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Process understanding of soil BVOC fluxes in natural ecosystems: a review

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Key Points:

- We present biotic and abiotic drivers for soil BVOC emissions and sinks
- We summarize the often-reported compounds and key processes regulating their fluxes
- We propose a generic framework for including soil BVOCs in ecosystem models

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Abstract

Biogenic volatile organic compounds (BVOCs) can be released from soils to the atmosphere through microbial decomposition of plant residues or soil organic carbon, root emission, evaporation of litter-stored BVOCs, and other physical processes. Soils can also act as a sink of BVOCs through biotic and abiotic uptake. Currently, the source and sink capabilities of soils have not been explicitly accounted for in global BVOC estimates from the terrestrial biosphere.

In this review, we summarize the current knowledge of soil BVOC processes and aim to propose a generic framework for modelling soil BVOCs based on current understanding and data availability. To achieve this target, we start by reviewing measured sources and sinks of soil BVOCs and summarize commonly reported compounds. Next, we strive to disentangle the drivers for the underlying biotic and abiotic processes. We have ranked the list of compounds, known to be emitted from soils, based on our current understanding of how each process controls emission and uptake. We then present a modelling framework to describe soil BVOC emissions. The proposed framework is an important step towards initializing modelling exercises related to soil BVOC fluxes. Finally, we also provide suggestions for measurements needed to separate individual processes, as well as explore long-term and large-scale patterns in soil BVOC fluxes.

Plain Language Summary

Living plants emit biogenic volatile organic compounds (BVOCs), which have impacts on regional and global climate. However, BVOCs can also be released from fallen leaf litter, plant roots, and soil organic matter, and some compounds are also consumed by soil microbes. In this article, we begin by sorting out the processes that govern soil emissions and uptakes of BVOCs, and summarize the current understanding and available data for each process. Furthermore, we propose a generic modelling framework to add soil BVOC-related processes into the typical structure existing in many ecosystem models. We also provide suggestions for future measurements that would help with model-data integration.

1 Introduction

Plant-emitted biogenic volatile organic compounds (BVOCs) have been extensively studied and the regional and global estimates of plant BVOC emissions are used as key drivers for atmospheric chemistry models to study the impacts of terrestrial BVOCs on the climate system (Guenther et al., 2012). Soil-related BVOC emissions could also contribute to ecosystem emissions, and thereby impact atmospheric chemistry (Kramshøj et al., 2016; Mochizuki et al., 2015; Nölscher et al., 2016), but they have been less well-studied than plant emissions. BVOCs can be released through microbial decomposition of plant residues or soil organic carbon (SOC) (Aaltonen et al., 2013; Insam & Seewald, 2010; Leff & Fierer, 2008; Stahl & Parkin, 1996), evaporation of litter-stored BVOCs (Aaltonen et al., 2011) and other physical processes (e.g., desorption from leaf litter tissue (Warneke et al., 1999), and from soil organic matter (Bachy et al., 2018; Schade & Custer, 2004)). Moreover, plant roots can also emit BVOCs (Kreuzwieser & Rennenberg, 2013). Similar to aboveground plant volatiles, soil BVOCs are produced for signaling, communication, defense, and stimulation or inhibition of plant or microbial growth (Delory et al., 2016; Insam & Seewald, 2010). Soils can also act as a sink of BVOCs through both abiotic (Ruiz et al., 1998) and biotic uptake (Cleveland & Yavitt, 1998; Owen et al., 2007). Currently, neither the source nor the sink capabilities of soils have been explicitly accounted for in the global BVOC estimates from the terrestrial biosphere (Sindelarova et al., 2014). However, the importance of soil emissions, including those from litter, roots, and SOC, in ecosystem BVOC exchange are increasingly acknowledged (Aaltonen et al., 2011; Bourtsoukidis et al., 2018; Kramshøj et al., 2016), for their contributions to total BVOC inventories (Gray et al., 2014; Janson, 1993) and the seasonal patterns observed at the ecosystem level (Aaltonen et al., 2011; Hakola et al., 2003; Hellén et al., 2006; Mäki et al., 2019).

Current field estimates of the contribution of soil emissions to the total ecosystem fluxes of BVOCs range from less than one percent (Asensio et al., 2007b) to tens of percent (Aaltonen et al., 2013; Kramshøj et al., 2016; Schade & Goldstein, 2001), with large variations between ecosystems, litter types, and seasons. In the Arctic, with low plant biomass, soil emissions can contribute up to 20% of the ecosystem emission (Kramshøj et al., 2016). Soil BVOC emissions from the boreal pine forest floor can exceed branch-level emissions in spring and autumn, when photosynthesis is limited by low temperature and light (Hellén et al., 2006) but litter is in a relatively early stage of decomposition (Isidorov et al.,

2010; Mäki et al., 2019; Rantala et al., 2015). Hakola et al. (2003) measured BVOC concentrations above a Finnish coniferous forest and found that the atmospheric monoterpene concentration in autumn was close to summer concentrations, and suggested that needle litter is an important autumn source of BVOCs. Bourtsoukidis et al. (2018) found that sesquiterpene emissions from Amazonian soils were of comparable magnitude to the canopy emissions during dry seasons, and also illustrated the important role of soil sesquiterpene emissions on O₃ reactivity at the forest floor. Staudt et al. (2019) reported that a Maritime pine forest ground was a large source of pinenes. However, other studies suggest that soil emissions play an insignificant role because they only constitute a very small fraction of ecosystem emissions (Asensio et al., 2007a; Greenberg et al., 2012; Hayward et al., 2001). The relative contribution of soil emissions to ecosystem fluxes is expected to vary with ecosystem, litter and soil types, but the methods applied to measure these two levels of fluxes can also have an impact on the concluded soil contributions. Nevertheless, a few global estimates of soil sources and sinks have been described based on limited site measurements: Sawada and Totsuka (1986) estimated that global ethylene emissions from the soil A0 layer amounts to 3.7 Tg/yr, which is around 22% of the total biogenic emission. Warneke et al. (1999) extrapolated from laboratory studies and concluded that globally, around 6-8 Tg/yr of acetone and 18-40 Tg/yr of methanol are emitted into the atmosphere from soil. Cleveland and Yavitt (1997) suggested that soil provides a global isoprene sink of 20.4 Tg/yr. These global numbers bear great uncertainties, with a very low geographical coverage of measurements and poor understanding of the underlying processes.

The potential impacts of soil BVOC emissions on atmospheric chemistry are even less well-understood than emission magnitudes. Faiola et al. (2014) found that litter-derived emissions can facilitate the formation of organic aerosols in spring and autumn in a temperate pine forest. Furthermore, the potential role of soil (including litter) BVOC emissions in decreasing reactive hydroxyl radical (OH) has been hypothesized based on atmospheric chemistry models and OH reactivity measurements. Studies of OH reactivity often indicated incompletely determined sources of BVOCs, and suggested a missing OH sink within the canopy (Di Carlo et al., 2004; Nölscher et al., 2016; Sinha et al., 2010).

BVOCs can also influence soil biogeochemical processes. E.g., BVOCs increase microbial respiration at the soil-litter interface (Ramirez et al., 2010), and negatively impact soil N transformations (Smolander et al., 2006) and methane oxidation (Amaral & Knowles,

1998); BVOCs are also involved in the regulation of plant and root growth (Ditengou et al., 2015; Ryu et al., 2003), plant-plant and plant-other organisms interactions (Delory et al., 2016; Insam & Seewald, 2010; Wenke et al., 2010). BVOC-mediated interactions in soils were reviewed by Peñuelas et al. (2014) and Insam and Seewald (2010), so will not be addressed here. The work by Insam and Seewald (2010) focuses on soil microbial BVOCs and presents literature regarding emission and uptake patterns of BVOCs for different soil organisms, mainly bacteria and fungi. It further outlines potential directions for attaining a better understanding of soil BVOC emission profiles. The review by Peñuelas et al. (2014) covers topics ranging from the potential source and sink strength of soil BVOCs to multi-dimensional interactions of volatile compounds in soil systems. Both papers give an excellent overview of the current state of understanding for soil BVOCs and clearly express perspectives on future directions in this field. In contrast, our review covers literature with the main focus on processes understanding of soil BVOC sinks and sources, and proposes a framework for modelling soil BVOCs in existing ecosystem models. We start by reviewing measured sources and sinks of soil BVOCs and disentangling the biotic and abiotic processes controlling BVOC fluxes. Next, we summarize the most-often reported compounds and present generic mathematical equations for each process. Finally, we provide suggestions for conducting soil BVOC measurements in the laboratory and field.

