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Review

Interactions and Regulatory Functions of Phenolics in Soil-Plant-Climate Nexus

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Abstract: Phenols are major compounds produced by plant species as a peripheral stimulus or as a regulatory defense mechanism under different environmental biotic stresses. These secondary metabolites are generated from shikimic and acetic acid metabolic pathways. The aromatic benzene ring compound plays an important role in plant development, especially in the defense forefront. They provide structural integrity and support to the plants. Phenolic phytoalexins released by pathogen/arthropod-attacked or wounded plants nullify or repel organisms for the advantage of the host. The allelopathic potential of phenolic compounds is observed in both natural and managed ecosystems. The global impacts of climatic variabilities such as drought, increased carbon dioxide, or greenhouse gas emissions alter the quantitative response of plant phenols. This review primarily discusses the different aspects of phenolic interactions concerning health, antioxidant properties, and insect-plant interaction as a nexus of soil and plant relations in response to variable climatic conditions.

Keywords: secondary metabolites; phenol; allelochemicals; soil interaction; plant-pathogen interaction; antioxidant; climate change

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1. Introduction

Primary plant metabolites, such as carbohydrates, amino and organic acids, and enzymes, exhibit essential physiological pathways such as glycolysis, the Krebs cycle, and the Calvin cycle that are important for plant growth, reproduction, and metabolism [1]. Metabolic pathways are enzyme-mediated chemical reactions and metabolites are organic compounds synthesized by the host [2]. In contrast, secondary metabolites such as phenols, alkaloids, flavonoids, and terpenoids play a significant role in stress and the defense mechanism of the plant [3] and are not directly associated with plant growth. They are responsible for attracting pollinators and seed dispersion [4,5] and are distributed within the taxonomic groups in the plant kingdom. The functions of secondary metabolites are particular to the plant species in which they occur [6]. The primary metabolites contribute to the production of secondary metabolites biosynthetically. Their deficiency does not cause dreadful effects on the plants [7]. The secondary metabolite content in plants is far less than the primary metabolites. Most of the facts, questioned by the shared efforts of photochemistry and plant physio-biology, depicted that secondary metabolite is a way out through which the plants respond to peripheral stimulus [8,9]. Bioactive compounds collected in plant tissues through biochemistry mechanisms are encrypted by other mechanisms of regulation. So, it is assumed that each plant species has progressed up to a remarkable set of machinery for the biosynthetic regulation of secondary metabolites, from previous generations, which effectively articulated these strategies [10]. Secondary metabolites provide (i) defense against other bacteria, fungi, amoebae, plants, insects, and large animals; (ii) metal transporting agents; (iii) agents of the relationship between microorganisms and plants, nematodes, insects, and higher animals; (iv) sexual hormones; and (v) differentiation effectors. Although antibiotics are not compulsory for sporulation, some secondary metabolites (including antibiotics) stimulate spore formation and inhibit or stimulate germination.

According to the British Nutrition Foundation, secondary metabolites are broadly divided into phenols, terpenoids, alkaloids, and sulphur-containing compounds [11]. Phenol and polyphenolic compounds are characterized by phenolic ring structure that includes flavonoids, lignans, and phenolic acids. Huge numbers of plant secondary metabolites validate the quest for bioactive and defensive compounds, which are elicitors and phytoalexins. One of the important compounds in the research area is known as capsidiol, present in tobacco leaves from *Vitis vinifera,* which is a terpenic ancestoral, aristolochene. It is seen in *Nicotiana tabacum*, among the diverse isoforms of terpene synthase, that the prenyl phosphate units are cyclized to form the aristolochene carbon form [12]. This bicyclic unit of alkene is designed as the most central biosynthetic step in the biogenesis of capsidiol. In this biosynthetic pathway, the terpene synthase transcripts level specifically is influenced by *Manduca sexta* infestation of shoots in *Nicotiana attenuate* leaves [13]. In this review, we discuss plant phenolics and their importance in soil-plant relations under global climatic variabilities. The manuscripts describe the need to integrate plant phenolics in agroecological systems, the biosynthetic pathways in plant systems, antioxidant properties, allelopathic interactions and their role in plant systems including the regulatory and inhibitory actions in the rhizosphere. We have also presented the agro-industrial integration of phenolic compounds and finally the impact of climate variabilities on the physiological and chemical fate of phenolics in plants.

2. Bio-Synthesis of Phenolic Compounds in Plant System

In response to several potential enemies in the vicinity, plants often produce secondary metabolites as their second line of defense, apart from the cuticle or/and the periderm, which acts as a physical barrier. Secondary metabolites produced by plants are usually phenolic in nature [14]. The two major metabolic pathways involved in synthesizing phenols in plants are the shikimate pathway and the malonate acetate pathway [15]. The seven enzymatic steps in the shikimate pathway (Figure 1) are the primary source of producing phenolic compounds, related to glycolysis (phenylalanine and tyrosine as end products; tryptophan as intermediate) in plants [16]. The important amino acids are produced in the plastid, clearly indicating the absence of such pathways in animal cells. Some of the steps of the pathway are also performed in the cytosol, where intermediate proteins and enzymes are also found. Apart from phenolic compounds, indole-3-acetic acid (IAA), tetrahydrofolate (vitamin B9), salicylic acid, some plant pigments, and quinones are also producing indole-3-acetic acid (IAA), tetrahydrofolate (vitamin B9), salicylic acid, and some plant pigments, and quinones other than the phenolic compounds are important components for transducing energy which is essential for electron transport chains in plant organs such as thylakoids and mitochondria [14,17]

