

## ESSAY REVIEW

# Plant secondary metabolites: a key driver of litter decomposition and soil nutrient cycling

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## Summary

1. A broad and diversified group of compounds, secondary metabolites, are known to govern species interactions in ecosystems. Recent studies have shown that secondary metabolites can also play a major role in ecosystem processes, such as plant succession or in the process of litter decomposition, by governing the interplay between plant matter and soil organisms.

2. We reviewed the ecological role of the three main classes of secondary metabolites and the methodological challenges and novel avenues for their study. We highlight emerging general patterns of the impacts of secondary metabolites on decomposer communities and litter decomposition and argue for the consideration of secondary compounds as key drivers of soil functioning and ecosystem functioning.

3. *Synthesis.* Gaining a greater understanding of plant–soil organisms relationships and underlying mechanisms, including the role of secondary metabolites, could improve our ability to understand ecosystem processes. We outline some promising directions for future research that would stimulate studies aiming to understand the interactions of secondary metabolites across a range of spatio-temporal scales. Detailed mechanistic knowledge could help us to develop models for the process of litter decomposition and nutrient cycling in ecosystems and help us to predict future impacts of global changes on ecosystem functioning.

**Key-words:** ecosystem processes, functional traits, litter decomposition, phenolic compounds, plant–soil (below-ground) interactions, secondary metabolites, soil organisms, tannins, terpenes

## Introduction

Plant secondary metabolites (PSM) are a very broad group of chemical compounds that are generally considered to be produced by the majority of plant species to cope with biotic and abiotic stresses. The term 'secondary metabolites' has historically been used to refer to all compounds that are not 'primary metabolites', that is those metabolites not essential for the growth, development and reproduction of an organism (Hartmann 2007). However, this crude classification

underestimates the importance of secondary metabolites for plants and their interactions with other organisms, and the wider effects that PSM can have on ecosystem functioning.

Plant secondary metabolites can be distinguished roughly into three classes of chemical compounds, namely alkaloids, phenolic compounds and terpenes. Each of these broad classes is comprised of many thousands of different individual compounds and this diversity is one of the primary challenges associated with studying the ecological roles of PSM. Nonetheless, a growing body of research on PSM has revealed the important roles they can play in plant–plant and plant–microbe/insect/mammal interactions. PSM govern the mechanisms of allelopathy, influencing intra- and interspecific competition between plants (Fernandez *et al.* 2006, 2013;

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Ormeño, Fernandez & Mévy 2007). Conversely, they can also act as mutually beneficial communication signals between plants, for example alerting neighbouring plants to the presence of herbivores (Arimura *et al.* 2000; Karban, Yang & Edwards 2014). Likewise, secondary metabolites can play a central role in a plants defence against herbivores and pathogens, but can also attract pollinators helping plants to complete their life cycles. All these interactions between plants and other organisms can be key components of the overall functioning of an ecosystem.

While secondary metabolites have been largely studied in the above-ground compartment of ecosystems, they have been poorly studied in the below-ground compartment. PSM are mainly released into the ecosystem by four pathways: (i) volatilization and diffusion away from plant tissues, (ii) leaching of above-ground plant material, (iii) exudation from plant roots and (iv) litter decomposition (Rice 1984). The later three pathways release important quantities of secondary metabolites into the soil and influence numerous soil processes. For example, tannins have been shown to slow decomposition rates and C and N cycling (Hättenschwiler & Vitousek 2000), while phenolic compounds can delay the colonization of litter by decomposers (Ormeño *et al.* 2006; Chomel *et al.* 2014). Soil organisms, from bacteria to invertebrates, drive the relationship between plant communities and soil processes (Wardle & van der Putten 2002). Indeed, the impact of PSM in soil processes is mainly driven by their impact on soil organisms.

The study of PSM in soils is challenging for three main reasons: the large diversity and complexity of compounds, their chemical transformation in soils and their biological transformation by soil organisms. Indeed, the fate of PSM in soil is far from being understood. Recent advances in methodology and our greater understanding of the ecology of secondary metabolites now provide opportunities to explore the wider roles of PSM in ecosystem processes, such as litter decomposition, and in the complexities of the soil food web. Here, we argue that secondary metabolites influence litter decomposition through interactions with the soil food web and that these interactions should be the main focus of future experiments attempting to better understand litter decomposition and organic matter cycling.

In this paper, we review current experimental and theoretical evidence for the importance of plant secondary metabolites in soil processes and the plant–soil relationship. We argue the need for a greater inclusion of secondary metabolites in litter decomposition studies and the exploration of the relationships between plant and soil communities. Accordingly, we provide (i) an overview of knowledge regarding the ecology of the main classes of plant secondary metabolites and (ii) the methodological challenges and novel avenues for their study. We then (iii) review the role of PSM in the litter decomposition process and their influence on decomposer communities, and go on to (iv) argue for the consideration of secondary compounds as key drivers of soil and ecosystem functioning.

## Definition and ecological roles of secondary metabolites

Secondary metabolites can be roughly divided into three main groups of chemical compounds, alkaloids, phenolic compounds and terpenoids (Hopkins 2003; see Table 1).

### ALKALOID COMPOUNDS

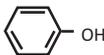
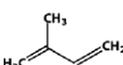
#### Definition

Some 200 years of alkaloid chemistry has resulted in the isolation of about 10 000 alkaloid compounds. Alkaloids are found in bacteria, fungi, plants and animals, although their distribution within each kingdom is quite limited (Cushnie, Cushnie & Lamb 2014). They occur in circa 300 plant families, with specific compounds typically confined to certain families (e.g. hyoscyamine in Solanaceae; Evans 2009). Alkaloids are characterized by at least one nitrogen atom, and most of them are well-defined crystalline substances that exist in a free state as N-oxides or unite with acids to form salts, both readily soluble in water (Evans 2009). In contrast, alkaloid freebases are frequently sparingly soluble in water but soluble in organic solvents (Evans 2009). Alkaloids usually have a marked physiological action on animals; for example, many of them have analgesic or toxic properties (e.g. cocaine or morphine) (Hopkins 2003). For these properties, alkaloids have been mainly studied in pharmacology and have been used throughout history in traditional medicine as well as currently in modern medical practice. Nonetheless, they have been little studied in the context of litter decomposition, soils and the decomposer subsystem.

