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Anthropogenic Stress and Phenolic Compounds: An Environmental Robustness Diagnostics Compound Family in Stress Ameliorations

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Abstract

Natural ecosystems are progressively vulnerable to a number of multiple anthropogenic stressors, particularly with water, ozone, air pollutants, pesticides, heavy metals (HMs), deforestation, artificial lightening, agriculture intensification, and land use pattern changes. All of them have risen in ecosystem imbalance, climate change, global warming, and many other natural disasters as abiotic stresses. These stressors cause imbalance in physiological, biochemical, and molecular traits at different levels and under different environmental components, which they are subjected. Therefore, to diminish the catastrophic consequences on ecological sustainability, the present chapter focuses on the role and mechanisms of secondary metabolites (SMs) especially phenolic compounds (PCs) for environmental robustness diagnostics via adaption or avoidance from these stressors. The prime objective of this chapter tends to explore the functions and responses of PCs in respect to elevated CO_2 (eCO_2), heavy metal (HM) stress, salinity, pollutant translocations, and transformations in ecosystem. For instance, it will help in understanding the different anthropogenic stressors, their impact on environmental components, PC response, and pathway or mechanisms by which these PCs nullify the drastic consequences of anthropogenic stressors.

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18.1 Introduction

Human developmental activities such as overpopulation, industrialization, urbanization, transportation, pharmaceutical, cosmetic industry, mining, manufacturing, energy industry, fishing and farming (use of fertilizer and pesticide), infrastructure building, and drainage of factory and municipal influence the biophysical environments, leading to a change in ecosystem, natural resources, and biodiversity (*https://en.wikipedia.org/wiki/Humanimpactontheenvironment*). In addition to these, deforestation and mining, intensified agriculture, altered land use pattern, excess artificial lightening (AL), and excess pesticides and fertilizers magnify the concentrations of pollutants in water, soil, and atmosphere, becoming the determining factors in affecting the environmental sustainability (Morand and Lajaunie 2017). These factors are known as anthropogenic stressors, and substantially disturb the natural environment by altering the ecosystem services and functions of terrestrial as well as of aquatic one, which lead~~s~~ to ecological imbalances, climate change, global warming, and other abiotic stresses (heat, chilling, freezing, high irradiation, salinity, drought, flooding, and mineral deficiency) (Dukhovskis et al. 2003; Midgley and Thuiller 2011; Häder and Gao 2015).

The plethora of these stresses leaves some pessimistic consequences on biodiversity, human health, as well as plant's survival and also impairs the basic structure, mechanisms, and functions of plants (Dukhovskis et al. 2003). Considering the drastic impacts of growing anthropogenic stress, scientists are continuously working to find the mechanism and novel strategies to mitigate/ameliorate its impacts on ecosystem. The common mechanism, followed by all the plants during stress conditions, is the production of reactive oxygen species (ROS) or oxidative stress. This condition can be mitigated by improving defense mechanism of plants or by improving the level of antioxidant compounds. These compounds have the dexterity to boost up the plant's immune system in coping both biotic and abiotic stresses. Antioxidant compounds such as PCs, terpenes, and alkaloids participate in defense mechanism which are developed by plants in a wide range, under the adverse situation (Isah 2019). In this consequence, phenols are ubiquitous in plant's kingdom, helping in overwhelmed stress constraints and survival under suboptimal conditions. The antioxidant properties and nature of phenolics are by virtue of the ring structure containing phenolic hydroxyl groups and effective against multiple stresses (Edreva et al. 2008). Considering the discussed facts, this chapter covers the response of various anthropogenic stressors such as deforestation, mining, pesticides, fertilizers, and artificial light on plant system and mechanism involved in amelioration of these stressors, especially by phenolic compounds.

18.2 Effect of Various Anthropogenic Stressors on Plant System

18.2.1 Deforestation and Mining

Removing of forest (vegetation) from any part of the planet for agriculture, industrialization, and urbanization purpose leads to diminishing carbon sequestration, and causes imbalance in atmospheric gases by overemission of greenhouse gases especially CO_2 that has increased from 280 to 405 ppm (Houghton 2005; IPCC 2014). This imbalance in gaseous concentration leads to degradation of air quality, acid deposition, ozone hole, sea-level rise, alterations in rainfall, and storm pattern (Keller et al. 1991). These changes are endangered for flora and fauna biodiversity and have drastic impacts on all living organisms. Water scarcity and other unfavorable conditions due to climate change impact on agriculture production system and food security associated with damaging the crops and irrigation systems (Lawrence and Vandecar 2015). Mining of natural resources such as fuels, coals, and ore of metals is a profitable activity for promoting industrial development, but it causes the accumulation of hazardous gases, surface logging, and deforestation (Anonymous 2011; Chakravarty et al. 2012).

