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RESEARCH REVIEW

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Decoupling the direct and indirect effects of climate on plant litter decomposition: Accounting for stress-induced modifications in plant chemistry

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Abstract

Decomposition of plant litter is a fundamental ecosystem process that can act as a feedback to climate change by simultaneously influencing both the productivity of ecosystems and the flux of carbon dioxide from the soil. The influence of climate on decomposition from a postsenescence perspective is relatively well known; in particular, climate is known to regulate the rate of litter decomposition via its direct influence on the reaction kinetics and microbial physiology on processes downstream of tissue senescence. Climate can alter plant metabolism during the formative stage of tissues and could shape the final chemical composition of plant litter that is available for decomposition, and thus indirectly influence decomposition; however, these indirect effects are relatively poorly understood. Climatic stress disrupts cellular homeostasis in plants and results in the reprogramming of primary and secondary metabolic pathways, which leads to changes in the quantity, composition, and organization of small molecules and recalcitrant heteropolymers, including lignins, tannins, suberins, and cuticle within the plant tissue matrix. Furthermore, by regulating metabolism during tissue senescence, climate influences the resorption of nutrients from senescing tissues. Thus, the final chemical composition of plant litter that forms the substrate of decomposition is a combined product of presenescence physiological processes through the production and resorption of metabolites. The changes in quantity, composition, and localization of the molecular construct of the litter could enhance or hinder tissue decomposition and soil nutrient cycling by altering the recalcitrance of the lignocellulose matrix, the composition of microbial communities, and the activity of microbial exoenzymes via various complexation reactions. Also, the climate-induced changes in the molecular composition of litter could differentially influence litter decomposition and soil nutrient cycling. Compared with temperate ecosystems, the indirect effects of climate on litter decomposition in the tropics are not well understood, which underscores the need to conduct additional studies in tropical biomes. We also emphasize the need to focus on how climatic stress affects the root chemistry as roots contribute significantly to biogeochemical cycling, and on utilizing more robust analytical approaches to capture the molecular composition of tissue matrix that fuel microbial metabolism.

KEYWORDS
climate change, drought, environmental stress, litter decomposition, lignins, nutrient cycling, soil carbon, tannins, warming

1 | INTRODUCTION

Litter decomposition is a fundamental process that sustains the productivity of terrestrial ecosystems through the recycling of nutrients in senesced plant biomass (Adair et al., 2008; Gholz, Wedin, Smitherman, Harmon, & Parton, 2000; Schlesinger, 1997). The rate of nutrient release from plant litter depends on multiple biotic and abiotic factors interacting at finer spatial and temporal scales. Predominant among those factors are the chemical composition of the litter matrix that regulates the nutrient release rates, the composition of the soil heterotrophic community that decomposes the litter, and climatic factors, including temperature and moisture that influence various reaction kinetics and the physiology of soil heterotrophs, and hence the decomposition process (Aerts, 1997; Cleveland et al., 2014; Cornwell et al., 2008; Lehmann & Kleber, 2015; Tamura, Suseela, Simpson, Powell, & Tharayil, 2017). The direct effects of each of these factors and their interactions on litter decomposition have been evaluated extensively in continent-scale studies that span different species and climates (Austin, Vivanco, Gonzalez-Arzac, & Perez, 2014; Prescott, 2010; Preston, Nault, Trofymow, Smyth, & Grp, 2009). A majority of these decomposition studies have primarily focused on the direct influence of climate on processes downstream of tissue senescence. However, climatic perturbations can induce morphological and physiological changes in plants, most of which alter the chemical composition of plant tissues (Le Gall et al., 2015). Since the chemical (molecular) composition of senesced litter fuels microbial metabolism and thus the recycling of nutrients, the changes in litter chemistry that occur upstream of tissue senescence could also influence terrestrial nutrient cycling, which surprisingly is poorly understood (Figure 1). Thus, there exists a critical knowledge gap in our understanding of how plant physiological alterations under changing climate could feed back to ecosystem productivity via their influence on plant litter chemistry.

The projected increase in temperature accompanied by frequent drought imposes severe abiotic stress on the growth and survival of plants (Ahuja, De Vos, Bones, & Hall, 2010; IPCC, 2013), and many plants adapt to these environmental stressors by reprogramming their cellular metabolism, which results in unique metabolite profiles (Gargallo-Garriga et al., 2015; Moura, Bonine, Viana, Dornelas, & Mazzafera, 2010; Top & Filley 2014; Suseela, Tharayil, Xing, & Dukes, 2013, 2015). Similar to climate-induced changes in the production of metabolites, future stressful climate scenarios may potentially regulate the retranslocation of nutrients from plant tissues during senescence (Norby, Long, Hartz-Rubin, & O'neill, 2000; Suseela et al., 2015). Thus, the final chemical composition of the plant litter that is available for microbial decomposition would be the combined product of presenescence physiological processes through the production and resorption of metabolites (Figure 2). Furthermore, along with the well-studied dynamics of extractable metabolites, climate stress also influences the composition of nonextractable, structural components of the plant tissues that form the bulk of the carbon that reaches the soil (Cabané, Afif, & Hawkins, 2012; Dixon & Paiva, 1995; Moura et al., 2010; Suseela, Triebwasser, Linsched,

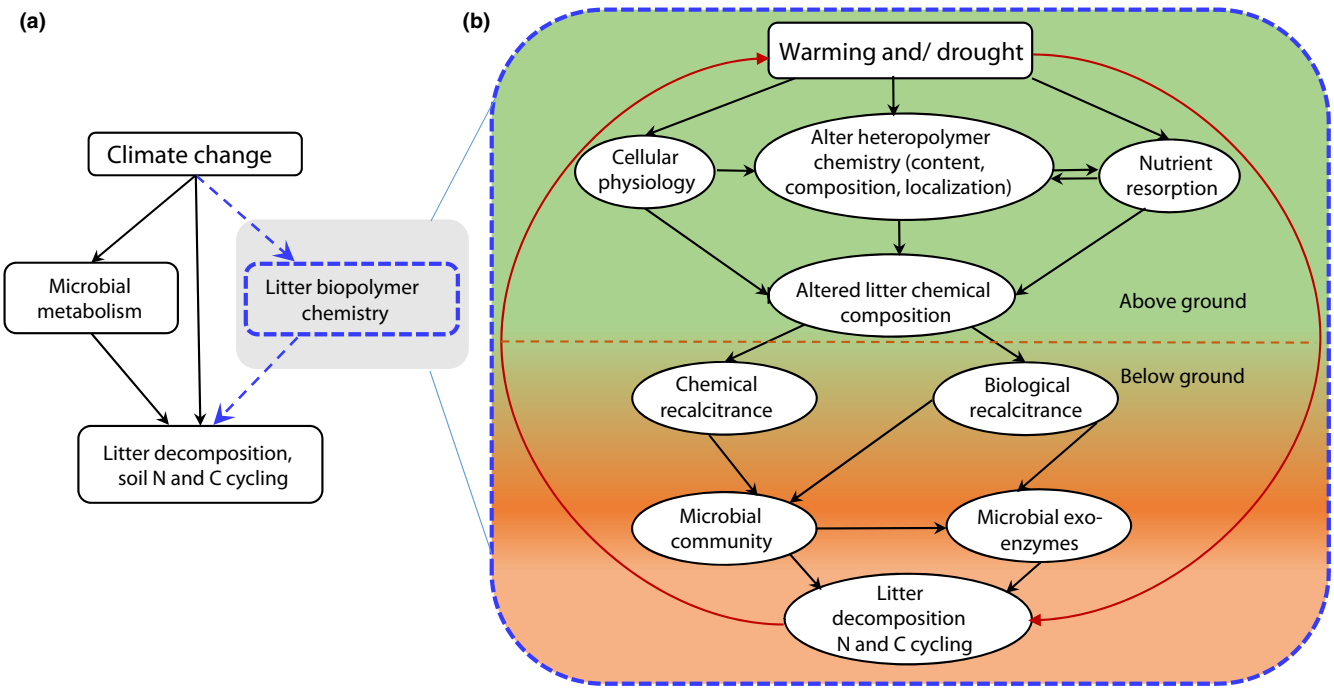


FIGURE 1 Schematic of the current knowledge on the influence of climate on litter decomposition, which regulates the cycling of soil nutrients and carbon (a). Although climate is known to affect plant physiology, the ramifications of stress adaptations in plants on the cycling of soil nutrients and carbon are surprisingly unknown (highlighted with blue broken boxes and arrows). Potential mechanisms by which climate-induced physiological changes in plants could influence litter heteropolymer chemistry and result in changes in litter chemical composition that alters soil nutrient and carbon cycling (b) [Colour figure can be viewed at wileyonlinelibrary.com]

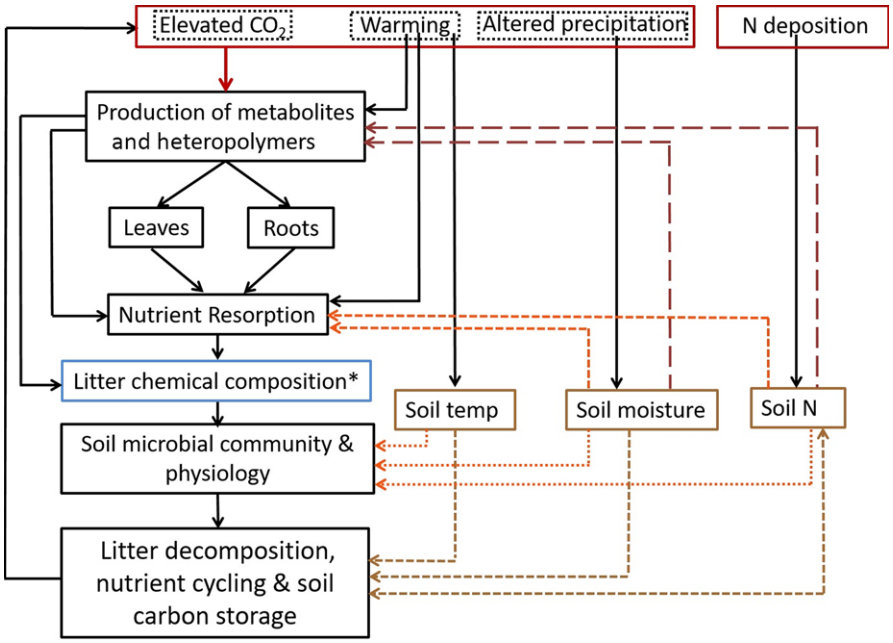


FIGURE 2 Schematic representation of the effect of global changes [elevated CO_2, warming, altered precipitation, and nitrogen (N) deposition] on the chemical composition of plant litter via alterations in both production and resorption metabolism. Altered litter chemical composition further influences the microbial community and hence litter decomposition, nutrient cycling, and soil carbon storage. The effects of global change factors mediated via changes in soil temperature and soil resource availabilities (soil moisture, N) and their subsequent influence on plant and soil processes are depicted by broken lines and arrows. *Litter chemical composition refers to the molecular identity of litter in terms of quantity, composition and localization of compounds [Colour figure can be viewed at wileyonlinelibrary.com]

Morgan, & Tharayil, 2014). However, limited data are available on the effect of climatic stresses on the chemical composition of the structural components of plant litter during the presenescence stage, and the subsequent influence of these changes on the decomposability of litter. This information is critical for accurately forecasting the rate of nutrient supply that sustains ecosystem productivity under future climates, especially because the terrestrial C cycle and its feedback to climate change depends on a close balance between the net primary productivity and the release of carbon from soils through heterotrophic respiration.