We included three types of articles in our review: (1) laboratory and field studies presenting the measured SOC, root and litter BVOC emissions, separately or as a whole; (2) papers that summarized the processes influencing soil BVOC fluxes; and (3) modelling papers with a focus on general gas (not only BVOCs) transport and biogeochemical cycling in soils. We also included papers presenting forest floor emissions with clear indications of soil emissions, but want to acknowledge that in these papers, emissions of understory vegetation and soil cannot be completely separated. We have excluded papers dealing with soil BVOC measurement techniques, BVOCs from cultivated ecosystems, anthropogenic soil volatile organic compounds (VOCs), and BVOC measurements right after cutting the aboveground vegetation (attempting to exclude induced BVOC emission (Loreto et al., 2006; Rinnan et al., 2013)). We also included a few studies conducted on agricultural soils which contain clear discussions on the underlying process of the measured fluxes and compounds of interest. For papers linking BVOC emissions with bacterial or fungal community variations, we refer the reader to the reviews by Insam and Seewald (2010) and Peñuelas et al. (2014).

2 Soil BVOC sources and sinks

Literature focusing on the quantification of soil BVOC fluxes is limited compared to the number of studies on plant emissions. Studies that have measured BVOC release from litter and SOC under laboratory conditions (Leff & Fierer, 2008; Svendsen et al., 2018), in contrast to *in situ* measurements, allow for separation of the sources of the release. Root emissions (including emissions from the root itself and associated fungi and bacteria) are generally difficult to separate from other sources (Lin et al., 2007) and can often be induced due to stress (Ali et al., 2011; Chiriboga et al., 2018; Kelsey et al., 2016) or responses to other environmental factors to mediate plant-plant and plant-soil organism interactions (Delory et al., 2016; Peñuelas et al., 2014; Walker et al., 2003; Wenke et al., 2010). To identify whether soils can function as a sink for BVOCs, soil samples are typically exposed to known concentrations of BVOCs, and reductions in these concentrations are attributed to soil uptake (Owen et al., 2007; Ramirez et al., 2010). Under field conditions, soil chambers have often been utilized for measurements of net soil BVOC fluxes (Mäki et al., 2017; Owen et al., 2007).

2.1 BVOC sources

Soils emit BVOCs as a result of microbe-mediated decomposition of SOC and plant residues, evaporation of stored compounds in leaf litter, and release of plant-metabolized BVOCs from roots. Below, we describe BVOC sources in detail, based on the different substrate types.

2.1.1 Litter emissions

Plant litter-emitted compounds vary in quantity and type for different plant species, and the types of BVOCs emitted during decomposition processes can also vary over time (Gray et al., 2010; Leff & Fierer, 2008). The leaf litter of closely related plant species (with similar structure and harbored microbial communities) tends to have similar BVOC emission profiles (Gray et al., 2010; Svendsen et al., 2018). Litter BVOCs are comprised of compounds produced in living plants and stored in leaves (Aaltonen et al., 2013; Svendsen et al., 2018), as well as new compounds produced by microbes during decomposition (Leff & Fierer, 2008). Generally, leaf litter exhibits higher emission rates than SOC (Hayward et al., 2001; Leff & Fierer, 2008; Ramirez et al., 2010; Sawada & Totsuka, 1986) because of the larger fraction of labile carbon and/or the release of stored BVOCs (Aaltonen et al., 2011;

Svendsen et al., 2018). Litter has often been suggested as the main BVOC source in a forest besides vegetation (Asensio et al., 2008a; Hellén et al., 2006; Mäki et al., 2017; Schade & Goldstein, 2001).

2.1.2 SOC emissions

BVOCs produced from SOC can originate from different pathways of microbial metabolism (e.g., aerobic decomposition, fermentation, and terpenoid biosynthesis). Measuring BVOC fluxes on bare soil or on soils with litter and vegetation removed could potentially separate SOC emissions from litter sources, but will not allow for quantification of the root contribution (Asensio et al., 2008b; Kramshøj et al., 2016; Rasheed et al., 2017). Similar to measurements of root-only emission, determination of BVOC fluxes from SOC alone, from an *in situ* vegetated area or under laboratory conditions, is difficult because removal of the roots and/or moss layer will destroy the soil structure. Therefore, reported fluxes or compound profiles from SOC alone include the side-effects (changed soil structure, altered microsites, and conditions for microorganisms) from manual removal of roots and/or moss layers within soils (Rinnan et al., 2013). Nevertheless, through laboratory measurements of root-free soils across a wide range of ecosystems, a large variety of compounds were detected by Leff and Fierer (2008). However, 70% of the compounds could not be identified with high confidence based on the method used. Rinnan et al. (2013) detected some terpenoids from temperate heath soils under off-season (outside of growing season) conditions. Kramshøj et al. (2018) found a wealth of BVOCs from Greenlandic permafrost soils upon thawing. Through desiccation experiments, both Veres et al. (2014) and Bourtsoukidis et al. (2018) found diverse compounds released from SOC. In brief, SOC is responsible for a diverse array of soil BVOC emissions.

2.1.3 Root emissions

Plant roots (including their associated mycorrhizal fungi and microbes) can synthesize and emit different compounds in the rhizosphere. In our review, the mycorrhizal microorganism-related emissions (i.e., from fungi and microbes) are all lumped into “root” emissions. Fluxes from roots may contribute considerably to total soil BVOC emissions (Gray et al., 2014). However, this is not consistently observed. While some studies have shown that the presence of roots increased BVOC emissions (Gray et al., 2014; Rinnan et al., 2013), others have reported reduced emissions (Asensio et al., 2007a) or no impact (Mäki et

al., 2017) on soil emissions. Direct measurement of root BVOC production without destroying the rhizosphere is difficult (Lin et al., 2007). The common strategy of separating root emissions from the remainder of soil emissions is to compare emissions from root-free soils with those from intact soils, attributing the difference to the root contribution. For instance, through comparison of soil BVOCs emitted from control plots with girdled plots, in which no flow of photosynthetic C takes place from shoots to roots, Gray et al. (2014) found that tree roots contribute half of the total C emitted from soils as BVOCs in a subalpine forest ecosystem. However, contrasting results were obtained by Mäki et al. (2017) in a boreal forest through trenching and placing isolating meshes to inhibit tree root growth. In that study, the authors found no significant differences between the control and the trenched plots. They concluded that plant-derived C flow into soil via roots did not clearly impact soil BVOC emissions and suggested that the C flow to the rhizosphere favors microbes that use BVOCs as a C source. This is also supported by Asensio et al. (2007a), who found that the presence of roots decreased the emissions of many compounds due to microbial decomposition. Disagreements regarding root contributions to soil BVOC emissions between studies may also result from differences in the plant species or experimental setup.

2.2 Soil as a BVOC sink

Soils can act as a sink of BVOCs through physical processes (adsorption to soil particles (Ruiz et al., 1998; van Roon et al., 2005) and dissolution in soil water), chemical processes (reactions with NO₃, OH radicals, ozone, and hydrogen peroxide (Insam & Seewald, 2010)), and biological processes (microbes using BVOCs as carbon and energy sources (Cleveland & Yavitt, 1997; Owen et al., 2007)). A loamy sand soil has been shown to consume up to 80% of BVOCs released during the litter decomposition period (Ramirez et al., 2010). Spielmann et al. (2017) exposed mountain grassland mesocosms and bare soils to increasing concentrations of isoprene and α -pinene (0–10 ppbv) in a laboratory setting and found soils to be the dominant sink for both compounds. Albers et al. (2018), through isotopic labelling, found that 5 out of 6 investigated BVOCs were rapidly mineralized by microbes in four different soils and illustrated that microbes could completely degrade BVOCs to CO₂. Gray et al. (2015) found that a large fraction (~68%) of isoprene was consumed by soils after 45 days of incubation and the uptake rate increased with increasing mixing ratios, reflecting the growth of microorganisms with increased exposure to isoprene (Cleveland & Yavitt, 1998).

Eddy covariance (EC)-measured BVOC fluxes point out the significance of BVOC uptake by ecosystems (Karl et al., 2004; Laffineur et al., 2012), but this approach alone cannot separate soil from vegetation uptake (deposition to vegetation surface and stomatal uptake).

