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Role of phenolic substances from decomposing forest litter in plant–soil interactions

A. T. KUITERS

Department of Ecology & Ecotoxicology, Faculty of Biology, Free University, De Boelelaan 1087, 1081 HV Amsterdam, The Netherlands

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INTRODUCTION

Phenolic substances are an important constituent of forest leaf material. Within living plant tissue they occur as free compounds or glycosides in vacuoles or are esterified to cell wall components (Harborne 1980). Major classes of phenolic compounds in higher plants are summarized in Table 1. 'Phenolics' are chemically defined as substances that possess an aromatic ring bearing a hydroxyl substituent, including functional derivatives (esters, methyl esters, glycosides, etc.). 'Polyphenols' are those phenols with two or more hydroxyl-groups. The term 'polymeric phenol' will be used for compounds composed of two or more rings (e.g. condensed tannins, flavenoids).

Table 1. The major classes of phenolics in plants

Number of carbon atoms	Basic skeleton	Class	Examples
6	C_6	Simple phenols	Catechol, hydroquinone
		Benzoquinones	2,6-Dimethoxybenzoquinone
7	C_6–C_1	Phenolic acids	*p*-Hydroxybenzoic, salicylic
8	C_6–C_2	Acetophenones	3-Acetyl-6-methoxybenzaldehyde
		Phenylacetic acids	*p*-Hydroxyphenylacetic
9	C_6–C_3	Hydroxycinnamic acids	Caffeic, ferulic
		Phenylpropenes	Myristicin, eugenol
		Coumarins	Umbelliferone, aesculetin
		Isocoumarins	Bergenin
		Chromones	Eugenin
10	C_6–C_4	Naphthoquinones	Juglone, plumbagin
13	C_6–C_1–C_6	Xanthones	Mangiferin
14	C_6–C_2–C_6	Stilbenes	Lunularic acid
		Anthraquinones	Emodin
15	C_6–C_3–C_6	Flavenoids	Quercitin, cyanidin
		Isoflavenoids	Genestein
18	$(C_6$–$C_3)_2$	Lignans	Pinoresinol
		Neolignans	Eusiderin
30	$(C_6$–C_3–$C_6)_2$	Biflavenoids	Amentoflavone
n	$(C_6$–$C_3)_n$	Lignins	—
	$(C_6)_6$	Catechol melanins	—
	$(C_6$–C_3–$C_6)_n$	Flavelans (condensed tannins)	

Data from Harborne (1989).

Phenolics in plant litter are to a small extent water soluble, are released by rain water and can be detected in small amounts in throughfall and stem flow (Bruckert *et al.* 1971). However, their main origin is their release from decomposing leaf litter deposited on the soil surface and from decomposing fine roots. Phenolics act as intermediates in the formation of humic compounds in the soil environment (Stevenson 1982). By condensation and polymerization reactions mediated by soil microbes (Bailly & Raboanary 1986), simple low molecular weight phenolic compounds together with amino acids and proteins are chemically altered into the more stable higher molecular weight fulvic acids, humic acids and finally into humins (Martin & Haider 1980). After reaching the soil, the effects of phenolics on the functioning of forest ecosystems are many and drastic. Soil phenolic substances directly affect bacteria, the development of mycelia and spore germination of saprotrophic and mycorrhizal fungi, and the germination and growth of higher plants (Hartley & Whitehead 1985). The process of humification is also largely directed by the polyphenol content of litter (Duchaufour 1983). Thus, site quality characteristics such as mineralization rate, nitrification rate and soil productivity are highly influenced by phenolics, released from living, senescent and decomposing plant tissue.

Soil factors, i.e. clay particles, oxyhydroxides, organic matter and pH, determine the concentrations of phenolic substances in soil solutions. Numerous workers have

investigated these factors (Kassim *et al.* 1982; Tee Boon Goh *et al.* 1986; Blum *et al.* 1987; Dao & Lavy 1987; Lehmann *et al.* 1987; McBride 1987; Federle 1988; Lehmann & Cheng 1988; McBride *et al.* 1988), but they will not be discussed here.

At the ecosystem level, phenolic substances from litter and humus layers have effects on species composition and dynamics of forest vegetation. Knowledge of the role of phenolic substances may contribute to a better understanding of vegetation succession in forest ecosystems and phenomena such as the regeneration failure observed in many natural or planted forest stands (Becker & Drapier 1984, 1985; André *et al.* 1987). The aim of this contribution is to review recent literature on the effects of phenolic substances on plant growth, particularly in forest systems. Both direct effects of phenolics on germination, seedling development and further plant growth, often indicated by the term 'allelopathy' (Rice 1984) as effects on site conditions, by affecting decomposition, mineralization rate and bacterial and fungal flora, will be discussed.

PHENOLIC SUBSTANCES AND SITE QUALITY

Polyphenol–protein complexes

Brown colouring of leaves and needles that have fallen on the ground is caused by the formation of insoluble polyphenol–protein complexes, the so-called 'brown pigments' (Toutain 1987a). Polyphenols present in the cell vacuoles form insoluble complexes with proteins of the cytoplasm after degradation of the cell structure. In living plants they serve as protective agents against herbivory and parasitism. Brown pigments can represent more than 20–25% of leaf dry weight (Stevenson 1982; Duchaufour 1983). These products are difficult to biodegrade and represent more than 60% of leaf nitrogen. Without this tanning process, leaf nitrogen would be mineralized very rapidly and would be set free as nitrate and ammonium during the season when the activity of the vegetation is low and would be lost from the ecosystem or stored only by those plant species which develop new roots during winter (Ernst 1979; Ellenberg *et al.* 1986). This tanning phenomenon of forest leaves allows the storage of nitrogen until the more active periods of plants, particularly spring and early summer with strong activity of soil micro-organisms.

