


Review

Plant Secondary Metabolites—Missing Pieces in the Soil Organic Matter Puzzle of Boreal Forests

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Received: 9 December 2017; Accepted: 29 December 2017; Published: 8 January 2018

Abstract: Processes underlying soil organic matter (SOM) transformations are meeting growing interest as SOM contains more carbon (C) than global vegetation and the atmosphere combined. Therefore, SOM is a crucial element of the C cycle, especially in ecosystems rich in organic matter, such as boreal forests. However, climate change may shift the fate of this SOM from C sink into C source, accelerating global warming. These processes require a better understanding of the involved mechanisms driving both the C cycle and the interlinked nitrogen (N) cycle. SOM transformations are balanced by a network of interactions between biological, chemical and physical factors. In this review, we discuss the findings of the most recent studies to the current state of knowledge about the main drivers in SOM transformations. We focus on plant-derived secondary metabolites, as their biochemical traits, especially interactions with soil microbial communities, organic N compounds and enzymes make them potential regulators of SOM decomposition. However, these regulatory abilities of plant-derived compounds are not fully explored.

Keywords: enzymatic activity; forest soil; tannins; terpenes

1. Introduction

Mechanisms controlling soil organic matter (SOM) formation and decomposition are meeting growing interest as they are critical for soil nutrient cycling and carbon (C) stabilization processes, particularly in ecosystems rich in organic matter, such as boreal forests. These northern forests play a crucial role in the global C cycle due to their high C storage of which significant amounts are fixed in SOM [1]. However, the fate of this C is uncertain in the view of climate change as C in the forest ecosystem might shift from sink to source, thereby accelerating global warming [2]. The decomposition of SOM is regulated by microbial responses to environmental conditions, that is, temperature and precipitation [3], chemical and physical protection of SOM [4], as well as chemical recalcitrance of SOM [5]. Furthermore, plant secondary metabolites (PSM), for example, tannins and terpenes, synthesized to cope with numerous environmental stressors influence these processes via different mechanisms [6,7]. Overall, the mechanisms underlying SOM transformations are not well known yet. As recently underlined, we need better understanding of plant-soil-microbial interactions to improve models of SOM decomposition [8–11]. In this mini-review, we present the current state of the art on SOM transformations in boreal forests with particular focus on the role of tannins and terpenes, dominating PSM.

2. SOM Decomposition in Boreal Forests

Decomposition processes in boreal forests are very slow due to numerous factors influencing the underlying mechanisms, such as specific climatic conditions, with low temperatures and a short growing season. The low C turnover rates of SOM in these forests might be driven by nitrogen (N) limitation [12–14]. Although boreal forest soils are rich in N, this N is mostly present in organic forms that are bound to or complexed with other soil compounds, including minerals and organic compounds such as polyphenols and polysaccharides [3,5]. Thus, the crucial step in SOM decomposition is the release of N from these boundaries, that is, the depolymerization of large N-containing molecules to organic small-molecular-weight compounds [15,16] which can be taken up directly from the soil [17–22]. Knowledge on the fate of N released from litter into the plant-microbe-soil system is scarce, although litter decomposition has been studied extensively in various biomes [23–27]. This is particularly relevant when the decomposition of root litter is investigated, which has only been done in some studies [28–30], and overall knowledge on the fate of root-litter derived N is still missing.