The effect of climate on litter decomposition and hence on soil nutrient cycling occurs on different spatial and temporal scales (Bardgett, Manning, Morrien, & De Vries, 2013). Over longer time scales, climate modifies ecosystem processes by altering plant species composition (Kardol et al., 2010; Yang et al., 2011). However, over shorter time scales, plant physiological adaptations to changing climate alter the litter chemical composition. This change in substrate chemistry further modulates the composition and activity of soil heterotrophs and could modify soil biogeochemical cycles (Cleveland et al., 2014; Fanin & Bertrand, 2016; Carillo et al., 2017; Koyama, Steinweg, Haddix, Dukes, & Wallenstein, 2017). The short-term changes resulting from plant adaptations and the ensuing changes in biogeochemistry would also partially influence plant species composition on longer time scales (Bardgett et al., 2013; Wu, Dijkstra, Koch, Penuelas, & Hungate, 2011). Here, we synthesize the current understanding on how climatic stress alters the quantity, composition and localization of the molecular construct of plant litter, and we further discuss the potential impacts of such changes on decomposition and soil nutrient cycling across different biomes.

In addition to warming and altered precipitation, other global change factors, such as elevated CO_2 and nitrogen deposition, also alter the chemistry and quantity of plant litter (see reviews by Norby, Cotrufo, Ineson, O'neill, & Canadell, 2001 and Van Diepen et al., 2015; Figure 2). However, elevated CO_2 and nitrogen deposition may not directly instigate physiological stress responses in plants. Thus, in this review, we focus on the responses of plants to climatic stressors, mainly high temperature and drought. We elaborate on how stress responses are manifested in the chemical composition of plant tissues, the potential consequences of these changes on the bioavailability of C and N to decomposers, and the ensuing nutrient cycle. In this synthesis, we highlight the dynamics of small molecules and heteropolymers in plants as the molecular identity of litter that fuel microbial metabolism could be more mechanistically correlated with fundamental ecosystem processes including litter decomposition and nutrient cycling. The changes in elemental composition as a function of climate variability have been elegantly reviewed elsewhere (Sardans, Penuelas, & Ogaya, 2008; Sardans, Rivas-Ubach, & Penuelas, 2012; Sardans et al., 2017; Yuan & Chen, 2015). Biosynthetic pathways and chemical structures are provided to highlight the potential diversity that could arise in chemical composition of plant heteropolymers under environmental stress, which in turn could influence their biological reactivity, and/or susceptibility to decomposition.

2 | EFFECT OF CLIMATIC STRESS ON THE CHEMICAL COMPOSITION OF PLANT TISSUES DURING THEIR FORMATIVE STAGES

Plants require the balanced availability of nutrients for optimal growth; hence, any factor that perturbs the nutrient acquisition ability of the plant or the supplying capacity of the soil will elicit responses in plants to counter these imbalances (Orcutt & Nielsen, 2000; Suzuki, Rivero, Shulaev, Blumwald, & Mittler, 2014). Plant responses to abiotic stresses are initiated through the transcription of a large number of genes and a complex network of signals and

signaling cascades, which include reactive oxygen species and hormones, such as abscisic acid, jasmonic acid, and salicylic acid (Cramer, Urano, Delrot, Pezzotti, & Shinozaki, 2011; Foyer & Noctor, 2005; Pinheiro & Chaves, 2011; Xiong, Schumaker, & Zhu, 2002). These responses are followed by changes in metabolites, with plants preferentially allocating more assimilated C to the production of compounds that would better acclimatize them to environmental stress (Bohnert & Sheveleva, 1998; Osakabe, Osakabe, Shinozaki, & Tran, 2014; Riipi et al., 2002). Plant biomass is a complex, polydisperse, matrix consisting of labile compounds (e.g., carbohydrates and proteins) and relatively recalcitrant heteropolymeric compounds (e.g., lignins, tannins, suberins, and cuticular matrix); thus, stress-induced changes can occur in any or all of these compounds. Moreover, the changes could encompass modifications in the quantity as well as the composition and localization of compounds within the plant tissue matrix, which alter the overall biochemical and /or biophysical construct of the tissue (Cabané et al., 2012; Moura et al., 2010)

2.1 | Change in extractable labile metabolites under environmental stress

Stress-induced metabolic reprogramming in plants results in the upregulation of several compound classes, such as amino acids, phenolic acids, sugars, organic acids, sugar alcohols, polyamines, and polyols (Bohnert, Nelson, & Jensen, 1995; Penuelas et al., 2013; Suseela et al., 2015). In plants, this upregulation of the extractable metabolite pool indicates a distinct adaptive stress response that corresponds to the inhibition/activation of specific metabolic pathways, rather than the general stress-induced changes in metabolism (Obata & Fernie, 2012). Many of these metabolites function as osmoregulators, scavenge free radicals, and maintain the structural integrity of proteins, enzymes, and other macromolecules (Akashi, Miyake, & Yokota, 2001; Alcazar et al., 2006, 2010; Bohnert et al., 1995; Galston, 1991; Groppa & Benavides, 2008; Kaplan et al., 2004; Matysik, Alia, Bhalu, & Mohanty, 2002; Szabados & Savoure, 2010; Wang et al., 2014), thus enabling plants to maintain the cellular homeostasis under stress. Climatic stress also often results in the reorganization of cellular proteins. Temperature stress reduces the synthesis of normal proteins and increases the transcription and translation of heat shock proteins (Bita & Gerats, 2013; Bray, Bailey-Serres, & Weretilnyk, 2000). Heat shock proteins play an important role in plant stress tolerance by acting as molecular chaperones, thereby preventing protein degradation and assisting in protein refolding (Ahuja et al., 2010; Gorantla et al., 2007; Scharf, Berberich, Ebersberger, & Nover, 2012; Sun et al., 2012; Wang, Vinocur, Shoseyov, & Altman, 2004). Climatic stress also increases the content of soluble proteins in tissue, which is more amenable for resorption during tissue senescence (Suseela et al., 2015).

Under natural settings, plants experience a combination of multiple stress factors (e.g., warming and drought) that elicit unique metabolic responses that cannot be extrapolated based on responses to individual stress factors (Obata & Fernie, 2012; Suseela et al., 2015). Multiple stress factors often stimulate different signaling pathways and the cross-talk between these pathways resulting in complex plant responses (Suzuki et al., 2014), which could even be antagonistic (Suseela, Tharayil, Xing, & Dukes, 2015; Suseela, Triebwasser, et al., 2014). Recent studies have indicated that the co-occurrence of warming and drought has resulted in the production of several metabolites in the tricarboxylic acid cycle, amino acids, polyamines, and polyols, that were not elicited when subjected to individual stress factors (Gargallo-Garriga et al., 2015; Suseela et al., 2015). In general, compared to plants growing in optimal environments, plants exposed to climatic stress tend to have a higher content of extractable compounds, which provide efficient protection against specific environmental stressors. Also, it should be noted that plants respond to environments that impose physiological stress rather than responding to an absolute temperature or drought regimen. Hence, the magnitude of stress response in plants could vary based on the local environmental conditions to which they are adapted.

2.2 | Change in recalcitrant macromolecular composition of tissues under environmental stress

Although the extractable metabolites in plant litter form a readily available source of energy for microbes that facilitate the initial decomposition of senesced tissues, compared with the structural components, the extractable metabolite pool constitutes a smaller fraction of the plant biomass. More than 80% of the dry mass across many plant species is composed of structural biopolymers, including homopolymers (composed of similar monomeric units; for example, cellulose) and heteropolymers (composed of different monomeric units; for example, lignins, tannins, suberin, and cuticular matrix), both of which are critical for maintaining the overall structure and functions of plants (Ding et al., 2012). For example, cellulose, the most abundant molecule in plant tissue, has *ca*. 40 times more load beading capacity than lignin (Gibson, 2012), the second most abundant molecule in many plants. However, the deposition of lignin that occurs during secondary cell wall formation provides chemical and physical recalcitrance to plant tissues through the formation of lignocellulosic complex, and enhances the structural integrity, stiffness, and hydrophobicity of the cell wall (Boerjan, Ralph, & Baucher, 2003; Maeda, 2016; Rogers & Campbell, 2004; Vanholme et al., 2012). The overall plant structural matrix including cellulose and lignins undergoes significant modifications under environmental stress (Le Gall et al., 2015). Other biopolymers, such as tannins, and cuticular matrices also enhance the recalcitrance of plant biomass by regulating the activity of microbial exo-enzymes and overall tissue hydrophobicity, respectively. In plants, many of the recalcitrant polymeric compounds originate from the phenylpropanoid pathway, which is directly modulated by environmental stressors.