The growth of fungal species occurring naturally on decomposing leaf litter is often inhibited by condensed polyphenols as demonstrated *in vitro* by Harrison (1971) for leaf leachates of *Quercus petraea* and *Q. robur*. The extra-cellular enzymes of the saprotrophic fungi are deactivated by forming complexes with the tannins. Only two groups of organisms are able to metabolize these brown pigments: leaf-inhabiting basidiomycetes with polyphenol oxidase activity (causing bleaching of the litter analogous to that caused by white-rot fungi in wood) and earthworms (Toutain 1987a,b). These organisms have an enzymatic potential to transform brown pigments. Mycelia of the typical litter-decomposing fungi are able to biodegrade brown pigments after having penetrated the epidermis and parenchyma cells of decaying leaves. By doing so they release a considerable quantity of water-soluble organic matter which is rapidly made insoluble after contact with mineral soil particles. Earthworms can directly utilize a large part of the nitrogen enclosed in the polyphenol–protein complexes. Well-structured organo-mineral particles with bacterial aggregates are formed inside the digestive system and are added to the soil in the form of faecel pellets. The brown pigments thus have an important impact on transformation rates of litter material and subsequently on the rate of nutrient cycling, an important feature of the functioning of forest ecosystems.

Litter quality and humus formation

'Site quality', defined here as soil fertility, is closely related to humus-type formation in forest ecosystems (Duchaufour & Toutain 1985). Humification is the transformation of organic materials by biological and physico-chemical reactions. The process of humification in forest systems in lowland, sub-alpine and alpine forest systems has been thoroughly investigated on contrasting mineral soil substrates (Bruckert *et al.* 1971; Toutain & Vedy 1975; Duchaufour 1976; Duchaufour & Souchier 1978; Duchaufour 1983; Duchaufour & Toutain 1985; Monrozier & Duchaufour 1986; Toutain 1987a,b). These investigations have resulted in a profound insight into the process of humification and soil development. In fact, two distinctive patterns of litter decay and humification can be recognized, leading to different kinds of soil profile development.

Mull humus formation. As found in brown acid forest soils: these soils are characterized by a rapid mineralization of organic matter, related to a high microbial activity and resulting in high soil fertility. Mull humus is formed where parent materials have moderate to high contents of iron and clay particles (Toutain & Vedy 1975; Duchaufour & Souchier 1978). Mullhumus site conditions are favourable for white-rot fungi and earthworms (Lumbricidae), organisms that are able to metabolize the 'brown pigments', thus removing the blockage of leaf litter decomposition. Soluble organic substances, including (poly)phenols released from decomposing litter are precipitated immediately after contacting mineral soil particles, i.e. by amorphous iron and aluminium oxyhydroxides.

Mor humus formation. Often related to podzolization: these soils have a low microbiological activity and low soil fertility due to a slow turnover of soil organic matter (Duchaufour & Souchier 1978). Site conditions are unfavourable for white-rot fungi and earthworms. The soil fauna is dominated by Enchytreae and microarthropodes that fragment litter materials. These organisms are not able to transform the polyphenol–protein complexes. The complexes pass through the digestive system of the soil fauna chemically unchanged and accumulate as faecal pellets in the fermentation and humus layers where the polyphenol complexes can remain for several decades (Toutain 1987a). Soluble low molecular weight organic substances are released in high amounts from these litter types and are percolated to deeper soil layers without being precipitated, transporting Fe and Al cations by complexing them. Parts of these complexes are precipitated in deeper soil layers. Mull and morhumification are in fact the two extremes of a continuum of different humus forms, with moder as the intermediate type.

Litter quality, particularly C/N ratio and polyphenol content, plays an important role in the humus type formed (Toutain & Vedy 1975; Vance *et al.* 1986), although the mineral composition of the soil is often of primary importance. Examples of forest species with mull humus formation, i.e. ameliorating species, are *Betula, Fraxinus, Populus, Tilia* and *Ulmus* (Miles 1985). Forest species with moder or mor humus type formation, the so-called acidifying species, include most coniferous species (*Picea* and *Pinus*) and species of the *Ericaceae*. There are also litter types such as *Fagus* and *Quercus* which can give rise to different types of humification depending on the physico-chemical characteristics of the soil substrate, especially the presence of free iron (Toutain & Vedy 1975).

Site quality and plant phenolics

The production of phenolics in plants is highly variable between plant species (Ricklefs & Matthew 1982), but is also under environmental control. The production of phenolics

may be increased by solar radiation, resulting in higher phenol contents of leaves in sun (McClure 1979). Site quality, especially the nutrient status of the soil has a large impact on phenolic contents of plant tissue. The results of Muller *et al.* (1987, 1989) suggest a trend of increasing phenolic production in foliar and fine root tissue (as found for beech, hickory and oak) along gradients of declining soil fertility. Staaf & Berg (1981) also found polyphenolic substances in conifer litter to vary with nutrient status of the soil. The overall effect of higher levels of phenolic compounds in litter material is a reduction of the turnover rate of organic material with, as a consequence, a reduced rate of mineralization of associated nutrients. Moreover, the high ratios of carbon to nutrients, especially nitrogen, in litter produced on nutrient-poor sites leads initially to an immobilization of nutrients in microbial biomass. Thus a positive feedback exists, whereby vegetation on poor sites produces increased amounts of phenolic compounds which further reduces site quality through a reduction in turnover rates of soil organic matter (Chapin *et al.* 1986; Horner *et al.* 1988).