#### Ecological role

Alkaloids are toxic compounds with multiple roles in plants, acting as feeding deterrents and allelochemicals, as well as protection against infection (Faeth & Saari 2012; Cushnie, Cushnie & Lamb 2014). Research has consistently shown not only that alkaloids participate in plant metabolism over the long term, but also that daily variation in alkaloid content (qualitative and quantitative) is very common in some species (Evans 2009). In several plant families (e.g. Poaceae), alkaloids are not synthesized by the plant but by fungal endophytes that control the types of alkaloids produced and their accumulation levels (Scharidl *et al.* 2013). This endophytic production of alkaloids in plants has been shown to slow litter decomposition rates by influencing the activity of microorganisms and detritivores (Omacini *et al.* 2004; Lemons, Clay & Rudgers 2005; Purahong & Hyde 2011; Iqbal *et al.* 2012). In contrast, when decomposition of fresh alkaloid-laden leaves was compared with alkaloid-free litter, alkaloids were quickly lost from the fresh leaves and differences in decomposition were only slight (Siegrist *et al.* 2010). However, to date there are too few studies to generalize the impact of alkaloids on decomposition processes or establish their fate in soils.

**Table 1.** Summary of the three main groups of secondary metabolites, their characteristics and examples of their ecological roles

Group	Classification	Structure	Diversity	Biological source	Ecological roles
Alkaloids	Highly diverse and complex but generally contain N		>12 000 isolated compounds	Plants (~300 families); bacteria; (endophytic) fungi	Plant defence against herbivores because of toxic properties on animals or feeding deterrence (bitter taste), antimicrobial activity Can slow decomposition rate
Phenolic compounds	One or more hydroxylated aromatic rings		>10 000 Isolated compounds		
Phenolic acids		C6-C1 or C6-C3		Plants, bacteria, fungi	Allelopathy; antibacterial activity Slows decomposition rate
Flavonoids		C6-C3-C6		Plants, bacteria, fungi	Pigments and scents; antioxidants; UV protectants; antifungal and antibacterial
Tannins	Polymers	(C6-C3-C6) <sub>n</sub>		Most abundant polyphenol in woody species; seldom found in grasses	Antiherbivore and protection against pathogens Complex with proteins and inhibition of enzyme activities Slows decomposition rate
Terpenes	Based on isoprene units		>30 000 isolated compounds	Plants	Scents and chemical signalling between plants and between plants and (in)vertebrates; resistance to biotic (insecticidal) and abiotic stress
Monoterpenes	Two isoprene units	C10			
Sesquiterpenes	Three isoprene units	C15			
Diterpenes	Four isoprene units	C20			

## PHENOLIC COMPOUNDS

### Definition

Around 10 000 phenolic compounds have been isolated. They are highly diverse, ranging from simple phenolic acids to large complex polymers, such as tannins and lignins (Hopkins 2003). These compounds can be produced by plants, bacteria and fungi. In plants, they can constitute from 1% to more than 25% of total green leaf dry mass (Hättenschwiler & Vitousek 2000). Phenolic compounds are characterized by the presence of at least one hydroxylated aromatic ring. Within this family of secondary metabolites, varying terms are used to characterize certain compounds and confusion arises because of the different criteria used in their classification. The term polyphenol, which strictly means compounds containing several hydroxyl groups on one or several aromatic rings, is often used in reference to a whole family of tannin compounds or even all phenolic compounds. The latter can also be qualified as the 'total phenols' fraction. However, a more precise classification of phenolic compounds based on their structure should be used to differentiate simple phenols (C<sub>6</sub> skeleton), phenolic acids (C<sub>6</sub>-C<sub>1</sub> or C<sub>6</sub>-C<sub>3</sub>), flavonoids (C<sub>6</sub>-C<sub>3</sub>-C<sub>6</sub>) and tannins ((C<sub>6</sub>-C<sub>3</sub>-C<sub>6</sub>)<sub>n</sub>). In some cases, they can be further classified by their degree of polymerization: (i) low molecular weight phenolic compounds are found in most plants in glycosylated and soluble form and are readily used as carbon sources by most decomposer organisms, but some of them also possess specific biological activities, for example cinnamic acids, (ii) high molecular weight phenolic

compounds such as tannins which are highly polymerized water-soluble compounds that belong to two subfamilies having different characteristics. Hydrolysable tannins are mainly present in dicot angiosperms. Condensed tannins are polymers of flavan-3-ols (flavonoids), sometimes referred to as proanthocyanidins (Hagerman 2002). Tannins are the most abundant polyphenolics found in woody species, but are generally absent from herbaceous plants (Hättenschwiler & Vitousek 2000).

### Ecological role

*Phenolic acids* are substances containing a phenolic ring and an organic carboxylic acid function. Whereas low molecular weight phenolic acids are easily degraded by microorganisms, others such as caffeic acid, p-coumaric acid and vanillic acid are known to have allelopathic activities (Rice 1984; Fernandez *et al.* 2008). As an example, caffeic acid is one of the most ubiquitous cinnamic acids isolated from a variety of crops, weed residues and other plants. It inhibits the growth of fungi (Harrison *et al.* 2003), bacteria (Bowles & Miller 1994) and plants (Rice 1984), including early root growth (Batish *et al.* 2008).

*Flavonoids* are a highly diverse group of molecules based on C<sub>6</sub>-C<sub>3</sub>-C<sub>6</sub> skeleton with various biological activities. They play important roles in providing colour, fragrance and taste to fruits, flowers and seeds (Mierziak, Kostyn & Kulma 2014). Due to their physical and chemical properties they have strong antioxidative properties. They can also act as

direct oviposition and feeding attractants or deterrents, and they can protect plants against insect pests by affecting their behaviour, growth and development (Mierziak, Kostyn & Kulma 2014). Flavonoids can also transmit information to symbiotic bacteria; for example, they are well known to be involved in the signalling between Rhizobia and the roots of legumes to initiate nodulation (Mierziak, Kostyn & Kulma 2014). These compounds also influence plant–plant interactions, such as allelopathic inhibition of germination in target species (Weston & Mathesius 2013).

*Tannins* are best known for their defensive action against herbivores and pathogens (Hättenschwiler & Vitousek 2000), but they have received special attention in studies of ecosystem functioning for their various biological and chemical

properties. It has been widely demonstrated that tannins can form insoluble complexes with proteins and other biological polymers or with metal ions during litter decomposition. These complexes render the organic matter inaccessible to further decomposition, and so tannins are increasingly recognized for their below-ground effects (Hättenschwiler & Vitousek 2000). They can also be toxic to microorganisms and inhibit enzyme activities, thereby affecting multiple aspects of nitrogen and carbon transformations in soils (Schimel *et al.* 1996; Bradley, Titus & Preston 2000; Hättenschwiler & Vitousek 2000; Fierer *et al.* 2001; Schofield, Mbugua & Pell 2001; Kraus, Dahlgren & Zasoski 2003). In most studies, nitrogen and carbon mineralization rates were reduced by the addition of tannins (Table 2). Their production is genetically

