Reactive Oxygen Species Generation, Scavenging and Signaling in Plant Defense Responses

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Abstract

Plants grow in an environment of abiotic stresses such as drought, high light (HL) intensity, heat, salinity, metal/metalloid, or a combination of these environmental stresses requires a delicate balance between energy production and consumption, to mention normal energy. Reactive oxygen species (ROS), a by-product of aerobic metabolism, are key signaling molecules which play a significant role in plants' responses to myriad of abiotic and biotic stresses. ROS initially evidenced as only damaging factors in plants further were found to play an important role in numerous signaling pathways that mediate plants' acclimatory and defense responses. The production and scavenging of ROS are accomplished in various cellular compartments such as the apoplast, cell membrane, mitochondria, chloroplasts, peroxisomes, and endoplasmic reticulum. Under abiotic stresses, an imbalance between ROS biosynthesis and scavenging and elimination in favor of biosynthesis with certain consequences for plant cell physiology has been termed as "oxidative stress." Regulation of redox environment and ROS signals via the cross talk of ROS with various signaling agents within plants' cell requires a high degree of coordination in different cellular compartments. In this present chapter, we provide an update on ROS generation, scavenging, and redox signaling in the context of plant abiotic stress tolerance. Unraveling destabilizing and stabilizing factors of ROS homeostasis and signaling in plants under biotic and abiotic stress environment

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may provide a detailed exploration of ROS/antioxidative signature-related kinetics that can help in designing new and sustainable innovative ways and means for (a) mounting proper acclimation response, (b) monitoring/increasing overall plants' fitness in improving health and productivity of plants under the influence of various stress conditions, and (c) identification and characterization of new targets and key regulator ROS-signaling transduction pathways which may provide excellent future candidates for breeding/engineering stress-resilient crop plants.

Keywords
Reactive oxygen species · Oxidative signaling · Oxidative stress · Plant defense responses

7.1 Introduction

Various abiotic pressures orchestrate the formation of reactive oxygen species (ROS) in plants, thus leading to severe alterations in plants' physiological, biochemical, and molecular process (Mahmud et al. 2017; Wani et al. 2018b). The ROS homeostases are most crucial events during oxidative stress-related metabolism in plants because ROS play a dual role in plants in a dose-dependent fashion, by acting as signaling molecules at low levels, and inducers of oxidative stress at the high levels (Chen et al. 2015; Requena et al. 2017; Mohanta et al. 2018; Wani et al. 2018a). As ROS accumulation poses negative impacts on plant cells, however, they regulate processes like systemic acquired resistance (SAR) and systemic acquired acclimation (SAA) during acclimation and defense responses in plants (Abdelrahman et al. 2016, 2017b; Czarnocka and Karpiński 2018). Thus, it cannot be ruled out that ROS are involved in diverse facets of development and metabolism of plants by regulating a plethora of oxidative and reductive signals and by acting as potential regulators of metabolic and energy fluxes in living organisms.

Superoxide radical ($O_2^{\cdot -}$), hydroxyl radical ($OH^{\cdot}$), hydroperoxyl radical ($HO_2^{\cdot}$), alkoxy radical ($RO^{\cdot}$), peroxy radical ($ROO^{\cdot}$), excited carbonyl (RO^{*}) are free radical and hydrogen peroxide (H_2O_2) and singlet oxygen ($^1\blacktriangle g$ or $^1O_2$), are non-radical molecular forms which are partially reduced or activated forms of atmospheric molecular oxygen (O_2), and are considered as ROS, and their high concentrations are considered as cytotoxic to plants tissues (Gill and Tuteja 2010; Vellosillo et al. 2010; Karuppanapandian et al. 2011; Abdelrahman et al. 2017a; Del Río 2015; Choudhury et al. 2017) (Fig. 7.1). ROS are regarded as unavoidable biochemical by-products of normal aerobic life that appeared on the surface of the Earth about 2.2–2.7 billion years ago, and their production is generally confined to cellular organelles having high flow of electrons like chloroplast, mitochondria, and peroxisomes (Choudhury et al. 2013) in addition to the apoplast

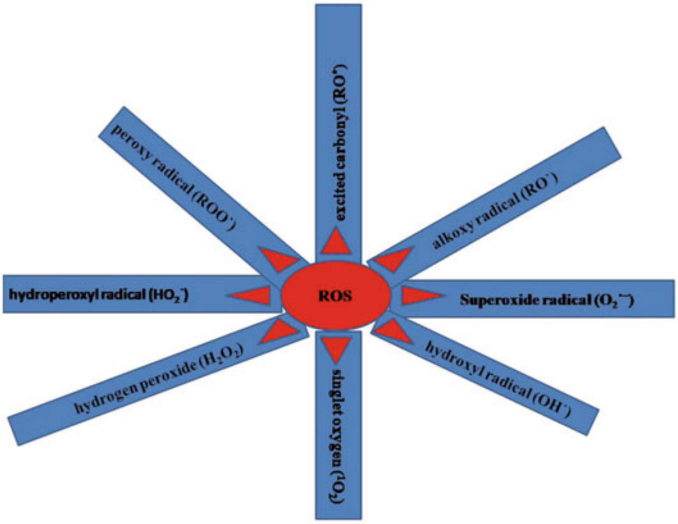

Fig. 7.1 A schematic representation showing free radical and non-radical forms of reactive oxygen species

(Roychoudhury and Basu 2012). About 1–2% of the molecular O_2 which is utilized by plants is sidetracked to lead the generation of ROS (Bhattacharjee 2005; Banerjee and Roychoudhury 2017). O_2 is a free radical and strong oxidant molecule because it contains two unpaired electrons having the same spin quantum number. This property makes it able to accept electrons, consequently leading to the generation of ROS in aerobic organisms. Anaerobic organisms also produce ROS and are thus having a well ROS detoxification system (Ślesak et al. 2012). Thus, we can say that both prokaryotic evolution and eukaryotic evolution took place in the presence of ROS-rich environment. In addition to various abiotic and biotic stress conditions, ROS are also produced under controlled conditions which lead to oxidative signaling in plants if they are consequently sequenced by antioxidants and osmolytes (Wani et al. 2018a, b). Under physiological circumstances, ROS are indispensable players for maintaining proper cellular metabolism, regulation of essential processes like proliferation, differentiation, and development of cells, light acclimation, cytoplasmic signaling reactions, pathogen resistance, hormonal signal transduction, and programmed cell death (Swanson and Gilroy 2010; Karpiński et al. 2013; Foyer and Noctor 2013; Gilroy et al. 2016; Mittler 2017).

However, biotic and abiotic perturbations such as high salt concentrations (Rasool et al. 2013; Ahmad et al. 2018), incidence of UV radiation and ozone (Yu et al. 2004; Yan et al. 2016; Chen et al. 2018), occurrence of drought (Huseynova et al. 2016; Sezgin et al. 2018), high and low temperature

(Li et al. 2015; Sailaja et al. 2015; Tahmasebi and Pakniyat 2015; Muneer et al. 2017; Abdelrahman et al. 2017a), heavy metal/metalloid accumulation (reviewed by Wani et al. 2018b; Kohli et al. 2018; Shi et al. 2018; Zaid et al. 2019), deficiency of mineral nutrients (Gill and Tuteja 2010; Liu et al. 2018), air pollution (Lodovici and Bigagli 2011; Lakey et al. 2016), hazardous gases (Muneer and Lee 2018), herbicides (Islam et al. 2016), and pathogen attack (De Gara et al. 2003; Torres et al. 2006; Torres 2010) lead to abrupt increase in endogenous ROS levels which in turn can lead to a state of "oxidative stress," thereby altering normal activities and causing cell death (Fig. 7.2) by damaging genetic makeup, oxidation of proteins, peroxidation of lipid bilayer, and leakage of ions. ROS accumulation due to various environmental stresses is a principal factor of decrease in global crop productivity (Khan and Singh 2008; Tuteja 2010; Khan and Khan 2017). In the complete sequence of events, ROS can lead to the initiation of new responses by triggering the expression of new genes. However, plants employ a sessile lifestyle and for countering oxidative stress-induced ROS bioaccumulation, they have evolved antioxidant defense systems that include enzymatic antioxidants which include battery of scavenger proteins, such as superoxide dismutase (SOD), monodehydroascorbate reductase (MDHAR), dehydroascorbate reductase (DHAR), catalase (CAT), ascorbate peroxidase (APX), glutathione reductase (GR), glutathione peroxidase (GPX), and peroxiredoxin (PRX) and non-enzymatic antioxidants, such as ascorbic acid (vitamin C), reduced glutathione (GSH), tocopherols (vitamin E), carotenoids, and phenolic compounds (Ahmad et al. 2010; Rejeb et al. 2014; Inupakutika et al. 2016; Dar et al. 2017; Pandey et al. 2017; Abdelrahman et al. 2018; Mohanta et al. 2018). Also, osmolytes such as proline and glycine betaine present in microbes, animals, and plants are known to alleviate the inhibitory effects of ROS (Kumar and Yadav 2009; Iqbal et al. 2015; Noreen et al. 2018) (Fig. 7.2).