SOLUBLE PHENOLICS IN DECOMPOSING LEAF LITTER

Leaching of phenolics from canopy and leaf litter

Soluble phenolic substances are leached by rainwater from the forest canopy and are present in throughfall. Concentrations in leaf tissue are generally highest in spring, immediately after budbreak during the period of rapid leaf expansion, and in autumn during abscision and leaf fall (Dormaar 1970; McClaugherty 1983; Kuiters & Sarink 1986). Throughfall percolating through the litter layer is enriched further with soluble phenolics released from the decomposing leaf litter. The presence of leaf-decomposing fungi on the leaf material increases the rate of leaching of soluble phenolics (Dix & Simpson 1984). The amounts released from decomposing leaf litter are generally much higher relative to amounts present in throughfall. Amounts of soluble phenols are much lower in coniferous litter than in leaves from deciduous trees. In a forest stand with *Acer saccharum*, the amounts reaching the soil by throughfall and leached from decomposing leaf litter amounted to 23 and 196 kg ha^{-1} $year^{-1}$, respectively (McClaugherty 1983).

During leaching, the soluble phenolics may undergo polymerization and condensation reactions and are thus transformed into insoluble and recalcitrant humic-like substances, as observed by Bruckert *et al.* (1971) for litter leachates of *Pinus sylvestris* and *Fagus sylvatica*. Soluble nitrogen in fresh leaf litter is transformed with these polycondensates into insoluble forms (Handley 1961). Fungal phenol-oxidases probably play an important role in these reactions in litter leachates (Lindeberg 1948).

Soluble phenolics from broad-leaved trees are generally rapidly leached from freshly fallen leaf litter. Three months after leaf fall most soluble phenolics have been released from decomposing litter (Olsen *et al.* 1971; McClaugherty 1983; Kuiters & Sarink 1986). In contrast, coniferous needle litters have low leaching rates, with the exception of *Larix decidua* needle litter (Kuiters & Sarink 1986).

Monomeric phenolics

The low molecular weight simple phenolics, i.e. the monomeric benzoic and cinnamic acid derivatives occur universally in higher plants, predominantly in the vacuoles bound to a sugar as a glycoside or an ester (Harborne 1980). Seasonal variation has been observed in phenol leaf tissue concentrations (Dormaar 1970; Olsen *et al.* 1971; Schütt & Blaschke 1980) with highest amounts in young leaves. With ageing phenolic monomers decrease.

Table 2. Amounts of water-soluble monomeric phenolics in freshly fallen leaf litter from several tree species collected in early autumn (October) on different stands in The Netherlands

Tree species	Phenolics ($\mu g\ g^{-1}$ dry weight)
Deciduous species	
Carpinus betulus	2552
Corylus avellana	2534
Betula pendula	2295
Fagus sylvatica	1759
Fraxinus excelsior	1331
Acer pseudoplatanus	1329
Quercus robur	813
Coniferous species	
Larix decidua	907
Pinus sylvestris	514
Pseudotsuga menziesii	259
Picea abies	45

Data from Kuiters (1987).
Phenolics in aqueous extracts of intact litter material were quantified by gas–liquid chromatography.

During senescence and shortly after leaf drop, soluble phenol concentrations are increased and phenolics are leached (Kuiters & Sarink 1986), and ester bonds are often broken down. Lignin degradation also gives rise to the release of monomeric phenolic acids and aldehydes, although this process proceeds very slowly (Martin & Haider 1980; Ander *et al.* 1984). The amount and type of monomeric phenolics in leaf litter leachates shows variation among tree species. A comparison of the leaf litter leachates of common tree species in European forests revealed the presence of 18 different benzoic and cinnamic acid derivatives and aldehydes (Kuiters & Sarink 1986). The relative amounts of these compounds differed between litter types. Highest amounts were released from broad-leaved tree species (Table 2), particularly from hornbeam (*Carpinus betulus*) hazelnut (*Corylus avellana*) and birch (*Betula pendula*). The compounds found in highest concentrations were gallic, *p*-hydroxybenzoic, vanillic, ferulic, caffeic, *p*-coumaric and *o*-coumaric acid (up to 5 $\mu mol\ g^{-1}$ dry weight leaf material). The same phenolic acids were found in leaf leachates of *Salix caprea* (Schütt & Blaschke 1980), in the leaves of *Quercus borealis* and *Q. alba* (Lohdi 1978), and the leaves of *Castanea crenata* (Cortizo & Mantilla 1981).

Polymeric phenolics

The higher molecular weight polymeric phenolics are generally present in the form of hydrolysable and condensed tannins. They may represent up to 40% of leaf dry weight (Baldwin *et al.* 1983; Baldwin & Schultz 1984; Racon *et al.* 1988). *Quercus* spp. are particularly well known for the high contents of hydrolysable tannins in their leaves. These can be leached by water from intact leaf litter or degraded by litter-inhabiting fungi such as *Aspergillus niger*, releasing breakdown products in the form of gallic, digallic and ellagic acid (Haslam & Tanner 1970).

Substantial tannin losses occur within the first 4 weeks after leaf drop (McClaugherty 1983). Baldwin & Schultz (1984) found that 70 and 90% of hydrolysable tannins were lost in the first month after leaf fall from sugar maple (*Acer saccharum*) and yellow birch (*Betula allegheniensis*), respectively. However, the loss rates of tannins from leaf litter have been found to be strongly dependent on site conditions (Baldwin & Schultz 1984), although the site characteristics responsible for these differences are unknown. It is likely that temperature and/or soil moisture acting through their effects on the microbiological community play an important role.