2.2.1 | Phenylpropanoid metabolism under environmental stress

More than 20% of organic molecules in many woody plants are derived from the phenylpropanoid pathway, of which phenylalanine is the precursor (Figure 3). The products of the phenylpropanoid pathway, including polyphenols, such as lignins, flavonoids, and tannins,

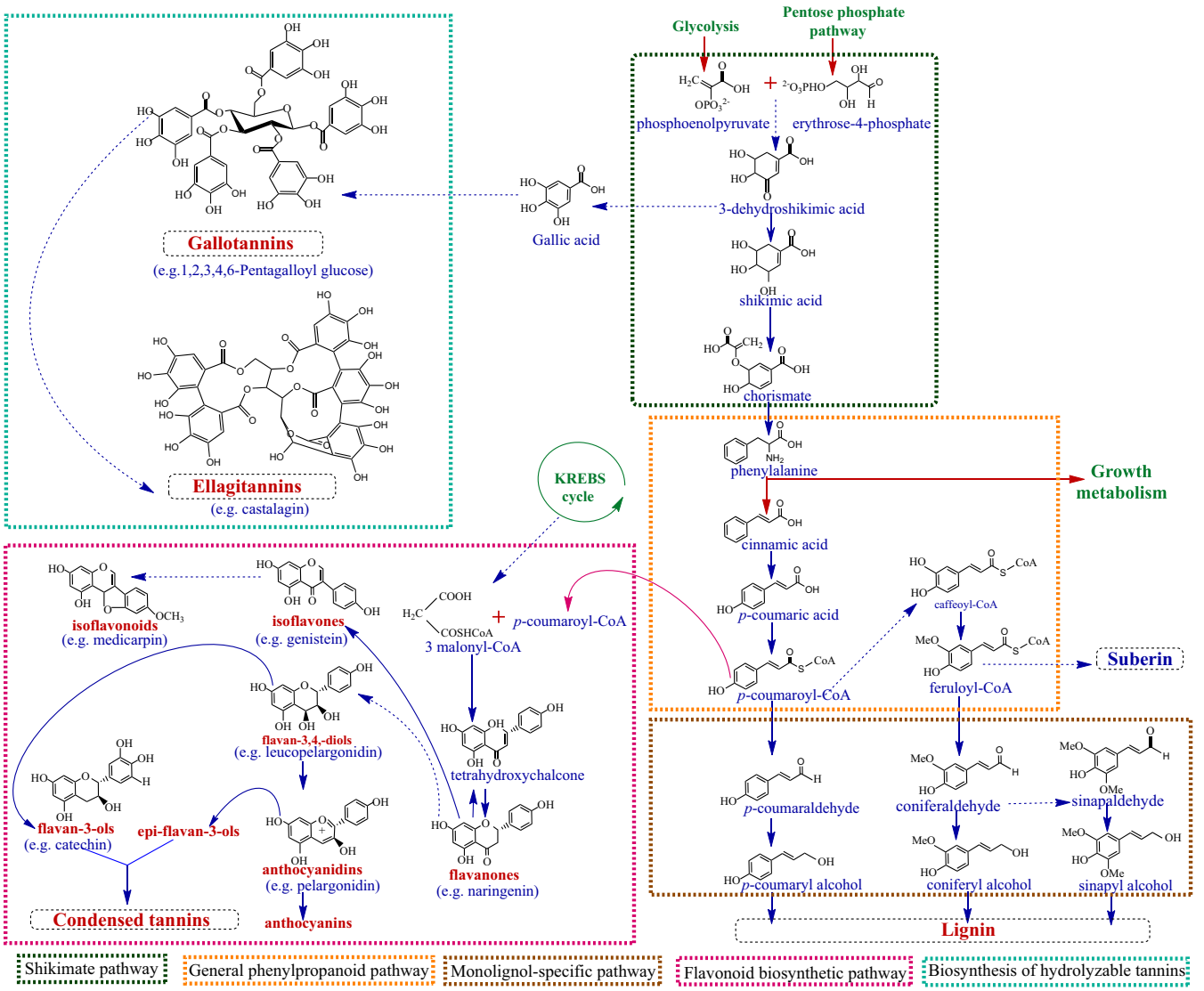


FIGURE 3 Pathways that are involved in the production of phenolic compounds in plants. Arrows with dotted lines indicate that several unknown intermediate steps are involved. For certain compound classes, an example of a compound is provided in parentheses (Lepiniec et al., 2006; Vanholme et al., 2010; Pouysegu, Deffieux, Malik, Natangelo, & Quideau, 2011) [Colour figure can be viewed at wileyonlinelibrary.com]

not only protect the plants from pests and diseases during the presenescence stage but also regulate the decomposition of these tissues during the postsenescence stage. In addition to an increase in the total quantity of phenylpropanoids from the reprogramming of metabolic pathways (Dixon & Pavia, 1995; Munne-Bosch, Queval, & Foyer, 2013), environmental stressors can also alter the chemical composition of these heteropolymers. The chemical reactivity and hence the biological function of heteropolymeric compounds is influenced by their chemical composition through the identity of monomers, the interunit linkages that connect the monomers within the polymer, the degree of polymerization, and the localization of these polymers within the three-dimensional tissue matrix (Ding et al., 2012; Gibson, 2012; Kraus, Yu, Preston, Dahlgren, & Zasoki, 2003; Tharayil et al., 2011; Top, Preston, Dukes, & Tharayil, 2017). These changes in the structural matrix, which is generally retained in the senesced litter, could influence the susceptibility of tissues to microbial decomposition via changes in biological reactivity or reductions in the accessibility of microbial enzymes to easily degradable substrates. Thus, it is critical to understand the molecular-level changes in heteropolymers that are imposed by environmental stresses during the formative stage of the tissue. Here, we focus on the stress-induced compositional changes in lignins, tannins, cuticle, and suberin, which are four important structural heteropolymers that together account for up to 30% of plant biomass.

Lignin

Lignin is a hydrophobic, aromatic heteropolymer that is mostly embedded in the polysaccharide matrix of the secondary cell wall, and it is the second most abundant biopolymer after cellulose (Boerjan et al., 2003). Lignin originates from the phenylpropanoid pathway, where phenylalanine is first deaminated to form cinnamic acid, which then undergoes a series of hydroxylation and methoxylation

reactions to form the respective lignin monomers (Bonawitz & Chapple, 2010). Lignin is a primarily composed of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) monomers produced from *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, respectively (Whetten & Sederoff, 1995; Figure 4a). The methyltransferase activity catalyzes the step-wise methylation of coumaroyl-CoA at positions *ortho* to the phenolic hydroxyl group to produce the S and G units of lignin (Whetten & Sederoff, 1995). The monomer composition of lignin is predominantly a characteristic of the plant lineage, where the G units predominate in gymnosperms, the G and S units predominate in angiosperms, and H, G, and S units predominate in grasses. Governed by their degree of methylation at the C3 and C5 positions, the G, S, and H monomers differ in the number of sites available for cross-linking during lignin polymerization (Figure 4a). Thus, the intramolecular linkages within the heteropolymeric lignin are a function of the proportional abundance of the S, G, and H units. Depending on the availability of the C3 and C5 position of the phenolic rings, the different monomeric units of lignin are bonded together through a series of noncondensed C-O-C ether (β-O-4) linkages or condensed C-C linkages (5-5′, β-5′, β-β, β-1; Terashima & Fukushima, 1988; Figure 4b).

Compared with homopolymers, such as cellulose, where the monomer units are polymerized directly by a polymerizing enzyme, the polymerization of lignin monomers is not directly under enzymatic regulation (Barros, Serk, Granlund, & Pesquet, 2015). Lignin polymerization proceeds mostly through the radical recombination coupling reaction of the oxidized mono/oligolignol, where peroxidase/H_2O_2 or laccase/O_2 act as oxidizing agents (Boerjan et al., 2003; Zhao et al., 2013). Thus, the rate-limiting step in lignin formation is the abundance of the monomer units and the rate of radical generation (Terashima et al., 1995; Van Parijs, Morreel, Ralph, Boerjan, & Merks, 2010). The nonenzymatic nature of polymerization results in the incorporation of nonmonolignol units into the lignin polymer. This nonspecificity of lignin polymerization is evidenced by the presence of a diverse array of cinnamate, hydroxybenzoate, and flavonoid conjugates in lignin (Karlen et al., 2016), which could alter the susceptibility of lignin to enzymatic deconstruction (Li, Pu, & Ragauskas, 2016).

The proportion of individual monomers of lignin differs among different cell types, among different regions in the cell wall and among different plant species. Moreover, the proportion of different lignin monomers is not a species-specific characteristic but rather is highly influenced by developmental and environmental cues (Carpita, 1996; Whetten & Sederoff, 1995). The metabolic reprogramming of the monolignol pathway under stress (Dixon & Paiva, 1995) could change the type of monomer and the rate at which monomers are supplied to lignin nucleation sites, which could alter the molecular identity of the lignin polymer. The randomness in the monomer identity of the lignin polymer could be further facilitated by the nonspecificity of the monolignol transporters in the cells (Liu, 2012).

Through the above conduits, environmental stress influences both the composition and localization of lignins in the cells (Cabané et al., 2012; Hawkins & Boudet, 2003; Moura et al., 2010). For example, although lignification is limited to secondary cell walls, under environmental stress, lignin impregnates the primary cell walls, which are normally nonlignified (Barros et al., 2015). Integration of lignins with cellulose matrix is enhanced through ester-ether cross linkages mediated by hydoxycinnamates (Ralph, 2010). These cross linkages that enhance the overall rigidity and stability of cell wall matrix increase under environmental stress (Le Gall et al., 2015). In addition, lignin produced during stress, which is termed stress lignin, is compositionally different from the constitutive lignin of the same plant species. For example, stress lignin has a higher abundance of G and H units and a lower abundance of S units, which results in highly branched lignin polymers with more interunit C-C bonds and more dimer units; thus, stress lignin is more condensed than constitutive lignin (Lange, Lapierre, & Sandermann, 1995). Lignin units that are acetylated at the γ-carbon of the side chain (predominantly at the S-unit) are reported in different angiosperms (Del Rio, Marques, Rencoret, Martinez, & Gutierrez, 2007; Del Rio et al., 2008). The resultant lignin polymer formed from acylated monolignols is more hydrophobic than normal lignin and hence is thought to be an adaptation for drought tolerance (Del Rio et al., 2007, 2008). Because the biodegradation of lignin is primarily dependent on microbial exoenzymes (Wong, 2009), the increased hydrophobicity could increase the recalcitrance of lignin as it repels microbial enzymes and prevents the accessibility to cellulose (Li et al., 2016).

Although stress significantly alters the biosynthesis of lignin and generally increases its quantity (Dos Santos et al., 2015; Le Gall et al., 2015; but see van der Weijde et al., 2017), the deposition of lignin is not uniform across all tissues and cell types. For example, in maize subjected to drought, an increase in lignin deposition was observed in the basal part of the roots, which reduced the growth in the basal region and induced a corresponding decrease in lignin deposition in the apical region, which would help plants maintain growth in the apical regions under water stress (Fan & Neumann, 2004; Fan et al., 2006). Similarly, plants exposed to drought show increased deposits of lignin in the exodermis and endodermis of the roots, which reduce the loss of water from internal tissues (Cruz, Jordan, & Drew, 1992). This differential deposition of lignin as well as the altered quantity and composition of lignin modify the pattern of plant tissue decomposition under drought. However, these changes must be investigated in different plant species because they differ in their ability to adapt to climate stressors.