2.3 Compounds and processes

Soil emissions differ from plant emissions, both in magnitude and chemical composition. Kesselmeier and Staudt (1999) gives an overview of plant emission inventories and Seco et al. (2007) focuses on plant-emitted, short-chained oxygenated BVOCs. Here, we list compounds known to be emitted from, and taken up by, soils and rank the level of understanding of the processes responsible for the sources and sinks (Table 1).

Methanol is the second most abundant hydrocarbon, next to methane, in the atmosphere, and is one of the dominant BVOCs emitted from soil (Asensio et al., 2008b; Oikawa et al., 2011; Ramirez et al., 2010; Schade & Goldstein, 2001). Methanol emissions originate from both biotic (Gray et al., 2010; Ramirez et al., 2010) and abiotic processes (Bachy et al., 2018; Warneke et al., 1999). Turnover of plant material (lignin and pectin) is one of the major biogenic sources of methanol (Fall & Benson, 1996; Schink & Zeikus, 1980). Methanol is also emitted from roots (Folkers et al., 2008; Oikawa et al., 2011), probably as a result of plant growth and maintenance processes (Folkers et al., 2008). SOC can also be a significant source of methanol through physico-chemical processes (Schade & Custer, 2004) and microbial activities (Asensio et al., 2008b; Bourtsoukidis et al., 2018). Methylophilic bacteria are common inhabitants in soils (Fall & Benson, 1996) and they can consume methanol, causing a net uptake in soil in different ecosystems (Asensio et al., 2007a; Kramshøj et al., 2018). Albers et al. (2018) showed very high and rapid methanol mineralization rates by microbes in four soil types.

Ethanol is a typical product of anaerobic fermentation and has been shown to be released from flooded roots (Kreuzwieser & Rennenberg, 2013). Gray et al. (2014) compared ethanol emissions from control and girdled plots (without active root systems) and found that the absence of active roots caused soils to shift from emission to uptake of ethanol. This alcohol has also been detected in litter emissions of beech (Warneke et al., 1999), pine, and spruce (Isidorov et al., 2003). Kramshøj et al. (2018) reported that ethanol was the compound emitted from permafrost soils upon thawing at the highest rates. They speculated that the

source of ethanol was likely fermentative decomposition of plant materials in anoxic soils. In plant leaves, ethanol is easily oxidized to acetaldehyde and further, to acetic acid (Kreuzwieser & Rennenberg, 2013) and its high water solubility makes it easily accessible to microorganisms. The uptake of ethanol by organic and mineral soils has been shown by Kramshøj et al. (2018).

Short-chain aldehydes, formaldehyde and acetaldehyde, are emitted by plant leaves (Kreuzwieser et al., 1999b; Seco et al., 2007). Formaldehyde is ubiquitous in the atmosphere and often regarded as an oxidation product of other VOCs. Formaldehyde emissions from plant leaves are thought to be due to the oxidation of methanol (Seco et al., 2007). DiGangi et al. (2011) found high emission rates of formaldehyde from soils under ponderosa pine forest based on *in situ* enclosure experiments, and suggested that formaldehyde emissions originated from ground litter. We are unaware of any laboratory data on litter-alone emissions of formaldehyde, although one study reported SOC formaldehyde production under aerobic conditions (Mancuso et al., 2015) and another study under anaerobic conditions (Kramshøj et al., 2018). Mancuso et al. (2015) explained that formation of formaldehyde was most probably linked to methylotrophic bacteria and occurred as a result of demethylation reactions. However, soil uptake of formaldehyde has also been shown both by soil samples under laboratory conditions (Kramshøj et al., 2018) and in a field setting (Gray et al., 2014). Formaldehyde, together with isoprene, were the two dominant compounds taken up by sandy soil in a subalpine ecosystem (Gray et al., 2014). Gray et al. (2014) did not identify the key process (es) for this uptake, but suggested that adsorption and dissolution might be responsible for the uptake. Acetaldehyde is known to be produced by flooded roots (Kreuzwieser et al., 1999a; Seco et al., 2007) and also from leaf litter (Greenberg et al., 2012; Schade & Goldstein, 2001; Warneke et al., 1999), but it could also be an oxidation product of ethanol. Acetaldehyde emissions from permafrost SOC and uptake by mineral and organic soils have been reported by Kramshøj et al. (2018), and the uptake has been shown to be of microbial origin.

Many studies reviewed by Kesselmeier and Staudt (1999) indicated that acetic and formic acids are the two most prominent volatile acids emitted by plants and emissions of both acids have subsequently been measured from 12 litter types during decomposition (Gray et al., 2010). Soil emissions of formic and acetic acid during the dry season in a savanna ecosystem were highlighted to be a significant source to the atmosphere (Sanhueza &

Andreae, 1991). A recent laboratory study reported high emission rates of both acids from ponderosa pine forest soil and found emissions to increase exponentially with soil temperature (Mielnik et al., 2018). However, net emission depends on the balance between production and uptake. For example, Gray et al. (2014) found that formic acid was emitted from soils containing active roots, but observed net uptake in soils without roots.

Acetone emissions from litter have been widely reported in both laboratory (Greenberg et al., 2012; Warneke et al., 1999) and field conditions (Greenberg et al., 2012; Schade & Goldstein, 2001). Heating and wetting plant materials can produce a large amount of acetone through physico-chemical reactions (Warneke et al., 1999). The same phenomenon also takes place in nature, where wetting of the warm top soil can largely contribute to the canopy-level acetone emissions (Schade & Goldstein, 2001). The EC measurements in this study by Schade and Custer (2004) indicated that acetone and methanol were the compounds emitted with the highest rates from bare soil during a heat wave in 2003. But the authors could not find any relationship between acetone emissions and the measured meteorological parameters, and instead suggested that the acetone emissions in the dry soils originated from biological production in deep soil, with higher water availability.

Bourtsoukidis et al. (2018) found that acetone emissions from SOC in aerobic conditions were an order of magnitude higher than those from the canopy. In contrast, Kramshøj et al. (2018) found that permafrost-released acetone can be taken up by overlying mineral and organic soils.

Isoprene emission from ecosystems is mainly associated with plant photosynthesis, although soil microorganisms also produce isoprene in pure cultures (Insam and Seewald (2010) and references therein). Isoprene emissions from forest floors can unfortunately, not be distinguished between vegetation and soil sources (Aaltonen et al., 2013; Hellén et al., 2006; Wang et al., 2018). Warneke et al. (1999) provided the only study we found reporting isoprene emissions from beech, oak, spruce, and grass leaf litter in response to heating and wetting. Mancuso et al. (2015), through comparisons of emissions and soil biochemical properties among three different kinds of soils, found higher isoprene emissions were from soils with higher microbial biomass and nutrient availability under aerobic conditions. Thus, isoprene was thought to be produced in soils as a microbial metabolite. Many soils contain isoprene-degrading microorganisms (Cleveland & Yavitt, 1997; Pegoraro et al., 2005) and the uptake of isoprene is closely linked to microbial activity (Gray et al., 2015). As such, low

or negligible net isoprene emissions can likely be attributed to a large soil uptake by microbes.

Monoterpenes are often the most emitted terpenoids from conifer litter (Hellén et al., 2006; Isidorov et al., 2010; Isidorov et al., 2003) and evergreen shrub litter (Svendsen et al., 2018). The monoterpenes emitted from litter could originate from the storage pools in needles, but also from microbial decomposition processes. Through comparisons of monoterpene concentrations in forest and clear-cut soils, Paavolainen et al. (1998) suggested that Norway spruce roots were a source of monoterpenes. Monoterpene emissions from coniferous roots (Lin et al., 2007) and elevated concentrations in the coniferous soil rhizosphere (Smolander et al., 2006) have also been reported. Asensio et al. (2007a) discovered both emissions and uptake of monoterpenes in the top 20 cm of soils from a natural holm oak forest. The uptake of monoterpenes increased with increasing soil moisture and the authors suggested that this was likely due to enhanced microbial activity when water limitations were relieved.

Sesquiterpenes are highly reactive compounds with moderate volatility and might easily be consumed or oxidized before escaping from soils. A few studies have linked soil sesquiterpene emissions to fungi (Horváth et al., 2012; Mäki et al., 2017). Lin et al. (2007) reported sesquiterpenes to be amongst the most emitted compounds from pine roots and Asensio et al. (2008b) also suggested high sesquiterpene emissions from roots in a Mediterranean shrubland. A recent study by Bourtsoukidis et al. (2018) reported strong sesquiterpene emissions from Amazonian soils (SOC only) and suggested they originate from soil microorganisms. Like monoterpenes, sesquiterpenes have also been shown to be released from the litter of evergreen conifers and shrubs (Isidorov et al., 2003; Svendsen et al., 2018).