The malonate acetate pathway is a comparatively less impactful biosynthesis pathway [18]. Phenylalanine ammonia-lyase (PAL) from the shikimic acid pathway catalyzes the production of phenolic compounds. Phenylalanine ammonia-lyase is a vital gateway enzyme in the secondary metabolic pathway, chief to the synthesis of phenolic compounds. It initiates the formation of cinnamic acid (CIN) from phenylalanine (Phe), important in regulating the formation of many phenolic acids [19]. The cell walls contain phenolic acid due to biotic stress, which increases the phenylpropanoid pathway where cinnamic acid and benzoic acid synthesis [20]. The PAL activity is hindered by 2-aminoindan-2-phosphonic acid (AIP) and is reported to have stronger inhibition capability in comparison to 2-aminooxyacetate (AOA) and 2 aminooxy-3-phenylpropanoic acid [21]. Due to the inhibitory effect of PAL by the enzyme AIP, there resulted in an accumulation of phenolic compounds in lettuce which limited browning in cut lettuce [22]. Another study reported a decrease in phenol accumulation in response to the inhibitory effect of PAL by AIP treatment [23]. The PAL also plays important role in producing phenol and flavonoids in response to biotic stresses in the fruiting bodies of the crops [24].

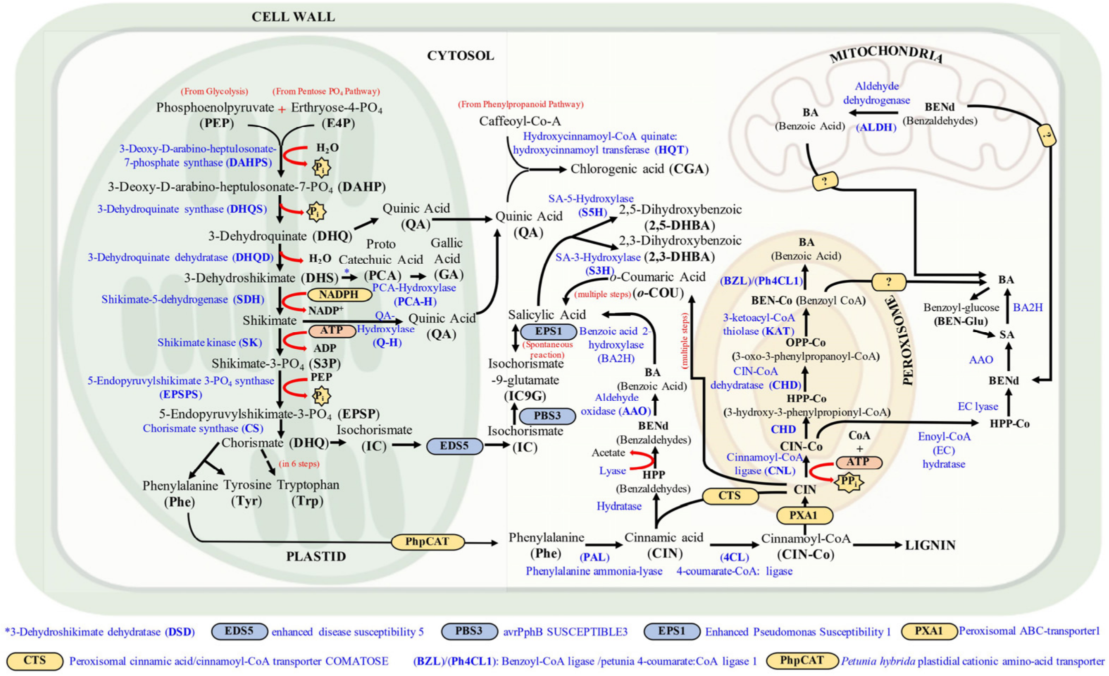


Figure 1. Biosynthesis of phenolic compounds in the plant cell [14–24].

3. Antioxidant Properties of Phenols

Reactive oxygen species (ROS) are important signaling molecules and free radicals that respond to cell signaling in plants due to stress [25]. The most popular ROS are superoxide radical, hydrogen peroxide and hydroxyl radical originating from electron transfers to dioxygen [26]. Reactive oxygen species (ROS) increases due to an imbalance in cellular homeostasis to maintain balance [27]. Reactive oxygen species (ROS) and reactive nitrogen species (RNS) are produced continuously by normal cellular environmental factors and are extremely responsive to the oxidized molecule. This mode of action in the mitochondrial respiratory chain and inflammation might lead to damage to other biotic molecules, such as proteins and DNA [28–30]. To avoid this damage, plants develop enzymatic and non-enzymatic defense mechanisms in which antioxidant metabolites (and enzymes) neutralize ROS [31]. A variety of responses were drawn, where some authors found a correlation between the polyphenol content and the antioxidant activity, while others found no such relationship [32]. The author [33] mentioned a parallel increase between phenol content and antioxidant activity during the germination of *Pangium edule* Reinw, whereas [34] an increase in the antioxidant activity of lupin seed (*Lupinus albus* ssp. Graecus), was observed and phenolic compounds, peptides/amino acids, and phospholipids are responsible for this increased production [34]

There is an ambiguity in the correlation between the polyphenol content and the antioxidant activity [26]. In response to plant stress, flavonoid and phenylpropanoid compounds, present mostly in plant cell vacuoles and apoplast (exterior to plasma cell and within cell wall), detoxify hydrogen peroxide by donating electrons to guaiacol peroxidases and forming their respective phenoxyl radicals [35]. Dimers or trimers of flavonoids are produced due to oxidization (reaction I below) in H_2O_2-peroxidase (enzyme) system (Figure 2).