Recently an interesting observation was made by Von Lioba and Schütt (1987) who found that ground vegetation composed of *Carex brizoides* deteriorated under beech (*Fagus sylvatica*) which showed symptoms of forest decline. Bioassays revealed that leaf litter leachates of declining beech trees inhibited germination and seedling development of seven understorey plant species. A similar observation was made by Hoque (1985) for Norway spruce (*Picea abies*), showing die-back symptoms.

PHENOLICS AND SOIL MICRO-ORGANISMS

Saprotrophic fungi

Leaf-litter inhabiting fungi occur mainly in the genera *Mycena, Marasmius, Collybia* and *Clitocybe* (Hering 1967, 1982; Dickinson & Pugh 1974; Cooke & Rayner 1984). Their spore germination and hyphal growth show both positive and negative responses when in contact with phenolic compounds. Stimulatory effects of phenolics have been found for basidiomycetes found on pine needles, i.e. *Marasmius androsaceus* and *Collybia peronata.* These fungi were found to be stimulated by flavenoids, especially taxifolin glucoside and taxifolin (Lindeberg *et al.* 1980), which occur in pine needles up to 1–2% of dry weight. Two other saprotrophs which specialize on conifer needle litter (*Dothichiza pityophila* and *Thysanophora penicilloides*), were found to be stimulated by ferulic acid, in contrast to several saprotrophs inhabiting deciduous leaf litter (Black & Dix 1976). Gallic acid has been shown to be inhibitory to some basidiomycetes and microfungi from leaf surfaces (Dix 1974, 1979). The growth promoting and inhibiting effects of water-soluble organic (phenolic) compounds present in forest litter probably determine to a great extent the distribution and activity of different litter-decomposing fungi (Lindeberg *et al.* 1980), which may explain substrate preference often found among litter-decomposing saprotrophs. Further research may support the hypothesis that substrate preference of many litter-inhabiting fungi is closely related to secondary plant chemistry.

Litter decomposers produce extracellular polyphenol oxidases (Lindeberg 1948; Dix 1979), which make them less vulnerable to the inhibiting activity of polyphenols, present in high amounts in decomposing leaf litter. The bleaching and softening of leaf litter through the action of such enzymes is thought to detoxify the litter and promote decay by increasing the palatability of the litter for soil fauna. Blaschke (1981) reported that respiration and cellulase activity in decaying conifer litter increased with a decrease of phenolics in the substrate.

The slower decay of certain litter species, often ascribed to high polyphenol contents, has been questioned recently. Dix & Simpson (1984) investigated the decomposing activity of *Collybia peronata*, a leaf-litter inhabiting basidiomycete with high polyphenol oxidase production and a high tolerance of tannins. Under experimental conditions it decomposed beech, oak and birch leaf litter at the same rate, irrespective of high variations in polyphenol content. They suggested that differences in the rate of decay of

different leaf litter species in the field is not directly caused by the effects of polyphenols on fungal growth but rather arises from differences in the water-holding capacity of litter, resulting in a different availability of water to fungi (Dix 1984).

Mycorrhizal fungi

Amino acids and carbohydrates initially released in high amounts from decaying plant litter may stimulate the growth of mycorrhizal fungi, but there are strong indications that phenolic substances have negative effects. Compared to the litter-inhabiting saprotrophs, ectomycorrhizal fungi are generally more sensitive to phenolic substances. This has been demonstrated in *in-vitro* tests by Olsen *et al.* (1971) who found litter decomposing *Marasmius* species to be less inhibited by benzoic acid and catechol than mycorrhizal fungi of the genus *Boletus*. Investigations of Robinson (1972), Rose *et al.* (1983) and Coté & Thibault (1988) affirmed the sensitivity of mycorrhizal fungi to phenolics.

These findings may partly explain tree regeneration failure observed in certain lowland and mountainous forest stands of Central Europe. By inhibiting germination and growth of mycorrhizal fungi, phenolic substances released from decomposing litter may hinder tree seedling establishment (Rose *et al.* 1983; Becker & Drapier 1984, 1985; Coté & Thibault 1988). However, if mycorrhizal fungi are able to infect tree roots, they may render trees less vulnerable to the negative effects of phenolics (Hanson & Dixon 1987). They found leachates of a fern (*Osmunda claytoniana*) reduced survival and growth of red oak seedlings (*Quercus rubra*). However, if oak seedlings were inoculated with the ectomycorrhizal fungus *Suillus luteus*, they were able to withstand the deleterious effects of the fern leachates. Hanson & Dixon (1987) hypothesized that organic molecules from the leachate reduced water uptake by roots, resulting in seedling mortality. The increased surface area for water uptake, known to be associated with ectomycorrhizae, might explain the ameliorating influence of the inoculum on seedling mortality.

Actinorhizal actinomycetes

Actinorhizal tree species are often used to increase soil nitrogen levels in forestry practice and so raise stand productivity. Thus black alder (*Alnus glutinosa*) with the N-fixing actinomycete *Frankia* in its root system, is often used as a nurse species interplanted with other tree species such as black walnut (*Juglans nigra*) or poplar species. However, it has often been observed that after a few years the black alders exhibit sudden decline. This has been ascribed to the release of phenolic substances from (decaying) leaves of the interplanted trees, an effect that becomes more and more manifest with increased leaf litter production. Well known examples in this respect are the release of juglone (5-hydroxy-1,4-naphthoquinone) by walnut trees (Rietveld *et al.* 1983; Ponder & Tadroo 1985) and phenolics such as catechol and benzoic acid by poplar trees (Dormaar 1970; Olsen *et al.* 1971). These phenolics may assert negative effects on *Frankia*.