Tannins

Tannins are the second most abundant polyphenol in many plants after lignins, and they are broadly classified as condensed tannins or proanthocyanidins (CT; Figure 5) and hydrolysable tannins (HT). Hydrolysable tannins are further classified as gallotannins and ellagitannins (Figure 6), and biosynthesis of HTs branches off from shikimate pathway, with 3-Dehydroshikimate as the precussor. Angiosperms produce pure CT or HT or a mixture of both CT and HT, whereas gymnosperms produce mostly pure CT (Triebwasser, Tharayil, Preston, & Gerard, 2012). When present in green tissue, tannins play a critical role in plant–herbivore and plant-to-plant interactions (Barbehenn & Constabel, 2011; Kraus, Dahlgren, & Zasoski,

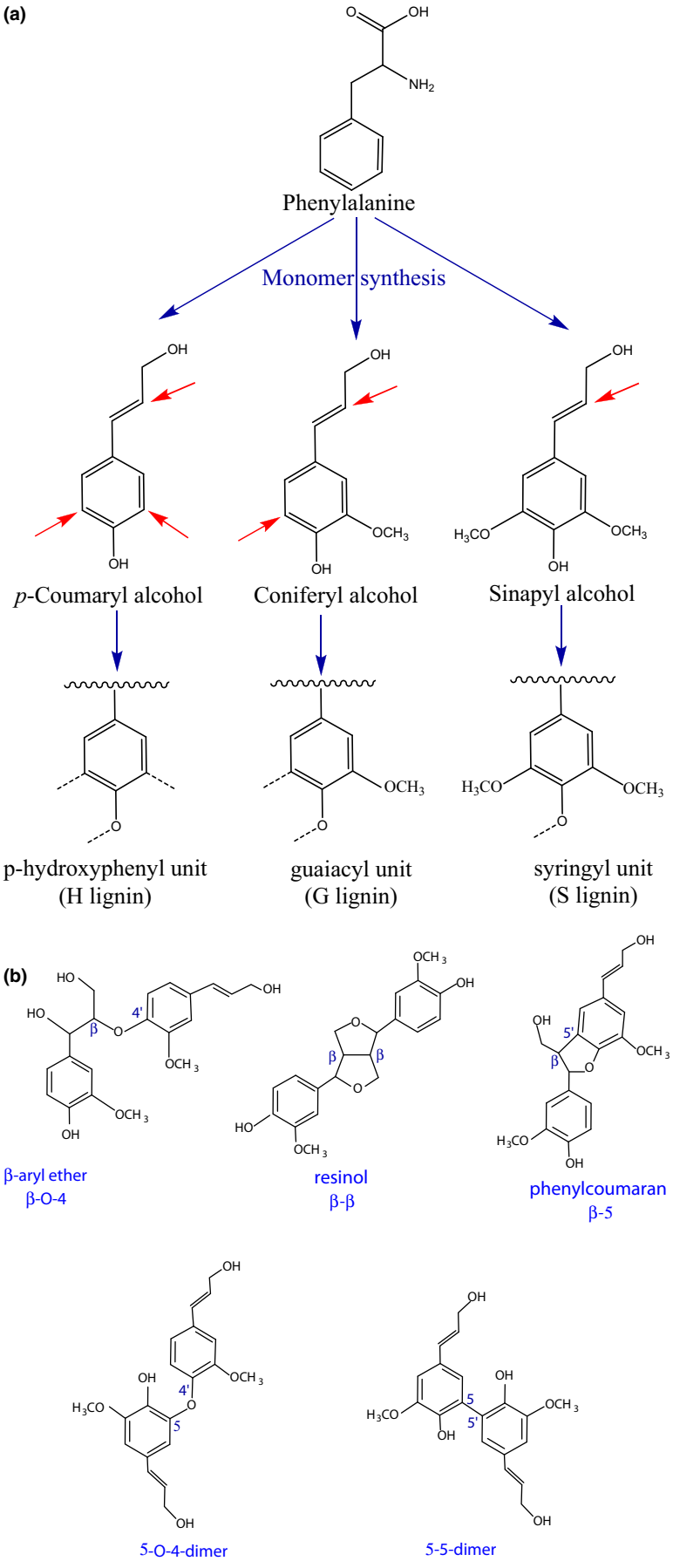
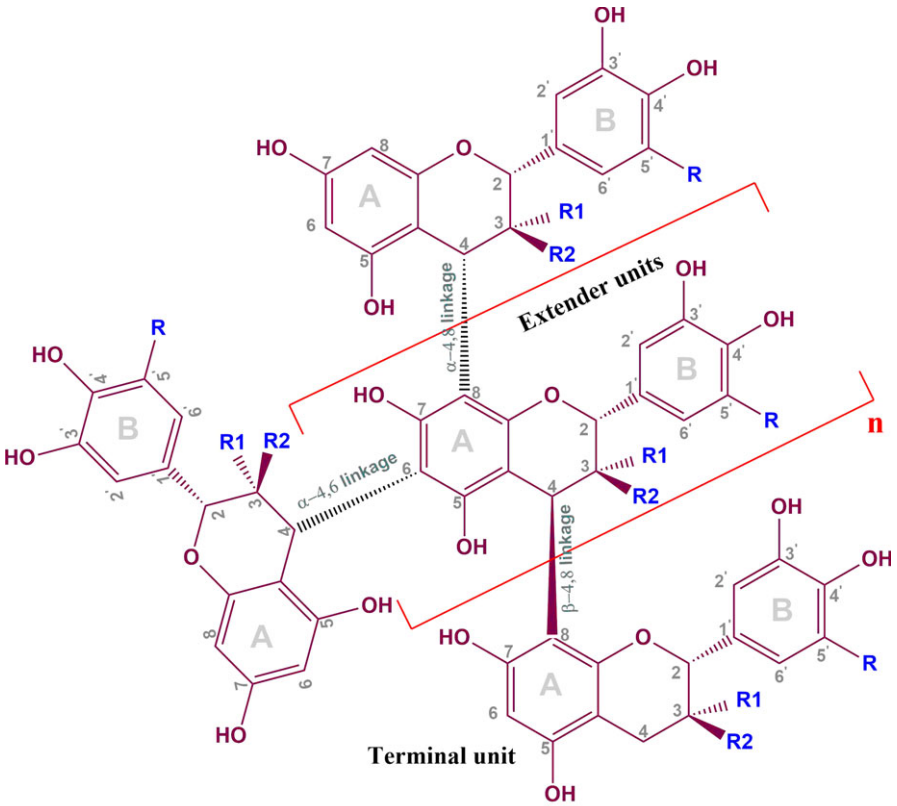


FIGURE 4 (a) Structure of monolignols p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol that forms H (p-hydroxyphenyl), G (guaiacyl), and S (syringyl) lignin, respectively (red arrows represent potential sites for cross-linkage with other lignin monomers), and (b) representation of linkages typically found in different types of lignin. Adapted from Hatfield & Vermerris, 2001. Also see Bonawitz & Chapple, 2010; Vanholme et al., 2010. Recalcitrance of lignin to decomposition is partly regulated by the interunit linkages connecting the monomers, which are governed by the number of sites available for cross-linkages in the monomer units (red arrow). H-lignin with nonmethoxylated C3 and C5 sites forms more cross-linked lignins that are more resistant to decomposition because of direct C-C linkages compared with S-lignin, where the cross-linkage is limited to labile β-O-4 linkages. Although the activation of the monomers is catalyzed by plant peroxidases, the formation of lignin polymer in plants is not under direct enzymatic control. Hence, the monomer composition of lignin and the interunit linkages are primarily governed by the rate at which monomers are supplied to lignin nucleation sites. Climatic stress that influences the phenylpropanoid pathway can thus potentially alter lignin composition by modifying the relative proportion of monomers that are synthesized and exported to the lignin nucleation sites [Colour figure can be viewed at wileyonlinelibrary.com]



MONOMERS	R	R1	R2
Procyanidin			
Catechin	H	H	OH
Epicatechin	H	OH	H
Prodelphinidin			
Gallocatechin	OH	H	OH
Epigallocatechin	OH	OH	H

FIGURE 5 Representative structure of condensed tannins depicting the potential chemical diversity. Chemical diversity can be contributed by the identity of monomers based on the number and position of hydroxylation, the number of extender units (n) that regulate the chain length of the tannin polymer, and the type of interflavan linkages connecting the monomers. Although the β-4,8 linkage more commonly results in a linear chain of tannins, the β-4,6 linkage results in the branching of the polymer, which potentially results in a greater association between tannins and cell walls. The trihydroxy B-ring is more reactivate in inactivating enzymes than the dihydroxy B-rings. Although the polymerization of tannins is enzymatically regulated, the degree of hydroxylation of the monomers is catalyzed by the same enzyme, which could result in substrate competition for hydroxylation, thereby altering the tannin composition. Climate stress that alters the carbon flow through the phenylpropanoid pathway could also change the polymer chain length of tannins and their association with cell wall components [Colour figure can be viewed at wileyonlinelibrary.com]

2003; Salminen & Lempa, 2002), and they also protect the plants from harmful radiation and oxidative stress (Close & McArthur, 2002).

Similar to lignin, the quantity and composition of tannins also vary with the plant species, plant age, tissue type, and environmental conditions (Schweitzer et al., 2008). Tannins provide protective functions; thus, climatic stresses, such as warming, together with limited soil moisture have been shown to increase the content of tannins in plant tissues. Previous studies have primarily emphasized the quantity of tannins in ecosystem C regulation and nutrient cycling. However, along with the total quantity of tannins, plants can also alter the structure of tannins by altering the hydroxylation pattern of the B-ring, the substitution pattern of the A-ring, the extent of polymerization, the type of linkage connecting the monomeric units, and the cis vs. trans conformation at C2—C3 (Kraus, Zasoski, Dahlgren, Horwath, & Preston, 2004; Nierop, Preston, & Verstraten, 2006; Figure 5). These compositional changes, in turn, can modify the reactivity of tannins and their protein precipitation capacity. This change in the overall biological reactivity of tannins is particularly important under abiotic stress conditions because plants might attain better protection by producing tannins with a higher reactivity than by producing a greater quantity of tannins. For example, resource-limited environments favor the production of more reactive HT that are metabolically cheaper (0.27 ATP equivalent per gram, Atkinson, 1977) than CT, which are 45% more metabolically expensive. Along this line, *Acer rubrum* exposed to high temperature and drought has been shown to produce a higher proportion of HT (Tharayil et al., 2011). In addition, environmental stressors, including low N and drought, have been shown to increase the polymer chain length of CT (Cohen & Kennedy, 2010; Kennedy, Matthews, & Waterhouse, 2002), which increases the biological reactivity of tannins (Kraus, Dahlgren, et al., 2003). Along with the content and composition, the localization of tannins within the tissue has a significant influence on the overall tissue recalcitrance. In young leaves, tannins are primarily stored in cell vacuoles (Marles, Ray, & Gruber, 2003; Stafford, Smith, & Weider, 1989) and thus are sequestered away from potential interactions with other plant metabolites. During the maturation of leaves, tannins penetrate the cell walls (Bussotti, Gravano, Grossoni, & Tani, 1998), resulting in an increase in the fiber-bound proportion of tannins via their interactions with pectin. Drought stress has been shown to influence the proportion of tannins associated with cell walls (Top et al., 2017).