SOC and litter have been found to release benzenoids both under laboratory and field conditions (Aaltonen et al., 2013; Kramshøj et al., 2018; Leff & Fierer, 2008; Svendsen et al., 2018). Svendsen et al. (2018) found benzenoids to be a significant fraction (~32%) of total BVOCs (measured using GC-MS) emitted from deciduous *Salix* litter. Both Isidorov and Jdanova (2002) and Leff and Fierer (2008) reported emissions of a variety of benzenoids from different kinds of litter samples. Wheatley et al. (1996) reported benzenoid emissions from agricultural soil under both aerobic and anaerobic laboratory incubations. Fast microbial mineralization of benzaldehyde in four different soils was shown by Albers et al. (2018), suggesting that soils can also take up benzenoids.

Both litter and SOC have been found to emit dimethyl sulfide (DMS) under laboratory (Jardine et al., 2015; Kesselmeier & Hubert, 2002; Mancuso et al., 2015) and field conditions (Staubes et al., 1989; Yi et al., 2010), with possible sources from the aerobic microbial metabolism of sulfur-containing amino acids (Jardine et al., 2015). Yi et al. (2010) found three types of forest soils were sources of DMS and also illustrated the contribution of litter-emitted DMS to the total soil emissions. Jardine et al. (2015), through measurement of real-time DMS ambient mixing ratios within and above a primary rainforest in central Amazon, showed that soil can contribute to the strong buildup of DMS mixing ratios during nights. They also demonstrated that soil can take up DMS.

Furan and its derivatives can be formed in soils through oxidation by iron and hydrogen peroxide (Huber et al., 2010). Kramshøj et al. (2019) reported 2-Methylfuran emissions from permafrost soils at 10 °C and 20 °C in laboratory incubations. Mancuso et al. (2015) reported methylfuran emissions from three different kinds of soils (one agricultural soil and two forest soils) under laboratory conditions.

3 Biotic and abiotic processes

The sources and sinks of BVOCs between soils and the atmosphere were introduced in section 2. Here, we review the drivers of the biotic and abiotic processes that need to be defined to link the processes to mathematic equations in a suggested model framework in section 4. Biotic processes include microbial decomposition, release from litter-storage, and root production. Abiotic processes include physical and chemical processes. Furthermore, the physical processes listed in Figure 1 are known to exist for general gas dynamics in soils, though some of these processes are still lacking supporting measurements for the compounds listed in Table 1. We describe these abiotic processes in this section and list literature (and mathematical methods), which may be useful for modelling these processes once soil BVOC data becomes available.

3.1 Biotic processes

Leff and Fierer (2008) found a positive correlation between both respiratory CO₂ emissions and microbial biomass, with BVOC production. Besides the release of BVOCs during microbial decomposition, microbes also consume a wide range of volatile compounds. Factors influencing microbial metabolism (like water content, and nutrient and oxygen availability) influence both the production and consumption of BVOCs by microbes and

therefore, affect the chemical composition and magnitude of fluxes (Cleveland & Yavitt, 1997; Insam & Seewald, 2010; Owen et al., 2007). For instance, lowering the water table depth of peat cores significantly reduced monoterpene emissions (Faubert et al., 2010). Sawada and Totsuka (1986) found that the soil A0 layer (containing litter) emitted considerable amounts of ethylene under aerobic conditions and Kramshøj et al. (2018) found that ethanol was produced in large quantities under anaerobic conditions as permafrost thawed. Litter age and quality, and the labile and recalcitrant fractions of SOC, affect microbial decomposition, and thus, the production rates of BVOCs. Decomposition of fresh litter requires less energy than the decomposition of aged leaves with more recalcitrant organic matter. Then, the decomposition of needle litter may take longer than for broadleaf litter (Cornwell et al., 2008), which may also affect the temporal dynamics of BVOC emissions (Svendsen et al., 2018).

Plant-synthesized BVOCs contribute to soil emissions via root exudates in the rhizosphere and leaf compounds stored in the litter. Kainulainen and Holopainen (2002) showed slow release of terpenoids from storage in needle litter over 19 months of decomposition, but so far no study has specifically identified potential drivers of the release of compounds from litter storage. The processes and associated drivers (stress-induced response and/or different levels of interactions, e.g., plant-plant, plant-soil organisms) of root emissions are varied and complex (Delory et al., 2016; Peñuelas et al., 2014). Furthermore, root exudates can also be rapidly used by microbes as C and energy sources (Kuzyakov & Larionova, 2005). Therefore, separating root production of BVOCs from emissions related to rhizosphere microbial activity is difficult (Lin et al., 2007) and some studies report emissions from the entire rhizosphere instead (Rasheed et al., 2017).

3.2 Abiotic processes

The exchange of gaseous BVOCs in soil air with the atmosphere above depends on the physical conditions for diffusion. Compounds retained in soil can dissolve in water, stay in gas phase, or be adsorbed to soil particles (Fig. 1). Dissolution and adsorption depend on gas concentrations in the soil and can be enhanced or reversed when the concentrations change.

Although a few laboratory studies (Gray et al., 2010; Leff & Fierer, 2008) have indicated that abiotic sources of BVOCs are generally less important than biotic ones, abiotic

processes might play a role in regulating the short-term patterns in BVOC fluxes: e.g., methanol emissions correlated with (high) soil temperature observed under drought conditions was interpreted as a sign of abiotic methanol desorption from heated soils (Schade & Custer, 2004). An increase in temperature could also concurrently increase microbial metabolism and therefore, it is generally difficult to separate temperature-induced increases in abiotic (e.g., physico-chemical) processes from biotic (microbial) responses.

3.2.1 Dissolution

Isoprenoids (e.g., isoprene, α -pinene, β -caryophyllene) and aromatic compounds are generally poorly water-soluble. Lower molecular weight compounds listed in Table 1, such as methanol, ethanol, formaldehyde, and acetone, are water soluble and can dissolve in soil water and evaporate to the atmosphere when conditions change. Henry's law is used to describe the solubility of gases in water; that is, the concentration of gas in water is proportional to the partial pressure of gas in the air above the solution. Henry's law constant varies between compounds and depends on temperature. At a fixed temperature, the higher the value of the Henry's constant, the more volatile the compounds are. Dissolved BVOCs can be adsorbed by soil particles, which will be discussed further in the next section.

3.2.2 Adsorption-Desorption

Adsorption and desorption of organic compounds can occur in both vapor and dissolved phases (Breus & Mishchenko, 2006; Ruiz et al., 1998). Organic vapors adsorb to soil particles through their affinity for ionically charged surfaces (Arocha et al., 1996; Morrissey & Grismer, 1999; Petersen et al., 1995). Total soil surface area (determined by soil particle size, particle density, and porosity) regulates soil adsorption capacities for organic gases (Petersen et al., 1994). Water vapor in soil pore spaces can compete for adsorption surfaces with organic vapors and therefore, it may be essential to consider the interactions and impacts of water vapor on adsorption (Site, 2001). Adsorption of gas-phase organic compounds is often described by the Brunauer-Emmett-Teller (BET) model, which defines the relationship between vapor pressure and the amount of adsorbed gas per unit of surface area. At low vapor pressure, the BET model is reduced to a linear adsorption isotherm, where gas-solid partitioning is mainly influenced by vapor pressure (Petersen et al., 1995). At high vapor pressure, the BET model accounts for surface area adsorption and vapor condensation (Ong & Lion, 1991).

Once compounds are dissolved in soil water, the adsorption-desorption relationship depends on the concentration in solution and the adsorbed amount of organic compounds on soil particles, which has been described by various linear and non-linear isotherms (Hinz, 2001; Kothawala et al., 2008). There are generally more studies regarding the adsorption-desorption of dissolved organic compounds than organic gases, and the current literature covering the adsorption of volatiles on soil particles addresses mainly the impacts on contaminant transport in soils.

3.2.3 Diffusion

Gas diffusion in soils is driven by concentration gradients and is modulated in Fick's law with a diffusion coefficient. Gas diffusion in water is about 10000 times lower than in air, so soil water content can be used to determine effective gas diffusion in soils (Borggaard & Elberling, 2007). Gas diffusion is often thought to be the main mechanism of gas transport in vadose zone. Kramshøj et al. (2019) found that drainage of meltwater from permafrost significantly increased BVOC emissions from fen soils and the authors attributed this phenomenon to the low diffusion rates in water-logged soils.