In-vitro experiments have revealed that actinorhizal actinomycetes of the genus *Frankia* are inhibited by some common plant phenolic compounds. Perradin *et al.* (1983) have demonstrated that *in-vitro* growth of *Frankia* isolates was significantly affected by the addition of certain phenolic acids in concentrations higher than 0·5 mM in the nutrient solution. Benzoic acid derivatives are generally less inhibitory than cinnamic acid derivatives (Vogel & Dawson 1986). Juglone has also been found to have a negative impact on *Frankia* isolates and inhibits the nodulation of black alder seedlings in soils (Dawson & Seymour 1983; Vogel & Dawson 1985).

Nitrogen fixation and nitrification

Microbial processes which have been reported to be influenced by phenolics are those concerned with the transformation of nitrogen, in particular nitrogen fixation and nitrification. The growth of *Rhizobium* spp. was found to be inhibited by several phenolic acids at concentrations of 0·5 mM (Purushothaman & Balaraman 1973). Neera & Garg (1989) compared the influence of the chemical structure of the phenolic acids on nodulation. They observed that monohydroxyl phenolics inhibited nodulation, whereas di- or polyhydroxyl compounds, such as caffeic and chlorogenic acid stimulated nodulation and the subsequent growth of leguminous plants.

That phenolics may also interfere with the process of nitrification was suggested by Rice & Pancholy (1972, 1973, 1974). Polyphenols, especially the condensed tannins, may influence nitrification by binding proteins. Condensed tannins isolated from balsam fir (*Abies balsamea*) or from balsam poplar (*Populus balsamifera*) were found to inhibit nitrification under experimental conditions (Thibault *et al.* 1982; Baldwin *et al.* 1983; Olson & Reiners 1983). Turtura *et al.* (1989) showed that simple phenolic acids inhibited nitrification at concentrations beyond 10 $\mu g\, g^{-1}$ soil. Rice & Pancholy (1974) found *Nitrosomonas* to be more susceptible than *Nitrobacter* to the inhibiting effects of phenolic acids. Lohdi & Killingbeck (1980) found soil extracts of *Pinus pondorosa* to inhibit *Nitrosomonas* and attributed this to various phenolic compounds present in the soil extract. Rice (1984), hypothesizing on the significance of this relationship for ecosystem functioning, suggested that inhibition of nitrification will result in the formation of relatively less nitrate-N and more ammonium-N. As positively charged nitrogen species are less vulnerable to leaching, this finally leads to a conservation of nitrogen in the soil system. He stated that climax species in particular have high amounts of condensed tannins in their tissue and this might be a mechanism for nitrogen conservation in mature ecosystems. However, the investigations of McCarty & Bremner (1986) were not in agreement with this hypothesis. They carried out *in-vitro* experiments with phenolic acids and tannins and at concentrations as high as 250 $\mu g\, g^{-1}$ soil, none of the compounds had an appreciable effect on nitrification. They explained these results by noting that Rice & Pancholy (1972, 1973, 1974) performed their experiments in nutrient solution whereas they added phenolics to soil. Their results supported the hypothesis that in soils under climax vegetations, it is not the rate of nitrification but the rate of ammonification of organic nitrogen that is inhibited. This controversy in the literature deserves further research.

Soil activity

Microbial populations are frequently stimulated by phenolic acids at concentrations below 5 $mg\, g^{-1}$ soil, utilizing them as a C-source (Sparling *et al.* 1981; Blum *et al.* 1987; Blum & Shafer 1988). After addition of phenolic acids to the soil, respiration increases to a maximum after 3–7 days (Sparling & Vaughan 1981; Sparling *et al.* 1981). Thus, the toxicity of phenolic acids to plants can be suppressed by the activity of microbes (Vaughan *et al.* 1983). However, the utilization and subsequent depletion of phenolic acids by microbial populations is dependent on the nutrient status of the soil. Blum & Shafer (1988) observed that when the populations of micro-organisms are nutrient limited, the use of phenolic acids as a C-source is restricted. This observation suggests that plant–plant interactions by allelopathic interference are presumably particularly present on soils with a low nutrient status.

DIRECT EFFECTS ON PLANTS

As the 'mineral theory' (Von Liebig 1865) has been generally accepted, plants are assumed not to need organic substances for optimal growth, although organic substances in the rhizosphere may interfere seriously with the availability and uptake of nutrients. Phenolic substances may affect the permeability of root membranes and may thereby alter the uptake and efflux of nutrients. Moreover, they can be taken up by plant roots and influence physiological processes. These aspects will be discussed here in further detail.

Soluble phenolics in soils

When studying the potential effects of phenolics on plants, it is important to know soluble concentrations in the soil rather than total amounts. Concentrations in the soil solution are strongly dependent on soil texture, soil pH, content of organic matter and vary with depth, season and composition of the vegetation. Water-soluble concentrations of individual phenolic acids were found not to exceed 10–15 $\mu g\ g^{-1}$ (Whitehead *et al.* 1981; Jalal & Read 1983a,b; Kuiters & Denneman 1987). Concentrations are positively correlated with organic matter content and are highest in the superficial organic layers (litter and fermentation layer). Moreover, species composition of the vegetation cover has a profound effect on type and amount of individual compounds (Whitehead *et al.* 1982, 1983; Kuiters & Denneman 1987). In forests of the temperate zone, highest concentrations are often found during the period from June to September (Jalal & Read 1983a,b; Kuiters & Denneman 1987), when microclimatic soil conditions for microbial activity are optimal.

