aaltonen *et al*. 2013). However, other studies observed no significant deposition (Schade & Custer 2004). It is likely that differences in the soil characteristics and environmental conditions affect these results. Although laboratory experiments have shown that soils can absorb 80% of the VOCs produced by litter (Ramirez *et al*. 2009), the importance of the soil sink activity under field conditions requires further investigation.

Diffusion and emission of VOCs in the soil

The fluxes of VOCs in the soil are thus bidirectional, that is, from the soil to the atmosphere (efflux or emission) and from the atmosphere to the soil (influx or uptake). The exchange of VOCs between the soil and the atmosphere occurs due to diffusion and advection mechanisms. Diffusion is driven by concentration gradients and is the dominant mechanism in the surface of unsaturated soils (Scanlon *et al*. 2002; Rolston & Møldrup 2012). After a concentration gradient is established between the soil and the atmosphere, the gases will move from regions of higher concentration to regions of lower concentration. Advection is driven by pressure gradients that develop due to changes in the barometric pressure, temperature or soil water content or to wind blowing across the soil surface (Scanlon *et al*. 2002; Rolston & Møldrup 2012).

According to Fick's laws of diffusion, soil-gas diffusion is governed by the gas diffusion coefficient D_p ($m^2\ s^{-1}$), which is highly dependent upon the physical properties of soil, such as total porosity, air-filled porosity and tortuosity of the pore system. The physical properties of soil are ultimately dependent upon the soil texture (silt, clay and sand) and organic matter content. Variations in the gas diffusivity can affect the emission and storage processes of VOCs in the soil system (Petersen *et al*. 1994; Scanlon *et al*. 2002; Rolston & Møldrup 2012). The soil organic matter that contributes to the formation of the structure of soil pores can therefore increase the diffusivity of gases in the soil (Boyle *et al*. 1989). However, some modelling studies have reported that the soil organic matter decreases gas diffusivity and volatilization likely due to an increased pore network tortuosity (Hamamoto *et al*. 2012) or the adsorption of VOCs to organic matter (van Roon *et al*. 2005b). Several mechanistic models have been developed during the past decades: from simple models focusing upon the variability of gas diffusion with respect to soil texture, soil organic matter content, root influence or soil water content (e.g. Arthur *et al*. 2012; Hamamoto *et al*. 2012; Uteau *et al*. 2013; Moldrup *et al*. 2000) to more complex models coupling the physics-based description of soil with soil biology (reviewed by Blagodatsky & Smith 2012). Despite all this information, mechanistic models considering the physical transport processes of non-methane, non-anthropogenic soil VOCs are almost non-existent (van Roon *et al*. 2005a,b).

Techniques and measurements of VOCs in the soil

Chambers (or 'enclosures') and/or passive sampler techniques are used to measure soil VOC fluxes in the field at particular sites or locations using point-based observations, whereas micrometeorological techniques are used for ecosystem-based observations. The chamber technique is the most widely used technique, most likely because of its suitability for all types of terrain and because of its specificity for soils. Two methods are commonly used to measure soil VOC fluxes: static and dynamic measurements.

The soil chamber method provides direct measurements of the soil VOC fluxes. However, this method has some limitations. Because soil VOC fluxes are generally diffusive, the chamber headspace concentration can affect the gradient driving the flux. Additionally, perturbations in the chamber pressure relative to that of the soil may induce a bulk flow of VOCs. Moreover, increases in the temperature and humidity inside the chamber can have opposite effects on the soil VOC fluxes (Greenberg *et al*. 2012; Aaltonen *et al*. 2013). In addition, roots can be damaged during the installation of the soil chambers, which may result in the release of several VOCs. These emissions can be persistent over time, which would result in the generation of artefacts in the measurements (Hayward *et al*. 2001; Smolander *et al*. 2006; Asensio *et al*. 2008a; Ketola *et al*. 2011).

The use of micrometeorological techniques to quantify the canopy-scale VOC fluxes has increased in the past few years. However, to the best of our knowledge, only two studies have applied eddy covariance (EC) (Schade & Custer 2004) or gradient-flux techniques (Greenberg *et al*. 2012) to measure soil VOC fluxes; the principles, assumptions and

Table 1b. Maximum or average biogenic volatile organic compound (VOC) fluxes measured in mesocosm and laboratory studies

Biogenic VOCs source or sink	VOC type	Emission rate	Emission temperature	Immission rate	Immision temperature	Units	Method	Reference
Soil	Sesquiterpenes	8.5[a]	13.6[b]	NR	NR	$\mu g\ m^{-2}\ h^{-1}$	Dynamic push-pull/GC-MS	Rinnan *et al.* 2013
Soil	Other VOCs	7[a]	13.6[b]	NR	NR	$\mu g\ m^{-2}$ h–1	Dynamic push-pull/GC-MS	Rinnan *et al.* 2013
Soil	Total VOCs	4[a]	18[b]	NR	NR	$\mu g\ m^{-2}\ h^{-1}$	Dynamic push-pull/GC-MS	Rinnan *et al.* 2013
Soil	Isoprene	NR	NR	–4029[c]	20[d]	$\mu g\ m^{-2}\ h^{-1}$	Static chamber/PTR-MS	Pegoraro *et al.* 2006
Fagus sp. litter	Acetone	0.6[e]	58	NR	NR	$\mu g\ g^{-1}$ DW h^{-1}	Dynamic glass cell/PTR-MS	Warneke *et al.* 1999
Fagus sp. litter	Acetaldehyde	0.4[e]	58	NR	NR	$\mu g\ g^{-1}$ DW h^{-1}	Dynamic glass cell/PTR-MS	Warneke *et al.* 1999
Fagus sp. litter	Methanol	0.35[e]	58	NR	NR	$\mu g\ g^{-1}$ DW h^{-1}	Dynamic glass cell/PTR-MS	Warneke *et al.* 1999
Pinus sylvestris litter	Total terpenes	7.5[e]	20	NR	NR	$\mu g\ g^{-1}$ DW h^{-1}	SPME/GC-MS	Isidorov *et al.* 2010
Picea abies litter	Total terpenes	1.3[e]	20	NR	NR	$\mu g\ g^{-1}$ DW h^{-1}	SPME/GC-MS	Isidorov *et al.* 2010
Larix decidua litter	Total terpenes	1.1[e]	20	NR	NR	μg g–1 DW h^{-1}	SPME/GC-MS	Isidorov *et al.* 2010
Populus deltoides litter	Ion *m*/*z* 33 + 51 (methanol)	7.0[f,g]	22	NR	NR	$\mu mol\ g^{-1}$ DW h^{-1}	Dynamic jar headspace/PTR-MS	Gray *et al.* 2010
Eucalyptus sp. litter	ion *m*/*z* 33 + 51 (methanol)	5.9[f,g]	22	NR	NR	$\mu mol\ g^{-1}$ DW h^{-1}	Dynamic jar headspace/PTR-MS	Gray *et al.* 2010
Pinus ponderosa litter	Ion *m*/*z* 33 + 51 (methanol)	2.5[f,g]	22	NR	NR	$\mu mol\ g^{-1}$ DW h^{-1}	Dynamic jar headspace/PTR-MS	Gray *et al.* 2010
Rhododendron maximum litter	Ion *m*/*z* 33 + 51 (methanol)	1.6[f,g]	22	NR	NR	$\mu mol\ g^{-1}$ DW h^{-1}	Dynamic jar headspace/PTR-MS	Gray *et al.* 2010
Centaurea maculosa litter	Ion *m*/*z* 33 + 51 (methanol)	0.6[f,g]	22	NR	NR	$\mu mol\ g^{-1}$ DW h^{-1}	Dynamic jar headspace/PTR-MS	Gray *et al.* 2010
Eucalyptus sp. litter	ion *m*/*z* 81 + 137 (monoterpenes)	0.4[f,g]	22	NR	NR	$\mu mol\ g^{-1}$ DW h^{-1}	Dynamic jar headspace/PTR-MS	Gray *et al.* 2010
Eucalyptus sp. litter	Ion *m*/*z* 59 (propanal/acetone)	0.3[f,g]	22	NR	NR	$\mu mol\ g^{-1}$ DW h^{-1}	Dynamic jar headspace/PTR-MS	Gray *et al.* 2010
Thinopyrum intermedia litter	Ion *m*/*z* 33 + 51 (methanol)	0.2[f,g]	22	NR	NR	$\mu mol\ g^{-1}$ DW h^{-1}	Dynamic jar headspace/PTR-MS	Gray *et al.* 2010
Acer rubrum litter	Total VOCs	~1425[e]	21	NR	NR	μg C-VOC g^{-1} DW h^{-1}	Dynamic/PTR-MS	Ramirez *et al.* 2009
Acer rubrum litter	Ion *m*/*z* 33 (methanol)	~967[f]	21	NR	NR	μg C-VOC g^{-1} DW h^{-1}	Dynamic/PTR-MS	Ramirez *et al.* 2009
Pinus taeda litter	Total VOCs	~579[e]	21	NR	NR	μg C-VOC g^{-1} DW h^{-1}	Dynamic/PTR-MS	Ramirez *et al.* 2009
Pinus taeda litter	Ion *m*/*z* 81 + 137 (monoterpenes)	~117[f]	21	NR	NR	μg C-VOC g^{-1} DW h^{-1}	Dynamic/PTR-MS	Ramirez *et al.* 2009
Pinus taeda litter	Ion *m*/*z* 59 (acetone)	~75[f]	21	NR	NR	μg C-VOC g^{-1} DW h^{-1}	Dynamic/PTR-MS	Ramirez *et al.* 2009
Pinus taeda litter	Ion *m*/*z* 33 (methanol)	~67[f]	21	NR	NR	μg C-VOC g^{-1} DW h^{-1}	Dynamic/PTR-MS	Ramirez *et al.* 2009
Acer rubrum litter	Ion *m*/*z* 59 (acetone)	~43[f]	21	NR	NR	μg C-VOC g–1 DW h^{-1}	Dynamic/PTR-MS	Ramirez *et al.* 2009
Soil alone	Total VOCs	~0.6[e]	21	~–0.8[e]	NR	μg C-VOC g^{-1} DW h^{-1}	Dynamic/PTR-MS	Ramirez *et al.* 2009

Fluxes are not temperature normalized.
[a]Average value before treatment (cutting all aboveground plant parts).
[b]Mean 24-h air temperature at the level of vegetation.
[c]Results may not be extrapolated to natural conditions: elevated isoprene concentration inside the mesocosm result in high diffusion gradient to the soil and high consumption fluxes.
[d]Minimum nighttime air temperature.
[e]Maximum value during the study period.
[f]Average value during the study period.
[g]Study performed with leaf litter from 12 plant species. Data in the table correspond to the most abundant VOCs within the studied plant types (Angiosperms: deciduous trees, evergreen shrubs, herbs and grasses; Gymnosperms: evergreen trees).
DW, dry weight; NA, not applicable; NR, not reported; NS, not significant; PTR-MS, proton-transfer reaction mass spectrometry; SPME, solid-phase microextraction.

mathematical elaborations for such measurements are complex (Lenschow 1995) and are not always appropriate in forest systems (Baldocchi 1997).