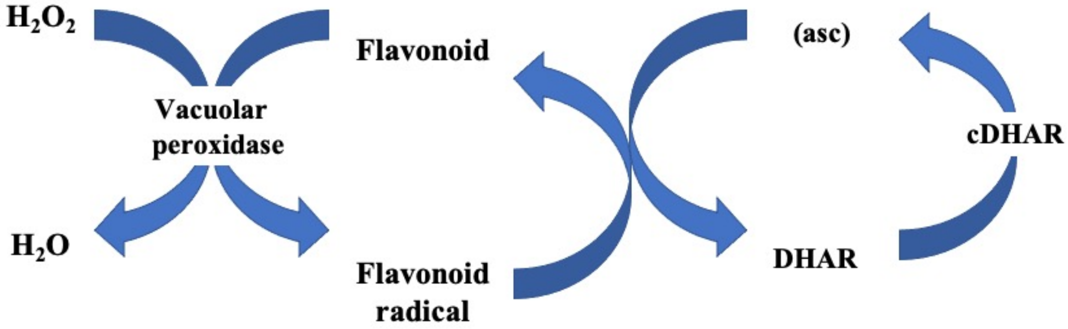


Figure 2. Schematic diagram of scavenging mechanism of flavonoids or polyphenols [26,35–37].

I $2FlavOH + H_2O_2 \rightarrow 2FlavO\cdot + 2H_2O$

In this reversible cycle (reaction II below), the phenoxyl radicals (i.e., FlavO·) are converted to their phyto phenols (i.e., flavonols–FlavOH) in enzymatic presence of ascorbate (asc), delimiting the degradation of products [36] while in absence of (asc) polymerization products are produced irreversibly.

II $2FlavO + (asc) \rightarrow 2FlavOH + 2MDA$ (monodehydroascorbate radical)

Monodehydroascorbate radical is transported to the cytoplasm and is reduced there by (Gsh)-dependent glutathione reductase (DHAR) to (asc) and dehydroascorbic acid (DHA) [37]

III $MDA + MDA \rightarrow (asc) + DHA$

Ascorbate regeneration by cytosolic DHA reductase (cDHAR) and Gsh-DHAR when coupled the flavonoids peroxidase system act as stress protectants by scavenging hydrogen peroxide, similar to ascorbate.

IV Summary of the three steps of reaction: $H_2O_2 + (asc) \rightarrow 2H_2O + DHA$

Though phenols show antioxidant properties, the prolonged presence of phenoxyl radicals can be responsible for cell mortality [38]. Antagonistically, reports have shown that extracts from berries have shown the presence of anthocyanins, quercetin, esters of coumaric acid, etc. with anticancer efficacy against different human cell lines [39]. Inhibition in tumor growth due to the polyphenol content from tea extracts has been noteworthy while working with rat cell lines, holding epigallocatechin gallate and theaflavin as the responsible polyphenols [40,41]. Inhibition of tumours is brought about by apoptosis or cell cycle arrest. The cells usually then undergo DNA fragmentation or chromatin condensation. Polyphenols such as flavonoids such as quercetin, rutin, and apigenin, phenolics acids such as gallic acid, tannic acid, caffeic acid, as well as delphinidin, resveratrol, and curcumin have shown oxidative DNA strand breakage, bringing about apoptosis and with anti-cancer drug developing properties [39,42].

4. Role of Phenol and Phenolic Compounds in Plant Systems

Secondary metabolites secreted from plants are of great importance in defense growth, and development. They are associated with various processes together with rhizogenesis [43,44], resistance to biotic and abiotic stress, and redox reactions in soils [45]. Also, they are related to flowering pigments and act as constitutive guards against intruders. They play an important role as allelopathic compounds and signal molecules. These compounds have an important role as natural animal toxicants [46] and function as pesticides [47,48]. They are also useful constituents of the rhizosphere. For weed control, the compounds are recognized as allelochemicals and in animals as phytoestrogens [49]. Effective allelochemicals can be present as volatile terpenoids, contaminated water-soluble hydroquinone, hydroxycinnamates, and 5-hydroxynapthoquinone. Several simple and complex phenolic compounds accumulated in plant tissues act as phytoalexins, phytoanticipins, and nematicides against many pathogens and insects [50]. Phenolic compounds have been used to serve as a valuable alternative to the chemical control of pathogens in crops.

When infection is caused by micro symbionts such as rhizobium as well as pathogen attack, then the herbivory phenols are synthesized and released [51]. These metabolites intra- and extra-cellular to plant tissues are known to function as phytoalexins, phytoanticipins, and node gene inducers. Many studies showed that phenolic metabolites are toxic to plants and a level determined in a higher range affects soils [52–55]. Phenolic acid concentrations in soil can range from 2.1% to 4.4% for monocot roots and from 0.1% to 0.6% for dicot roots [56]. The phenolics might have a beneficial or negative impact on the availability of plant mineral elements in the rhizosphere. Through rainfall leachate of phenolic as chromogenic acid or through a variety of other methods that alter phenolic synthesis, green leaves and decomposing plant litter can regulate the rhizosphere and dynamics [56]. The development of protein complexes delays the decomposition and mineralization of organic matter, increases microbial activity when utilized as a carbon source, results in immobilization, and directly inhibits nitrification [57–61]. The effects of soil-borne diseases in modern agricultural systems may help varied defense mechanisms used by rhizosphere-dwelling plants. The effects of soil-borne diseases in modern agricultural systems may help varied defense mechanisms used by rhizosphere-dwelling plants. The production, release, and addition of numerous phenolic chemicals serve as the plant's defense mechanism against diseases, nematodes, and phytophagous insects [62,63]. The alfalfa root releases isoflavonoid 2-(35-dihydroxyphenyl)-5, 6-dihydroxybenzofuran which acts as a phytoalexin to defend against root infections such as *Fusarium oxysporum* f. sp. Phaseoli [64]. When released into the soil through seeds, roots, or residue decomposition, these chemicals play a significant role in defense and protection against soil-borne diseases and root-feeding insects [18,65]. Due to the ecological potential of these macromolecules from symbiotic legumes in the rhizosphere as a sustainable method of lowering soil-borne diseases in the ecosystems, they have attracted more scientific interest [66].