7.2 Types of ROS, Their Chemistry, and the Underlying Detoxification Systems

As mentioned in the above section, there are various types of ROS which are generated under various stressful environments. According to Temple et al. (2005), the presence of atmosphere O_2 enabled metabolism of respiration and energy transfer systems to use O_2 as terminal oxidant. This leads to ROS formation in cells. Atmospheric O_2 can relatively give rise to various intermediate ROS by the univalent reduction reactions, which otherwise is non-reactive in its ground state (Scandalios 2005). Also, the availability of d block elements such as copper and iron, which further catalyze the reactions through the Haber-Weiss mechanism or the Fenton reaction, gives rise to the formation of $OH^{\cdot}$, which is regarded as the most reactive chemical species in the biological systems. In the accompanying section, we are schematically representing the formation of various ROS in biological world.

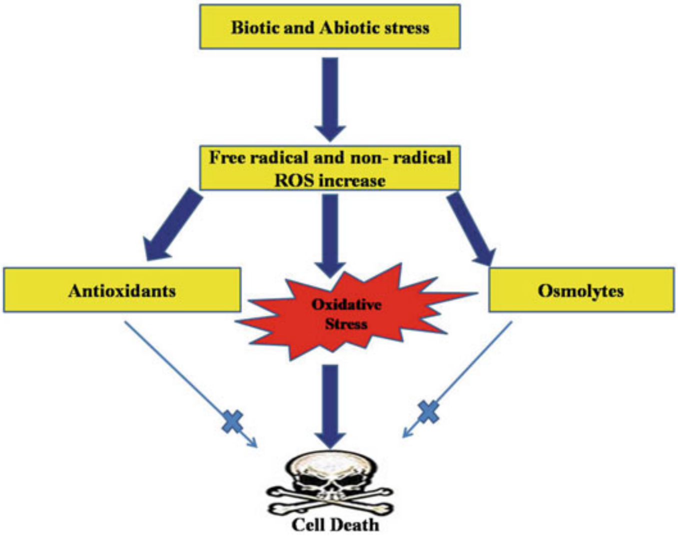

Fig. 7.2 A schematic representation depicting the production and detoxification of reactive oxygen species in plants through the antioxidant defense system

(1) Hydroxyl radical ($OH^{\cdot}$)

$$H_2O_2 + O_2^{\cdot-} \xrightarrow{Fe2+,3+} OH^- + O_2 + OH^{\cdot}$$

(2) Superoxide radical ($O_2^{\cdot-}$)

$$O_2^{\cdot-} + Fe^{3+} \rightarrow {}^1O_2 + Fe^{2+}$$

$$2O_2^{\cdot-} + 2H^+ \rightarrow O_2 + H_2O_2Fe^{3+}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^- \text{ (Fenton reaction)}$$

(3) Singlet oxygen ($^1O_2$)

$$Chl \rightarrow {}^3Chl$$

$$3Chl + {}^3O_2 \rightarrow Chl + {}^1O_2$$

(4) **Hydrogen peroxide (H_2O_2)**

$$2O_2^{\cdot -} + 2H^+ \rightarrow H_2O_2 + O_2$$

$$2O_2^{\cdot -} + 2H^+ \overset{SOD}{\rightarrow} H_2O_2 + O_2$$

These ROS are generated continuously at chloroplast, mitochondria, endoplasmic reticulum, peroxisomes, apoplast, cell membrane, and cell wall. The generation of ROS in different cell components has been depicted in Fig. 7.3.

A brief description of their generation in cell compartments is as follows:

Hydroxyl radical ($OH^{\cdot}$) is generated by Fenton reaction and is most reactive ROS known. In cell systems, ($OH^{\cdot}$) radicals are largely responsible for oxidation of DNA, lipids, proteins (Sharma et al. 2012; Sewelam et al. 2016). They have the distinction in cells in the manner that ($OH^{\cdot}$) radicals do not have any enzymatic antioxidants for their elimination (Vranová et al. 2002, Pinto et al. 2003; Gill and Tuteja 2010).

Operation of photosynthesis under stress conditions results in absorption of light energy in excess more than the capacity of photosynthetic machinery to utilize it through photosynthetic electron transport chain (Végh et al. 2018). This results in the formation of singlet oxygen ($^1O_2$) at photosystem PS (II) and superoxide radical ($O_2^{\cdot -}$) at PSI and PSII, respectively (Schmitt et al. 2014; Foyer 2018). As represented in Fig. 7.3, singlet oxygen ($^1O_2$) is formed by the reaction of triplet state of chlorophyll (^{3}Chl) with molecular O_2 (Das and Roychoudhury 2014). At PSII, the excess energy absorbed by the ^{3}Chl is transferred to molecular O_2 to give rise to the $^1O_2$. $^1O_2$ is thus a strong oxidant molecule that causes oxidation of macromolecules leading to cellular "damage" (Watabe et al. 2007). Singlet oxygen ($^1O_2$) is thus responsible for much of the oxidative inactivation during over-excitation of the photosynthetic electron transport chain (Telfer 2014). Superoxide radical ($O_2^{\cdot -}$) is the first ROS to be formed in plant tissues as only 1–2% of total O_2 consumption in cell tissues leads to their formation (Puntarulo et al. 1988). $O_2^{\cdot -}$ radicals may further lead to the generation of more toxic ROS like ($OH^{\cdot}$) and ($^1O_2$) as depicted above (Halliwell 2006; Gill and Tuteja 2010). H_2O_2 among all ROS is moderate ROS species and plays a dual role in plant signaling at low concentrations, it acts as a signaling molecule to mitigate biotic and abiotic stresses, at high levels, and it triggers cell death (Hossain et al. 2015; Cuypers et al. 2016; Khan et al. 2018). Production of H_2O_2 involves two-step electron reduction of $O_2^{\cdot -}$ (reaction 4). As represented in reaction 4, superoxide dismutase (SOD) catalyzes the second reduction step of $O_2^{\cdot -}$ which is finally converted into H_2O_2 (Sharma et al. 2012). As compared to other ROS, H_2O_2 has got a long half-life of 1 ms (Møller et al. 2007).

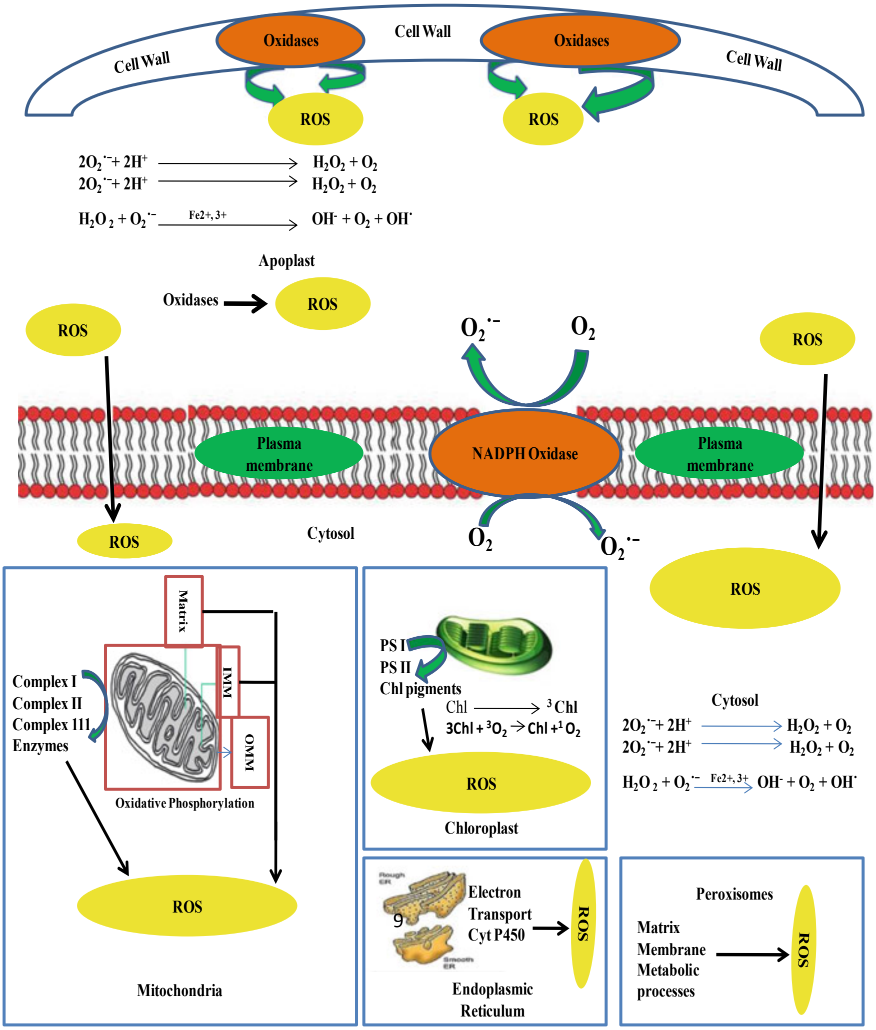

Fig. 7.3 Production sites of different reactive oxygen species (ROS) in plants. ROS are biosynthesized at various locations in the cells like chloroplast, mitochondria, plasma membrane, peroxisomes, apoplast, endoplasmic reticulum, and cell wall. The figure also shows the components of cell structures where ROS are produced

7.3 Antioxidant Batteries in Plants for Excess ROS Detoxification

As mentioned in the introductory part that plant stress tolerance mechanisms involve activation of the antioxidant defense system. The antioxidant defense system among others consists of antioxidants which are present in almost all cellular compartments that demonstrate their ability to detoxify ROS for plant survival. As ROS trigger the gene expression and signal transduction pathways in response to various stress-response programs, thus the antioxidant proteins are activated as and when ROS concentration exceeds the threshold. Here in the present section, we have covered the components of an antioxidant defense system that include enzymatic (SOD, CAT, APX, MDHAR, DHAR, and GR) and non-enzymatic (GSH, ASA, carotenoids, and tocopherols) antioxidants which are directly or indirectly engaged in the detoxification of ROS.