Online analytical methods include proton-transfer reaction mass spectrometry (PTR-MS) and membrane inlet mass spectrometry (MIMS). The MIMS technique separates organic compounds from water or air using a thin silicone membrane, which is installed between the sample and the ion source of a mass spectrometer (Wong *et al*. 1995). Ketola *et al*. (2011) showed that the MIMS technique is rapid and easy to use and allows the direct on-site screening of soil VOCs with a simple sampling probe. Another online monitoring technique is the 'electronic nose'. The crucial features of this technique are the low specificity of the sensor and a high selectivity, which results in representative 'olfactory fingerprints' that include (almost) all VOCs concurrently perceived (De Cesare *et al*. 2011). Bastos & Magan (2007) established the e-nose technology for qualitative soil VOC fingerprinting.

Gas chromatography–mass spectrometry (GC-MS), gas chromatography with flame ionization detector (GC-FID) and headspace gas chromatography with flame ionization detector (HSGC-FID) are off-line techniques and require the pre-concentration of VOCs in adsorption traps, which are generally hydrocarbon adsorbents packed in stainless steel or glass tubes (Brancaleoni *et al*. 1999). Thus, sample air is entrained through the adsorbent tube, and the VOCs are trapped inside. After collection, the sample tubes are thermally desorbed at high temperature using a thermodesorption instrument or chemically desorbed with a disulphide–methanol solution. The VOCs are then subjected to GC-MS, GC-FID or HSGC-FID for analyses (Hayward *et al*. 2001; Schade & Goldstein 2001; Smolander *et al*. 2006; Asensio *et al*. 2007a; Aaltonen *et al*. 2011; Ketola *et al*. 2011). Soil VOCs collected using passive samplers are eluted with dichloromethane and analysed by HSGC-FID (Smolander *et al*. 2006).

With respect to the available tools for the high-throughput analysis of complex VOC blends and the corresponding statistical tools, many studies have attempted to obtain high-quality data and improve data normalization and mining (De Bok *et al*. 2011). To gain further insights into the complexity of soil VOC emissions and biosyntheses, fingerprints based upon VOC profiling should be combined with microbial, fungal and plant marker techniques (Insam & Seewald 2010).

Contribution of soil VOC emissions to the ecosystem

In general, oxygenated VOCs and terpenoids dominate soil emissions in the field (Table 1a). Methanol, acetaldehyde, acetone and acetic acid are generally the highest soil VOCs measured in a ponderosa pine plantation (Schade & Goldstein 2001; Greenberg *et al*. 2012), agricultural bare soil (Schade & Custer 2004) and Mediterranean ecosystems such as a holm oak forest (Asensio *et al*. 2007c) and shrubland (Asensio *et al*. 2008b). Monoterpene and sesquiterpene emissions are also significant in conifer forests (Table 1a), although terpene fluxes are usually lower than those of the main VOCs (Smolander *et al*. 2006; Aaltonen *et al*. 2011; Greenberg *et al*. 2012). Minor fluxes of other common soil VOCs have been reported (Table 1a): propanal, pentanal and pentanal isomers (Greenberg *et al*. 2012), C3 and C4 carbonyls (Asensio *et al*. 2008b), methyl-2-ethylhexanoate and 2-methylfuranmethyfuran (Rinnan *et al*. 2013).

Although almost all studies indicate that the emissions of VOCs are lower from soils than from aboveground vegetation, some discrepancies remain regarding the significance of the contribution of soil VOCs to the overall ecosystem fluxes (Table 1a). For instance, within the same ecosystem type, that is, a ponderosa pine plantation, Schade & Goldstein (2001) estimated that soil exhibited a relatively high contribution to the methanol, acetone and acetaldehyde canopy fluxes (20–40, 30–45 and 20–65%, respectively), whereas Greenberg *et al*. (2012) reported very low soil contributions for the same oxygenated VOCs (less than 1%). The differences between both studies may be due to the methodology (chamber versus flux-gradient method), environmental conditions (temperature and moisture) and/or seasonality. In summer, the contribution of soil VOCs to terpene ecosystem fluxes in conifer forests was not significant (Hayward *et al*. 2001; Greenberg *et al*. 2012), whereas in spring and autumn, these VOCs amounted up to 10% of the terpene canopy-level fluxes (Hellen *et al*. 2006; Aaltonen *et al*. 2011). The observed seasonal differences may be due to increases in the plant VOC emissions during summer (Llusià *et al*. 2013; Oderbolz *et al*. 2013), which can hide the soil VOC sources, and to the increased fall of litter in autumn.

Studies showing soil emissions reaching similar rates than canopy emissions are unusual (Janson 1993; Schade & Goldstein 2001). These two studies were performed using the soil chamber technique, and the high fluxes were found under specific conditions, such as after rain (Schade & Goldstein 2001) or due to unknown reasons, like high terpene emissions in October not explained by the seasonal needle drop (Janson 1993). Therefore, the current available data show that soil VOC emissions are one to two (zero to three) orders of magnitude lower than canopy emissions, but that can reach the same order of magnitude under specific conditions depending upon ecosystem type, season, environmental conditions or biogenic VOC type.

It is remarkable that most of the studies on soil VOC fluxes in the field have been conducted in temperate, boreal and Mediterranean ecosystems. There is no information regarding the soil VOC fluxes in other ecosystems, such as tropical forests. In these highly productive ecosystems, the source/sink activity of soils could have a greater impact on the canopy-level fluxes of VOCs. Further field measurements are thus warranted.

VOCs FROM SOIL MICROORGANISMS

Structural diversity of volatiles from bacteria and fungi and volatile-based fingerprinting

The soil is a treasure chest for (yet unknown) microbial VOCs because soil microorganisms produce large quantities

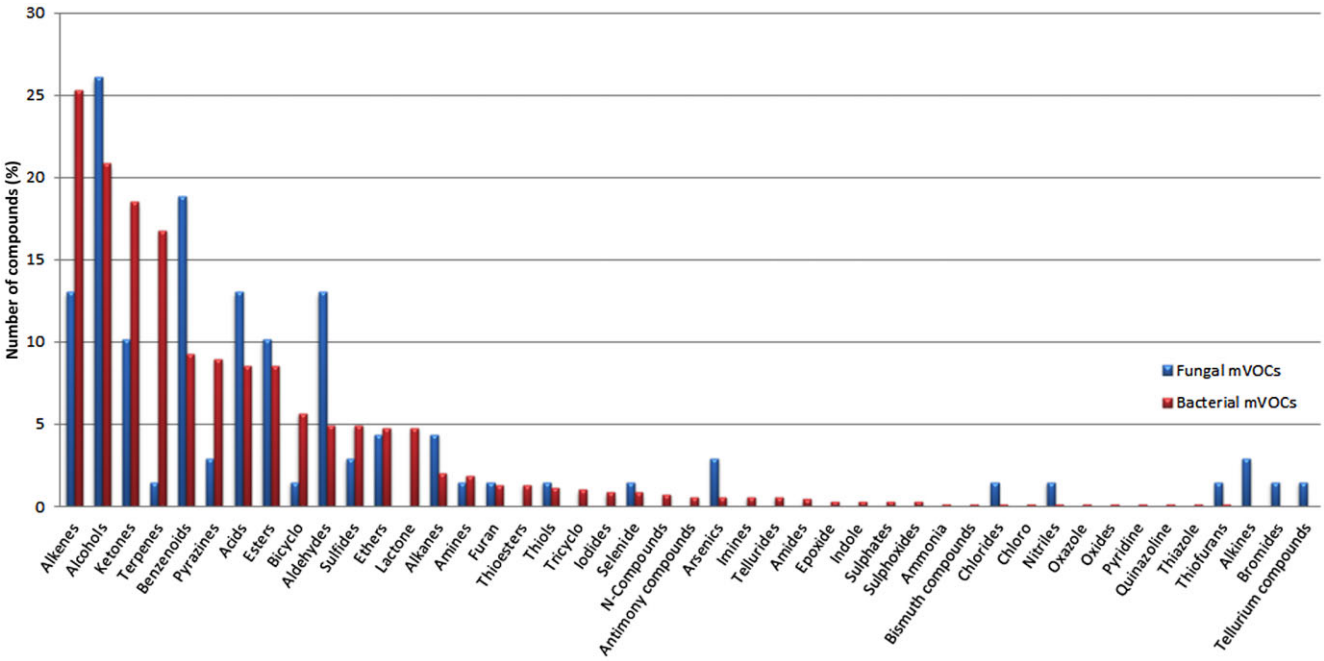

Figure 1. Distribution of microbial volatile organic compound (VOC) emission. Volatiles emitted by bacteria (red columns) and by fungi (blue columns). Chemical classes are ordered due to the number of different compounds within a class. Bacterial VOC profiles are rich in alkenes, alcohols, ketones and terpenes; fungal VOCs are dominated by alcohols, benzenoids, aldehydes, ketones and arsenics (descending order).

of diverse volatiles (Stotzky & Schenck 1976; Linton & Wright 1993; Schulz & Dickschat 2007; Effmert *et al*. 2012). In addition to inorganic volatiles (CO_2, CO, H_2, N_2, N_2O, NO, NO_2, NH_3, H_2S and HCN) (Gottschalk 1986; Kai & Piechulla 2009), many VOCs are emitted by microorganisms. The detectable microbial VOC profiles, however, depend on the presence of substrates and growth conditions (Fiddaman & Rossall 1994; Kai *et al*. 2010; Blom *et al*. 2011) and on the detection techniques used (Rowan 2011; Wenke *et al*. 2012). Consequently, a measured VOC profile might not reflect the complete and complex potential of volatile emission of a microorganism but rather presents a snapshot. Furthermore, the identification of microbial VOCs was limited because the NIST, Wiley and other volatile libraries were originally a compilation of volatiles primarily obtained from animals and plants. Therefore, unusual and unknown bacterial and fungal VOCs have to be structurally elucidated through other analytical means [e.g. nuclear magnetic resonance (NMR)]. For example, sodorifen, a major VOC released by the rhizobacterial isolate *Serratia plymuthica* 4R × 13, is a compound with a structure that is new to science (Kai *et al*. 2010; Von Reuss *et al*. 2010; Weise *et al*. 2014). Therefore, it can be envisioned that new and interesting structures may be found in the future.

So far, literature search of compounds with low molecular mass, high vapour pressure (>0.01 kPa), low boiling point and low polarity, which are properties that support evaporation and diffusion through air spaces in soil habitats, resulted in the compilation of approximately 1000 microbial VOCs released from approximately 350 bacterial and 80 fungal species. This compilation is now included in the 'mVOC' database (http://bioinformatics.charite.de/mvoc/) (Lemfack *et al*. 2014). Considering the number of microorganismal species that exist on earth, one can estimate that the number of microbial VOCs in the database will rapidly increase in the future. In this database, the microbial VOCs are organized into 45 chemical categories, which allow a quick search of VOCs released by bacteria and fungi. Figure 1 shows the distribution of compound classes emitted by bacteria (red columns) and fungi (blue columns). In general, the bacterial VOC profiles contain more alkenes, ketones, pyrazines and terpenes than those obtained from fungal species, whereas fungi emit more benzenoids, aldehydes, arsenics, chlorides, nitriles, thiofurans, alkines and bromides than bacteria. However, it also should be kept in mind that differences in emission profiles occur at the level of genus, species or strain/isolate as documented for several rhizobacterial isolates (e.g. Kai *et al*. 2007; Blom *et al*. 2011). This observation paves the way for a non-destructive way to monitor microbial populations and compositions of microbiomes (McNeal & Herbert 2009).