18.2.2 Pesticide and Heavy Metal (HM) Accumulation

Due to industrialization, urbanization, and modern agricultural practices, several toxic chemicals like pesticides, herbicides, insecticides, fungicides, and HMs are applied for crop productions in excess quantities (Rashid et al. 2010; Kumar et al. 2021). The use of pesticide significantly increased with time, and it is estimated that 2 MT of pesticides is utilized annually, which can be increased up to 3.5 million tons by 2020. Excess use of pesticides can alter the plant's physiological and biosynthetic reactions and molecular composition. Moreover, it can influence the growth of beneficial rhizosphere microorganism interactions and hampers the soil fertility and productivity (Sharma et al. 2019).

Heavy metals like Cd, Hg, As, Pb, Ni, Cu, Zn, Cr, Co, and Se are highly toxic, and act as nondegradable pollutants and become hazardous for plants as well as humans, even at minute concentrations (Nagajyoti et al. 2010; Singhal et al. 2022). Nevertheless, some metals are essential for normal metabolic activities of plants and considered as micronutrients (Fe, Zn, Mn, Cu, and Mo), which are required in very trace amounts (Hänsch and Mendel 2009). HMs emanate from natural sources such as volcanic eruption, weathering of rocks, and biogenic sources and anthropogenic sources such as industrial waste, burning of fossil fuels, application of fertilizer and pesticide, municipal and agriculture wastewater, and mining and accumulated in soil, water, and air by physical and chemical processes (Mohammed et al. 2011). Heavy metals can be absorbed by crops' rhizosphere, and their accumulation and toxicity are affected by a variety of factors including sand, silt, clay proportions in soil, temperature, cation exchange capacity, pH, organic and inorganic matter content, etc. (Kim et al. 2012).

The native soil fauna is altered by heavy metals which ultimately affects the ability of soil microorganisms to carry out the mineralization process and subsequent nutrient availability. Heavy metal caused oxidative damage and alters membrane permeability and modulates sugar and protein metabolism (Fryzova et al. 2017). Germination of seeds, root and shoot elongation, fresh and dry weight, soluble sugar content, α-amylase enzyme activity, and protein content in various crops are affected by toxic levels of heavy metals resulting in disruption in plant metabolism and growth (Goyal et al. 2020).

18.2.3 Rise of Pollutants in Water, Soil, and Air

Pollution is a widespread problem affecting environmental health. Various substances are responsible for rising pollution (i.e., pollutant) and that have undesired and adversely effects the usefulness of a resource, introducing from various anthropogenic sources like industries by product and sewage seepage, transportation contaminant and agricultural waste disposal, which congregated and remained for ever since in soil, air, and water (Popescu and Ionel 2010; Gheorghe and Ion 2011). Pollutant can be alienated in several categories includes Hg and other HMs, persistent organic pollutants such DDT, polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) (Kodavanti et al. 2017; Rose and Fernandes 2017), ozone (O_3), particulate matter (PM), persistent pharmaceutical pollutants such as tetracycline, ciprofloxacin, ibuprofen, diclofenac, carbamazepine, cetirizine, polycyclic aromatic hydrocarbons (PAHs) like naphthalene, fluorene, anthracene (Maliszewska-Kordybach and Smreczak 2000), secondary metabolites like terpenoids and volatile organic molecules like alkanes, alkenes, alcohols, esters, etc. (Kesselmeier and Staudt 1999). These pollutants are bioaccumulated in the environment and enter in the food web and drastically affect the livings (She et al. 2016).

Discharge of above waste can be excess in soil and water bodies (eutrophication) causes acidity and negatively influences soil and water microorganism and associated plants (Porter et al. 2013). Pollutants have several detrimental effects on plants, including germination and leaf and root damage, which interrupt photosynthetic properties and ultimately caused *stunted* growth and poor biomass production. Pollutants are also responsible for *obstruction in stomata, respiration,* and damage which appears *in the form of chlorosis, bronzing, and mottling at severe conditions (*Maliszewska-Kordybach and Smreczak 2000; Pourkhabbaz et al. 2010; Kreslavski et al. 2017).

18.2.4 Use of Artificial Lightening

The process of photosynthesis can be always affected by a specific spectrum of light within a notable time period, although plants are exposed with a wide range of visible spectrum of light over the lifespan that are responsible for their normal growth and functions; however, excessive visible and UV radiation impairs plant productivity (Häder and Gao 2015). Disturbance in natural cycle of diurnal rhythm affects arguably the ecosystem (Singhal et al. 2019a; Meravi and Kumar Prajapati 2020; Singhal et al. 2021b). Artificial lighting emits a variable intensity of light (Darko et al. 2014). When plants are exposed with continuous street light during dark hours, plants experience stress, and Fv/Fm value of photosystem II was lower (Meravi and Kumar Prajapati 2020). Light pollution strongly depends on source and emission color of light (Falchi et al. 2011). Light pollution significantly influences germination, vegetative growth, and flowering of crop plants (Singhal et al. 2019b; Meravi and Kumar Prajapati 2020; Sodani et al. 2021).