7.3.1 Enzymatic Antioxidants

7.3.1.1 Superoxide Dismutase (SOD, EC 1.15.1.1)

SOD is an intracellular ubiquitous enzymatic antioxidant which belongs to the metalloenzyme family present universally in all aerobic organisms. SOD is known to provide first the line of defense against excess ($O_2^{\cdot-}$) in the chloroplast, mitochondria, peroxisomes, and cytosol (Gill and Tuteja 2010).

$$O_2^{\cdot-} + O_2^{\cdot-} + 2H^+ \overset{SOD}{\rightarrow} H_2O_2 + O_2$$

The reaction shows the dismutation of $O_2^{\cdot-}$ radical into molecular oxygen and hydrogen peroxide, and the reaction rate is 10,000 times faster than the spontaneous dismutation (Das and Roychoudhury 2014). SOD contains isoenzyme cofactors, viz. Mn-SOD, Fe-SOD, and Cu/Zn-SOD (Alscher et al. 2002), all of which function in the dismutation of $O_2^{\cdot-}$, thus overcoming $O_2^{\cdot-}$ radical-induced oxidative stress. An increase in SOD activity has been reported in diverse plants subjected to various environmental pressures such as salt stress (Ahmad et al. 2018), heavy metal toxicity (Zaid and Mohammad 2018; Zaid et al. 2019), pesticide stress (Fatma et al. 2018), ozone (Chen et al. 2018), wounding (Si et al. 2017, 2018), cold stress (Wani et al. 2018c; Sheteiwy et al. 2018), and drought (Ahmad et al. 2017; Moazzam-Jazi et al. 2018).

7.3.1.2 Catalase (CAT, EC 1.11.1.6)

Catalases are heme-possessing antioxidant enzymes having ability to directly scavenge H_2O_2 into H_2O and O_2.

$$2H_2O_2 \overset{CAT}{\rightarrow} 2H_2O + O_2$$

As reviewed by Gill and Tuteja (2010), CAT has highest reaction turnover rates and one molecule of CAT can dismute approximately 6 million molecules of H_2O_2 to H_2O and O_2 in the 60 s time span. Animal cells contain only one CAT isoform, while plant cells are characterized by a couple of CATs (Iwamoto et al. 1998). As peroxisomes are the main sites of H_2O_2 production, however, CATs in plants also exist in chloroplasts, mitochondria, and cytosol. The expression and activity of CATs are triggered when plants are exposed to various kinds of abiotic stresses such as nematode (Vicente et al. 2015), arbuscular mycorrhizal fungi (Hashem et al. 2018), heavy metal (Zaid and Mohammad 2018), drought (Wang et al. 2018a), salinity (Fariduddin et al. 2018), cold (Jan et al. 2018a), heat (Rai et al. 2018), and UV radiation (Mariz-Ponte et al. 2018).

7.3.1.3 Enzymes of Ascorbate–Glutathione (AsA-GSH) Cycle

The AsA-GSH pathway consists of four enzymes, namely ascorbate peroxidase (APX), monodehydroascorbate reductase (MDHAR), dehydroascorbate reductase (DHAR), and glutathione reductase (GR) (Fig. 7.4), and two non-enzymatic antioxidant proteins, viz. ascorbate (AsA) and glutathione (GSH). In the accompanying section, we are discussing them one by one that how ASA-GSH pathway operates to eliminate excess ROS in plants.

7.3.1.4 Ascorbate Peroxidase (APX, E.C.1.1.11.1)

APX is the first enzyme of the AsA-GSH cycle, which detoxifies H_2O_2 by causing peroxidation of AsA and yielding water and monodehydroascorbate (MDHA) radical (Asada 1999; Pandey et al. 2015) (Fig. 7.4). MDHA is then either converted to dehydroascorbate (DHA) non-enzymatically or reduced back to AsA by an enzyme (MDHAR). The reaction involved is represented below:

$$\mathrm{H_2O_2} + 2\mathrm{AsA} \overset{\mathrm{APX}}{\rightarrow} 2\mathrm{H_2O} + 2\mathrm{MDHA}\ (\rightarrow 2\mathrm{DHA})$$

Five APX isoforms have been discovered in plants, namely cytosolic (cAPX), mitochondrial (mitAPX), stromal (sAPX), membrane-bound APXs present in chloroplasts (tAPX), and peroxisomes/glyoxysomes (Asada 1999; Caverzan et al. 2012; Anjum et al. 2014). Over-expression of genes related to APX has been shown to mediate stress tolerance to various abiotic stresses in various crop plants.

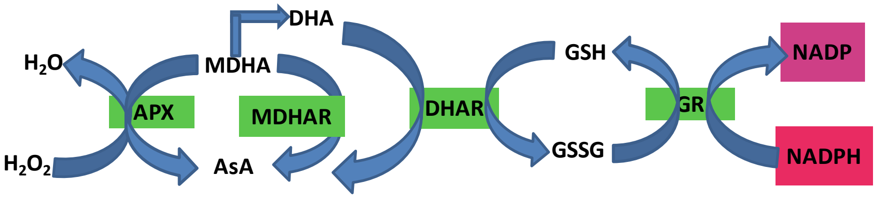

Fig. 7.4 Schematic representation of ascorbate–glutathione cycle showing enzymes and formation of reducing equivalents. Details are described in the text

For example in *Jatropha curcas* plants, quantitative polymerase chain reaction (qPCR) analysis showed over-expressing a thylakoid APX was responsible for conferring salt stress tolerance (Liu et al. 2013). In another study, ectopic over-expression of the peroxisomal APX gene (*SbpAPX*) conferred salt stress tolerance in *Arachis hypogea* plants (Singh et al. 2014). In a recent study, Balfagón et al. (2018) found that APX is the chief protein to be involved in citrus tolerance to combined conditions of drought and high temperatures. In sorghum, Akbudak et al. (2018) reported the genome-wide identification and expression profiling of APX gene families under drought stress conditions and found that APX families in leaves and roots showed significant changes in their expression levels, which, therefore, regulate drought stress tolerance. Employing bioinformatics approaches, Ozyigit et al. (2016) presented a comparative evaluation of APX gene/protein families in 18 different plant species. They analyzed the exon/intron organization of APX, studied and identified conserved motif signatures of APX, constructed the phylogenetic trees and 3D models of APX families, and analyzed the APX gene expression profiles. They conclude that APX is major H_2O_2-scavenging enzymes in plants.

7.3.1.5 Monodehydroascorbate Reductase (MDHAR, E.C.1.6.5.4)

MDHAR is a flavin adenine dinucleotide (FAD) enzyme which is responsible for rejuvenating AsA from the short-lived MDHA radical by using NADPH as an electron donor agent, thus maintaining reduced AsA pool in cellular tissues (Sharma et al. 2012). MDHA can react non-enzymatically to form DHA (Fig. 7.4). The reaction catalyzed by MDHAR is represented below:

$$\begin{tikzcd}
\mathrm{NADPH} + \mathrm{H}^+ + 2\mathrm{MDHA} \arrow[r, "\mathrm{MDHAR}"] \arrow[d] & 2\mathrm{AsA} + \mathrm{NADP}^+ \\
2\mathrm{DHA} &
\end{tikzcd}$$

MDHAR contains several isozymes present in the chloroplast, mitochondria, peroxisomes, cytosol, and glyoxysomes (Foyer and Halliwell 1976; Reumann and Corpas 2010). Modulated MDHAR activity has been observed in diverse crop plants in response to various abiotic stresses such as salinity (Ahanger et al. 2018), metal toxicity (Jan et al. 2018b; Hasanuzzaman et al. 2017), drought stress (Sharma and Dubey 2005), ultraviolet-B stress (Shiu and Lee 2005), and high-temperature stress (Nahar et al. 2015). Nevertheless, over-expression of MDHAR gene (*AtMDAR1*) in the cytosol has been shown to minimize the deleterious effects of ozone, salt, and polyethylene glycol-induced stress in transgenic tobacco plants (Eltayeb et al. 2007). These transgenic plants were found to exhibit up to 2.1-fold higher MDHAR activity as compared to wild-type plants. In yet another experiment, Li et al. (2010) observed that over-expression of chloroplastic MDHAR increased tolerance to temperature and methyl viologen-induced oxidative stresses by alleviating photoinhibition of PSI and PSII and elevating AsA pool. These results suggest that an over-expressed MDHAR level confers enhanced tolerance against multiple abiotic stresses in plants.

7.3.1.6 Dehydroascorbate Reductase (DHAR, EC.1.8.5.1)

DHAR brings the reduction of DHA to AsA using reduced glutathione (GSH) as the reducing substrate (Ushimaru et al. 1997; Das and Roychoudhury 2014) (Fig. 7.4). It is thus the second enzyme apart from MDHAR which maintains the redox pool of AsA in plant cells (Qin et al. 2011). The reaction catalyzed by DHAR is given below:

$$\mathrm{DHA} + \mathrm{GSH} \overset{\mathrm{DHAR}}{\rightarrow} \mathrm{AsA} + \mathrm{GSSG}$$

DHAR also showed tolerance to abiotic stress. In an experiment, Eltayeb et al. (2011) demonstrated that transgenic potato plants over-expressing Arabidopsis *AtDHAR1* gene showed tolerance against herbicide, drought, and salt stresses.