The concept of volatile-based fingerprinting to detect or identify microbes is quite old. In 1956, Hunt and co-workers worked on the taxonomy of the genus *Ceratocystis* and described different odours within this genus. With the analysis of 34 strains of 10 species of *Ceratocystis* spp., Sprecher & Hanssen (1983) concluded that fungal volatile blends could serve as *in vitro* taxonomic markers under standardized conditions. Similarly, bacterial VOCs were used as a chemotaxonomic marker. Henis *et al*. (1966) observed

species- and even strain-specific VOC peak signatures of 29 bacteria. This work was supported by Tracey *et al*. (1986) who proposed the use of microbial VOCs for the characterization and identification of bacteria. Our literature survey-based comparison of fungal and bacterial VOCs showed also characteristic differences (Fig. 1) (Lemfack *et al*. 2013). The VOC compounds of more than 400 microbial strains and isolates were plotted and revealed characteristic volatile patterns emitted by specific taxonomic groups (Fig. 2). The VOC clusters of typical soil-dwelling representatives (Fig. 2, groups 1, 2, 4, 5 and 7 in green) are highlighted by circles. The VOC spectra of *Pseudomonas* species (7) are dominated by alcohols, aldehydes, ketones, alkanes and alkenes. *Aspergillus* and *Penicillium* (1) species release distinct alcohols, ketones and furans. Conspicuous is the clustering of S-containing volatiles especially in the blends of soil-borne genera (*Streptomyces*, *Bacillus* and *Pseudomonas*). Geosmin, for example, is primarily produced by members of the genus *Streptomyces* (2) (Gerber 1968; Medsker *et al*. 1968, 1969; Dickschat *et al*. 2005) but also by cyanobacteria (8) (Izaguirre *et al*. 1982; Watson 2004) and by some fungal genera (not shown in Fig. 2) (Mattheis & Roberts 1992; Breheret *et al*. 1999; La Guerche *et al*. 2004). Stahl & Parkin (1996) used geosmin and 2-methylisoborneol as indicators of the activity of actinomycetes, bacteria and fungi by measuring their microbial production directly in the soil. These researchers concluded that the investigations of the microbial VOC compositions of soil microbiome require sophisticated well-rethought GC-MS analytical systems and methods (see the section Techniques and measurements of VOCs in the soil). Nevertheless, the detection of trace emissions can be quite valuable and useful for applied problems, such as early diagnosis of microbial diseases *in situ* (Turner & Magan 2004; Statham Thorn & Greenman 2012; Zhu *et al*. 2013), detection of microbial contamination of food products and potable water (Bastos & Magan 2007; De Bok *et al*. 2011; Falasconi *et al*. 2012), detection of fungi (Joblin *et al*. 2010) and discrimination of plant pathogens (e.g. *Erwinia amylovora*) from other plant-associated bacteria (Spinelli *et al*. 2012). Since several soil-borne microorganisms, such as *Phytophthora infestans*, *Pythium ultimum*, *Botrytis cinerea*, or *Erwinia carotovora* and *Fusarium oxysporum* are responsible for immense crop losses during the long-term storage of fruits and vegetables (e.g. potato, onion), an early and non-invasive valid diagnosis and discrimination of diseases by VOC fingerprinting may lead to the reduction of crop losses (Prithiviraj *et al*. 2004; Lui *et al*. 2005).

Although previous studies of VOCs revealed insights into microbial activity and community structure, a recent comprehensive study performed by Müller *et al*. (2013) was the first to uncover the possibility of identifying the functional groups of root-associated fungi (ectomycorrhizal, pathogenic and saprophytic species). Additionally, statistical tools enabled focusing upon specific compounds of the different chemotypes for the prediction of functional groups. However, the extent to which this can be applied in field studies remains to be analysed in the future.

Biosynthesis of microbial VOCs

Bacteria and fungi occur ubiquitously; subsequently, it is often impossible to assign microbial genera or species exclusively to one particular or certain habitat. This paragraph summarizes microbial metabolic pathways related to volatile production. Many VOCs are produced during primary metabolism and energy generation in microorganisms. The underlying biosynthetic pathways are aerobic heterotrophic carbon metabolism, fermentation, amino acid degradation, terpenoid biosynthesis and sulphur reduction.

Bacteria use three major pathways to degrade sugars, preferentially glucose: (1) the Embden–Meyerhof pathway; (2) the Entner–Doudoroff pathway; and (3) the heterolactic/homolactic pathways (Gottschalk 1986; Effmert *et al*. 2012). Pyruvate, glyceraldehyde-3-phosphate, lactate, acetate and CO_2 are the resulting intermediates, and these compounds, with the exception of CO_2, are then used as precursors for the biosynthesis of various VOCs. Ethanol can be synthesized by *Saccharomyces* (*S. cerevisiae* and *S. paradoxus*; Sniegowski *et al*. 2002) and a few other bacteria. Heterolactic fermentation (*Lactobacillus*, Yanagida *et al*. 2006; *Lactococcus*, Kljin *et al*. 1995) results in lactic acid, ethanol and CO_2, and mixed acid fermentations conducted with Enterobacteriaceae (Degelmann *et al*. 2009) result in ethanol and other products. 2,3-Butanediol and acetoin are the major products of *Bacillus* species (e.g. *B. subtilis*; Ryu *et al*. 2003), whereas butyric acid, butanol and acetone are the fermentation products of *Clostridium* species (Smith 1975). Acids, particularly keto acids (2-oxoglutarate, oxaloacetate, pyruvate, 2-oxoisovalerate, 2-oxoisocaproate and 2-oxo-2-methylvalerate) are generated by the oxidative deamination of amino acids (glutamate, aspartate, alanine, valine, leucine and isoleucine, respectively) catalysed by cytochrome-linked oxidases, NAD(P)-linked dehydrogenases, transaminases or other specific enzymes. The subsequent decarboxylation and reduction reactions (the latter depends upon the redox status of the microorganism) further convert these acids into aldehydes/ketones and alcohols. Methane (CH_4) is an important greenhouse gas, and microbes play major roles in both emission and uptake (Nazaries *et al*. 2013). CH_4 is produced by methanogens (Archaea) (Großkopf *et al*. 1998) as part of the anaerobic degradation of organic matter. Methanogenesis is a complex form of anaerobic respiration and requires six unusual co-enzymes for the conversion of CO_2, acetate and methyl group-containing compounds. In contrast, CH_4 consumption is mainly achieved by methanotrophs (Kolb *et al*. 2003), which are often found at the anoxic/oxic interface of various habitats associated with high CH_4 emissions. The anaerobic oxidation of CH_4 involves the use of sulphate or nitrite as an electron acceptor and results, for example, in the formation of methanol by methane monooxygenase and the further formation of formaldehyde by methanol dehydrogenase via two pathways (ribulose monophosphate pathway and serine pathway lead to the assimilation of formaldehyde).

Many microbial volatile blends contain C6 to C16 hydrocarbon compounds, mainly alkenes and aliphatic alcohols

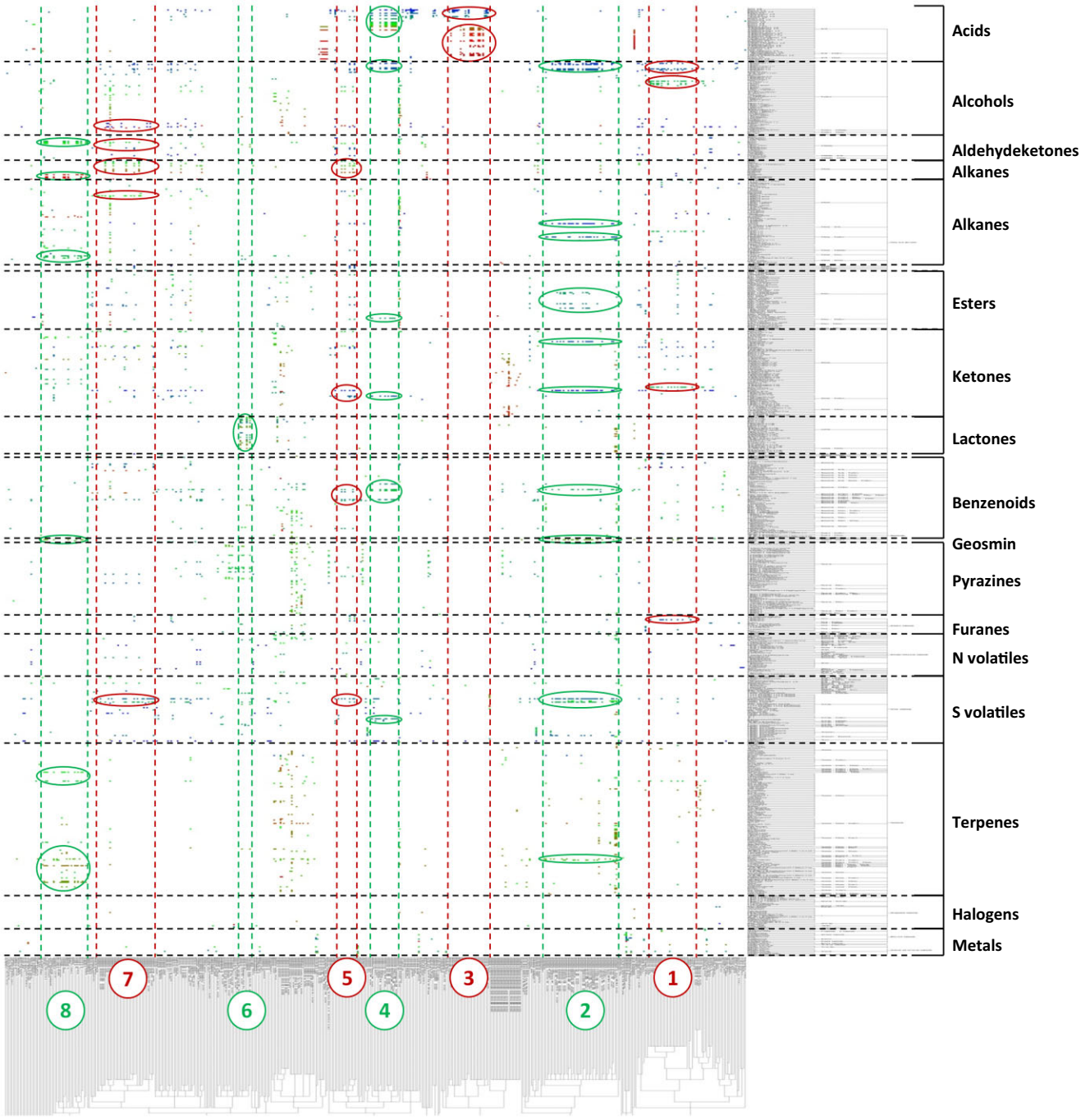

Figure 2. Distribution of microbial volatile organic compounds (VOCs) in fungal and bacterial groups. Vertically, 852 volatile compounds are listed and sorted by their chemical class. Horizontally, 461 microbial strains are ordered based upon their taxonomic classification (Sayers *et al*. 2010). (1) *Aspergillus*, *Penicillium;* (2) *Streptomyces*; (3) *Prevotella*, *Porphyromonas*, *Bacteroides;* (4) *Leuconostoc*, *Lactobacillus*; (5) *Bacillus*; (6) *Dinoroseobacter*, *Loktanella*; (7) *Pseudomonas*; (8) cyanobacteria. Typical soil-borne microbes are marked in green, and untypical soil-borne representatives are marked in red. One dot represents one single compound. Colour code of dots: dark blue >0 Da, blue green 100 Da, red green 200 Da, dark red >300 Da. Circles highlight remarkable clusters of volatiles emitted by the eight designated microbial groups.