18.2.5 Increase in Agriculture Intensification and Change in Land Use Pattern

Agriculture-intensifying practices promote to fulfill the demand of increasing population (Rodriguez Garcia et al. 2018) by increasing productivity per unit area (Byerlee et al. 2014). As a consequence of intensifying production practices, the demand of inputs like fertilizers, pesticides, water for irrigation, farm machinery, and labor has been increased. Intensification of crops like wheat, rice, and cowpea leads to land sparing (Folberth et al. 2014; Garcia et al. 2020), causing mineral deficit. Emission of CO_2 and N_2O is increased by intensive agriculture practices and leads to global climate change and loss of biodiversity. Altered land use pattern due to overpopulation can lead to alteration in surface temperature (Chakraborti et al. 2019), loss of groundwater quality (Sarkar et al. 2020), and nutrient criteria (Liu et al. 2018), which influence climate (Llopart et al. 2018).

18.3 Modulations of Physiological, Biochemical, and Molecular Traits by Anthropogenic Activity

Release of injurious gases, HMs, and other chemicals such as pesticides into the environment from anthropogenic activities disrupts physiological processes and metabolic functions of plants by forming anthropogenic and natural stress circumstances. Higher dose of pesticides and HMs also acts as stressor and affects the nontargeted plants (Shakir et al. 2018).

According to various reports, these stresses adversely affect crop yield-related attributes and amplify ROS generation which alter the cellular redox homeostasis and affect plant's immune system, causing damage of cell organelles, resulting in hindrance of many physiological functions in plants (Fryzova et al. 2017; Shakir et al. 2016, Shakir et al. 2018). Oxidative stress perturbs the photosynthetic process by generation of singlet oxygen in chloroplasts. Mitochondrial activities also influenced ROS production, where H_2O_2 is rapidly generated (Asati et al. 2016). These ROS also decline phospholipid and saturated fatty acid contents, thus causing membrane damage by lipid peroxidation (Asati et al. 2016; Shakir et al. 2018) among various other biomacromolecular assembly disruptions (Gill and Tuteja 2010).

Nevertheless, plants have evolved several mechanisms at the morphological, physiological, biochemical, and molecular levels to protect themselves via adaptation or avoidance against these unfavorable circumstances and sustain their lifecycle. To diminish the adverse effects of these stresses, plants need to improve their performance and tolerance to these stresses by enhancing antioxidant defense system (Shakir et al. 2018), supporting in detoxifying ROS with using superoxide dismutase (SOD), catalase (CAT), peroxidase (POD), ascorbate peroxidase (APX), glutathione reductase (GR), glutathione peroxidase (GPX), glutathione *S*-transferase (GST), monodehydroascorbate reductase (MDHAR), dehydroascorbate reductase (DHAR), and quinine reductases (QR) enzymes (Ahmad et al. 2008; Das and Roychoudhury 2014; Shakir et al. 2018). Likewise, nonenzymatic antioxidant compounds such as ascorbate (AsA), glutathione (GSH), carotenoids, ascorbate, amino acids like proline and proteins like LEA protein, dehydrins (DHN), antifreezing proteins, mRNA-binding protein, and chaperons (Akula and Ravishankar 2011) stimulate the enduring capability of the system to face the destructive effects of oxidative stress.

Secondary metabolites, consisting PCs like flavonoids, isoflavonoids, and terpenoids, and nitrogen-containing metabolites like alkaloids (dos Reis et al. 2012) are found to contribute in stress-tolerant mechanism (Kumar et al. 2020a, b, c). Plants under stress condition also respond through synthesizing some specific, endogenous, and low-molecular-weight stress hormones such as salicylic acid, jasmonic acid, ethylene, and abscisic acid (Fujita et al. 2006; Hayat et al. 2014). Higher accumulation and activities of these antioxidants in plant tissue impart stress tolerance directly or indirectly (Sharma et al. 2019; Kumar et al. 2020).

18.4 Role and Mechanisms of SMs Especially PCs in Environment Robustness Diagnostics Via Adaption or Avoidance from Stresses

Basic cellular process requires energy and oxygen saturation environment for normal functioning. The energy demand and oxygen are derived from the primary metabolites which are accumulated through photosynthesis and later on yield ATP and oxygen via respiration (Hussein and El-Anssary 2018). Apart from primary metabolites, there are also other low-molecular-weight compounds which do not participate in basic cellular constitution and thermodynamics. The later are known as secondary metabolites and can be often seen as the derived products of primary metabolism (Thirumurugan et al. 2018). Responses to changing environmental cues are mediated by secondary metabolites which make the plants eligible to withstand climate adversaries, and even the plants can maintain optimal growth and development (Isah 2019; Tyagi et al. 2020; Tak and Kumar 2020; Wagay et al. 2020).