7.3.1.7 Glutathione Reductase (GR, E.C.1.6.4.2)

GR is a flavoprotein having a disulfide bond which catalyzes the NADPH-dependent reduction of oxidized glutathione (GSSG) to reduce glutathione (GSH), is thus important for maintaining the reduced redox pool of GSH, and thus maintains homeostatic redox balance in cellular environment (Ghisla and Massey 1989; Gill and Tuteja 2010; Achary et al. 2015) (Fig. 7.4). As depicted in Fig. 7.4, GSH is used to regenerate AsA from DHA by DHAR enzyme and is itself converted to GSSG. GR is thus a crucial enzyme in AsA-GSH cycle to maintain GSH/GSSG ratio. The reaction involved is:

$$\mathrm{GSSG} + \mathrm{NADPH} \overset{\mathrm{GR}}{\rightarrow} \mathrm{GSH} + \mathrm{NADP}$$

7.3.2 Non-enzymatic Antioxidants

7.3.2.1 Reduced Glutathione (GSH)

GSH is a tripeptide (γ-glutamyl-cysteinyl-glycine) molecule, having a low molecular weight, and is one of the crucial nonprotein sulfur-containing thiols in plants to scavenge ROS and ROS-induced oxidative damage. It has been detected abundantly in reduced form (GSH) and is present in all cellular compartments like apoplast, endoplasmic reticulum, cytosol, vacuole, mitochondria, chloroplasts, peroxisomes (Foyer and Noctor 2003). GSH provides a reducing environment by functioning as an antioxidant molecule in several ways. In plants, GSH production imparts chilling stress tolerance (Lukatkin and Anjum 2014), metal/metalloid tolerance (Per et al. 2017; Kim et al. 2017), high-temperature stress tolerance (Nahar et al. 2015), and salt stress tolerance (Zhou et al. 2018). GSH is involved in redox signaling, regulation and modulation of enzymatic activities, and expression of defense gene during biotic and abiotic stresses (Zechmann 2014; Anjum et al. 2012). In the AsA-GSH cycle, as represented in Fig. 7.4, GSH acts as a reductant to reduce DHA to AsA enzymatically and is itself oxidized to GSSG which indicates that GSH plays a crucial role in maintaining AsA pool in the cellular environment (Noctor et al. 1998). On the other hand, GSSG is reduced back to GSH by GR in the presence of reducing equivalents. This process replenishes and maintains a cellular redox of GSH which provides a reducing environment during stress conditions.

7.3.2.2 Ascorbate

AsA (vitamin C) is the most abundant water-soluble antioxidant molecule and is regarded as a key electron donating substrate to detoxify excess ROS (Khan et al. 2011; Qian et al. 2014; Akram et al. 2017). In plant cells, biosynthesis of AsA takes place in mitochondria as a result of the Smirnoff-Wheeler pathway (Wheeler et al. 1998). AsA protects cells and their organelles from toxic ROS produced as a result of biotic and abiotic stresses (Khan et al. 2012; Naz et al. 2016), controls division of cells, and acts as a cofactor of many enzymes (Lisko et al. 2014). Exogenous application of AsA increases resistance in plants against various abiotic stresses. In a study involving young peach trees, Penella et al. (2017) applied foliar AsA to improve their performance after rewatering the plants. Their results suggested that AsA improved water stress tolerance under suboptimal water regimes. In yet another study, Xu et al. (2015) found that AsA mitigated the water stress-induced root growth in tall fescue by increasing the antioxidative defense system. In wheat plants, Alamri et al. (2018) applied AsA to improve their tolerance against lead toxicity. They concluded that AsA-induced lead stress tolerance was associated with improved plants' defense systems, content of essential nutrients, reduced chlorophyll degradation, increased cysteine accumulation, maintained relative water content, and the enhancement in the activities of enzymes like ATP sulfurylase, ribulose-1,5-bisphosphate carboxylase/oxygenase, nitrate reductase, and O-acetylserine(thiol)lyase. In *Arabidopsis*, AsA has been shown to trigger the release of the cytosolic-free calcium, which is essential in plant signaling phenomenon (Makavitskaya et al. 2018). Thus, it is evident from the above discussion that AsA imparts stress tolerance by modulating various plant mechanisms.

7.3.2.3 Carotenoids

Carotenoids are a class of lipophilic antioxidant molecule present in plants, algae, and microorganisms (Young 1991; Ahmad et al. 2010; Abdelrahman et al. 2016; Patias et al. 2017). Carotenoids play an essential role in different plant processes and are characterized with antioxidant potential during plant stress signaling by acting as light harvesters by dissipating excess light as heat, light quenchers, and their ability to scavenge the triplet chlorophyll (3Chl*) state and ROS (Uarrota et al. 2018). They are also precursors of abscisic acid and strigolactones (Ruiz-Sola and Rodríguez-Concepción 2012). As ROS scavenger, carotenoids prevent oxidative stress and confer abiotic stress in plants. Carotenoids protect the photosynthetic machinery from ROS-induced oxidative stress (Srichandan et al. 1989). In a study carried out by Wang et al. (2018c), over-expression of alfalfa gene (*MsOr*) in tobacco increased tolerance to multiple abiotic stresses along with enhanced carotenoid content showing possible cross talk between stress tolerance and carotenoid accumulation. In a classical study involving cyanobacterial species, Patias et al. (2017) found that the carotenoid extracts were shown to be a potent scavenger of peroxyl radical, having peroxyl radical scavenger ability. In mango plants during ROS stress signaling, Rosalie et al. (2018) proposed a link made between antioxidant system defense and carotenoid metabolism. In response to drought stress, over-expression of a carotenoid ε-hydroxylase gene (*SlLUT1*) in transgenic tobacco plants improved drought stress tolerance by maintaining photosynthesis as well as scavenging of ROS (Wang et al. 2018b). In *Arabidopsis thaliana*, Caliandro et al. (2013) highlighted the proper regulation of altered α- and β-branch carotenoid biosynthesis in maintaining leaf photoprotection and whole-plant acclimation in response to photooxidative stress.

7.3.2.4 Tocopherols

Tocopherols are considered as lipid-soluble antioxidant molecules which contribute to plant resistance to biotic and abiotic stresses (Munne-Bosch 2005; Cela et al. 2018). Tocopherols are exclusively present in thylakoid membranes or in plastids and have four isomers (α-, β-, γ-, and δ-) with α-tocopherol (vitamin E) possessing highest biological activity and antioxidant capability. Along with other antioxidants, tocopherols play a principal role in reducing ROS level in photosynthesizing apparatus and protect photosynthetic membranes from lipid peroxidation to maintain the stability of membranes under various stress environments (Munné-Bosch and Alegre 2002; Munné-Bosch et al. 2013). Supply of tocopherols increases resistance in plants against various abiotic stress conditions. In water-stressed *Vigna radiata* cultivars, Sadiq et al. (2017) applied tocopherol which considerably improved antioxidant enzyme activities (SOD, POD, and CAT), chlorophyll content, and also the composition of fresh pods in both the cultivars. In *Arabidopsis thaliana*, vitamin E played an essential role in enhancing tolerance to metal-induced oxidative stress (Collin et al. 2008). In response to 75 μM Cu and Cd treatment, transcript levels of genes encoding enzymes of the vitamin E biosynthetic pathway were found to be increased, while tocopherol-deficient (*vte1*) mutant showed an enhanced sensitivity toward 75 μM Cu and Cd treatment as compared to the relative wild-type (WT) control. As tocopherols protect PSII from photoinhibition, lack of tocopherol modulates the PSII antenna and thus the functioning of PSI and II under light conditions (Niewiadomska et al. 2018); however, in tocopherol mutants (*vte1*) action of ROS ($^1O_2$) on PSII resulted in permanent damage at light-harvesting complex II and at PSII core. In response to biotic stress, an alteration in the composition of tocopherol in chloroplasts negatively influences the *Arabidopsis thaliana* response to stress condition by causing marked changes in fatty acid membrane composition, highest peroxidation of lipids, and altered activation of the defense system (Cela et al. 2018).

7.3.2.5 Phenolic Compounds

Phenolics are diverse secondary metabolites found widely in plant tissues. These possess antioxidant capacity. Commonly studied plant phenolics in relation to abiotic stress are flavonoids, tannins, hydroxycinnamate esters, and lignins. Antioxidative properties of polyphenols are due to

(1) ability to chelate ions of heavy metals,
(2) high reactivity as a donor of electrons or hydrogen,
(3) radical derived from polyphenols which stabilize unpaired and unstable electrons which have chain-breaking functions (Rice-Evans et al. 1997).

Phenolic compounds engineer plants' stress tolerance. In a study involving *Scrophularia striata* plants, Falahi et al. (2018) showed that water stress alleviation by phenolic compounds is mediated by cross talk between nitric oxide and H_2O_2. Key enzymes of phenolic pathways like phenylalanine ammonia-lyase (PAL) and tyrosine ammonia-lyase (TAL) were increased and were deployed in response to the stress mitigation. In a recent study, Siddiqui et al. (2018) found that PAL in beetroot increased when plants were infected with pathogenic microbes. Thus, these pieces of evidence clearly indicate that phenolic compounds are directly or indirectly involved in imparting resistance to a range of stresses in plants.