5. Regulatory and Inhibitory Interactions of Phenolic Compounds in the Rhizospheric Soil Matrix

Phenolic compounds enter the soil systems as exudates from roots or as leachates or particulate matter from plants [67,68]. The release of phenolic compounds from decomposing leaf litter and roots on upper soil layers of the horizon is mediated by soil microbes. Phenolic compounds in soils exist in three forms—free or dissolved, absorbed or reversibly bound by clay minerals or chelated complexes with metals and proteins, and polymerized [67]. In soil formation and pedogenesis, phenolics and other organic molecules from the root and seed exudates, leaf leachates, and decaying plant residues play a key role. The degradation of phenols and their reactivity depends on the chemical structure and forms of phenol [69,70]. Many phenolics such as phenolic acids and tannins are water-soluble. These forms remain in solution between soil particles leading to reversible sorption through hydrophobic, hydrogen, and ionic interactions. These microbial condensation and polymerization reactions of phenolic compounds with amino acids and proteins in the soil matrix release soil organic acids of higher molecular weights such as fulvic acids, humic acids, and humin [60,71,72]. This process of humification alters the physicochemical processes in soils based on alterations in soil health and qualitative characteristics. The resulting humic substances are generated by polymeric combinations of phenolic compounds and soil organic matter [67]. The recalcitrant structure of phenols makes them resistant to natural biodegradation and decomposition. However, the phenolic compounds are highly soluble in water up to 10g L^{-1} [73]. These properties possess serious risks of environmental pollution [74–76].

The phenolic compounds are also known for inhibiting the oxidation of ammonia by nitrifying microorganisms during nitrification [77–79]. Contrastingly, low contents of phenolic acids in rhizospheric soils have indicated increased nitrogen (N) mineralization rates, and enhancement in ammonium content, resulting in increased conservation of soil N [80]. Contrastingly, phenolic compounds can enhance the mobility of soil phosphorus (P) depending on soil properties such as pH and organic chelates. The addition of phenolic compounds decreases the pH of saturation paste extract of calcareous and aluminum-dominated soils [81]. Phenols synergized with organic acids (chelates before biodegradation) alter the stable and sparingly soluble forms of soil phosphorus (P) to easily dissolvable forms [81]. The abundance of phenols can absorb large quantities of heavy metals such as cadmium in soils [82].

These abundances can lead to ecological consequences in the growth and development of plants, mainly impacting the germination stage. In woodland or forestry, regenerative practices and reforestation problems are attributed to the phenolic compounds polymerized with high organic matter and deposited in the soils. These depositions can be due to former tree species [81]. The phenolic compounds also impact other physiological responses during plant growth such as cellular expansion, membrane permeability, nutrient mobility, soil-plant relations for respiration, and water uptake [83].

6. Phenolic Compounds in Plant-Pathogen Interaction

Plant phenols constitute one of the common and important groups of defensive secondary metabolites compounds, that play a vital role against herbivores, including insects [71,84,85]. Insect attacks or defense mechanisms alter and elevate the qualitative and quantitative measures and elevation in activities of the oxidative enzyme [84]. For example, lignin is a phenolic heteropolymer and plays a significant role in plant defense against insects and pathogens [86] by physically blocking or increasing the leaf toughness, diminishing the nutritional content of the leaf, and restricting the entry of pathogens and feeding behaviour of herbivores (Figure 3) [87]. Lignin synthesis is induced by herbivore or pathogen attack and the rapid deposition reduces further growth of the pathogen or herbivore productivity. Some genes involved in lignin expression, such as (CAD/CAD-like genes) at times, are noted to increase in amount when studied on plants infected with pests and pathogens [86]. Due to the phenolic oxidation catalyzed by polyphenol oxidase (PPO) and peroxidase (POD), there is a potential defense mechanism in plants. To leaf proteins, the quinones are formed due to the oxidation of phenols binding covalently, and also hinder protein digestion in herbivores [88]. Also, quinones show direct toxicity to insects [88,89]. The nutritional value of plant proteins for insects is reduced due to the alkylation of amino acids, which in turn adversely affects insect growth and development [88]. Other than the mentioned roles there is evidence showing the role of phenols in the cyclic reduction in ROS such as superoxide anion and hydroxyl radicals, H_2O_2, and singlet oxygen, which activate a cascade of reactions leading to the activation of defensive enzymes [8]. *Operophtera brumata* (L.) in Salix leaves, the simple phenolics (salicylates) act as an antifeedant, and there is an adverse correlation between the salicylate levels and the larval growth; still, salicylic acid (SA) is much more important as phytohormone than as deterrent [90].

Some phenolic compounds are soluble in organic solvents, whereas some are soluble in water, such as carboxylic acid and glycosides [91]. Phenolics also play important by attracting pollinators and fruit dispersers, absorbing harmful ultraviolet radiation as a mechanical support in the plant, and limiting the growth of nearby competing plants [92]. There are a wide number of examples of phenolics used in defense against insect herbivores. Wheat cultivars which contain phenolic compounds are much less attractive to *Rhopalosiphum padi* (Cereal aphid) [93]. Catechol-based phenolics present in the leaves of Fragaria (strawberry) provide resistance to *Tetranychus urticae* (two-spotted spider mite) [94]. It is noticed that the cotton phenolic pigment gossypol has repellent effects against abundant insects and is lethal to *Heliothis virescens* (tobacco bollworm), *Heliothis zea* (bollworm), and quite a few other insects [95].