Germination and early seedling development

Many studies have shown that phenolic acids are able to affect germination, but usually with respect to germination rate (time needed for germination) rather than total seed germination. Inhibition of germination of many agronomic species is only observed at concentrations beyond 1·0 mM (Rasmussen & Einhellig 1977; Einhellig & Rasmussen 1978; Lynch 1980; Sparling & Vaughan 1981; Williams & Hoagland 1982; Blum *et al.* 1984). Although available data for wild plant species, particularly forest herbs, are scarce, they show the same manner of insensitivity of germination to phenolic acids (Kuiters 1989). The adverse effects of phenolic acids on the germination rate might at least be due partly to a retardation of water uptake by seeds as has been shown recently for water-soluble plant constituents (Krogmeier & Bremner 1989b).

Seedling development is more sensitive to phenolic acids than seed germination (Hartley & Whitehead 1985). Typical symptoms are brown colouring of the roots, effects on root and shoot growth and changing of geotropy. Most phenolics tested are inhibitory at millimolar concentrations, but are stimulatory at micromolar levels (Rasmussen & Einhellig 1977; Blum & Dalton 1985; Hartley & Whitehead 1985; Kobza & Einhellig 1987; Müller *et al.* 1988). Early seedling growth of the two forest floor species *Deschampsia flexuosa* and *Senecio sylvaticus* in contact with ferulic and *p*-coumaric acid was studied in detail (Kuiters 1987, 1989). It was found that besides primary root elongation, number and length of secondary roots and root dry weight were stimulated at 0·01 mM but were inhibited at concentrations beyond 1 mM. The strongest inhibitive effects have been found for cinnamic acid derivatives, particularly ferulic and *p*-coumaric acid (Müller *et al.* 1988). When these bioassays are carried out in soil, effects on seedling development are strongly reduced or may totally disappear (Krogmeier & Bremner 1989a), related to a strong adsorption of phenolic acids to soil particles.

Summarizing, the seedling stage seems to be a sensitive phase in the life cycle of plants with respect to phenolic compounds occurring in the litter and humus layer of the forest floor. Effects of litter type on herbaceous species composition may partly be mediated by interference of phenolics, released from decomposing litter at the early seedling stage.

Mineral nutrition

Experimental data indicate that an alteration of nutrient balance may be one mechanism of growth inhibition by phenolic acids. Effects of phenolic acids on the nutrient uptake of plants have been reported both from nutrient culture and soil studies. Glass (1973, 1974) found that the absorption of K and P by excised roots of barley was inhibited to some degree by each of 12 benzoic and cinnamic acid derivatives tested. McClure *et al.* (1978) also found a reduced uptake of phosphate by soybeans exposed to ferulic acid. Alsaadawi *et al.* (1986) found syringic, caffeic and protocatechuic acid to inhibit the uptake of N, P, K, Fe and Mo by cowpea (*Vigna sinensis*). Kobza & Einhellig (1987) showed that addition of 0·5 mM ferulic acid to the nutrient solution of sorghum reduced P content in shoots and P, K and Mg in root tissue. Kuiters & Sarink (1987), investigating the effects of phenolic acids on the mineral nutrition of five woodland herbs, found effects on the uptake of K, Ca, Mg, Fe, Mn and Zn. In most cases phenolic acids resulted in a reduced uptake and translocation of the elements, with the exception of Mn uptake, which was stimulated at higher phenolic acid concentrations. The effects were strongly dependent on phenolic acid type and concentration, mineral nutrient and plant species.

Related to the diminished uptake of elements often found in the presence of phenolic acids, Stowe & Osborn (1980) suggested that plants growing on nutrient-deficient sites are more sensitive to phenolic acids, although there is little experimental evidence to support this hypothesis. Experiments carried out by Kuiters *et al.* (1987) with two woodland herbs grown under P stress in the presence of phenolic acids could not confirm this hypothesis.

Experiments testing the effects of phenolic acids on plant growth are seriously hindered by the fact that phenolics are easily degraded by micro-organisms. Their half-life is less than 10 days (Blum *et al.* 1984). Sparling & Vaughan (1981), who demonstrated the modifying effects of micro-organisms in nutrient culture, stated that nutrient solutions should be changed at least every 3 days and that experiments should be carried out under aseptic conditions.

A persistent question in this research area is whether the available concentrations of phenolic substances in the soil environment are actually able to interfere with plant growth. Estimates of phenolic acids in the rhizosphere soil solution are generally low, less than 0·1 mM (Whitehead *et al.* 1982; Kuiters & Denneman 1987), and are below concentrations required for inhibition of plant growth or reduction of seed germination. However, under natural soil conditions it is probably a mixture of phenolic substances that causes growth-modifying effects whereby synergistic effects between individual compounds are likely to occur (Rasmussen & Einhellig 1977; Einhellig & Rasmussen 1978; Blum *et al.* 1985a).

Outside the plant, phenolic substances may improve nutrient availability by solubilization of cations from the mineral and organic soil particles due to complexation or reduction reactions. These effects have been reported for Fe and Mn (Vance *et al.* 1986).