Soil organic C derives from plant material [31] and enter the soil with photosynthates and litter passing through soil microbial biomass before transformation into SOM [32]. Soil microorganisms have a dual mode of control over SOM: catabolic, as they decompose organic compounds, or anabolic, as they stabilize C, forming thus more stable SOM [11]. In boreal forests, mycorrhizal fungi (MF) fueled by plant C allocation of recent photosynthates may significantly contribute to the SOM decomposition and mining for N from soil [33,34]. However, competition between MF and saprotrophic fungi might retard SOM decomposition and lead to a build up of SOM [35–37], especially at low fertility soils [38]. Competition between different fungal guilds is not as intensive as previously believed due to vertical separation; saprotrophs occupy mainly the litter layer and upper layer of humus, whereas mycorrhizal fungi occur mostly at deeper humus layers [39,40]. Moreover, living roots can significantly accelerate or retard the decomposition of old recalcitrant C in the soil via root exudates (so called “priming effect”) [41]. The mechanism of priming has been studied intensively and is reviewed extensively, for example, in Kuzyakov et al. [41]. In contrast to the intensively studied allocation of plant photosynthates belowground fueling soil microbes, the role of other plant-derived compounds shaping microbial communities and affecting SOM decomposition is far from being understood. Among plant-derived compounds, some PSM in particular affect soil processes due to their biochemical traits [7,42–45], that is, by affecting microbial communities (toxicity vs. C source), binding of organic compounds and metal ions, antioxidant activity and modifying enzyme activity [46]; however, research on these effects is scarce.

3. Effects of PSM on SOM Transformations

3.1. Plant Synthesis of PSM and Soil Concentrations

Plant secondary metabolites are not essential for plant growth, but rather control the interactions of plants with the environment, that is, as defense against pathogens and herbivores [47,48], as allelopathic agents [49], and/or as antioxidants protecting leaves from UV radiation and excess of light [50]. Extractable PSM can comprise even up to 30% of the dry weight (DW) of plants, especially in forest ecosystems [51], and their concentrations are species-, age-, season- and organ-specific, as well as affected by soil nutrient deficiency, light, temperature, elevated CO₂ and drought [52–57]. Plant secondary metabolites consist of two major groups: terpenes and phenolic compounds (including tannins).

Tannins are polyphenols usually separated into hydrolysable tannins (HT) and condensed tannins (CT) (Figure 1). Tannins are the fourth most abundant compounds in vascular plant tissue after cellulose, hemicelluloses and lignin [58]. For example, tannin concentration in pine leaves and roots can reach up to 15–20% DW [54,59,60]. Many studies have shown that high tannin concentration can be found in plants living in conditions of low soil fertility and low pH [61]. The most diverse group of PSM are terpenes, built up from isoprene units. Terpenes include monoterpenes (having two isoprene units, IU), sesquiterpenes (three IU), diterpenes (four IU), triterpenes (six IU), tetraterpenes (eight, IU),

and polyterpenes (more than eight IU) [62] (Figure 1). Terpene concentrations in leaves range from 1% to 2% DW [62].