7.4 Conclusion and Future Directives

During the last few decades, a rich development in our knowledge of ROS chemistry, biosynthesis, and regulation in the context of abiotic stress tolerance has emerged. However, the exact underlying ROS-signaling pathways largely remain a mystery. In the present chapter, we attempt to address the regulatory role of ROS in plant abiotic defense responses and discuss at length how batteries of the antioxidant defense machinery, the antioxidant enzymes, and the non-antioxidant metabolites work in coordination to alleviate the oxidative damage induced by various ROS to engineer tolerance against various environmental stress conditions. By collecting the literature, we have tried here to unravel the basic chemistry of various ROS and the ameliorative role of various enzymatic and non-enzymatic antioxidants in imparting plant abiotic stress tolerance. Undoubtedly, the current concept may increase our understanding of the field of ROS biosynthesis and signaling in plant defense responses. Further research is needed to accurately explain the complex regulatory mechanisms that integrate ROS-signaling pathways for regulating growth and development of plants under abiotic stresses. Functional genomic techniques, along with metabolomics and proteomics, will give detailed insights into the regulation of ROS-signaling networks and the crucial role played by the antioxidant defense system during plants' responses to various environmental pressures. These concepts might pave the way for the development of transgenic approaches to engineer tolerance for optimization of crop performance, under multiple stresses in the future.

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References

Abdelrahman M, Abdel-Motaal F, El-Sayed M, Jogaiah S, Shigyo M, Ito S-I, Trane LP (2016) Dissection of *Trichoderma longibrachiatum*-induced defense in onion (*Allium cepa* L.) against *Fusarium oxysporum* f. sp. cepa by target metabolite profiling. Plant Sci 246:128–138

Abdelrahman M, Burritt DJ, Tran LP (2017a) The use of metabolomic quantitative trait locus mapping and osmotic adjustment traits for the improvement of crop yields under environmental stresses. Semin Cell Dev Biol 83:86–94

Abdelrahman M, Mahmoud HYAH, El-Sayed M, Tanaka S, Tran LP (2017b) Isolation and characterization of Cepa2, a natural alliospiroside A, from shallot (*Allium cepa* L. Aggregatum group) with anticancer activity. Plant Physiol Biochem 116:167–173

Abdelrahman M, Jogaiah S, Burritt DJ, Tran LP (2018) Legume genetic resources and transcriptome dynamics under abiotic stress conditions. Plant, Cell Environ 41:1949–2225

Achary VMM, Reddy CS, Pandey P, Islam T, Kaul T, Reddy MK (2015) Glutathione reductase a unique enzyme: molecular cloning, expression and biochemical characterization from the stress adapted C 4 plant, *Pennisetum glaucum* (L.) R. Br. Mol Biol Rep 42:947–962

Ahanger MA, Alyemeni MN, Wijaya L, Alamri SA, Alam P, Ashraf M, Ahmad P (2018) Potential of exogenously sourced kinetin in protecting *Solanum lycopersicum* from NaCl-induced oxidative stress through up-regulation of the antioxidant system, ascorbate-glutathione cycle and glyoxalase system. PLoS ONE 13(9):e0202175

Ahmad P, Jaleel CA, Salem MA, Nabi G, Sharma S (2010) Roles of enzymatic and nonenzymatic antioxidants in plants during abiotic stress. Crit Rev Biotechnol 30:161–175

Ahmad J, Bashir H, Bagheri R, Baig A, Al-Huqail A, Ibrahim MM, Qureshi MI (2017) Drought and salinity induced changes in ecophysiology and proteomic profile of *Parthenium hysterophorus*. PLoS ONE 12(9):e0185118

Ahmad P, Abd Allah EF, Alyemeni MN, Wijaya L, Alam P, Bhardwaj R, Siddique KH (2018) Exogenous application of calcium to 24-epibrassinosteroid pre-treated tomato seedlings mitigates NaCl toxicity by modifying ascorbate–glutathione cycle and secondary metabolites. Sci Rep 8(1):13515

Akbudak MA, Filiz E, Vatansever R, Kontbay K (2018) Genome-wide identification and expression profiling of ascorbate peroxidase (APX) and glutathione peroxidase (GPX) genes under drought stress in sorghum (*Sorghum bicolor* L.). J Plant Growth Regul 1–12

Akram NA, Shafiq F, Ashraf M (2017) Ascorbic acid—a potential oxidant scavenger and its role in plant development and abiotic stress tolerance. Front Plant Sci 8:613

Alamri SA, Siddiqui MH, Al-Khaishany MY, Nasir Khan M, Ali HM, Alaraidh IA, Mateen M (2018) Ascorbic acid improves the tolerance of wheat plants to lead toxicity. J Plant Interact 13:409–419

Alscher RG, Erturk N, Heatrh LS (2002) Role of superoxide dismutases (SODs) in controlling oxidative stress in plants. J Exp Bot 53:1331–1341

Anjum NA, Ahmad I, Mohmood I, Pacheco M, Duarte AC, Pereira E, Prasad MNV (2012) Modulation of glutathione and its related enzymes in plants' responses to toxic metals and metalloids—a review. Environ Exp Bot 75:307–324

Anjum NA, Gill SS, Gill R, Hasanuzzaman M, Duarte AC, Pereira E, Tuteja N (2014) Metal/metalloid stress tolerance in plants: role of ascorbate, its redox couple, and associated enzymes. Protoplasma 251:1265–1283

Asada K (1999) The water–water cycle in chloroplasts: scavenging of active oxygen and dissipation of excess photons. Annu Rev Plant Physiol Plant Mol Biol 50:601–639

Balfagón D, Zandalinas SI, Baliño P, Muriach M, Gómez-Cadenas A (2018) Involvement of ascorbate peroxidase and heat shock proteins on citrus tolerance to combined conditions of drought and high temperatures. Plant Physiol Biochem 127:194–199

Banerjee A, Roychoudhury A (2017) Abiotic stress, generation of reactive oxygen species, and their consequences: an overview. In: Reactive oxygen species in plants: boon or bane—revisiting the role of ROS, p 23

Bhattacharjee S (2005) Reactive oxygen species and oxidative burst: roles in stress, senescence and signal transducation in plants. Curr Sci 1113–1121

Caliandro R, Nagel KA, Kastenholz B, Bassi R, Li Z, Niyogi KK, Matsubara S (2013) Effects of altered α-and β-branch carotenoid biosynthesis on photoprotection and whole-plant acclimation of Arabidopsis to photo-oxidative stress. Plant, Cell Environ 36:438–453

Caverzan A, Passaia G, Rosa SB, Ribeiro CW, Lazzarotto F, Margis- Pinheiro M (2012) Plant responses to stresses: role of ascorbate peroxidase in the antioxidant protection. Genet Mol Biol 35:1011–1019

Cela J, Tweed JK, Sivakumaran A, Lee MR, Mur LA, Munné-Bosch S (2018) An altered tocopherol composition in chloroplasts reduces plant resistance to *Botrytis cinerea*. Plant Physiol Biochem 127:200–210

Chen G-Q, Ren L, Zhang J, Reed BM, Zhang D, Shen Xh (2015) Cryopreservation affects ROS-induced oxidative stress and antioxidant response in Arabidopsis seedlings. Cryobiology 70:38–47

Chen YJ, Wen MX, Sui JX, Yan YQ, Yuan W, Hong L, Zhang L (2018) Ameliorating effects of leaf water extract of three aromatic plant species on ozone-polluted snap bean (*Phaseolus vulgaris* L. 'Jiangjunyoudou'). Bull Environ Contam Toxicol 100:849–855

Choudhury S, Panda P, Sahoo L, Panda SK (2013) Reactive oxygen species signaling in plants under abiotic stress. Plant Signal Behav 8(4):e23681

Choudhury FK, Rivero RM, BlumwaldE Mittler R (2017) Reactive oxygen species, abiotic stress and stress combination. Plant J 90:856–867

Collin VC, Eymery F, Genty B, Rey P, Havaux M (2008) Vitamin E is essential for the tolerance of *Arabidopsis thaliana* to metal-induced oxidative stress. Plant, Cell Environ 31:244–257

Cuypers A, Hendrix S, Amaral dos Reis R, De Smet S, Deckers J, Gielen H, Jozefczak M, Loix C, Vercampt H, Vangronsveld J, Keunen E (2016) Hydrogen peroxide, signaling in disguise during metal phytotoxicity. Front Plant Sci 7:470. https://doi.org/10.3389/fpls.2016.00470

Czarnocka W, Karpiński S (2018) Friend or foe? Reactive oxygen species production, scavenging and signaling in plant response to environmental stresses. Free Radic Biol Med 122:4–20

Dar MI, Naikoo MI, Khan FA, Rehman F, Green ID, Naushin F, Ansari AA (2017) An introduction to reactive oxygen species metabolism under changing climate in plants. In: Reactive oxygen species and antioxidant systems in plants: role and regulation under abiotic stress. Springer, Singapore, pp 25–52