**Table 2.** Reported effects of secondary metabolites or groups of metabolites on soil organisms and processes

Effect	Direction	Secondary metabolite	Plant species	Studies
<b>Soil organisms</b>				
Colonization, reproduction and moulting of springtails	–	Polyphenols, tannins, lignin	<i>Acacia</i> , <i>Shorea</i> , <i>Cassia</i> and <i>Dalbergia</i>	Das & Joy (2009)
Fitness of gypsy moths and forest tent caterpillar	–/+	Phenolic glycosides	<i>Populus</i>	Hwang & Lindroth (1997)
Soil respiration	–	Condensed tannins	<i>Populus tremuloides</i>	Madritch, Jordan & Lindroth (2007)
Microbial activity	–	Batatasin III (phenol)	<i>Empetrum hermaphroditum</i>	Nilsson, Gallet & Wallstedt (1998)
Microorganisms	–/+	Condensed tannins	<i>Populus</i>	Schweitzer <i>et al.</i> (2007)
Arthropods	–/+	Condensed tannins	<i>Populus</i>	Whitham <i>et al.</i> (2006)
<b>Litter decomposition</b>				
Biotic decomposition	–	Lignin	Herbaceous	Austin & Ballaré (2010)
Abiotic decomposition (photodegradation)	+	Lignin	Herbaceous	Austin & Ballaré (2010)
Mineralization	–	Phenolic compounds	<i>Cistus albidus</i>	Castells, Penuelas & Valentine (2004)
Litter mass loss	–	Condensed tannins	16 woody species	Coq <i>et al.</i> (2010)
Litter decomposition	+	Total phenolic compounds	4 woody species	Hättenschwiler & Jorgensen (2010)
Litter decomposition	–	Condensed tannins	4 woody species	Hättenschwiler & Jorgensen (2010)
Litter decomposition	–/+	Condensed tannins	<i>Populus</i>	Madritch, Donaldson & Lindroth (2006)
Litter decomposition	–	Condensed tannins, lignin	<i>Populus fremontii</i> , <i>P. angustifolia</i> and their hybrids	Schweitzer <i>et al.</i> (2004)
Litter decomposition/nutrient immobilization	–	Condensed tannins	<i>Populus</i>	Schimel <i>et al.</i> (1996)
<b>N cycle</b>				
Sequestration of organic N sources	–	Condensed tannins	<i>Kalmia angustifolia</i> and <i>balsam fir</i>	Bradley, Titus & Preston (2000)
Nitrification	–/+	Monoterpenoids	<i>Pinus ponderosa</i>	Bremner & McCarty (1988)
N <sub>2</sub> fixation	–	Condensed tannins	<i>Populus</i>	Cates & Rhoades (1977)
N mineralization	–/+	Condensed tannins	<i>Populus</i>	Fierer <i>et al.</i> (2001)
Respiration and N mineralization	–	Condensed tannins	<i>Picea abies</i> and <i>Pinus sylvestris</i>	Kanerva & Smolander (2008)
Nitrification	–	Monoterpenoids	<i>Picea abies</i>	Paavolainen, Kitunen & Smolander (1998)
N mineralization	–	Condensed tannins, lignin	<i>Populus fremontii</i> , <i>P. angustifolia</i> and their hybrids	Schweitzer <i>et al.</i> (2004)
Nitrification	–	Monoterpenoids	<i>Pinus ponderosa</i>	White (1991)
<b>Others</b>				
C and N mineralization	–/+	Condensed tannins	10 woody and shrub species	Norris <i>et al.</i> (2011)
Photosynthesis and growth of birch seedlings	–	Batatasin III (phenol)	<i>Empetrum hermaphroditum</i>	Wallstedt <i>et al.</i> (2001)
Beta-glucosidase and acid-phosphatase activities	–	Tannins	<i>Kalmia angustifolia</i> , <i>Picea mariana</i>	Joanisse <i>et al.</i> (2007)

determined with constitutive function in some species, but their production can also be induced as a response to environmental stresses such as herbivory. At the genetic level, Schweitzer *et al.* (2004) found marked differences among cottonwood hybrids (*Populus fremontii* L. × *P. angustifolia* James) in terms of foliar levels of condensed tannins, which ranged from 1% to 10% of leaf dry matter. The composition and activity of tannins can also change considerably during tissue senescence (Gallet & Lebreton 1995; Nierop, Preston & Verstraten 2006).

## TERPENES

### Definition

With more than 30 000 known metabolites, terpenes or terpenoids are the most diverse group of PSM (Hartmann 2007). These compounds are mainly produced by plants, and their concentrations usually range from 1% to 2% of dry matter content, although greater concentrations may be found in leaves or in specific plant structures, such as trichomes (Langenheim 1994). These generally lipophilic compounds are based on a simple five-carbon building block (isoprene unit). Monoterpenes are composed of two isoprene units (C<sub>10</sub>); they include, for example, alpha-pinene, which is widespread in plants. Sesquiterpenes possess three isoprene units (C<sub>15</sub>, e.g. thunbergol), while diterpenes have four (C<sub>20</sub>). Some terpenes, mainly mono- and sesquiterpenes, are volatile (Langenheim 1994) and are often referred to as volatile organic compounds (VOCs). The terpene family includes hormones, carotenoid pigments, latex and most essential oils (Hopkins 2003).

### Ecological role

Terpenes first became known in their volatile forms, for their role in chemical communication among organisms and their involvement in resistance mechanisms against both biotic and abiotic stresses. Terpenes have varied roles, from attracting pollinators, protecting plants from herbivores (Langenheim 1994), or acting as toxic insecticides and insect repellents (Hopkins 2003). The impact of monoterpenes on soil microorganisms is complex, as they can inhibit the activity and growth of certain microbial groups while stimulating others (Amaral & Knowles 1998). Several studies have shown that monoterpenes inhibit N mineralization (White 1986, 1991, 1994; Bremner & McCarty 1988) and net nitrification in the soil (White 1986, 1991, 1994; Paavolainen, Kitunen & Smolander 1998; Table 2). Causes of this inhibition are still not fully understood, but may be due to a direct action of monoterpenes on an enzyme involved in the ammonium oxidation pathway (White 1988), or inhibition of growth in *Nitrosomonas europaea*, a bacterium that oxidizes ammonium to nitrite (nitrification; Ward, Courtney & Langenheim 1997). These authors also noted that other terpenes, such as beta-pinene, seem to have stimulatory effects on *Nitrosomonas europaea* growth.

## Methods for quantifying secondary metabolites

Technical issues are among some of the most important limitations when studying PSM due to the complex nature of their characterization and analysis. These issues are particularly relevant in heterogeneous substrates like leaf litter and soils. First, the type of material (leaves, litter), the moment of sampling (plant life cycle or phase of litter decomposition), the sample collection method, the storage conditions and the physical processing (grinding) of material can alter the results of the extraction and subsequent quantitative analysis of PSM. Secondly, there is a wide variety of analytical methods for characterizing these compounds, which makes comparisons among studies difficult. Thirdly, since PSM are not essential for the growth and development of plants, they can be continuously modified and adapted to the demands of changing environmental pressures (Hartmann 2007), resulting in a highly heterogeneous content from one individual to another. Some of the most common, the more useful and also some of the emergent analytical techniques for quantifying and characterizing PSM are described below.