The role of phenolic substances as plant-growth regulating substances has also been studied in more complete plant/soil test systems. These are *in-vitro* experiments where test plants are grown in soils to which intact litter materials have been mixed. Schütt *et al.* (1981) tested the growth-modifying effect of needle litter from pine (*Pinus sylvestris*) and

Douglas fir (*Pseudotsuga menziesii*) on the seedling growth of pine, Douglas fir and spruce (*Picea abies*). In the first year, negative effects on growth were observed, mainly for pine seedlings. At the end of the second year, only positive effects on shoot length and biomass were observed for all test species and were most pronounced for spruce seedlings. Moreover, the litter additions generally had a strong positive effect on mycorrhizal infection of tree seedlings, whereby the effects of douglas fir litter were most pronounced. Among test species, pine seedlings were more sensitive than seedlings of spruce or douglas fir. Kuiters (1987) compared the effect of fresh and aged leaf litter of several tree species on seedling survival and growth of several woodland herbaceous species. Strong negative effects were observed for soils mixed with needle litter of pine even when the litter was aged (6 months old). Although leaf litter of the deciduous trees birch (*B. pendula*), oak (*Q. robur*) and beech (*Fagus sylvatica*) also impeded seedling development initially, these effects rapidly disappeared and 6-month-old litter improved seedling growth when mixed with the soil.

Of course, the interpretation of these experiments is difficult due to the simultaneous occurrence of direct effects of the organic substances released from the litter on plant roots, the effects these substances have on soil microbial activity thereby influencing rate of mineralization and nutrient availability, and the addition of extra amounts of nutrients with the added litter material. Nevertheless, these experiments may provide useful information about the overall effect of particular litter types on plant growth under more natural conditions.

Permeability of root membranes

Physiological experiments with excised roots (Glass 1973, 1974; Glass & Dunlop 1974) support the hypothesis that the influence of phenolic acids on ion uptake is mediated largely through direct, non-specific effects on the semipermeability of the root cell membrane. The inhibitory effects are strongly correlated with their lipid solubilities as reflected by their octanol–water partition coefficients. Membrane potential is readily depolarized in the presence of phenolic acids, by cinnamic acid derivatives more than by benzoic acid derivatives. Related to this depolarization is an increase in permeability of the root cell membrane, resulting in an increased efflux of ions, to equalize internal and external ion concentrations (Glass & Dunlop 1974). Root tissue has the ability to detoxify phenolic acids by forming glycosides, reducing their lipid solubility and thereby their toxicity. However, *o*-substituted compounds such as salicylic acid are not easily esterified, which explains their toxicity.

The permeability of root membranes for phenolic acids is pH-dependent. Harper & Balke (1981) in their studies with the model compounds salicylic and ferulic acid, observed that root membranes are more permeable to the undissociated form of the phenolic acid. A similar observation was reported by Shann & Blum (1987) for ferulic and *p*-hydroxybenzoic acid. Blum *et al.* (1989) found that the effectiveness of phenolic acids on cucumber seedlings was higher at lower pH values.

Uptake of phenolics

Due to their water solubility and their relatively simple molecular structure, phenolic acids are taken up by plant roots and are partly translocated to shoot tissue (Flaig 1973). Accurate determinations of phenolic acid uptake by plants have been carried out with radioactive (ring)-labelled compounds. In this way the rate of uptake, transport and the transformation of the phenolic acids added to the plant can be followed. Numerous experiments have been carried out with wheat seedlings and ^{14}C-labelled vanillic,

p-hydroxybenzoic and syringic acid (Harms *et al.* 1969a,b). After 6 days of incubation, the seedlings had taken up 1–3% of the labelled phenolic acids, of which 60% was found in the roots and 40% in shoot tissue. Part of the activity taken up was found as assimilated CO_2 due to the decarboxylation of phenolic acids. This occurred particularly in the root by phenoloxidases. The phenolic acids were transported as free acids to the shoot where they were glycosylated. About 60–80% of the activity was found to be glucose esters or glucosides of the glucose esters of the added acids. After splitting the glucosides in the cells by a β-glucosidase, lignin formation may start.

Differences in uptake rate have been found between phenolic acids. In cucumber bioassays, the uptake rate of ferulic acid was 50–75% higher than for *p*-hydroxybenzoic acid (Shann & Blum 1987). Moreover, the uptake of *p*-hydroxybenzoic acid was affected not only by its own concentration but also by the presence of ferulic acid. So, the uptake of a certain phenolic acid can be modified by the presence of other phenolic compounds.

Interference with physiological processes

Inside the plant, direct effects of phenolics on plant growth may include inferference with metabolic processes such as mitochondrial respiration (Demos *et al.* 1975), photosynthetic rate (Einhellig *et al.* 1970; Patterson 1981), stomatal aperture (Einhellig & Kuan 1971), chlorophyll content (Einhellig & Rasmussen 1979; Alsaadawi *et al.* 1986; Kuiters & Sarink 1987) or protein synthesis (Danks *et al.* 1975; Cameron & Julian 1980) and water potential (Blum *et al.* 1985a,b).

Effects of mixtures of phenolic acids may be synergistic, additive or antagonistic. Experimental data also indicate that the effects are often reversible. Once the phenolic acids are removed from the root environment, physiological processes are often restored (Blum *et al.* 1985a).

CONCLUSIONS

Forest litter is often rich in phenolic substances which are added to the soil by leaching and decomposition. They include simple phenols, phenolic acids and polymeric phenols. Once released in the soil environment they influence plant growth directly by interfering with plant metabolic processes and by effects on root symbionts and indirectly by affecting site quality through interference with decomposition, mineralization and humification.

Site quality effects

Phenolic substances (particularly polyhydroxy compounds e.g. the condensed tannins) can seriously delay decomposition of plant litter by the formation of recalcitrant complexes with proteins after mixing of the cell contents during senescence. An effect of this 'tanning process' is that leaf nitrogen is initially immobilized and stored in these polyphenol–protein complexes and is only gradually released in the course of decomposition.