Das K, Roychoudhury A (2014) Reactive oxygen species (ROS) and response of antioxidants as ROS-scavengers during environmental stress in plants. Front Environ Sci 2:53

De Gara L, de Pinto MC, Tommasi F (2003) The antioxidant systems vis-à-vis reactive oxygen species during plant–pathogen interaction. Plant Physiol Biochem 41:863–870

Del Río LA (2015) ROS and RNS in plant physiology: an overview. J Exp Bot 66:2827–2837

Eltayeb AE, Kawano N, Badawi GH, Kaminaka H, Sanekata T, Shibahara T, Tanaka K (2007) Overexpression of monodehydroascorbate reductase in transgenic tobacco confers enhanced tolerance to ozone, salt and polyethylene glycol stresses. Planta 225:1255–1264

Eltayeb AE, Yamamoto S, Habora MEE, Yin L, Tsujimoto H, Tanaka K (2011) Transgenic potato overexpressing Arabidopsis cytosolic AtDHAR1 showed higher tolerance to herbicide, drought and salt stresses. Breed Sci 61:3–10

Falahi H, Sharifi M, Chashmi NA, Maivan HZ (2018) Water stress alleviation by polyamines and phenolic compounds in *Scrophularia striata* is mediated by NO and H_2O_2. Plant Physiol Biochem 130:139–147

Fariduddin Q, Khan TA, Yusuf M, Aafaqee ST, Khalil RRAE (2018) Ameliorative role of salicylic acid and spermidine in the presence of excess salt in *Lycopersicon esculentum*. Photosynthetica 1–13

Fatma F, Kamal A, Srivastava A (2018) Exogenous application of salicylic acid mitigates the toxic effect of pesticides in *Vigna radiata* (L.) Wilczek. J Plant Growth Regul 1–10

Foyer CH (2018) Reactive oxygen species, oxidative signaling and the regulation of photosynthesis. Environ Exp Bot. https://doi.org/10.1016/j.envexpbot.2018.05.003

Foyer CH, Halliwell B (1976) The presence of glutathione and glutathione reductase in chloroplasts: a proposed role in ascorbic acid metabolism. Planta 133:21–25

Foyer CH, Noctor G (2003) Redox sensing and signalling associated with reactive oxygen in chloroplasts, peroxisomes and mitochondria. Physiol Plant 119:355–364

Foyer CH, Noctor G (2013) Redox signaling in plants. Antioxid Redox Signal 18:2087

Ghisla S, Massey V (1989) Mechanisms of flavoprotein-catalyzed reactions. EJB Rev 29–45

Gill SS, Tuteja N (2010) Reactive oxygen species and antioxidant machinery in abiotic stress tolerance in crop plants. Plant Physiol Biochem 48:909–930

Gilroy S, Białasek M, Suzuki N, Górecka M, Devireddy AR, Karpiński S, Mittler R (2016) ROS, calcium, and electric signals: key mediators of rapid systemic signaling in plants. Plant Physiol 171:1606–1615

Halliwell B (2006) Reactive species and antioxidants. Redox biology is a fundamental theme of aerobic life. Plant Physiol 141:312–322

Hasanuzzaman M, Nahar K, Anee TI, Fujita M (2017) Exogenous silicon attenuates cadmium-induced oxidative stress in *Brassica napus* L. by modulating AsA-GSH pathway and glyoxalase system. Front Plant Sci 8:1061

Hashem A, Alqarawi AA, Radhakrishnan R, Al-Arjani ABF, Aldehaish HA, Egamberdieva D, Abd_Allah EF (2018) Arbuscular mycorrhizal fungi regulate the oxidative system, hormones and ionic equilibrium to trigger salt stress tolerance in *Cucumis sativus* L. Saudi J Biol Sci 25:1102–1114

Hossain MA, Bhattacharjee S, Armin SM, Qian P, Xin W, Li HY, Burritt DJ, Fujita M, Tran LSP (2015) Hydrogen peroxide priming modulates abiotic oxidative stress tolerance: insights from ROS detoxification and scavenging. Front Plant Sci 6:420. https://doi.org/10.3389/fpls.2015.00420

Huseynova IM, Rustamova SM, Aliyeva DR, Babayev HG, Aliyev JA (2016) Photosynthesis, antioxidant protection, and drought tolerance in plants. In: Drought stress tolerance in plants, vol 1. Springer, pp 349–378

Inupakutika MA, Sengupta S, Devireddy AR, Azad RK, Mittler R (2016) The evolution of reactive oxygen species metabolism. J Exp Bot 67:21

Iqbal N, Nazar R, Khan NA (2015) Osmolytes and plants acclimation to changing environment: emerging omics technologies. https://doi.org/10.1007/978-81-322-2616-1_5

Islam F, Ali B, Wang J, Farooq MA, Gill RA, Ali S, Zhou W (2016) Combined herbicide and saline stress differentially modulates hormonal regulation and antioxidant defense system in *Oryza sativa* cultivars. Plant Physiol Biochem 107:82–95

Iwamoto M, Maekawa M, Saito A, Higo H, Higo K (1998) Evolutionary relationship of plant catalase genes inferred from exon-intron structures: isozyme divergence after the separation of monocots and dicots. Theor Appl Genet 97:9–19

Jan N, Majeed U, Andrabi KI, John R (2018a) Cold stress modulates osmolytes and antioxidant system in *Calendula officinalis*. Acta Physiol Plant 40:73

Jan S, Alyemeni MN, Wijaya L, Alam P, Siddique KH, Ahmad P (2018b) Interactive effect of 24-epibrassinolide and silicon alleviates cadmium stress via the modulation of antioxidant defense and glyoxalase systems and macronutrient content in *Pisum sativum* L. seedlings. BMC Plant Biol 18:146

Karpiński S, Szechyńska-Hebda M, Wituszyńska W, Burdiak P (2013) Light acclimation, retrograde signalling, cell death and immune defences in plants. Plant, Cell Environ 36:736–744

Karuppanapandian T, Moon JC, Kim C, Manoharan K, Kim W (2011) Reactive oxygen species in plants: their generation, signal transduction, and scavenging mechanisms. Aust J Crop Sci 5:709

Khan MIR, Khan NA (eds) (2017) Reactive oxygen species and antioxidant systems in plants: role and regulation under abiotic stress. Springer, Singapore

Khan NA, Singh S (2008) Abiotic stress and plant responses. IK International, New Delhi, pp 205–215

Khan T, Mazid M, Mohammad F (2011) A review of ascorbic acid potentialities against oxidative stress induced in plants. J Agrobiol 28:97–111

Khan TA, Mazid M, Mohammad F (2012) Potential of ascorbic acid against oxidative burst in plants under biotic stress: a review. J Ind Res Technol 2:72–80

Khan TA, Yusuf M, Fariduddin Q (2018) Hydrogen peroxide in regulation of plant metabolism: signalling and its effect under abiotic stress. Photosynthetica 56:1237. https://doi.org/10.1007/s11099-018-0830-8

Kim YO, Bae HJ, Cho E, Kang H (2017) Exogenous glutathione enhances mercury tolerance by inhibiting mercury entry into plant cells. Front Plant Sci 8:6

Kohli SK, Handa N, Sharma A, Gautam V, Arora S, Bhardwaj R, Alyemeni MN, Wijaya L, Ahmad P (2018) Combined effect of 24-epibrassinolide and salicylic acid mitigates lead (Pb) toxicity by modulating various metabolites in *Brassica juncea* L. seedlings. Protoplasma 255:11–24

Kumar V, Yadav SK (2009) Proline and betaine provide protection to antioxidant and methylglyoxal detoxification systems during cold stress in *Camellia sinensis* (L.) O. Kuntze. Acta Physiol Plant 31:261–269

Lakey PS, Berkemeier T, Tong H, Arangio AM, Lucas K, Pöschl U, Shiraiwa M (2016) Chemical exposure-response relationship between air pollutants and reactive oxygen species in the human respiratory tract. Sci Rep 6:32916

Li F, Wu QY, Sun YL, Wang LY, Yang XH, Meng QW (2010) Overexpression of chloroplastic monodehydroascorbate reductase enhanced tolerance to temperature and methyl viologen-mediated oxidative stresses. Physiol Plant 139:421–434

Li X, Ahammed GJ, Zhang YQ, Zhang GQ, Sun ZH, Zhou J, Shi K (2015) Carbon dioxide enrichment alleviates heat stress by improving cellular redox homeostasis through an ABA-independent process in tomato plants. Plant Biol 17:81–89

Lisko KA, Aboobucker SI, Torres R, Lorence A (2014) Engineering elevated vitamin C in plants to improve their nutritional content, growth, and tolerance to abiotic stress. In: Jetter R (ed) Phytochemicals, biosynthesis, function and application. Springer International Publishing, Switzerland, pp 109–128

Liu Z, Bao H, Cai J, Han J, Zhou L (2013) A novel thylakoid ascorbate peroxidase from *Jatrophacurcas* enhances salt tolerance in transgenic tobacco. Int J Mol Sci 15:171–185

Liu Z, Ren Z, Zhang J, Chuang CC, Kandaswamy E, Zhou T, Zuo L (2018) Role of ROS and nutritional antioxidants in human diseases. Front Physiol 9

Lodovici M, Bigagli E (2011) Oxidative stress and air pollution exposure. J Toxicol. https://doi.org/10.1155/2011/487074