The most common method used to study the phenolic fraction in litter or plants is the Folin–Ciocalteu method, which estimates the concentration in –OH phenolic groups, that is bonded to a benzene aromatic ring (Bärlocher & Graça 2005). This method is based on oxidative properties of phenolic groups, which react with the Folin–Ciocalteu reagent to form a blue complex. However, this reagent is not specific to polyphenols and reacts with other compounds, such as aromatic amino acids and proteins (Everette *et al.* 2010). Indeed, some authors argue that this method is more a measure of total antioxidant capacity rather than phenolic content (Everette *et al.* 2010). Moreover, each molecule reacts with its own specificity. As such, concentrations have to be expressed with respect to a standard compound (gallic acid, for instance). This makes absolute quantification impossible with the Folin–Ciocalteu method and the use of this reactant should be restricted to intraspecific comparisons (Appel *et al.* 2001). However, it is far quicker and more accessible than an exhaustive determination of all phenolic structures by chromatographic techniques [gas chromatography coupled with mass spectrometry (GC-MS)].

There are some specific chemical analyses for different functional phytochemical groups of phenolics, for example the acid butanol method or the vanillin method for condensed tannins (Hagerman 2002).

The only method for the analysis of terpenoids is by GC-MS after a non-polar solvent extraction of the organic substrate. Unlike phenolics, there is no global method for quantifying the 'terpene fraction', and the only option for this is by summation of individual compounds.

However, emergent holistic techniques have been developed and offer promising alternatives to characterize relationships between plant secondary metabolites and soil organisms (Fortunel *et al.* 2009; Parsons *et al.* 2011). For example, near-infrared spectrometry (NIRS) is a highly precise physical

method based on the selective absorption of near-infrared electromagnetic radiation by organic molecules (Birth & Hecht 1987). This technique generates spectra reflecting the total organic makeup of the material (N, lignin, cellulose, hemicelluloses, etc.). Fortunel *et al.* (2009) demonstrated that decomposition rates could be predicted via spectral data provided by NIRS. This method has a more powerful integrative capacity than chemical analysis of single compounds. This could be related to the technical features of NIRS, which involve no extraction procedures in contrast to chemical extractions that are critical steps in the precise quantification of insoluble macromolecules, such as cellulose or lignins.

Metabolomics is another recently developed holistic method that permits the identification and quantification of all metabolites of a tissue or organ through various analytical techniques involving gas and/or liquid chromatography coupled with mass spectrometry or nuclear magnetic resonance (NMR) spectroscopy (Fiehn 2002; Weston *et al.* 2015). The information provided by metabolomics is a complete snapshot of the chemical composition of a tissue (e.g. a leaf) at a particular point in time and this method allows one to focus on chemistry that is not well understood, and evaluate and identify metabolites for which there is limited knowledge (Breitling *et al.* 2013). Metabolomics is now becoming an important tool in understanding the systematic responses of many organisms to changing environmental conditions. Using this method in litter decomposition studies enables the tracking of slight changes in the chemical composition of litter during decomposition in a way never before possible (Wallenstein *et al.* 2010, 2013).

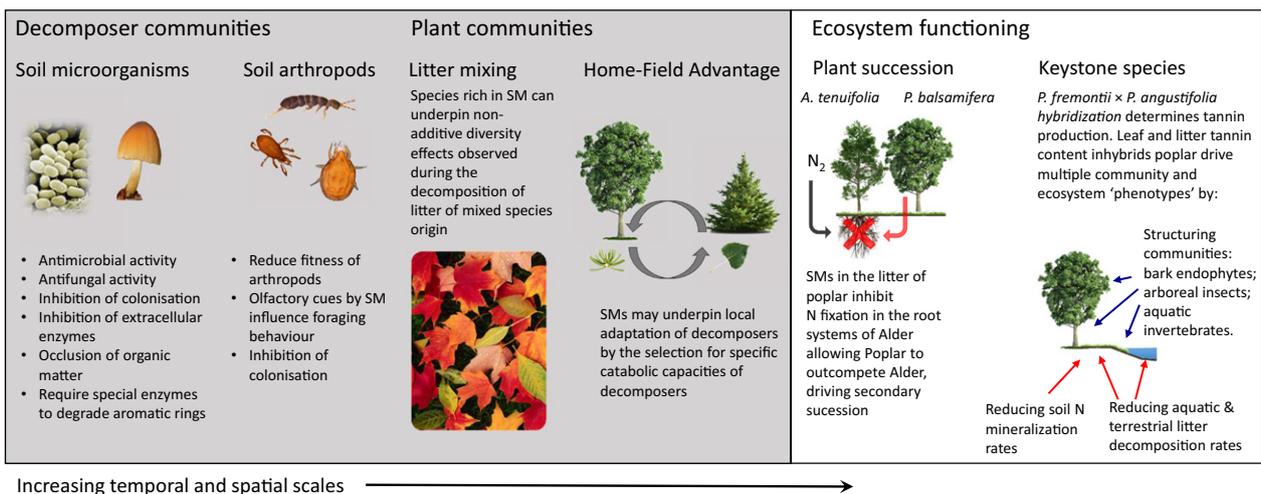
Another recent method for sampling secondary metabolites in soils that heralds new possibilities is the silicone tubing microextraction, or STME, developed by Mohney *et al.*

(2009). Sorbent microtubes are placed directly in soil and permit the *in situ* monitoring of the release of allelochemicals from roots (Mohney *et al.* 2009; Barto *et al.* 2011; Weidenhamer *et al.* 2014). The ability to profile the dynamics of these metabolites in soil provides a tool for further investigation of their ecological role in the rhizosphere and their fate in the soil. The STME method has been used in two studies and led to the discovery of tremendous spatial and temporal heterogeneity of the release of allelochemicals in root exudates (Weidenhamer *et al.* 2014). Further they were able to demonstrate movement of root exudates and allelochemicals through mycorrhizal fungal networks from plant to plant (Barto *et al.* 2011).

## Secondary metabolites in litter decomposition

PSM are now recognized as having a major role in ecosystem processes such as litter decomposition and nutrient cycling (see Table 2; Fig. 1), and can ultimately impact the structure and function of ecosystems (Hättenschwiler & Vitousek 2000; Iason, Dicke & Hartley 2012). At small spatio-temporal scales (i.e. at the level of individual organisms) PSM can have effects (i) on the activity of soil organisms, (ii) on the litter decomposition process. At a broader scale (i.e. plant community level), PSM may help explaining, (iii) the idiosyncratic effect of litter mixtures on litter decomposition rates and (iv) the adaptation/selection of soil organisms that lead to a 'home-field advantage' (i.e. when litter decomposes more rapidly in its 'home' environment). Finally, we illustrate the importance of PSM as drivers of ecosystem functioning with two key studies where an ecosystems approach provided new insight of the importance of PSM (Fig. 1).