and ketones. These compounds are typically the result of fatty acid metabolism. Fatty acid biosynthesis starts with acetyl-CoA, which is subsequently extended by acetyl units obtained from malonate. The reverse reaction during fatty acid degradation (β-oxidation) releases acetyl-CoA. The intermediates of both pathways are potential precursors for microbial VOCs. Many transformation reactions occur; for example, decarboxylation yields alkanes, 1-alkenes or methyl ketones. Another possibility is the reduction of the carboxy group, which leads to the generation of aldehydes and

1-alkanols. Odd numbers of aliphatic chains are generated when, for example, propionyl-CoA is used as the starter molecule. The structural diversity also increases when methylmalonate rather than malonate is used for the elongation steps. Methyl ketones with an odd number of carbon atoms are derived from even-numbered beta-keto acids by decarboxylation, whereas even-numbered methyl ketones arise from fatty acids with an odd number of carbons and are quite rare. Unbranched aldehydes also occur rarely, most likely because of their high reactivity (Schulz & Dickschat 2007). Acids are also easily converted into esters and are quite common aroma compounds due to their elevated volatility. Lactones are formed by the oxidation of the acid chain, leading to hydroxyl acid intermediates with low volatility, which subsequently undergo cyclization reaction.

Aromatic compounds are generated in microbes and plants by the shikimate pathway or by the degradation of L-phenylalanine or L-tyrosine. 2-Phenylethanol, which is one of the most widespread volatile aromatic compounds, can be synthesized from phenylalanine through its transamination to phenylpyruvate, which is catalysed by aromatic aminotransferase (AraT), a subsequent oxidative decarboxylation to phenylacetaldehyde, and a reduction reaction. The respective enzymes have been purified from several species (Schulz & Dickschat 2007). Unusual phenone derivatives, such as 1-phenylnonan-1-one, 1-phenyldecan-1-one and methyl-branched derivatives, are formed by an unusual head-to-head coupling of benzyl-CoA and an alkyl acyl-CoA and subsequent decarboxylations. Two alternative pathways are known to produce benzyl-CoA: the ammonia lyase pathway and the phenylpyruvate-phenylacetate-phenylglyoxylate pathway (Schulz & Dickschat 2007). In both cases, phenylalanine ammonia lyase (PAL) catalyses the initial reaction.

Pyrazines are also major VOCs produced by bacteria. These produce a strong odour and are used as important flavouring compounds. The biosynthesis of pyrazines is not well established (Schulz & Dickschat 2007). The lower methyl and ethyl pyrazines appear to be synthesized non-enzymatically by the amination of acyloins, and in bacteria via dihydropyrazines, which are unstable and easily oxidized to pyrazines. Higher alkyl pyrazines obviously require enzymatic activity, and amino acids often serve as precursors (Schulz & Dickschat 2007). Other N-containing VOCs, such as trimethyloxazoline (*Bacillus thuringiensis* and *Bacillus popilliae*), indole (e.g. many *Escherichia coli* strains) and skatole (*Calothrix*), are synthesized from amino acids and other compounds found widely in nature (Davis *et al*. 2013).

Geosmin and 2-methylisoborneol are VOCs with a musty and earthy smell emitted by actinomycetes, myxobacteria and cyanobacteria (Schulz & Dickschat 2007; Citron *et al*. 2012). Both compounds are important drinking water contaminants with an unpleasant taste and smell, which results in numerous consumer complaints. Although it has known for decades that geosmin is a terpene, its biosynthesis remains elusive until recently. A PCR-based approach and the genomic data mining of many *Streptomyces* species highlighted sesquiterpene (geosmin) synthases producing geosmin (Cane & Watt 2003; Gust *et al*. 2003; Citron *et al*. 2012). Interestingly, two evolutionary distant geosmin synthase types were found: one is present in myxobacteria and cyanobacteria, and the other is found in actinomycetes. Furthermore, other terpene synthases (TPS) were obtained from *Streptomyces* species and *Nostoc punctiforme* PCC 73102 (summarized by Nakano *et al*. 2011). Recently, a new (+)-caryolan-1-ol cyclase was isolated from *Streptomyces griseus* (Nakano *et al*. 2011). The first fungal *TPS* gene was isolated from *Penicillium roqueforti* (Caruthers *et al*. 2000). A genome comparison revealed the *TPS* class I genes in *Trichoderma* species and their orthologs in ascomycetes (Gibbons *et al*. 2012). A novel class of sesquiterpenes, as well as its gene cluster, was recently described for *Trichoderma virens* (Crutcher *et al*. 2013).

Microbial monoterpene synthases have been studied less than sesquiterpene synthases because few specific geranyl pyrophosphate (GPP) synthases are found in microorganisms, unlike in plants. In yeast, both GPP and farnesyl pyrophosphate (FPP) synthase activities are shared by one enzyme called farnesyl pyrophosphate synthase (FPPS) (Fischer *et al*. 2012). *Streptomyces citreus* and *Streptomyces caviscabis* emit monoterpenes (Schulz & Dickschat 2007). To date, only a few bacterial and fungal *TPS* genes have been reported, likely due to the low amino-acid-sequence identities of these compared with those of the respective enzymes in eukaryotes (Yamada *et al*. (2012).

Volatile sulphur compounds play an important role in the global biogeochemical cycle of sulphur. H_2S, methanethiol, dimethyl sulphide (DMS), dimethyl disulphide (DMDS) and dimethyl trisulphide (DMTS) are the most important volatile sulphur compounds. Lactic bacteria contribute to the formation of flavour compounds including H_2S, methanethiol, DMS and DMDS in dairy products through the degradation of L-methionine either by the direct cleavage of the amino acid by L-methionine gamma-lyase or by its transamination to alpha-keto-gamma-methylbutyric acid and subsequent reductive demethiolations. Two other enzymes, namely cystathionine beta-lyase and cystathionine gamma-lyase, may also be involved in the production of these volatiles (Schulz & Dickschat 2007). DMDS and DMTS are most likely formed via autoxidation mediated by ascorbate and transition metal ions in many bacteria. Methanethiol, the proposed parent compound, is more difficult to detect because of its high volatility, but it has nevertheless also been reported in the headspace of bacteria (Weise *et al*. 2012).

VOCs FROM PLANT ROOTS AND RHIZOMES

Biosynthetic and tissue-specific diversity of root VOCs

Belowground plant tissues produce VOCs with similar diversity as those of aboveground organs. Numerous reports (too many to be listed individually) have documented VOCs as constituents of essential oils extracted from roots and rhizomes, although only a limited number of studies have measured actual VOC emissions from these tissues (Table 2).

One of the smallest VOCs emitted by plants is methanol. The aboveground phytogenic emissions of methanol are

Table 2. Biogenic volatile organic compounds (VOCs) and their biosynthetic genes from roots and rhizomes of different plant species

Plant species (Family)	Volatile organic compounds (VOC sampling/analysis method)	Treatment (multiple treatments according to different references)	Root-expressed genes involved in VOC biosynthesis	References
Arabidopsis thaliana (Col ecotype) (Brassicaceae)	1,8-Cineole; (*Z*)-γ-bisabolene; rhizathalene; ethanol; ethyl acetate; aldehydes; ketones (SPME, PTR-MS, solvent extraction)	Untreated jasmonic acid *Bradysia* spp. *Pseudomonas syringae* DC3000 *Alternaria brassicicola* *Diuraphis noxia*	TPS23/27 – 1,8-cineole synthases TPS12/13 – (*Z*)-γ-bisabolene synthases TPS08 – rhizathalene synthase	Chen *et al.* 2004 Chen *et al.* 2011 Ro *et al.* 2006 Steeghs *et al.* 2004 Tholl & Lee 2011 Vaughan *et al.* 2013
Artemisia tridentata (sage brush) (Asteraceae)	Camphor; 1,8-cineole; nerol; neryl isovalerate; sesquiterpene hydrocarbons (e.g. caryophyllene); acetylenic spiroethers (dynamic headspace extraction, HSME, HSPME)	Untreated	None characterized	Jassbi *et al.* 2010
Asclepias syriaca (common milkweed) (Apocynaceae)	Monoterpene hydrocarbons (e.g. limonene); 1,8-cineole; veratrole; acetophenones; 2-methoxy-3-isopropyl pyrazine (dynamic headspace sampling, SPME)	Untreated *Tetraopes tetrophthalmus* (red milkweed beetle)	None characterized	Rasmann *et al.* 2011
Brassica nigra (Brassicaceae)	Glucosinolate breakdown products; methanethiol; sulphides (DMS, DMDS, DMTS) (PTR-MS)	*Delia radicum* (cabbage root fly)	Glucosinolate biosynthesis genes – *Brassica oleracea* treated with jasmonic acid	Crespo *et al.* 2012 Tytgat *et al.* 2013
Citrus paradise × *Poncirus trifoliata* *Poncirus trifoliata* *Citrus aurantium* (Rutaceae)	α-Pinene; β-pinene; limonene; pregeijerene; geijerene (dynamic *in situ* collection)	Untreated *Diaprepes abbreviatus* (root weevil)	None characterized	Ali *et al.* 2011
Curcuma longa (Zingiberaceae)	Monoterpenoids; sesquiterpenoids, e.g. 1,8-cineole, α-zingiberene, β-sesquiphellandrene, α-turmerone, β-turmerone (organic solvent extraction)	Untreated	2 monoterpene synthases 3 sesquiterpene synthases (TPS products, see Koo & Gang 2012)	Koo and Gang 2012
Gossypium herbaceum (Malvaceae)	Sesquiterpene hydrocarbons (SPME)	Untreated *Diabrotica balteata* (banded cucumber beetle)	None characterized	Rasmann & Turlings 2008
Lycopersicon esculentum (Solanaceae)	Methyl salicylate; β-phellandrene (traces) (saturated $CaCl_2$ extract, SPME)	Untreated	LeMTS2 (SlTPS4) – β-phellandrene, β-myrcene, sabinene synthase	van Schie *et al.* 2007
Matricaria recutita (chamomile) (Asteraceae)	Sesquiterpene hydrocarbons including tricyclic sesquiterpenes (α-isocomene); geranyl valerate (organic solvent extraction)	Untreated	MrTPS2 – (−)-α-isocomene synthase	Irmisch *et al.* 2012
Nicotiana attenuata *Nicotiana sylvestris* (Solanaceae)	Capsidiol (organic solvent extraction)	Untreated	5-epi-aristolochene synthase (producing precursor of capsidiol)	Bohlmann *et al.* 2002
Pinus pinea (Pinaceae)	Monoterpene hydrocarbons; sesquiterpene hydrocarbons and oxides; anisole; 2,4-dimethoxyallylbenzene (dynamic bag enclosure method; passive diffusion method)	Untreated Drought stress	None characterized	Lin *et al.* 2007