Lukatkin AS, Anjum NA (2014) Control of cucumber (*Cucumis sativus* L.) tolerance to chilling stress—evaluating the role of ascorbic acid and glutathione. Front Environ Sci 2:62

Mahmud JAL, Hasanuzzaman M, Nahar K, Rahman A, Hossain MS, Fujita M (2017) gamma-aminobutyric acid (GABA) confers chromium stress tolerance in *Brassica juncea* L. by modulating the antioxidant defense and glyoxalase systems. Ecotoxicology 26:675–690

Makavitskaya M, Svistunenko D, Navaselsky I, Hryvusevich P, Mackievic V, Rabadanova C, Voitsekhovskaja O (2018) Novel roles of ascorbate in plants: induction of cytosolic Ca^{2+} signals and efflux from cells via anion channels. J Exp Bot 69:3477–3489

Mariz-Ponte N, Mendes RJ, Sario S, de Oliveira JF, Melo P, Santos C (2018) Tomato plants use non-enzymatic antioxidant pathways to cope with moderate UV- A/B irradiation: a contribution to the use of UV-A/B in horticulture. J Plant Physiol 221:32–42

Mittler R (2017) ROS are good. Trends Plant Sci 22:11–19

Moazzam-Jazi M, Ghasemi S, Seyedi SM, Niknam V (2018) COP1 plays a prominent role in drought stress tolerance in Arabidopsis and Pea. Plant Physiol Biochem 130:678–691

Mohanta TK, Bashir T, Hashem A, Abd Allah EF, Khan AL, Al-Harrasi AS (2018) Early events in plant abiotic stress signaling: interplay between calcium, reactive oxygen species and phytohormones. J Plant Growth Regul 1–17

Møller IM, Jensen PE, Hansson A (2007) Oxidative modifications to cellular components in plants. Annu Rev Plant Biol 58:459–481

Muneer S, Lee JH (2018) Hazardous gases (CO, NO_x, CH_4 and C_3H_8) released from CO_2 fertilizer unit lead to oxidative damage and degrades photosynthesis in strawberry plants. Sci Rep 8 (1):12291

Muneer S, Park YG, Kim S, Jeong BR (2017) Foliar or subirrigation silicon supply mitigates high temperature stress in strawberry by maintaining photosynthetic and stress-responsive proteins. J Plant Growth Regul 36:836–845

Munne-Bosch S (2005) The role of α-tocopherol in plant stress tolerance. J Plant Physiol 162:743–748

Munné-Bosch S, Alegre L (2002) The function of tocopherols and tocotrienols in plants. Crit Rev Plant Sci 21:31–57

Munné-Bosch S, Queval G, Foyer CH (2013) The impact of global change factors on redox signaling underpinning stress tolerance. Plant Physiol 161:5–19

Nahar K, Hasanuzzaman M, Alam MM, Fujita M (2015) Exogenous glutathione confers high temperature stress tolerance in mung bean (*Vigna radiata* L.) by modulating antioxidant defense and methylglyoxal detoxification system. Environ Exp Bot 112:44–54

Naz H, Akram NA, Ashraf M (2016) Impact of ascorbic acid on growth and some physiological attributes of cucumber (*Cucumis sativus*) plants under water-deficit conditions. Pak J Bot 48:877–883

Niewiadomska E, Brückner K, Mulisch M, Kruk J, Orzechowska A, Pilarska M, Luchowski R, Gruszecki WI, Krupinska K (2018) Lack of tocopherols influences the PSII antenna and the functioning of photosystems under low light. J Plant Physiol 223:57–64

Noctor G, Arisi ACM, Jouanin L, Kunert KJ, Rennenberg H, Foyer CH (1998) Glutathione: biosynthesis, metabolism and relationship to stress tolerance explored in transformed plants. J Exp Bot 49:623–647

Noreen S, Akhter MS, Yaamin T, Arfan M (2018) The ameliorative effects of exogenously applied proline on physiological and biochemical parameters of wheat (*Triticum aestivum* L.) crop under copper stress condition. J Plant Interact 13:221–230

Ozyigit II, Filiz E, Vatansever R, Kurtoglu KY, Koc I, Öztürk MX, Anjum NA (2016) Identification and comparative analysis of H_2O_2-scavenging enzymes (ascorbate peroxidase and glutathione peroxidase) in selected plants employing bioinformatics approaches. Front Plant Sci 7:301

Pandey P, Singh J, Achary V, Reddy MK (2015) Redox homeostasis via gene families of ascorbate-glutathione pathway. Front Environ Sci 3:25

Pandey S, Fartyal D, Agarwal A, Shukla T, James D, Kaul T, Negi YK, Arora S, Reddy MK (2017) Abiotic stress tolerance in plants: myriad roles of ascorbate peroxidase. Front Plant Sci 8:581. https://doi.org/10.3389/fpls.2017.00581

Patias LD, Fernandes AS, Petry FC, Mercadante AZ, Jacob-Lopes E, Zepka LQ (2017) Carotenoid profile of three microalgae/cyanobacteria species with peroxyl radical scavenger capacity. Food Res Int 100:260–266

Penella C, Calatayud Á, Melgar JC (2017) Ascorbic acid alleviates water stress in young peach trees and improves their performance after rewatering. Front Plant Sci 8:1627. https://doi.org/10.3389/fpls.2017.01627

Per TS, Masood A, Khan NA (2017) Nitric oxide improves S-assimilation and GSH production to prevent inhibitory effects of cadmium stress on photosynthesis in mustard (*Brassica juncea* L.). Nitric Oxide 68:111–124

Pinto E, Sigaud-Kutner TCS, Leitao MAS, Okamoto OK, Morse D, Colepicolo P (2003) Heavy metal induced oxidative stress in algae. J Phycol 39:1008–1018

Puntarulo S, Sánchez RA, Boveris A (1988) Hydrogen peroxide metabolism in soybean embryonic axes at the onset of germination. Plant Physiol 86:626–630

Qian HF, Peng XF, Han X, Ren J, Zhan KY, Zhu M (2014) The stress factor, exogenous ascorbic acid, affects plant growth and the antioxidant system in *Arabidopsis thaliana*. Russ J Plant Physiol 61:467–475

Qin A, Shi Q, Yu X (2011) Ascorbic acid contents in transgenic potato plants overexpressing two dehydroascorbate reductase genes. Mol Biol Rep 38:1557–1566

Rai KK, Rai N, Rai SP (2018) Salicylic acid and nitric oxide alleviate high temperature induced oxidative damage in *Lablab purpureus* L plants by regulating bio-physical processes and DNA methylation. Plant Physiol Biochem 128:72–88

Rasool S, Ahmad A, Siddiqi TO, Ahmad P (2013) Changes in growth, lipid peroxidation and some key antioxidant enzymes in chickpea genotypes under salt stress. Acta Physiol Plant 35:1039–1050

Rejeb KB, Abdelly C, Savouré A (2014) How reactive oxygen species and proline face stress together. Plant Physiol Biochem 80:278–284

Requena ME, Egea-Gilabert C, Candela ME (2017) Involvement of reactive oxygen species and the induction of the cellular antioxidant machinery in the necrotic death of two *Capsicum annuum* cultivars with different sensitivity to *Phytophthora capsici*. J Plant Pathol 99:185–195

Reumann S, Corpas FJ (2010) The peroxisomal ascorbate–glutathione pathway: molecular identification and insights into its essential role under environmental stress conditions. In: Anjum NA, Chan M-T, Umar S (eds) Ascorbate–glutathione pathway and stress tolerance in plants. Springer, Dordrecht, The Netherlands, pp 387–404

Rice-Evans C, Miller N, Paganga G (1997) Antioxidant properties of phenolic compounds. Trends Plant Sci 2:152–159

Rosalie R, Léchaudel M, Dhuique-Mayer C, Dufossé L, Joas J (2018) Antioxidant and enzymatic responses to oxidative stress induced by cold temperature storage and ripening in mango (*Mangifera indica* L. cv. 'Cogshall') in relation to carotenoid content. J Plant Physiol 224:75–85

Roychoudhury A, Basu S (2012) Ascorbate-glutathione and plant tolerance to various abiotic stresses. In: Oxidative stress in plants causes, consequences and tolerance. IK International Publishing House Pvt. Ltd., New Delhi, pp 177–258

Ruiz-Sola M, Rodríguez-Concepción M (2012) Carotenoid biosynthesis in Arabidopsis: a colourful pathway. Arab Book 10:e0158

Sadiq M, Akram NA, Ashraf M (2017) Foliar applications of alpha-tocopherol improves the composition of fresh pods of *Vigna radiata* subjected to water deficiency. Turk J Bot 41:244–252

Sailaja B, Subrahmanyam D, Neelamraju S, Vishnukiran T, Rao YV, Vijayalakshmi P, Mangrauthia SK (2015) Integrated physiological, biochemical, and molecular analysis identifies important traits and mechanisms associated with differential response of rice genotypes to elevated temperature. Front Plant Sci 6:1044

Scandalios JG (2005) Oxidative stress: molecular perception and transduction of signals triggering antioxidant gene defenses. Braz J Med Biol Res 38:995–1014

Schmitt FJ, Renger G, Friedrich T, Kreslavski VD, Zharmukhamedov SK, Los DA, Allakhverdiev SI (2014) Reactive oxygen species: re-evaluation of generation, monitoring and role in stress-signaling in phototrophic organisms. Biochim Biophys Acta 1837:835–848