Because of the ability of tannins to complex with proteins and thus to inactivate enzymes, tannins are less actively resorbed during

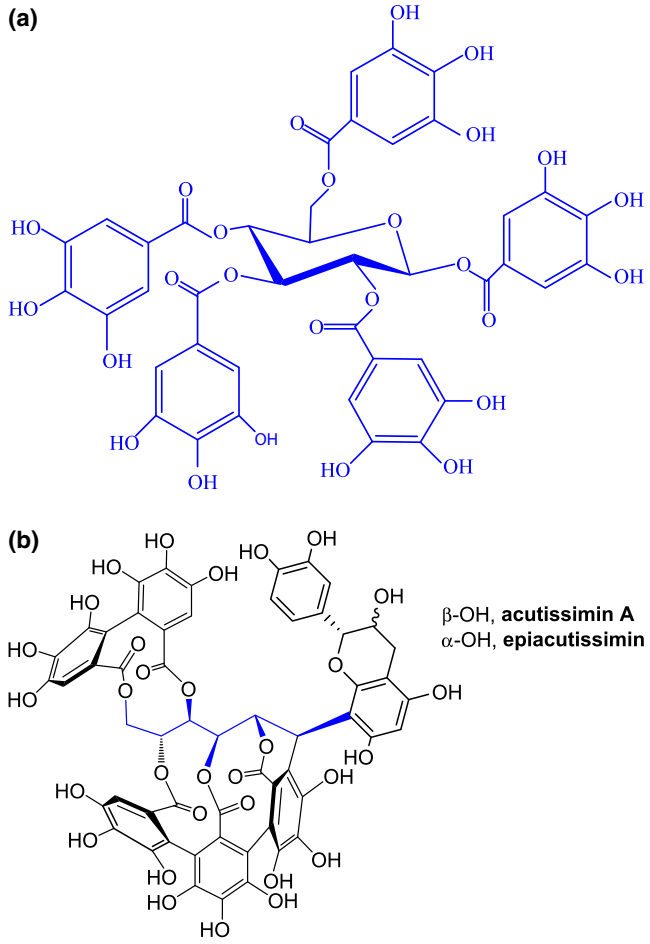


FIGURE 6 Representative structure of (a) gallotannins and (b) ellagitannins. Drier climates have been shown to induce the production of a greater proportion of hydrolysable tannins (HT) than wetter climates, and the enzyme inactivation capacity of HT is generally higher than that of condensed tannins (Tharayil et al., 2011) [Colour figure can be viewed at wileyonlinelibrary.com]

tissue senescence (Top et al., 2017), resulting in a relative enrichment of tannins in senesced litter. Tannins in senesced litter can account for up to 25% of the tissue dry weight (Kraus, Dahlgren, et al., 2003) and thus is a major form of carbon input to soils. Tannins in senesced tissues retain their biological reactivity (Hagerman, Rice, & Ritchard, 1998) and could inactivate soil enzymes (Triebwasser et al., 2012), which could alter soil N mineralization (Adamczyk, Kitunen, & Smolander, 2009; Kraus, Dahlgren, et al., 2003; Kraus, Yu, et al., 2003; Madritch & Lindroth, 2015; Nierop et al., 2006; Suseela, Alpert, Nakatsu, Armstrong, & Tharayil, 2016; Tharayil, Alpert, Bhowmik, & Gerard, 2013; Zucker, 1983;). Thus, changes in the quantity, composition, and localization of tannins that occur during the growth-phase of the plant could influence the litter decomposition and soil nutrient cycling.

Cuticle

The cuticle framework is the largest interface between the biosphere and atmosphere, and it functions as a barrier that prevents nonstomatal water loss from the leaves and contributes to plant defenses against pests and pathogens, UV radiation, and mechanical damage (Bargel, Koch, Cerman, & Neinhuis, 2006; Gniwotta et al., 2005; Heredia, 2003; Onoda, Richards, & Westoby, 2012). The cuticle consists of cutin, a polyester polymer of C16 and C18 fatty acids, and cutan, a long-chain (up to C33) hydrocarbon-polymer (alkenes and alkanes), which are interlaid and overlaid with cuticular waxes. The highly heterogeneous chemical structure of cuticle allows this heteropolymer to perform multiple functions. Cuticular wax is also a multiphase system consisting of crystalline domains composed of polymers of very long chain (C24–C34) saturated fatty acids and an amorphous domain composed of short-chain aliphatics and non-aliphatic compounds (Dominguez, Heredia-Guerrero, & Heredia, 2011; Johnson, Dorot, Liu, Chefetz, & Xing, 2007).

The amount of cuticular matrix in plants is regulated by environmental cues and can change within weeks of exposure to environmental stress (Franke & Schreiber, 2007; Kim, Park, Kim, & Jenks, 2007; Kosma et al., 2009; Meyer & Peterson, 2011; Seo et al., 2011; Shepherd & Griffiths, 2006). Water deficits promote the production of cuticular waxes in several plant species (Cameron, Teece, & Smart, 2006; Kosma et al., 2009). Cutan is an aliphatic hydrophobic biopolymer that increases in plants under drought stress (Boom, Damste, & De Leeuw, 2005). However, the barrier properties of the cuticle are more likely associated with the chemical composition of cuticular components (Kerstiens, 2006; Riederer & Schreiber, 2001). Plants exposed to lower irradiation levels and higher temperatures show increased production of fatty acids, aldehydes, primary alcohols, and esters, whereas those exposed to high irradiation and lower temperatures show increased production of alkanes, secondary alcohols, and ketones. Environmental perturbations also lead to changes in the chain-length distributions in waxes (Shepherd & Griffiths, 2006), which is evident in plants adapted to warmer and drier climates, such as the Mediterranean, with these plants showing a greater proportion of longer chain (C34-C37) alkanes in their waxes than plants adapted to cooler and wetter climates (Dodd & Poveda, 2003). Because of the depolymerization susceptibility of the ester linkages in cutin, this polymer is labile, whereas cutan and crystalline waxes are more recalcitrant and hydrophobic (Boom et al., 2005; Shechter, Xing, & Chefetz, 2010; Stimler, Xing, & Chefetz, 2006). Thus, along with the quantitative increase in cuticular matrices, the acclimation by plants to stressful climates could be caused by increases in cutan and crystalline waxes in the cuticle.

Suberin

Similar to cuticle in leaves, in roots, suberin functions as an apoplastic barrier to control the movement of water, solutes, and gases. Suberin also helps in defending roots against pathogens and toxic compounds in the rhizosphere. In plant roots, suberization occurs in the exodermis and the casparian strip of the endodermis. Suberin is an extracellular biopolymer consisting of a polyaliphatic (ω-hydroxyacids, α, ω-diacids, fatty acids, and primary alcohols) and polyphenolic domain (hydroxycinnamic acid and especially ferulic acid; Bernards, 2002; Ranathunge, Schreiber, & Franke, 2011). The phenolic and aliphatic

domain have differential effects on pathogens, with the aliphatic domain providing resistance against fungal attack and the phenolic domain contributing resistance to bacterial attacks (Lulai & Corsini, 1998). Similar to other plant heteropolymers, such as lignins and tannins, the quantity, composition, and spatial distribution of suberin also vary under biotic and abiotic conditions. Abiotic stresses, such as drought and salinity, were found to increase the quantity of suberin in roots (Franke & Schreiber, 2007; Schreiber, Franke, & Hartmann, 2005). During drier soil moisture conditions, suberin deposits in the exodermis can protect the roots from drying (Enstone, Peterson, & Ma, 2002). Suberin is also deposited as needed in response to environmental cues and forms a variable boundary that separates plant tissue from the environment (Baxter et al., 2009; Ranathunge et al., 2011; Schreiber, Hartmann, Skrabs, & Zeier, 1999). For example, in wetland grasses, suberin deposition in the exodermis of the subapical region of roots acts as a barrier against radial oxygen loss and solute penetration (Kotula, Ranathunge, Schreiber, & Steudle, 2009). Because uniform heteropolymer deposition prevents the entry of water and limits the association between roots and mycorrhizal fungi, suberin lamellae are not produced in all roots and do not form uniformly in every cell of the endodermis of the root (Peterson & Enstone, 1996). The variable nature of heteropolymer deposition enables roots to adopt different strategies to balance the goals of protection against absorptive and transport functions. For example, roots may develop completely suberized long cells alternating with short passage cells with suberin limited to the radial walls. This organization enhances root protection but still allows mycorrhizal fungi to penetrate the roots through these short passage cells (Enstone et al., 2002). Additionally, suberization is much lower in the root apex to maintain an active zone for resource acquisition, which leads to differences in the deposition patterns of heteropolymers moving from the root apex to more basal root tissue (Soukup, Armstrong, Schreiber, Franke, & Votrubova, 2007). Global changes may affect the quantity and composition of suberin through changes in aboveground and belowground resource availability. For example, plants exposed to elevated CO_2 and warming had higher abundance of suberin in the roots compared with that of plants exposed to ambient conditions (Suseela, Tharayil, Pendall, & Rao, 2017). In addition to changes in the quantity of suberin, roots of plants exposed to warming and elevated CO_2 had higher ω-hydroxyacids compared with plants grown under ambient conditions thus indicating a change in the composition of suberin with climate.

Plants exhibit high plasticity in the quantity, composition and localization of heteropolymers in response to climatic stresses that alters the structural chemistry of plant litter. Although plasticity in the heteropolymeric cell wall components enables both aboveground and belowground plant organs to adapt to environmental stresses, this remodeling of structural chemistry may enhance or hinder tissue decomposability by altering the microbial C use efficiency. However, our understanding of the effect of multiple environmental stresses on the molecular-level chemistry of plant tissues, particularly in the roots (Brunner, Herzog, Dawes, Arend, & Sperisen, 2015; Carrillo et al., 2014), as well as tissue decomposition and soil nutrient cycling is still nascent.

2.3 | Effect of climatic stress on the resorption of plant metabolites

Stress-induced changes in the chemical composition of plant tissues may influence belowground processes only if these changes are preserved or further amplified in the senesced tissues. Thus, the influence of climate on the resorption metabolism is a key link connecting plant stress physiology with belowground processes. Globally, perennial plant species are estimated to retranslocate ~60% of nitrogen and phosphorus from their senescing tissues (Vergutz, Manzoni, Porporato, Novais, & Jackson, 2012). Thus, nutrient resorption forms an important strategy through which perennial plants conserve already acquired resources for the subsequent season (Chapin & Kedrowski, 1983). Climate-induced change in the availability of soil moisture can alter nutrient resorption. For example, drought alone or in combination with high warming dramatically decreased the resorption of nitrogen from the leaves of *Quercus rubra* compared with plants exposed to ambient and wet treatments (Suseela et al., 2015). Soil moisture limitation can affect the extent of resorption in plants since moisture stress often results in impairing the phloem-loading capacity (Hill, 1980; Pugnaire & Chapin, 1992). Several studies have also shown a decrease in the resorption of nitrogen with increase in temperature (Oleksyn, Reich, Zytkowiak, Karolewski, & Tjoelker, 2003; Oyarzabal, Paruelo, Federico, Oesterheld, & Lauenroth, 2008; Yuan & Chen, 2009). In addition to soil moisture, any climate-induced change in the availability of soil nutrients could also alter nutrient resorption in plants (Yuan & Chen, 2009).