Similar to modelling other gases, such as CH_4 and CO_2 , the diffusion coefficient of BVOCs in Fick's law depends on soil temperature and a series of soil properties, such as texture, porosity, and tortuosity of the pore system. Moldrup et al. (2000) provided a detailed review on different algorithms for estimating gas diffusion coefficient in soils. Ambient BVOC concentrations near the soil surface are necessary for determining the magnitude and direction of diffusion.

3.2.4 Advection

Gas transport in the vadose zone can also be caused by changes in atmospheric pressure (Elberling et al., 1998; Tillman et al., 2003), which is often ignored in soil gas transport models (Tillman et al., 2003). However, Smith et al. (1996) found large discrepancies between the measured total fluxes of trichloroethene vapor and the calculated diffusion fluxes, and pointed to the importance of advection-driven gas transport. Choi et al. (2002) illustrated the importance of advection fluxes under natural conditions based on a comparison of laboratory and field measurements with model simulations. In particular, when soil moisture increased near the soil surface, a large reduction in diffusion occurred relative to advection fluxes.

Tillman et al. (2003) applied a one-dimensional advection-diffusion equation for simulating trichloroethene fluxes. Simulated fluxes were comparable to field-measured total fluxes. Chen et al. (1995) successfully simulated the measured fluxes of 1,3-dichloropropene during a 2-week period after fumigant injection, which was based on an adapted Richard's equation that considers atmospheric pressure changes. However, the abovementioned research investigating advection process is limited to contaminant gas transport.

3.2.5 Ebullition

Methane emissions through rapid bubbling have often been observed from wetlands and inclusion of ebullition in CH₄ flux modelling is essential. However, similar observations of BVOC ebullition from water-logged soils have not yet been reported. Ebullition happens when the built-up gas concentration in soil reaches a certain threshold and the gas forms bubbles. Modelling CH₄ ebullition is often based on threshold approaches and links ebullition events with either pore water CH₄ concentrations or pressure of free-gas volume (Peltola et al., 2018). Further investigation is required to determine whether ebullition is an important process for BVOC transport.

4 Generic model framework

Here, we present a framework designed to integrate soil BVOC processes into the typical/basic structure existing in many ecosystem models. The proposed framework, based on our current understanding and data availability originated from a wide range of ecosystems under different conditions, is applicable for modelling at large-scales with different ecosystem types. As many large-scale ecosystem models are also applicable for site-level studies, the proposed framework for modelling soil BVOCs could also work for site-level modelling, after adjustments (calibrating model parameters and/or adjusting initial conditions) have been made to include site-level information. Here, we specifically assess the environmental drivers, as well as vegetation and soil information that determine the process rates.

Before presenting mathematical equations for modelling purposes, a few assumptions and simplifications have to be made to account for the modelling scale and data availability of soil BVOCs: (1) Many compounds could originate not only from decomposing SOC and litter, but also from intermediate products of chemical reactions, e.g., formaldehyde could be produced from methanol oxidation before forming CO₂. Oxidation and reduction processes

can happen simultaneously and rapidly. Separating between a biochemical and chemical origin of certain compounds in soil might be challenging, due to the difficulty in representing the concentrations of mixed compounds, the rapidly shifting redox potential (due to oxygen dynamics), and co-occurrence of oxidative and reductive processes at different microsites. (2) A few studies have suggested that the chemical composition of BVOC emissions changes during litter decomposition (Gray et al., 2010; Svendsen et al., 2018), which may be linked to changes in the microbial community during decomposition (Svendsen et al., 2018). Linking compound emissions with microbial diversity is generally challenging for modelling, considering difficulties in representing microbial diversity and micrometeorological variations at the scales targeted by ecosystem models (Wieder et al., 2015). Thus, no change in compound composition (i.e. BVOC profile) is assumed during the progression of litter and SOC decomposition. Furthermore, the compounds emitted by decomposition of SOC and uptake by soil microbes in this model framework are frequently reported (see Table 1), which might indicate that the microbial processes producing these compounds are common in soils. Following these two assumptions, the proposed framework only requires often-available climate and/or landscape variables as drivers. Thus, modelling the emission and uptake of microbially-driven compounds is a function of soil environmental variables.

A large variety of compounds can be emitted from soils but the suggested model solutions below will mainly refer to the compounds listed in Table 1. In Fig. 2, we present a possible framework for modelling soil BVOC fluxes that accounts for the basic structure present in many ecosystem models. We have divided this framework into: model inputs and three modules representing the main drivers (vegetation model, soil climate, and soil biogeochemistry (BGC) model), which are linked and can influence each other. The vegetation and soil environments can also be directly obtained from other input datasets (remote sensing or model-based). Here, we focus on a description of the BVOC-related processes (red arrows in Fig. 2) in the soil BGC module.

Similar to modelling soil nitrous oxide (N_2O) (Butterbach-Bahl et al., 2013), soil BVOC models can be based on two different levels of complexity: 1) at a more generic level, one only considers biotic production and uptake, and assumes that the net production of compounds in soils is equal to the flux at the soil-atmosphere interface; or 2) at a more detailed level, with a representation of within-soil dynamics, the physical transfer of gasses (also oxygen) in soil, and the fraction of aerobic-anaerobic conditions. Here, we start by

describing the biotic production and uptake of BVOCs, followed by a section briefly describing the physical transfer of compounds. The level of complexity that should be chosen for implementation depends on the availability of observations, not only of net fluxes at the soil surface, but also those that can help to separate individual processes.

4.1 Litter BVOC production

Modelling BVOCs produced from leaf litter (P_L in Eq. 1) requires inclusion of both microbially-produced and storage-derived BVOCs (Eq. 1). Storage-derived compounds are only considered important for some plant species.

$$P_L = k_L f(T_L) f(M_L) f(Q_L) C_L \Gamma + S(\tau, T_L) C_{LS}$$

(Eq. 1)

where P_L is the production rate from leaf litter ($\mu\text{gC m}^{-2} \text{h}^{-1}$), k_L is the standardized emission rate ($\mu\text{gC gdw}^{-1} \text{h}^{-1}$), and $f(T_L)$, $f(M_L)$ and $f(Q_L)$ are unit-less response functions of the production to litter temperature, moisture, and biochemical characteristic, respectively. C_L is litter available C (gC m^{-2}). Γ is the conversion from dry biomass to C content (gdw gC^{-1}). $S(\tau, T_L)$ is the relative emission rate (h^{-1}) from storage as a function of averaged residence time τ and litter temperature T_L , and C_{LS} is the storage pool size ($\mu\text{gC m}^{-2}$).

For microbial production, the key factors to consider are substrate availability and physiological controls on microbes. Similar to modelling plant BVOCs, standardized conditions (e.g., litter temperature of 30 °C and moisture level of 6 % as in Greenberg et al. (2012), temperature of 30 °C or 20 °C as in Zimmerman et al. (1978) and Isidorov et al. (2010), respectively) could be defined. Then the measured emission rates at different temperature and moisture levels could be standardized to the same conditions before using these as model parameters (Guenther et al., 1995). Such a standardized rate (k_L in Eq. 1) could then be combined with unit-less response functions to litter biochemical characteristics ($f(Q_L)$), environmental variables (temperature $f(T_L)$), and moisture $f(M_L)$). Modelling litter-produced BVOCs can be defined at grouped plant species level (e.g., plant functional types) by assuming that litter emissions from closely related plant species have similar litter properties and harbored microbes. The standardized production rates (k_L), as well as the types of compounds emitted from plant litter, need to be pre-defined for each group of litter (based on plant species origin). The C readily available for producing BVOCs decreases with litter age, as labile carbon is first utilized by microbes, and it is common to use litter C:N and/or

lignin content to quantify the effects of litter biochemical characteristics on decomposition in models (Parton, 1996; Paudel et al., 2015; Zhang et al., 2008). The direct response of litter BVOC production to temperature ($f(T_L)$), moisture ($f(M_L)$), and litter quality ($f(Q_L)$) can be obtained from laboratory studies (Gray et al., 2010; Greenberg et al., 2012). The available C amount for leaf litter (C_L in Eq. 1) can be obtained from terrestrial ecosystem models or from other data sources.