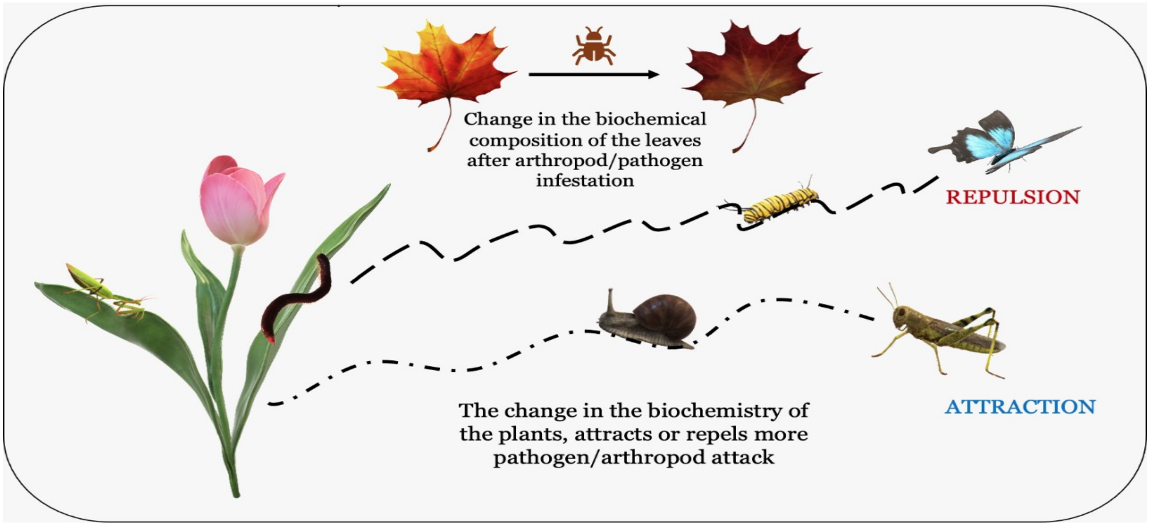


Figure 3. Changes in the biochemical composition of the plants (infected or attacked by arthropods or pathogens) attract or repel other agents to the affected host plant [86,87].

7. Allelopathic Interactions

Allelochemicals mostly spread via the roots and soil of plants many biotic and abiotic factors contribute to the allelopathic interactions among organisms. Phosphorus, nitrogen content, water stress, temperature, and microbes and their metabolites play a role of high significance [96,97]. Soil fatigue is a phenomenon in agriculture where the accumulation of fungi secreting mycotoxins in the soil hinders the productivity of plants [98]. Such toxins have an upper hand in the soil-microbes-plant interaction and have survived or endured in the community interaction with a myriad of biological effects [99]. These mycotoxins vary in their potential impact on plants and/or animals, belonging to various groups of cyclic terpenoids, polyketides, and cyclic polypeptides [100]. Polyketides include many potent mycotoxins with not only zootoxic but also phytotoxic properties: alternariol from *Alternaria* spp., aflatoxin from *Aspergillus* spp., fumigatin and zearalenone from *Fusarium* spp., trichodermin from *Trichoderma* spp., patulin, citrinin, rubratoxin from *Penicillium* spp. [98]. Microorganisms in interaction with plant and soil secrete a large number of allelochemicals (lytic enzymes such as glucanases, chitinases, etc.) and influence and causes several plant diseases. β-1,3-glucanase among many other cell wall degrading enzymes (CWDEs), destroys the cell walls causing the root rot *Pythium aphanidermatum* and the fusarial rot *Fusarium oxysporum* [99,101].

Among various metabolic compounds secreted by plants in response to interaction, phenols play a major role and constitute a major group of plant allelochemicals in the ecosystem (Figure 4) [102]. Phenolic allelochemicals play a role in root elongation, observed in *Lactuca sativa* L. [103] by cell division, and interfering with the development of the plant [104] growth of wheat (*Triticum aestivum* var. PBW) has been significantly reduced when their seeds were soaked in root leachates or root and leaf extract of various weeds such as *Parthenium hysterophorus*, *Asphodelus tenuifolius*, and *Pluchea lanceolata*, revealing a high phenolic content [105].

The phenolic allelochemicals based on their structure can be broadly divided into the following categories [107] (Table 1).