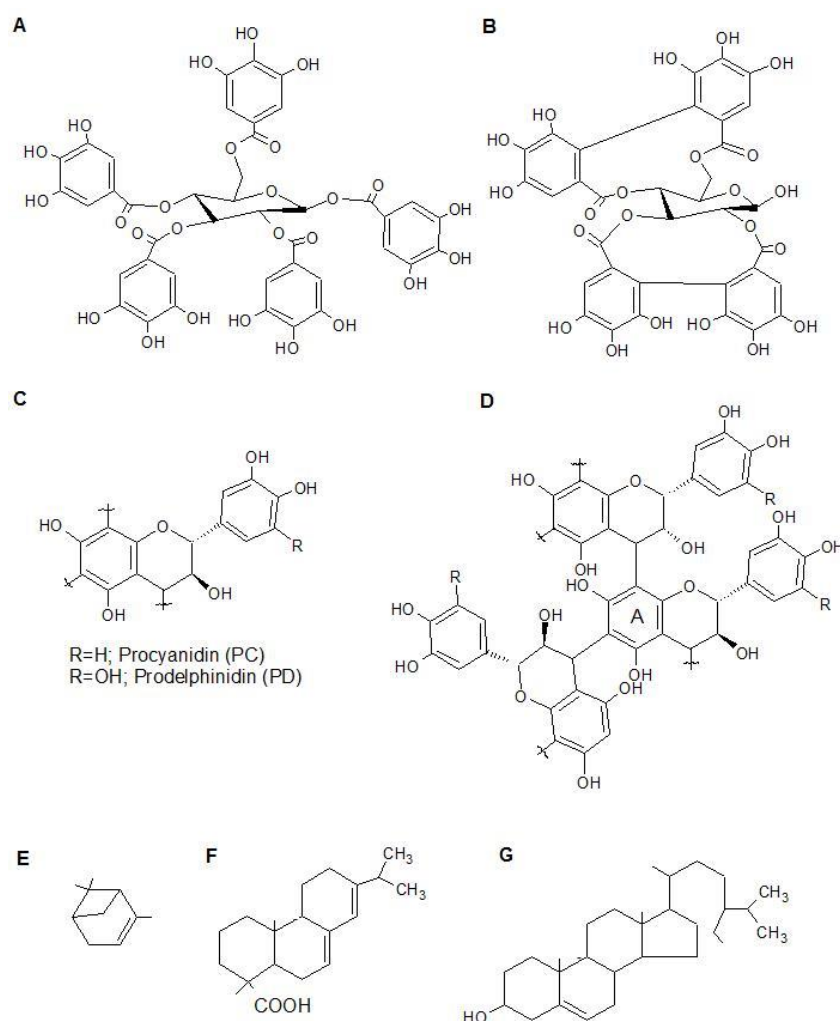


Figure 1. Tannin and terpene chemistry. Hydrolysable tannins are basically divided into gallotannins (A) and ellagitannins (B), which are made up of gallic acid or hexahydroxydiphenic acid esters, respectively, linked to a sugar moiety. Monomers of condensed tannins (CT) can be divided into procyanidins and prodelfinidins (C); Condensed tannins (proanthocyanidins) are polymers of three-ring flavanols joined by C–C bonds (D); Terpenes are based on isoprene units; examples of common terpenes: (E) alpha-pinene (monoterpene); (F) abietic acid; (G) beta-sitosterol.

Soil concentrations of PSM depend on litter input and degradation rate regulated by plant species, environmental conditions and microbial community structure but also forest management [54,63–68]. For example, the concentration of terpenes was higher in litter than in the organic layer [63,69]. In the organic layer, concentrations of mono-, di-, and triterpene reached up to 0.2 g/kg SOM with total concentration of sesqui-, di-, and triterpene reaching up to 5 g/kg SOM [54]. Hydrolysable tannin concentrations in boreal forest soils are very low [64,67], likely due to generally low HT concentrations in plant litter or fast decomposition rates. On the contrary, CT concentrations are significantly higher, reaching up to a few g per kg SOM [63,64,66]. However, the actual concentrations of tannins in the soil are unknown, because significant amounts of tannins are undetectable due to complexation with proteins and sorption to other compounds in the soil, which strongly decreases the recovery of CTs [46,70].