For leaf litter with specialized storage organs, like needles, emissions from storage need to be considered (Isidorov et al., 2010). The emissions from the stored pools can be formulated as a function of an average residence time under standard conditions (τ), litter temperature (T_L), and storage pool size (C_{LS}), the same way that the pool emissions are assumed to be a continuous source and not influenced by light in plant emission models (Schurgers et al., 2009). For litter, the storage pool size (C_{LS}) can be simulated in ecosystem models and without an input of new compound to the storage pool in litter, the emissions will decrease with time.

4.2 Soil organic carbon BVOC production

Generally, soil carbon in ecosystem models is often discretized into several carbon pools with different turnover rates (Eleanor & Keith, 2015; Wieder et al., 2015). Modelling production of trace gases from microbial decomposition of SOC often follows first-order decay kinetics and is a multiplier of SOC pool size and relative decomposition/decay rate (the inverse of turnover time). The decomposition rate varies with different soil climate variables (e.g., soil temperature, pH, water content, soil texture) (Wieder et al., 2015). The same scheme could also be applied to microbially-produced BVOCs from SOC. The compounds that are produced from SOC (following Table 1) as well as their relative production rates (k_{SOC} , Eq.2) need to be specified for aerobic and anaerobic conditions.

The temperature response of BVOC production from SOC has been explored by Veres et al. (2014) and a Q_{10} value ranging from 2 to 3 has been reported. Both Mielnik et al. (2018) and Paulot et al. (2011) observed that there was an exponential dependence of formic and acetic acid emissions with temperature. Beyond the often-used exponential Q_{10} function, different formulas describing the temperature response of microbial activities (Reichstein & Beer, 2008) could be tested in models as well.

Based on desiccation experiments in the laboratory, Bourtsoukidis et al. (2018) found a relationship between sesquiterpene emissions from Amazonian soils and soil water-filled pore space (WFPS) at a constant temperature. This relationship depicts an initial peak of sesquiterpenes at high WFPS, potentially linked to anaerobic production, and a second peak at moderate WFPS associated with aerobic production. Similar peaks in emissions have been found by Rossabi et al. (2018) after rewetting of dry soils. At relatively high WFPS, emissions have been observed to decrease when anaerobic conditions shift to aerobic (and hence fermentation decreases) in permafrost soils (Kramshøj et al., 2018) and peat (Faubert et al., 2010; Tiiva et al., 2009). In general, WFPS is often used for modelling soil N₂O fluxes (Tian et al., 2018) and we would suggest including WFPS to account for the impacts of soil water content on BVOC production. To simulate this abovementioned behavior, individual emission response function to WFPS would need to be determined empirically for different compounds, considering differences in optimal WFPS (most favorable conditions for microbial activities) (Bourtsoukidis et al., 2018). Furthermore, WFPS should be also used to separate aerobic and anaerobic decomposition and to differentiate compounds that are specific to the two regimes, e.g., ethanol production typically occurs under anaerobic conditions and acetone is normally found under aerobic conditions.

$$P_{\text{SOC}} = k_{\text{SOC}} f_{\text{SOC}}(\text{WFPS}) f_{\text{SOC}}(T_s) C_{\text{SOC}}$$

(Eq. 2)

Here, P_{SOC} is the production rate from SOC ($\mu\text{gC m}^{-2} \text{h}^{-1}$); k_{SOC} is the relative production rate (h^{-1}) at specific soil temperature and WFPS level, $f_{\text{SOC}}(\text{WFPS})$ is SOC emission rate in response to soil WFPS, $f_{\text{SOC}}(T_s)$ is SOC emission rate in response to soil temperature, and C_{SOC} is the soil C pool size integrated over the soil depth (gC m^{-2}), obtained from the soil BGC module.

4.3 Root BVOC production

Large-scale ecosystem models often allocate a fraction of synthesized C to root growth and root exudates and this fraction varies between different plant species (Grayston et al., 1997; Hütsch et al., 2002). Root-produced BVOCs released via root exudates have been recognized (Delory et al., 2016). In general, we would assume that C allocated to root-produced BVOCs should be less than the total C assigned for the root exudates.

At this stage, it is not possible to separate root emission profiles for different plant groups, as we suggested for litter. Instead, we would suggest modelling a list of often-reported root-emitted compounds (methanol, ethanol, acetaldehyde, and monoterpenes) with no differentiation in the relative production rates (k_{root} , Eq. 3) for different plant species. Compounds like ethanol and acetaldehyde that are known to be produced by flooded roots (Bracho-Nunez et al., 2012; Drew, 1997; Seco et al., 2007), should only be turned on within the model when soil conditions surrounding the root become anaerobic (soil anaerobiosis). Using WFPS to separate aerobic and anaerobic conditions, the root production rates of BVOCs under both conditions are expected to vary with soil temperature ($f_{\text{root}}(T_s)$) and soil water content ($f_{\text{root}}(\text{WFPS})$) at root depth. However, the measurement data to support a parameterization for root BVOC in response to soil environmental variables are not available so far, and we would alternatively suggest using the response of root respiration to these environmental variables, which has been intensively studied (Bååth & Wallander, 2003; Reichstein & Beer, 2008). The measured root-emitted gases are often given in the unit of produced compounds per root biomass (Lin et al., 2007), so it might be straightforward to use the measured data if we link the produced BVOC with root C content (C_{root}), although a linkage to plant assimilation rates may also be valid for some compounds (Ghimire et al., 2013).

$$P_{\text{root}} = k_{\text{root}} f_{\text{root}}(T_s) f_{\text{root}}(\text{WFPS}) C_{\text{root}} \quad (\text{Eq. 3})$$

Here, P_{root} is the production rate from roots ($\mu\text{gC m}^{-2} \text{h}^{-1}$), k_{root} is the relative production rate (h^{-1}) at specific soil temperature and WFPS, $f_{\text{root}}(T_s)$: root emission in response to soil temperature at the root depth; $f_{\text{root}}(\text{WFPS})$: root emission in response to WFPS, and C_{root} (gC m^{-2}) is the root C content, obtained from the vegetation module.

4.4 Microbial uptake

Microbial uptake of the often reported compounds, such as methanol, isoprene and monoterpenes, should be considered in models. Modelling microbial uptake of methane, i.e. methanotrophy, is typically based on quantification of diffusive fluxes and microbial oxidation (Murguia-Flores et al., 2018). Methane oxidation rates are often based on the first-order equation, where the rate is a function of methane concentration in soils and oxidation

activity. The microbial oxidation activity is formulated by an oxidation rate and a few environmental variables (Curry, 2007; Ridgwell et al., 1999).

Similar to modelling the soil uptake of methane, microbial uptake of some BVOCs can be parameterized by a relative uptake/mineralization rate with its response to soil environmental variables, and this relative uptake rate might vary among different compounds in different soils. Cleveland and Yavitt (1998) quantified isoprene uptake rates of temperate forest soils and their relationships with temperature and soil moisture. An exponential increase in isoprene uptake with temperature (with a Q_{10} value of 1.42) was found between 5 °C and 25 °C and the rate declined when temperatures exceeded the optimal 30 °C. An increase in soil moisture can increase microbial activity at low soil moisture content, resulting in an increase in soil BVOC uptake, but also in a decrease of the amount of gas accessible to soil microbes (Asensio et al., 2007a; Cleveland & Yavitt, 1997). Once soils begin to turn anaerobic, a further increase in soil moisture may inhibit aerobic microbial activities (Kramshøj et al., 2019), while less-efficient anaerobic microbes start to convert BVOCs to methane (CH_4). Furthermore, if soils encounter drought, a decrease in soil moisture can reduce microbial activities through cell desiccation, and hence reduce uptake.

$$U = k_u f_u(T_s) f_u(\text{WFPS}) C_{\text{BVOC}}$$

(Eq. 4)

Here, k_u (h^{-1}) is the relative uptake/mineralization rate, $f_u(T_s)$ is the unit-less response of soil uptake of BVOCs to soil temperature (T_s), $f_u(\text{WFPS})$ is the uptake rate in response to soil water conditions; and C_{BVOC} (gC m^{-2}) is the C content of the soil BVOC pool (Fig. 2).

4.5 Physical transfers

Soil BVOCs in different phases (gas, dissolved, and adsorbed, see Fig. 2) are not specified in this framework, but could be specified in models if the soil environmental parameters are available to represent shifts in the compounds between these three phases. The physical characteristics of compounds (e.g., volatility, solubility) can be found in chemical databases. Moreover, if the modelling exercises are about BVOC fluxes at the soil surface at daily or longer timescales, it might not be that crucial to describe these three phases explicitly.