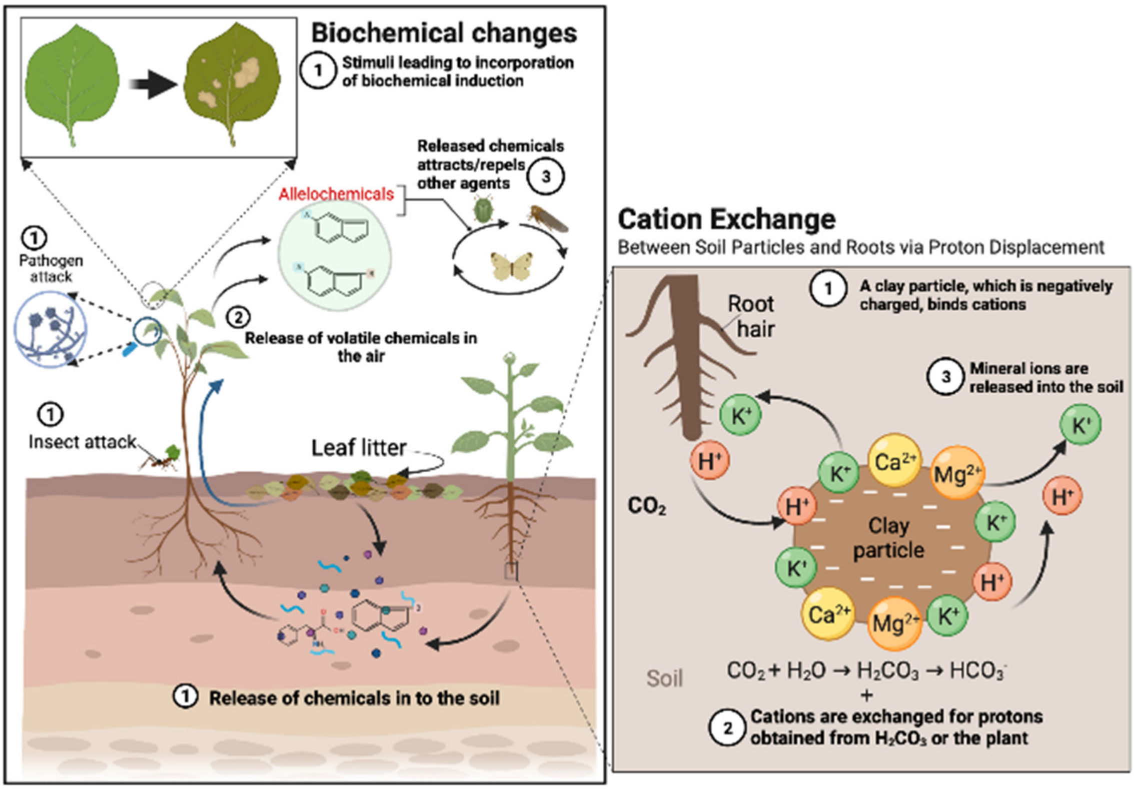


Figure 4. Plants use allelopathy by their roots to absorb more nutrients along with water from the soil and eventually hinder the growth of neighbouring plants. Pathogen or arthropod attacks also bring about biochemical changes in the host plant indirectly [102–105]. The cationic changes brought about by the release of allelochemicals in the soil redirect the change in the nutrient uptake of the effector plant [106].

Table 1. Phenolic allele-chemical compounds and their mode of action.

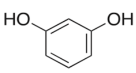
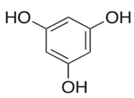
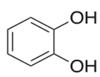
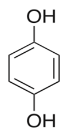
Phenolic Compounds	Some Examples with Their Structure	Function or Mechanism of Action	Reference
C_6 compounds Simple Phenols 1. Resorcinol 2. Phloroglucinol 3. Catechol 4. Hydroquinone	 Resorcinol  Phloroglucinol  Catechol  Hydroquinone	Have various inhibitory effects against enzyme activities. Catechol acts as inhibitors of phosphorylase. The acylphloroglucinol structure might play a significant role in inhibiting plant transpiration.	[107,108]

Table 1. *Cont.*

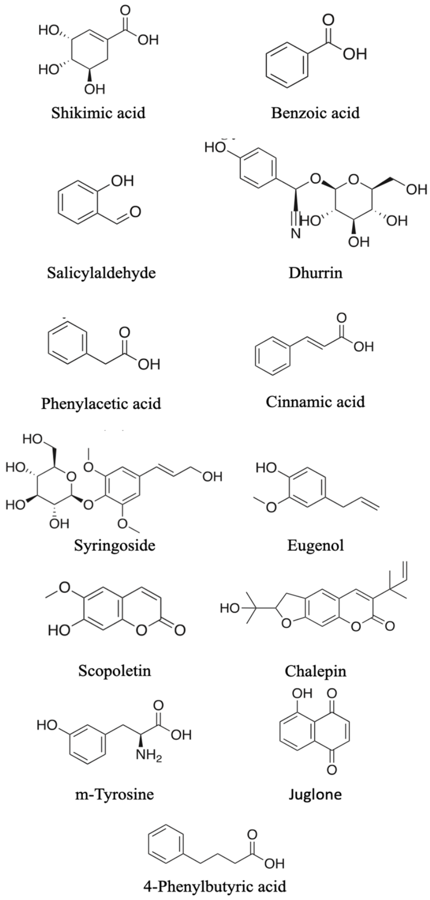
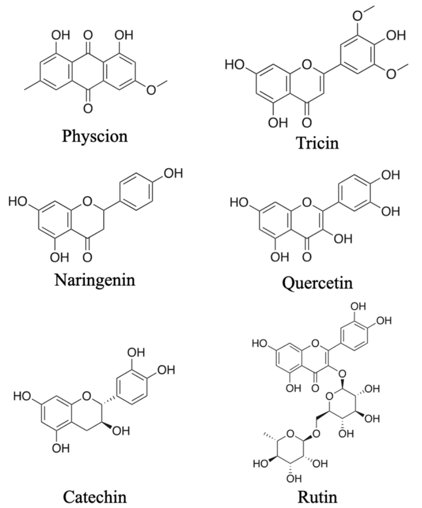
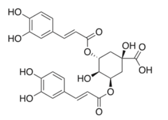
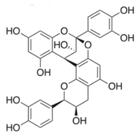
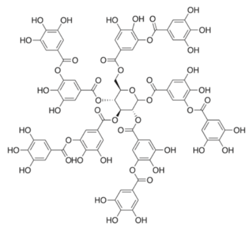
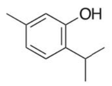
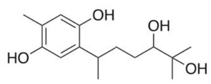
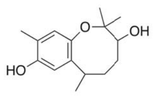
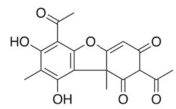
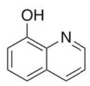
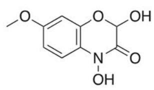
Phenolic Compounds	Some Examples with Their Structure	Function or Mechanism of Action	Reference
C_6-C_n compounds *n* = 1 1. Shikimic acid 2. Benzoic acid and derivatives 3. Phenolic aldehydes 4. Phenolic glycosides *n* = 2 1. Phenylacetic acids 2. Acetophenones 3. Styrenes 4. Phenethylamines *n* = 3 1. Cinnamic acid and derivatives 2. Phenolic glycosides 3. Phenolic propanoids 4. Coumarins 5. Furanocoumarins 6. Aromatic amino acids *n* = 4 1. Naphthoquinone 2. Phenylbutyric acids		Effect on membrane permeability hormonal activity, respiration, photosynthetic activity, synthesis of organic compounds and plant growth as a whole	[108]
C_6-C_n-C_6 compounds *n* = 2 1. Anthraquinones *n* = 3 1. Flavones 2. Flavanones 3. Flavonols 4. Catechins 5. Epicatechins 6. Flavan-3,4-diols 7. Pterocarpanes 8. Flavonoid glycosides		Inhibit the germination of seeds and growth of plants. Release of flavonoid compounds into the rhizosphere plays an important role in the supply of phosphorus to plants.	[97]