3.2. Influence of PSM on SOM Transformations

The effects of PSM on SOM are complex and depend on their chemical structure [43,71]. For example, both tannins and terpenes can affect net N mineralization and nitrification, soil microbial biomass C and N and microbial community structure [6,45,72–75]. The main probable mechanism by which tannins affect soil N transformations is via binding to proteins. The formation of such tannin-protein complexes depends on the biochemical characteristics of both, the involved protein and tannin as well as the pH of the soil solution [73,76]. It was suggested by Northup et al. that most of the dissolved organic N (DON) is associated with protein-tannin complexes, thus conserving litter-derived N in the forest ecosystem [77]. Furthermore, high levels of tannins present in the litter shift N cycling from mineral to organic dominated pathways [72,73,77,78]. These tannin-protein complexes are recalcitrant mainly due to decreased solubility, thus the formation of complexes stabilize C and build up more stable SOM. Moreover, the addition of tannin-protein complexes to the soil decreased net N mineralization, respiration, and microbial biomass as compared to protein addition alone [43,79,80]. Although tannin-protein complexes seem to be recalcitrant, this source of N can be accessed by saprotrophs, as well as plants via mycorrhiza (both, ericoid and ectomycorrhiza) [81,82]. These fungi slowly release N from complexes using a set of enzymes, including at first step oxidoreductases [81,82]. Recently, Adamczyk et al. [43,44] showed that tannins interact not only with proteins, but also with other organic N compounds present in the soil, that is, arginine, polyamines, chitin and N bases. Thus, Northup's theory [73] should be extended to include also other organic N containing compounds. Overall, the role of other PSM-N complexes other than tannin-protein remain unknown, although tannin-chitin complexes seems to act similarly to tannin-protein complexes [43]. The complexation of chitin by tannins may be a relevant process at ecosystem scale, as roots are tannin-rich and the neighboring ectomycorrhizal symbiont biomass is estimated to range from 100 to 600 kg·ha⁻¹ [83]. In addition, higher terpenes, that is, abietic acid, colophony (i.e., a mixture of diterpenes) and beta-sitosterol can also precipitate protein. However, the affinity of terpenes to proteins seems to be lower than affinity of tannins [84]. All in all, according to laboratory experiments, additions of PSM to soil affect numerous processes in the forests N cycle (Figure 2) [30,54]. However, the relationship between PSM and N cycling has not been found as clear under field conditions [54]. Soil is a highly heterogenic environment, with myriads of compounds which can affect interaction between PSM and organic nitrogen. For example, PSM interaction with minerals is potentially important in mineral soils, although knowledge about it is scarce. It has been shown in laboratory study with quartz sand and sand coated with goethite or ferrihydrite that tannins strongly bind to minerals [85]. Protein-tannin complexes and condensed tannins showed lower recovery after addition to more mineral soil than to highly organic soil [70]. Sorption to soil depends on chemical structure of tannins [46]. Interaction of PSM with other soil compounds, as for example with minerals, can contribute to C stabilization, but it can also inactivate tannins and terpenes, affecting their effect on N cycling.

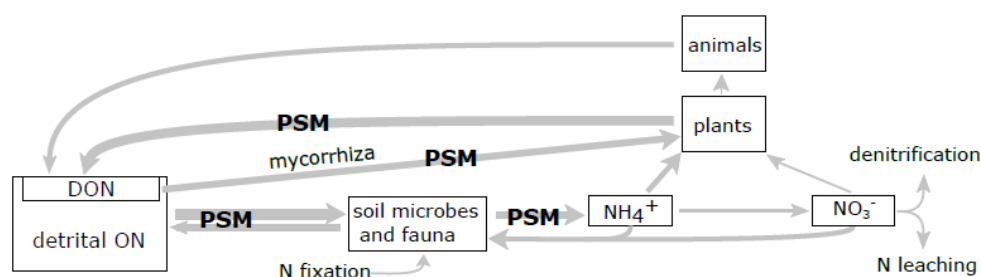


Figure 2. Potential effects of plant secondary metabolites (PSM) on forest N cycling. The model of main fluxes (arrows) and pools (boxes) of N in terrestrial ecosystems [58,86]. Arrow thickness is proportional to the magnitude of net flux. Processes affected by tannins and terpenes are marked “PSM”. DON—dissolved organic nitrogen; ON—organic nitrogen.

3.3. Effects of PSM on SOM Degradation via Regulation of Enzymatic Activity

SOM decomposition is driven by a multiple set of microbial enzymes. Extracellular hydrolytic enzymes convert organic polymers of C and nutrients to forms available for soil microorganisms and plants. However, the complexation of PSM with organic N compounds (see Section 3.2) decreases SOM degradation rates via the formation of recalcitrant substrates. As PSM interact with proteins, also the effect of PSM on enzymes should be included in models concerning ecosystem functioning. To date, tannins have been viewed as potential enzyme inhibitors [75,87–89], thus potential interactions of tannins with enzymes represent one mechanisms regulating SOM decomposition and explain the low rates of decomposition in tannin-rich ecosystems. However, this effect was not consistent throughout studies, as sometimes no decrease in activity was observed [90]. A recent study conducted with and without soil provided first evidence of the different effects tannins have on enzymatic activity; (1) Additions of low tannin concentrations led to an increase in catalytic activity of enzymes, whereas (2) higher tannin concentrations resulted in a decrease in enzymatic activity [42]. Mechanically, this dual effect of tannins on enzymatic activity is due to changes in the secondary conformation of enzymes after tannin addition [42] (Figure 3). However, even tannin-enzyme complexes exerted some activity [42], which may lead to stabilization of enzymes in the soil. Such stabilization can exert positive effect on soil decomposition processes in the long term. Tannin-bound enzymes may act as a reservoir of enzymatic activity ready to react with changing fluxes of substrate [91]. Monoterpenes have been also proposed as potential enzyme inhibitors, for example, inhibiting ammonia monooxygenase through non-competitive inhibition [92,93]. A recent study in vitro and in soil showed that both, monoterpenes and higher terpenes can inhibit activity of chitinase and beta-glucosidase [94]. Overall, PSM should be seen as potential regulators of SOM decomposition at PSM-rich sites.