Climatic stresses also alter the resorption of the metabolites by regulating the plant physiological processes during senescence (Brant & Chen, 2015). The pattern and extent of resorption is influenced by the enzymatic remobilization process and could be affected by the unique composition of the polymers produced during climatic stress. Climate stress often results in the production of tannins and lignins that are open to a higher degree of complexation/cross-linkages with proteins (Tenhaken, 2015), which interferes with normal N resorption. This increase in polyphenol content could interfere with N resorption by binding with the proteins to form tannin–protein complexes that resist the activity of plant proteases during tissue senescence or by reducing the activity of proteases through tannin–protease complexation. For example, the N resorption efficiency of *Quercus rubra* exposed to a combination of warming treatments was strongly correlated with the total tannin content of the mature leaves, where the N resorption decreased with higher tannin content of tissues. (Suseela et al., 2015).

2.4 | Potential impacts of altered tissue chemistry on decomposition and nutrient cycling

Although extractable metabolites constitute <20% of the litter biomass in many plant species (Horwath, 2007), these labile compounds directly promote microbial metabolism and thus shape the initial trajectory of decomposition of the senesced litter (Berg & McClaugherty, 2008; Suseela et al., 2013). Thus, compositional changes during

production, and an extended resorption of labile metabolites from senescing tissues could change the rate and trajectory of litter decomposition and nutrient cycling. The altered nutrient resorption under climatic stress may also influence the bioavailability of C and N from these litters. For example, the lower degree of resorption of osmoprotectants such as as sugars and amino acids that are produced under climatic stress, can result in litter matrix abundant in labile substrates (van der Weijde et al., 2017) that are of high nutritive value to soil heterotrophs, which could facilitate rapid decomposition of the litter produced under drought. Alternatively, the polyphenols produced in response to stress can complex with cellular proteins, thereby preventing N resorption and resulting in a low C: N ratio in the senesced litter (Suseela et al., 2015). However, because of the recalcitrance of the protein–polyphenol complex, the N in these tissues could be less available to microbes; thus, litter from stressful environments might exhibit a lower rate of decomposition despite a higher N content. In addition, soil microbial communities utilize labile compounds in plant litter to subsidize the energy requirement for the production of exo-enzymes that degrade the more recalcitrant polyphenols (i.e., priming effect; Rasmussen, Southard, & Horwath, 2007; Fontaine, Mariotti, & Abbadie, 2003; Chapman & Koch, 2007). Thus, the formation of polyphenol–protein complexes could hamper this cometabolism and further augment the recalcitrance of litter produced under climatic stress, thereby decreasing the initial rate of nutrient release (Figure 1).

From an enzymatic perspective, the relative resistance of a polymer to degradation (recalcitrance) is often positively correlated with the type of monomers and the molecular linkages connecting the monomers. Thus, because of its linear homopolymeric construction through β-1,4 linkages, cellulose undergoes rapid enzymatic depolymerization. Protective heteropolymers in plants possess multiple types of intermolecular linkages that have varied cleavage propensities (Vanholme, Demedts, Morreel, Ralph, & Boerjan, 2010; reviewed by Boerjan et al., 2003). For example, the abundance of S units results in less polymerized, linear lignins dominated by β-O-4 (β-aryl ether) bonds that are more susceptible to chemical cleavage (Bahri et al., 2006; Stewart, Akiyama, Chapple, Ralph, & Mansfield, 2009). The abundance of H and G units result in more branched lignins, that contain a greater proportion of direct C-C linkages between monomers (Figure 4a), which are less prone to cleavage (Bahri et al., 2006; Faix, Mozuch, & Kirk, 1985). The diversity of interunit linkages in heteropolymers necessitates multiple classes of enzymes working in tandem for the deconstruction of lignins. Thus, lignins that are abundant in G and H units that increase the diversity of interunit linkages tend to degrade more slowly (Talbot, Yelle, Nowick, & Treseder, 2012; Triebwasser-Freese, Tharayil, Preston, & Gerard, 2015). In addition, the abundance of G and H units that produce more networked lignin prevents fiber swelling, thereby hindering the accessibility of the microbial enzymes to the biomass (Ramos, Breuil, & Saddler, 1992). Along this line, recent research has demonstrated that the catalytic efficiency of microbial peroxidase enzymes in soil is more influenced by the monomer composition of lignin than by the total quantity of lignin (Triebwasser-Freese et al., 2015). More compact arrangement of linear S-rich lignin is also thought to reduce the degradation susceptibility of plant biomass (Skyba, Douglas, & Mansfield, 2013).

Plant biomass can be considered as a polydisperse matrix consisting of both labile and relatively recalcitrant structural compounds. Thus along with the inter-unit linkages within the heteropolymers, the overall recalcitrance of such composites is enhanced by cross linkages between various components within the tissue matrix. The abundance of cross-linker units such as hydroxycinnamates and their dehydrodimers, that integrates lignins to the cellulose matrix increases the overall resilience of the plant tissues (Ralph, 2010). The influence of cross-linkers is often reflected during the progression of litter decomposition, where the litter matrix becomes preferential enriched with carbohydrates that are cross-linked to lignins, which then reduces the rate of decomposition (Suseela et al. 2013, 2014).

Similar to lignins, stress-induced quantitative and compositional changes in tannins also alter litter decomposition and soil nutrient cycling. The inherent recalcitrance together with the protein complexation capacity make the content and composition of tannins in senesced tissues highly significant in regulating ecosystem C and N cycling (Northup, Yu, Dahlgren, & Vogt, 1995). Tannins form strong complexes with most proteins through H-bonding and hydrophobic interactions that can (i) reduce the catalytic efficacy of enzymes and (ii) reduce the substrate suitability for proteolytic enzymes, thereby decreasing the decomposition of organic matter and interfering with soil N mineralization (Tharayil et al., 2013; Triebwasser et al., 2012). Similarly, tannins exhibit a two-fold increase in the inhibition of microbial peroxidase enzymes compared with hydrolases because of their ability to function as efficient redox buffers (Triebwasser et al., 2012) that quench the active intermediates of peroxidases. Because lignin degradation primarily depends on microbial exo-enzymes (Wong, 2009), an abundance of tannins, through their redox-buffering capacity and complexation reactions, can deactivate peroxidases and slow down lignin degradation.

In addition to their abundance, the localization of tannins can also influence tissue decomposition. For example, tannins that form complexes with the cell wall through tannin–pectin complexes (Jakobek, 2015; Watrelot, Le Bourvellec, Imberty, & Renard, 2013) may decrease the decomposition susceptibility of senesced litter compared with vacuolar tannins that are susceptible to leaching losses during early stages of decomposition (Schofield, Hagerman, & Harold, 1998). Thus, the decomposition susceptibility of senesced litter is often robustly correlated with the proportion of fiber-bound tannins than with total tissue tannins. Additionally, vacuolar tannins that leach from the litter into the soil undergo condensation and polymerization reactions with proteins, thereby protecting nitrogenous compounds in the soil, and potentially leading to long-term N storage (Kleber, Sollins, & Sutton, 2007; Kraus, Dahlgren, et al., 2003; Madritch & Lindroth, 2015; Tharayil et al., 2013). Tannin concentrations as low as 2 mg/g soil significantly reduce N mineralization (Kraus et al., 2004; Tharayil et al., 2013). Complexation with proteins makes tannins resistant to tannases (microbial enzymes that degrade

HT; Belmares, Contreras-Esquivel, Rodriguez-Herrera, Coronel, & Aguilar, 2004), whereas tannin complexation protect the proteins from the activity of proteases, thereby increasing the overall recalcitrance of tannin–protein complexes in the soil (Adamczyk et al., 2009). Apart from the quantity, the monomeric composition and polymer chain length of tannins strongly influence the N and P mineralization rates in soil, where tannins with a greater proportion of prodelphinidins being more inhibitory to mineralization (Nierop et al., 2006). Thus based on species-specific stress response in plants, tannins produced under stress could have contrasting influence on litter decomposition and soil N and C cycling. For example, abundance of vacuolar tannins that are of shorter chain length produced in *Acer rubrum* exposed to drought (Tharayil et al., 2011) could result in inhibition of soil N cycling than the repression of decomposition of this stressed litter, due to the leaching of these tannins to soil during early stages of decomposition (Schofield, Hagerman, & Harold, 1998). Similarly, from a tannin perspective, the litter of *Quercus rubra* produced under wet treatments was proposed to be have a greater resistance to decomposition due to the abundance of fiber-bound, polymerized tannins (Top et al., 2017). However, when carbon-normalized extracts of this *Quercus* litter was applied to soils acclimatised to various climatic treatments, the extracts from litter produced under drought treatments, despite a higher amount of sugars (Suseela et al., 2015), significantly inhibited soil microbial respiration across all treatments due to the relative abundance of specific phenolic compounds that interrupted microbial metabolism (S. Top & N. Tharayil, unpublished). Thus based on the influence of climate (through changes in production and/or resorption) on the proportional abundance of various compounds in litter, the same litter could have contrasting influence on litter decomposition and soil nutrient cycling. In addition, high tannin content in litter could increase the abundance of fungi (slow decomposers adapted to phenol-rich conditions; Mutabaruka, Hairiah, & Cadisch, 2007) relative to the bacterial community (fast decomposers), thereby reducing the rate of organic matter decomposition.

Similarly, under climatic stresses that limit resource availability, acclimatization can occur by the selective enhancement of cutan and crystalline wax production relative to cutin and amorphous wax production, which would increase the rigidity of the cuticular matrix (Takahashi, Tsubaki, Sakamoto, Watanabe, & Azuma, 2012) and lower the decomposability of these tissues. The change in the composition of suberin in roots with greater abundance of monomers of higher chain length could potentially decrease the decomposability of roots produced under global change (Angst, Heinrich, Kogel-Knabner, & Mueller, 2016; Suseela et al., 2017). Thus, climatic stress can induce quantitative and qualitative changes in heteropolymer chemistry that may further alter the bioavailability of C and N.

The climate-induced changes in litter chemical composition would impose selection pressure on soil heterotrophs through the altered composition and bioavailability of substrates (Carillo et al., 2017; Koyama et al., 2017). This, in turn, could change the composition of heterotrophic community and thus the overall functioning of soil biota. The magnitude of these changes would be partly regulated by the contrast in litter chemistry that is produced under climatic stress. For example, a palpable change in litter chemical composition that has a lower influence on the overall nutritive quality of the tissue might cause a shift in community composition of soil heterotrophs, but not in the overall functional attributes. However, significant shifts in litter chemical composition resulting in the abundance of substrates that are less readily bioavailable would shift the microbial community composition, which would alter the mineralization of nutrients in the litter. Climatic stress also directly act as a selection pressure on soil microbes. Climatic stressors influence the physiology, functional activities and community composition of soil microbes which decomposes the litter (Bouskill, Wood, Baran, Hao, et al., 2016; Bouskill, Wood, Baran, Ye, et al., 2016). Thus, the decomposition dynamics of plant litter would potentially be a product of the decomposer responses to both the direct effect of climate and the climate-induced altered litter chemistry. A detailed synthesis of the effects of global change on soil microbes has been reviewed elsewhere (Classen et al., 2015; Mohan et al., 2014; Singh, Bardgett, Smith, & Reay, 2010).