Table 2. *Continued*

Plant species (Family)	Volatile organic compounds (VOC sampling/analysis method)	Treatment (multiple treatments according to different references)	Root-expressed genes involved in VOC biosynthesis	References
Quercus petraea × *Quercus robur* (Fagaceae)	anisole, (*R*)-1-octen-3-ol; 2-ethyl-hexan-1-ol; nonanal; decanal; octan-3-one; 6-methyl-5-hepten-2-one; 1,8-cineole; linalool-oxide; camphor; borneol; geranyl acetone (dynamic headspace sampling, SPME)	Untreated Mechanical damage *Melolontha hippocastani* (cockchafer)	None characterized	Weissteiner *et al.* 2012
Thapsia laciniata Rouy *Thapsia garganica* *Thapsia villosa* (Apiaceae)	δ-Cadinene; α- and δ-guaiene; elemol; guaiols (SPME, hydrodistillation)	Untreated	5 predicted sesquiterpene synthases TgTPS1 – δ-cadinene synthase TgTPS2 – 6-β-hydroxygermacra-1(10),4-diene (kunzeaol) synthase	Drew *et al.* 2012 Drew *et al.* 2013 Pickel *et al.* 2012
Trifolium pratense (Fabaceae)	Ethanol; (*E*)-2-hexenal; hexanal; 3-octanone; limonene; α-pinene (SPME)	*Hylastinus obscures* (clover root borer)	None characterized	Palma *et al.* 2012
Valeriana officinalis (Valerianaceae)	Valerenadiene (isobutenyl-containing sesquiterpene); valerianol; valerenal; valeranone; bornyl acetate; camphene; fenchene (basic essential oil components)	Untreated	7 VoTPS genes VoTPS1 – valerena-1,10-diene synthase VoTPS3 and 4 – monoterpene synthases VoTPS5 – sesquiterpene synthase VoTPS7 – germacrene C synthase	Pyle *et al.* 2012 Raal *et al.* 2008 Yeo *et al.* 2013
Vitis berlandieri Planch. × *Vitis riparia* Michx. *Vitis vinifera* (Vitaceae)	C6-compounds; terpenes (including modified terpenes); aromatic compounds; alcohols and *n*-alkanes (SPME)	Untreated *Daktulosphaira vitifoliae* (phylloxera)	VvPNRLin – (3*R*)-linalool synthase VvPNLinNer1, 2 – (3*S*)-linalool, (*E*)-nerolidol synthases VvPNLNGI1, 2, 3 ((3*S*)-linalool, (*E*)-nerolidol, (*E*,*E*)-geranyl linalool synthases	Lawo *et al.* 2011 Matarese *et al.* 2013
Zea mays (Poaceae)	(*E*)-β-caryophyllene and other sesquiterpene hydrocarbons; hexadecanal, tetradecanal; β-bisabolene, β-macrocarpene (SPME)	Untreated *Diabrotica virgifera virgifera* (Western corn root worm) *Diabrotica balteata* *Spodoptera littoralis* (aboveground)	TPS6 and TPS11 – (*S*)-(β-macrocarpene, (*S*)-β-bisabolene synthases TPS23 – (*E*)-β-caryophyllene synthase	Rasmann *et al.* 2005 Rasmann & Turlings 2008 Kollner *et al.* 2008a Kollner *et al.* 2008b
Zingiber officinale (Zingiberaceae)	Monoterpenoids; sesquiterpenoids, e.g. 1,8-cineole, α-zingiberene, β-sesquiphellandrene	Untreated	14 monoterpene synthases 15 sesquiterpene synthases (TPS products, see Koo & Gang 2012)	Koo and Gang 2012

Only plant species are listed, from which root VOC emissions were measured with different sampling techniques and/or root-expressed genes involved in VOC biosynthesis have been identified.
DMS, dimethyl sulphide; DMDS, dimethyl disulphide; DMTS, dimethyl trisulphide; HSME, headspace solvent microextraction; HSPME, headspace solid-phase microextraction; PTR-MS, proton-transfer reaction mass spectrometry; SPME, solid-phase microextraction.

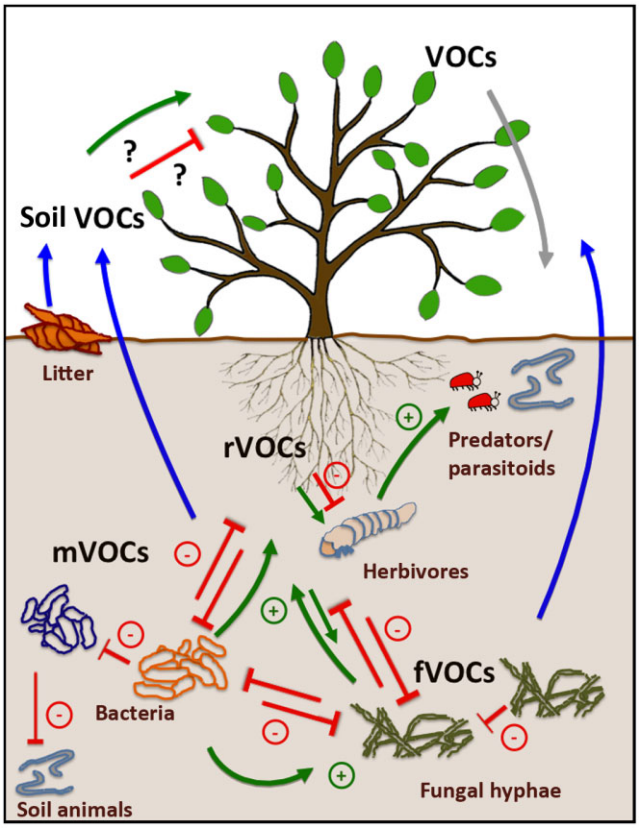

Figure 3. Schematic scheme of biogenic volatile organic compounds (VOCs) emissions and biotic interactions in the soil. VOCs (blue arrows) emitted by bacteria (mVOCs), fungi (fVOCs), roots (rVOCs) and litter (bVOCs). Direct negative effects (e.g. growth inhibition, toxicity) of VOCs are indicated by red arrows. Direct positive (growth promotion) and indirect (attractance for predators in tri-trophic interactions) effects are indicated by green arrows.

primarily associated with leaf expansion and cell elongation (Galbally & Kirstine 2002; Hueve *et al*. 2007). In this process, which involves cell wall extension and stiffening, methanol is produced through the demethylation of pectin by the enzyme pectin methylesterase (PME) to allow the cross-linking of pectin polymers and the stabilization of cell walls. PME activity is also found in roots (Oikawa *et al*. 2011), where it is involved in root elongation (Palin & Geitmann 2012) and the separation of root border cap cells (Driouich *et al*. 2007). Moreover, AtPME3, one of the major PME isoforms in Arabidopsis, has been shown to play a role in adventitious root formation (Guenin *et al*. 2011). Methanol emission and PME activity have been associated with the induced responses to herbivore feeding, and these are most likely associated through the change in cell wall properties (Peñuelas *et al*. 2005; von Dahl *et al*. 2006; Körner *et al*. 2009). The extent to which methanol emissions respond to or influence belowground herbivores is not well understood. However, root-produced methanol may be used as a carbon source by methylotrophic symbionts, which induce root nodule formation (Sy *et al*. 2005) (Fig. 3).

VOC mixtures emitted by roots often contain non-oxygenated or oxygenated fatty acid derivatives such as aldehydes, ketones and alcohols (Table 2). For example, the two aldehydes, hexadecanal and tetradecanal, are released together with terpene volatiles from maize roots in response to feeding damage by larvae of the Western corn root worm (*Diabrotica virgifera*) and may play a role as background odours in the attraction of *D. virgifera* (Robert *et al*. 2012). Furthermore, short-chain C6 volatiles, such as (*E*)-hex-2-enal, (*E*)-hex-2-en-1-ol, have been detected in the volatile blends emitted by grape roots infested with phylloxera (*Daktulosphaira vitifoliae*) (Lawo *et al*. 2011) and in roots of *Trifolium pratense* in response to root borer feeding (Palma *et al*. 2012). C6 volatiles are produced from the polyunsaturated fatty acids linoleic acid (18:2) or linolenic acid (18:3) by the activity of 13-lipoxygenases (LOX) and hydroperoxide lyase (Dudareva *et al*. 2006). It can be assumed that the wound-induced C6 volatiles released by roots have functions similar to those observed aboveground: these exhibit bactericidal and fungicidal activities (e.g. Prost *et al*. 2005) and activate defence responses through intra-plant signals (Frost *et al*. 2008). Depending upon their diffusion radius in the soil, C6 volatiles may also serve as short-range attractive cues for herbivores and their parasites or as in-between plant signals (Fig. 3). 13-Lipoxygenases also catalyse the first step in the allenoxide synthase-specific branch of the LOX pathway leading to the biosynthesis of jasmonic acid and its volatile derivative, methyl jasmonate (Schaller & Stintzi 2009). In Arabidopsis, one of four 13-lipoxygenases, LOX6, is specifically expressed and essential for stress-induced jasmonate accumulation in roots (Grebner *et al*. 2013). However, the methylation of jasmonic acid by jasmonate carboxyl methyltransferase (Seo *et al*. 2001) and the release of methyl jasmonate has, to the best of our knowledge, not yet been reported from herbivore-damaged belowground tissues.

Reflective of their diversity in aboveground tissues, terpenes are among the most prominent VOCs emitted from belowground tissues. Plants produce terpenes from isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP) generated by the cytosolic mevalonate (MVA) or plastidic MEP pathways. The condensation of the C5 units gives rise to all-*trans* or all-*cis* prenyl diphosphate precursors that are converted by the TPS enzymes of different subfamilies into acyclic, mono-, bi- or tri-cyclic C10 -monoterpenes, C15-sesquiterpenes or semi-volatile C20-diterpenes (Chen *et al*. 2011). The primary terpene skeletons may then be further modified through secondary enzymatic reactions, such as dehydrogenations, hydroxylations, methylations and acylations (Dudareva *et al*. 2006). Volatile terpenes are common components of the extracts and essential oils of many aromatic plants. For instance, a large variety of monoterpenes and sesquiterpenes are produced in the roots of Vetiver grass (*Vetiveria zizanioides*) (Champagnat *et al*. 2006) and in the rhizomes of ginger (*Zingiber officinale*) and turmeric (*Curcuma longa*) (Koo & Gang 2012). Comparatively few studies have measured direct emissions of terpenes from root tissues. Table 2 summarizes investigations on constitutive or pathogen- and herbivore-induced emissions of VOCs from

the roots of crops (maize, cotton, red clover and grape), trees and shrubs (pine, citrus, oak and sagebrush), Arabidopsis and other herbaceous species (milkweed). Several root-expressed *TPS* genes responsible for the formation of terpene volatiles have been identified (Table 2), although a large number of biosynthetic genes remain to be characterized. Roots have also been shown to produce irregular terpenes, which are derived by degradation of regular terpenes, but these compounds have so far been observed only in extracts of roots (e.g. Havlik *et al*. 2009) or their emission might be limited as indicated for C13- and C14-apocarotenoids produced in mycorrhizal roots (Walter *et al*. 2010).