Secondary metabolites involve in defense mechanism against pathogens and abiotic stresses such as atmospheric pollution and extreme environmental conditions which represents the main array of innate immune system of plants; these properties of SMs make it essential as primary metabolites (Kliebenstein 2013).

Secondary metabolites involve in several important processes, representing physiological, metabolic, and reproductive ones, and improve biomass production of plants. However, metabolites do not take part directly in growth and developmental processes but execute their roles in signaling, in stimulating and inhibiting enzymatic activities, and in defense mechanism and also involve in an interaction with other organisms too. Secondary metabolites have a wide-ranging importance including pharmaceuticals, agrochemicals, food additives, flavors, fragrances, colors, and other industrial materials and are applicable as antioxidants, bioremediation agents, allelochemicals, plant growth regulators, and metal ion chelators (Tiwari and Rana 2015). Besides antioxidants, it has also an antimicrobial activity and inhibitory role on lipid peroxidation and carcinogenesis (Mojzer et al. 2016). Phenolic compound influences several processes such as seed germination, cell division, growth and development process, and photosynthetic activity of plants. Alteration in germination and photosynthetic activity occurs due to change in germinating enzyme's activity such as amylase, peroxidase, and chlorophyll content. Plant phenolics act as regulatory signal for modulating both physiological and developmental phases through regulation at transcription and translation levels, signal transduction, and modification in membrane dynamics. Taken all together these series of regulation can bring about the tolerance against abiotic and biotic stresses (Cheynier et al. 2013). Phenolic and flavonoid have potential to scavenge free radicals (Chan et al. 2008).

During chemical stress, plants trigger synthesis of phenolics like isoflavones, phenolic acid, and hydroxycinnamic acid derivatives (Akula and Ravishankar 2011). These PCs have potential to inhibit the germination as well as growth process of plants by reducing leaf water and stomatal conductance. The higher production of PCs in plant tissue induces stress condition which inhibits the growth of plants via two ways, either by inhibition of chlorophyll biosynthesis or via accelerating chlorophyll degradation, both of which lead to retardation of photosynthesis and decrease in photosynthates with decreased net assimilation rate (NAR). Phenolic compound is derived primarily from the phenylpropanoid pathway (Dixon and Paiva 1995); during stress situation the activity of phenylpropanoid pathway is emanated; hence, the synthesis of phenolic acid is increased to intensify the detoxifying activity of PCs (Mahdavi et al. 2015). Phenylalanine is involved in biosynthesis of phenolic antioxidant, but under stress condition, a transient decline in phenylalanine is exhibited, which significantly rises at later stage. Similarly, shikimic acid also decreases due to overuse at early phase of stress, which is an essential component of the shikimate pathway (Dixon et al. 2002).

Primary metabolites, having more carbon and nitrogen, may be used for the generation of various SMs as per demand, opting related pathways through phenylpropanoid, mevalonate, glucose, amino acid, and acetate-malonate via acting as a sink, depending upon the requirement; further it can also be recycled again in primary metabolites through the degradation process (Collin 2001). Chemical elicitation also can induce stress responses and stimulate synthesis and accumulation of

SMs in plant tissue (Naik and Al-Khayri 2016). Exogenous application of Ca^{++} affects PC metabolism and influences the activities of enzymes such as phenylalanine ammonia-lyase (PAL), polyphenol oxidase (PPO), and peroxidase (POD) in tobacco (*Nicotiana tabacum* L.) leaves under normal condition (Ruiz et al. 2003), while in wheat, the expression of phenylalanine ammonia-lyase (PAL), 4-coumaric acid-CoA ligase (4CL), cinnamic acid 4-hydroxylase (C4H), caffeic acid O-methyltransferase (COMT), and p-coumarate 3-hydroxylase (C3H) is noted to influence under UV-B radiation, and phenolic contents either free or in bound form significantly increased during germination, which in turn contributes to improved antioxidant capability (Chen et al. 2017, 2019a, b).

18.5 Function and Responses of Phenolic Compounds in Respect to Elevated CO_2, Heavy Metal Stress, Salinity, Pollutant Translocations, and Transformations in Ecosystem

During stressful condition SM content is raised, which indeed confers higher tolerance to plant against stressful situation. Under these stresses, plants have potential to synthesize additional SMs especially phenolic compounds through upregulation of genes conferring synthesis of regulatory enzymes of phenylpropanoid pathway, which are capable of scavenging free radicals and preventing cell membrane damages by peroxidation (Koopmann et al. 1999; Selmar 2008).