Sewelam N, Kazan K, Schenk PM (2016) Global plant stress signaling: reactive oxygen species at the cross-road. Front Plant Sci 7:187. https://doi.org/10.3389/fpls.2016.00187

Sezgin A, Altuntaş C, Sağlam A, Terzi R, Demiralay M, Kadıoğlu A (2018) Abscisic acid cross-talking with hydrogen peroxide and osmolyte compounds may regulate the leaf rolling mechanism under drought. Acta Physiol Plant 40:141

Sharma P, Dubey RS (2005) Drought induces oxidative stress and enhances the activities of antioxidant enzymes in growing rice seedlings. Plant Growth Regul 46:209–221

Sharma P, Jha AB, Dubey RS, Pessarakli M (2012) Reactive oxygen species, oxidative damage, and antioxidative defense mechanism in plants under stressful conditions. J Bot. https://doi.org/10.1155/2012/217037

Sheteiwy MS, An J, Yin M, Jia X, Guan Y, He F, Hu J (2018) Cold plasma treatment and exogenous salicylic acid priming enhances salinity tolerance of *Oryza sativa* seedlings. Protoplasma 1–21

Shi WG, Liu W, Yu W, Zhang Y, Ding S, Li H, Luo ZB (2018) Abscisic acid enhances lead translocation from the roots to the leaves and alleviates its toxicity in *Populus canescens*. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2018.09.024

Shiu CT, Lee TM (2005) Ultraviolet-B-induced oxidative stress and responses of the ascorbate–glutathione cycle in a marine macroalga *Ulva fasciata*. J Exp Bot 56:2851–2865

Si T, Wang X, Wu L, Zhao C, Zhang L, Huang M, Jiang D (2017) Nitric oxide and hydrogen peroxide mediate wounding-induced freezing tolerance through modifications in photosystem and antioxidant system in wheat. Front Plant Sci 8:1284

Si T, Wang X, Zhao C, Huang M, Cai J, Zhou Q, Jiang D (2018) The role of hydrogen peroxide in mediating the mechanical wounding-induced freezing tolerance in wheat. Front Plant Sci 9:327

Siddiqui ZA, Khan MR, Abdallah EF, Parveen A (2018) Titanium dioxide and zinc oxide nanoparticles affect some bacterial diseases, and growth and physiological changes of beetroot. Int J Veg Sci 1–22. https://doi.org/10.1080/19315260.2018.1523267

Singh N, Mishra A, Jha B (2014) Ectopic over-expression of peroxisomal ascorbate peroxidase (SbpAPX) gene confers salt stress tolerance in transgenic peanut (Arachis hypogaea). Gene 547(1):119–125

Ślesak I, Ślesak H, Kruk J (2012) Oxygen and hydrogen peroxide in the early evolution of life on earth: in silico comparative analysis of biochemical pathways. Astrobiology 12:775–784

Srichandan SC, Choudhury NK, Biswal UC (1989) Carotenoid degradation during in vitro aging of wheat chloroplasts. Photosynthetica 23:687–690

Swanson S, Gilroy S (2010) ROS in plant development. Physiol Plant 138:384–392

Tahmasebi A, Pakniyat H (2015) Comparative analysis of some biochemical responses of winter and spring wheat cultivars under low temperature. Int J Agric Agric 7:14–22

Telfer A (2014) Singlet oxygen production by PSII under light stress: mechanism, detection and the protective role of beta-carotene. Plant Cell Physiol 55:1216–1223

Temple MD, Perrone GG, Dawes IW (2005) Complex cellular responses to reactive oxygen species. Trends Cell Biol 15:319–326

Torres MA (2010) ROS in biotic interactions. Physiol Plant 138:414–429

Torres MA, Jones JD, Dangl JL (2006) Reactive oxygen species signaling in response to pathogens. Plant Physiol 141:373–378

Tuteja N (2010) Cold, salt and drought stress. In: Hirt H (ed) Plant stress biology: from genomics towards system biology. Wiley-Blackwell, Weinheim, Germany, pp 137–159

Uarrota VG, Stefen DLV, Leolato LS, Gindri DM, Nerling D (2018) Revisiting carotenoids and their role in plant stress responses: from biosynthesis to plant signaling mechanisms during stress. In: Antioxidants and antioxidant enzymes in higher plants. Springer, Cham, pp 207–232

Ushimaru T, Maki Y, Sano S, Koshiba K, Asada K, Tsuji H (1997) Induction of enzymes involved in the ascorbate-dependent antioxidative system, namely, ascorbate peroxidase, monodehydroascorbate reductase and dehydroascorbate reductase, after exposure to air of rice (*Oryza sativa*) seedlings germinated under water. Plant Cell Physiol 38:541–549

Végh B, Marček T, Karsai I, Janda T, Darkó É (2018) Heat acclimation of photosynthesis in wheat genotypes of different origin. South Afr J Bot 117:184–192

Vellosillo T, Vicente J, Kulasekaran S, Hamberg M, Castresana C (2010) Emerging complexity in reactive oxygen species production and signaling during the response of plants to pathogens. Plant Physiol 154:444–448

Vicente CS, Ikuyo Y, Shinya R, Mota M, Hasegawa K (2015) Catalases induction in high virulence pinewood nematode *Bursaphelenchus xylophilus* under hydrogen peroxide-induced stress. PLoS ONE 10:e0123839

Vranová E, Atichartpongkul S, Villarroel R, Van Montagu M, Inzé D, Van Camp W (2002) Comprehensive analysis of gene expression in *Nicotiana tabacum* leaves acclimated to oxidative stress. Proc Natl Acad Sci 99:10870–10875

Wang X, Zhang X, Chen J, Wang X, Cai J, Zhou Q, Dai T, Cao W, Jiang D (2018a) Parental drought-priming enhances tolerance to post-anthesis drought in offspring of wheat. Front Plant Sci 9:261. https://doi.org/10.3389/fpls.2018.00261

Wang S, Zhuang K, Zhang S, Yang M, Kong F, Meng Q (2018b) Overexpression of a tomato carotenoid ε-hydroxylase gene (SlLUT1) improved the drought tolerance of transgenic tobacco. J Plant Physiol 222:103–112

Wang Z, Xu W, Kang J, Li M, Huang J, Ke Q, Kwak SS (2018c) Overexpression of alfalfa Orange gene in tobacco enhances carotenoid accumulation and tolerance to multiple abiotic stresses. Plant Physiol Biochem 130:613–622

Wani SH, Tripathi P, Zaid A, Challa GS, Kumar A, Kumar V, Bhatt M (2018a) Transcriptional regulation of osmotic stress tolerance in wheat (*Triticum aestivum* L.). Plant Mol Biol 1–19

Wani W, Masoodi KZ, Zaid A, Wani SH, Shah F, Meena VS, Mosa KA (2018b) Engineering plants for heavy metal stress tolerance. Rend Lincei Sci Fis Nat 1–15

Wani MA, Jan N, Qazi HA, Andrabi KI, John R (2018c) Cold stress induces biochemical changes, fatty acid profile, antioxidant system and gene expression in *Capsella bursa pastoris* L. Acta Physiol Plant 40:167

Watabe N, Ishida Y, Ochiai A, Tokuoka Y, Kawashima N (2007) Oxidation decomposition of unsaturated fatty acids by singlet oxygen in phospholipid bilayer membranes. J Oleo Sci 56:73–80

Wheeler GL, Jones MA, Smirnoff N (1998) The biosynthetic pathway of vitamin C in higher plants. Nature 393:365–369

Xu Y, Xu Q, Huang B (2015) Ascorbic acid mitigation of water stress-inhibition of root growth in association with oxidative defense in tall fescue (*Festuca arundinacea* Schreb.). Front Plant Sci. 6:807. https://doi.org/10.3389/fpls.2015.00807

Yan F, Liu Y, Sheng H, Wang Y, Kang H, Zeng J (2016) Salicylic acid and nitric oxide increase photosynthesis and antioxidant defense in wheat under UV-B stress. Biol Plant 60:686–694

Young AJ (1991) The photoprotective role of carotenoids in higher plants. Physiol Plant 83:702–708

Yu J, Tang XX, Zhang PY, Tian JY, Cai HJ (2004) Effects of CO_2 enrichment on photosynthesis, lipid peroxidation and activities of antioxidative enzymes of *Platymonas subcordiformis* subjected to UV-B radiation stress. Acta Bot Sin Engl Ed 46:682–690

Zaid A, Mohammad F (2018) Methyl jasmonate and nitrogen interact to alleviate cadmium stress in *Mentha arvensis* by regulating physio-biochemical damages and ROS detoxification. J Plant Growth Regul 1–18

Zaid A, Mohammad F, Wani SH, Siddique KM (2019) Salicylic acid enhances nickel stress tolerance by up-regulating antioxidant defense and glyoxalase systems in mustard plants. Ecotoxicol Environ Saf. 180:575–587

Zechmann B (2014) Compartment-specific importance of glutathione during abiotic and biotic stress. Front Plant Sci 5:566

Zhou Y, Diao M, Cui JX, Chen XJ, Wen ZL, Zhang JW, Liu H (2018) Exogenous GSH protects tomatoes against salt stress by modulating photosystem II efficiency, absorbed light allocation and H_2O_2-scavenging system in chloroplasts. J Integr Agric 17:60345–60347