### Effects of plant secondary metabolites on ecosystem processes and implicated communities



**Fig. 1.** Influence of secondary metabolites at different temporal and spatial scales. At the small scale end of the spectrum, studies have shown various effects of PSM on soil biotic communities, and on decomposition rate and nutrient cycling. At broader scales, secondary metabolites can influence plant-decomposer interactions and outweigh the effects of the other functional traits especially with mixed litter. A plant species producing high concentrations of secondary metabolites can promote specialization of decomposer communities to degrade its litter (home field advantage). At the scale of an ecosystem, secondary metabolites can govern the plant succession process and have major effect on ecosystem functioning.

## PLANT FUNCTIONAL TRAITS AND LITTER DECOMPOSITION

Litter decomposition is a complex ecosystem process dependant on prevailing climatic conditions but also driven by three interacting factors, namely plant community composition, soil characteristics and soil organisms (Wall *et al.* 2008; Garcia-Palacios *et al.* 2013; Bradford *et al.* 2016). Differentiating the influence of each of these factors is a significant ongoing challenge. In particular, the complexity of relationships between soil organisms in the soil food web has long been a barrier to understanding their influence on the overall process of litter decomposition. The use of plant functional traits to predict litter decomposition rates has greatly advanced our understanding of litter quality in driving litter decomposition processes (Cornwell *et al.* 2008). For example, leaf dry matter content (LDMC) is a measure of leaf structural components (the non-labile parts, such as lignin and fibres) relative to total leaf mass. Leaves with high LDMC, in addition to containing

large concentrations of primary structural components, may or may not also be rich in high molecular weight secondary metabolites, such as tannins (Wright *et al.* 2004), that generally slow the decomposition rates of litter. Integrative traits such as LDMC and leaf nitrogen content (LNC) are often good predictors of decomposition rates often being strongly correlated with decomposition rates (Kazakou *et al.* 2006, 2009; Quedsted *et al.* 2007; Pakeman, Eastwood & Scobie 2011). However, the functional traits used are often too general to explain complex relationships and often fail to explain the variability of litter decomposition rates observed across experimental systems, especially when litter mixtures are considered. The strength of the relationships between these functional traits and litter decomposition rates often appear idiosyncratic, varying widely between studies (see Table 3 for examples) with these discrepancies often attributed implicitly to the complex interactions between the drivers of decomposition. We argue that some of these discrepancies may result

**Table 3.** Reported coefficients of determination ( $R^2$ ) between plant functional traits and litter decomposition rate (k) or litter mass loss from selected studies

Studies	LDMC	LNC	SLA	Lignin	C/N	LCC	Tannins	Lignin/N	Phenols	Study area	Study level
Cornelissen & Thompson (1997)		(+) 0.48	(+) 0.31							<i>In situ</i>	Specific
Cortez <i>et al.</i> (2007)	(-) 0.66	(+) 0.56	(+) 0.52							<i>In situ</i>	CWM
Cortez <i>et al.</i> (2007)		(+) 0.71		(ns) 0.01	(-) 0.71	(+) 0.35				<i>In situ</i>	Specific
Fortunel <i>et al.</i> (2009)	(-) 0.17	(+) 0.10	(ns) 0.02			(-) 0.09				Microcosm	CWM
Garnier <i>et al.</i> (2004)	(-) 0.66	(+) 0.55	(+) 0.61							<i>In situ</i>	CWM
Kazakou <i>et al.</i> (2006)	(-) 0.56	ns	ns			ns			ns	Microcosm	Specific
Kazakou <i>et al.</i> (2009)	(-) 0.62	ns	ns			ns				Microcosm	Specific
Kurokawa, Peltzer & Wardle (2010)	(-) 0.16		(+) 0.11	(ns) 0.04	(-) 0.13		(ns) 0.09		(-) 0.26	Microcosm	CWM
Pakeman, Eastwood & Scobie (2011)	(-) 0.48	(+) 0.20	(ns) 0.006		(-) 0.25	(-) 0.34				<i>In situ</i>	CWM
Pakeman, Eastwood & Scobie (2011)	(-) 0.30	(+) 0.07	(ns) 0.008		(-) 0.12	(-) 0.16				<i>In situ</i>	Specific
Perez-Harguindeguy <i>et al.</i> (2000)		(+) 0.23			(-) 0.27	(-) 0.22				Exp. garden	Specific
Qusted <i>et al.</i> (2007)	(-) 0.66	(ns) 0.19	(+) 0.47		(-) 0.33	(-) 0.57				<i>In situ</i>	CWM
Qusted <i>et al.</i> (2007)		(ns) 0.27		(-) 0.35				(-) 0.65		<i>In situ</i>	Specific
Schweitzer <i>et al.</i> (2004)		(ns) 0.02		(ns) 0.81			(ns) 0.76	(ns) 0.37		Exp. Garden	Specific
Wardle, Bonner & Barker (2002)		(+) 0.04		(-) 0.22			(-) 0.07	(-) 0.14		Microcosm	Specific

LDMC, leaf dry matter content; LNC, leaf nitrogen content; SLA, specific leaf area; LCC, leaf carbon content; Exp. garden, experimental garden; CWM, community-weighted mean.

from the key roles played by secondary metabolites that are not considered or captured by the analysis of so called integrative functional traits.