18.5.1 Response of Phenolics Under Elevated CO_2 and Their Role

A major portion of available fixed carbon are diverted to form carbon-based secondary metabolites, while the remaining carbon increases the intracellular CO_2 concentration (Becker and Kläring 2016; Huang et al. 2017; Sabagh et al. 2021). Elevated CO_2 affects important plant traits by generating ROS and improves the level of defensive compound (total phenolics) which positively correlated with leaf C:N ratio (Karowe and Grubb 2011). Accumulation of PCs under enriched CO_2 levels is due to the upregulation of phenol biosynthetic (phenylpropanoid pathway) enzymes including PAL, *β-glucosidase, and flavanone-3-hydroxylase* (Peltonen et al. 2005). Elevated CO_2 and UV-B radiation in combination lead to a significant increase in the allocation of carbon between biomass and secondary metabolites (phenolic acids, flavonoids, condensed tannins), due to interrelation of primary and secondary metabolism and triggered by the enzyme activity such as phenylalanine ammonia-lyase (PAL), peroxidase, and PPO (Mattson et al. 2005). Enhanced PCs and flavonoids by elevated CO_2 and UV light levels have indirect and direct impacts on the insect performance and behavior, herbivory rates, and pathogen attack (Bidart-Bouzat and Imeh-Nathaniel 2008).

The enzymatic activity of PAL, biomass production, and lignin content in four plant species, namely, *Spergula arvensis*, *Poa annua*, *Senecio vulgaris*, and *Cardamine hirsuta*, are indicated to alter under elevated CO_2 (Hartley and Jones 2003). Penuelas et al. (1996) observed that in leaves of wheat, the phenolic concentration was increased, while it reduced in pine and no significant change was noted in orange, under enrichment of CO_2, and they also indicated an inverse linear relation between PC content and biomass production. Flavonoid (quercetin, rutin, catechin, epicatechin, kaempferol, naringenin, fisetin, and morin) and phenolic acid (gallic acid, vanillic acid, ferulic acid, tannic acid, cinnamic acid, and salicylic acid) profiles were influenced by elevated carbon dioxide (400–1200 μmol mol^{-1} CO_2), which might upregulate the antioxidant activity in three varieties (alata, pumila, and lanceolata) of Malaysian *Labisia pumila* (Myrsinaceae) (Jaafar et al. 2012). Kim et al. (2005) noted that UV exposure and other environmental factors have critical impacts on cellular damage and aging via working through free radicals and ROS; they further reported that metabolic excess of carbon also rises flavonoid content in *Acer palmatum* and in wheat leaves (isoorientin and tricin concentration) at high CO_2. Impacts of elevated CO_2 and modulation of plant traits and PCs are presented in Table 18.1.

18.5.2 Responses of Phenolic Under Heavy Metal and Their Role

Anthropogenic activity introduces heavy metals (HMs) as one of the persistent abiotic stress factors through overaccumulation which causes oxidative stress by producing ROS that leads to disorganization of lipids in cell membrane and alters physiological and metabolic processes, thus ultimately reducing in growth. However, protective mechanism initiated in that condition enhanced the production of stress-related proteins, antioxidants, SMs, hormone, and signaling molecules (Ghori et al. 2019). Accumulation of phenolic compounds such as flavonoid and phenolic acid in plants has been an effective defense response to heavy metal stress, and the protective role of these compounds might be associated with their ability to scavenge ROS (Izbiańska et al. 2014; Chen et al. 2019a, b). Under HM stress condition, an excess amount of flavonoids and polyphenols was observed in various crops such as in alfalfa treated with Pb (Sima et al. 2012; Maslennikov et al. 2018) and isoflavonoids (like anthocyanin) in cabbage (Posmyk et al. 2009).

Higher synthesis of phenolic compound is depending on the upregulation of PAL and chalcone synthase (CHS) activity, stimulated by HM stress (Winkel-Shirley 2002). Silicon and selenium (Se) enhanced the production of phenolic compound in maize and rice, respectively (Mihaličová Malčovská et al. 2014; Chauhan et al. 2017). Shikimate dehydrogenase (SKDH), peroxidase, glucose-6-phosphate dehydrogenase (G6PDH), PAL, cinnamyl alcohol dehydrogenase (CAD), caffeic acid peroxidase (CA-POD), chlorogenic acid peroxidase (CH-POD), PPO, and b-glucosidase (b-GS) also increase in metal stress condition; these enzymes are associated with synthesis of PCs as well as lignin accumulation (Ali et al. 2006). Flavonoid has the ability to chelate metals (Keilig and Ludwig-Müller 2009) and

Table 18.1 Highlight the impacts of elevated CO_2 on phenolic content and modulation of plant traits