Direct effects of phenolic substances on the activity of litter decomposers have been reported. Spore germination and hyphal growth of leaf litter-inhabiting saprotrophic fungi can be influenced both positively and negatively by phenolic compounds in leaf materials. Decomposers that produce extracellular polyphenol oxidases such as white-rot fungi are generally less vulnerable to the inhibiting effects of polyphenols.

Related to the inhibiting effects of phenolics on the decomposition of primary resources are the influence of phenolics on humus-type formation and thereby site quality. These effects are highly dependent on vegetation type and partly of soil characteristics. In this respect, a distinction is made between 'ameliorating' and 'acidifying' species. Leaf litter of

typical 'ameliorating' tree species like *Populus, Betula, Tilia* or *Fraxinus* contain polyphenols with low 'tanning' abilities. Decomposition of these litter types proceeds relatively quickly and results in mullhumus formation, i.e. humus where biological activity and mineralization of nutrients are high, and soil fertility is subsequently high. In contrast, leaf litter of 'acidifying' species like *Picea, Pinus* and *Ericaceae* contain high amounts of tanning polyphenols, leading to morhumus formation, i.e. a humus type where decomposition and mineralization rates are slow due to a low biological activity.

Root symbionts and other micro-organisms

Plant growth is also influenced by effects of phenolics on root symbionts.

Mycorrhizal fungi, which as root symbionts have an important function in the establishment and growth of many tree species, have been found to be relatively sensitive to phenolic substances. This has been demonstrated particularly for phenolic acids. This mechanism may contribute to an explanation of the phenomenon of tree regeneration failure often encountered in natural or planted forest stands.

Other root symbionts, such as actinomycetes in the roots of N_2-fixing trees have also been found to be negatively influenced by leaf phenolics. In mixed stands where actinorhizal trees are used as nurse species, a decline of the nurse species is often observed after certain years and this has been explained by the increasing production of phenol-rich leaf litter by the other tree species.

Finally, several micro-organisms involved in nitrogen transformations in the soil have been found to be sensitive to phenolics. N_2-fixing bacteria, e.g. *Rhizobium* spp., are reported to be inhibited by monohydroxyl phenols, whereas polyhydroxyl compounds stimulate nodulation and subsequent plant growth. Nitrifying species such as *Nitrosomonas* and *Nitrobacter* have also been found to be susceptible to the effects of phenolic substances, although in the literature there is some controversy on this point.

Direct effects on plants

Many reports describe the direct effects phenolics may have on the development of higher plants. Most experiments have been carried out with agricultural species, few with forest species.

Generally, seed germination is not dramatically influenced. Only at unrealistic high concentrations beyond 10^{-3} M have negative effects been found. Seedling development is more sensitive, and most phenolic acids tested are inhibitory at millimolar concentrations and stimulatory at micromolar levels. Cinnamic acid derivatives seem to be somewhat more effective than benzoic acid derivatives.

Reports on the effects of phenolics on plants include almost all plant metabolic processes, e.g. mitochondrial respiration, photosynthetic rate, chlorophyll synthesis, water relations, protein synthesis and mineral nutrition. With respect to the uptake of nutrients an important effect caused by phenolic acids is the alteration of root membrane permeability, especially occurring at lower pH conditions. The result is an efflux of ions, as has been demonstrated for K and P. Effects on the uptake of micro-nutrients (Fe, Mn, Zn, Cu) have also been reported. It has been suggested that the allelopathic activity of phenolics is especially through these effects on nutrient uptake.

Final remarks

A few final remarks should be made with respect to the implications of phenolic substances for plant growth in relation to physico-chemical soil conditions. Both from the

interference of phenolics with site quality and the effects they may exert on physiological functioning of individual plants, it can be concluded that the role of phenolic substances in plant–soil interactions is closely related to pH and soil nutrient status. Phenolic substances will affect plant performance especially under acidic soil conditions, where several mechanisms act additionally or even synergistically.

(1) In acidic, poorly buffered soils, phenolic substances released from decomposing plant litter are less immobilized by clay, organic matter or Fe- and Al-oxyhydroxides. They remain in the soluble phase, maintaining their effectiveness. Microbial activity here is generally low, and micro-organisms are less able to use phenolic substances as C-sources under nutrient stress conditions, implicating that the life-time of phenolic acids in these soils is prolonged as has been demonstrated for morhumus sites.

(2) Phenolic acids are physiologically more active in the undissociated form, i.e. at low pH conditions. Their lipid solubility is higher and they are taken up more easily by the root membrane, exerting their physiological effect (photosynthesis, respiration, water relations, mineral nutrition, etc.).

(3) Plants grown on acidic, nutrient poor sites have elevated levels of phenolics in their leaf and root tissue. Thus higher amounts of phenolics are returned to the soil by litter production. By inhibiting decomposition rates and finally nutrient cycling, site quality is deteriorated even further by the phenolics.

In contrast, in calcareous soils most phenolics are rapidly metabolized by microbial activity and adsorption is high, leading to a rapid removal of phenolics from the soil solution. Moreover, most phenolics are present in the (partly) dissociated, less toxic state. Finally, under these soil conditions plants generally have lower phenolic concentrations in their shoot and root tissue and lower amounts of phenolics are returned to the soil by litter. Therefore, interference between phenolics and vegetation may be expected to occur, especially at acidic, nutrient-poor sites. Indeed, many reports have been published on phenolic–plant interactions for systems such as *Calluna* vegetation (Robinson 1972; Carballeira & Cuervo 1980; Ballester *et al.* 1982; Jalal & Read 1983a,b) and coniferous forest systems, well known for their acidification of the soil, i.e. *Pinus, Picea,* and *Abies* spp. (Shütt *et al.* 1981; Becker & Drapier 1984, 1985; André *et al.* 1987).

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