Phenylpropanoid and benzenoid VOCs, which are frequently detected as VOCs in trichomes and flowers (Gang *et al*. 2001; Dudareva *et al*. 2006), are also common constituents of VOC mixtures in plant roots and rhizomes. Insect-induced emissions of phenylpropanoids (e.g. eugenol, phenylethyl alcohol), benzenoids such as benzaldehyde and methyl salicylate, and acetophenones have been recorded from the roots of milkweed and grape, respectively (Lawo *et al*. 2011; Rasmann *et al*. 2011) (Table 2). As demonstrated by studies of aboveground tissues, most phenylpropanoids and benzenoids are biosynthesized from phenylalanine via *trans*-cinnamic acid in the core phenylpropanoid pathway (Dudareva *et al*. 2006; Qualley *et al*. 2012). By contrast, phenylacetaldehyde is produced directly from phenylalanine through a single or two-enzyme decarboxylation-amine oxidation reaction (Kaminaga *et al*. 2006; Tieman *et al*. 2006; Gutensohn *et al*. 2011), and phenylethyl alcohol is biosynthesized by subsequent reduction (Tieman *et al*. 2006) or via an alternative biosynthetic route through phenylpyruvate (Boatright *et al*. 2004). Despite the elucidation of multiple steps in the phenylpropanoid/benzenoid biosynthetic pathways, there is currently no good understanding of these pathways and their regulation in belowground tissues.

Volatile S-containing compounds produced by the breakdown of glucosinolate metabolites are characteristic defence compounds of plants in the crucifer family (Halkier & Gershenzon 2006). Glucosinolates are classified by their amino acid precursors as aliphatic, aromatic or indole glucosinolates. The glycosides are hydrolysed by endogenous thioglucosidases called myrosinases upon tissue damage to release glucose and an aglycone that is rearranged into volatile isothiocyanates, thiocyanates and nitriles (Halkier & Gershenzon 2006). Volatile glucosinolate-breakdown products have been found in the dried and fresh roots of crucifers (e.g. Afsharypuor & Sepehrnejad 2006; Aissani *et al*. 2013; Blazevic & Mastelic 2009), and their emission has been monitored directly by PTR-MS from *Delia radicum* (cabbage root fly)-infested roots of *Brassica nigra* (Crespo *et al*. 2012). Belowground herbivory can increase glucosinolate levels, as was shown for indole glucosinolates in *B. nigra* roots upon *D. radicum* feeding (van Dam & Raaijmakers 2006). The glucosinolate-breakdown products exhibit toxic or deterrent activities against herbivores, including nematicidal activity (Buskov *et al*. 2002) (Fig. 3), although there is still limited evidence supporting this role and the effect of ecotype-specific differences of glucosinolate profiles *in planta* (van Leur *et al*. 2008). The accumulation of glucosinolates in roots appears to be the result of shoot-to-root transport but is also due to root-specific biosynthesis, as shown by recent micrografting experiments (Grube Andersen *et al*. 2013). In line with these findings, the expression of several glucosinolate biosynthesis genes has been shown to increase in roots of *Brassica oleracea* upon treatment with jasmonic acid (Tytgat *et al*. 2013).

PTR-MS analysis has also revealed the emission of other S-containing VOCs, such as methanethiol, DMS, DMDS and DMTS from *Delia*-infested *B. nigra* roots (Crespo *et al*. 2012). DMDS functions as an attractant of soil-dwelling beetles, which are predators of root fly larvae (Ferry *et al*. 2007). The sulphides are thought to be biosynthesized from the amino acids cysteine and methionine through endogenous transferase and lyase enzyme activities (Chin & Lindsay 1994; Attieh *et al*. 2002).

Finally, a few other types of root-derived volatile or semi-volatile compounds with known defensive activities and/or occurrence in specific plant families should be mentioned, even though these compounds have been primarily detected in root extracts and their direct release from roots is currently unknown.

Medium chain length methyl ketones are volatile fatty acid derivatives, which can be produced by the enzymatic hydrolysis of 3-ketoacyl-acyl carrier proteins and the decarboxylation of 3-keto fatty acids (Yu *et al*. 2010). Methyl ketones are potent defence compounds against different pests (Williams *et al*. 1980; Kennedy 2003), including nematodes (Ntalli *et al*. 2011). The identification of the C11 and C13 methyl ketones 2-undecanone and 2-tridecanone, respectively, in the roots of different species (e.g. Viana *et al*. 2002) support their role as belowground defences.

Among the volatile or semi-volatile compounds typically produced by roots of species belonging to the Apiaceae are aliphatic polyacetylenes and volatile phthalides (e.g. Chaughan *et al*. 2012; Rivero *et al*. 2012; Sellami *et al*. 2012). Some of the most well-known polyacetylenes are falcarinol and falcarindiol, whose biosynthesis from oleic acid includes multiple steps of dehydrogenation by acetylenases and desaturases to form the characteristic triple bonds (Minto & Blacklock 2008). Both compounds have antimicrobial and antifungal activities and show elevated levels in response to different stresses (Christensen & Brandt 2006; Seljasen *et al*. 2013).

Roots of species in the Asteraceae plant family produce another group of sulphurous compounds named thiophenes. Thiophenes are derived from polyacetylenes by thiophene ring formation (Arroo *et al*. 1995). Less polar C12-thiophenes, such as BBT (5-(3-buten-1-ynyl)-2,20-bithienyl) extracted from roots of *Tagetes* (French marigold), can be considered moderately volatile (Szarka *et al*. 2006). Thiophenes are known for their strong phototoxic bioactivity but also exhibit nematicidal effects belowground that are likely caused by enzymatic activation in roots (Hudson *et al*. 1991). Roots of medicinal vegetables in the Asteraceae family are also known to accumulate pyrazines, specifically methoxypyrazines (Shimizu *et al*. 2011), which are frequently

associated with an earthy or bell pepper-like aroma. Little information is available regarding the biosynthesis of methoxypyrazines from amino acid precursors, although a methyltransferase involved in the formation of 3-isobutyl-2-methoxypyrazine was recently characterized in grape berries (Dunlevy *et al*. 2013).

Taken together, belowground plant tissues represent a large reservoir of volatile compounds of different biosynthetic origins. Root-derived VOCs are often distinct from those produced by the aboveground tissues. For example, the composition of the volatile terpene blend found in Arabidopsis roots shows no overlap with that obtained in flowers and leaves. Accordingly, above- and belowground organs exhibit different expression profiles of members of the *TPS* gene family (Tholl *et al*. 2005; Huang *et al*. 2010; Tholl & Lee 2011; Vaughan *et al*. 2013). Several Arabidopsis root-specific *TPS* genes exhibit basal constitutive expression levels in contrast to genes that are expressed in response to herbivory and pathogen infection in leaves (Chen *et al*. 2004; Attaran *et al*. 2008; Huang *et al*. 2010).

Similarly, van Dam *et al*. (2009) described distinct differences in the glucosinolate profiles observed in the roots and shoots of Brassicaceous plants: the root profiles exhibit higher concentrations and a greater diversity of glucosinolates. In particular, the roots maintain higher levels of the aromatic 2-phenylethyl glucosinolate, which allows the release of a volatile breakdown product with greater toxicity in the soil. The ability of the roots to maintain a more potent constitutive defence against belowground pathogens or pests is reflected in the largely constitutive production of glucosinolates and the weaker increase in the glucosinolate levels in response to biotic stress compared with those found in shoots (van Dam *et al*. 2009). In line with these findings, a survey of the root VOC compositions indicates that specific terpenoids, such as 1,8-cineole and camphor, are frequently found in the extracts of roots or rhizomes and thus may have been selected for their antimicrobial and insecticidal activities. In fact, (−)-camphor has been shown to act synergistically with 1,8-cineole (Chen *et al*. 2013). In addition, shoot- and root-specific differences in specialized metabolites and VOCs may contribute to the differences in the endophytic bacterial community compositions observed in naturally grown Arabidopsis (Bodenhausen *et al*. 2013).

As in aboveground tissues, root VOCs can accumulate in specialized secretory tissues or cells. For example, Vetiver grass roots produce essential oils in cortical parenchymatous secretory cells (Del Giudice *et al*. 2008). Similarly, in carrot roots, terpenes are primarily synthesized in the upper part of the root in an interconnected network of oil ducts located in the phloem (Senalik & Simon 1986). VOCs stored in these tissues are likely to be released upon wounding or infection rather than from intact roots. In the absence of specialized secretory structures and storage pools, VOCs have to be produced constitutively at non-toxic levels or are immediately emitted under stress-induced conditions. Depending upon their polarity, many VOCs may remain in the intercellular space or rhizosphere, whereas others diffuse further into the soil and function as 'long-distance' info-chemicals, as has been demonstrated for insect-induced sesquiterpenes (Turlings *et al*. 2012) (see Fig. 3). Even if the production of VOCs is not confined to secretory cells or ducts, their biosynthesis can be rather cell-type-specific. According to *TPS* gene transcriptional maps and promoter-reporter gene studies in Arabidopsis roots, different volatile terpenoids are biosynthesized in the stele, cortex and epidermis (Tholl & Lee 2011). The recently discovered Arabidopsis diterpenes named rhizathalenes are produced by TPS08 in the root stele, where they exhibit anti-feedant activities against the opportunistic root herbivore *Bradysia* (Vaughan *et al*. 2013). The exact reason for the cell-type-specific formation of VOCs in roots is not well understood. Glucosinolates have been demonstrated to occur at their highest levels in the outer periderm of canola roots, and their breakdown products are believed to protect the xylem from intruding fungal pathogens (van Dam *et al*. 2009). It is possible that overlapping gradients of VOCs form complex multi-layered chemical defence barriers that may also be important for the establishment of distinct associations with opportunistic and competent microbes in specific niches in the endosphere or the vascular tissue. Moreover, the VOC mixtures produced by plant roots are likely to be modified by microbial or fungal colonizers due to detoxification processes or the breakdown of compounds as carbon source. For example, the catabolism of sesquiterpenes by bacteria associated with roots of vetiver grass was found to strongly alter the root-specific volatile terpene bouquets (Del Giudice *et al*. 2008).