Plants	Trait influenced	Change in phenolic contents	References
Dactylis glomerata and *Bromus erectus*	Biomass, nonstructural carbohydrates	Increase in phenolic acid (gallic acid)	Castells et al. (2002)
Labisia pumila Benth	Increasing radical scavenging activity and ferric reducing antioxidant potential	Increase in phenolic acid and flavonoid (gallic acid, caffeic acid, pyrogallol and quercetin, myricetin, kaempferol, rutin, and naringenin) and enhanced PAL activity	Jaafar et al. (2012)
Strawberry (*Fragaria x ananassa* Duch.)	Alteration in ascorbic acid (AsA), glutathione (GSH), altered ratios of AsA to dehydroascorbic acid (DHAsA) and GSH to oxidized glutathione (GSSG), reduced content of DHAsA with elevated ROS absorbance activity	High anthocyanin and phenolic content (p-coumaroyl glucose, dihydroflavonol, quercetin 3-glucoside, quercetin 3-glucuronide, and kaempferol 3-glucoside contents, cyanidin 3-glucoside, pelargonidin-3-glucoside, and pelargonidin-3-glucoside-succinate content	Wang et al. (2003)
Soybean (*Glycine max* L)	Changes in antioxidant enzyme and growth attributes	Increase in isoflavones like genistein and daidzein and the flavonols like quercetin and kaempferol, and naringenin	O'Neill et al. (2010)
Malaysian herb Kacip Fatimah (*Labisia pumila* Blume)	High ROS production, higher GSH, GSSG, soluble carbohydrate, and antioxidant activities observed	Increase in total phenolics and total flavonoids	Ibrahim and Jaafar (2011)
Labisia pumila Benth.	Decrease in chlorophyll content, total soluble sugar, starch, and TNC	Upregulation in SM production via shikimic acid pathway and increased starch content	Ibrahim et al. (2014)
Rice (*Oryza sativa* L.)	Change in C:N ratio and total nonstructural carbohydrates	Increase in total PC and flavonoid contents under elevated CO_2 at maturity but decrease during germination and flowering stage and total nonstructural carbohydrate contents are increased	Goufo et al. (2014)
Strawberry	Increase in antioxidants like SOD	Increases in total polyphenol such as catechin, pelargonidin-3-glucoside, quercetin-3,4-di-glucoside, p-coumaric, ferulic acid,	Balasooriya et al. (2019)

(continued)

Table 18.1 (continued)

Plants	Trait influenced	Change in phenolic contents	References
		coumaroyl, kaempferol-3-glucuronide, resveratrol, flavonoid, and anthocyanin	
Lettuce	Modulation of antioxidant enzymes and SMs	Increase in flavonoid, quercetin-3-O-glucoside, quercetin-3-O-glucuronide, luteolin-7-O-glucoside, kaempferol, myricetin, chlorogenic, chicoric, gallic, protocatechuic, caffeic, and p-coumaric, vanillic, syringic acids	Pérez-López et al. (2018)

provide protection against HMs (Kidd et al. 2001). Hydroxyl (–OH) and carboxylic acid (–COOH) of PCs help in binding metals (Michalak 2006). Impacts of HMs on plant's growth traits and PCs are represented in Table 18.2.

18.5.3 Responses of Phenolic Compounds Under Salinity and Their Role

Salinity is the consequence of accumulation of salts by anthropogenic activities; it is a major constraint on the survival and synthesis of bioactive compounds of plants (Isah 2019; Singhal et al. 2021a; Sabagh et al. 2021). Salinity intensifies overproduction of ROS that induces oxidative stress and causes alteration in the defense responses and production of antioxidants including plant's SMs (Gill and Tuteja 2010). They have an influential scavenging property to ROS in plant under salt stress. Moreover, the induction of secondary metabolic pathway gets initiated by salt stress, resulting in higher production of SMs that have potential antioxidative capacity.

Biosynthesis of PCs enhanced by the overexpression of transcriptional regulator (gene) such as VvbHLH1 in *Arabidopsis thaliana* (Wang et al. 2016), NtMYB4 mediate NtCHS1 in tobacco (Chen et al. 2019a, b) and NHX in *Olea europaea* (Rossi et al. 2016); results in upregulation of key genes of the phenylpropanoid pathway PAL, cinnamate-4-hydroxylase (C4H), 4-coumarate-CoA ligase (4CL), chalcone synthase (CHS) and chalcone isomerase (CHI); DFR, FLS, and ANS (Wang et al. 2016; Rossi et al. 2016) that significantly enhanced the biosynthesis and accumulation of flavonoid like kaempferol and quercetin (Wang et al. 2016). Bistgani et al. (2019) reported that total phenolic contents increased up to 20%, leaf flavonoid (38.6%), cinnamic acid (31.4%), gallic acid (20.4%), rosmarinic acid (27.6%), in *Thymus vulgaris* and *Thymus daenensis* after application of 60 mM NaCl and suggested that increased PCs associated with enhanced antioxidant property under salinity stress. Similarly, Linić et al. (2019) suggested that PCs are associated with short-term adaptation to salinity tolerance, although it is species

Table 18.2 represents the impacts of heavy metal on phenolic contents and modulation of plant traits