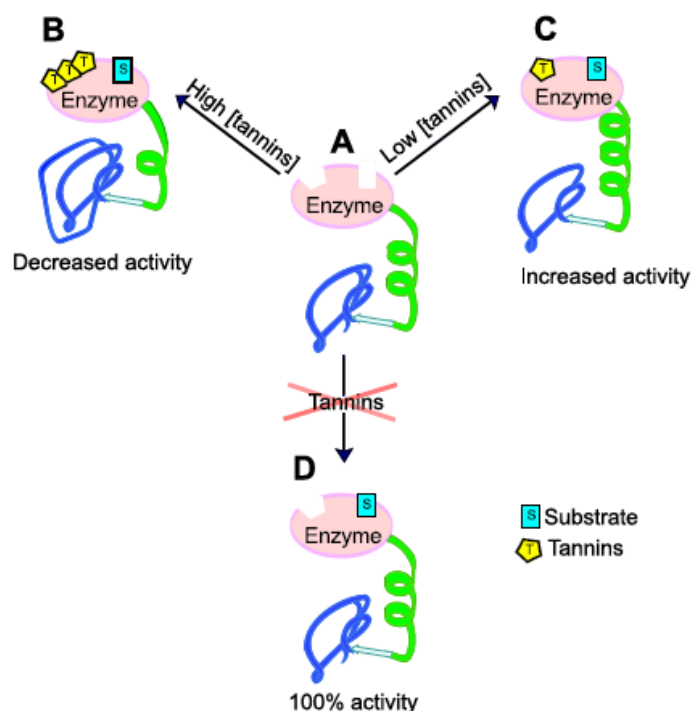


Figure 3. Simplified scheme showing possible effects of tannins on enzymatic activity. (A) enzyme without tannins and substrate; (B) enzyme after reaction with high concentration of tannins; activity is decreased, in secondary structure, more irregular (in blue) and less regular (in green) structures are present; (C) enzyme after reaction with low concentration of tannins, activity is increased; in secondary structure, more regular (in green) and less irregular (in blue) structures are present; (D) enzyme without tannins, 100% activity.

4. Conclusions and Directions of Future Studies

Future studies on SOM transformations should take into account the complicated plant-soil microbial interactions, and how these are affected by different PSM. Furthermore, as projections for future climate change suggest an increase in temperature, prolonged periods of drought, as well as increased greenhouse gas emissions [95], plant production of PSM is likely to be affected [96]. For example, trees produce tannins that are more likely to form complexes with proteins in response to climatic stress [52]. Furthermore, the concentrations of PSM such as terpenes are increasing with elevated temperature and CO₂ levels [53]. Therefore, the effects of PSM on SOM transformations in response to varying climate conditions are likely to change. Moreover, global change may also result in the threat of invasive species, which may provide PSM of different quantity and quality.

Acknowledgments: B.A. is funded by the Finnish Cultural Foundation and J.S. is funded by a Heisenberg Fellowship from the German Research Foundation (DFG).

Author Contributions: B.A. and J.S. wrote the paper with important input from other co-authors.

Conflicts of Interest: The authors declare no conflict of interest.

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