BVOC diffusion is considerably impacted by soil properties, including grain size distribution, soil pH, SOC content, and soil porosity (Peñuelas et al., 2014; Petersen et al.,

1995). Ruiz et al. (1998) found that the adsorption capacity of BVOCs to clay can be an order of magnitude higher than sand and two orders of magnitude higher than limestone. van Roon et al. (2005) found that soil organic matter reduced volatilization and leaching losses, due to the increase of pore network tortuosity and/or sorption of BVOCs on organic matter. Serrano and Gallego (2006) investigated the impacts of soil pH on the sorption ability of 25 BVOCs and found that alkaline soils adsorbed more compounds than acidic soils. These relationships might be of use for modelling if the samples used in the studies are relevant for large areas, but there is a general lack of quantitative information on the importance of these processes impacting the fluxes measured at the soil surface.

5 Suggestions for soil BVOC measurements

Much of our present understanding about soils as a sink or source of BVOCs is influenced by measurement methods and compounds that can be detected. For instance, methanol might be one of the dominant BVOCs released from soil and/or litter (Gray et al., 2010), but this compound has not been investigated in many studies due to limitations in the compound trapping method (Greenberg et al., 2012; Leff & Fierer, 2008; Mäki et al., 2017).

A separation of understory plant emission from belowground emissions is difficult to conduct in the field (Janson, 1993) and the methods based on removal of understory vegetation (Faubert et al., 2012; Greenberg et al., 2012; Mäki et al., 2017), inevitably expose the remaining root-soil-litter system to alterations, including changed root emission and/or microbial community composition (Lin et al., 2007). As a result, we know very little about the contribution of soils to the ecosystem emissions *in situ*. Advances in measuring approaches to separate belowground-derived from aboveground-derived BVOCs would allow us to further explore the contribution of soil emissions to within-canopy atmospheric chemistry and total ecosystem emissions. Nevertheless, the suggestions we give below are motivated by a desire to quantify different processes and to reveal long-term and large-scale patterns in soil BVOC fluxes.

5.1 Process-oriented laboratory and field measurements

In general, measurements resolving individual processes controlling BVOC production and uptake (e.g., Greenberg et al. (2012), Asensio et al. (2007a) and Cleveland and Yavitt (1998)) can greatly benefit model parameterization. For litter BVOC production, we lack knowledge about the residence time of stored compounds in litter and the response of

their emission rates to different environmental conditions. Furthermore, there is a lack of consistency in laboratory measurements of litter BVOC production rates across different studies, differing in compound detection methods, sampling frequency, and experiment duration (Gray et al., 2010; Isidorov et al., 2010; Ramirez et al., 2010; Svendsen et al., 2018), making it hard to compare rates from different studies. A consistent laboratory sampling of litter emissions from different ecosystems could reveal important patterns in this potentially large source of soil BVOCs. For SOC emission, we need more laboratory experiments assessing how different environmental factors control SOC-related emissions in major soil types. For example, the laboratory study investigating SOC-produced compounds in response to changing soil water by Bourtsoukidis et al. (2018) have demonstrated useful and systematic relationships that can be readily applied in models.

Sampling approaches that allow separating root emissions from SOC-emitted BVOCs without excavation of roots from soil are essential for characterizing compounds emitted by roots in undisturbed systems. Delory et al. (2016) suggested using a mass spectrometer in selective ion monitoring mode to separate the known root-emitted VOCs from the volatile background in soil. Eilers et al. (2015) suggested a direct static sampling of root-only BVOCs using polydimethylsiloxane (PDMS) tubes buried in soil to sample various volatiles with different polarity and volatility. Delory et al. (2016) discussed the limitations of both static and dynamic root sampling methods. The static method allows for a comparison of emission profiles, but does not yield absolute emission rates. The dynamic sampling, based on flushing the soil with (typically) BVOC-free air, allows for measurement of root emission rates, but the altered soil atmospheric composition might impact the emissions. Because of these measurement challenges, there is little information about the linkage between soil environmental variables and compounds released from roots. Additionally, this review has not explored stress related root emissions (Ali et al., 2011; Kelsey et al., 2016; Chiriboga M. et al., 2018) or root emissions in plant-plant (Delory et al., 2016) and plant-soil organisms (Wenke et al., 2010) interactions, which might further complicate the detected linkage between emissions and environmental variables. Nevertheless, isotopic labelling might enable us to reveal patterns in how root emissions respond to changes in the soil environment (Kuz'yakov & Larionova, 2005). The solution proposed in this review, using the summarized compounds from the collected literature to specify the chemical composition of root emissions, might require modification once the mechanisms controlling specific compound emissions under certain conditions are better understood.

Albers et al. (2018) discussed a potential overestimation of BVOC uptake rates in experiments when soils are exposed to BVOC concentrations that are a few orders of magnitude higher than ambient concentrations, which is likely to stimulate BVOC degradation. Using isotopic labelling and exposing soils to natural mixing ratios is needed for quantification of microbial uptake rates of BVOCs. Furthermore, exposing soils to different conditions (e.g., varying temperature, moisture, or pH) is also needed to investigate the response of microbial uptake to these changes.

In order to effectively measure litter or SOC emissions under laboratory conditions, samples are often incubated at optimal temperature and moisture, litter samples are chopped/ground into smaller pieces, and soil samples are sieved in order to decrease heterogeneity (Gray et al., 2010; Leff & Fierer, 2008; Ramirez et al., 2010). This pre-handling of litter and soil samples can lead to losses of BVOCs. Furthermore, during the incubation periods, a wide range of BVOCs can be removed by microbial metabolism and/or sorption on mineral particles. In contrast, the grinding of litter and sieving of soil samples may maximize emission rates due to the breakdown of sample structure but may also increase uptake rates due to the increased surface area the microbes that can reach. Furthermore, these handling procedures might also break down fungal hyphae, and therefore impair the activity of the soil fungal community. Such disturbances render the potential emission rates and emitted compound composition measured under laboratory conditions to be only indirectly comparable to fluxes measured *in situ*. Work focused on evaluating the differences between laboratory- and field-measured BVOC emissions could help to better quantify potential uncertainties for integrating laboratory-based data into models.

5.2 Measurements to cover temporal variation

To separate vegetation and soil emissions and their temporal variation, it might be necessary to combine automatic soil chamber, EC, and online BVOC analysis technologies for measuring fluxes continuously and then analyzing which compounds could originate from soils. The advantage of using high-frequency and continuous measurements for disentangling soil emissions is that we can potentially attribute measured fluxes for non-photosynthetic periods (like before and after growing seasons or night-time emissions) to soil processes. Aaltonen et al. (2013) used automatic flow-through chambers with proton transfer reaction-mass spectrometry (PTR-MS) to measure BVOC fluxes during snow-free seasons (from May to November, 2010) from a boreal forest floor. These kind of chamber-based measurements

provide high temporal resolution data and can exclude emissions from forest trees, but may not sufficiently represent spatial heterogeneity (Butterbach-Bahl et al., 2013). Combining EC with PTR-MS can average over the heterogenic area and provide ecosystem-level fluxes for a continuous period (Park et al., 2013; Ruuskanen et al., 2011). However, EC measurements cover the whole ecosystem and the measured flux cannot separate between vegetation and soil emissions (Cappellin et al., 2017; Karl et al., 2004; Park et al., 2013). Together with continuous measurements from soil chambers, it might be possible to distinguish soil fluxes from vegetation.

5.3 Geographical focus areas

Broad spatial coverage of measurements is important, especially for understanding differences in the driving processes for observed soil BVOCs across different ecosystems. We have identified some geographic areas that deserve attention.

Coniferous needle litter can emit high amounts of BVOCs (Aaltonen et al., 2011; Greenberg et al., 2012; Isidorov et al., 2010) and has been more widely studied than other types of litter. Although coniferous litter might contribute largely to ecosystem emissions, due to its sources from storage as well as wide distribution of the forest, deciduous litter, with faster decomposition rates than needle litter, should also be equally investigated, especially in warmer climate.

Around 50% of global SOC is estimated to be stored in the northern permafrost (Tarnocai et al., 2009), where the greatest climatic warming is predicted to occur. The long-term accumulated belowground SOC could provide large carbon sources for microbes in a warmer future, and Kramshøj et al. (2018), as the first study, elucidated that permafrost soils can be a considerable source of BVOCs. More quantification of BVOCs released from the regions with high SOC contents could provide insights into potential contributions to the atmosphere. Furthermore, Bourtsoukidis et al. (2018) found sesquiterpene emissions from carbon-rich tropical forest soils (Terra Firme) to be of comparable magnitude to forest emissions during the dry season, highlighting the importance of further characterizing soil emissions from this region.