Table 1. *Cont.*

Phenolic Compounds	Some Examples with Their Structure	Function or Mechanism of Action	Reference
Phenolic dimers (C_6-C_3)$_2$ Compounds 1. Coumaric acids and derivatives (C_6-C_3-C_6)$_2$ compounds 1. Biflavonoids and poly flavonoids Phenolic hybrids(C_6-C_1)$_{10}$ Compounds 1. Tannins	 3,5-Dicaffeoylquinic acid  Procyanidin A2  Tannic acid	Tannic acid is an inhibitor of peroxidase, catalase, and cellulase	[97]
Others 1. Phenolic monoterpenes 2. Phenolic lipids 3. Phenolic sesquiterpenes 4. Dibenzofurans 5. Quinolines 6. Benzoxazinones	 Thymol  Helibisabonol A  Heliannuol A  Usnic acid  8-Hydroxyquinoline  2,4-Dihydroxy-7-methoxy-1,4-benzoxazin-3-one	Effect on all mitosis stages, respiration, and membrane permeability	[108,109]

C_6 compounds—Simple phenols. C_6-C_n compounds—Benzoic acid (n = 1) and derivatives; phenylacetic acid and acetophenones (n = 2); phenylpropanoids, coumarins, phenylalanine, and derivatives (n = 3); naphthoquinones and phenyl butyric acids (n = 4). C_6-C_n-C_6 compounds—anthraquinones (n = 2); flavonoids (n = 3). Other complex structures—phenolic dimers and hybrids.

8. Phenolic Compounds from Agro-Industrial Byproducts

From agricultural and industrial residues, the abundance of phenolic compounds and their extraction and antioxidant activity has been widely researched [110]. Several agricultural byproducts have been identified which contain phenolic compounds with antioxidant activity such as rice hulls, [111] buckwheat hulls, [112] and almond hulls [113]. The total cinnamic acid content of the hulls of Swedish oats (*Avena sativa* L.) [114] was found higher than that of the groats (23.6 compared to 3.6 mg kg^{-1} dry matter) [115]. Another source of phenolic antioxidants is pistachio hulls, which may contain up to 34 mg tannic acid equivalents phenolics/g dry weight [115].

Citrus industry byproducts, if utilized, could be key sources of phenolic compounds, as the peels in particular have been found to contain advanced amounts of total phenolics in comparison to the edible portions [116]. Phenolic compounds, various phenolic acids, and flavonoids are present in tomato waste [117]. There are reports that dry onion skin waste is one of the agro-industrial wastes which is high in flavonoids and phenolic acids and has a role in antioxidant activity [118]. Similarly, potato, which is one of the most widely used vegetables around the world, has been reported to have peel waste that has glycoalkaloids [119].

Another important source of phenolic compounds is the byproducts of the olive industry, with much attention focused on olive mill wastes. In the olive fruits, the phenolic compounds are distributed into the olive oil or may be present in the aqueous phase wastewater or the solid phase pomace, with nearly 1–2% partitioning into the former [120]. Therefore, a major potential source of phenolics, particularly in consideration that annual production exceeds 7 million tons, is the olive mill wastes [121]. The phenolic content of the olive mill wastewater (OMWW) is reported to vary between 1.0% and 1.8% depending on varietal factors and processing effects. Hydroxytyrosol, tyrosol, oleuropein, and a variety of hydroxycinnamic acids are major components of OMWW [122]. Olive leaves are another byproduct of the olive industry and can be also referred to as a source of phenolics, though to a lesser extent [123] there are some reports where it is mentioned that wines made from blueberries have higher total phenolic content (600–1860 mg Gallic acid equivalents L^{-1}) than white wines (191–306 mg Gallic acid equivalents L^{-1}) [124]. Collectively, the information provided gives an outline idea about phenols and phenolic compounds related to agro-waste and its impact.