RELEVANCE OF SOIL VOCs AND VOCs-MEDIATED INTERACTIONS

Interactions mediated by root-released VOCs

Root VOCs play a role in insect–nematode interactions

VOCs-mediated interactions between plants and arthropods in the aboveground environment are a well-recognized phenomenon that allowed the development of scientific concepts for direct and indirect defence strategies (Agrawal 1998; De Moraes *et al*. 1998; Dicke & Sabelis 1998; Dicke *et al*. 2003) (Fig. 3). These concepts have drawn increasing attention to the testing of whether belowground interactions follow the same ecological principles. It is known that the belowground parts of plants emit VOCs upon insect attack, similarly to the green parts of plants (Aratchige *et al*. 2004; Rasmann *et al*. 2005; Crespo *et al*. 2012). Due to their very low experimental accessibility, the belowground VOC emission rates and the physicochemical properties of soils are less explored, even if their importance for plant survival and ecological balance in small habitants is recognized. In the past decade, the finding that the herbivory-induced volatiles of roots attract entomopathogenic nematodes (Boff *et al*. 2001; van Tol *et al*. 2001; Bertin *et al*. 2003; Rasmann *et al*. 2005; Degenhardt *et al*. 2009) gained increased attention. Similarly, a tri-trophic underground interaction has been shown for predatory mites (Aratchige *et al*. 2004) and parasitoids (Neveu *et al*. 2002) that are attracted by root-derived VOCs.

The specific VOCs that are responsible for the belowground signalling sent by the roots depend upon the plant species and the attacking herbivore. One of the main volatile cues used by insects for belowground orientation is respiratory CO_2 (Johnson & Nielsen 2012). Insects and plant-parasitic nematodes (Wenke *et al*. 2010) are able to follow the CO_2 gradient towards the roots. Reinecke *et al*. (2008) described, however, that the presence of VOCs in the soil headspace might diminish the influence of CO_2.

To date, terpenoids have received little attention in this context, even if their roles can be diverse (Lin *et al*. 2007). The belowground VOC patterns are often not comparable to the odour profiles emitted by the green parts of plants. Hiltpold & Turlings (2008) tested the diffusivity of biogenic VOCs in soil and investigated why maize roots solely release (*E*)-*β*-caryophyllene even if the leaves emit a bouquet of different compounds. These researchers showed that the best-diffusing compounds in a soil environment are sesquiterpenes and that (*E*)-*β*-caryophyllene is less costly to synthesize than the best-diffusing compound *α*-copaene. (*E*)-*β*-Caryophyllene can also function as an attractant for nematodes (Hiltpold *et al*. 2010).

Ali *et al*. (2011) identified the sesquiterpene pregeijerene (1,5-dimethylcyclodeca-1,5,7-triene) as a bioactive compound released by citrus trees after *Diaprepes abbreviatus* attack. As an indirect defence compound, this sesquiterpene increased herbivore mortality by attracting different native entomopathogenic nematodes. Pregeijerene also functions in other systems, such as in the protection of blueberry fields from herbivorous larvae (Ali *et al*. 2011).

As another example, the red clover root borer (*Hylastinus obscurus*) detects several volatiles emitted by red clover (*T. pratense* L.) plants, as determined by EAG. The male borer, and not the female, is able to use the plant volatiles to search for the host, as determined through bioassays (Palma *et al*. 2012). Previously, Tapia *et al*. (2007) showed that the response of *H. obscurus* differs according to the VOC profile, which changes during plant ontogenesis. In their study, different concentrations of the VOCs were the cause of the different responses observed. Similarly, the concentrations of VOCs from conifer roots were found to be crucial for the orienting behaviour of *Hylobius abietis* (Nordlander *et al*. 1986).

The mechanism through which root-emitted VOCs directly affect root herbivore behaviour was explored by Robert *et al*. (2012), who described that the root feeder *D. virgifera* is attracted and better off on roots already fed on by its conspecifics (Fig. 3). In contrast, plants infested with a leaf herbivore were found to be less attractive to the root feeder. Two possible VOCs originating from roots mediate this signalling: induced (E)-*β*-caryophyllene as an attractant and suppressed ethylene as a repellent (Robert *et al*. 2012).

Moreover, a few studies have connected the above- and belowground interactions: Pierre *et al*. (2011) showed that dual herbivory (root and shoot herbivory by *D. radicum* and *Pieris brassicae*, respectively) of turnip plants (*Brassica rapa*) induces novel compounds compared with one-organism-based herbivory. However, these researchers did not test whether the tri-trophic interactions are affected. The first study including both below- and aboveground herbivory and tri-trophic signalling at both levels was conducted by Rasmann & Turlings (2007). These researchers showed that the entomopathogenic nematode *Heterorhabditis megidis* and the parasitic wasp *Cotesia marginiventris* are highly attracted to their hosts, *D. virgifera* and *Spodoptera littoralis*, respectively, only when the host was feeding on the plants. The simultaneous occurrence of below- and aboveground herbivory negatively influenced the tri-trophic signalling (Rasmann & Turlings 2007). Another multi-trophic study (Olson *et al*. 2008), which included cotton (*Gossypium* spp.), *Helicoverpa zea*, *Meloidogyne incognita* and the parasitic wasp *Microplitis croceipes*, showed that root feeding had little influence on the VOC odour profile and hence the tri-trophic interaction (Fig. 3).

The specificity of these VOCs signals is a less explored topic: De Moraes *et al*. (1998) provided the first demonstration that aboveground tri-trophic interactions employ a high level of specificity. In fact, the belowground responses of plants and insects at the levels of the induced plant VOCs, the elicitation by herbivores and the behaviour of nematodes also appear to be highly specific (Rasmann & Turlings 2008; D'Allessandro *et al*. 2014).

Root VOCs play a role in interactions with microbes

Plants need to constantly defend and cope with various pathogenic microbial species. Plant VOCs play several roles in these interactions. For example, plant VOCs may exert direct antimicrobial activity that inhibits the spread of plant pathogens (Cardoza *et al*. 2003; Huang *et al*. 2003). VOCs can also inhibit microbial growth (Lin *et al*. 2007; Wenke *et al*. 2010) and function as carbon source for microbes (Zak *et al*. 1994; Gramms & Bergmann 2008). Gramms & Bergmann (2008) observed that VOCs could be a significant source of carbon, thus promoting the growth of certain basidiomycetous soil fungi in poor natural soils. *Pseudomonas fluorescens* and *Alcaligenes xylosoxidans* are even able to use the monoterpene *α*-pinene as a sole carbon source (Kleinheinz *et al*. 1999).

Similarly to animals, microbes are also attracted by the CO_2 gradient (Bécard & Piché 1989). Other root-based VOCs of different biosynthetic origins as reviewed above are been found to have a defensive function: for example, the monoterpene *β*-phellandrene is an effective bioagent against the pathogen *Fomes annosus*, and emissions of 1,8-cineole help defend against several microbes (Wenke *et al*. 2010). In addition, VOCs, mostly oxygenated fatty acid derived C6 and C9 alcohols, emitted by wheat and chickpea roots were found to impair the growth of pathogenic *Fusarium* spp. in the field (Cruz *et al*. 2012).

Ecological studies of the soil system are even more complex because the emitted VOC themselves, as well as their oxidation products, have ecological effects. As shown earlier, (*E*)-*β*-caryophyllene itself plays many ecological roles in soil environments, but its epoxide has shown a much

stronger repellent effect on diverse fungal species (Hubbell *et al*. 1983). In fact, reliable ecological studies should take into account the wide spectrum of different factors that participate in the maintenance of the balance of soil habitats.

VOC-based plant–plant belowground interactions

Some rare plant-to-plant interactions have been described in the literature at the root level: VOCs from snapdragon flowers inhibit Arabidopsis root growth (Horiuchi *et al*. 2007), and the VOCs from Echinacea roots exert allelopathic effects on several different plant species (Viles & Reese 1996). Belowground VOCs can also mediate the priming of defence responses in neighbouring plants. Falik *et al*. (2011) showed that unstressed plants are able to perceive stress cues sent by the roots of their drought-stressed neighbours. Moreover, the unstressed plants were found to be able to send the signal further, thereby eliciting stress responses in other unstressed plants (Falik *et al*. 2011).

Interactions mediated by microbial VOCs

Bacterial VOCs

Exposure to bacterial VOCs can reduce growth and inhibit spore germination in various fungi (Moore-Landecker & Stotzky 1972; Wright & Thompson 1985; McKee & Robinson 1988; Fiddaman & Rossall 1993). The mechanism through which bacterial VOCs affect fungal growth thus depends upon different factors, such as the environmental constrains, the fungal age and the species (Mackie & Weatley 1999).

Bacteria appear to employ their volatile profiles according to the environmental conditions, such as the presence of neighbouring plants, other bacteria or fungi (Kai *et al*. 2009). Comprehensive summaries of the effects of bacterial VOCs on fungal growth are documented in recent surveys (Wheatley 2002; Zou *et al*. 2007; Kai *et al*. 2009). These surveys clearly demonstrate that the most prominent effect of bacterial VOCs is, indeed, growth inhibition resulting in fungistasis. Soil fungistasis, that is, inhibition of fungal propagules, is a phenomenon that is apparently largely mediated by VOCs. In fact, several bacterial isolates have fungistatic activities (Effmert *et al*. 2012), and only a few tested fungal species remain unaffected when confronted with bacterial volatiles (Kai *et al*. 2007). For example, the VOCs of several antagonist bacterial species are effective growth-inhibiting agents of the soil-borne phytopathogenic fungus *Rhizoctonia solani*. *R. solani* can cause serious damage in agricultural systems and natural forests; thus, it would be economically interesting to develop VOC-based biological control methods (Kai *et al*. 2007). In another study, Mackie & Weatley (1999) tested the survival of different fungal species growing in atmospheric contact with soil bacteria and showed that VOCs from all of the bacterial species tested negatively affected the hyphal growth of at least one fungal species. Overall, half of the tested bacterial VOC profiles possessed both stimulative and inhibitory activity, and some exerted only growth inhibitory effects. However, none of the bacteria tested was found to exert only stimulatory effects (Mackie & Weatley 1999). In addition, the VOCs from the bacteria *Bacillus subtilis*, *Bacillus pumilus* and *Paenibacillus polymyxa* inhibit the growth of several common fungal species (Fiddaman & Rossall 1994; Campos *et al*. 2010).

The bacterial bioactive VOCs of interest are trimethylamine, benzaldehyde and *N*,*N*-dimethyloctylamine. These exhibit very strong antifungal activity even at low levels in soils (Chuankun *et al*. 2004). Campos *et al*. (2010) summarized several other microbial VOCs with antibiotic properties and suggested that VOC-mediated interactions may be far more widespread than presently thought.

In contrast to the increasing knowledge of how bacterial VOCs impair fungal fitness, almost nothing is known regarding the impact of these volatiles on the bacteria itself. It is well known that bacterial species communicate with each other through cell-to-cell communication, but the extent of this communication that is mediated by VOCs is unknown (Ryan & Down 2008; Kai *et al*. 2009). A few studies have demonstrated the effect of bacterial VOCs on the growth of other bacterial species: the volatiles emitted by *Veillonella* species and *Bacteroides fragilis* caused growth inhibition in different enteropathogenic bacteria (Hinton & Hume 1995; Wrigley 2004). In addition, Kai *et al*. (2009) demonstrated that the metabolism of *Burkholderia cepacia* changed in a bipartite Petri dish with *S. plymuthica*.