6 Summary

Regional and global estimations of BVOC budgets and their feedbacks to the atmosphere so far only include plant emissions, but more and more laboratory and field studies have indicated the importance of BVOC fluxes from soils. Soil emissions specifically affect the seasonal emission patterns, atmospheric chemistry during shoulder seasons, and the within-canopy OH sink. In this study, we summarize the current knowledge about sources and sinks of soil BVOCs and unravel biotic and abiotic drivers behind the processes. We also present a list of often-reported compounds for soils, which can serve as the focus group for modelling. Based on the current data, we further propose a generic framework for taking into account soil BVOC fluxes in ecosystem models. The proposed framework in this study could potentially initiate modelling attempts to quantify soil emissions at different scales.

Process-oriented measurements are required not only to provide quantitative information for model parameterization and evaluation, but also to gain a predictive understanding of soil BVOC fluxes under changing climate. Based on the current status of measurement techniques, root emissions of BVOCs in natural systems have been the least studied. Understanding processes regulating root emissions, as well as responses to different soil conditions at the plant species level, should be one of the foci in future studies. Furthermore, attention should be devoted to consistent sampling of litter emissions, investigating the responses of SOC emissions to different soil environmental variables in major soil types and developing approaches for long-term monitoring of soil BVOC emissions *in situ*.

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Table 1 List of soil biogenic volatile organic compounds, with suggested sources and sinks in soil. The current process understanding is divided into the following levels: ++good, +reasonable, n.a.: no supporting study. For sinks, the related processes for each compound (compound group) are listed in the last column.

Compounds	Chemical formula	Sources			Sinks		Related sink processes*
		Litte r	Aerobi c	Anaerobi c	Roo t	Sink s	
Methanol	CH ₄ O	++	++	+	++	++	Microbial uptake, Solubility
Ethanol	C ₂ H ₆ O	++	n.a.	++	++	++	Microbial uptake
Formaldehyde	CH ₂ O	+	+	+	n.a.	+	Adsorption Dissolution
Acetaldehyde	C ₂ H ₄ O	++	+	+	++	+	Microbial uptake
Acetic acid	C ₂ H ₄ O ₂	++	++	n.a.	+	+	Microbial uptake
Formic acid	CH ₂ O ₂	+	++	n.a.	+	+	Microbial uptake
Acetone	C ₃ H ₆ O	++	++	+	+	++	Microbial uptake
Isoprene	C ₅ H ₈	+	+	n.a.	n.a.	++	Microbial uptake
Monoterpenes	C ₁₀ H ₁₆	++	+	n.a.	++	++	Microbial uptake
Sesquiterpenes	C ₁₅ H ₂₄	++	+	n.a.	+	n.a.	n.a.
Benzenoids	Contain benzene ring	++	+	+	n.a.	+	Microbial uptake
Dimethyl sulfide (DMS)	C ₂ H ₆ S	++	++	n.a.	n.a.	+	n.a.
Furans	5-membered ring		++	n.a.	n.a.	n.a.	n.a.

* Only indicates processes mentioned in the literature.

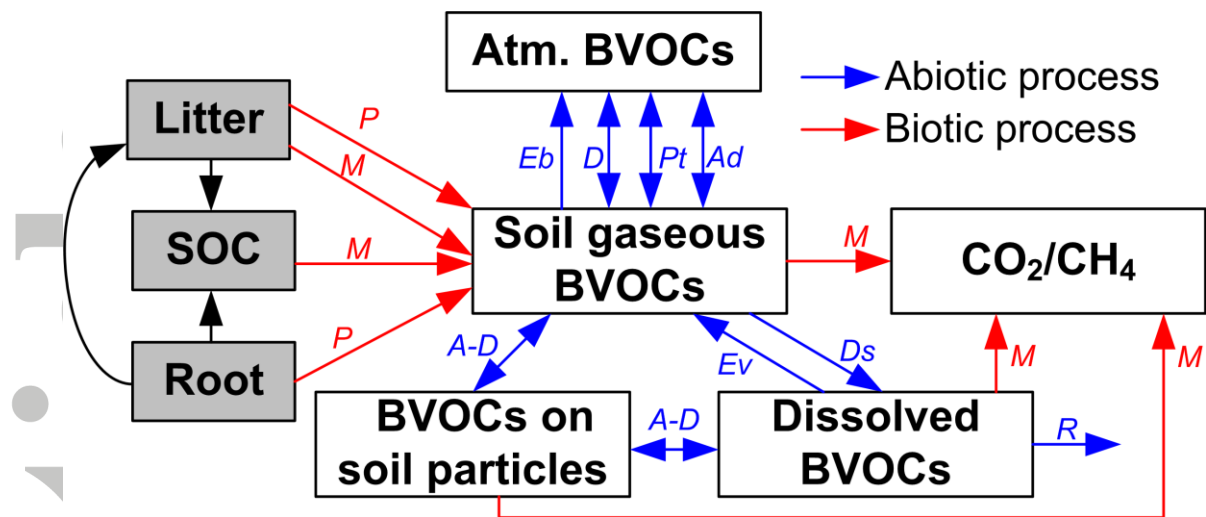


Figure 1. Overview of biotic (red arrows) and abiotic (blue arrows) processes influencing soil BVOCs. *Atm.*: Atmospheric; *Ad*: Advection; *A-D*: Adsorption-Desorption; *D*: Diffusion; *Ds*: Dissolution; *Eb*: Ebullition; *Ev*: Evaporation, *M*: Microbial decomposition/mineralization; *P*: Plant originated. *Pt*: Plant transportation; *R*: Runoff export. No chemical reactions are considered.

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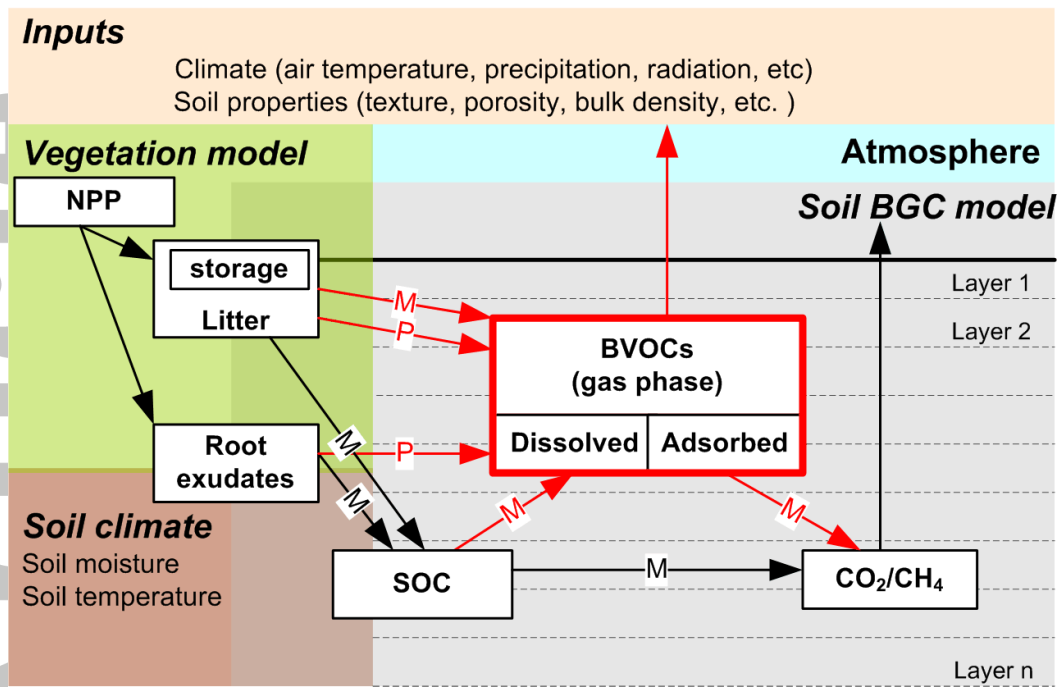


Figure 2. Schematic drawing of soil BVOC model. The red box and arrows are the new processes related to soil BVOCs, while the black arrows show processes that have been traditionally included in ecosystem models. BGC: biogeochemistry; SOC: soil organic carbon; M: microbial decomposition/mineralization; P: plant originated; Layer 1, Layer 2, ...Layer n, represent different soil layers in models.

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