9. Phenol as Contaminants

Phenols are organic contaminants present and regarded as one of the most toxic pollutants in wastewater; they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants with direct harmful effects on human health at low concentrations [125,126]. Oil refineries and the petrochemical industry, tanneries, olive mills, cork-producing industry, and pulp and paper mills, contribute to the use and disinfectants of the pesticide [127–130]. Phenols are extensively distributed as environmental pollutants. From many industrial processes, including synthetic rubber, plastics, paper, oil refineries, petrochemical, ceramic, steel, conversion processes, and phenolic resin industries, the concentration of phenolic compounds varies widely. Natural forest fires are also a source of phenol contamination [131]. Phenol's presence in water and wastewater could be toxic to plants if this water is reused for irrigation, while it may also be toxic for bacteria as well [126,132]. There is a serious discharge problem due to their poor biodegradability, high toxicity, and ecological aspects when wastewater containing phenolic compounds is discharged [133]. Industrial use is gradually avoided due to the high toxicity of phenols; they are subjected to specific regulations by substituting them with harmless compounds [134]. A crucial step is taken by the Environmental Protection Agency (EPA) which calls for lowering the phenol content in the wastewater to less than 1mg L^{-1} [134]. Wastewaters containing phenols and other toxic compounds need careful treatment before discharge into the receiving bodies of water. Additionally, biological treatment, activated carbon adsorption, solvent extraction, chemical oxidation, and electrochemical methods are the most widely used methods for removing phenol and phenolic compounds from wastewater [135–137].

10. Response of Phenolics to Climate Change

Plant growth and physiological functions are globally impacted by climate change. Elevated levels of CO_2, temperature together with phytopathogenic infection or arthropod herbivory significantly modify plant biochemistry and likewise their defense responses. By the year 2100, the global mean surface temperature is predicted to increase by at least 1.5 degrees Celsius compared to that in 1850–1900 [138]. Plant phenolics play an important role in plant protection against abiotic stressors due to climatic variabilities such as drought, salinity, and ultraviolet (UV) radiations [139,140]. These stressors increase the expression of phenolic compounds and impact decomposition and nutrient cycling [140,141]. Plants originating from a cold climate, higher altitude, or semi-arid environment have been reported to have the highest phenolic compound contents in their organs [142]. The strong oxidant property of phenolic compounds protects the cellular structure by increasing ROS production and avoiding cell damage [143,144]. Increased production of polyphenols by many plant species is indicative of protection against oxidative damage by drought [145]. Depending on the plant genotype and water deficit conditions, phenolic compounds such as tannins and flavonoids are synthesized to protect the cell membrane and photosynthesis mechanism, protein denaturation, and plant growth inhibition [146,147]. The study by Varela and colleagues measured polyphenols in shrublands and detected variability in concentrations of phenolic compounds among different species of Patagonian shrublands [145]. In *Larrea divaricata* production of phenolic compound, synthesis increased during the season of greatest drought, while *Larrea chilense* has lower production of phenolic compounds without variation between seasons. Similarly, another group of scientists experimented on five different genotypes of peanuts to study the impact of drought on phenolic compounds where drought significantly increased the phenolic content in leaves and stems at midseason [148].

Globally, climatic variabilities particularly increased temperature, are strongly correlated to increased carbon dioxide in the atmosphere [149]. In plant systems, increased temperature and elevated carbon dioxide levels increase phenolic compounds in foliar tissues and decrease concentrations in woody parts of the plants. Drought and UV radiations influence the accumulation of phenolic compounds in some cultivars of Solanaceous and leafy vegetables [150–152]. Salt stress in soils is also a major environmental stressor due to climate change. The salinity stress can significantly reduce the photosynthetic electron chain reaction and can promote ROS leading to oxidative stress in plants [153]. The phenolic compounds such as flavonoids and pro-anthocyanidins play an important role by acting as free radical scavengers [154]. The flavonoid accumulation induced by UV-B radiations protects the cellular system by potentially acting as a ROS scavenger [143,154,155].

Climate plays a key role in the biochemical contents of fruits and plants, leading to variation in the phenolic content of the same species of different regions [156]. Besides the climate impacts on the plant, the field performance of any microbial herbicide in terms of virulence and host range depends on several biological traits of the organisms and their environmental conditions, which directly and indirectly can leave ecological and economic consequences on the mutually interacting species [157].

11. Conclusions

Secondary metabolites such as phenols and polyphenolic compounds are regulatory and have inhibitory effects on plants in response to abiotic stresses or external stimuli. It generates defense mechanisms against harmful microbiota, chelating transport agents, sexual hormones, and differentiation effectors. These compounds provide significant benefits for human health and therefore the manuscript provides a forum to understand the nexus benefits of plant phenols as an integrative balance of soil, rhizosphere, plant, and climate change. The redoximorphic features of phenolic hormones concerning plant hormones (such as resveratrol (which improves impaired glucose) and streptozotocin (beneficial impacts on β-cells)) play a vital role in chronic metabolic disorders in humans. Therefore, understanding the biosynthetic pathway and the mechanism of phenolic compounds in agroecological systems is important for further research and development in this area.

The two major biosynthetic pathways—shikimic acid and malonic acetate pathways—are primary sources of producing phenolic compounds, followed by the glycolytic pathway and cinnamic acid which are the intermediate product. The polyphenolic compounds enhance vegetable products' nutritional and functional values and further evolve into strong complexation with digestive enzymes when consumed. The presence in plants makes phenolic compounds as precursors during the decomposition of soil organic matter specifically for humic acid in soils.

This leads to the synergistic impact of these secondary metabolites as functions of pedogenetic processes in soil. The defense mechanism against feeding herbivores and allelopathic interaction is majorly in response to the release of phenolic compounds. Phenolic compounds are impacted by variable climate and inductive or natural stresses such as drought and salinity. These stresses impact the physicochemical mechanisms of phenols, primarily increasing the reactive oxygen species. Therefore, the beneficial impacts of phenolic compounds as integrative balance in soil and plant systems, presented in this study concerning global climatic changes, aim to advance further research of these compounds under external environmental stimuli or abiotic stresses.

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