Heavy metal	Plant	Growth trait	Phenolic contents	Reference
Chromium (Cr)	Rice (*Oryza sativa*)	High MDA, high proline, increased antioxidant enzymes such as GST, APX, and SOD including DPPH	Higher phenolic and flavonoid content evaluation	Dubey et al. (2018)
Lead (Pb)	Lupine (*Lupinus luteus* L.)	Significant increase in the root length and accumulation of both H_2O_2 and O_2 and TBARS content	Increased flavonoid contents	Izbiańska et al. (2014)
Copper (Cu)	Cabbage (*Brassica oleracea*)	Enhanced in TBARS content, and SOD, CAT, POX, APX, GPX, and GR	Levels of anthocyanin and sinapoyl derivatives	Posmyk et al. (2009)
Cadmium and zinc (Cd and Zn)	*Kandelia obovata*	Effects on antioxidant capacity and growth	Increase in phenolic acids including pyrogallic acid, coumaric acid, protocatechuic acid, chlorogenic acid, and salicylic acid	Chen et al. (2020)
Copper (Cu) stress	Pepper (*Capsicum annuum* L.)	Decrease in the plant growth	Increase in SKDH and peroxidase, and isoperoxidases, PRX-B, and PRX-A3	Diaz et al. (2001)
Aluminum and cadmium	Blueberry (*Vaccinium corymbosum* L.)	Increase in MDA and H_2O_2 contents and antioxidant SOD	Increase in PCs (gallic, chlorogenic and ellagic phenolic acids)	Manquián-Cerda et al. (2018)
Lead (Pb)	*Prosopis farcta* shoots	Increase in aspartic acid and glycine content but glutamic acid significantly decreased	Enhanced PAL activity, increase in phenolic acids and flavonoids; daidzein, vitexin, ferulic acid, and SA	Zafari et al. (2016)
Zn and Cd	*Arabidopsis thaliana*	Reduced antioxidant enzyme	Induction of phyto-chelation genes (*AtPCS1*, *AtPCS2*) by flavonoid (quercetin and naringenin)	Keilig and Ludwig-Mueller (2009)
Copper (Cu)	*Panax ginseng*	Increased cysteine, NPSH contents and DPPH activity; the induced activities of substrate-specific peroxidases like caffeic	Increase in activities of G6PDH, SKDH, PAL, and CAD; increase in accumulation of phenolics (phenolic	Ali et al. (2006)

(continued)

Table 18.2 (continued)

Heavy metal	Plant	Growth trait	Phenolic contents	Reference
		acid peroxidase, and CA-POD; chlorogenic acid peroxidase (CH-POD), polyphenol oxidase (PPO) and b-glucosidase (b-GS)	acid and flavonoids) and lignin	

specific. Effects of salinity stress on plant functional traits and PCs are represented in Table 18.3.

18.5.4 Responses of Phenolics by Pollutant and Their Role

Systemic pesticide generates the chemical stress in soybean that triggers the production of phenolic compound, and it is observed that total phenols in leaf, shoot, and fruit are noted to increase by 114 and 220% at vegetative stage and 50, 166, and 163% at late fruiting stage (Siddiqui and Ahmed 2006). Nitrogen and phosphorus are key nutrients, and both play an imperative role in the plant growth and development and application of nitrogenous and phosphoric fertilizers, which have potential to change the flavonoid content in St. John’s Wort plant (*H. perforatum*) (Azizi 2004). Impacts of different pesticides on plant traits and PCs are represented in Table 18.4.

Furlan et al. (1999) reported that the valley of Piloes River (no air pollution) and valley of Mogi River (severely affected by air pollutions) showed the increase in N, leaf palatability and nutrition value and a decrease in SMs (phenol and tannins) production in valley of Mogi River weaken the defense capacity and future fitness. In *Lotus corniculatus* L., *Trifolium montanum* L., *T. pratense* L. and *T. repens* L. While the leaves were subjected to pollution, generated by human activities and cement factories, then the accumulation of PCs in epidermis, assimilatory mesophyll, and vascular tissue is noted to be associated with ensuring tolerant capacity, and plants have shown less injury (Gostin 2009). Similarly, it was suggested that a progressive shift in ozone-treated leaves leads to a faster senescence, and most surface phenolic compounds showed a declining trend, although some metabolic shift toward few phenolics is associated with higher antioxidant capacity (Saviranta et al. 2010; Khoddami et al. 2013). Herbicide and nitrate enrichment are major problems of aquatic ecosystem and affect plant growth, structural integrity, and PCs (Nuttens et al. 2016). Acid rain influences physiological, biochemical, and molecular change and leads to degradation of pigments, cellular components, and structure by the overproduction of ROS. This kind of digastric effects can be coped with the accumulation of vitamin C, carotenoids, and phenols and exogenous application of polyamines, salicylic acid, and β-aminobutyric acid (Xalxo and Sahu 2017).