2.4.1 | Indirect effect of climate on litter decomposition in different biomes

The indirect effect of climate change on litter decomposition may vary with different biomes because climate factors that act as an environmental stress in one biome may present favorable conditions for growth and decomposition in another biome. For example, in tropical biomes, elevated temperatures together with a reduction in soil moisture may pose severe abiotic stress to plants, which may potentially result in metabolic perturbations with the ability to further alter the litter chemical composition and decomposability. However, in high-latitude ecosystems, warming may accelerate plant growth, particularly under nonlimiting soil resource conditions (Elmendorf et al., 2012). Thus, in high-latitude ecosystems, any change in litter chemistry caused by climatic factors that impose favorable conditions for growth may not translate to altered litter decomposability. Such characteristics are further evident from a comprehensive litter decomposition experiment that utilized litter from different combinations of global change treatments in high-latitude ecosystems (Table 1; Aerts, Van Bodegom, & Cornelissen, 2012). The results revealed that the global change factors resulted in a threefold variation in litter stoichiometric ratios, with treatments that included warming increasing the tissue C:N by an average of 17% and those that included elevated CO_2 increasing the tissue C:N by an average of 12%. However, the overall response in the rate of decomposition was an order of magnitude lower than the response ratio of litter C:N, which may be related to a lack of structural changes in litter in these colder biomes where warming, in general, does not result in environmental stress. This finding suggests that changes in elemental ratios (e.g. C:N) may not translate to corresponding changes in litter decomposability (Aerts et al., 2012). In high-latitude ecosystems, climate factors also had less of an effect

TABLE 1 Litter decomposition experiments that employed litter from plants exposed to global change factors

Global change experiments	Treatments	Plant species used for the decomposition experiment	Changes in measured chemical parameters between control and global change treatments	Time of decomposition	Major conclusion	Key references
Warming experiments						
Harvard Experimental Forest, MA, USA	Warming (ambient + 5°C), ambient temperature	*Quercus sp*., *Betula sp*., *Acer saccharum* and *Pinus strobus*	N increased by 40% and P decreased by 100% in the heated treatment compared to the ambient treatment.	56-day lab incubation and field mesocosm study	Decomposition of leaves from the ambient treatment increased total P by 115% in the mesocosms than the leaves from the heated treatment. The magnitude of N release did not differ between leaves from the heated and ambient treatment	Fey, Mertens, Beversdorf, Mcmahon, and Cottingham (2015)
Subalpine meadow at the Rocky Mountain Biological Laboratory, CO, USA	Warming (infrared radiation at an intensity 22W/m^2), ambient temperature	*Artemisia tridentata*, *Festuca thurberi*, *Delphinium nuttallianum*, *Erigeron speciosus*, *Erythronium grandiflorum*, *Pentaphylloides floribunda*, *Ligusticum porter*	*A. tridentata* in heated plots had lower lignin and lower C:N ratio than the control. *E. grandiflorum* had higher C:N ratio and a trend of higher lignin: N ratio in the heated plots relative to control. Other species did not exhibit differences in litter chemistry due to warming.	Field incubation (~275 days)	*A. tridentata* from heated plots had higher rates of decomposition than those from the control plots.	Shaw and Harte (2001)
Multifactor global change experiments						
33 Arctic and Alpine Field experiment	Warming (W), Fertilizing (F), Irrigation (I), Elevated CO_2 (CO_2), Elevated UVB irradiance (UV), Shading (S) (24 W, 17 F, 4 I, 2 CO_2, 4 UV, 3 SH, 8 W*Fd, 3 F*I, 1 W*CO_2, 1 W*UV, 1 CO_2*UV, 1 CO_2*I, 1 UV*I, 1 CO_2*UV*I)	Deciduous dwarf shrubs, evergreen dwarf shrubs, grasses, sedges, forbs, wood-rushes, sedges, mosses	Elevated CO_2 increased C: N ratio by 12% and warming increased C: N ratio by 17%.	Two year field incubation	The response ratio of decomposition rate was an order of magnitude less than the change in the C: N ratio of the litter.	Aerts et al. (2012); Cornelissen et al. (2007)
Jasper Ridge Global Change Experiment, California, USA	ECO_2 (680 ppm), N, warming (1°C), increased precipitation (+50%)	Grasses (*Avena* spp) and forbs	Lignin increased in grasses and forbs exposed to elevated CO_2, lignin decreased in grasses exposed to warming and forbs exposed to increased precipitation. N increased with nitrate application.	October 2002-summer 2003	Change in litter quality due to elevated CO_2 did not alter mass loss of the litter in the short term.	Henry, Cleland, Field, and Vitousek (2005)

(Continues)

TABLE 1 (Continued)

Global change experiments	Treatments	Plant species used for the decomposition experiment	Changes in measured chemical parameters between control and global change treatments	Time of decomposition	Major conclusion	Key references
Old Field Community Climate and Atmosphere Manipulation (OCCAM), Oak Ridge, Tennessee, USA	Ambient CO_2, ECO_2 (ambient + 300 ppm), warming (ambient + 3°C), ambient temperature, differential irrigation (dry/wet: 2 mm/25 mm per week)	Fine roots of *Festuca pretense*, *Trifolium repens*, *Lespedeza cuneata*	No change in C: N ratio of roots of all species due to elevated CO_2. *Lignin concentration F. pratense*: 16% and 18% in ambient and ECO_2, respectively. *L. cuneata*: 14% and 16% in ambient and ECO_2, respectively.	120-day lab incubation	Slower decomposition of *T. repens* and *L. cuneata* exposed to ECO_2 than that of ambient. No change in decomposition of *F. pratense*.	De Graaff et al. (2011)
Biodiversity, CO_2 and Nitrogen (BioCON), Minnesota, USA	Ambient CO_2, ECO_2 (560 ppm), N addition (4 g N m^{-2} yr^{-1})	Combined litter from selected plant species from a mixture of C4 grasses, C3 grasses, and legumes.	Elevated CO_2 decreased percent N and percent acid-hydrolyzable residue or Klason lignin.	Two year field incubation	Decomposition of litter from elevated CO_2 had only 2.5% decrease in carbon loss.	Knops et al. (2007)
Warming & Nitrogen addition experiment, Ontario, Canada	Warming (ambient + 2–3°C); ambient temperature, N addition (6 g N m^{-2} yr^{-1})	*Bromus inermis*, *Poa pratensis*	–	Two years field incubation	Warming induced changes in litter quality had a significant effect on mass loss than the direct effect of warming.	Henry and Moise (2015)
Boston Area Climate Experiment, Waltham, MA, USA	Warming (ambient, +1, +2.5, +4°C); Precipitation [ambient, wet (ambient + 50%), dry (ambient-50%]	*Quercus rubra*, *Quercus alba*	Litter exposed to the dry treatment had higher abundance of alkyl compounds and lignin compared to litter exposed to the wet treatment.	Two years of field incubation. Litter collected from the ambient, wet and dry treatments were placed in all precipitation treatments.	After the first year of decomposition, compared to the ambient and wet treatment litter, the litter from the dry treatment had higher abundance of alkyl C irrespective of the precipitation treatments where the litter was decomposing.	Suseela V, unpublished.
California grassland, Irvine, CA, USA	Drought (50% reduction in annual rainfall), N addition (60 kg N ha^{-1})	Grasses and forbs	Litter exposed to drought had higher C: N ratio, higher lignin, less cellulose and hemicellulose, higher sugar, starch, and fats.	One year field incubation	Microbial communities exposed to drought litter had higher abundance of fungi which in turn altered litter decomposition in the initial stages.	Allison et al. (2013)
Warming and ozone experiment, Finland	Warming (ambient, ambient + 2.1–4.2°C), Ozone (ambient, elevated ozone-1.4 × times the ambient)	*Betula pendula* Roth (clones gt14 and gt15)	Litter exposed to warming had higher C:N ratio gt14 clone (C:N ratio was 14.4 and 18.4 in ambient and warming treatments, repectively) gt15 clone (C:N ratio was 16.2 and 18.6 in ambient and warming treatments, repectively).	257 days of field incubation	For gt14, litter from warming treatment decomposed slower than litter exposed to ambient treatment, while for gt15, the trend was opposite which could be attributed to changes in other chemical or physical litter parameters.	Kasurinen, Silfver, Rousi, and Mikola (2017)

(Continues)

TABLE 1 (Continued)

Global change experiments	Treatments	Plant species used for the decomposition experiment	Changes in measured chemical parameters between control and global change treatments	Time of decomposition	Major conclusion	Key references
Elevated Atmospheric Carbon Dioxide & Warming Experiment, Corvallis, OR	Ambient CO_2, ECO_2 (ambient + 180 ppm), warming (ambient + 3.8°C), ambient temperature,	Douglas-fi r *(Pseudotsuga menziesii* (Mirb.) Franco)	Fine roots exposed to ECO_2 had higher concentration of water-soulble extractives (%WSE). Warming incresed the %WSE and decreased % lignin content of fine roots.	Three-year field incubation	Short-term (≤ 9 months) indicated that roots from the ambient CO_2 and ambient temperature had the slowest rate of decomposition.	Chen et al. (2008)
Warming and drought experiment, Lusignan, France	Summer regrowth exposed to drought and elevated temperature (+3°C) by infrared heating of the canopy for 3 weeks	*Festuca arundinacea*, *Dactylis glomerata*	Warming treatment resulted in a decrease in VSC lignin in both species due to a stimulation of plant growth under warmer comditions. Non-cellulosic sugars increased in *D. glomerata* exposed to warming.	40 days of lab incubation	Addition of litter to soil led to priming of native soil organic matter. *D. glomerata* exposed to summer drought or heating treatment showed higher net positive priming.	Sanaullah et al. (2014)

Searches were done using the ISI Web of Science with the search terms "litter decomposition climate"; "litter quality drought litter decomposition"; "litter quality warming litter decomposition"; and supplemented with references from published articles on this topic. Experiments that had elevated carbon dioxide as the only global change factor were not included in this table (but see Norby et al. 2001).

on nutrient resorption (Aerts, Cornelissen, Van Logtestijn, & Callaghan, 2007). However, a shift in plant species due to climate change may have a greater effect on litter decomposition in colder biomes than change in litter quality within species (Cornelissen et al., 2007). For example, a decrease in lichens and vascular plants may alter the rate of litter decomposition (Aerts, 2006; Cornelissen et al., 2001; Hobbie et al., 2017).