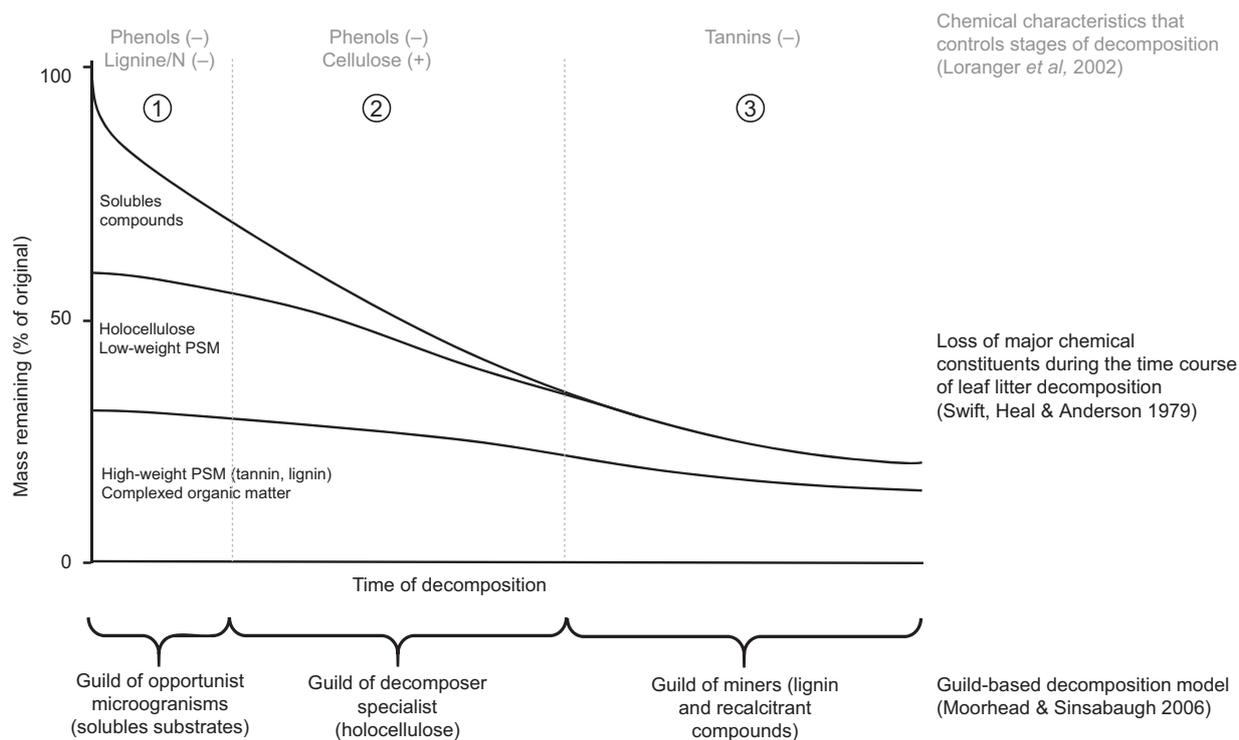
## SECONDARY METABOLITES AND DECOMPOSER ORGANISMS

Many studies examining the relationship between PSM and arthropods have focused on herbivory, pest control or pollination above-ground (Hadacek 2002). However, few studies have addressed the direct impact of secondary metabolites on the abundance and specific or functional diversity of soil microorganisms and fauna (see Table 2 for rare examples). Certain secondary metabolites can limit growth and activity of decomposers, from microorganisms to macroarthropods (Kuiters 1990; Hättenschwiler & Vitousek 2000; Chomel *et al.* 2014), because they are directly toxic to these organisms, or because they exhibit structural features (like aromatic rings) that require specialized enzymes in order to be degraded.

Many secondary metabolites have antibacterial and antifungal activities to protect plants against pathogens, but these properties may persist through senescence to be released into soil during litter decomposition with consequent impacts on

the soil food web. For example, phenolic compounds in leaf litter can have antifungal properties, inhibiting spore development and hyphal growth, or antibacterial properties inhibiting bacterial adhesion and cell envelope transport proteins (Kuiters 1990; Mierziak, Kostyn & Kulma 2014). Several studies in Mediterranean environments have shown that the concentration of phenolic compounds in litter is one of the principal factors influencing their colonization by saprotrophic fungi (Ormeño *et al.* 2006; Chomel *et al.* 2014). Another important effect of PSM on microbial activity is the inhibition of extracellular enzymes, reducing the ability of microorganisms to degrade substrates (Schimel *et al.* 1996; Joannis *et al.* 2007).

We suggest that the cocktail of secondary metabolites that are present in litter and, subsequently in soils, should be considered more explicitly as a key factor influencing rates of litter decomposition, through their effects on decomposer activity and the wider soil food web. For example, Loranger *et al.* (2002) showed that secondary metabolite contents were closely correlated with litter mass loss and that different phases of the decomposition process were influenced by different groups of compounds (Fig. 2). The rate of decomposition was first negatively related to the concentration of phenolic compounds and to the lignin/N ratio. After two and a half months of decomposition, the authors observed a



**Fig. 2.** Proposed alignment of the time course of the decomposition of major litter constituents (from Swift, Heal & Anderson 1979, main graph), the microbial interaction model of litter decomposition (Moorhead & Sinsabaugh 2006, below the graph), and the control of each phase of decomposition by different chemical constituents including plant secondary metabolites (Loranger *et al.* 2002, above the graph). The first phase of litter decomposition (1) corresponds to leaching / degradation of soluble compounds and is dominated by a guild of opportunistic microorganisms with a high growth rate. The decomposition rate of this phase was negatively correlated to phenol and lignin/N characteristics of litter. The second phase (2) corresponds to the colonization by the guild of decomposer specialists that grows more slowly and has high affinity for holocellulose substrates. The decomposition rate of this phase was positively correlated with cellulose content and negatively with phenol content. In the last phase of the decomposition process (3), the litter is mostly constituted by recalcitrant compounds and lignin and is colonized by a guild of miners that grows very slowly and is specialized in degrading lignin and recalcitrant compounds. The decomposition rate of this phase was negatively correlated to tannin content.

negative correlation with the concentration of phenolic compounds, but a positive correlation with cellulose concentration. Finally, after 9 months of decomposition, the process was negatively related to tannins.

We can link these 'recalcitrant compound phases' to the microbial interaction model of litter decomposition ('guild-based decomposition model' (GDM)) that was proposed by Moorhead & Sinsabaugh (2006) (Fig. 2). This model defines the functional role of microbial communities by separating out three distinct guilds of organisms according to their use of substrates. A first guild is composed by opportunistic microorganisms that grow quickly and have high affinities for soluble substrates. A second guild is made up of decomposers that are specialized in the degradation of holocellulose substrates and with a moderate growth rate, while a third guild of miners grow very slowly and are specialized in lignin degradation (Moorhead & Sinsabaugh 2006). In a study of Aleppo pine (*Pinus halepensis* Miller) needle decomposition in the Mediterranean region, Chomel *et al.* (2014) analysed the dynamics of secondary metabolites that were linked with the metabolic profiles of the bacterial communities. These communities preferentially used simple sugars at the beginning of the decomposition process, while carboxylic acids and amino acids were preferentially used from the second year onwards. After 30 months, the catabolic activity of the microbial community was focused on the breakdown of highly polymerized substances after which the total mass of the highest molecular weight phenolic compounds decreased. Thus, catabolic activity may be an important trait to consider when assessing secondary metabolite effects on decomposer communities. Moreover, catabolic diversity seems to be a key tool for determining the functional dynamics of communities of microorganisms.

Secondary metabolites can also act as an important factor for the colonization of litter by invertebrates by providing olfactory cues that affect food choice/preference. For instance, condensed and hydrolysable tannins extracted from oak leaves are toxic to Collembola (Poinsot-balaguer *et al.* 1993). Further, olfactory experiments have shown that springtails are able to differentiate fungi and litter of different toxicity/palatability, moving towards fungal strains with suppressed secondary metabolite contents (Staadén *et al.* 2011; Stotefeld, Scheu & Rohlf 2012). Another study showed that the colonization rate of springtails was lower in litters containing higher quantities of secondary compounds but similar macronutrient profiles (C, N and P) (Das & Joy 2009). Furthermore, individuals that remained in contact with litters containing greater quantities of secondary metabolites exhibited lower growth performance, lower fecundity and fewer moults (Das & Joy 2009). At the same time, detritivorous macrofauna play an important functional role in the detoxification of litter, for example by reducing condensed tannins in their faecal pellets to negligible levels compared to initial litter content (Coulis *et al.* 2009). This reduction of tannin concentrations is due to their degradation by gut microorganisms or by complexation into insoluble high molecular weight structures.