Table 18.3 highlights the impacts of salinity stress on plant traits and phenolic compounds

Plant	Plant trait influenced	Phenolic compounds	References
Phaseolus vulgaris L.	Decreased biomass and photosynthetic pigment, increased MDA content, antioxidant enzymes, and ascorbic acid	Increase in amounts of total flavonoids	Taïbi et al. (2016)
Sesuvium portulacastrum L.	Accumulated high contents of proline	Higher polyphenols, anthocyanins and carotenoids at moderate salinity	Slama et al. (2017)
Roselle (*Hibiscus sabdariffa* L.)	Decreased plant height, fresh weight of shoot and flower	Increase phenolic and anthocyanin content	Hashemi and Shahani (2019)
Lettuce	High antioxidant enzymes SOD, POD, CAT; and enhanced carotenoid	Increase in phenolics biosynthesis (phenolic acids and flavonoids);	Mahmoudi et al. (2010)
Thymus vulgaris L. and *T. daenensis* Celak)	Decreased plant dry matter production	Increased total phenolic and flavonoid content (Cinnamic acid, gallic acid)	Bistgani et al. (2019)
Lettuces	p-Hydroxybenzoic and syringic acids, caffeic acid, gallic, protocatechuic, caffeic, p-coumaric, and ferulic acids	Induce flavonoids quercetin, quercetin-3-O-glucoside, quercetin-3-O-glucuronide and quercitrin.	Sgherri et al. (2017)
Amaranthus tricolor	Enhanced pigments (anthocyanins, carotenoids, β-cyanin, β-xanthin, and betalain); β-carotene, vitamin C	Increase in phenolic acids and flavonoids (Salicylic acid, vanilic acid)	Sarker and Oba (2018)
Clary sage (*Salvia sclarea* L.)	Decrease in fatty acid such as palmitic, stearic, and arachidic acids; linolenic at appreciable percentage	Increase in total phenolic contents	Taârit et al. (2012)
Salvia mirzayanii	Higher in amount of volatile oil components, oxygenated monoterpenes comprising of α-terpinyl acetate, 1,8-cineole, and sesquiterpene hydrocarbons	Increase in total phenolic content	Valifard et al. (2014)
Rapeseed (*Brassica napus*)	Reduced growth and yield attributes	Increase in total phenolics, non-flavonoids	Falcinelli et al. (2017)

Table 18.4 Impacts of different pesticides on phenolic compounds and plant's growth traits

Pesticide used	Plant/ vegetation	Phenolic compounds	Trait observed	Reference
Emamectin benzoate, alpha-cypermethrin, and imidacloprid	Tomato (*Solanum lycopersicum*)	Decline in secondary metabolic synthesis	Loss in cell viability and decrease in total soluble sugar (TSS) and total soluble proteins (TSP). Higher cell injury due to high ROS (H_2O_2) production and TBARS content. Increases in antioxidant activities SOD, CAT, GR, POD, APX, and proline	Shakir et al. (2018)
Topsin, benlate, Demacron, and chlorsulfuron	Soybean (*Glycine max*)	Total phenol contents increased leaf (114%) and shoot (220%)	Decrease in leaf area ratio, leaf area index, specific leaf area, net assimilation rate, leaf weight ratio, leaf area duration, RGR, CGR Increase in total phenolic	Siddiqui and Ahmed (2006)
Pyridine; IPP	Wheat (*Triticum aestivum* L.)	Modulation of polyphenol oxidase activity	Increase thiobarbituric acid (TBA), PPO, total protein, water-soluble carbohydrate	Wang et al. (2014)
Imidacloprid (IMI)	*Brassica juncea* L.	Modulation of the expression of nonylphenol isomers, (1E)-1-ethylidene-7a methyloctahydro-1H-indene	Synthesis of phytochemicals such as nonylphenol isomers, linoleic acid, ethyl 2-isopropylphenyl ester, oxalic acid, etc.	Sharma et al. (2015)
Diazinon	Rice (*Oryza sativa* L.)	Expression of valine, ferulic acid, sinapic acid, and phenylalanine	Biosynthesis and metabolism of 30 sugars, amino acids, organic acids, and phenylpropanoids, 31 metabolites including (hydroxybenzoic acid and ferulic acid)	Mahdavi et al. (2015)

Therefore, different atmospheric pollutants influence plant traits, and PC modulation helps in tolerance capacity up to a certain extent.

18.6 Summary

Human activity will exacerbate climatic conditions. Allelopathic nature of phenolic compounds could solve numerous ecological problems with respect to sustainable development of agriculture, forestry, natural resources, and environmental conservation. Every stress condition produces highly reactive oxygen species, responsible for oxidative stress. These PCs have potential to reduce the drastic adverse effects of oxidative stress in various plant species by elevating antioxidant defense. However, PCs are ubiquitous compounds generated during stress situations, and their higher expressions provide tolerance capacity. Although PCs are very less studied in this respect, more research should be carried out to understand the molecular mechanisms of these PCs. This chapter signifies on PCs under various anthropogenic stresses and concludes the mechanism of tolerance under this circumstance.

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