In temperate biomes, warming with a reduced frequency of precipitation results in limited soil moisture. These adverse conditions impose severe stress on plant tissues during their formative stages and result in changes to the structural chemistry (Tharayil et al., 2011; Suseela et al., 2015; Suseela, Triebwasser, et al., 2014; Top et al., 2017; Figure 2). In temperate biomes, similar to altering the chemistry of green tissues, climate also differentially influences nutrient resorption, which further alters the litter chemistry (Norby et al., 2000). Compared with temperate regions, plants in the tropics already experience high temperature and high UV radiation that predisposes them to upregulating their defense systems, which results in an increase in heteropolymers and phenolic compounds (Coley & Aide, 1991). Future changes in climatic conditions, including extreme droughts, may alter plant litter chemistry and decomposition in the tropics. However, the magnitude and direction of these changes in the subtropics, dry tropics, and wet tropics may depend on the precipitation patterns, including the intensity as well as the frequency of precipitation. Models predict less precipitation in the subtropics and dry tropics (Collins et al., 2013), which may amplify the effect of climatic stress on plant litter chemistry. For example, trees in seasonally dry tropical forest ecosystems with limited rainfall had a higher abundance of cutin and suberin, which increases the chemical recalcitrance of plant litter (Campo & Merino, 2016). Similarly, plants adapted to dry Mediterranean ecosystems that are rich in phenolic compounds show further increases in lignin content and the C: N ratio when exposed to drought (Sardans, Roda, & Penuelas, 2006; Sardans et al., 2012). In wet tropical biomes, both temperature and precipitation are predicted to increase (Collins et al., 2013), and the effect on litter quality may depend on the interaction between warmer and wetter conditions. However, in different tropical biomes, few studies have directly investigated climate-induced changes in litter chemistry and the subsequent effect of these changes on litter decomposition.

2.4.2 | Effect of climate-induced altered litter quality on decomposition: Insights from empirical studies

Much of the current knowledge on the effect of global climate change on litter chemistry is based on stoichiometric ratios. The effect of elevated CO_2 and warming on litter stoichiometry in different environments has been elegantly reviewed by Sardans and Penuelas (2012). However, current knowledge on the subsequent effect of these changes on litter decomposition is mainly obtained from CO_2 enrichment experiments. The effect of elevated CO_2 on leaf chemistry and decomposition is highly variable. Studies have reported an increase in C-based compounds and free phenolics

under elevated CO_2 (Couteaux, Kurz, Bottner, & Raschi, 1999; Couture, Holeski, & Lindroth, 2014; Meehan, Crossley, & Lindroth, 2010; Norby et al., 2001; Parsons, Bockheim, & Lindroth, 2008; Parsons, Lindroth, & Bockheim, 2004), whereas others have not found changes in litter chemistry (Billings et al., 2003; Finzi, Allen, Delucia, Ellsworth, & Schlesinger, 2001; Finzi & Schlesinger, 2002; Hall, Stiling, Moon, Drake, & Hunter, 2006; Huttunen et al., 2009; King et al., 2001; Liu, King, & Giardina, 2005). Although in green tissues, the N content decreased by ~14% under elevated CO_2, this change was not translated to the senesced litter chemistry because of incomplete nutrient resorption. For example, a meta-analysis indicated that in senesced leaf litter, the difference in tissue N between ambient and elevated CO_2 was only 7% (Norby et al., 2001). Despite the increase in the C:N ratio of litter under CO_2 enrichment, the decomposition rates of these tissues were independent of CO_2 enrichment (De Graaff, Six, Blum, & Van Kessel, 2006; Kainulainen, Holopainen, & Holopainen, 2003; Knops, Naeemw, & Reich, 2007; Liu et al., 2009; Norby et al., 2001). However, few studies have reported slower decomposition (Parsons et al., 2004, 2008), and others have reported accelerated decomposition of litter exposed to elevated CO_2 (Carney, Hungate, Drake, & Megonigal, 2007; Talhelm, Pregitzer, & Zak, 2009). In general, elevated CO_2 does not act as a plant stress factor, and many plant responses under high temperature and drier conditions that lead to metabolic and structural chemistry changes may be absent under elevated CO_2 alone. Similarly, elevated CO_2 may not influence tissue nutrient resorption (Billings et al., 2003) compared with other climate change factors, such as warming and altered precipitation. Additionally, under future climate scenarios, the effect of CO_2 enrichment on litter chemistry and decomposition will depend largely on the interaction of elevated CO_2 with other climate change factors, such as warming, drought, and nitrogen deposition (Huang, Houlton, Marklein, Liu, & Zhou, 2015; Sardans & Penuelas, 2012). In general, warming and a combination of warming and drought increase the C:N and C:P ratios in plant litter, with a higher production of stress-related C compounds observed in hot/dry environments (Sardans & Penuelas, 2012). However, to our knowledge, few studies have evaluated the molecular-level changes in litter chemistry, and exceedingly few decomposition studies that include climate experiments with warming and drought manipulation treatments have been performed using climatically stressed litter (Table 1).

3 | CONCLUSIONS AND FUTURE PERSPECTIVES

Plant litter decomposition is a fundamental ecosystem process that regulates ecosystem productivity via nutrient recycling. Our synthesis suggests that climatic stresses, such as high temperature and drought, either alone or in combination can dramatically alter the chemical composition of labile metabolites as well as heteropolymers in plant tissues. These changes could lead to a cascade of belowground interactions with the potential to affect nutrient cycling under future climate scenarios, which remain less known. Understanding the magnitude and direction of these infrequently explored changes in litter chemical composition is critical to predicting nutrient cycling and the productivity of ecosystems under future climate scenarios. However, surprisingly, few studies have investigated the effect of climatic stress on molecular-level litter chemical composition. To achieve a better understanding of the effect of warming and drought on litter chemical composition, we propose the following measures.

TABLE 2 Common methods and instrumentation that could enhance the molecular-level understanding of plant tissue matrices

Plant chemical composition	Method &/Instrumentation	Key references
Extractable, small (<1500 Da) metabolites	Gas chromatography- Mass spectrometry (GC-MS)	Fiehn et al. (2000); Lisec, Schauer, Kopka, Willmitzer, and Fernie (2006)
	High Pressure Liquid Chromatography-Tandem Mass spectrometry (HPLC-MS/MS)	De Vos et al. (2007)
	Nuclear Magnetic Resonance (NMR) Spectroscopy	Kim, Choi, and Verpoorte (2010)
Lignins (SVC)	CuO oxidation followed by GC-MS analysis	Kaiser and Benner (2012)
Tannins		
Condensed tannins- quantity	Acid-butanol assay followed by quantifying the amount of depolymerized anthocyanidin by spectrophotometer	Porter, Hrstich, and Chan (1985); Shay, Trofymow, and Constabel (2017)
Condensed tannins- Degree of polymerization & monomer identity	Depolymerization of CT in excess nucleophile followed by HPLC-UV/MS analysis; NMR Spectroscopy	Kennedy and Jones (2001); Gea, Stringano, Brown, and Mueller-Harvey (2011); Zeller et al. (2015)
Hydrolyzable tannins	Methanolysis followed by quantification of ellagic acid and methyl gallate by HPLC-UV, MS/MS	Hartzfeld, Forkner, Hunter, and Hagerman (2002)
Cutin, Suberin	Base hydrolysis followed by GC-MS analysis of monomers	Jarvinen et al. (2009)
Bulk carbon chemistry of plant tissues	Fourier Transform Infrared (FTIR) spectroscopy	Lammers, Arbuckle-Keil, and Dighton (2009)
	Nuclear Magnetic Resonance (NMR) Spectroscopy	Mansfield, Kim, Lu, and Ralph (2012)
	Pyrolysis GC-MS	Ralph and Hatfield (1991); van Erven et al. (2017)

1. Including various analytical techniques that meaningfully capture the finer level changes in litter chemical composition is pivotal to understanding the decomposability of the litter matrix (Table 2). The content of lignin and N and other stoichiometric ratios that are commonly used to define litter quality, such as C:N, help us understand the overall elemental cycling in ecosystems. However, many recent studies have shown that litter decomposition rates cannot be robustly predicted from C:N ratios alone (Aerts, 1997; Aerts et al., 2012; Cornwell et al., 2008; Hobbie, Oleksyn, Eissenstat, & Reich, 2010). This is particularly true under environmental stress because the compositional changes in litter that alter the microbial carbon use efficiency and enzyme activities are captured only to a lower extent by elemental ratios. Processes that facilitates decomposition could be more robustly linked to the molecular identity of the substrates in litter that fuels the heterotrophic metabolism than to their elemental composition. Thus, probing deeper into the molecular composition of compounds would provide a mechanistic insight and predictive understanding of the rate of litter decomposition and nutrient cycling. For example, stress-induced changes in lignin captured by measuring 'true lignin,' which provides information about the monomer composition (ratios of C/V, S/V, and SVC), would better predict the decomposability of litter than coarser parameters, such as Klason lignin (Preston & Trofymow, 2015; Preston et al., 2009). In addition to employing wet chemistry analyses to capture the quantity and composition of the litter matrix, changes in the overall compositional chemistry of litter can be effectively captured using other techniques, such as Fourier Transform Infrared spectroscopy (McKee, Soong, Calderon, Borch, & Cotrufo, 2016; Nault, Preston, & Trofymow, 2009; Suseela, Tharayil, Xing, & Dukes, 2014; Suseela et al., 2015).
2. Few studies have measured stress-induced changes in the litter chemistry of tropical biomes and their influence on litter decomposition, which precludes our ability to predict the direction and magnitude of the indirect effect of climatic stress on litter decomposition in the tropics. There is an evident need for such studies in the subtropics, dry tropics, and wet tropics using plants with different functional traits. Conducting coordinated climate manipulation experiments across different biomes would facilitate comparisons of the results, and such experiments would also require collaboration and coordinated efforts between scientists from developed and developing countries (Knapp et al., 2016). Furthermore, the aboveground and belowground tissues exposed to different climatic stresses in the different biomes must be analyzed via decomposition studies in their respective ecosystems to decouple the direct and indirect effects of climate on terrestrial nutrient cycling.
3. The current emphasis on litter chemistry and decomposition is focused on aboveground litter, mainly foliar litter. However, a majority of soil carbon sequestration is achieved by plant roots. As roots occupy a heterogenous soil environment, they rely heavily on the integration of heteropolymers such as lignins, suberins and tannins to protect the tissues from pathogens and harmful chemicals (Mandal, Das, & Mishra, 2011; Thomas et al., 2007) and to maximize their resource uptake functions (Baxter et al., 2009; Schreiber, 2010). Roots possess high plasticity in response to abiotic stresses, particularly drought (Brunner et al., 2015), which can alter the root heteropolymer chemistry. These chemical changes in roots may include change in the quantity, monomer composition and spatial organization of heteropolymers within the three-dimensional root tissue matrix, which can potentially alter root decomposability. Hence, the responses of root chemical composition to climatic stresses and the influence of roots on soil nutrient cycling must be investigated.

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