## SECONDARY METABOLITES AND DECOMPOSITION AT THE PLANT COMMUNITY LEVEL

At the plant community level, studies have shown that aggregated traits, that is traits that are weighted by the abundance of each species, can be closely correlated with the decomposition rate of the litter mixtures (Garnier *et al.* 2004; Quedérou *et al.* 2007; Quérier, Thebault & Lavorel 2007; Fortunel *et al.* 2009). Rather than aggregated traits values, the dissimilarity of litter traits within plant communities can also be used to explain how the plant community composition influences the decomposition of mixed litter (Epps *et al.* 2007; Barantal *et al.* 2011). However, these approaches do not account for the widely observed synergistic or antagonistic interactions between the decomposing litter of different plant species through litter mixing effects (Gartner & Cardon 2004; Santonja *et al.* 2015; Chomel *et al.* 2016). One mechanism by which these litter mixing effects occur is through disproportionate effects of individual species, whose influence on decomposition outweighs those of surrounding species (Diaz *et al.* 2007; Quérier, Thebault & Lavorel 2007; Barantal *et al.* 2011). These disproportionate effects can be attributed to nutrient-rich plant species but also to species that are large producers of secondary metabolites (Hättenschwiler, Tiunov & Scheu 2005; Viard-Cretat *et al.* 2009; Barantal *et al.* 2011).

Several studies have shown that plant litter decomposes faster when placed in the habitat from which it was derived than in a foreign habitat, which has been termed the home-field advantage (HFA) of litter decomposition (Hunt *et al.* 1988; Gholz *et al.* 2000; Ayres, Dromph & Bardgett 2006; Vivanco & Austin 2008; Ayres *et al.* 2009a,b; Strickland *et al.* 2009; Veen *et al.* 2014; Chomel *et al.* 2015). It has been suggested that this HFA results from the local adaptation of soil communities to decompose the litter that they encounter most often (Wardle & van der Putten 2002; Ayres *et al.* 2009b; Wang, Zhong & He 2013; Austin *et al.* 2014). This knowledge has raised other questions: Which plant traits could control this long-term 'co-evolution' between plant and decomposer communities? Some studies found that this home-field advantage is more pronounced with more recalcitrant litter, rich in secondary metabolites, because fewer soil communities include biota able to degrade these compounds (Ayres *et al.* 2009a; Wallenstein *et al.* 2013).

## CASCADING EFFECTS OF SECONDARY METABOLITES

In addition to their role in litter decomposition, secondary metabolites may have important roles in wider processes operating in soils through continued input and persistence in the environment. We highlight here two relevant examples of how the effects of secondary metabolites cascade across trophic levels to affect long-term changes in ecosystem functioning. The first and perhaps best example placed secondary metabolites at the core of the succession process in an Alaskan taiga floodplain (Schimel *et al.* 1996; Schimel, Cates & Ruess 1998; Fierer *et al.* 2001). The transition during secondary forest succession from grey or speckled alder (*Alnus*

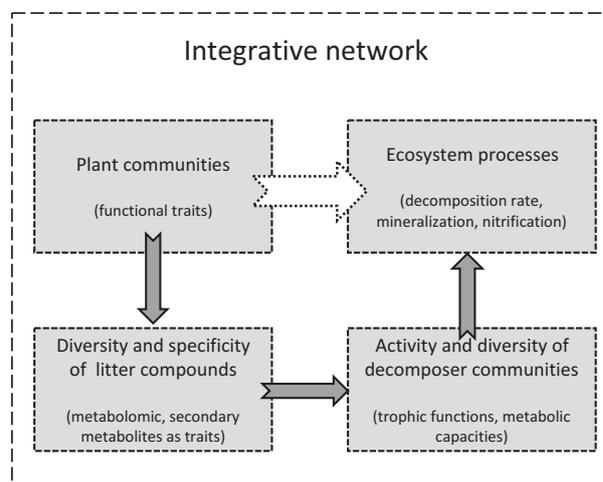
*incana* ssp. *tenuifolia* (Nutt.) to balsam poplar (*Populus balsamifera* L.) in this system was associated with major changes in the dynamics of carbon and nitrogen in the soils. These changes in soil processes were linked to the presence of secondary metabolites produced by balsam poplar. Alders in general, and grey alder in particular are actinorhizal shrubs or trees in endosymbiotic association with filamentous bacteria of the genus *Frankia*. Balsam poplar releases tannins via its litter that i) inhibits nitrogen fixation by *Frankia* (Schimel *et al.* 1996), ii) inhibits N mineralization by forming decomposition-resistant and recalcitrant protein complexes in the soil and (iii) forms complexes with microbial extracellular enzymes, thereby inhibiting their activity (Scalbert 1991). These authors observed a significant reduction in nitrogen availability within the soil, making this environment more favourable for balsam poplar, which through its strong competitiveness for resources outgrows the alder, accelerating the successional transition.

The second example highlighting the central role that PSM can play in the functioning of an ecosystem is the 'gene-to-ecosystems' approach used in a well-studied riparian forest system of *Populus angustifolia* × *P. fremontii* throughout the western USA (Schweitzer *et al.* 2004, 2007, 2008, 2012; Bailey *et al.* 2005, 2009; LeRoy *et al.* 2006; Whitham *et al.* 2006). This body of work is based on the genetic variation between the two species and their hybrids in foliar condensed tannin concentration; low concentrations of tannins occur in the leaves of *P. fremontii* (close to 0 mg g<sup>-1</sup> of leaf), high concentrations in the leaves of *P. angustifolia* (more than 50 mg g<sup>-1</sup> of leaf), while their hybrids contain intermediate concentrations (Whitham *et al.* 2006). These differences in tannin content seemed to drive the 'phenotypes' of many communities, such as arthropods living in the tree canopies (Whitham *et al.* 2006), endophytic fungi (Bailey *et al.* 2005) and aquatic macro-invertebrates that consume poplar litter in nearby water courses (LeRoy *et al.* 2006). Furthermore, condensed tannins also explained the 'phenotypes of the ecosystem', such as nitrogen mineralization (condensed tannins explained 63% of the variation in net nitrogen mineralization in the soils; Schweitzer *et al.* 2004) or decomposition of litters in aquatic environment (condensed tannins explained 97% of the variation in leaf decomposition in the stream; LeRoy *et al.* 2006).