Fungal VOCs

Several reports have shown the broad and complex spectra of the VOCs released by fungi (Kramer & Abraham 2012; Müller *et al*. 2013). However, the ecological impact of fungal VOCs in the soil system remains mostly unexplored (Fig. 3). Fungal VOCs, similar to other VOCs, often have antibiotic activity. For example, the antagonistic fungal species *Trichoderma* spp. can inhibit the growth of pathogenic fungi on a plant by producing VOCs and other antibiotics (Chakraborty & Chatterjee 2008). The odour profile of the fungus *Muscodor albus* can have drastic effects, including the killing of several pathogenic fungi and bacteria (Strobel *et al*. 2001). Schalchli *et al*. (2011) reported the fungicide effects of VOCs released by the saprobiont *Schizophyllum commune* against the plant pathogens *B. cinerea* and *Mucor miehei*. Fungal volatile isolates not only reduce the fitness of other fungi but can also affect bacteria; however, studies of VOCs acting as bactericides are scarce. In addition, short-chain semi-volatile fatty acids from *B. fragilis* and from *Veillonella* species have growth-reducing effects on several enteropathogenic bacteria (for a review, see Campos *et al*. 2010).

As in the plant kingdom, fungus-to-fungus interactions involve VOCs. For example, the basidiomycetes *Hypholoma fasciculare* and *Resinicium bicolor* change their emission profiles when their mycelia come into physical contact (Hynes *et al*. 2007). These changes apparently inform the fungi about each other and appear to inhibit the growth of the fungi in unbeneficial directions.

Interesting observations regarding fungus-to-fungus communication revealed that the wild-type *F. oxysporum* MSA 35 strain is able to reduce the growth of and the expression of virulence genes by the pathogenic *F. oxysporum* through VOCs. The volatile profile of these two strains of *F. oxysporum* differed in the presence of sesquiterpenes, which were emitted only by the antagonist wild-type fungus. Sesquiterpenes were missing completely from the VOCs profile of the pathogenic fungus (Minerdi *et al*. 2009).

Microbial VOCs involved in the communication of plants and animals

Bacteria interact with plants by VOCs that either promote plant fitness (Ryu *et al*. 2003) or reduce it (Kai *et al*. 2008; Blom *et al*. 2011). Kai *et al*. (2009) provided a nice overview of the so-far published effects of bacterial VOCs on plants. The inhibitory effect of bacterial VOCs on plants is often growth reduction (Vespermann *et al*. 2007; Tarkka & Piechulla 2007; Kai *et al*. 2008; Kai *et al*. 2010). Some bacterial VOCs, such as hydrogen cyanide, can even be deadly to plants (Blom *et al*. 2011). However, the bacterial volatile 2,3-butanediol confers growth-promoting effects (Ryu *et al*. 2003). Experimentally, the plant growth promotion effects of VOCs need to be investigated under ambient CO_2 conditions because high CO_2, for example, in sealed Petri dishes, act as a fertilizer and can enhance plant fitness (Kai & Piechulla 2009). A microarray analysis of Arabidopsis grown in the presence of *B. subtilis* VOCs revealed that more than 600 genes change their expression levels (Zhang *et al*. 2007), underlining the importance of bacterial VOCs in the triggering of plant responses.

Microbial VOCs can also inhibit the development and well-being of animals. The VOCs emitted by several different bacterial species (*B. subtilis*, *P. fluorescens*, *S. plymuthica* 4R × 13 and *Xanthomonas campestris* pv. *vesicatoria*) impair the growth of the protozoan *Acanthamoeba castellanii* and are even lethal to the protozoan *Paramecium caudatum* (Kai *et al*. 2008). Another study demonstrated that bacterial VOCs affect the well-being of nematodes (Gu *et al*. 2007). Nematodes such as *Caenorhabditis elegans*, a common nematode in soils, can detect bacterial VOCs through their chemoneurons for orientation purposes (Sengupta *et al*. 1996).

Similar to bacteria, fungal VOCs also affect plant and animal fitness. The volatile isolates of *Muscodor albus* and those of *F. oxysporum* exhibit a nematicidal effect (for review, see Campos *et al*. 2010). Truffles also produce a wide blend of VOCs. Splivallo *et al*. (2007) provided the first demonstration of an ecological role of these volatiles: these volatiles are considered phytotoxic because they cause rapid and efficient leaf bleaching and inhibit root growth in *Arabidopsis thaliana* (Splivallo *et al*. 2007).

Mycorrhization is well known for its growth-promoting effects (Sharma *et al*. 1997; Jung *et al*. 2012). This symbiosis may also influence the plants' VOC emission and indirectly affects its defence responses (Fig. 3). In the context of VOCs, a mycorrhizal fungus helps plants activate immune responses and set a primed state that speeds up the plant's acute defence responses, for example, by VOCs in stressed plants (Jung *et al*. 2012). Rapparini *et al*. (2007) reported changes in the sesquiterpene emissions from *Artemisia annua* L. after infection with arbuscular mycorrhiza (*Glomus* spp.). Mycorrhization also induces the emission of green leaf volatiles (degradation products due to lipoxygenase activity) in *Plantago lanceolata* by herbivory or mechanical wounding (Fontana *et al*. 2009). Interestingly, herbivore infection in combination with mycorrhization, however, resulted in a lower sesquiterpene emission from *P. lanceolata* plants than that obtained by herbivory alone. The induction of VOC emissions was also described in peppermint (*Mentha piperita*) infected by an endophytic fungus (Mucciarelli *et al*. 2007). The above-mentioned examples are a few of the initial reports that have shown the functions of VOCs in mycorrhization. To better understand the impacts of mycorrhizal associations on the defence response of a broad range of plant species and their effects on different trophic levels, additional investigations are needed.

Minerdi *et al*. (2010) described the ability of fungal VOCs to promote plant growth. The cultivation of lettuce plants in airborne contact with *F. oxysporum* MSA 35 VOCs (in consortium with bacteria) stimulated increased shoot growth and overall biomass, as well as higher chlorophyll content. These researchers identified β-caryophyllene as at least one of the VOCs responsible for this growth-promoting effect (Minerdi *et al*. 2010). Because *F. oxysporium* MSA 35 lives naturally in consortia with bacteria, it is likely that either both organisms synthesize sesquiterpenes or each organism influences the other to stimulate synthesis. Indeed, there is growing evidence that fungal VOCs can have positive effects on plants; for example, Hung *et al*. (2012) described the plant growth-promoting activity of fungal VOCs. Arabidopsis seedlings grown in aerial contact with *Trichoderma viride* were taller and larger, flowered earlier and had more lateral roots than the control plants. Recently, the plant growth-promoting effects of selected compounds (2-methyl-propanol and 3-methyl-butanol) from the VOC blend produced by the plant growth-promoting fungus *Phoma* sp. GS8-3 were verified in *Nicotiana attenuata* (Naznin *et al*. 2013). However, the underlying mechanisms in the plants and the ecological relevance of these effects are unknown.

VOC-based multi-trophic interactions – microbes, animals and plants

Plants constantly live in connection with different environmental constrains. Thus, comprehensive ecological studies should pay attention to the multi-trophic interactions that occur in the soil system. The fungi–plants–insects interactions are complex and highly balanced (Gao *et al*. 2005; Márquez *et al*. 2007; Kai *et al*. 2009). Due to the large number of unexplored fungal species in soil, a high amount of information remains to be elucidated (Kramer & Abraham 2012). Some studies have shown that these multiple chemical networks are modulated in concert with fungi, bacteria and even viruses (Márquez *et al*. 2007). Indeed, several interacting microorganisms maintain the ecological and functional

balance of the soil system. In coffee plantations, VOCs from antagonist fungal species, for example, act mutually as biocontrol agents limiting the survival rate of parasitic nematodes. In addition, these same species (fungi and nematodes), together with the VOCs from bacterial microbes, limit the growth of the nematode-predator fungus *Arthrobotrys conoides* (Freire *et al*. 2012).

Microorganisms can also act as mediators of plant–herbivore interactions in the soil (Jallow *et al*. 2008). Fungal VOCs can, for example, function as vector attractants, for example, *Fusarium verticillioides* causes widespread mould disease in maize, releases a bouquet of volatiles including alcohols, acetaldehyde and ethyl acetate that have been proven to attract sap beetles. Sap beetles feed on maize but function also as vectors by spreading the fungal species (Bartelt & Wicklow 1999).

Many studies have demonstrated that pathogen infection in plants can change the plant's defence responses against herbivores (e.g. Erb *et al*. 2011). In tomato plants (*Lycopersicon esculentum*), changes in the tri-trophic defence responses were observed after infection with the endophytic fungus *Acremonium strictum*. Thus, the tomato plants became more attractive to the polyphagous moth *Helicoverpa armigera* due to a change in their VOC profile (Jallow *et al*. 2008).

In contrast, symbiotic fungi are known to have many positive effects on plants. Recently, the consequences of root microbes on aboveground tri-trophic signalling were explored (Pineda *et al*. 2013), and the findings showed that beneficial root-colonizing microbes can trigger an adjustment of the herbivory-induced VOC emissions in Arabidopsis and thereby change the attraction of the parasitoid *Diaeretiella rapae* foraging the leaf herbivore (Pineda *et al*. 2013).

FUTURE PERSPECTIVES

Further extensive, qualitative and quantitive measurements of soil VOCs exchange are clearly warranted in all ecosystems but especially in less known, highly productive, and diverse tropical forests, in order to shed light on the actual role and the quantification of soil as source or sink in the soil-atmosphere VOC exchange budget.

Nevertheless, thanks to the enormous progress in analytical techniques, which allow analysis and identification of traces of VOCs in soils and isolates from roots, bacteria and fungi, the structural diversity, concentrations and emissions of soil-born VOCs have now been partly described as reported in this review. The generally low emission rates and low air space concentrations of these soil-borne VOCs facilitate their signalling role. Furthermore, this signalling role might explain why emission rates from non-decomposition processes are much lower than emission rates from decomposition processes.

Progress in cultivation of yet not-culturable bacteria and fungi in combination with the various molecular tools and genomic resources will dramatically enlarge the known number of VOCs emitted by soil organisms in the next years. This progress in structure identification in combination with molecular and genetic markers will speed up the development of VOCs-based phenotyping of microbes with multiple applications in ecology, biotechnology, and food and health control. At the moment, we only see the tip of the iceberg on the diversity of biological interactions active in the soil system and the rhizosphere between plants, microbes and arthropods. It will be interesting to understand whether the functions of VOCs in direct and indirect defence aboveground are conceptually applicable to the soil system. Progress has been made in determining the function of root-derived VOCs as defences or attractants in interactions with soil-borne herbivores and their parasites. However, much remains to be learned about the role of different plant-derived VOC signals in the soil, especially in associations of roots with microbial colonizers (i.e. growth-promoting bacteria, various types of mycorrhiza, N-fixing nodules). Mutant-based approaches, which rely upon an improved understanding of the biosynthesis of VOCs in roots of different model systems, in conjunction with microbial metagenomic analyses, may help dissect the function of different classes of compounds in selecting root-zone microbial communities. Likewise, effects of soil microbial VOCs as elicitors of plant signalling responses and gene regulatory networks will require further attention.

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