The ecosystem approach used in these two studies illustrates how secondary metabolites (tannins in particular) can govern the structure of an ecosystem and could help to elucidate complex ecological interactions in other ecosystems.

### Challenges and perspectives

The major problem in studying the process of litter decomposition lies in addressing the feedback loops between all the drivers and components of this process. The use of plant functional traits to link plant community structure and ecosystem processes is a good attempt to simplify this complexity; however, idiosyncratic results can appear. We now need to gain mechanistic understanding of the relationships between



**Fig. 3.** Research perspectives to improve understanding of the link between plant communities and the process of litter decomposition. Knowledge gaps on the relationship between plant chemistry and decomposer communities limit our mechanistic understanding of how plant communities influence ecosystem processes. Solid arrows represent areas that need to be better understood in order to predict the overall impact of a plant community on the key ecosystem process of litter decomposition.

plant chemistry, including secondary metabolites, and the activity of soil organisms during the litter decomposition process to be able to understand the relationship between plant community structure, the soil food web and ecosystem processes (Fig. 3). This requires explicit consideration of how the effects of individual PSM cascade through the soil food web.

### QUANTIFYING SECONDARY METABOLITES

Ecological studies often restrict their analyses to broad classes of PSM such as 'total phenols' or 'total tannins', while the identification of specific compounds requires both the technical capacity and time, and as is often more costly. But the use of new techniques can help us to have more accurate analysis of PSM. Standardization of methods and a systematic, accurate description of environmental variables are also necessary to carry forward research more efficiently. Difficulties with PSM studies arise from the fact that tissue PSM content can show temporal variations due to ontogenic and seasonal changes (Koricheva *et al.* 1998; Barton & Koricheva 2010), abiotic stresses such as nutrient limitation (De Long *et al.* 2016) and the influence of herbivory (Ibanez *et al.* 2013; Jackrel & Wootton 2015). Knowledge on the distribution of secondary metabolites within plants is still scant, and probably most of the PSM are found in higher concentrations in young rather than mature leaves (Barton & Koricheva 2010). During the senescence phase, resorption or chemical transformation of PSM could occur and potentially induce drastic changes between green and senescent leaves, but these processes are far from elucidated.

The example of Whitham *et al.* (2006) discussed above demonstrated that genetics offers a promising way to study

the impact of secondary metabolites in ecosystems. Using metabolomics to link genotype and phenotype could extend the study of secondary metabolites to several ecological levels. Simultaneous identification and quantification of all the metabolites of an organism produces a complete profile of the physiological behaviour of these organisms in response to environmental changes (Hartley *et al.* 2012). This is a significant advance; instead of crude total quantification of a group of PSM, key mechanisms or key molecules underlying a process or interactions can be elucidated even if the compounds are not known initially. For example, Wallenstein *et al.* (2010, 2013) were interested in the degree to which leaf litter chemistry is altered by different soil communities during decomposition. Using metabolomics they were able to reveal specific differences in the function of decomposer communities, where the most important factor may be the specific and differing ways they transform litter rather than the rate at which it is decomposed.

Thus, ecometabolomics (metabolomics applied to ecology) could help us to interpret the response of different groups of organisms in the allocation of resources to growth, storage and defence (Sardans, Penuelas & Rivas-Ubach 2011). Most metabolomics studies have focused on the response of an individual (plant or animal) to biotic or abiotic factors such as environmental changes or parasite attack (Sardans, Penuelas & Rivas-Ubach 2011). We have to go further and apply the metabolomics approach across multiple organisms and several trophic levels including plants and soil organisms, in order to obtain an overview of the ecosystem and the phenotypes of the different compartments and to improve our mechanistic understanding of the litter decomposition process.

#### THE SOIL FOOD WEB

We need to better understand the relationship between soil organisms and how they interact with each other to understand their influences on soil processes. Soil food webs have for a long time been considered as a 'black box' but recent advances in measuring soil food-web structure and function offers new possibilities. The use of stable isotopes (C and N) have been increasingly used to understand the relationship between each trophic level, giving new insight into C resources and trophic position or feeding preferences of soil fauna (Albers, Schaefer & Scheu 2006; Crotty *et al.* 2014; Pausch *et al.* 2016). Another promising avenue is apply the functional traits approach to soil organisms (Cragg & Bardgett 2001; Pey *et al.* 2014). The majority of studies dealing with functional traits of invertebrates have focussed on assessing the effect of environmental changes on soil organisms (Pey *et al.* 2014), such as the responses of springtails to climate (Makkonen *et al.* 2011) or those of oribatid mites and springtails communities to management intensity (Farska, Prejzkova & Rusek 2014). Farska, Prejzkova & Rusek (2014) showed that feeding guilds and reproduction mode were useful functional traits to observe changes in mesofauna communities in response to land management intensity. However, the

use of functional traits of decomposers to explain decomposition is scarce.

In the same way that palatability of living tissues is directly linked to the occurrence and concentration of secondary metabolites, plant litter decomposability can be defined by its content in secondary metabolites (Grime *et al.* 1996; Kurokawa, Peltzer & Wardle 2010; Mason *et al.* 2011; Asplund & Wardle 2013). In that way, secondary metabolites can play a significant role as functional traits linking plants, litter, decomposer communities and decomposition rate (Cortez *et al.* 2007; Pakeman, Eastwood & Scobie 2011). The possibility to link plant chemistry with metabolic functional traits of decomposers is a promising avenue for our mechanistic understanding of ecosystem functioning concerning plant–soil interactions and decomposition processes. Exploration of the effects that secondary metabolites have on these communities by measuring their metabolic capacities, trophic functions and the shifts between different guilds within communities during the decomposition process may provide long needed insight into the 'black box' of the decomposer subsystem.

#### Conclusion

In this review, we highlight how plant secondary metabolites have a major and often overlooked role in the process of litter decomposition with wider consequences for nutrient cycling and so ultimately on the structure and function of ecosystems. PSM have a major influence on litter decomposition principally through their impacts on the activity of soil organisms. In this review, we present examples of key studies where PSM underpin mechanisms driving variation in decomposition processes and nutrient cycling. PSM can outweigh the effects of other plant functional traits on litter decomposition rates and so help to explain the often idiosyncratic results of, for example, litter mixings studies. They are also strongly implicated in structuring decomposer communities, supported by the findings of greater HFA effects with the presence of PSM-rich recalcitrant litter. There is also evidence for implication of PSM at broader spatial and temporal scales, as they can drive plant succession and the structuring of ecosystems. However, in many circumstances PSM are overlooked and the underlying mechanisms by which they interact with ecosystem processes are still to be elucidated. We argue that studies covering interactions of PSM across a range of spatio-temporal scales (organisms, communities and ecosystem) are needed to further understand their importance in ecosystems. We present in this review examples of new methodology and approaches that may help to motivate further research.

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## Data accessibility

This paper does not use data.

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